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Thermodynamics of plane-parallel emulsion and foam films

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Abstract. Studies on the thermodynamics of plane-parallel thin liquid films (emulsion and foam films) are surveyed. Various approaches to the thermodynamics of planar non-interacting interfaces in thick liquid films (Gibbs dividing surface method, Rusanov's method based on a layer with a finite thickness, Hansen's method) as well as the thermodynamics of plane-parallel thin liquid films based on different models [membrane of zero thickness, membrane of finite thickness, two interacting dividing (as defined by Gibbs) surfaces] are examined. The bibliography includes 56 references.

I. Introduction

The interaction between the particles of a disperse phase in emulsions and foams takes place through thin layers—microscopic liquid films (MLF) of the dispersion medium. This interaction determines the stability and the structural-mechanical properties of disperse systems.

Despite the strikingly non-equilibrium character of processes involved in the formation and breakdown of MLF under real emulsification and foam-formation conditions, equilibrium thermodynamics can serve as a first approximation in the description of the properties of such films, which is more accurate the lower the rate of change of the external perturbing influences compared with the rates of internal relaxation processes (hydrodynamic and adsorption processes, surfactant reconformation processes on interfaces, etc.) in such films. The effects associated with the non-equilibrium nature of the physicochemical processes can be described under such conditions as excess effects compared with standard effects in equilibrium thermodynamics. This guarantees that they are unambiguous.

The difficulty of the thermodynamic description of MLF consists in the lack of a generally recognised definition of the concept of interfacial interaction in the so-called transition region in the film. The forces of the interaction between the surfaces of the film in the transition region vary in magnitude and sign (Figs. 1*a* and 1*b*), vanishing on emerging from the film into the bulk phase α of the Plato region of the film meniscus, where the wedging pressure is zero (Fig. 1*c*). No problems arise in describing the interaction with the central part of the plane-parallel film because thermodynamic methods for plane-parallel liquid films have been developed.[1–10] But the thermodynamics of the transition region of the film have as yet been inadequately developed. In particular, there is no generally recognised way of determining and describing the disjoining pressure in the transition region of the film, which leads to ambiguous and inconsistent estimates of the interaction energy in this region of the film.

If the area corresponding to the transition region of the film constitutes a small fraction of the plane-parallel region, then one can neglect the contribution by the energy of the interaction of the transition region to the overall interaction energy in such a film. However, with decrease in the size of the MLF, the contribution to the interaction energy in the transition region is appreciable and cannot be disregarded. In the latter case, the thermodynamic description of the interaction in the MLF is based on idealised models. For example, the real film, having a complex profile in the transition region, is replaced by a plane-parallel film with a thickness H_f and a radius r_f and two lateral surfaces having a constant average curvature and a constant interfacial tension. The excess amounts of the thermodynamic quantities are then referred to the contact (dividing according to Gibbs[11]) line separating the plane-parallel region of the film from the bulk phase α. For example, the concept of the linear tension, which represents the excess free energy of the film referred to a unit length of the contact line, has thus arisen.[12–14]

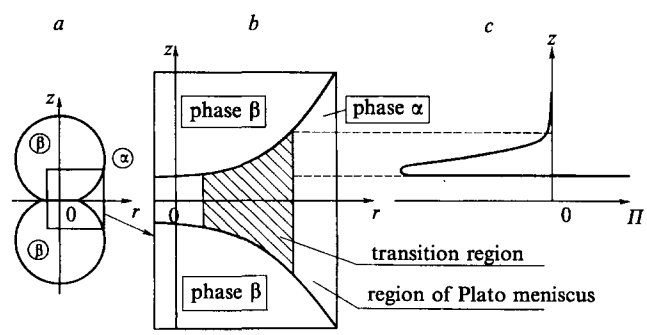


Figure 1. Thermodynamics of liquid films (see text): (*a*) a symmetrical microscopic liquid (emulsion or foam) film arises between two identical flowing (liquid or gaseous) particles of a phase β in a liquid phase α; (*b*) in a symmetrical liquid film one can distinguish a central plane-parallel region, the transition region, and the region of the bulk-phase meniscus of the phase α; (*c*) the disjoining pressure $\Pi(H)$ isotherm in the transition region ($H = 2z$ is the local thickness of the film in the transition region).

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represents the excess free energy of the film referred to a unit length of the contact line, has thus arisen.[12-14]

At the same time, it is evident that the use of idealised (reference according to Gibbs[11]) thermodynamic models, which is undoubtedly convenient in a formal thermodynamic description of thin liquid films, does not solve the problem of calculating the excess quantities arising under these conditions (for example, the linear tension) in the films. It is therefore necessary to devise the thermodynamics of the transition region of thin liquid films. Such thermodynamics can be defined as a self-consistent and closed system of concepts and relations between parameters characterising the interfacial interaction in the transition region of the film (for example, the disjoining pressure) and other thermodynamic parameters and functions.[13-15] The thermodynamics of the transition region of the film reduces to the thermodynamics of plane-parallel films and the thermodynamics of free interfaces in the appropriate regions where determinations are carried out.[16]

Problems of the thermodynamics of plane-parallel liquid films, which constitute the basis for the construction of the thermodynamics of the transition region of the liquid films,[13,16,17] are discussed in this review.

II. Thermodynamics of planar free interfaces

We shall consider briefly the principal definitions and postulates of the thermodynamics of planar free interfaces, which in fact constitute the thermodynamics of thick plane-parallel liquid films where the interfaces bounding them do not interact by definition. The thermodynamics of such surfaces, developed by Gibbs,[11] has been described in detail in a number of publications.[8,18-23]

1. Description of the thermodynamic system

We shall consider, with reference to Fig. 2, a multicomponent two-phase thermodynamic system with a volume V containing two liquid phases, α and β (or a liquid phase β and a gaseous phase α) and a planar interface dividing them, whose area $A = Ll$, where L is the length and l the width. Under equilibrium conditions, the temperature T as well as the chemical potentials μ_i of the ith components ($i = 1, 2, ..., N$; N is the number of components) are equal in all parts of the system under consideration. We shall neglect the effect of the force of gravity, i.e. we shall assume that the hydrostatic pressures P_α and P_β in the macroscopic phases α and β are the same and equal to P.

We shall postulate that the right-hand wall of the cell is mobile and that it is acted upon by an external force f_e, which balances the forces of the interfacial tension σ_0 of the planar surface. If necessary, the chemical potentials μ_i of the ith components can be varied or kept constant with the aid of a material source v_i.

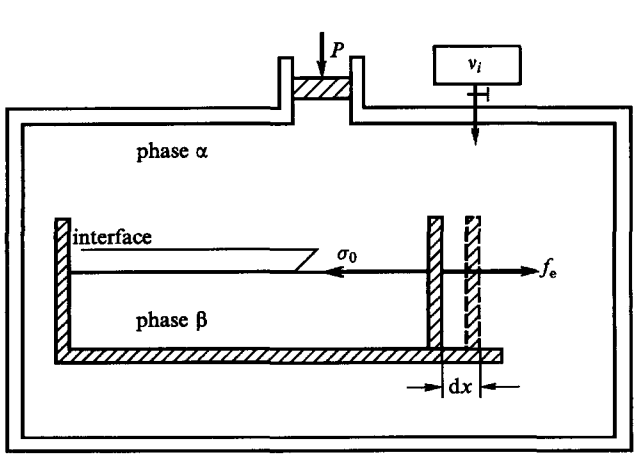


Figure 2. Thermodynamic system containing a flowing (liquid or gaseous) phase β, a liquid phase α, and the interface.

2. Hydrostatic description of the interface

Within the framework of local thermodynamics (which is also known as quasi-thermodynamics or microscopic thermodynamics[21]), one uses a hydrostatic description of the interface, in which the latter is represented as an anisotropic continuous medium in each microscopic volume for which the principal thermodynamic relations hold.[15,19,21-27]

Despite the artificiality of the concept of the interface as a continuous medium with a thickness of ~ 1 nm, such representation is internally consistent, i.e. it constitutes a non-contradictory system of concepts and equations and, furthermore, is extremely clear. In order to formulate the thermodynamic equations, it is necessary to define the concept of the hydrostatic pressure in the medium.

The components of the intermolecular interaction due to the thermal motion of the molecules, short-range forces (Born repulsion, hydrogen bonds), and long-range forces (van der Waals attraction, electrostatic interaction between the electrical double layers) are usually included in the pressure tensor.[28,29] The mechanical equilibrium in the mixture is then fully determined by this generalised hydrostatic pressure tensor and external (for example, gravitational) forces. Sometimes only the short-range intermolecular forces and thermal motion are included in the pressure tensor, with the assumption that the long-range forces are external with respect to the volume elements of the medium.[30-32]

The condition for mechanical equilibrium in the medium is formulated as follows within the framework of local thermodynamics:[8,19,21,22,27,33]

$$\operatorname{div} \boldsymbol{P} = 0, \tag{1}$$

where $\boldsymbol{P}$ is the generalised hydrostatic pressure tensor. In an isotropic medium, the tangential components of the pressure tensor are zero. The normal components of the tensor are equal to one another (Fig. 3*a*):

$$P_{xx} = P_{yy} = P_{zz} = P.$$

In a continuous anisotropic medium, with the aid of which the transition region of the interface is modelled, the tangential components of the pressure tensor are also zero, and the normal components are

$$P_{zz} = P_N(z), \quad P_{xx} = P_{yy} = P_T(z).$$

The qualitative dependence of the components of the pressure tensor $P_N(z)$ and $P_T(z)$ on the coordinate z in the case of a planar interface is presented in Figs. 3*b* and 3*c*. In the region of the bulk phases α and β, these components are equal: $P_N = P_T = P$. In the transition layer with a thickness δ, the component P_N does not change and remains equal to P, while $P_T(z)$ becomes negative and greatly exceeds the compressive pressure P in absolute magnitude. We may note that, in the case of a curved interface, the component

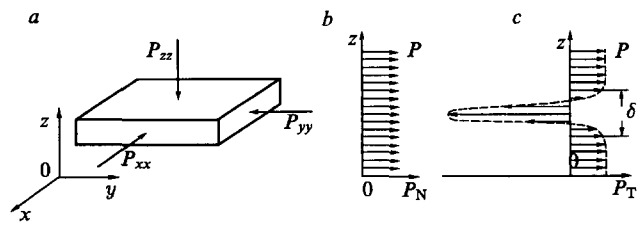


Figure 3. Description of the interface in terms of local thermodynamics: (*a*) different components of the hydrostatic pressure tensor in a system containing an interface; (*b*) and (*c*) dependence of the components P_N and P_T of the hydrostatic pressure tensor on the coordinate z.

P_N does vary in the transition layer with a thickness δ but remains positive (i.e. the pressure P_N remains compressive).

3. Fundamental equation of a system containing a planar free interface

When the mobile lateral wall of the cell (see Fig. 2) moves by dx, the area of the interface increases by $dA = l\,dx$, and the external force f_e executes an amount of work

$$dW_\sigma = \sigma_0\,dA. \tag{2}$$

The volume of the system V may then change by dV and the work performed by forces external to the system is

$$dW_P = -P\,dV. \tag{3}$$

Furthermore, as a result of adsorption on the newly formed surface, the number of moles N_i of the ith components changes by dN_i and the amount of work then performed is

$$dW_\mu = \sum_i \mu_i\,dN_i. \tag{4}$$

Thus the Helmholtz free energy of the system changes by

$$dF = -S\,dT + \sum_i \mu_i\,dN_i - P\,dV + \sigma_0\,dA, \tag{5}$$

where S is the entropy of the system. Eqn. (5) is called the fundamental equation of a system containing a planar free interface.

In the study of the mechanical equilibrium in the energy properties of liquid films, it is convenient to operate with the intensive variables T and μ_i instead of T and N_i. Instead of the Helmholtz free energy F, one therefore uses the grand thermodynamic potential

$$\Omega = F - \sum_i \mu_i N_i,$$

whose differentiation and combination of the resulting expression with Eqn. (5) yields the fundamental equation of the system under consideration in the form

$$d\Omega = -S\,dT - \sum_i N_i\,d\mu_i - P\,dV + \sigma_0\,dA. \tag{6}$$

The following definitions of the interfacial tension σ_0 for a planar free interface follow from Eqns. (5) and (6):

$$\sigma_0 = \left.\frac{\partial F}{\partial A}\right|_{T,V,N_i} = \left.\frac{\partial \Omega}{\partial A}\right|_{T,V,\mu_i}. \tag{7}$$

4. Thermodynamic description of the interface

The interface is described on the basis of different thermodynamic models. The Gibbs method of excess quantities, based on the modelling of the interface by the so-called dividing surface, i.e. an imaginary surface which has a zero thickness but is characterised by a finite surface energy, entropy, mass, etc. has come to be most widely used. This method is convenient also for thin liquid films.

The method based on a layer with a finite thickness, developed by Rusanov[18, 19] and Hansen,[34] and subsequently developed in the studies of Motomura,[35] Markin, Volkov,[36] and others, is convenient for the description of the physicochemical properties of adsorbed surfactant layers. On the other hand, this method is not used for interacting interfaces in thin liquid films.

Brief characteristics of these methods are given below from the standpoint of their possible extension to thin liquid films.

a. The dividing surface method

In this method, a real system with a volume V, containing an interface with a thickness δ (Fig. 4*a*), is replaced by an idealised model consisting of two reference phases α and β separated by a dividing surface of zero thickness and we have

$$V = V_\alpha + V_\beta, \tag{8}$$

where $V_\alpha = Al_\alpha$ and $V_\beta = Al_\beta$ are the volumes of the reference phases. The extensive parameters, the local densities of which change sharply in the transition region, are represented by the sum of the bulk-phase components and surface excess amounts:

$$S = S_\alpha + S_\beta + S_s, \tag{9}$$

$$N_i = N_{i\alpha} + N_{i\beta} + N_{is}, \tag{10}$$

$$\Omega = \Omega_\alpha + \Omega_\beta + \Omega_s, \tag{11}$$

where S_α and S_β, $N_{i\alpha}$ and $N_{i\beta}$, and Ω_α and Ω_β are respectively the bulk-phase entropies, numbers of moles of the ith components, and grand thermodynamic potentials of the reference phases α and β, while S_s, N_{is}, and Ω_s are the excess values of these quantities for the reference phases referred to the dividing surface.

Fundamental equation for a planar free dividing surface. Having substituted Eqns. (8)–(11) in the fundamental equation for system (6), we obtain

$$d\Omega = d\Omega_\alpha + d\Omega_\beta + d\Omega_s, \tag{12}$$

where

$$d\Omega_\alpha = -S_\alpha\,dT - \sum_i N_{i\alpha}\,d\mu_i - P\,dV_\alpha, \tag{13}$$

$$d\Omega_\beta = -S_\beta\,dT - \sum_i N_{i\beta}\,d\mu_i - P\,dV_\beta, \tag{14}$$

$$d\Omega_s = -S_s\,dT - \sum_i N_{is}\,d\mu_i + \sigma_0\,dA. \tag{15}$$

Eqns. (13)–(15) are fundamental for the reference phases α and β and the planar dividing surface respectively. The Gibbs method of excess quantities described here makes it possible to extract from the fundamental equation for a system containing a planar interface the so-called surface component, i.e. Eqn. (15), which describes the thermodynamic properties of the dividing surface. However, one should bear in mind that the excess amounts S_s and N_{is} depend on the location of the dividing surface. The method of establishing this location must be specially stipulated for an unambiguous thermodynamic description of the dividing surface. On the other hand, for constant T and μ_i, the interfacial tension σ_0, defined by the relation

$$\sigma_0 = \left.\frac{\partial \Omega_s}{\partial A}\right|_{T,\mu_i}, \tag{16}$$

is independent of the location of the interface, like the excess grand thermodynamic potential Ω_s. Indeed, bearing in mind that Ω_s is a homogeneous first-order function relative to the extensive parameter A for constant intensive parameters T and μ_i and applying Euler's theorem to Eqn. (15), we obtain

$$\Omega_s = \sigma_0 A. \tag{17}$$

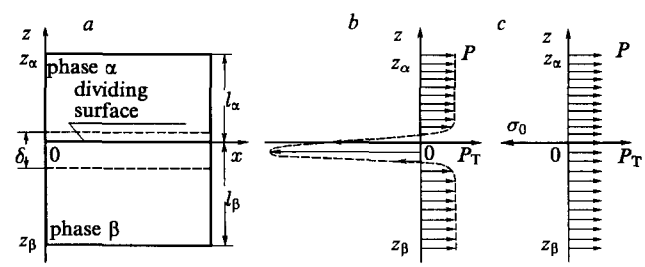


Figure 4. Illustration of the dividing surface (as defined by Gibbs) method in the thermodynamics of a planar free interface: (*a*) open system containing an interface; (*b*) dependence of the component P_T of the hydrostatic pressure tensor on z; (*c*) result of the replacement of the interface by a dividing surface.

In this connection we may note that, by virtue of the invariance of the function Ω_s as regards the choice of the dividing surface, its use for the thermodynamic description of the interface is preferable to the use of the Helmholtz free energy, whose excess amount

$$F_s = \sigma_0 A + N_i \mu_i, \tag{18}$$

depends on the position of the dividing surface.

The Gibbs–Duhem equation. On differentiating Eqn. (17) and combining it with Eqn. (15), we obtain the familiar Gibbs–Duhem equation for a planar free dividing surface:

$$d\sigma_0 = -S_s\, dT - \sum_i \Gamma_i\, d\mu_i, \tag{19}$$

where $S_s = S_s/A$ and $\Gamma_i = N_{is}/A$ are the specific excess entropy and excess number of moles (adsorption) of the ith component referred to the dividing surface. If the procedure used to derive the Gibbs–Duhem equation is applied to the grand thermodynamic potential Ω of a system containing a planar free interface [see Eqn. (6)], we obtain the following expression:[35]

$$A\, d\sigma_0 = -S\, dT - \sum_i N_i\, d\mu_i + V\, dP. \tag{20}$$

Hydrostatic representation of the interfacial tension. Within the framework of the ideas of local thermodynamics it is possible to express the force f with which the system acts on a surface area element $\Delta A = z_\alpha z_\beta l$ (where $l = 1$) of a mobile wall (see Fig. 4*a*) by the component $P_T(z)$ of the pressure tensor in terms of the relation (Fig. 4*b*):

$$f = \int_{z_\beta}^{z_\alpha} P_T(z)\, dz. \tag{21}$$

When the real system is replaced by an idealised system containing two reference phases α and β and the dividing surface, the corresponding force f^{id} (Fig. 4*c*) is

$$f^{id} = \int_{z_\beta}^{z_\alpha} P dz - \sigma_0. \tag{22}$$

The minus sign of σ_0 reflects the direction of the action of the interfacial tension.

The familiar Bakker formula[37] for the interfacial tension of a planar free dividing surface can be obtained from the condition for the mechanical equivalence of the real and idealised systems, i.e. from the conditions $f = f^{id}$:

$$\sigma_0 = \int_{-\infty}^{+\infty} [P - P_T(z)] dz, \tag{23}$$

where the integration limits have been replaced by infinity, bearing in mind that outside the transition region with thickness δ we have the equality $P_T(z) = P$.

The influence of pressure on the interfacial tension. According to Gibbs,[11] the derivative $(\partial\sigma_0/\partial P)_T$ represents a volume decrement associated with the specific expansion of the interface. Such interpretation of the $\sigma_0(P)$ relation apparently follows from the Gibbs–Duhem equation [Eqn. (20)], which can be transformed into

$$d\sigma_0 = -\frac{S}{A} dT - \left(\frac{\Gamma_1}{n_{1\alpha}} \frac{1-\varphi_2}{1-\varphi_1\varphi_2} + \frac{\Gamma_2}{n_{2\beta}} \frac{1-\varphi_1}{1-\varphi_1\varphi_2}\right) dP + \sum_{i=3}^{N} \left(\frac{\Gamma_1}{n_{1\alpha}} \frac{n_{i\alpha} - \varphi_2 n_{2\beta}}{1-\varphi_1\varphi_2} + \frac{\Gamma_2}{n_{2\beta}} \frac{n_{i\beta} - \varphi_1 n_{i\alpha}}{1-\varphi_1\varphi_2} - \Gamma_i\right) d\mu_i, \tag{24}$$

by eliminating the intensive parameters μ_1 and μ_2 (it is assumed that the components $i = 1$ and $i = 2$ correspond to water and oil molecules), where $n_{i\alpha} = N_{i\alpha}/V_\alpha$ and $n_{i\beta} = N_{i\beta}/V_\beta$, $\varphi_1 = n_{1\beta}/n_{1\alpha}$, and $\varphi_2 = n_{2\alpha}/n_{2\beta}$. If one considers a two-component system in which the two components are immiscible, for example with $n_{1\beta} = 0$ and $n_{2\alpha} = 0$, then we obtain from Eqn. (24):[38]

$$\left.\frac{\partial\sigma_0}{\partial P}\right|_T = -\left(\frac{\Gamma_1}{n_{1\alpha}} + \frac{\Gamma_2}{n_{2\beta}}\right). \tag{25}$$

If the dividing surface has been chosen in such a way that either $\Gamma_1 = 0$ or $\Gamma_2 = 0$, we obtain from Eqn. (25)

$$\left.\frac{\partial\sigma_0}{\partial P}\right|_T = -\frac{\Gamma_2}{n_{2\beta}} = -\frac{\Gamma_1}{n_{1\alpha}}. \tag{26}$$

Since $v_1 = 1/n_{1\alpha}$ and $v_2 = 1/n_{2\beta}$ are the molar volumes of components 1 and 2 respectively and the quantities Γ_1 and Γ_2 have the dimensions mol m^{-2}, the right-hand side of Eqn. (26) has the dimensions $m^3\, m^{-2}$ and has therefore been interpreted by Gibbs[11] as a decrease in volume associated with the specific expansion of the interface.

At the same time, one should note that, since the signs of Γ_1 and Γ_2 are not known beforehand, one cannot say whether the interfacial tension σ_0 will increase or decrease with increase in P. This applies also to the specific change in the volume of the interface.

The experimental results obtained from measurements of the $\sigma_0(P)$ relation are contradictory: a negative value $(\partial\sigma_0/\partial P)_T = -0.07$ Å has been obtained[39] for the benzene–water systems; a positive value $(\partial\sigma_0/\partial P)_T \simeq +0.025$ Å has been found[38,40–42] for the hexane–water system, and this decreased to +0.01 Å after the addition of tetradecanol to the system.[35] It follows from Eqn. (23) that, with increase in pressure, the interfacial tension should not change if the interfacial layer is liquid-like. In this case, an increase in hydrostatic pressure is transmitted in all directions without change, i.e. P and $P_T(z)$ increase by the same amount, and the integral (23) does not change.

On the other hand, if the structure of the layer is such that it exhibits 'solid-like' properties, the increase in σ_0 with increase in the pressure P is induced by the 'shielding' effect. Indeed, if it is assumed that the increase in pressure dP is not transmitted at all to the narrow transitional interfacial layer (Fig. 4), then the depth of the minimum in the $P_T(z)$ curve does not change and the external force acting on the mobile wall from the right increases. In this case, the derivative $(\partial\sigma_0/\partial P)_T$ has the physical significance of the thickness of the interfacial layer. If the interfacial layer is structured but not so much that it can be regarded as 'solid-like', then its effective thickness

$$h_f = \left(\frac{\partial\sigma_0}{\partial P}\right)_T, \tag{27}$$

is less than δ.

In connection with the proposed interpretation of the influence of hydrostatic pressure P on the interfacial tension σ_0 we may note that the results of Motomura and coworkers[35,40–42] agree with the conclusion that σ_0 should increase with increase in P for a two-component system. It has been shown[42] that in the water–hexane–octadecanol system the interfacial tension σ_0 decreases with increase in P and the decrease is fairly considerable $[(\partial\sigma_0/\partial P)_T = -2$ Å] in the phase transition from extended octadecanol monolayers to condensed (i.e. 'solid-like') monolayers. This result conflicts with the proposed interpretation of the influence of P on σ_0.

b. The method based on a layer with a finite thickness

This method[6,18,19] is based on the replacement of a real system with a volume V, containing a planar interface, by an idealised system incorporating two phases, α and β, with volumes $V_\alpha^f = l_\alpha A$ and $V_\beta^f = l_\beta A$ respectively (Fig. 5*a*) and a layer with a thickness h_f and a volume $V_f = h_f A$ dividing them, i.e.

$$V = V_\alpha + V_\beta + V_f. \tag{28}$$

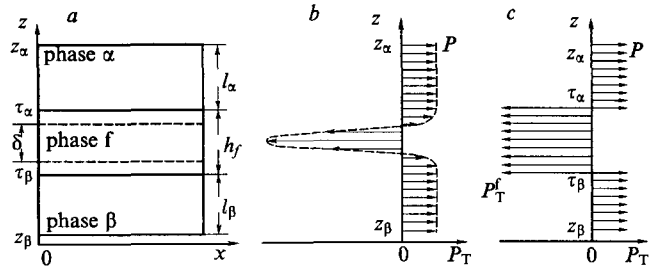


Figure 5. Illustration of the method of the finite thickness layer method in the thermodynamics of a planar free interface: (*a*) open system containing an interface; (*b*) dependence of the component P_T of the hydrostatic pressure tensor on z; (*c*) result of the replacement of the interface by a layer of finite thickness.

The extensive parameters S, N_i, and Ω are also represented by sums of the corresponding bulk-phase components referring to the reference phases α and β and of the excess amounts S_f, N_{if}, and Ω_f referring to the volume V_f of a layer having a finite thickness, i.e.

$$S = S_\alpha + S_\beta + S_f, \tag{29}$$

$$N_i = N_{i\alpha} + N_{i\beta} + N_{if}, \tag{30}$$

$$\Omega = \Omega_\alpha + \Omega_\beta + \Omega_f. \tag{31}$$

Fundamental equation of a layer with a finite thickness. Having substituted Eqns. (28)–(31) in the fundamental equation for the system [Eqn. (6)], we obtain

$$d\Omega = d\Omega_\alpha + d\Omega_\beta + d\Omega_f, \tag{32}$$

where

$$d\Omega_\alpha = -S_\alpha\,dT - \sum_i N_{i\alpha}\,d\mu_i - P\,dV_\alpha, \tag{33}$$

$$d\Omega_\beta = -S_\beta\,dT - \sum_i N_{i\beta}\,d\mu_i - P\,dV_\beta, \tag{34}$$

$$d\Omega_f = -S_f\,dT - \sum_i N_{if}\,d\mu_i - P\,dV_f + \sigma_0\,dA. \tag{35}$$

Eqns. (33)–(35) are fundamental for the reference phases α and β and the layer with a finite thickness, respectively.

Hydrostatic description of the layer with a finite thickness. The force f with which the real system acts on the mobile wall is described by Eqn. (21). For the description of the force f^{id} with which the idealised system, containing a layer with a finite thickness h_f, acts on the same surface element of the wall, one has to refine the concept of the layer. If the layer is assumed to be a formation uniform along its thickness and characterised by constant volume densities of the thermodynamic quantities, for example, the entropy

$$s_f = \frac{S_f}{V_f}, \tag{36}$$

and the number of moles of the ith component

$$n_i = \frac{N_{if}}{V_f}, \tag{37}$$

but anisotropic as regards mechanical properties [for example, the layer is extended by the operation of the pressure $P_T^f = P_{xx} = P_{yy}$ (Fig. 5*c*)], then the force f^{id} can be formulated thus:

$$f^{id} = \int_{z_\beta}^{\tau_\beta} P\,dz + \int_{\tau_\beta}^{\tau_\alpha} P_T^f\,dz + \int_{\tau_\alpha}^{z_\alpha} P\,dz, \tag{38}$$

where τ_α and τ_β are the coordinates of the upper and lower surfaces of the layer with $h_f = \tau_\alpha - \tau_\beta$. Taking into account Eqn. (23), we obtain from the condition for the mechanical equivalence of the systems $f = f^{id}$

$$P_T^f h_f = P h_f - \sigma_0. \tag{39}$$

Having substituted Eqn. (39) in Eqn. (35), we find the fundamental equation for a layer of finite thickness:

$$d\Omega_f = -S_f\,dT - \sum_i N_{if}\,d\mu_i - PA\,dh_f - P_T^f h_f\,dA. \tag{40}$$

If it is assumed that a layer uniform with respect to its thickness and having a volume V_f is a liquid phase, then the hypothesis that its properties are anisotropic is unjustified (an isotropic pressure P operates in the liquid phase). In this case, we are forced to consider two dividing surfaces[43] to which the excess pressure P_T^f is referred, assuming that the pressure in the layer is isotropic and equal to P. We may note that the excess amounts of the other thermodynamic quantities are referred to a layer with a thickness h_f, i.e. only the excess pressure, which we shall call the interfacial tension σ_0, is referred to two dividing surfaces.

For this representation of a layer of finite thickness, the force acting on a surface element of the mobile wall is

$$f^{id} = \int_{z_\alpha}^{z_\beta} P\,dz - \sigma_0. \tag{41}$$

From the condition for the mechanical equivalence of the systems $f = f^{id}$, we obtain an expression for σ_0 which agrees in form with Eqn. (23). However, in this case it is implied that both dividing surfaces are equivalent as regards mechanical properties (unless the difference between them is specially stipulated), i.e. it is assumed that

$$\sigma_0 = \sigma_{0\alpha} + \sigma_{0\beta}, \tag{42}$$

where $\sigma_{0\alpha}$ and $\sigma_{0\beta}$ are the interfacial tensions of the dividing surfaces of finite thickness.

Hansen's method. Hansen[34] proposed a modified finite thickness layer method for the description of systems with a planar interface. He used the model of a layer containing a liquid phase and two dividing surfaces which are placed in such a way that the degrees of adsorption Γ_1 and Γ_2 of the components, which are solvents for phases α and β respectively, are zero. The distance between such dividing surfaces with the coordinates τ_α^H and τ_β^H is

$$\tau^H = \tau_\alpha^H - \tau_\beta^H. \tag{43}$$

By applying to Eqns. (33)–(35) the procedure used to obtain equations of the Gibbs–Duhem type, we obtain

$$s_\alpha\,dT + n_{1\alpha}\,d\mu_1 + n_{2\alpha}\,d\mu_2 + \sum_{i=3}^{N} n_{i\alpha}\,d\mu_i = dP, \tag{44}$$

$$s_\beta\,dT + n_{1\beta}\,d\mu_1 + n_{2\beta}\,d\mu_2 + \sum_{i=3}^{N} n_{i\beta}\,d\mu_i = dP, \tag{45}$$

$$-d\sigma_0 = \frac{S_f}{A}dT + \tau^H n_{1f}\,d\mu_1 + \tau^H n_{2f}\,d\mu_2 + \sum_{i=3}^{N}\frac{N_{if}}{A}d\mu_i - \tau^H\,dP, \tag{46}$$

where $n_{1\alpha} = N_{i\alpha}/V_\alpha$, $n_{i\beta} = N_{i\beta}/V_\beta$, $n_{if} = N_{if}/V_f$, $V_f = A\tau^H$, and $s_{\alpha,\beta} = S_{\alpha,\beta}/V_{\alpha,\beta}$.

Assuming that $n_{1f} = n_{1\beta}$ and $n_{2f} = n_{2\alpha}$, which is equivalent to the conditions $\Gamma_1 = 0$, $\Gamma_2 = 0$, and $\varphi_1 = n_{1\beta}/n_{1\alpha}$, $\varphi_2 = n_{2\alpha}/n_{2\beta}$, we obtain from Eqns. (44)–(46)

$$d\sigma_0 = -s_f\,dT + \frac{(1-\varphi_1)(1-\varphi_2)}{1-\varphi_1\varphi_2}\tau^H\,dP - \sum_{i=3}^{N}\left[\Gamma_i - \frac{\varphi_1(n_{i\alpha}-\varphi_2 n_{i\beta}) + \varphi_2(n_{i\beta}-\varphi_1 n_{i\alpha})}{1-\varphi_1\varphi_2}\right]d\mu_i, \quad (47)$$

where $\Gamma_i = N_{if}/A$, and $s_f = S_f/A$.

In the case of a two-component system, the following relation follows from Eqn. (47):

$$d\sigma_0 = -s_f\,dT + \frac{(1-\varphi_1)(1-\varphi_2)}{1-\varphi_1\varphi_2}\tau^H\,dP, \quad (48)$$

For immiscible components (for example, for component 1, forming phase α, and component 2, forming phase β) and when account is taken of the conditions $\varphi_1 = \varphi_2 = 0$, Eqn. (48) is converted into

$$d\sigma_0 = -s_f\,dT + \tau^H\,dP. \quad (49)$$

In this case,[34,35] the distance between the dividing surfaces, for which $\Gamma_1 = 0$ and $\Gamma_2 = 0$, is

$$\tau^H = \left.\frac{\partial\sigma_0}{\partial P}\right|_T, \quad (50)$$

which agrees with the result obtained by Good and Buff.[38] The expression obtained agrees with the conclusion reached by Gibbs,[11] who noted that the derivative $(\partial\sigma_0/\partial P)_T$ characterises the distance between the two equimolecular surfaces. Having compared Eqn. (50) with Eqn. (26), we obtain

$$\tau^H = -\left.\frac{\Gamma_2}{n_{2\beta}}\right|_{\Gamma_1=0} = -\left.\frac{\Gamma_1}{n_{1\alpha}}\right|_{\Gamma_2=0}. \quad (51)$$

In the case of a three-component system (for example, water–oil–surfactant) subject to the additional condition that the oil and water are immiscible, Eqn. (47) gives rise to the following relation:[34,35]

$$d\sigma_0 = -s_f\,dT - \Gamma_3\,d\mu_3 + \tau^H\,dP. \quad (52)$$

In this representation, a layer with a thickness τ^H is filled solely with component 3 (i.e. the surfactant) and can be regarded as a phase. Attention must be drawn to the fact that the quantity τ^H, defined by Eqn. (43), may be negative (even in the absence of a surfactant or for a constant μ_3), whereupon the concept of a layer with a finite thickness τ^H and filled with the surfactant is not quite so clear. In particular, it has been found[42] for the water–hexane–octadecanol system that σ_0 diminishes from 35 to 25 mJ m^{-2} with increase in P from 0.1 to 50 MPa for a constant mole fraction of the surfactant in the oil $x_3 = 2.21 \times 10^{-3}$. Since the chemical potential μ_3 changes with increase in pressure, Motomura[35] suggested that one goes over to the variables T, P, and x_3 (the mole fraction of component 3 in one of the phases) by replacing μ_3 in Eqn. (52) by x_3 in accordance with the relation

$$d\mu_3 = \frac{\partial\mu_3}{\partial T}dT + \frac{\partial\mu_3}{\partial P}dP + \frac{\partial\mu_3}{\partial x_3}dx_3. \quad (53)$$

Then instead of Eqn. (52), we obtain at a constant temperature T

$$d\sigma_0 = \left(\tau^H - \Gamma_3\frac{\partial\mu_3}{\partial P}\right)dP - \Gamma_3\frac{\partial\mu_3}{\partial x_3}dx_3. \quad (54)$$

If the solvent is ideal in relation to the surfactant, one can write[35]

$$\mu_3 = \mu_3^0(T,P) + RT\ln x_3, \quad (55)$$

and instead of Eqn. (54) we have

$$d\sigma_0 = \left(\tau^H - \Gamma_3\frac{\partial\mu_3^0}{\partial P}\right)dP - RT\Gamma_3\,d\ln x_3, \quad (56)$$

where μ_3^0 is the standard value of the chemical potential μ_3, i.e. its value at $x_3 = 1$. Since $\partial\mu_3^0/\partial P$ can be interpreted as the volume of one surfactant molecule $v_3 \simeq 10^{-29}$ m^3 and the adsorption Γ_3 is $\sim 10^{-6}$ mol m^{-2}, the product $\Gamma_3(\partial\mu_3^0/\partial P)$ in Eqn. (56) increases from 0 to ~ 1 Å with increase in x_3 from 0 to the value corresponding to a surfactant monolayer on the interface.

If the thickness of the layer τ^H does not change as x_3 increases, then the quantity

$$\tau_*^H = \tau^H - \Gamma_3\frac{\partial\mu_3}{\partial P} = \left.\frac{\partial\sigma_0}{\partial P}\right|_{T,x_3} \quad (57)$$

should diminish with increase in x_3, which was observed by Motomura and coworkers[35,40–42] for tetradecanol and octadecanol. However, for a water-soluble surfactant (NaDDS) τ_*^H does not vary with increase in x_3,[41] which may indicate the simultaneous increase in τ^H in Eqn. (57). Furthermore, an abrupt decrease in τ_*^H from positive ($\sim +0.2$) to negative (~ -0.2) values at a certain critical pressure P has been observed for octadecanol, which has been attributed[35–41] to a phase transition within the surfactant adsorption layer.

Thus the finite thickness layer method, in particular Hansen's method improved by Motomura,[35] permits certain definite conclusions concerning the structure of interfacial (adsorption) layers. On the other hand, the mechanism of the influence of hydrostatic pressure P on the interfacial tension σ_0 is not entirely clear. For example, it follows from Eqn. (49) that a layer with a thickness τ^H is 'solid-like' (if one uses the ideas of local thermodynamics), i.e. an increase in pressure in the bulk phase is not transmitted to the mobile wall in contact with this layer (Fig. 2). The interfacial layer with a thickness τ^H as it were shields the wall from the external pressure and an increase in pressure dP leads to an increase in interfacial tension by $d\sigma_0 = \tau^H\,dP$. The decrease in σ_0 with increase in P proves to be difficult to express in terms of local thermodynamics, since it is not clear why an increase in pressure leads in this instance to a marked decrease in the depth of the minimum on the $P_T(z)$ curve (Fig. 3), which is greater than the increase in P in the system.

III. Thermodynamics of plane-parallel thin liquid films

1. Definition of a thermodynamic system incorporating a thin liquid film

We shall consider a system (Fig. 6) incorporating a plane-parallel liquid film with an area A fixed on a rigid frame which can be moved without friction by an external force f_e.[10,13,44] The film is in mechanical equilibrium with the flowing (liquid or gaseous) phase β surrounding it and the liquid phase α from which it is formed. The chemical potentials μ_i of the ith components are equal in all the phases of the system and in the film. The external force f_e is balanced by the tension of the film γ. A force f_α is applied to the left-hand piston. With its aid, the pressure P_α within phase α in this piston is controlled. The chemical potentials (the numbers of moles of the components) can be varied with the aid of a material source ν_i.

An open subsystem with a volume V (Fig. 6) (containing phase β and the film element) in thermal, material, and mechanical equilibrium with the system considered above is examined simultaneously.

2. Fundamental equation of a system containing a thin liquid film

If the variable parameters of the system are the temperature T, the volume of the system V, the area of the film A, and the number of moles N_i of the ith component, then the fundamental equation for such a system can be written in the form[4,9,10,13,45]

$$dF = -S\,dT - P_\beta\,dV + \sum_i \mu_i\,dN_i + \gamma\,dA.$$

In terms of the variables T, V, μ_i, and A, the fundamental equation for the system becomes[13, 16, 46, 47]

$$d\Omega = -S\,dT - P_\beta\,dV - \sum_i N_i\,d\mu_i + \gamma\,dA, \tag{58}$$

where $\Omega = F - \sum \mu_i N_i$ is the grand thermodynamic potential and F is the Helmholtz free energy of the system.

3. Membrane model of a thin liquid film

By analogy with Gibb's approach[11] to the thermodynamic description of free interfaces, Deryagin and coworkers[1,2] developed the thermodynamics of thin liquid films using a membrane of zero thickness as the reference thermodynamic model of the film. They determined the excess thermodynamic quantities relative to this membrane.

Within the framework of this model, the volume of the system V is equal to the volume of the reference phase β, i.e. $V_\beta = V$, and one assumes arbitrarily that

$$N_i = N_{i\beta} + \tilde{N}_{if}, \tag{59}$$

$$S = S_\beta + \tilde{S}_f, \tag{60}$$

where $N_{i\beta}$ and S_β are the number of moles of the ith component and the entropy of the reference phase β, and $\tilde{N}_{if}$ and $\tilde{S}_f$ are the corresponding excess values of these quantities for the reference phase referred to the membrane. The free energy of the system Ω is also expressed by the sum

$$\Omega = \Omega_\beta + \tilde{\Omega}_f, \tag{61}$$

where Ω_β and $\tilde{\Omega}_f$ are the free energy of the reference phase β and the excess free energy referred to the membrane, respectively.

The fundamental equation (58) for the system is written in the form

$$d\Omega = d\Omega_\beta + d\tilde{\Omega}_f, \tag{62}$$

where

$$d\Omega_\beta = -S_\beta\,dT - P_\beta\,dV_\beta - \sum_i N_{i\beta}\,d\mu_i \tag{63}$$

is the fundamental equation of the reference phase β and

$$d\tilde{\Omega}_f = -\tilde{S}_f\,dT - \sum_i \tilde{N}_{if}\,d\mu_i + \gamma\,dA \tag{64}$$

is the fundamental equation for the membrane.

a. Hydrostatic pressure in a thin liquid film

A thin liquid film cannot be regarded as a phase because, as within the transition region of the interface, intensive thermodynamic parameters (such as the pressure and the densities of matter, internal energy, entropy, etc.) change sharply within it perpendicular to its plane. Within the framework of local thermodynamics,[26–29, 47, 48] thin liquid films are represented as an anisotropic medium in each microscopic volume of which the fulfillment of the principal thermodynamic relations is postulated. In particular, the fulfillment of the condition for mechanical equilibrium [condition (1)] is postulated, whereas in an isotropic medium the tangential components of the hydrostatic pressure tensor $\boldsymbol{P}$ are zero, while the normal components P_{xx}, P_{yy}, and P_{zz} are equal to the hydrostatic pressure P in the isotropic medium. As in interfaces (Fig. 3), the tangential components within the liquid film are zero, while the normal components (Fig. 7*a*) are

$$P_{xx} = P_{yy} = P_T(z), \tag{65}$$

$$P_{zz} = P_N = P. \tag{66}$$

In the case of a plane-parallel thin liquid film, the pressure tensor component P_N is independent of the coordinate z. Within curved thin liquid films of constant thickness, the pressure P_N varies, remaining nevertheless compressive (positive).

b. Film tension

In the membrane approach, the film tension γ is understood as the specific excess pressure $P_T(z)$ (per unit length) relative to the isotropic hydrostatic pressure P_β in the reference phase β acting in the direction tending to reduce the film area:[7, 9, 26–29, 45, 47, 48]

$$\gamma = -\int_{-\infty}^{+\infty} [P_T(z) - P_\beta]dz = -\int_{-\infty}^{+\infty} [P_T(z) - P_N]dz, \tag{67}$$

where the integration with respect to z is carried out in the region of the inhomogeneity of the film and the minus sign before the integral is selected in conformity with the definition of the film tension as the force tending to reduce the length of the film.

Fig. 7*b* shows that in the membrane approach the plane bounding the system on the right is acted upon by the pressure P_β directed to the right and the film tension γ directed to the left. These forces are balanced by the force of the pressure P_β acting on the plane from the right and by the external force f_e directed to the right. Thus the specific force (per unit length of the film) is equal in magnitude to the film tension γ.

The following definition of the film tension follows from the fundamental equation (64):

$$\gamma = \left.\frac{\partial \tilde{\Omega}_f}{\partial A}\right|_{\mu_i, T}, \tag{68}$$

$$\gamma = \left.\frac{\partial \Omega}{\partial A}\right|_{\mu_i, T, V_\beta}. \tag{69}$$

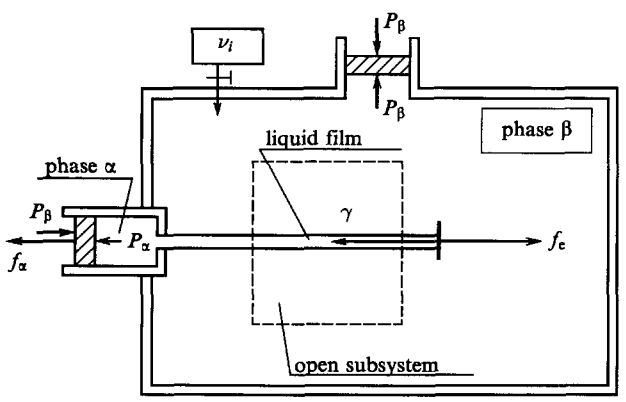


Figure 6. A closed system incorporating a flowing (liquid or gaseous) phase β and a plane-parallel liquid film formed from the liquid phase α.

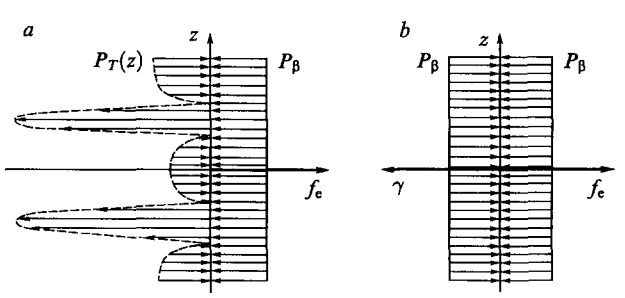


Figure 7. The membrane model of a liquid film: (*a*) equilibrium in a section of the vertical plane of the film holder acted upon by an external force f_e and the hydrostatic pressure P_β from the right and by the local pressure $P_T(z)$ from the direction of the film on the left; (*b*) result of the replacement of the film by a membrane of zero thickness.

This actually means that the film is stretched when the piston comprising the cylinder containing phase α is stationary (the volume of phase β is then also kept constant).

4. The model of the film based on the concept of two dividing surfaces

The thermodynamics of thin liquid films, based on this idea, was first worked out by Rusanov[3-5,8] and was subsequently developed in a number of other studies.[6,7,9,16,17,44-47]

In this model, the thin liquid film is represented by a thin layer of the reference phase α with a finite thickness H, separated from the external reference phase β by the dividing surfaces (as defined by Gibbs) (Fig. 8). The volume of the open subsystem V is equal to the sum of the volumes of the reference phase β and phase α from which the film has been obtained:

$$V = V_\beta + V_\alpha. \tag{70}$$

Under these conditions, $V_\alpha = V_f$, and $dV_\alpha = -dV_\beta$ (if V = const.) and the following relation also holds:

$$dV_f = dV_\alpha = A\,dH + H\,dA. \tag{71}$$

The grand thermodynamic potential of the system Ω is now formulated as the sum

$$\Omega = \Omega_\beta + \Omega_\alpha + \tilde{\Omega}_s, \tag{72}$$

where Ω_β and Ω_α are the free energies of the reference phases β and α respectively and $\tilde{\Omega}_s$ is the excess grand thermodynamic potential for the reference phases β and α referred to the two dividing surfaces.

The fundamental equation for the system is written in the form

$$d\Omega = d\Omega_\beta + d\Omega_\alpha + d\tilde{\Omega}_\sigma, \tag{73}$$

where the fundamental equations for phases β and α are respectively

$$d\Omega_\beta = -S_\beta\,dT - \sum_i N_{i\beta}\,d\mu_i - P_\beta\,dV_\beta, \tag{74}$$

$$d\Omega_\alpha = -S_\alpha\,dT - \sum_i N_{i\alpha}\,d\mu_i - P_\alpha\,dV_\alpha, \tag{75}$$

where P_α is the pressure in phase α, which is the reference phase for the film:

$$S = S_\beta + S_\alpha + \tilde{S}_s, \tag{76}$$

$$N_i = N_{i\beta} + N_{i\alpha} + \tilde{N}_{is}. \tag{77}$$

Here $\tilde{S}_s$ and $\tilde{N}_{is}$ are the excess entropy and the excess number of moles of the ith component respectively for the reference phases β and α relative to the two dividing surfaces.

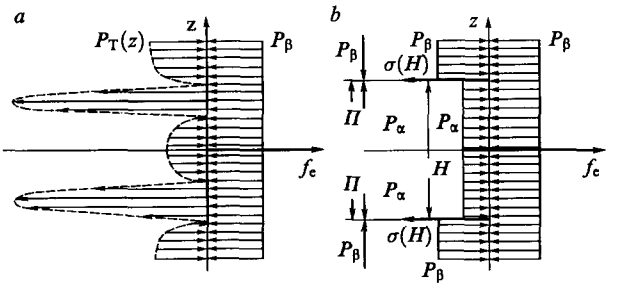


Figure 8. Illustration of the model of the liquid film based on the concept of two dividing surfaces in the film: (*a*) equilibrium in the film holder acted upon by $P_T(z)$, P_β, and f_e; (*b*) result of the replacement of the film by an idealised model comprising two interacting dividing surfaces and a layer of phase α having a thickness H.

The fundamental equations for two interacting dividing film surfaces is obtained from Eqns (58), (70), and (73)–(77):[13,16,47]

$$d\tilde{\Omega}_s = -\tilde{S}_s\,dT - \sum_i \tilde{N}_{is}\,d\mu_i - (P_\beta - P_\alpha)\,dV_\alpha + \gamma\,dA. \tag{78}$$

Taking into account Eqn. (71) as well as the definition of the disjoining pressure[28,29]

$$\Pi = P_\beta - P_\alpha, \tag{79}$$

and the definition[5,8,17,44] of the interfacial tension $\sigma(H)$ in a film with a thickness H, i.e.

$$\gamma = 2\sigma + \Pi H, \tag{80}$$

the fundamental equation for interacting dividing surfaces was obtained:[16]

$$d\tilde{\Omega}_s = -\tilde{S}_s\,dT - \sum_i \tilde{N}_{is}\,d\mu_i - \Pi A\,dH + 2\sigma\,dA. \tag{81}$$

a. The disjoining pressure in a liquid film

According to the formal definition, the disjoining pressure Π in a film[28,29] is equal to the difference between the hydrostatic pressures in the two reference phases β and α under the conditions of the equilibrium between the film and these phases. Since, as shown above [see Eqn. (66)], the normal component of the pressure $P_{zz} = P_N$ in the film is equal to the pressure P_β in phase β, Eqn. (79) can be rewritten in the following form:

$$\Pi = P_N - P_\alpha, \tag{82}$$

which corresponds best, according to a number of workers,[6,7,8,20,28,29] to the physical significance of the disjoining pressure.

There exist two points of view on the interpretation of the physical significance of the disjoining pressure Π. One group of workers[9,28,29,45,49,50] understand the disjoining pressure as the manifestation of forces of the 'second kind',[28,29,51] which arise in the region of the mutual overlap of the "surface forces of the first kind", i.e. two interfacial discontinuity surfaces (dividing surfaces according to Gibbs). The disjoining pressure is then represented as a pressure acting within the bulk of the film and existing, as it were, independently of the dividing surfaces of the film. The dividing surfaces are assumed not to interact with one another, so that the interfacial tension remains constant in magnitude as the film thickness diminishes and is equal to σ_0 (i.e. to the interfacial tension of the boundary of the bulk phases). The reference pressure in the film (the Gibbs reference pressure) chosen in some investigations[9,45,50] is not the hydrostatic pressure P_α but the hydrostatic pressure P_β. It has been shown[16] that this choice of reference pressure leads to the appearance of a pressure gradient in the transition region of the film and to difficulties in the determination of the disjoining pressure in this region.

The second group of workers[10,13,14,16,17,44,52-54] use the concept of the disjoining pressure as a specific force (per unit area) of the interaction between the dividing surfaces in the film. The chosen reference phase and pressure in the film are α and P_α respectively, so that a pressure gradient does not arise in the transition region of the film.[16]

The interfacial tension $\sigma(H)$ corresponding to this concept of the pressure is a function of the film thickness H. The following expression for the disjoining pressure arises from the fundamental Eqn. (81):

$$\Pi = -\frac{1}{A}\left.\frac{\partial\tilde{\Omega}_s}{\partial H}\right|_{T,\mu_i,A}, \tag{83}$$

where $\tilde{\Omega}_s$ has the significance of the excess free energy of the interacting dividing surfaces in a film with a thickness H. The function $\Pi(H)$ is called the isotherm of the disjoining pressure in the film. Despite the fact that the film thickness was chosen arbitrarily, the disjoining pressure is independent of the choice of the parameter H, i.e. is invariant for a fixed physical state of the film (is determined by the parameters T, μ_i, P_α, and P_β).

b. The interfacial tension in a thin liquid film

According to the definition, the interfacial tension σ [Eqn. (80)] depends on the choice of the positions of the dividing surfaces in the film (i.e. on the parameter H) for a fixed physical state of the film. If the film tension γ and the disjoining pressure Π are invariant and independent of the parameter H for the constant T, μ_i, P_α, and P_β, then σ depends linearly on H:

$$2\{\sigma\} = \gamma - \Pi\{H\}, \tag{84}$$

(the braces denote that the parameter H varies virtually for a fixed physical state of the system).

The interfacial tension σ is by definition the specific (referred to unit length) excess pressure $P_T(z)$ from the reference phases β and α compared with the isotropic pressures P_β and P_α in the reference phases relative to the dividing surfaces[6,9,10,16] (Fig. 8):

$$2\sigma(H) = -\int_{-\infty}^{-H/2} [P_T(z) - P_\beta]\,dz - \int_{-H/2}^{+H/2} [P_T(z) - P_\alpha]\,dz - \int_{+H/2}^{+\infty} [P_T(z) - P_\beta]\,dz. \tag{85}$$

If the film thickness really increases, which may be indicated by a decrease in the difference between the hydrostatic pressures $\Pi = P_\beta - P_\alpha$ (for $P_\beta \geqslant P_\alpha$), then it follows from Eqn. (67) that the film tension γ also varies and tends to γ_0, corresponding to the condition $\Pi = 0$. Then, according to Eqn. (80), the interfacial tension also tends to its limiting value σ_0 corresponding to the absence of interaction between the dividing surfaces and we have $\gamma_0 = 2\sigma_0$. As was to be expected, under these conditions the interfacial tension in such a thick liquid film is independent of the position of the dividing surfaces.

c. The specific free energy of the interaction in the film

For a real increase in film thickness from a certain value H to infinity for constant parameters T, μ_i, and A, the disjoining pressure executes an amount of work which is given by the following expression according to the fundamental Eqn. (81):

$$\tilde{\Omega}_s(\infty) - \tilde{\Omega}_s(H) = -A\int_H^\infty \Pi(H)\,dH. \tag{86}$$

Having put

$$\Delta\Omega(H) = \frac{\tilde{\Omega}_s(H) - \tilde{\Omega}_s(\infty)}{A}, \tag{87}$$

where $\Delta\Omega(H)$ is the specific (referred to unit surface area) free energy (grand thermodynamic potential) of the interaction between the dividing surfaces in a film with a thickness H, we obtain a relation which is valid for constant T, μ_i, and A:

$$\Delta\Omega(H) = \int_H^\infty \Pi(H)\,dH. \tag{88}$$

By putting

$$\tilde{S}_s = 2As_s, \tag{89}$$

$$\tilde{N}_{is} = 2A\Gamma_i, \tag{90}$$

we can rewrite the fundamental Eqn. (81) in the form

$$d\tilde{\Omega}_s = -2As_s\,dT - 2A\sum_i \Gamma_i\,d\mu_i - \Pi A\,dH + 2\sigma\,dA, \tag{91}$$

where s_s and Γ_i are the specific (referred to one of the dividing surfaces of a film with a thickness H) excess entropy and number of moles of the ith component respectively and Γ_i is referred to as the adsorption of the ith component on the film surface.

When the surfaces in the film are really moved apart an infinitely great distance, the disjoining pressure Π tends to zero and we obtain the following expression for free non-interacting surfaces in a plane-parallel film when account is taken of Eqn. (91):

$$d\Omega_s^0 = -2As_s^0\,dT - 2A\sum_i \Gamma_i^0\,d\mu_i + 2\sigma_o\,dA, \tag{92}$$

where the superscript 0 means that the corresponding quantity refers to a free planar surface.

By integrating the fundamental Eqn. (91) with respect to the film area A for constant T, μ_i, and H, we obtain[16]

$$\tilde{\Omega}_s(H) = 2\sigma(H)A. \tag{93}$$

If the film thickness is infinte in such integration (the case of non-interacting planar dividing surfaces), we have from Eqn. (92)

$$\tilde{\Omega}_s(\infty) = 2\sigma_o A. \tag{94}$$

An important relation of the thermodynamics of plane-parallel thin liquid films arises from Eqns. (86)–(88), (92)–(94):[16]

$$\Delta\Omega(H) = 2\Delta\sigma = 2\sigma(H) - 2\sigma_0 = \int_H^\infty \Pi(H)\,dH. \tag{95}$$

We recall that the definition (95) is valid for constant parameters T, μ_i, and A. Taking into account the relation between the grand thermodynamic potential Ω and the Helmholtz free energy F, i.e. $\Omega = F - \sum N_i\mu_i$, we obtain the following relation for the constant parameters indicated above:

$$\Delta F(H) = \Delta\sigma(H) - 2\sum_i \Delta\Gamma_i(H)\mu_i, \tag{96}$$

where

$$\Delta F(H) = \frac{F_s(H) - F_s(\infty)}{A}, \tag{97}$$

and

$$\Delta\Gamma_i(H) = \Gamma_i(H) - \Gamma_i(\infty), \tag{98}$$

Here $\Gamma_i(\infty)$ and $F_s(\infty)$ are the adsorption and the Helmholtz free energy of the non-interacting surfaces. Furthermore, the following relation holds:[16]

$$\Delta F(H) = \int_H^\infty \Pi(H)\,dA - 2\sum_i \Delta\Gamma_i(H)\mu_i. \tag{99}$$

d. The Gibbs–Duhem equation for a plane-parallel thin liquid film

On differentiating Eqn. (93) and combining the result with Eqn. (91), we obtain[13,16] the Gibbs–Duhem equation for interacting dividing surfaces in a thin liquid film with a thickness H:

$$2d\sigma = -2s_s\,dT - 2\sum_i \Gamma_i\,d\mu_i - \Pi\,dH, \tag{100}$$

which is converted into the familiar Gibbs–Duhem equation for free (non-interacting) planar surfaces:[11,23]

$$d\sigma_0 = -s_s^0\,dT - \sum_i \Gamma_i^0\,d\mu_i. \tag{101}$$

Evidently the disjoining pressure $\Pi(H)$ and the interfacial tension $\sigma(H)$ are linked by the relation

$$\Pi(H) = -2\left.\frac{\partial\sigma(H)}{\partial H}\right|_{T,\mu_i}, \tag{102}$$

which follows from Eqn. (100) and is also known as the Gibbs–Duhem equation for a plane-parallel film.

In thermodynamics based on the membrane approach, the Gibbs–Duhem equation

$$d\gamma = -s_f\,dT - \sum_i \Gamma_{if}\,d\mu_i, \tag{103}$$

is obtained from the fundamental Eqn. (64) in the same way as Eqn. (100), i.e. by integrating Eqn. (64) with respect to A for constant T and μ_i as well as P_α and P_β and subsequent differentiation and simultaneous solution with Eqn. (64). Here

$$s_f = \frac{\tilde{S}_f}{A}; \quad \Gamma_{if} = \frac{\tilde{N}_{if}}{A}, \tag{104}$$

are the specific (referred to unit area of a membrane of zero thickness) excess entropy and number of moles of the ith component.

We may note that s_f and Γ_{if} differ from the corresponding excess amounts s_s and Γ_i defined by Eqns. (89) and (90).

5. The film model based on the concept of a membrane of finite thickness

In the approach based on the concept of the film as a membrane of zero thickness, the film thickness naturally cannot be regarded as a thermodynamic parameter of the system. This approach can be used for the description of those experiments in which the film thickness H is not measured and the pressure in the reference phase α is also unknown.

If the change in the volume of the system dV can be measured experimentally with adequate accuracy (Fig. 6), then, for a known film area A, it is possible to determine the effective film thickness H^*. When the temperature T and the chemical potential μ_i of the ith components are kept constant, it is of interest to examine two situations.

1. If the hydrostatic pressure in phase β as well as the external force f_α are kept constant then, following an increase in the film area A by dA when the film is acted upon by f_e, the volume of the system increases by dV, while the effective film thickness can be determined from the relation

$$H^* = dV\,dA \quad .$$

The volume of the system then changes largely as regards the volume of phase α from which the film has been formed.

2. If the force f_α is constant (i.e. the pressure in phase α is constant although unknown) and the film area is likewise constant, then an increase in the pressure in phase β can lead to a measurable decrease in the volume of the system by an amount dV. This makes it possible to determine the change in the effective film thickness dH^* from the relation $dH^* = dV/A$. Furthermore, in the latter case it is possible to determine the change in the film tension γ, which is interpreted as the influence of the external pressure on the mechanical (energy) properties of the film.

We may note that in both cases it is assumed that the composition of phase α within the film and the constant pressure P_α are assumed to be unknown and the variable parameters are the pressure P_β, the temperature T, the chemical potentials μ_i of the ith components, and the film tension γ which is equal to the force f_e.

The film thermodynamics, based on the model of a membrane with a finite thickness, is constructed on the basis of the fundamental Eqn. (58) and the volume V of the open subsystem is represented by the sum

$$V = V_\beta + V_f, \tag{105}$$

where V_β is the volume of the reference phase β and V_f is the volume of the film which can be found by varying the volume of the reference phase β during the formation of a film having an area A for constant parameters T, μ_i, P_β, and P_α.

a. Fundamental equation for a membrane with a finite thickness

Having put the fundamental Eqn. (58) for an open subsystem containing a plane-parallel thin liquid film in the form

$$d\Omega = d\Omega_\beta + d\tilde{\Omega}_f^*,$$

having retained the previous form of the fundamental equation [Eqn. (63)] for the reference phase β, and using for the membrane the expression

$$d\tilde{\Omega}_f^* = -\tilde{S}_f^*\,dT - \sum_i \tilde{N}_{if}^*\,d\mu_i - P_\beta\,dV_f + \gamma\,dA, \tag{106}$$

($\tilde{S}_f^*$ and $\tilde{N}_{if}^*$ are the excess entropy and the number of moles of the ith component of the reference phase β on a membrane of finite thickness), we obtain the following equation defining the tension of a film of finite thickness:

$$\gamma = \left.\frac{\partial \tilde{\Omega}_f^*}{\partial A}\right|_{T,\mu_i,V_f}. \tag{107}$$

We may note that the excess entropy and the excess numbers of moles of components in Eqn. (106) differ from the corresponding excess amounts which enter into Eqn. (64) because the volumes of the reference phases β are different in the two cases.

b. The Gibbs–Duhem equation for a membrane of finite thickness

Having integrated the fundamental equation for a membrane of finite thickness [Eqn. (106)] with respect to the extensive parameters V_f and A for constant intensive parameters T and μ_i, we obtain

$$\tilde{\Omega}_f^* = -P_f V_f + \gamma A.$$

After differentiating the resulting equation and combining the result with Eqn. (106), we have

$$A\,d\gamma = -\tilde{S}_f^*\,dT - \sum_i \tilde{N}_{if}^*\,d\mu_i + V_f\,dP_\beta. \tag{108}$$

Introducing the effective film thickness

$$H^* = \frac{V_f}{A}, \tag{109}$$

and also the effective specific surface excess entropy and excess number of moles of the ith component, i.e.

$$s_f^* = \frac{\tilde{S}_f^*}{A} \qquad \Gamma_i^* = \frac{\tilde{N}_{if}^*}{A}, \tag{110}$$

which differ from the corresponding values defined by Eqn. (104), we obtain the Gibbs–Duhem equation for this case in the form

$$d\gamma = -s_f^*\,dT - \sum_i \Gamma_i^*\,d\mu_i + H^*\,dP_\beta. \tag{111}$$

c. Frumkin's equation

We may note that the effective film thickness H^*, defined by Eqn. (109), can be obtained from Eqn. (111):

$$H^* = \left.\frac{\partial \gamma}{\partial P_\beta}\right|_{T,\mu_i}. \tag{112}$$

It differs from the film thickness defined as the distance between two equimolecular (as defined by Gibbs) surfaces for which $\Gamma_1 = 0$ (Γ_1 is the adsorption of the solvent on the film interface) or in other ways (for example, as the distance between two tension surfaces, etc.).

Using the definitions of the disjoining pressure [see Eqns. (79) and (82)] and taking into account the fact that for a constant pressure P_α the relation $dP_\beta = d\Pi$ holds, one can rewrite Eqn. (112) as follows:[55]

$$H^* = \left.\frac{\partial \gamma}{\partial \Pi}\right|_{T,\mu_i}. \tag{113}$$

The relation obtained is known as Frumkin's equation in a differential form.[10, 45]

Integrating Eqn. (111) with respect to Π for constant T and μ_i, we find (in terms of our notation)

$$\gamma = \gamma^0 + H^*\Pi + \int_{H^*}^{\infty} \Pi \, dH. \tag{114}$$

Assuming that γ^0, the film tension at $\Pi = 0$ (i.e. in the case of an infinitely large H^*), can be replaced by $2\sigma_0$ (where σ_0 is the interfacial tension of a free planar surface), Eqn. (114) can be rewritten thus:[45, 55]

$$\gamma = 2\sigma_0 + H^*\Pi + \int_{H^*}^{\infty} \Pi \, dH. \tag{115}$$

This expression is known as the integral form of Frumkin's equation.

We may note that Eqn. (115) was derived for the special case corresponding to the special selection of the film thickness defined by Eqn. (190). In contrast to this, on taking into account Eqn. (95), Eqn. (80) can be written in the form

$$\gamma = 2\sigma_0 + H\Pi + \int_{H}^{\infty} \Pi \, dH, \tag{116}$$

and is valid for any choice of the positions of the dividing surfaces in the film and it is therefore more general than Eqn. (115).

The introduction into consideration of the disjoining pressure Π in the approach based on the concept of the film as a membrane of finite thickness is equivalent to the formal replacement of the pressure P_β by Π in the fundamental Eqn. (106) for the membrane. Such replacement was natural in the approach based on the concept of two dividing surfaces in the film [see Eqn. (78)], because the reference phase α with a pressure P_α was introduced into consideration in order to calculate the excess thermodynamic parameters relative to the dividing surfaces. On the other hand, in the case of a membrane of finite thickness, where the excess thermodynamic parameters are calculated relative to the entire membrane, the pressure P_α is assumed to be unknown (although it is kept constant with the aid of an external force f_α—see Fig. 6). The disjoining pressure Π in Eqn. (115) is also unknown because it was determined with an accuracy to within a constant quantity.

Thus the replacement of P_β by the disjoining pressure Π in Eqn. (106)[9, 45] is, strictly speaking, illegitimate. On the other hand, the Gibbs–Duhem equation, derived on the basis of a weaker condition, namely that $dP_\beta = d\Pi$, is more rigorous, like Frumkin's equation in the differential form (113), which follows from Eqn. (111) written in the form[45]

$$d\gamma = -s_f^* \, dT - \sum_i \Gamma_i^* \, d\mu_i + H^* \, d\Pi. \tag{117}$$

The discussion concerning the definition of the disjoining pressure in thermodynamics, based on the concept of a film as a membrane of finite thickness, was taken up by a number of workers.[9, 31, 44, 45] One of the considerations was the problem of the choice of the reference pressure for the film: de Feijter et al.[44] used P_α as the reference pressure, Toshev and Ivanov[6, 45] chose P_β. Whereas for plane-parallel films the choice of the reference pressure is insignificant, since it leads formally to the same Gibbs–Duhem equation for the film, it has been shown[16] that in the case of the transition region the second approach leads to difficulties associated with the need to take into account the hydrostatic pressure gradient in this region of the film.

IV. Conclusion

The above analysis of studies in the thermodynamics of plane-parallel liquid thick and thin films showed that three main approaches to the construction of such thermodynamics have now been developed.

The first approach, based on the thermodynamic film model as a membrane of zero thickness, developed by Deryagin and coworkers,[1,2] relates the excess free energy (grand thermodynamic potential) of the system $\widetilde{\Omega}_f$, referred to the membrane, to variable thermodynamic parameters: the temperature T, the chemical potentials μ_i of the ith components, and the film area A:

$$d\widetilde{\Omega}_f = -\widetilde{S}_f \, dT - \sum_i \widetilde{N}_{if} \, d\mu_i + \gamma \, dA,$$

where $\widetilde{S}_f$ and $\widetilde{N}_{if}$ are the excess entropy and the excess number of moles of the ith component of the reference phase β (Fig. 7), referred to the membrane, and γ is the film tension.

The Gibbs–Duhem equation for constant T, μ_i, and P_β assumes the form

$$d\gamma = -s_f \, dT - \sum_i \Gamma_{if} \, d\mu_i,$$

where s_f and Γ_{if} are the specific (referred to unit area of the membrane) excess entropy and excess numbers of moles of the ith components.

The membrane approach is convenient when a description of the mechanical and energy behaviour of thin liquid films, whose thickness is not measured experimentally, is required.

The second approach is based on the concept of the film as a membrane of finite thickness[6, 7, 9, 45, 56] and relates the excess free energy $\widetilde{\Omega}_f^*$ to the variable parameters T, μ_i, and A and also to the film volume V_f, which is assumed equal to the apparent change in the volume of the system (Fig. 7) on formation of a film with an area A for constant T, μ_i, P_β, and P_α [see Eqn. (106)]:

$$d\widetilde{\Omega}_f^* = -\widetilde{S}_f^* \, dT - \sum_i \widetilde{N}_{if}^* \, d\mu_i + H^* \, dP_\beta,$$

where the excess amounts $\widetilde{S}_f^*$ and $\widetilde{N}_{if}^*$ differ from the corresponding excess amounts in Eqn. (64).

The Gibbs–Duhem equation is written in this case in the form

$$d\gamma = -s_f^* \, dT - \sum_i \Gamma_{if}^* \, d\mu_i + H^* \, dP_\beta,$$

or, if $P_\alpha = \text{const.}$, then, taking into account that $dP_\beta = d\Pi$, it is formulated as follows:

$$d\gamma = -s_f^* \, dT - \sum_i \Gamma_{if}^* \, d\mu_i + H^* \, d\Pi,$$

where $H^* = V_f/A$ is the effective film thickness.

This approach is convenient when the experimental determination of the mechanical properties of a liquid film is accompanied by the measurement of the volume of the system containing the given film.

The third approach is based on the concept of two dividing surfaces in the film[3–5, 6] and relates the excess grand thermodynamic potential of the film $\widetilde{\Omega}_s$ to the variable parameters T, μ_i, A, and the film thickness by the equation

$$d\widetilde{\Omega}_s = -\widetilde{S}_s \, dT - \sum_i \widetilde{N}_{is} \, d\mu_i - \Pi A \, dH + 2\sigma \, dA,$$

in which the interfacial tension σ in a film having a thickness H is related to the tension γ by the expression

$$2\sigma = \gamma - \Pi H.$$

The corresponding Gibbs–Duhem equation is

$$2d\sigma = -2s_s \, dT - 2\sum_i \Gamma_i \, d\mu_i - \Pi \, dH.$$

The specific excess amounts s_s and Γ_i are referred to one of the dividing surfaces of the film.

This approach is convenient when the experimental measurement of the mechanical properties of the film is accompanied by the simultaneous measurement of its thickness at a known pressure P_α in phase α.

Thus the use of a specific approach to the description of the thermodynamic and mechanical behaviour of plane-parallel liquid (emulsion and foam) films is determined and limited by the possibility of the experimental measurement of the liquid film thickness and the pressure in the reference phase α from which the film has been formed. The approach based on the concept of two dividing surfaces in the film is optimum when it is extended to the transition region in liquid films within the limits of which the disjoining pressure varies sharply both in magnitude and in sign.

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