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Thermodynamics of free and of interacting curved interfaces in liquid films

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Abstract. Publications on the thermodynamics of free and of interacting curved interfaces in liquid films are reviewed. The approaches of Gibbs, Boruvka–Neumann, and others to the determination of the surface tension of free curved surfaces are compared. The dependences of differently defined interfacial tensions on the radius of curvature of the interface are obtained. The fundamental equilibrium equations for systems containing curved surfaces, including the transition region of the liquid film, are proposed. A generalised invariant of the profile of the liquid film is obtained, and used to derive all the known equilibrium equations for a liquid film with a bulk meniscus, including the equation for a liquid drop on a solid surface and precise analytical expressions describing the line tension for different thermodynamic models of the liquid film. The theory of the adhesion of fluid particles, which relates the adhesion force and the potential energy of the interaction between deformable particles to the parameters of the disjoining pressure isotherm, is discussed. The bibliography includes 88 references.

I. Introduction

Emulsion and foam films are formed at the contact between two liquid drops or gas bubbles (Fig. 1, phase β) in a liquid dispersion medium (Fig. 1, phase α).

The plane-parallel part of a liquid emulsion or foam film at the centre of the contact region is characterised by the equilibrium condition

$$\Pi = P_\beta - P_\alpha , \qquad (1)$$

where P_β and P_α are the hydrostatic pressures in the phases β and α respectively, and Π is the disjoining pressure in the film.

In the bulk meniscus region of the liquid film the interaction between the interfaces vanishes (i.e. $\Pi = 0$). Therefore the curvature of these surfaces is constant, and is determined exclusively by the difference between the hydrostatic pressures $P_\beta - P_\alpha$.

The profile of the liquid film $H(r)$ in the region of the meniscus [or the profile of the free curved surface $z(r)$] contains information on the contact force (compressive, f_p, or repulsive, f_a) applied to the fluid particles,[1–3] and on the integral characteristic of the surface forces [a large thermodynamic potential $\Delta\Omega(H_f)$]. Furthermore the experimental dependence of the contact angle θ_f on the radius of the film r_f contains information on the line tension in the liquid film, i.e. on the form of the profile of the disjoining pressure isotherm $\Pi(H)$ in the transition region.[4–6].

Unlike the region of the bulk meniscus the curvature of the interfaces in the transition region of a liquid film is not constant but shows a complicated dependence on the local thickness H of the film profile. Therefore the profile of the meniscus in the transition region of a liquid film contains information on the $\Pi(H)$ isotherm,[2, 3] which can be obtained from experimental plots of the contact angle against the thickness of the film in the transition region [$\phi(H)$]. Unfortunately the length of the transition region of the film is small, and therefore the disjoining pressure isotherm $\Pi(H)$ cannot be determined to within an acceptable precision from the $H(r)$ profile in this region, measured for example by the so-called topographic method.[7] In the region of the bulk meniscus this profile can be determined very accurately for small contact angles, and it is effectively the only meaningful source of information on surface forces.

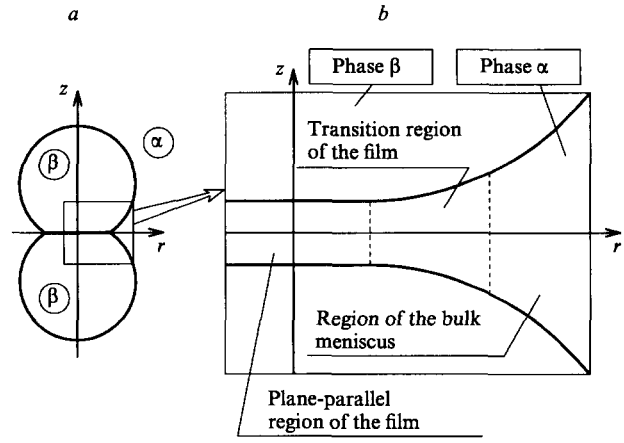


Figure 1. Thermodynamics of liquid films: (*a*) symmetrical microscopic liquid film (emulsion or foam) produced between two identical fluid particles (liquid or gaseous) of phase β in the liquid phase α; (*b*) central plane-parallel region, transition region, and region of the bulk meniscus (containing two non-interacting curved interfaces in the symmetrical liquid film).

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The thermodynamics of free curved surfaces in liquid films were established by Gibbs,[8] and further developed by Buff,[9] Ono and Kondo,[10] Rusanov,[11-13] Rowlinson and Widom,[14] Ivanov and Kralchevsky,[15] Markin et al.,[16, 17] Babak,[5, 18] and others.[19-21]

The next step forward in the development of the thermodynamics of free curved surfaces was its extension to the transition region of emulsion and foam films of variable thickness, in which a disjoining pressure is generated and which smoothly change into a plane-parallel film on one side and into a system of two free (non-interacting) curved interfaces in the region of the bulk meniscus.[1, 5, 18, 22] Clearly, the best thermodynamic model for this generalisation is the liquid film model, based on the assumption of two interfaces (in the Gibbs sense) defining a layer of finite thickness of a liquid reference phase (the Gibbs comparison phase). The thermodynamics of plane-parallel liquid films based on this model were developed by Rusanov,[11-13] and those of free curved interfaces in the region of the bulk meniscus by Gibbs.[8] However, neither of these models allows for the presence of a transition region characterised by a surface tension gradient.[1, 5, 18] As a result, the thermodynamics of plane-parallel liquid films and those of free curved surfaces are not mutually consistent.

The two approaches can be reconciled in terms of the thermodynamics of the transition region of the liquid film,[1, 5, 18] which naturally reduce to the thermodynamics of plane-parallel liquid films and to the thermodynamics of free curved interfaces in the appropriate regions of the system.

The aim of the present review is to discuss recent work on the thermodynamics of free and of interacting curved interfaces in emulsion and in foam films.

II. Thermodynamic description of free curved interfaces

The study of curved interfaces reveals a number of problems associated with the development of the thermodynamics of the transition region in thin liquid films.

First, the fundamental equation of the system containing a curved interface is no longer invariant with respect to the method of localisation of the curved interface. This is formally shown by the appearance in the fundamental equation of terms relating to the work of bending and twisting of the interface (whose magnitude depends on the mode of localisation of the interface).

Second, we find a problem in determining the interfacial tension, whose magnitude depends both on the position of the interface and on the method of selecting the reference system used to define the interfacial tension. The different possible choices of a reference system to determine the interfacial tension led to a discussion of the validity of the generalised Laplace equation.[15, 16, 19-21] We note that correct allowance for the bending and twisting moments in the generalised Laplace equation is essential also in the case of liquid particles with low and ultra-low interfacial tension, such as micelles, vesicles, and drops of a coacervate phase.

1. Cylindrical free interfaces

We shall begin our discussion of the thermodynamics of curved interfaces with the simplest case of cylindrical surfaces, i.e. surfaces having only one principal radius of curvature, thus avoiding mathematical difficulties due to the need to allow for the second radius of curvature without loss of generality.

Systems containing a free cylindrical interface. Let us consider a multicomponent system including two macroscopic phases α and β separated by a free cylindrical interface (Fig. 2). To simplify the discussion we shall ignore gravity, and we shall assume that the hydrostatic pressures P_α and P_β in the two phases are known. All the parts of the system in equilibrium have the same temperature T and the same chemical potential μ_i of the i-th component [$i = 1, 2, \ldots, N$; N is the number of components, of which the total number of moles (N_i) in the system is controlled by the material source ν_i].

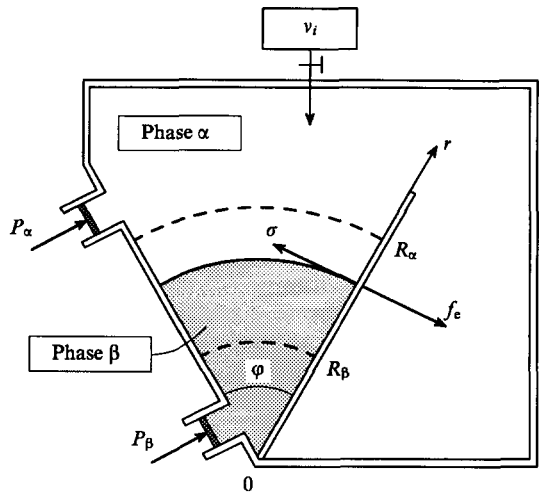


Figure 2. Thermodynamic system including a fluid (liquid or gaseous) phase β and a liquid phase α separated by a curved free cylindrical interface.

We shall also assume that the above system is in thermodynamic equilibrium with an open subsystem bounded on the right by a mobile side-wall (Fig. 2) forming a dihedral angle φ with the fixed left-hand wall, and by two arbitrarily located dividing surfaces having radii R_α and R_β (enclosing the interface) and two flat end faces forming a layer of thickness l_z. The moment of the external force f_e balances the moments of the interfacial tension σ and of the pressure force P_α and P_b acting on the system.

Hydrostatic description of the curved interface. The capillary properties of curved interfaces have been widely discussed in the framework of local thermodynamics.[9, 10-12, 16, 23, 24]

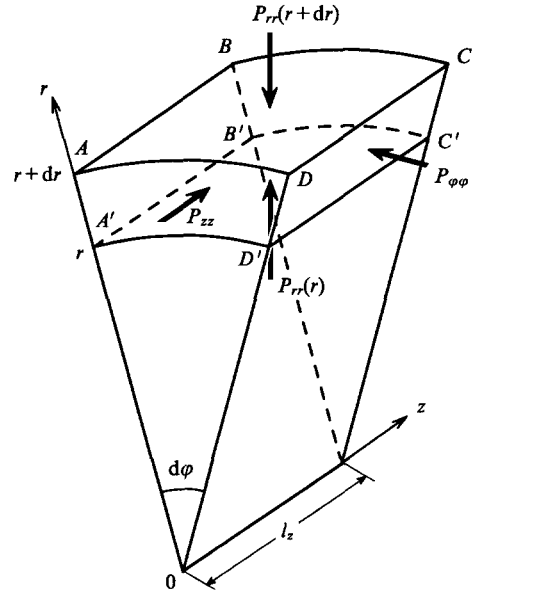


Figure 3. Element of volume of the thermodynamic system containing a cylindrical interface.

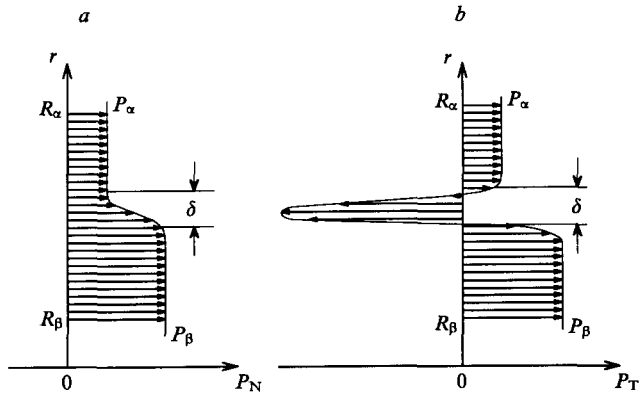


Figure 4. Distribution of the normal P_N (*a*) and of the tangential P_T component (*b*) of the hydrostatic pressure tensor in the transition region of a curved interface.

We shall use the following symbols for the non-zero components of the hydrostatic pressure $\hat{P}$ in cylindrical coordinates (Fig. 3):

$$P_N(r) = P_{rr}\,, \quad P_T(r) = P_{zz} = P_{\varphi\varphi}\,.$$

An idealised plot of the dependence of these components on the radius r is shown in Fig. 4. Unlike the planar interface[22] the normal component of the pressure tensor $P_N(r)$ (see Fig. 4*a*) varies sharply in a narrow region of the interfacial transition layer of thickness δ (see Fig. 4*b*). In the region of the bulk phases α and β the two components are equal to P_α and P_β respectively.

In cylindrical coordinates the hydrostatic equilibrium condition

$$\mathrm{div}\hat{P} = 0$$

becomes

$$\frac{dP_N}{dr} + \frac{P_N}{r} = \frac{P_T}{r} \tag{2}$$

and can be obtained from the mechanical equilibrium condition of the element of volume $ABCDA'B'C'D'$ (see Fig. 3) which experiences the pressure components $P_N = P_{rr}$ and $P_T = P_{\varphi\varphi} = P_{zz}$. Equating to zero the projection of the resulting force in the r direction and noting that

$$P_N(r+dr) = P_N(r) + \frac{dP_N}{dr}dr\,,$$

we find

$$-\left[P_{rr} + \frac{dP_{rr}}{dr}dr\right] l_z(r+dr)d\varphi + P_{rr}(r) l_z r\,d\varphi + P_{\varphi\varphi} l_z\,dr\,d\varphi = 0\,,$$

whence we obtain Eqn (2), which can also be rewritten

$$\frac{d(rP_N)}{dr} = P_T\,, \tag{3}$$

or

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

The mechanical equilibrium condition (2) is sometimes used in the form[25]

$$\frac{dP_N}{dr} = (P_T - P_N)k_1(r)\,, \tag{4}$$

where $k_1(r) = 1/r$ is the curvature of the interface.

The integral form of the equilibrium Eqn (4) is

$$P_\alpha - P_\beta = \int_{R_\beta}^{R_\alpha} [P_T(r) - P_N(r)]k_1(r)\,dr\,, \tag{5}$$

with integration limits R_α and R_β in the region of the macroscopic phases where the difference $(P_T - P_N)$ is zero, since the pressures P_T and P_N are P_α and P_β in the phases α and β respectively. Eqn (5) can also be obtained by integrating Eqn (3):

$$P_\alpha R_\alpha - P_\beta R_\beta = \int_{R_\beta}^{R_\alpha} P_T(r)\,dr\,. \tag{6}$$

Interfacial tension. Using the method of Gibbs excesses[8] we shall replace the real open subsystem containing a cylindrical interface (Fig. 5*a*) by an idealised system (Fig. 5*b*) including two reference phases α and β and an interface (according to Gibbs) having an arbitrary radius R.

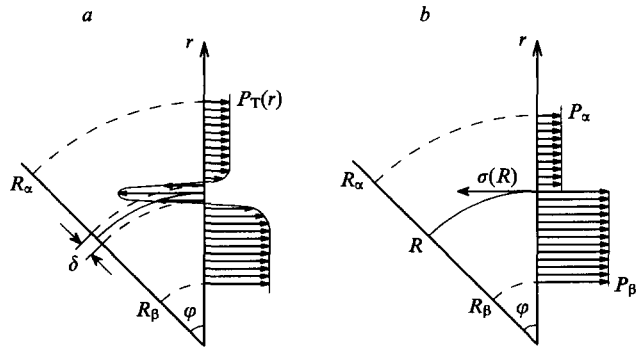


Figure 5. Definition of the interfacial tension of a cylindrical interface: (*a*) distribution of the pressure component $P_T(r)$ near the interface; (*b*) result of replacing the interface by a Gibbs cylindrical dividing surface.

The mechanical moment M applied by the real system to the right-hand (mobile) wall is

$$M = \int_{R_\beta}^{R_\alpha} P_T(r) r\,dr\,. \tag{7}$$

The mechanical moment is referred to unit length l_z of the cylindrical layer of the system (see Fig. 3).

The idealised system acts on a unit length of the mobile wall with a mechanical moment M^{id} equal to

$$M^{id} = \int_{R_\beta}^{R} P_\beta r\,dr + \int_{R}^{R_\alpha} P_\alpha r\,dr - \sigma(R)R\,, \tag{8}$$

where $\sigma(R)$ is the interfacial tension of the cylindrical surface of radius R. From the condition of mechanical equivalence between the idealised and the real system, i.e. for $M^{id} = M$, we obtain the following expression for the interfacial tension

$$\sigma(R) = \int_{R_\beta}^{R} [P_\beta - P_T(r)]\frac{r}{R}dr + \int_{R}^{R_\alpha} [P_\alpha - P_T(r)]\frac{r}{R}dr\,. \tag{9}$$

According to Kondo[26] the function $\sigma(R)$ has a single minimum σ_t at a radius R_t of the cylindrical surface, which Gibbs called the tension surface.[8]

The fundamental equation of the system containing a cylindrical interface. We shall derive the fundamental equation of a system containing a curved interface by considering the element of volume $ABCDA'B'C'D'$ shown in Fig. 3, of thickness $AA' = h$

and having a base area $A(r) = rl_z\,d\varphi$. The work done by the external forces in deforming this volume (at constant T and μ_i) is

$$\delta W = -P_N(r)A(r)\delta r - P_T(r)h\,\delta A(r)$$
$$= -P_N(r)\delta V + [P_N(r) - P_T(r)]h\,\delta A(r)\,, \qquad (10)$$

where $\delta V = A(r)\delta r + h\,\delta A(r)$ is the variation of the volume. Integrating (10) over the whole volume of the open subsystem gives

$$\Omega = \left\{-\int_{R_\beta}^{R_\alpha} P_N(r)r\,dr + \int_{R_\beta}^{R_\alpha}[P_N(r) - P_T(r)]r\,dr\right\}\varphi$$
$$= \left[\int_{R_\beta}^{R_\alpha} P_T(r)r\,dr\right]\varphi\,. \qquad (11)$$

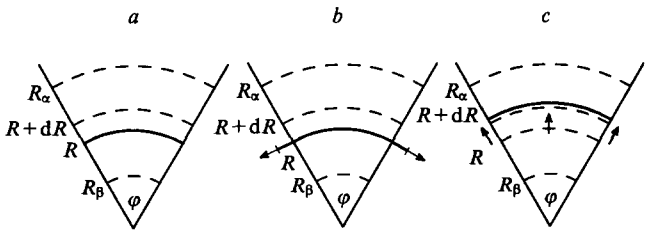


Figure 6. Derivation of the fundamental equation of a system containing a curved cylindrical surface of radius R. The deformation of the dividing surface produced by a change in the radius of curvature from R to $R + dR$ (*a*) includes the work of simple extension of the surface for constant R (*b*) and the work of simple bending of the surface for constant area (*c*).

Let us now consider an element of volume of the idealised system (Fig. 6) including a cylindrical interface of radius R, and let us calculate the work δW performed by the external forces in deforming this surface. It can be arbitrarily divided into four parts: the work of deformation of the phase α ($-P_\alpha\delta V_\alpha$, Fig. 6*a*), the work of deformation of the phase β ($-P_\beta\delta V_\beta$, Fig. 6*a*), the work of simple expansion of the interface with a constant radius of curvature $R[\sigma(R)\delta A(R)$, Fig. 6*b*], the work of simple bending of the interface with a constant area and a change in curvature of δk_1 ($C_1\delta k_1$, Fig. 6*c*).†

Thus the work of the external forces during the deformation of an element of volume of the idealised system (which includes the interface) can be written

$$\delta W = -P_\beta\,\delta V_\beta - P_\alpha\,\delta V_\alpha + \sigma(R)\delta A(R) + c_1A(R)\delta k_1\,. \qquad (12)$$

The fundamental equation for this system in the general case is

$$d\Omega^{id} = -S\,dT - \sum_i N_i\,d\mu_i - P_\beta dV_\beta - P_\alpha dV_\alpha$$
$$+\sigma(R)dA(R) + c_1A(R)dk_1\,, \qquad (13)$$

where S is the entropy of the open system.

By integrating this equation over the extensive parameters we obtain an expression for the grand thermodynamic potential of the idealised system:

$$\Omega^{id} = -P_\beta V_\beta - P_\alpha V_\alpha + \sigma(R)A(R)\,, \qquad (14)$$

† In the Gibbs terminology[8] the coefficient C_1 has the dimensions of J m^{-1}. Other workers refer this coefficient to unit surface area and express it as $C_1 = c_1A(R)$. In the case of a cylindrical surface the physical significance of the coefficient c_1 is that of a bending moment referred to unit width of the cylindrical surface.

which is easily converted into a form convenient for a comparison with Eqn (11):

$$\Omega^{id} = \left[-\int_{R_\beta}^{R} P_\beta r\,dr - \int_{R}^{R_\alpha} P_\alpha r\,dr + \sigma(R)R\right]\varphi\,. \qquad (15)$$

From the condition of energy equivalence of the real and the idealised system, $\Omega = \Omega^{id}$, we can obtain the expression (9) for the interfacial tension $\sigma(R)$.

Fundamental equation of a cylindrical separating surface. The separating surface method is based on the presentation of the extensive parameters Ω, S, V, N_i as sums of bulk parts, relating to the reference phases α and β, and excesses, relating to the separating surface. In this convention the fundamental equation (13) of the system can be written as follows for the reference phases:

$$d\Omega = d\Omega_\alpha + d\Omega_\beta + d\Omega_s\,, \qquad (16)$$

where

$$d\Omega_\alpha = -S_\alpha dT - \sum_i N_{i\alpha}d\mu_i - P_\alpha dV_\alpha\,, \qquad (17)$$

and

$$d\Omega_\beta = -S_\beta dT - \sum_i N_{i\beta}d\mu_i - P_\beta dV_\beta\,, \qquad (18)$$

where

$$d\Omega_s = -S_s dT - \sum_i N_{is}d\mu_i + \sigma(R)dA(R) + c_1A(R)dk_1 \qquad (19)$$

is the fundamental equation of the free curved (cylindrical) separating surface.

Eqn (19) differs from the corresponding equation for a planar separating surface[22] by the term $c_1A(R)dk_1$, equal to the work done by the external forces during the simple bending of the separating surface, and also by the dependence of the interfacial tension $\sigma(R)$ on the localisation of the curved separating surface. We note that the fundamental equation of the planar interface contains the interfacial tension σ_0, which is invariantly related to the position of the separating surface.[22]

The Gibbs–Duhem equation for a cylindrical separating surfaces. Integrating Eqn (19) over the parameter $A(R)$ for constant T, μ_i, and k_i gives

$$\Omega_s = \sigma(R)A(R)\,. \qquad (20)$$

By differentiating Eqn (20) and combining it with (18) we obtain the Gibbs–Duhem equation for this surface,

$$A(R)d\sigma(R) = -S_s dT - \sum_i N_{is}d\mu_i + c_1A(R)dk_1\,,$$

which can be written

$$d\sigma(R) = -s_s dT - \sum_i \Gamma_i\,d\mu_i + c_1dk_1\,, \qquad (21)$$

where $s_s = S_s/A(R)$ and $\Gamma_i = N_{is}/A(R)$ are the entropy excess and the excess in the number of moles of the ith component respectively referred to unit area of the separating surface.

Unlike the Gibbs–Duhem equation for a flat interface Eqn (21) is not invariant with respect to the position of the curved separating surface.[22]

Eqn (21) defines the relationship between the excesses of the thermodynamic quantities, but it contains no information on the condition of the equilibrium between this separating surface and the bulk reference phases α and β. This equilibrium condition can

be obtained only from the fundamental equation for the whole system containing the curved interface.

Fundamental equilibrium equation of a system containing a cylindrical interface. This equation can be obtained by minimising the grand thermodynamic potential of the system (13). The minimisation can be carried out by two methods: the imaginary displacement of the separating surface, i.e. a change in the radius R of this surface for a fixed physical state of the system, determined by the parameters T, μ_i, P_α, and P_β (Kondo's method[26]), or a real deformation of the separating surface with changes in the physical parameters P_β and P_α but constant T and μ_i (the method of Gibbs[8]).

Both methods lead to the same final equilibrium equation for a system containing a cylindrical interface.

By using Kondo's method,[26] i.e. by varying the grand thermodynamic potential of the system Ω^{id} in Eqn (14) over the radius R of the separating surface and equating the variation $\sigma\Omega^{id}$ to zero, we obtain

$$-P_\beta\left\{\frac{\partial V_\beta}{\partial R}\right\}\delta R - P_\alpha\left\{\frac{\partial V_\alpha}{\partial R}\right\}\delta R + \sigma R\left\{\frac{\partial A(R)}{\partial R}\right\}\delta R + A(R)\left\{\frac{\partial \sigma(R)}{\partial R}\right\}\delta R = 0 ,$$

where the braces denote a virtual differentiation. Allowing for the self-evident geometric relations

$$\frac{\partial V_\beta}{\partial R} = A(R) ; \quad \frac{\partial V_\alpha}{\partial R} = -A(R) ; \quad \frac{\partial A(R)}{\partial R} = \frac{A(R)}{R} ; \tag{22}$$

we can convert the resulting equation into the fundamental equilibrium condition for a system containing a cylindrical separating surface:

$$\frac{\sigma(R)}{R} + \left\{\frac{\delta\sigma(R)}{\partial R}\right\} = P_\beta - P_\alpha . \tag{23}$$

For the tension surface, where $\partial\sigma(R)/\partial R = 0$, $R = R_t$, and $\sigma(R_t) = \sigma_t$ (the subscript t denoting quantities referred to the tension surface) we obtain from (23) the Laplace equation for a cylindrical tension surface:

$$\frac{\sigma_t}{R_t} = P_\beta - P_\alpha . \tag{24}$$

By minimising Eqn (13) with respect to δR (for a real deformation of the interface) with constant T and μ_i we arrive at

$$-P_\beta\frac{\partial V_\beta}{\partial R}\delta R - P_\alpha\frac{\partial V_\alpha}{\partial R}\delta R + \sigma R\frac{\partial A(R)}{\partial R}\delta R + c_1 A(R)\frac{\partial k_1}{\partial R}\delta R = 0 .$$

Using the geometric relations (22) we can convert this equation into the fundamental equilibrium equation for a system containing a cylindrical separating surface:

$$\frac{\sigma(R)}{R} + c_1\frac{\partial k_1}{\partial R} = P_\beta - P_\alpha . \tag{25}$$

According to Gibbs[8] a separating surface having a zero bending moment is called a tension surface. On such a surface $c_1 = 0$, and Eqn (25) yields the Laplace equation (24).

Since according to the Gibbs–Duhem equation (21) we can write

$$c_1 = \left.\frac{\partial\sigma(R)}{\partial k_1}\right|_{T,\mu_i} , \tag{26}$$

Eqn (25) can be expressed as

$$\frac{\sigma(R)}{R} + \frac{\partial\sigma(R)}{\partial R} = P_\beta - P_\alpha . \tag{27}$$

Unlike Eqn (23) this equation contains the real derivative $\partial\sigma(R)/\partial R$.

By using the obvious relationship

$$\frac{\partial k_1}{\partial R} = -\frac{1}{R^2} = -k_1^2$$

we can convert (25) into

$$k_1\sigma(R) - c_1 k_1^2 = P_\beta - P_\alpha , \tag{28}$$

which is known as the Gibbs–Kelvin equation for a system containing a cylindrical separating surface.[9, 25] For a tension surface ($c_1 = 0$) the Gibbs–Kelvin equation is converted into the simpler Laplace equation

$$k_1\sigma_t = P_\beta - P_\alpha . \tag{29}$$

We note that Boruvka and Neumann[19] have doubted the validity of Eqn (28). They suggest that in the case of cylindrical surfaces the Laplace equation (29) is satisfied for any position of the separating surface.

The problem of determining the interfacial tension of curved surfaces. During the last decade the work of Boruvka and Neumann[19] has been widely quoted and discussed in relation to proposed generalisations of the Laplace equation to include non-spherical surfaces.[15, 16, 20, 21] Let us examine the main topics of these discussions.

By using their fundamental equation for a system containing a non-spherical interface with two different principal radii of curvature Boruvka and Neumann[19] obtained a fundamental equilibrium equation for the system (of the Laplace equation type), which in the case of a cylindrical separating surface in any position (i.e. of a surface having only one principal radius of curvature) takes the form

$$k_1\sigma_{BN} = P_\beta - P_\alpha . \tag{30}$$

They called σ_{BN} the interfacial tension,[19] and did not consider the possibility of inconsistency between the definitions of interfacial tension given by Eqns (30) and (28). [We shall arbitrarily call the interfacial tension in formula (28) the Gibbs interfacial tension σ_G.] Eqn (28) in the form

$$k_1\sigma_G - c_1 k_1^2 = P_\beta - P_\alpha \tag{31}$$

was criticised by Boruvka and Neumann, who believed it to be incorrect. The resulting controversy[20, 21] was widened by Markin et al.,[16] who pointed out that the interfacial tensions σ_G and σ_{BN} in the expressions (30) and (31) are defined in different ways, and therefore the two formulae for the generalised Laplace equation of non-spherical surfaces are both correct if allowance is made for the difference between σ_G and σ_{BN}. These workers[16] obtained expressions for σ_G and σ_{BN} within the scope of local thermodynamics and established a relationship between these quantities. For a cylindrical separating surface this relationship is

$$\sigma_G = \sigma_{BN} + c_1 k_1 . \tag{32}$$

We shall examine the physical meaning of the definitions of σ_G and σ_{BN} by considering a cylindrical separating surface.

From the fundamental Eqn (19) we obtain an expression for σ_G which is identically equal to $\sigma(R)$ for a cylindrical surface:

$$\sigma_G = \left.\frac{\partial\Omega_s}{\partial A}\right|_{T,\mu_i,k_1} . \tag{33}$$

A special feature of this definition is that the interfacial tension σ_G is interpreted as the increment of the specific excess of the grand thermodynamic potential resulting from an increase in the area $A(R)$ of a curved (rather than a planar) separating surface

having a constant curvature $k_1 = 1/R$. This means that σ_G includes both the intrinsic work of formation of a new separating surface and the work done in bending it. In fact, the interfacial tension σ_G is defined in terms of a reference system which includes the two phases β and α (with different hydrostatic pressures P_β and P_α: $P_\beta > P_\alpha$, see Fig. 2) and the curved separating surface.

Boruvka and Neumann used as a standard a hypothetical state of the system in which the interfacial surface has a zero curvature but the pressures in the phases α and β are different. In spite of the fact that this state of the system is not realisable in practice it allows an unambiguous definition of the interfacial tension, which we shall arbitrarily denote σ_{BN}:

$$\sigma_{BN} = \int_{R_\beta}^{R} [P_\beta - P_T(r)]dr + \int_{R}^{R_\alpha} [P_\alpha - P_T(r)]dr \,. \tag{34}$$

We note that an expression for σ_G [Eqn (9)] was obtained by using the principle of mechanical equivalence of the real and the idealised system, i.e. by equating the moments of the forces M and M^{id}, and that the expression for σ_{BN} follows formally from the condition of equality of the forces f and f^{id} which act on the side surface separating the real from the idealised system:

$$f = \int_{R_\beta}^{R_\alpha} P_T(r)dr \,;\; f^{id} = \int_{R_\beta}^{R} P_\beta dr + \int_{R}^{R_\alpha} P_\alpha dr - \sigma_{BN} \,. \tag{35}$$

According to the fundamental Eqn (19) the work done by external forces in increasing the area $A(R)$ of a cylindrical separating surface of radius R (with constant T, μ_i, and k_1) is $\sigma_G dA(R)$, as shown in Fig. 7*a*. According to Boruvka and Neumann[19] σ_{BN} is defined as the work which must be expended to create a unit area of planar interface by the deformation of the system illustrated in Fig. 7*b* (with constant T, μ_i, P_α, and P_β).

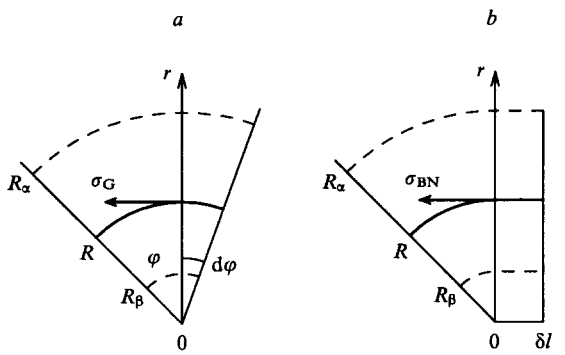


Figure 7. Illustration of the difference between the Gibbs (*a*) and the Boruvka–Neumann (*b*) definition of the interfacial tension.

The following expression has been proposed[19] for the fundamental equation in the case of the cylindrical separating surface:

$$d\Omega_s = -S_s dT - \sum_i N_{is} d\mu_i + \sigma_{BN} dA + c_1 d\tilde{K}_1 \,, \tag{36}$$

where

$$\tilde{K}_1 = \int_A k_1 dA \tag{37}$$

is the extensive parameter of the curvature, corresponding to the work needed to bend the separating surface.

It was also suggested[19, 21] that the free energy Ω_S is a uniform first-order function of the parameter $\tilde{K}_1$. Rowlinson rejected this suggestion,[20] and doubted the validity of the fundamental equation for the separating surface in the form of Eqn (36). The formal thermodynamic definition of σ_N follows from Eqn (36):

$$\sigma_{BN} = \left.\frac{\partial \Omega_s}{\partial A}\right|_{T, \mu_i, \tilde{K}_1} \,. \tag{38}$$

Since in the case of a cylindrical surface the right-hand side of Eqn (37) can be expressed as $k_1 A(R)$ we can apply Euler's theorem of uniform functions to Eqn (36) and write

$$\Omega_s = \sigma_{BN} A + c_1 \tilde{K}_1 \,. \tag{39}$$

By comparing (39) with the expression (20) previously obtained we obtain a relationship between σ_G and σ_{BN} [Eqn (32)]. Thus σ_{BN} is equal to the specific excess free energy at constant T and μ_i referred to unit area of a flat dividing surface, and σ_G includes also the excess free energy associated with the deformation (change in curvature) of the dividing surface.[16]

Dependence of the interfacial tensions on the radius of the dividing surface. The interfacial tensions σ_G and σ_{BN} depend on the method of localisation of the curved surfaces, i.e. on the subjective choice of a radius of curvature R for these surfaces. Analytical expressions for the functions $\sigma_G(R)$ and $\sigma_{BN}(R)$ in the case of cylindrical dividing surfaces can be obtained by using in the calculation an idealised function $P_T^0(r)$ in the form of a rectangular well with parameters Π_0 and Δ (Fig. 8*a*). The superscript '0' shows that the function $P_T^0(r)$ corresponds to a standard state, i.e. a flat dividing surface and pressures $P_\alpha = P_\beta$. Increasing the pressure P_β gives the function $P_T^0(r)$ a new form (Fig. 8*b*).

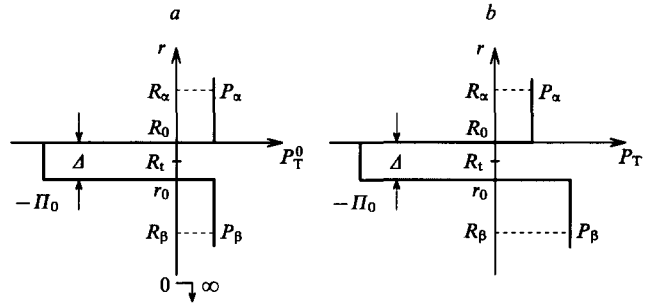


Figure 8. Representation of the function $P_T(r)$ as a rectangular well for a flat (*a*) and a curved interface (*b*).

One of the problems met when studying the bending of the interfacial surface is the ambiguous dependence of the parameters of the function $P_T(r)$ on the pressure P_β. In particular, it is not clear whether an increase in the pressure P_β affects the depth of the minimum (Π_0) in the $P_T(r)$ curve or the width Δ of the rectangular well, and we cannot describe the lower branch of the $P_T(r)$ curve (on the side of the phase β) analytically even when an analytical form of this curve is known for the $P_T^0(r)$ function when $P_\alpha = P_\beta$.

The interfacial tension σ_G and σ_{BN} can be calculated numerically when a complete and unambiguous description of the function $P_T(r)$ is available for any pressure P_β [i.e. when the function $P_T(r)$ is determined as a functional]. In the calculations shown below it is assumed that the parameters Π_0 and Δ of the function $P_T(r)$ are unaffected by an increase in the pressure P_β.

In particular, if the physical radius of the drop (in this case, a 'cylindrical' drop) is known, i.e. if we know the distance from the axis of curvature to some characteristic point of the $P_T(r)$ curve (which could be the radius r_0 or R_0 in the case of the rectangular well shown in Fig. 8*b*), we can use the hydrostatic equilibrium condition ($\operatorname{div} \hat{P} = 0$) to determine unambiguously the function

$P_N(r)$, and if the pressure P_α in the phase α is known the previously unknown pressure P_β in the phase β can be obtained from Eqn (6). Then, once P_β is known, the formulae (9) and (34) can be used to find the interfacial tensions σ_G and σ_{BN} for any radius R of the dividing surface.

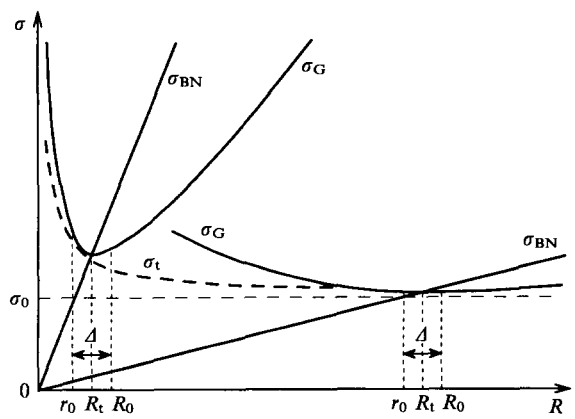


Figure 9. Dependence of the Gibbs and the Boruvka–Neumann interfacial tension on the radius of the cylindrical dividing surface for different values of the radius of the interfacial surface (see Fig. 7): σ_0 is the interfacial tension of the flat surface; R_t is the radius of curvature of the tension surface; $\sigma_t(r_0)$ is the interfacial tension of the Gibbs tension surface.

In Fig. 9 we show the dependence of σ_G and σ_{BN} on the radius of curvature R of the cylindrical dividing surface, calculated for the idealised form of the function $P_T^0(r)$ as a rectangular well with parameters Π_0 and Δ.

The $\sigma_G(R)$ functions calculated by Eqn (9) have a minimum (σ_t) at $R = R_t$ (the radius of the tension surface):

$$\frac{\sigma_G(R)}{R} + \frac{1}{2}\frac{\sigma_0}{r_0}\left(1 - \frac{R_t^2}{R^2}\right) = P_\beta - P_\alpha , \tag{40}$$

where

$$R_t = r_0(1+\alpha)^{1/2} , \tag{41}$$

$$\sigma_t = \sigma_0(1+\alpha)^{1/2} , \tag{42}$$

$$\sigma_0 = \int_{R_\beta}^{R_\alpha} [P_\alpha - P_T^0(r)]\mathrm{d}r = (\Pi_0 + P_\alpha)\Delta , \tag{43}$$

$$\alpha = \frac{\Delta}{r_0} .$$

We note an interesting property of the $\sigma_G(R)$ function. When the physical radius r_0 of the interface is decreased the radius of the tension surface R_t remains within the limits of the transitional interface layer, i.e. the system satisfies the condition

$$r_0 < R_t < R_0 = r_0 + \Delta ,$$

according to which the difference $\delta_t = R_t - r_0$ decreases from $\delta_t = \Delta/2$ for $r_0 \gg \Delta$ to zero for $r_0 \to 0$. Thus we may assume that the tension surface is almost indistinguishable from the Gibbs 'detachment surface', corresponding to a maximum density gradient in the inner phase. The interfacial tension σ_t increases as the radius r_0 decreases [see Eqn (42) and Fig. 9]. Eqn (40) is a generalised form of the Laplace equation, which in the case of the tension surface takes the simple form

$$\frac{\sigma_t}{R_t} = P_\beta - P_\alpha .$$

The interfacial tension σ_{BN} obtained from Eqn (34) is

$$\sigma_{BN} = \sigma_0 \frac{R}{r_0} . \tag{44}$$

The plots of the function $\sigma_{BN}(R)$ intersect those of $\sigma_G(R)$ at their minima (see Fig. 9). Under these conditions

$$\sigma_{BN}(R) = \sigma_t = \frac{\sigma_0 R_t}{r_0} .$$

Thus we may conclude that the Gibbs (σ_G) and the Boruvka–Neumann (σ_{BN}) interfacial tensions are indistinguishable for a tension surface of radius R_t.

With respect to this special property of the $\sigma_G(R)$ and $\sigma_{BN}(R)$ functions we note that some workers[10, 11, 14, 15] have calculated the radius of curvature R_t of the tension surface from the condition of simultaneous fulfilment of the equalities

$$f = f^{id} \quad \text{and} \quad M = M^{id} ,$$

but (as shown above) the condition $M = M^{id}$ leads to the Gibbs definition of the interfacial tension (σ_G) whereas the condition $f = f^{id}$ leads to the Boruvka–Neumann definition (σ_{BN}). Thus in that work the radius of curvature of the tension surface is obtained from the equality condition $\sigma_G(R_t) = \sigma_{BN}(R_t) = \sigma_t$.

For a cylindrical interfacial surface the generalised Laplace equation[19] is

$$\frac{\sigma_{BN}(R)}{R} = P_\beta - P_\alpha$$

for any radius of curvature R of the dividing surface (not only for the tension surface radius R_t) as function of $\sigma_G(R)$. The relationship between σ_G and σ_{BN} is obtained from Eqns (40) and (44):

$$\sigma_G = \frac{1}{2}\sigma_{BN}\left(1 + \frac{R_t^2}{R^2}\right) . \tag{45}$$

The choice of a standard state of the system in the determination of the interfacial tension. The difference between σ_G and σ_{BN} is significant (for all radii R of the dividing surface within the region $r_0 \leqslant R \leqslant r_0 + \Delta$) only when $r_0 \approx \Delta$ (a value typical of micelles and of nuclei of a new phase). A correct choice of the optimum reference system and of its standard state is very important for the thermodynamic description of these objects. The choice affects both the determination of the interfacial tension and the construction of the fundamental equation of the system and of the fundamental equilibrium equation in the most suitable form.

For example, in the Gibbs approach to the determination of σ_G [Eqn (9)] the fundamental equation for a cylindrical dividing surface (19) takes its simplest form for the tension surface of radius R_t:

$$\mathrm{d}\Omega_s = -S_s\mathrm{d}T - \sum_i N_{is}\mathrm{d}\mu_i + \sigma_t\,\mathrm{d}A_t ,$$

where $A_t = A(R_t)$ is the area of the tension surface, so that the excess in the grand thermodynamic potential is

$$\Omega_s = \sigma_t A_t ,$$

and the equilibrium equation of the system containing a cylindrical interfacial surface is the Laplace equation (24).

However, the interfacial tension σ_t and the radius of the tension surface are themselves dependent on the physical radius r_0 of the interfacial surface [see Fig. 9 and Eqns (41) and (42)], which complicates practical calculations of capillary effects.

Another method of determining the interfacial tension for a cylindrical surface relies on choosing as the standard state a state of the reference system for which $P_\beta^0 = P_\alpha^0$ and the interface is flat. The $P_T^0(r)$ function which corresponds to this interfacial surface is assumed to be known.

The deformation of a system containing a cylindrical interfacial surface can be arbitrarily divided into three stages: (1) the conversion of the curved surface into a flat surface by an imaginary change in the physical state of the system, i.e. by lowering the pressure from P_β to P_α^0; (2) stretching the flat interface to a new (larger) area; (3) bending the new surface to a new radius of curvature. Finally, by summing the amounts of work done in the three stages we obtain the fundamental equation for the excess in the grand thermodynamic potential (at constant T and μ_i) in the form

$$d\Omega_s = \sigma_0 dA_0 + dW_b(r_0) , \tag{46}$$

in which the dividing surface has a radius r_0, and the term $dW_b(r_0)$ is the work of bending the interface for an infinitesimally small change in curvature (the subscript b denotes a characteristic of the bending).

When the function $P_T^0(r)$ is modelled by a rectangular well (see Fig. 8) the work of bending $dW_b(r_0)$ for the cylindrical surface is zero. This follows from the fact that the interfacial tension σ_G calculated by Eqn (9) is independent of the pressure P_β and equal to σ_0. In this case Eqn (46) becomes

$$d\Omega_s = \sigma_0 dA_0 , \tag{47}$$

and the corresponding fundamental equation for the equilibrium of a system containing a cylindrical interface,

$$\frac{\sigma_0}{r_0} = P_\beta - P_\alpha^0 , \tag{48}$$

reduces to the Laplace equation (24), except that the pressure P_β is treated as arbitrary (not standard) and the interfacial tension σ_0 refers to a flat dividing surface with $P_\beta^0 = P_\alpha^0$.

We should stress the following advantages of the proposed thermodynamic description of a system containing a cylindrical interfacial surface which postulates a $P_T^0(r)$ function in the form of a rectangular well: (1) the dividing surface is identified with a physical surface of radius r_0 rather than with a tension surface of radius $R_t = r_0(1 + \Delta/r_0)^{\frac{1}{2}}$ (which depends on the radius of curvature r_0); (2) the interfacial tension σ_0 stays constant when the interface is bent, unlike the interfacial tension $\sigma_t = \sigma_0(1 + \Delta/r_0)^{\frac{1}{2}}$, which depends also on the radius of curvature r_0; (3) the Laplace equation is in its simplest form, and therefore makes the method very attractive for the thermodynamic description of systems in which the interfacial surface has a small radius of curvature.

When $P_T^0(r)$ is a function of arbitrary form the work of bending the dividing surface in (46) can be expressed as

$$dW_b(r_0) = c_1^0 A_0 dr_0 , \tag{49}$$

where

$$c_1^0 = \frac{1}{A_0}\frac{\partial \Omega_s}{\partial r_0}\bigg|_{T, \mu_i, A_0} .$$

The parameter r_0 must be chosen so as to make the interfacial tension $\sigma(R)$ equal to σ_0. We shall arbitrarily call this dividing surface a standard dividing surface.

2. Spherical free interfaces

Spherical free interfaces are characterised by two identical principal radii of curvature: $R_1 = R_2 = R$ (Fig. 10).

The work done by the tangential pressure $P_T(r)$ during changes in volume of a system containing a surface of this type (as a result of infinitesimally small changes $d\varphi_1$ and $d\varphi_2$ in the angles φ_1 and φ_2 at constant T and μ_i) can be expressed as

$$dW = \int_{R_\beta}^{R_\alpha} P_T(r) r\, d\varphi_1 r\, d\varphi_2 dr . \tag{50}$$

Replacing this real system by an idealised model formed by two reference phases α and β with a spherical dividing surface of

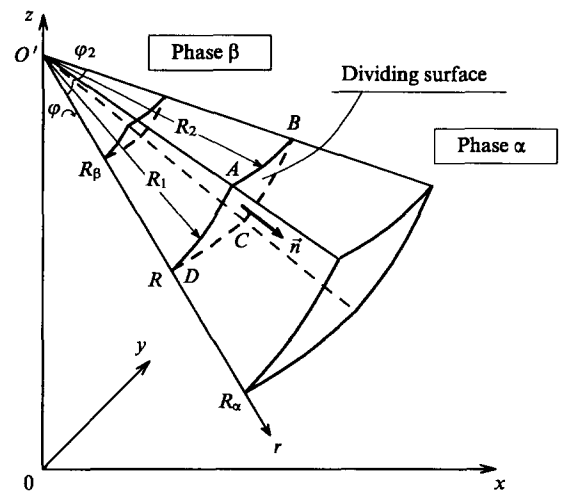


Figure 10. Element of volume of a system containing a spherical interface.

radius R gives an expression for the work dW^{id} in the form [see Eqn (15)]

$$dW^{id} = \left\{\int_{R_\beta}^{R} P_\beta r^2 dr + \int_{R}^{R_\alpha} P_\alpha r^2 dr - \sigma(R)R^2\right\} d\varphi_1 d\varphi_2 . \tag{51}$$

It follows from the condition of mechanical equivalence of the real system and of its idealised model.[11, 26] that

$$\sigma(R) = -\int_{R_\beta}^{R} [P_T(r) - P_\beta]\frac{r^2}{R^2} dr - \int_{R}^{R_\alpha} [P_T(r) - P_\alpha]\frac{r^2}{R^2} dr . \tag{52}$$

The fundamental equation of a system containing a spherical free interface is given as

$$d\Omega = -S dT - \sum_i N_i d\mu_i - P_\beta dV_\beta - P_\alpha dV_\alpha + \sigma(R) dA(R) + cA(R) dk , \tag{53}$$

where c is a coefficient for the differential of the average curvature k:

$$k = k_1 + k_2 = \frac{1}{R_1} + \frac{1}{R_2} = \frac{2}{R} . \tag{54}$$

Eqn (53) is the analogue of the fundamental equation for a cylindrical surface (13), but the coefficients c and c_1, and also the interfacial tensions, are differently defined in the two equations.

As in the case of the cylindrical surface we can obtain a fundamental equation for a spherical free dividing surface,

$$d\Omega_s = -S_s dT - \sum_i N_i d\mu_i + \sigma(R) dA(R) + cA(R) dk , \tag{55}$$

and the Gibbs–Duhem equation for this surface

$$d\sigma(R) = -s_s dT - \sum_i \Gamma_i d\mu_i + c\, dk . \tag{56}$$

By minimising the free energy in Eqn (53) through variations of the radius of curvature of the dividing surface we obtain the fundamental equilibrium equation of a system containing a spherical interface:

$$\frac{2\sigma(R)}{R} + c\frac{\partial k}{\partial R} = P_\beta - P_\alpha , \tag{57}$$

which reduces (allowing for the self-evident geometric relation $\partial k/\partial R = -k^2/2$) to an equation of the Gibbs–Kelvin type for a spherical surface,

$$k\sigma(R) - \tfrac{1}{2}ck^2 = P_\beta - P_\alpha . \tag{58}$$

For $c = 0$ (the condition for which the Gibbs tension surface is defined[8]) we obtain form (58) the familiar Laplace equation for a spherical surface

$$\frac{2\sigma_t}{R_t} = P_\beta - P_\alpha \,. \tag{59}$$

For the tension surface the fundamental equation of a system containing a spherical interface becomes[11]

$$d\Omega = -S\,dT - \sum_i N_i\,d\mu_i - P_\beta dV_\beta - P_\alpha dV_\alpha + \sigma_t dA_t \,. \tag{60}$$

Eqn (52) is the definition of the interfacial tension which may be called the Gibbs interfacial tension.[16] It is obtained from the condition of equality of the mechanical moments of the pressure forces $M = M^{id}$ acting in a plane drawn within an element of spherical volume (Fig. 10) of the real and of the idealised system respectively.

In the case of a spherical surface the Boruvka–Neumann interfacial tension,[19] defined by Eqn (34), does not follow from the condition of equality of the forces f and f^{id} acting on the side surface which limits the element of volume (see Fig. 10) of the real and the idealised system respectively, as it does in the case of a cylindrical interface.

On the other hand we obtain from the condition $f = f^{id}$ a new definition of the interfacial tension, denoted by the symbol σ_f:

$$\sigma_f(R) = \int_{R_\beta}^{R} [P_\beta - P_T(r)]\frac{r}{R}dr + \int_{R}^{R_\alpha} [P_\alpha - P_T(r)]\frac{r}{R}dr \,. \tag{61}$$

This parameter differs from the Gibbs and the Boruvka–Neumann interfacial tensions for spherical surfaces [Eqns (52) and (34), respectively], though its form is consistent with the expression (33) for σ_G in the case of a cylindrical surface.

Thus in the case of spherical dividing surfaces the interfacial tension can be defined in three ways: as σ_G, σ_f, or σ_{BN}. These quantities are different functions of the radius R of the spherical dividing surface. Some workers[10, 14, 19, 21] ignore this difference, or at least they fail to allow for it adequately: this accounts for the different version of the Gibbs–Kelvin equation which had been proposed.

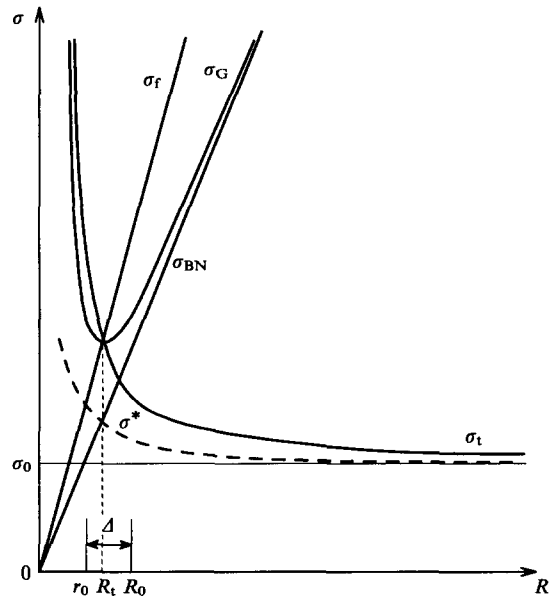


Figure 11. Dependence of the Gibbs and the Boruvka–Neumann interfacial tension and of σ_f [defined by Eqn (61)] on the radius of the spherical interface for $r_0 = \Delta$ (see Fig. 7): σ_0 is the interfacial tension of the flat surface; σ_t is the interfacial tension of the tension surface as a function of the radius of curvature r_0; σ^* is the interfacial tension defined by Eqn (37); R_t is the radius of curvature of the tension surface.

The dependences $\sigma_G(R)$, $\sigma_f(R)$, and $\sigma_{BN}(R)$, illustrated in Fig. 11, should be compared with Fig. 9, which shows similar plots of the functions $\sigma_G(R)$ and $\sigma_{BN}(R)$ for a cylindrical dividing surface.

The following relationships which follow from the condition of mechanical equilibrium $\operatorname{div}\hat{P} = 0$ for a spherical surface[10, 15] have also been used to calculate the hydrostatic pressure P_β and the interfacial tensions:

$$\frac{d(r^2 P_N)}{d(r^2)} = P_T \,, \tag{62}$$

$$\frac{dP_N}{dr} = \frac{2}{R}(P_T - P_N) \,, \tag{63}$$

$$\frac{d(r^3 P_N)}{dr} = r^2(P_N + 2P_T) \,. \tag{64}$$

Eqn (63) can also be written[25] as

$$\frac{dP_N}{dr} = k(r)(P_T - P_N) \,, \tag{65}$$

where $k(r) = 2/r$ is the curvature of a spherical dividing surface of radius r. In an integral form Eqn (65) becomes

$$P_\beta - P_\alpha = \int_{R_\beta}^{R_\alpha} [P_N(r) - P_T(r)]k(r)dr \,.$$

Integration of (62) leads to the equation[15]

$$\tfrac{1}{2}(P_\alpha R_\alpha^2 - P_\beta R_\beta^2) = \int_{R_\beta}^{R_\alpha} P_T(r) r\,dr \,.$$

We note that the plots of the functions $\sigma_G(R)$ and $\sigma_f(R)$ intersect at one point, corresponding to the values R_t and σ_t. As reported,[10, 11] the spherical tension surface is defined as the dividing surface which satisfies the condition

$$\sigma_G(R_t) = \sigma_f(R_t) \,, \tag{66}$$

where $\sigma_G(R)$ and $\sigma_f(R)$ are described by Eqns (52) and (61) respectively. Thus the values of R_t and σ_t given by the plots in Fig. 11 are respectively the radius and the interfacial tension of the tension surface. Fig. 11 also shows the $\sigma_t(R_t)$ dependence.

We also note that, in contrast to the cylindrical surface, in a spherical dividing surface the graphs of $\sigma_G(R)$ and $\sigma_{BN}(R)$ do not intersect anywhere.

As was pointed out above, in submicroscopic liquid drops (micelles, vesicles, coacervate drops), characterised by ultra-low interfacial tensions, a very important role is played by the form of the fundamental equation and of the generalised Laplace (or Gibbs–Kelvin) equation. Analytical equilibrium equations of the Gibbs–Kelvin type, obtained for the idealised profile of the $P_T(r)$ component of the hydrostatic pressure tensor shown in Fig. 8*a*, are given below for comparison.

The generalised Laplace equation for the tension surface is

$$\frac{2\sigma_t}{R_t} = P_\beta - P_\alpha \,. \tag{67}$$

Here

$$\sigma_t = \sigma_0\left[(1+\alpha)\left(1+\frac{\alpha}{2}\right)\right]^{2/3} \,,$$

$$R_t = r_0\left[\frac{(1+\alpha)^2}{1+\alpha/2}\right]^{1/3} \,, \tag{68}$$

where $\alpha = \Delta/r_0$, Δ is the width of the transition region, and σ_0 is the interfacial tension of the flat interfacial surface,

$$\sigma_0 = \int_{R_\beta}^{R_\alpha} [P_\alpha - P_T^0(r)]dr \,, \tag{69}$$

where the standard $P_T^0(r)$ function is a rectangular well (Fig. 8*a*), i.e. it corresponds to the condition $P_\alpha = P_\beta$.

For the Boruvka–Neumann interfacial tension[19, 21] the generalised Laplace equation is

$$\frac{2\sigma_{BN}}{R}\left(1+\frac{\alpha}{2}\right) = P_\beta - P_\alpha , \tag{70}$$

where

$$\sigma_{BN} = \sigma_0 \frac{R}{r_0} . \tag{71}$$

For the interfacial tension σ_0 defined by Eqn (69) we have

$$\frac{2\sigma_0}{r_0}\left(1+\frac{\alpha}{2}\right) = P_\beta - P_\alpha . \tag{72}$$

Lastly, for the interfacial tension σ^*, defined by the expression

$$\sigma^* = \int_{R_\beta}^{R_\alpha} [P_\alpha - P_T^0(r)]\frac{r}{r_0}\mathrm{d}r = \sigma_0\left(1+\frac{\alpha}{\Delta}\right) , \tag{73}$$

the generalised Laplace equation takes the very simple form

$$\frac{2\sigma^*}{r_0} = P_\beta - P_\alpha . \tag{74}$$

By comparing the generalised Laplace equations for different definitions of the interfacial tension and different radii of the spherical separation surfaces we may conclude that the simplest thermodynamic description of these surfaces is offered by using the interfacial tension σ_0, defined for flat interfaces, and the physical radius of curvature of the surface r_0 [see Eqn (72)]. On the other hand, the advantage of using the interfacial tension σ^* [defined by Eqn (73)] and the radius r_0 [see Eqn (74)] is not clear. In practical calculations of the Gibbs interfacial tension (including calculations of the tension surface) and of the Boruvka–Neumann interfacial tension slight deviations of the radius of the dividing surface from the chosen value (for example, from the value R_t) produce changes in the functions $\sigma_G(R)$ and $\sigma_{BN}(R)$, i.e. they complicate the form of the Laplace equation. However, we should stress that all these remarks are of practical significance only for the interfacial surfaces of submicroscopic objects, having radii commensurate with the transition region of the interfacial surface. For higher values of the radius r_0, i.e. $\alpha \to 0$, all the interfacial tensions are effectively equal.

3. Non-spherical free interfaces with two principal radii of curvature

By analogy with the cylindrical and the spherical interfacial surfaces we shall write the fundamental equation for systems containing a non-spherical free interface with two principal radii of curvature R_1 and R_2 in the form

$$\mathrm{d}\Omega = -S\mathrm{d}T - \sum_i N_i \mathrm{d}\mu_i - P_\alpha \mathrm{d}V_\alpha - P_\beta \mathrm{d}V_\beta + \sigma_G \mathrm{d}A + c_1 A \mathrm{d}k_1 + c_2 A \mathrm{d}k_2 , \tag{75}$$

in which $k_1 = 1/R_1$ and $k_2 = 1/R_2$ are the principal values of the surface curvature, c_1 and c_2 are the coefficients of the curvature differentials, and R_1 and R_2 are the radii (i.e the distances along the z axis from the points O_1 and O_2 to the dividing surface, see Fig. 12). Integrating Eqn (75) with respect to the extensive parameters V_α, V_β, and A with constant intensive parameters T, μ_i, k_1, and k_2 yields an expression for the grand thermodynamic potential of the system:

$$\Omega = -P_\alpha V_\alpha - P_\beta V_\beta + \sigma_G A , \tag{76}$$

where A is the area of interfacial surface generated by stretching with constant values of k_1 and k_2, and σ_G has the meaning of a Gibbs interfacial tension.

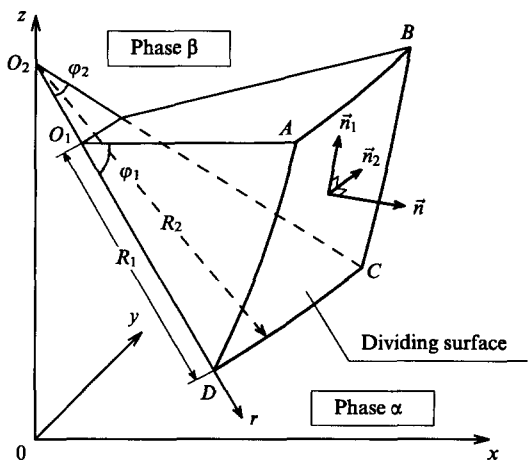


Figure 12. Element of volume of a system containing a non-spherical interface with two different principal radii.

By minimising the grand thermodynamic potential while varying the displacement of the separation surface in the direction of the normal $\vec{n}$ by δR and allowing for the obvious geometric relations

$$\frac{\partial V_\beta}{\partial R} = A ; \quad \frac{\partial V_\alpha}{\partial R} = -A ; \quad \frac{\partial A}{\partial R} = kA ;$$

$$k = k_1 + k_2 ; \quad c_1\frac{\partial k_1}{\partial R} + c_2\frac{\partial k_2}{\partial R} = \frac{\partial \sigma_G}{\partial R} ;$$

we obtain

$$k\sigma_G + \frac{\partial \sigma_G}{\partial R} = P_\beta - P_\alpha . \tag{77}$$

Eqn (77) is the fundamental equilibrium equation for a system containing a non-spherical separation surface.

The fundamental equation of the non-spherical separation surface itself is[8]

$$\mathrm{d}\Omega_s = -S_s\mathrm{d}T - \sum_i N_{is}\mathrm{d}\mu_i + \sigma_G \mathrm{d}A + c_1 A \mathrm{d}k_1 + c_2 A \mathrm{d}k_2 , \tag{78}$$

which should be compared with the equations (19) and (55) for cylindrical and for spherical surfaces respectively.

By applying Euler's theorem of homogeneous functions we find that, by analogy with (21) and (56), the Gibbs–Duhem equation for a non-spherical separation surface is

$$\mathrm{d}\sigma_G = -s_s\mathrm{d}T - \sum_i \Gamma_i \mathrm{d}\mu_i + c_1\mathrm{d}k_1 + c_2\mathrm{d}k_2 . \tag{79}$$

We shall now briefly review various approaches to the description of non-spherical free interfaces.

The concepts of average curvature (H) and of differential curvature (D) were first proposed by Gibbs,[8] who defined them as

$$H = \tfrac{1}{2}(k_1 + k_2) \quad \text{and} \quad D = \tfrac{1}{2}(k_1 - k_2) . \tag{80}$$

In these symbols the fundamental equation of the system is

$$\mathrm{d}\Omega = -S\mathrm{d}T - \sum_i N_i \mathrm{d}\mu_i - P_\alpha \mathrm{d}V_\alpha - P_\beta \mathrm{d}V_\beta + \sigma_G \mathrm{d}A + AB\mathrm{d}H + A\theta\mathrm{d}D , \tag{81}$$

where B and θ are the specific bending and torsion moment respectively (referred to unit area of the separation surface):

$$B = c_1 + c_2 , \quad \text{and} \quad \theta = c_1 - c_2 . \tag{82}$$

In his derivation of the fundamental equilibrium equation of the system Gibbs[8] ignored the torsion moment θ (a second-order quantity as compared with the bending moment B: in the case of spherical surfaces the condition $\theta = 0$ applies exactly). By applying also the condition $B = 0$ to the tension surface Gibbs obtained the Laplace equation from the fundamental equation of the system (81) (by minimising the grand thermodynamic potential):

$$k_t\sigma_t = P_\beta - P_\alpha , \tag{83}$$

where

$$k_t = k_{1t} + k_{2t} , \tag{84}$$

and k_{1t} and k_{2t} are the principal curvatures of the tension interface.

Later work on the thermodynamics of non-spherical free interfaces dealt with the effect of the torsion moment θ on the generalised Laplace equation,[15, 16, 19, 21, 25]

Applying the minimisation procedure to Eqn (81) while allowing for the moment θ gives the following fundamental equilibrium equation:[25]

$$2H\sigma_G - B(H^2 + D^2) - 2\theta HD = P_\beta - P_\alpha . \tag{85}$$

Eqn (85) known as the Gibbs–Kelvin equation for non-spherical surfaces.[25] By comparing it with (77) we obtain

$$\frac{\partial\sigma_G}{\partial R} = -B(H^2 + D^2) - 2\theta BD . \tag{86}$$

The condition

$$\frac{\partial\sigma_G}{\partial R} = 0 , \tag{87}$$

corresponding to a minimum in the interfacial tension, takes the form

$$B(H^2 + D^2) + 2\theta BD = 0 . \tag{88}$$

The interface which satisfies the condition (88) is called the surface of minimum tension, in contrast to the Gibbs tension surface, obtained for the condition $B = 0$. Thus Gibbs ignored the term $2\theta HD$ in his definition of the tension surface. Obviously, the spherical surfaces of tension and of minimum tension coincide when $\theta = 0$.

Some workers[16, 19, 21] have suggested replacing H and D by the principal (first) curvature J and the Gaussian (second) curvature K of the surface:

$$J = k_1 + k_2 , \quad \text{and} \quad K = k_1k_2 . \tag{89}$$

In this case the fundamental equation of the system for a nonspherical surface becomes

$$d\Omega = -S\,dT - \sum_i N_i\,d\mu_i - P_\alpha dV_\alpha - P_\beta dV_\beta + \sigma_G dA + AC_1 dJ + AC_2 dK , \tag{90}$$

and the fundamental equilibrium equation of the system is[16]

$$J\sigma_G - C_1(J^2 - 2K) - C_2JK = P_\beta - P_\alpha , \tag{91}$$

where

$$C_1 = \frac{c_1k_1 - c_2k_2}{k_1 - k_2} ; \quad C_2 = \frac{c_1 - c_2}{k_1 - k_2} \tag{92}$$

[the coefficients c_1 and c_2 occur in Eqn (79)].

The condition which defines the interface of minimum tension (88) can be written[16]

$$C_1(J^2 - 2K) + C_2JK = 0 . \tag{93}$$

The Laplace equation is obtained by inserting the condition (93) into (91):

$$k_0\sigma_G^0 = P_\beta - P_\alpha , \tag{94}$$

where $k_0 = J_0 = k_{10} + k_{20}$, k_{10} and k_{20} are the principal curvatures of the minimum tension surface, and σ_G^0 is the minimum tension of the nonspherical surface.

III. Equilibrium of interfaces in the bulk meniscus region of a liquid film

If the separation surfaces in a liquid film are assumed to be surfaces of minimum tension, and allowance is made for the close similarity of σ_G^0 with σ_t for the tension surface with σ_0 for plane-parallel surfaces (when the radius of curvature is much greater than the thickness of the transitional interfacial layer, i.e. in practical terms for $r_0 > 10$ nm) the equilibrium equation (85) becomes

$$k_0\sigma_0 = P_\beta - P_\alpha = \Delta P , \tag{95}$$

where $k_0 = k_1 + k_2$, and k_1 and k_2 are the first and the second principal curvatures of the surface.

1. Invariants of the profile of a liquid film

Since the profile of liquid films is determined experimentally by the topographic method[7] (from interference pictures of the film in reflected monochromatic light) it is convenient to use Eqn (95) in $z(r)$ coordinates (Fig. 13). This gives invariants of the profile of liquid films related to differences in geometry.

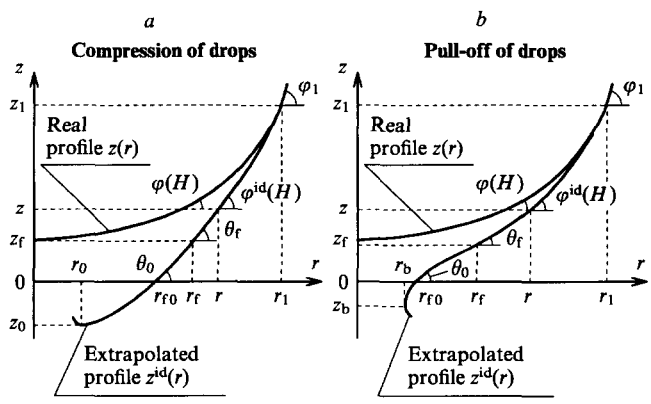


Figure 13. Form of the extrapolated profile of the surface of the liquid film between two liquid drops during compression by an external force (*a*) and pull-off (*b*).

It should be noted that because of the experimental difficulties in determining the real profile of a liquid film in the transition region a hypothetical profile (obtained by extrapolating the profile of the surface with a constant average curvature k_0 in the region of the bulk meniscus to the transition region) is often used in the thermodynamic description instead of the real profile, on the assumption that disjoining pressures are negligible (Fig. 13). This extrapolated (idealised) profile $z^{id}(r)$ differs from the real profile $z(r)$ in the transition region of the film, and coincides with the real profile in the region of the bulk meniscus.

The idealised profile can intersect the plane $z_f = H_f/2$ (where H_f is the thickness of the plane-parallel region of the film, and the subscript f denotes a quantity characteristic of the film) at a contact angle θ_f, or the plane $z = 0$ at a constant angle θ_0, whose values are used to calculate the specific free energy of the interaction in the flat part of the film.

For cylindrical interfaces, which have only one principal radius of curvature, Eqn (95) becomes

$$\sigma_0\frac{d\sin\varphi^{id}(r)}{dr} - \Delta P = 0 , \tag{96}$$

where $\varphi^{id}(r)$ is the local angle, formed by the surface of the idealised profile with the r axis. The equation

$$\frac{dz^{id}(r)}{dr} = \tan\varphi^{id}(r) \tag{97}$$

in conjunction with Eqn (96) forms a system which fully defines the profile of the film $H^{id}(r) = 2z^{id}(r)$ if the following boundary conditions are given: $\varphi^{id}(r) = \varphi_1$ and $z^{id}(r) = z_1$ for $r = r_1$, where r_1 is the radius of the film determined experimentally in the region of the bulk meniscus.

Integrating (96) over the idealised profile z^{id} from $z^{id}(r)$ to z_1 gives

$$\int_{z^{id}}^{z_1} \sigma_0 \frac{d\sin\varphi^{id}(r)}{dr} dz^{id} - \Delta P(z_1 - z^{id}) = 0 . \tag{98}$$

Since $[d\sin\varphi^{id}(r)/dr]dz^{id} = -\cos\varphi^{id}$ we obtain from (98) an invariant which is independent of the film thickness:

$$2\sigma_0\cos\varphi^{id}(r) + \Delta P H^{id}(r) = 2\sigma_0\cos\varphi_1 + \Delta P H_1 = \text{const} . \tag{99}$$

In the case of nonspherical interfaces characterised by two different radii of curvature the Laplace equation (95) becomes

$$\sigma_0 \frac{d\sin\varphi^{id}(r)}{dr} + \sigma_0 \frac{\sin\varphi^{id}(r)}{r} - \Delta P = 0 . \tag{100}$$

Integrating (100) as was done for the cylindrical surface gives an invariant independent of the local thickness of the idealised film profile $H^{id}(r)$:

$$2\sigma_0\cos\varphi^{id}(r) + \Delta P H^{id}(r) + 2\sigma_0 \int_{z^{id}}^{z_1} \frac{\sin\varphi^{id}(r)}{r} dz^{id}$$

$$= 2\sigma_0\cos\varphi_1 + \Delta P H_1 = \text{const} . \tag{101}$$

If the interfacial surface in the liquid film is spherical, i.e. if $k_1 = k_2$, the integral in Eqn (101) reduces to $\Delta P[H_1 - H(r)]/2$, and the invariant of the surface profile of the film takes the form

$$2\sigma\cos\varphi^{id}(r) + \tfrac{1}{2}\Delta P H^{id}(r)$$

$$= 2\sigma_0\cos\varphi_1 + \tfrac{1}{2}\Delta P H_1 = \text{const} . \tag{102}$$

2. Analytical expression for the idealised profile of the liquid film

Let us consider two fluid (liquid or gaseous) particles of the phase β forming a symmetrical liquid film in the phase α. To simplify the discussion we shall ignore the effect of gravity, and assume that the film is stable towards rupture and is not spontaneously thinned.

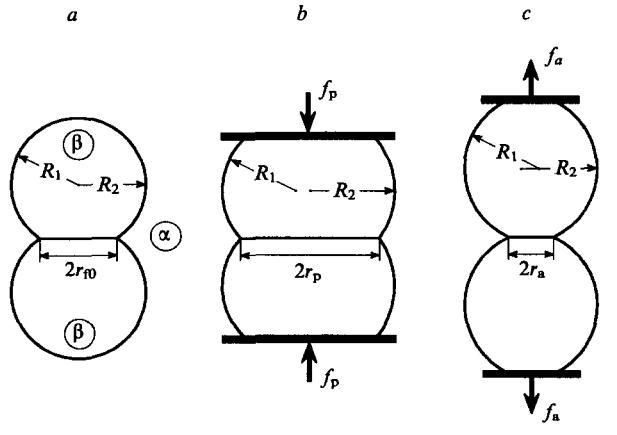


Figure 14. Shape of contacting drops in the absence of an external force (*a*), under compression (*b*), and during pull-off (*c*).

If the fluid particles do not experience an external force f_e (compressive, $f_p > 0$, or stretching, $f_a < 0$) the particles are spherical (Fig. 14*a*), and $k_1 = k_2 = k_0 = 2/R$, where R is the radius of the particles. In this case the profile of the surface of the particles, or the idealised profile of the film surface $z^{id}(r)$ [see Eqn (97)], is described by the equation

$$z^{id}(r) = z_1 - \int_{z^{id}}^{z_1} \tan\varphi^{id}(r) dr$$

$$= z_1 + R[\cos\varphi_1 - \cos\varphi^{id}(r)] . \tag{103}$$

If the particles are compressed by an external force f_p (Fig. 14*b*) the radius of the film increases to r_p, and the surface of the drops is no longer spherical, the radius R_2 increasing and R_1 decreasing. When a tensile force f_a is applied to the drops (Fig. 14*c*) R_2 decreases and R_1 increases.

By re-writing Eqn (100) as

$$\sigma_0 \frac{1}{r}\frac{d}{dr}[r\sin\varphi^{id}(r)] = \Delta P \tag{104}$$

and integrating it from r to r_1 we obtain the equation[1, 4]

$$\sin\varphi^{id}(r) = \frac{k_0}{2}r + \frac{B}{r} , \tag{105}$$

in which

$$k_0 = \frac{\Delta P}{\sigma_0} ,$$

$$B = r_1\sin\varphi_1 - \frac{k_0}{2}r_1^2 . \tag{106}$$

The physical significance of the parameter B can be understood by the following considerations. If the reference radius r_1 is taken to be R_2 (see Fig. 14*a*) we have $\varphi_1 = \pi/2$, and we arrive at the expression

$$B = \frac{k_{20} - k_{10}}{2k_{20}^2} = \frac{1}{k_{20}}\left(1 - \frac{k_0}{2k_{20}}\right) , \tag{107}$$

where k_{10} and k_{20} are the principal values of the curvature of the particle surfaces, corresponding to the 'equator', for which $\varphi_1 = \pi/2$. Obviously, the parameter B can be positive or negative, depending on the sign of the difference $(k_{20} - k_{10})$.

We shall now obtain expressions for the contact forces acting on fluid drops for the cases of mutual compression or pull-off.

In the case of a compressive force $f_e = f_p > 0$ the $z^{id}(r)$ profile has a maximum (see Fig. 13*a*) since, when $\varphi^{id}(r_0) = 0$, Eqn (105) has a real solution (allowing for the fact that $B < 0$):

$$r_0 = \sqrt{-\frac{2B}{k_0}} , \tag{108}$$

where k_0 is the average curvature.

From the condition of mechanical equilibrium of the drop we obtain the expression

$$f_p = \pi r_0^2 \Delta P = \pi r_0^2 \sigma_0 k_0 , \tag{109}$$

and in conjunction with (108) this gives

$$f_p = -2\pi\sigma_0 B . \tag{110}$$

The parameter B can be determined experimentally from the interference picture of the film.[27-29] The compressive force can also be determined[4] from Eqn (110). A mechanical interpretation of Eqn (109) is proposed in Fig. 15*a*. Evidently, the outer compressive force f_p is balanced by a pressure force of $\pi r_0^2\sigma_0 k_0$.

If a pull-off force $f_e = f_a < 0$ is applied to the drops (see Fig. 14*c*) it follows from (107) that $B > 0$, and Eqn (105) does not have a real solution for $\varphi^{id}(r) = 0$ [i.e. the profile $z^{id}(r)$ has no minimum].

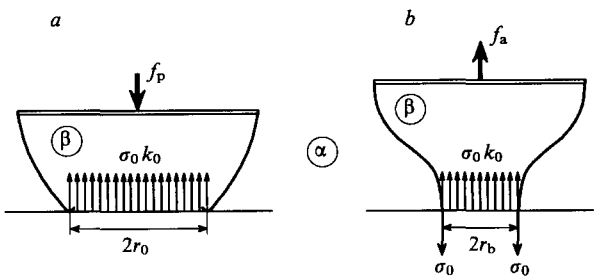


Figure 15. Equilibrium of a liquid drop under the influence of compression (*a*) and extension forces (*b*).

On the other hand for $\varphi^{id}(r) = \pi/2$, Eqn (105), written as

$$1 = \frac{k_0}{2} r + \frac{B}{r} , \tag{111}$$

has two real roots:

$$r_{(1)} = r_b = \frac{1 - \sqrt{1 - 2k_0 B}}{k_0} = \frac{1}{k_0}\left(1 - \frac{k_{10}}{k_{20}}\right) , \tag{112}$$

(see Fig. 13*b* for r_b), and

$$r_{(2)} = \frac{1}{k_{20}} = R_{20} . \tag{113}$$

The geometrical significance of the second root $r_{(2)} = R_{20}$ is illustrated in Fig. 13*b*. A positive value of the first root $r_{(1)} = r_b$ denotes the appearance of a 'neck' in the profile of the drop. Obviously, for $z^{id} = z_b$ (see Fig. 13*b*) the curvature $k_{20} = 1/r_b$ is positive, and $k_{10} = k_0 - k_{20}$ is negative for a positive average curvature k_0.

The relationship between r_b and f_a can be obtained by the following argument (Fig. 15*b*). Since the drop is assumed to be in equilibrium the resultant of all the forces acting on it must vanish. These forces are: the external pull-off force f_a; the interfacial tension force acting on the perimeter of the neck and equal to $-2\pi r_b \sigma_0$; and the hydrostatic pressure force, equal to $\pi r_b^2 \Delta P = \pi r_b^2 \sigma_0 k_0$. Equating their sum to zero gives

$$f_a - 2\pi r_b \sigma_0 + \pi r_b^2 \sigma_0 k_0 = 0 , \tag{114}$$

which becomes, when combined with (111),

$$f_a = 2\pi\sigma_0 \left[r_b - \tfrac{1}{2} k_0 r_b^2\right] = -2\pi\sigma_0 B . \tag{115}$$

Thus in the case of pull-off of the drops the parameter B is proportional to the applied negative force f_a.

Furthermore by using the sign convention for the force f_e, according to which $f_e = f_p > 0$ and $f_e = f_a < 0$, Eqn (110) and (115) can be re-written[4]

$$f_e = -2\pi\sigma_0 B , \tag{116}$$

while Eqn (105) becomes[4]

$$\sin\varphi^{id}(r) = \frac{k_0}{2} r - \frac{f_e}{2\pi\sigma_0} \frac{1}{r} . \tag{117}$$

Thus we may conclude that the extrapolated profile of the liquid film contains information on the external force f_e acting on the drop and on its sign: if $B > 0$ the drop is experiencing a pull-off force, whereas if $B < 0$ the applied force is compressive.

3. Various approximations to the idealised profile of the liquid film

The idealised profile of a curved liquid film (the profile of the film in the region of the bulk meniscus) contains information on the specific free energy of the interaction in the plane-parallel region of the film. Therefore measurements of the profile of these films are one of the main experimental methods of studying the energetics of thin liquid films.

Since the analytical expression for the function $z^{id}(r)$ usually contains elliptical integrals of the second kind various simplifications of the idealised profile have been suggested for practical use.[7, 28, 29] The approximating functions proposed by Kolarov et al.[7, 28] are among the most widely used:

$$z^{id}(r) = ar^2 + b , \tag{118}$$

$$z^{id}(r) = ar^2 + b' \ln r + c , \tag{119}$$

where a, b, b', and c are empirical coefficients, determined by measuring the profile of the film in the region of the bulk meniscus. The contact angles θ_f and θ_0 and the radii r_f and r_{f0} of the curved films (see Fig. 13) are found by extrapolating the approximating functions to the transition region of the film.

We should stress that the approximating functions (118) and (119) are obtained from the strict solution of the system of differential equations (97) and (117) for the following approximations: $\tan\varphi^{id} \simeq \sin\varphi^{id}$ and $f_e = 0$ for Eqn (118) and $\tan\varphi^{id} \simeq \sin\varphi^{id}$ for Eqn (119). For large enough values of the contact angle both these approximating functions are almost identical to the exact function. However, for the contact angles formed by the common black films or by the Newtonian black films, usually in the ranges $\lesssim 1°$ and $1° - 5°$ respectively, replacing the exact functions by the approximating functions can result in erroneous calculations of the contact angles.

In particular, an estimate of the precision of the approximated profile obtained by the functions (118) and (119) for a liquid film having an angle of contact of $\sim 1°$ has been reported.[30] It was shown that the function (119) satisfactorily describes the profile of these films. On the other hand, use of the parabola (118) introduces serious errors in the determination of the contact angles. It was also found[31] that the function (119) is convenient for describing the profiles of films which do not form contact angles θ_0 and θ_f (in the latter case the specific free energy of the interaction in the film is positive). On the other hand the use of the parabola to describe the profile of these films results in the formation of contact angles, i.e. it leads to the erroneous conclusion that the specific free energy is negative in these films.

4. Lens-like thickening in equilibrium with a thin liquid film

A lens-like thickening (or dimple) at the centre of a round liquid film is formed when two fluid drops (liquid or gaseous) are rapidly brought into contact in a liquid medium (Fig. 16*a*) or in the contact region between a drop and a solid surface (Fig. 16*b*).

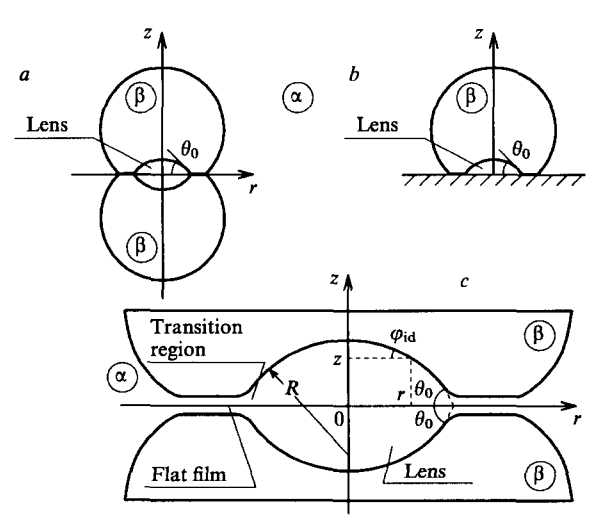


Figure 16. Lens-like thickening produced in the contact region between two fluid drops of phase β in the liquid phase α (*a*) and in the contact region between a fluid drop and a solid surface (*b*); geometric parameters of the liquid lens in equilibrium with the liquid film (*c*).

We shall obtain the equation for the profile of these lenses in the coordinates defined in Fig. 16c.

Since the first and the second principal curvature of the lens profile are given by the expressions

$$k_1 = -\frac{\mathrm{d}\sin\varphi^{\mathrm{id}}(r)}{\mathrm{d}r}\ ;\ k_2 = -\frac{\sin\varphi^{\mathrm{id}}(r)}{r}\ ,$$

the fundamental equilibrium equation (100) is[18]

$$\sigma_0\frac{\mathrm{d}\sin\varphi^{\mathrm{id}}(r)}{\mathrm{d}r} + \sigma_0\frac{\sin\varphi^{\mathrm{id}}(r)}{r} + \Delta P_\alpha = 0\ , \tag{120}$$

where $\Delta P = P_\alpha - P_\beta$ is the difference between the hydrostatic pressures in the lens and in the external medium (phase β).

Eqn (97) becomes

$$\frac{\mathrm{d}z^{\mathrm{id}}(r)}{\mathrm{d}r} = -\tan\varphi^{\mathrm{id}}(r)\ , \tag{121}$$

since $z^{\mathrm{id}}(r)$ decreases when r increases.

By integrating (120) with respect to r from zero to an arbitrary value of r corresponding to the bulk region of the meniscus (or to some point on the idealised profile coinciding with the real profile in the region of the bulk meniscus) we obtain

$$\sin\varphi^{\mathrm{id}}(r) = \tfrac{1}{2}k_0 r\ . \tag{122}$$

This expression is the equation for a region of radius $R = \frac{1}{2}k_0$, where $k_0 = \Delta P_{\mathrm{d}}/\sigma_0$. Extrapolating this profile to its intersection with the r axis gives the contact angle θ_0, which is used to calculate the specific free energy of the interaction in the plane-parallel region of the film.

This method of measuring the contact angle θ_0 is known as the floating lens method.[32] It has been used to measure the specific free energy of the interaction[33] in Newtonian black films of hydrocarbons (bilayer lipid membranes), within which microscopic lenses of liquid hydrocarbons had been formed.

We note that Eqns (120) and (121) are convenient for describing the profile of a liquid drop in contact with a flat solid surface under conditions of zero gravity, when the perturbing effect of the gravity forces on the profile of the drop can be neglected.

5. Vertical liquid films in a gravitational field

The effect of gravity on the form of the profile of liquid films will be examined by considering a vertical liquid film produced by drawing a flat plate (for example, a Wilhelmi plate) out of a liquid phase α into a fluid (liquid or gaseous) phase β (Fig. 17).[34]

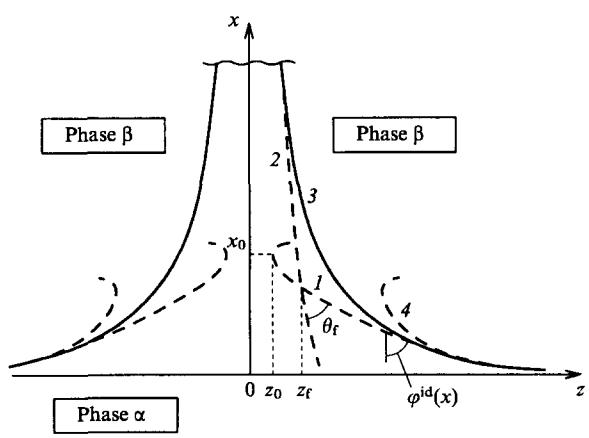


Figure 17. Vertical film in a gravitational force field: *1* and *4*, extrapolated profile of the cylindrical surface; *2*, extrapolated profile of the vertical film; *3*, real surfaces.

In this case the profile of the film in the region of the bulk meniscus is described by the system of equations

$$\sigma_0\frac{\mathrm{d}\sin\varphi^{\mathrm{id}}(x)}{\mathrm{d}x} = \Delta P\ ;\quad \frac{\mathrm{d}z^{\mathrm{id}}(x)}{\mathrm{d}x} = \tan\varphi^{\mathrm{id}}(x) \tag{123}$$

with the boundary conditions $x = 0$ and $\varphi^{\mathrm{id}}(x) = \pi/2$ for $z \to \infty$. Within the liquid film the difference in hydrostatic pressures is

$$\Delta P = P_\beta - P_\alpha = -\Delta\rho g x\ ,$$

i.e. ΔP is now no longer a constant, and Eqn (123), allowing for the chosen direction of the x axis and for the definition of the angle $\varphi^{\mathrm{id}}(x)$, takes the form

$$\frac{\mathrm{d}\sin\varphi^{\mathrm{id}}(x)}{\mathrm{d}x} = -\frac{\Delta\rho g x}{\sigma_0}\ , \tag{124}$$

where $\Delta\rho = \rho_\alpha - \rho_\beta$, and ρ_α and ρ_β are the densities of the phases α and β respectively. Since $\varphi^{\mathrm{id}}(0) = \pi/2$ for $x = 0$, the solution of (124) is

$$\sin\varphi^{\mathrm{id}}(x) = 1 - \frac{x^2}{a^2}\ , \tag{125}$$

where $a = \sqrt{2\sigma_0/\Delta\rho g}$ is the capillarity constant.

The idealised profile of the vertical liquid film in a field of gravity forces can be found by solving Eqn (123) with the boundary conditions $\varphi^{\mathrm{id}}(x) = 0$ and $z^{\mathrm{id}}(x) = z_0$ for $x = x_0$, where $x_0 = a$ [for which the idealised profile $z^{\mathrm{id}}(x)$ has a minimum].

Depending on the sign of the specific free energy of the interaction in the flat part of the film the idealised profile can pass either within the liquid film or outside it, i.e. in the phase β. The method of determining angles of contact in these films has already been discussed in depth.[18, 34]

IV. Thermodynamic description of interacting interfaces in the transition region of a liquid film

The main difficulty in constructing the thermodynamics of interacting interfaces in the transition region of liquid films is the absence of generally accepted views on the disjoining pressure. If the shear components of the generalised pressure tensor $\boldsymbol{P}$ are assumed to be zero in the plane-parallel region of the liquid film, and the tension γ is defined by the expression[22]

$$\gamma = \int_{-\infty}^{+\infty}[P_\beta - P_{\mathrm{T}}(z)]\mathrm{d}z\ , \tag{126}$$

in the transition region (and in particular in the symmetry plane for $z = 0$) the component P_{T} of the pressure tensor varies as a function of the coordinate r from a negative value at the centre of the circular thin liquid film (i.e. at $r = 0$) to a positive value for $r \to \infty$ (i.e. in the region of the bulk meniscus of the film). It is no longer convenient to use the tension γ to construct the fundamental thermodynamic equation of the system in the transition region of the film: firstly, because γ is now a function of the coordinate r, and secondly because shear components of the pressure tensor are now present in the transition region [due to the gradient $P_{\mathrm{T}}(z, r)$], and the relationship (126) ceases to be valid.

Thus we need to develop other approaches to the thermodynamics of the transition region in liquid films.

1. Various definitions of the disjoining pressure

An analysis of recent publications on this topic reveals two points of view on the physical nature of the disjoining pressure and on the mechanism of its action in the transition region of thin liquid films.

The disjoining pressure as a bulk force. According to this model[35–37] the disjoining pressure should be treated as a manifestation of 'forces of the second kind',[38] arising in the region of mutual overlapping of the 'surface forces of the first kind',

i.e. of the two phase separation surfaces (after Gibbs[8]). The disjoining pressure Π, defined by the expression[38]

$$\Pi = P_N - P_\alpha = P_\beta - P_\alpha , \quad (127)$$

is represented as a bulk pressure having tensor properties and existing independently of the separation surfaces of the film. According to this model the action of the disjoining pressure is normal to these surfaces in both the plane-parallel and the transition region of the film[37] (Fig. 18*a*). As a consequence of this model the separation surfaces in the film are treated as non-interacting, and therefore the interfacial tension is assumed to be constant over the whole of the transition region and equal to the interfacial tension σ_0 at the boundary of the bulk phases.[36, 37] The curved separation surfaces, characterised by a constant interfacial tension σ_0, are called 'surfaces of tension' by Eriksson and Toshev:[37] the fundamental equilibrium equation in the transition region of the film becomes[35, 37]

$$\sigma_0 k(H) + \Pi(H) - \Delta P = 0 , \quad (128)$$

where $\Pi(H)$ is the local value of the disjoining pressure (a function of the film thickness H); $\Delta P = P_\beta - P_\alpha$ is the difference between the hydrostatic pressures in the phases β and α; $k(H)$ is the local value of the curvature of the film surface in the transition region.

In the region of the bulk meniscus (Fig. 18*a*) $\Pi = 0$, and from Eqn (128) we obtain the Laplace equilibrium equation $\sigma_0 k_0 = \Delta P$, where k_0 is the constant average curvature of the free curved surface. Eriksson and Toshev[35, 39] define a reference pressure of the Gibbs type at the centre of the circular film, equal to the hydrostatic pressure in the phase β. This assumption formally leads to the creation of a hydrostatic pressure gradient in the transition region, since in the transition region of the bulk meniscus the hydrostatic pressure is P_α. Therefore Eriksson and Toshev[37] introduced into the model an additional force to balance the pressure gradient in the transition region. This expedient produced unnecessary complications in the thermodynamic description of this region of the film, including a number of inconsistencies. For example, the constancy of the interfacial tension σ_0, which follows from the assumption that the action of the disjoining pressure is in a direction normal to the dividing surfaces, is formally incompatible with the Gibbs–Duhem equation,[22] widely used (by Eriksson and Toshev,[37, 39, 40] among others, to describe plane-parallel films):

$$\Pi(H) = -2\frac{\partial\sigma}{\partial H}\bigg|_{T,\mu_i,A} . \quad (129)$$

This contradiction has been pointed out previously.[15]

The disjoining pressure as a specific interaction force between the dividing surfaces in the film has been discussed by the present writer[1–4] and by De Feijter et al.[41–43] The phase α and the pressure P_α are chosen as the reference phase and the reference pressure (in the Gibbs sense), and therefore no pressure gradient appears in the transition region in this model (Fig. 18*b*). An important assumption in this case is that the radial component of the disjoining pressure is zero: this leads to the following fundamental equilibrium equation for the film in the transition region:[1, 31, 44]

$$\sigma(H)k(H) + \Pi(H)\cos\varphi(H) - \Delta P = 0 , \quad (130)$$

where $\sigma(H)$ is the local value of the interfacial tension in the transition region; $\varphi(H)$ is the local contact angle of the real profile of the film surface.

Eqn (130) can be interpreted as the mechanical equilibrium condition of the dividing surface in a direction normal to this surface under conditions of an interfacial tension gradient $\sigma(H)$ in the transition region of the film. Diagrams illustrating the mechanical equilibrium of a dividing surface for a plane-parallel film in the transition region and in the region of the bulk meniscus are shown in Fig. 18*b*: here $\sigma_f = \sigma(H_f)$ is the interfacial tension in a plane-parallel film of thickness H_f. Thus the forces acting at right angles to the film surface in the transition region include the capillary pressure $\sigma(H)k(H)$, the hydrostatic pressures P_α and P_β, and also the projection of the disjoining pressure $\Pi(H)\cos\varphi(H)$, whose sum vanishes at equilibrium [see Eqn (130)].

Evidently, the equilibrium equation (130) reduces to the Eqns (127) and (95), which describe the equilibrium of the film in the plane-parallel region and in the region of the bulk meniscus respectively.

The fundamental equation (130) describes the equilibrium of the film surface in the transition region in a direction tangential to this surface, and allows it to be interpreted mechanically. The gradient of the interfacial tension $d\sigma(H) = \sigma(H + dH) - \sigma(H)$ in a direction tangential to the surface of the film is thus balanced by the force $-\Pi(H)\sin\varphi(H) \times dl$, which can be written

$$d\sigma(H) = \sigma(H + dH) - \sigma(H) = -\Pi(H)\sin\varphi(H) \times dl .$$

This equation is consistent with the Gibbs-Duhem equation (129), since the length of the element of surface dl under consideration is expressed in terms of dH and $\varphi(H)$ by the relation $dH = 2\sin\varphi(H) \times dl$.

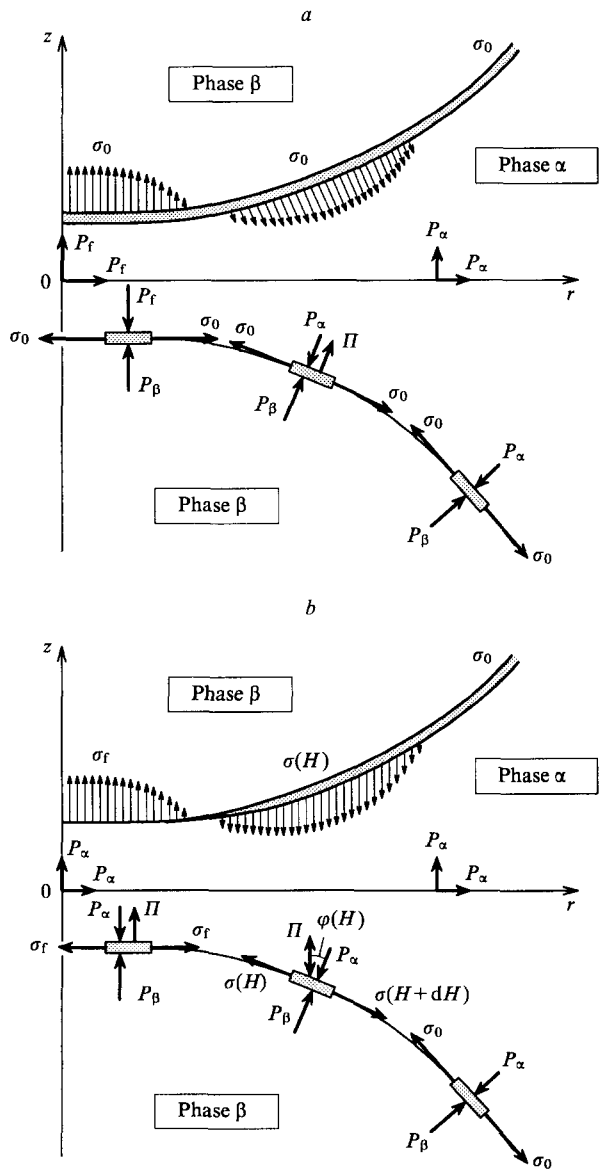


Figure 18. Representation of the disjoining pressure in a liquid film as a pressure tensor (*a*) and as a tensor of the specific interaction force between the dividing surfaces in the film (*b*).

2. The fundamental equation of a liquid film in the transition region

The writer has shown[22] that the fundamental equation of a system containing a plane-parallel film can be written in the form

$$d\Omega = -S\,dT - \sum_i N_i\,d\mu_i - \Delta P\,dV_\beta - \Pi(H)A\,dH + 2\sigma(H)\,dA\,. \quad (131)$$

We note that the layout of this equation does not require a subjective choice of the position of the dividing surfaces in the film, i.e. it is independent of H, even though $\sigma(H)$ and also V_α and V_β depend on the localisation of the dividing surfaces.

The fundamental equation of the system, including two curved non-interacting dividing surfaces of minimum tension in the region of the bulk meniscus, can be written in terms of the equation (90) and the condition (93) in the form[5]

$$d\Omega = -S\,dT - \sum_i N_i\,d\mu_i - \Delta P\,dV_\beta + 2\sigma_0 dA\,, \quad (132)$$

where $\sigma_0 \equiv \sigma_G^0$ [see Eqn (94) and discussion].

Eqn (131) has been used[1-5, 18, 44] as the fundamental equation for the transition region of a liquid film, the position of the dividing surfaces being chosen so as to satisfy the condition (94) over the whole of the transition region. In this case Eqn (131) is converted into Eqn (132) in the region of the bulk meniscus. Since the position of the dividing surfaces in the transition region is unambiguously fixed, the fundamental equation in the plane-parallel region of the film should be written[5]

$$d\Omega = -S\,dT - \sum_i N_i\,d\mu_i - \Delta P\,dV_\beta - \Pi(H_f)A\,dH + 2\sigma_f\,dA\,, \quad (133)$$

where $\sigma_f \equiv \sigma(H_f)$, since the minimum tension surfaces have now been chosen as the dividing surfaces in the plane-parallel film.

Minimising the functional (131) at constant T and μ_i in a direction normal ($\vec{n}$) to the surface of the film in the transition region leads to the expression

$$\delta\Omega = -\Delta P\frac{\partial V_\beta}{\partial \vec{n}_\beta}\delta\vec{n} - \Pi(H)A\frac{\partial H}{\partial \vec{n}}\delta\vec{n} + 2\sigma(H)\frac{\partial A}{\partial \vec{n}}\delta\vec{n}\,,$$

which is converted, allowing for the self-evident geometric relations

$$\frac{A\partial H}{\partial \vec{n}} = -\cos\varphi(H)\left(\frac{\partial V_\beta}{\partial \vec{n}}\right); \quad \frac{2\partial A}{\partial \vec{n}} = k(H)\left(\frac{\partial V_\beta}{\partial \vec{n}}\right),$$

into the fundamental equilibrium equation for the surface of the film in the direction of the normal [Eqn (130)].[1, 5, 18, 44] Under these conditions the Gibbs–Duhem equation (129) defines the equilibrium of an element of surface in a direction tangential to the surface.

The fundamental equation for interacting curved dividing surfaces of minimum tension in the transition region of the film can be obtained from Eqn (131) by subtracting from it the 'bulk' part, corresponding to the macroscopic phases α and β:[5, 18]

$$d\tilde{\Omega}_s = -\tilde{S}_s dT - \sum_i \tilde{N}_{is}\,d\mu_i - \Pi(H)A\,dH + 2\sigma(H)dA\,, \quad (134)$$

where the tilde sign denotes Gibbs excesses of the corresponding quantity.

In the region of the bulk meniscus Eqn (134) becomes

$$d\tilde{\Omega}_s = -\tilde{S}_s dT - \sum_i \tilde{N}_{is}\,d\mu_i + 2\sigma_0 dA\,, \quad (135)$$

and the fundamental equation for interacting surfaces of minimum tension in a plane-parallel is

$$d\tilde{\Omega}_s = -\tilde{S}_s dT - \sum_i \tilde{N}_{is}\,d\mu_i - \Pi(H_f)A\,dH + 2\sigma_f(H)dA\,. \quad (136)$$

3. Shape of the profile of a liquid film in the transition region

The shape of the real profile $H(r) = 2z(r)$ of a symmetrical circular liquid film (see Fig. 1) is uniquely described by the system of Eqns (129) and (130), together with

$$\frac{dH(r)}{dr} = 2\tan\varphi(H)\,. \quad (137)$$

In the region of the bulk meniscus the real profile $H(r)$ coincides with the ideal profile $H^{id}(r) = 2z^{id}(r)$, which can be determined experimentally with adequate precision.[7] The position of the point (r_1, z_1) can be used as a boundary condition: it is the same for the real and the idealised profile in the region of the bulk meniscus, in which the two profiles have the same angle of contact φ_1 (see Fig. 13).

In cylindrical films, having only one principal radius of curvature, integration of the fundamental equilibrium equation of the film (130) over the thickness of the real profile from a value H in the transition region to a value H_1 in the region of the bulk meniscus yields an invariant, independent of the thickness of the profile:[1, 5, 6, 18]

$$2\sigma(H)\cos\varphi(H) + \Delta PH(r) = 2\sigma_0\cos\varphi_1 + \Delta PH_1 = \text{const}\,. \quad (138)$$

The invariant (138) is the analogue of (99), obtained for noninteracting cylindrical surfaces. Since the right-hand sides of the two invariants are equal the left-hand sides must also be equal. This produces a new generalised invariant:[1, 5]

$$2\sigma(H)\cos\varphi(H) + \Delta PH(r) = 2\sigma_0\cos\varphi^{id}(H) + \Delta PH^{id}(r)\,, \quad (139)$$

which establishes a mutual relationship between the parameters which characterise the real [$H(r)$] and the idealised film profile [$H^{id}(r)$].

From the generalised invariant (139) we obtain well known expressions, widely used in the thermodynamics of thin liquid films, which are usually based on mechanical models of the liquid films, for example[46, 47]

$$\sigma_f = \sigma_0\cos\theta_f\,, \quad (140)$$

or (see Sheludko et al.[48] and Fig. 13)

$$\sigma_f = \sigma_0\cos\theta_0 - \tfrac{1}{2}\Delta PH_f\,. \quad (141)$$

We shall illustrate these assertions with a number of examples.[1, 5, 6, 18]

Let us insert into the left-hand side of the generalised invariant (139) values corresponding to the real profile $H(r)$: $H = H_f$, $\varphi(H_f) = 0$, and $\sigma(H_f) = \sigma_f$. Into the right-hand side we insert the corresponding values for the idealised profile $H^{id}(r)$: $H^{id} = H_f$, and $\varphi^{id}(H_f) = \theta_f$. The result is

$$2\sigma_f + \Delta PH_f = 2\sigma_0\cos\theta_f + \Delta PH_f\,,$$

from which we obtain Eqn (140).

On the other hand if the values $H_{id} = 0$ and $\varphi^{id}(0) = \theta_0$ are inserted into the right-hand side of the generalised invariant (139) they produce the equation

$$2\sigma_f + \Delta PH_f = 2\sigma_0\cos\theta_0\,, \quad (142)$$

from which (141) is obtained. Since γ is related to the interfacial tension σ_f in a film of thickness H_f by the expression[22]

$$\gamma = 2\sigma_f + \Delta PH_f\,, \quad (143)$$

Eqn (142) leads to the well known relation[48]

$$\gamma = 2\sigma_0\cos\theta_0\,. \quad (144)$$

By using the relationship [which follows from the Gibbs–Duhem equation (129)] between the specific free energy of

interaction (grand thermodynamic potential) in a plane-parallel film and the interfacial tension[34, 41, 45]

$$2\sigma_f - 2\sigma_0 = \Delta\Omega(H_f) = \int_{H_f}^{\infty} \Pi(H)\mathrm{d}H , \quad (145)$$

we obtain from Eqns (140) and (142) the familiar relations[46, 47]

$$\Delta\Omega(H_f) = 2\sigma_0(\cos\theta_f - 1) \quad (146)$$

or[48]

$$\Delta\Omega(H_f) = 2\sigma_0(\cos\theta_0 - 1) - \Delta P H_f . \quad (147)$$

Attention has been drawn[1, 5, 43] to the difference between the contact angles θ_f and θ_0 and to the need to allow for this difference when using the expressions (146) and (147) in order to avoid crude errors in the calculation of the specific energy of interaction in the film at low contact angles and relatively large thicknesses of the liquid films.

We shall now establish how the equilibrium equations of films with a bulk meniscus can be obtained from the universal invariant (139) when the contact angle θ_0 is not formed. For example, the common black films, also known as α-films, between drops in which the capillary pressure $P_c = \Delta P = P_\beta - P_\alpha$ is smaller than the height Π_2 of the coagulation barrier in the disjoining pressure isotherm. The profile of these films (curve *1* of Fig. 19*a*) is characterised by a relatively large thickness H_f^c of the central plane-parallel part: as a rule the idealised profile $H^{id}(r)$ does not form a contact angle θ_0 under these conditions.

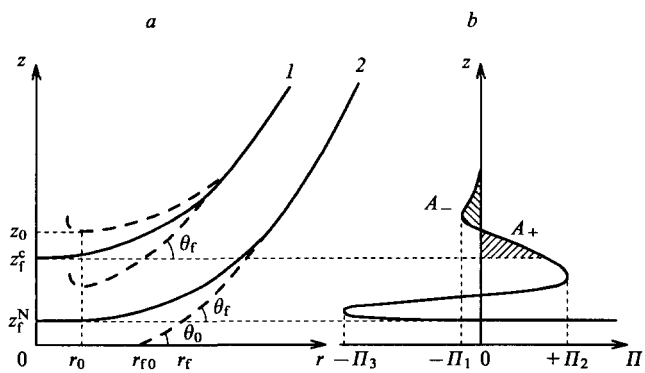


Figure 19. Creation of common and of Newtonian black films: (*a*) profiles of the common (*1*) and of the Newtonian black film (*2*); (*b*) profile of the disjoining pressure isotherm.

If $\Delta\Omega(H_f) < 0$, i.e. according to (145), the area of the cross-hatched negative region A^- (Fig. 19*b*) is greater than the area of the positive region A^+ (for example, for a high enough concentration of electrolyte in an aqueous dispersion medium, in which the coagulation barrier is low): the idealised profile $H^{id}(r)$ forms a contact angle θ_f and has a minimum $H_0 = 2z_0$, which is smaller than the film thickness $H_f^c = 2z_f^c$ (see Fig. 19*a*). On the other hand if $A^+ > A^-$ we have $\Delta\Omega(H_f) > 0$ and the idealised profile $H^{id}(r)$ lies above the real profile of the film $H(r)$, with $H_0 > H_f^c$.

Inserting into the right-hand side of the generalised invariant (139) the values $H^{id} = H_0$ and $\varphi^{id} = 0$, corresponding to a minimum on the $H^{id}(r)$ curve, we obtain the expression[18]

$$2\sigma_f + \Delta P H_f = 2\sigma_0 + \Delta P H_0 , \quad (148)$$

from which new relations are obtained:

$$\gamma = 2\sigma_0 + \Delta P H_0 , \quad (149)$$

$$\Delta\Omega(H_f) = \Delta P(H_0 - H_f) . \quad (150)$$

Thus, if $H_0 < H_f$ we have $\Sigma\Omega(H_f) < 0$. Eqn (150) for the case of $\Delta\Omega(H_f) > 0$ was obtained[45, 49, 50] for films with a cylindrical profile by applying the principle of detailed balancing developed by Deryagin for films.[51]

Newtonian black films, also known as β-films, are formed from the α-films when the height Π_2 of the coagulation barrier is lowered (for example, by increasing the concentration of electrolyte), or by increasing the capillary pressure P_c to a level higher than the coagulation barrier Π_2 (for example, by decreasing the radii of the liquid drops between which the liquid film is formed)[52] (see curve *2* of Fig. 19*a*).

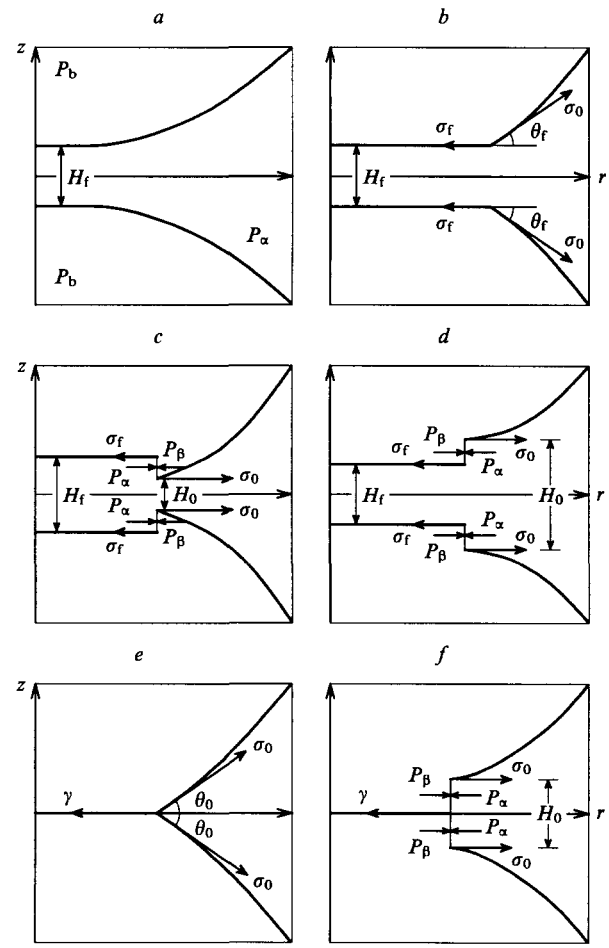


Figure 20. Equilibrium of a liquid film with a bulk meniscus (*a*) according to the thermodynamic model which stipulates two dividing surfaces (*b*–*d*) and according to the membrane model of the film (*e*, *f*).

The expressions (140), (144), (148), and (149) allow a clear mechanical interpretation of these effects (Fig. 20), which differs according to the thermodynamic model chosen to describe the thin liquid films.

If the model assumes two interacting dividing surfaces in the liquid film[53, 54] the equilibrium schemes illustrated in Fig. 20*b*–20*d* are usually adopted. Fig. 20*b* shows the equilibrium of the film with a meniscus, as in Eqn (140). When the contact angle θ_0 is not formed, and $H_0 < H_f$, Eqn (148) corresponds to the scheme shown in Fig. 20*c*. Under these conditions $\Delta\Omega(H_f) < 0$. If $\Delta\Omega(H_f) > 0$ we have $H_0 > H_f$, and the scheme shown in Fig. 20*d* corresponds to Eqn (148).

If the membrane model is chosen as a thermodynamic model of the film[55, 56] it is convenient to use the mechanical model shown in Fig. 20*e* [corresponding to Eqn (144)] for negative values of $\Delta\Omega(H_f)$, when the contact angle θ_0 is formed. On the other hand if the contact angle θ_0 is not formed we can use the mechanical model shown in Fig. 20*f*, corresponding to Eqn (149).

Under these conditions $\Delta\Omega(H_f)$ can take both negative and positive values.

The generalised invariant for circular liquid films can be obtained by integrating the fundamental equilibrium equation (130) over the thickness of the real profile [as was done for films with a cylindrical profile in the derivation of Eqn (138)], and combining the resulting expression with (101):

$$2\sigma(H)\cos\varphi(H) + \Delta PH(r) + \int_H^{H_1} \frac{\sigma(H)\sin\varphi(H)}{r}\,dH = 2\sigma_0\cos\varphi^{id}(H) + \Delta PH^{id}(r) + \int_{H^{id}}^{H_1} \frac{\sigma_0\sin\varphi^{id}(H)}{r}\,dH^{id} . \quad (151)$$

We shall show how accurate analytical expressions can be obtained from the generalised invariant (151) for circular films, allowing numerical estimates of the line tension.[1, 2, 5]

As was done for films with a cylindrical profile in the derivation of Eqns (140) and (146) we shall insert into the left-hand side of the invariant (151) the values $H = H_f$, $\varphi = 0$, and $\sigma = \sigma_f$, and into the right-hand side the values $H^{id} = H_f$ and $\varphi^{id} = \theta_f$, corresponding to the case of $\Delta\Omega(H_f) < 0$. The result is

$$2\sigma_f + \Delta PH_f + \int_{H_f}^{H_1} \frac{\sigma(H)\sin\varphi(H)}{r}\,dH = 2\sigma_0\cos\theta_f + \Delta PH_f + \int_{H_f}^{H_1} \frac{\sigma_0\sin\varphi^{id}(H)}{r}\,dH^{id} ,$$

which is usually written[41]

$$2\sigma_f + \frac{\tau}{r_f} = 2\sigma_0\cos\theta_f , \quad (152)$$

or

$$\Delta\Omega(H_f) + \frac{\tau}{r_f} = 2\sigma_0(\cos\theta_f - 1) , \quad (153)$$

where

$$\tau = r_f\left[\int_{H_f}^{\infty} \frac{\sigma(H)\sin\varphi(H)}{r}\,dH - \int_{H_f}^{\infty} \frac{\sigma_0\sin\varphi^{id}(H)}{r}\,dH^{id}\right] . \quad (154)$$

τ is the line tension in the film model based on the assumption of two dividing surfaces. Eqn (154) is the exact analytical expression[1, 18, 44] for the line tension τ, and differs substantially from the approximate expressions used by some workers.[36, 41] Detailed descriptions of the line tension theory and of results obtained in measurements of the line tension have already been published.[5, 6]

We shall now show how an expression for the line tension can be obtained in the membrane model of the film.[48, 57] To this end we shall insert into the right-hand side of the generalised invariant for a circular liquid film (151) the values $H^{id} = 0$ and $\varphi^{id} = \theta_0$ (postulating the formation of the contact angle θ_0). The result is

$$2\sigma_f + \frac{\varkappa}{r_{f0}} = 2\sigma_0\cos\theta_0 - \Delta PH_f , \quad (155)$$

or

$$\gamma + \frac{\varkappa}{r_{f0}} = 2\sigma_0\cos\theta_0 , \quad (156)$$

or

$$\Delta\Omega(H_f) + \frac{\varkappa}{r_{f0}} = 2\sigma_0(\cos\theta_0 - 1) - \Delta PH_f , \quad (157)$$

where

$$\varkappa = r_{f0}\left[\int_{H_f}^{\infty} \frac{\sigma(H)\sin\varphi(H)}{r}\,dH - \int_0^{\infty} \frac{\sigma_0\sin\varphi^{id}(H)}{r}\,dH^{id}\right] \quad (158)$$

is the line tension in the membrane model of the liquid film.[6]

We note that the equilibrium equations for circular films (152) and (156) differ from the analogous equations for cylindrical films (140) and (144) by including the terms τ/r_f and $\varkappa/r_{f0}$ in the left-hand side: these can be interpreted as 'two-dimensional' capillary pressures, associated with an inflection in the contact line (or dividing line according to Gibbs), by analogy with the capillary pressure $2\sigma_0/R$ (in the case of a sphere of radius R) created by the bending of the dividing surface.

The equations (154) and (158) give the relationship between the two types of line tension in the various thermodynamic models of liquid films:[1, 6]

$$\frac{\varkappa}{r_{f0}} = \frac{\tau}{r_f} - \int_0^{H_f} \frac{\sigma_0\sin\varphi^{id}(H)}{r}\,dH^{id} .$$

Expressions for the equilibrium of circular films with a meniscus, analogous to (148)–(150) for cylindrical films, have also been given[1, 18] (see Fig. 19*a*):

$$2\sigma_f + \Delta PH_f + \int_{H_f}^{H_1} \frac{\sigma(H)\sin\varphi(H)}{r}\,dH = 2\sigma_0 + \Delta PH_0 + \int_{H_0}^{H_1} \frac{\sigma_0\sin\varphi^{id}(H)}{r}\,dH^{id} , \quad (159)$$

$$\gamma + \frac{\tau_B}{r_0} = 2\sigma_0 + \Delta PH_0 , \quad (160)$$

$$\Delta\Omega(H_f) + \frac{\tau_B}{r_0} = \Delta P(H_0 - H_f) , \quad (161)$$

where

$$\tau_B = r_0\left[\int_{H_f}^{\infty} \frac{\sigma(H)\sin\varphi(H)}{r}\,dH - \int_{H_0}^{\infty} \frac{\sigma_0\sin\varphi^{id}(H)}{r}\,dH^{id}\right] \quad (162)$$

is the line tension.[1, 18, 44]

Profile of the lens-like thickening in equilibrium with a liquid film. In the transition region between the lens-like thickening and the plane-parallel liquid film (see Fig. 16) the first principal curvature changes sign from negative to positive, whereas the second principal curvature remains negative:

$$k_1 = -\frac{d\sin\varphi(H)}{dr} \text{ and } k_2 = -\frac{\sin\varphi(H)}{r} .$$

The average negative curvature of the surface in the transition region ($k = k_1 + k_2$) within the liquid lens decreases to zero in absolute value when r increases, then becomes positive, and finally decreases again to zero in the almost plane-parallel region of the liquid film surrounding the lens.

A characteristic feature of the lens–liquid system is its basic disequilibrium, due to the fact that the chemical potentials of the components μ_i within the lens exceed the corresponding values in the phase α. In particular, the hydrostatic pressure P_d within the lens is greater than the pressure P_α in the phase α, and therefore the material in the lens will tend to pass into the phase α by direct flow or as a result of bulk or surface diffusion. This tendency increases as the size of the lens decreases and as the pressure (i.e. the chemical potentials of the components) within the lens is increased.

If the rate of the hydrodynamic or diffusion processes is low the system can be treated as a quasi-equilibrium system. In a system of this type the energetics and the mechanical equilibrium can be described by the methods of equilibrium thermodynamics.

The main difficulty in the thermodynamic description of the lens–liquid film system is the lack of an unambiguous definition (in terms of the postulated presence of two dividing surfaces in the

film) of the reference system (in particular the Gibbs reference system) within the film itself, since a pressure gradient is formally present as a result of the obvious inequality $P_d > P_\alpha$. This gradient is increased by the flow of liquid from the lens.

Similar difficulties arise in the membrane approach to the description of the film, since the tension γ becomes a function of the coordinate r owing to the pressure gradient in the film in the direction of the r axis (see Fig. 16*c*).

A possible approach to the thermodynamic description of the transition region of the film at the boundary with the lens is described below.[18]

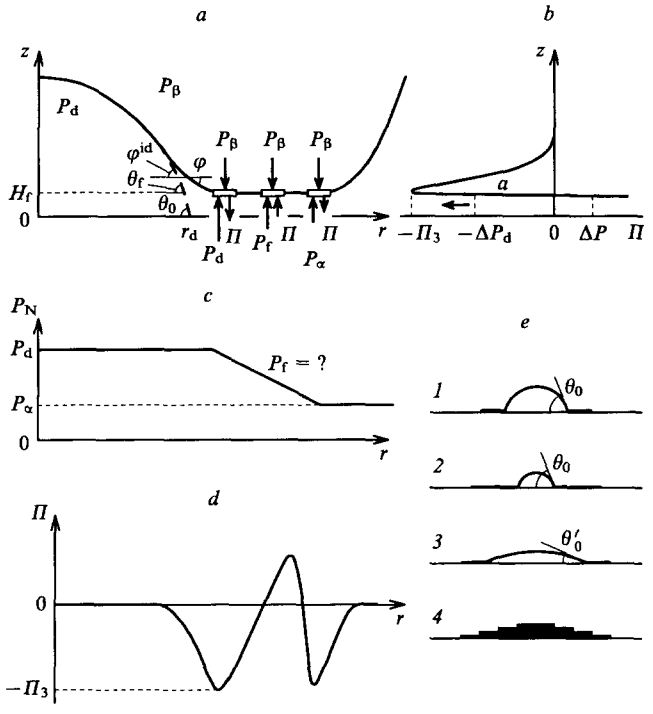


Figure 21. Equilibrium between the lens and the liquid film: (*a*) profile of the transition region between the liquid film and the lens; (*b*) profile of the disjoining pressure isotherm; (*c*) dependence of the normal component P_N of the reference pressure in the lens–liquid film system on the radius r; (*d*) distribution of the disjoining pressure in the lens–liquid film system; (*e*) evolution of the form of the liquid drop on a solid surface as a function of time.

The real profile of the film $z(r)$, including the profile of the lens itself (Fig. 21*a*), can be described by the Gibbs–Duhem equation or by the system of equations

$$\frac{dz(r)}{dr} = -\tan\varphi(H) , \tag{163}$$

$$\sigma(H)\frac{d\sin\varphi(H)}{dr} + \sigma(H)\frac{\sin\varphi(H)}{r} + \Pi(H)\cos\varphi(H) + \Delta P_f(r) = 0 , \tag{164}$$

where $\Delta P_f(r) = P_f(r) - P_\beta$, and $P_f(r)$ is the reference pressure in the film region. The form of the function $P_f(r)$ is not previously known, though it is obvious that $P_f(r) = P_d$ for $r < r_d$ (r_d is the radius of the lens) and $P_f(r) = P_\alpha$ in the bulk of the phase α. The form of the function $P_f(r)$ is shown schematically in Fig. 21*c*. The question mark in the symbol P_f = ? denotes the ambiguity in the choice of the form of this function in the film region.

In spite of this ambiguity we can assume that the film will be accurately plane-parallel because of the low compressibility of the liquid. We can therefore write the equilibrium equation (164) in the film region as

$$\Pi(H) + \Delta P_f(r) \simeq 0 . \tag{165}$$

This means that in the transition region of the lens, where $P_f \simeq P_d$ (see Fig. 21*c*), the disjoining pressure is negative, since

$$\Pi + P_d - P_\beta = 0 \quad \text{and} \quad P_d > P_\beta$$

(see Fig. 21*a*). We should note that a negative sign for the disjoining pressure denotes mutual attraction of the dividing surfaces in the film

As we move away from the transition region of the film along the r axis the disjoining pressure becomes positive (Fig. 21*d*) because of the decrease in the reference pressure P_f caused by the repulsion of the dividing surfaces in the film. In considering the changes in sign of the disjoining pressure it should not be forgotten that within the model of two dividing surfaces in the film the disjoining pressure is defined as the excess of the specific interaction force (between the surfaces) over the effect of the arbitrarily chosen reference pressure. Therefore both the magnitude and the sign of the disjoining pressure are arbitrary. For example, if P_d is chosen as the reference pressure the disjoining pressure within the film will be negative everywhere.

Let us assume that the choice of reference pressure shown in Fig. 21*c* is an optimum. Then the disjoining pressure Π changes sign once again and becomes negative when r is increased within the transition region between the film and the phase α (see Fig. 21*a*) for the choice of disjoining pressure isotherm shown in Fig. 21*b*: this effect is due to the capillary pressure forces (see Fig. 18*b*).

By using the procedure described above for applying the generalised invariant of the film profile to the lens–liquid film system we obtain[18]

$$2\sigma(H)\cos\varphi(H) + \int_H^{H_1}\Delta P_f(r)dH - \int_H^{H_1}\frac{\sigma(H)\sin\varphi(H)}{r}dH = 2\sigma_0\cos\varphi^{id}(H) + \Delta P_d[H_1 - H^{id}(r)] - \int_{H^{id}}^{H_1}\frac{\sigma_0\sin\varphi^{id}(H)}{r}dH^{id} , \tag{166}$$

where H_1 is the thickness of the profile in the region of the bulk phase of the lens.

Inserting into the left-hand side of the invariant (166) the parameters corresponding to the real profile of the film ($H = H_f$, $\varphi = 0$, and $\sigma = \sigma_f$) and into the right-hand side the parameters corresponding to the idealised profile ($H^{id} = 0$, $r = r_d$, and $\varphi^{id} = \theta_0$) gives the following equilibrium equation:

$$2\sigma_f + \int_{H_f}^{H_1}\Delta P_f(r)dH - \frac{\varkappa}{r_d} = 2\sigma_0\cos\theta_0 + \Delta P_d H_1 , \tag{167}$$

where $\varkappa$ is the line tension, defined by the expression

$$\varkappa = r_d\left[\int_{H_f}^{\infty}\frac{\sigma(H)\sin\varphi(H)}{r}dH - \int_0^{\infty}\frac{\sigma_0\sin\varphi^{id}(H)}{r}dH^{id}\right] . \tag{168}$$

On the other hand inserting into the right-hand side of (166) the parameters $H^{id} = H_f$, $r \simeq r_d$, and $\varphi^{id} = \theta_f$ gives

$$2\sigma_f + \int_{H_f}^{H_1}\Delta P_f(r)dH - \frac{\tau}{r_d} = 2\sigma_0\cos\theta_f + \Delta P_d(H_1 - H_f) , \tag{169}$$

where the line tension τ is given by the expression[18]

$$\tau = r_d\left[\int_{H_f}^{\infty}\frac{\sigma(H)\sin\varphi(H)}{r}dH - \int_{H_f}^{\infty}\frac{\sigma_0\sin\varphi^{id}(H)}{r}dH^{id}\right] . \tag{170}$$

The equilibrium equations (167) and (168) can be simplified if $dP_f(r)/dr \ll 1$. Under these conditions the reference pressure P_f in

the transition region of the film can be treated as constant and equal to P_d, which allows the equilibrium equation to be written in the form[18, 33]

$$2\sigma_f - \frac{\varkappa}{r_d} = 2\sigma_0 \cos\theta_0 + \Delta P_d H_f \tag{171}$$

or

$$2\sigma_f - \frac{\tau}{r_d} = 2\sigma_0 \cos\theta_f . \tag{172}$$

Replacing the film by a membrane of zero thickness and using the definition (143) for the tension γ of the film converts Eqn (171) into

$$\gamma - \frac{\varkappa}{r_d} = 2\sigma_0 \cos\theta_0 . \tag{173}$$

For the equilibrium of a fluid (liquid or gaseous) drop in contact with a solid substrate (see Fig. 16*b*) the relationships (171)–(173) become[6, 36, 58]

$$\sigma_f - \frac{\varkappa}{r_d} = \sigma_0 \cos\theta_0 + \Delta P_d H_f , \tag{174}$$

$$\sigma_f - \frac{\tau}{r_d} = \sigma_0 \cos\theta_f , \tag{175}$$

$$\gamma - \frac{\varkappa}{r_d} = \sigma_0 \cos\theta_0 . \tag{176}$$

Eqn (176) has been used[59, 60] to determine the line tension $\varkappa$ from the experimental dependence of the contact angle θ_0 on the drop radius r_d on a solid or a liquid support. In these measurements it is usually assumed[6] that the tension γ of the film stays constant when the size of the drop or lens is changed, and Eqn (176) is used in the form[59, 60]

$$\cos\theta_0 = \cos\theta_0(\infty) - \frac{\varkappa}{\sigma_0 r_d} , \tag{177}$$

where $\theta_0(\infty)$ is the constant value of the contact angle corresponding to the condition $r_d \to \infty$.

The line tension $\varkappa$ is treated as positive if the contact line (or dividing line, according to Gibbs) has an excess of positive free energy, i.e. if it tends to shorten itself.[6] In particular, reported[59, 60] positive values of the line tension $\varkappa$ correspond to an increase in the contact angle with decreasing drop size. In this connection it has been pointed out[6, 18] that the dependence of the contact angle θ_0 on the drop radius r_d could be associated with the changes in the film tension γ rather than with changes in the line tension. In this case Eqn (177) should be replaced by the more general relation

$$\cos\theta_0 = \cos\theta_0(\infty) - \frac{\varkappa}{\sigma_0 r_d} + \Delta\gamma(r_d) , \tag{178}$$

where $\Delta\gamma(r_d) = \gamma(r_d) - \gamma(\infty)$, and allowance should be made for the $\gamma(r_d)$ dependence, which is not previously known.

We note that according to the generalised theory of the line tension[2, 3, 5, 18] $\varkappa$ can take only negative values for systems characterised by finite values of the angle of contact. Numerical estimates of the line tension as a function of the physicochemical parameters (shape of the profile of the disjoining pressure isotherm, size of the contact angle, capillary pressure, film size) have been recently reviewed.[6]

We shall discuss the causes and the character of the changes in the film tension γ in the lens–film (or drop–solid support) system.[18] A possible evolution of the liquid drop–solid substrate system induced by decreasing the radius r of the drop is illustrated in Fig. 21*e*. The existence condition of the finite contact angle θ_0 is the inequality

$$\Pi_3 > \Delta P_d = P_\alpha - P_\beta , \tag{179}$$

where Π_3 is the depth of the short-range coagulation minimum in the disjoining pressure isotherm $\Pi(H)$ shown in Fig. 21*b*. The representative point *a* on the $\Pi(H)$ isotherm corresponds to the state *1* of the system in Fig. 21*e*. Decreasing the size of the drop (state *2*) raises the pressure P_d in the drop, and the representative point on the $\Pi(H)$ isotherm moves to the left in the direction of the arrow. Under these conditions the angle of contact θ_0 remains finite, but changes in size under the influence of the line tension, and also of the change in the film tension γ.

By postulating that the thickness of the liquid layer H_f is not affected by the displacement of the representative point *a* to the left we can treat the interfacial tension σ as constant [see Eqn (145)]: this leads to a decrease in the film tension $\gamma = 2\sigma_f - \Delta P_d H_f$ with decreasing radius r_d of the drop.

When the size of the drop is decreased to the critical radius r_d^*, for which the capillary pressure ($2\sigma_0/R = 2\sigma_0 \sin\theta_0/r_d^*$) reaches the value Π_3, i.e.

$$r_d^* = \frac{2\sigma_0 \sin\theta_0}{\Pi_3} , \tag{180}$$

the finite contact angle θ_0 can no longer exist, and the drop discontinuously changes to the new state *3* (Fig. 21*e*) with a smaller contact angle θ_0' [if the $\Pi(H)$ isotherm has a long-range coagulation minimum Π_1, see Fig. 19*b*]. Under these conditions the new state is stable if the drop radius is greater than the critical value, defined by the relation (180), with Π_3 replaced by the new value Π_1.

If the Π_1 minimum does not exist, or the drop is smaller than the critical size, we observe spreading of the drop over the liquid layer, sometimes accompanied by the formation of several layers of molecular dimension[61–63] (state *4* in Fig. 21*e*).

This discussion of the equilibrium in the lens–liquid film system would not be complete without a mention of the possibility of spontaneous formation of lens-like thickening within initially plane-parallel films, accompanied by the thinning down of these initial formations. This effect can occur as a result of a local decrease in the interfacial tension σ_0: for example, during the mass transfer of SAS through a phase separation surface from the film to the boundary phase.[64]

The spontaneous thinning of plane-parallel liquid films stabilised by SAS at concentrations higher than the CMC often takes place by the stratification mechanism, i.e. a gradual layer-by-layer thinning to give increasingly thin layers.[65–67] The mechanism of this phenomenon is not clear.[67]

4. Interaction of interfacial surfaces in microscopic films

The microscopic liquid films (MLF) formed in the region of the contacts between emulsion drops and foam bubbles have an extremely small (almost zero) plane-parallel region, i.e. they consist almost entirely of a transition region, characterised by its profile $H(r)$ (Fig. 22*a*). This feature greatly complicates their thermodynamic description, since in order to determine the parameters of the interaction between fluid particles in a liquid medium we require information on the profile of the film, including the transition region.

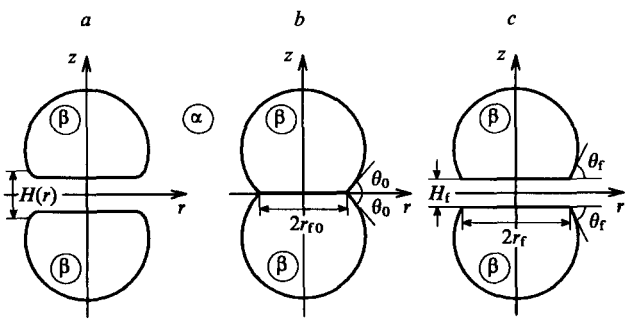


Figure 22. Representation of a microscopic liquid film (*a*) by the membrane model (*b*) and by a model which assumes two dividing surfaces in the film (*c*).

In particular this information is needed to calculate the grand thermodynamic potential Ω of the system which includes the volumes of the phases α and β, and also of the liquid film (for constant T and μ_i[5, 6, 14, 18]):

$$\Omega = -P_\alpha V_\alpha - P_\beta V_\beta + \int \sigma \, dA \,, \tag{181}$$

where the integration is carried out over the interfacial surface (the Gibbs dividing surface) allowing for the dependence of the interfacial tension σ on the position of the surface.

To simplify their thermodynamic description these systems are replaced by their analogues (reference or comparison systems), in which, for example, a circular membrane of zero thickness[55, 56] is used instead of the real microscopic liquid film (the membrane approach, Fig. 22*b*), or alternatively a circular plane-parallel film[12, 13] of thickness H_f (the approach based on the assumption of two dividing surfaces in the film, Fig. 22*c*). In this case the thermodynamic excess quantities are referred to the dividing (contact) lines. This creates the concept of linear thermodynamic excesses: for example, a line tension, representing the excess of the grand thermodynamic potential referred to unit length of the contact line.

In the membrane approach the expression for the grand thermodynamic potential of the idealised system is[5, 6, 14, 18]

$$\Omega^{id} = -P_\alpha V_\alpha^{id} - P_\beta V_\beta^{id} + \sigma_0 A^{id} + \pi r_0^2 \gamma + 2\pi r_{f0}^2 \varkappa \,, \tag{182}$$

where $\varkappa$ is the line tension of the film (or membrane) and the superscript id denotes quantities referred to the idealised system shown in Fig. 22*b* (in particular, A^{id} is the combined area of the two drops having a total volume V^{id} diminished by the two membrane areas πr_{f0}^2). The interfacial tension of this surface is arbitrarily taken to be equal to σ_0, even in the transition region, since it is assumed that no interaction exists between the drop surfaces (in keeping with stipulations of the method). By starting from the condition of energy equivalence of the real and the idealised system, i.e. $\Omega = \Omega^{id}$, we can define the line tension $\varkappa$ and calculate it. This approach has been fully discussed.[5, 6, 18]

When describing the interaction between drops in terms of the model of two dividing surfaces in the film the grand thermodynamic potential of the idealised system Ω^{id} is expressed[5, 6, 18] as (Fig. 22*c*)

$$\Omega^{id} = -P_\alpha V_\alpha^{id} - P_\beta V_\beta^{id} + \sigma_0 A^{id} + 2\pi r_f^2 \sigma_f + 2\pi r_f \tau \,, \tag{183}$$

where τ is the line tension, and the values V_α^{id}, V_β^{id}, and A^{id} differ from the corresponding quantities in Eqn (182), which relates to the membrane model of the film. Calculations of τ allowing for the condition $\Omega = \Omega^{id}$ have been reported.[5, 6, 18]

If the contact angles θ_0 and θ_f are not formed we can use idealised models (see Fig. 20*e*), relating to the membrane model and to the postulate of two dividing surfaces in the film respectively. The expressions for the grand thermodynamic potential corresponding to these models are

$$\Omega^{id} = -P_\alpha V_\alpha^{id} - P_\beta V_\beta^{id} + \sigma_0 A^{id} + \pi r_0^2 \gamma + 2\pi r_0 \varkappa_B \,, \tag{184}$$

$$\Omega^{id} = -P_\alpha V_\alpha^{id} - P_\beta V_\beta^{id} + \sigma_0 A^{id} + 2\pi r_0^2 \sigma_f + 2\pi r_0 \tau_B \,. \tag{185}$$

Calculations of the line tension τ_B have been reported.[5, 6]

5. Contact interactions in emulsions and foams

Theories of the adhesion of solid particles. The relationship between the adhesion force acting on solid (rigid) particles in liquid media and the parameters which characterise the interaction between phases in microscopic liquid films was established by Bradley[68] and Deryagin[69] during their development of the thermodynamic theory of solid particles. Their expression

$$f_a^* = \pi R \Delta F_a = \pi R \Delta \Omega(H_f) \,, \tag{186}$$

relates the force of adhesion f_a^* of solid non-deformable particles of radius R with the specific free energy of adhesion ΔF_a [equal to the specific grand thermodynamic potential of the interaction $\Delta\Omega(H_f)$ in a liquid film of thickness H_f for constant T and μ_i. In calculations of $\Delta\Omega(H_f)$ by formula (145) H_f is taken to be $\sim 0.2-0.5$ nm (see Refs 70 and 71), which corresponds to the short-range coagulation minimum on the $\Pi(H)$ isotherm.]

Eqn (186) can be used to calculate the influence of physicochemical factors (pH and ionic strength of the solution, surface charge, etc.) on the force of adhesion between the particles, since the effect of these factors on $\Delta\Omega(H_f)$ can be established on the basis of the Deryagin–Landau–Verwey–Overbeek theory[72, 73] or of the modern theories of the steric stabilisation of dispersions.[74–76]

The effect of the deformability of solid particles on the force of adhesion between them is allowed for in the Johnson–Kendall–Roberts theory,[77] according to which (in our symbols)

$$f_a^* = 0.75\pi R \Delta\Omega(H_f) \,. \tag{187}$$

The Muller–Yushchenko–Deryagin theory[78] led to the expression

$$f_a^* = \nu \pi R \Delta\Omega(H_f) \,, \tag{188}$$

in which the parameter ν takes values in the range 0.75–1, depending on the size of the particles, their elastic properties, the thickness of the film, and the Hamaker constant (which characterises the energy of the molecular attraction between the surfaces).

The theory of adhesion of fluid particles was constructed and applied,[4, 18] and then further developed.[5, 6, 79] The proposed equation

$$f_a^* = \nu_a \pi R \Delta\Omega(H_f) \tag{189}$$

has the same form as the relationship of the previous theory, but the parameter ν_a, which lies in the range $0.5 \leqslant \nu_a \leqslant 1.0$, is more easily accessible for numerical calculations. For example, for the disjoining pressure $\Pi(H)$ isotherm, characterised by a single coagulation minimum (Fig. 23), the parameter ν_a is expressed as follows:[5]

$$\nu_a \approx \frac{1 + 0.5\alpha_a}{1 + \alpha_a} \tag{190}$$

where

$$\alpha_a = \frac{|\Delta\Omega(H_f)|}{\Delta_3 \sigma_0 k_0} = \frac{\Pi_3}{\sigma_0 k_0} = \frac{\Pi_3}{P_c} \,, \tag{191}$$

Δ_3 is the effective width of the short-range coagulation minimum, and P_c is the capillary pressure. If the particles are in the long-range coagulation minimum we must replace Π_3 by Π_1 according to Eqn (191) (see Fig. 20*b*).

The parameter α_a is characterised by the deformability of the particles: the lower the deformability, the greater is the similarity in properties between the fluid particles and the rigid solid particles during extension. For example, for $\Pi_3 \ll P_c$ we have $\alpha_a \simeq 0$, and therefore $\nu_a \simeq 1$, which corresponds to the Bradley–Deryagin adhesion theory. If $\Pi_3 \gg P_c$ we have $\alpha_a \gg 1$, and $\nu_a \approx 0.5$, and (189) becomes

$$f_a^* = 0.5\pi R \Delta\Omega(H_f) \,.$$

The dependence of the radius of the liquid film r_f between particles on the external force f_e has been obtained[4] by numerical modelling of the contact interactions between two identical liquid particles. This involved numerically solving the system of differential equations (97), (117), (129), (130), and (137) for fixed values of σ_0 and P_c, and also of the parameters which characterise the shape of the disjoining pressure isotherm $\Pi(H)$, but with a variable external force f_e [compressing ($f_e = f_p > 0$) or extending the particle ($f_e = f_a < 0$)]. The results of one series of

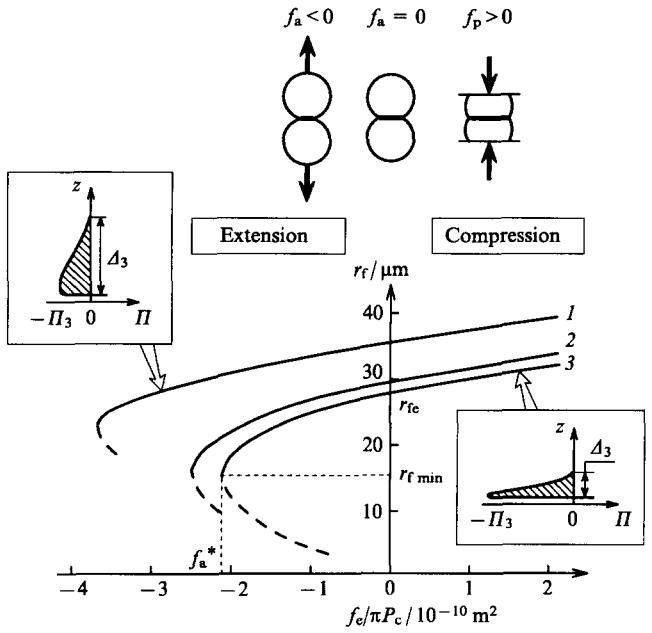


Figure 23. Dependence of the film radius on the reduced external force applied to a fluid particle of radius 1 mm ($\sigma_0 = 30$ mJ m^{-2}; $\Delta\Omega(H_f) = -60 \times 10^{-17}$ J m^{-2}) for different effective values of the parameter Δ_3, nm: (*1*) 10, (*2*) 10^2, (*3*) 10^3; $r_{f\,min}$ is the minimum stable radius of the film at the moment of detachment of the particle; r_{fe} is the equilibrium radius of the liquid film for $f_e = 0$.

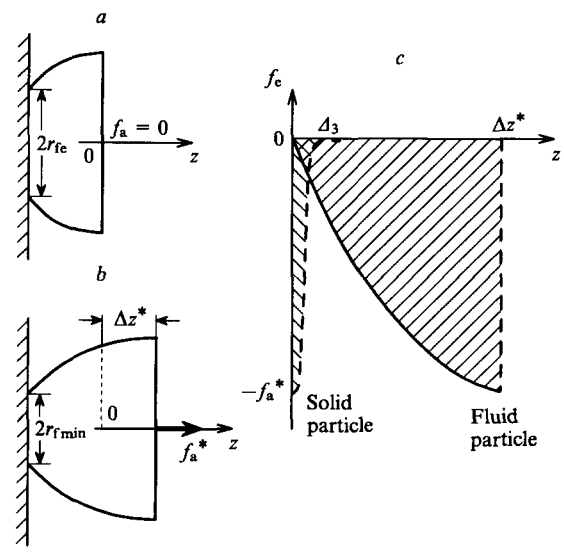


Figure 24. Illustration of the calculation of the work of removal of a fluid particle. Shape of the particle for $f_e = 0$ (*a*) and at the instant of removal f_a^* (*b*); dependence of the external force f_e on the displacement z for the removal of a solid or a liquid particle (*c*).

measurements of this type are shown in Fig. 23 as an illustration of the proposed method.[2, 4]

We should specially note that the shape of the $\Pi(H)$ isotherm (the width of the coagulation minimum Δ_3) for a given value of the free energy of interaction $\Delta\Omega(H_f)$ is strongly dependent on the force of adhesion f_a^* in the case of fluid particles, but in solid particles the dependence is negligibly small.

Work of separation of fluid particles. The strongest dependence on the shape of the disjoining pressure isotherm is seen in the work of separation of fluid particles W_a^f, which can exceed the work of separation of rigid solid particles W_a^s by more than a factor of 10^3 for equal values of $\Delta\Omega(H_f)$ and other parameters. The work W_a^f can be calculated by the relation (Fig. 24*c*)

$$W_a^f = \int_0^\infty f_e(H)\,dz \approx \tfrac{1}{2} f_a^* \Delta z^* , \tag{192}$$

where Δz^* is the displacement of the detachment force caused by the moment of the force which breaks the adhesion contact between the particles. The corresponding work W_a^s is

$$W_a^s = \int_0^\infty f_e(H)dz \approx \tfrac{1}{2} f_a^* \Delta_3 . \tag{193}$$

Obviously, the more deformable the particle, i.e. the greater the parameter α_a, the more markedly does the displacement Δz^* (Fig. 24*b*) exceed the radius of action of the molecular forces of attraction Δ_3, and the greater is W_a^f in comparison with W_a^s for a practically constant adhesive force f_a^*. In particular it has been shown[4, 5, 79] that

$$W_a^f \approx W_a^s\left(1 + \frac{\alpha_a}{2}\right) . \tag{194}$$

Eqn (194) provided the basis for the derivation of the criterion of the aggregation stability (stability towards coagulation) of emulsions,[5, 18] which for a disjoining pressure with one coagulation minimum takes the form

$$\nu_a \frac{R\Delta\Omega^2(H_f)}{\Pi_3}\left(1 + \frac{\alpha_a}{2}\right) \leqslant B , \tag{195}$$

where B is a parameter of the order of $10k_BT$, and k_B is Boltzmann's constant. If the emulsion is stable towards coalescence the relationship (195) is also the thermodynamic criterion for the spontaneous dispersing of the precipitate from such an emulsion.

In the cases of $\alpha_a = \Pi_3/P_c \to 0$ the liquid drops in the emulsion can be treated as completely rigid, and (195) is converted into the thermodynamic criterion of the aggregation stability of sols,[80, 81] i.e. (in our symbolism)

$$\frac{R\Delta\Omega^2(H_f)}{\Pi_3} \leqslant B . \tag{196}$$

For emulsions with a low value of the interfacial tension σ_0 and $\alpha_a \gg 1$ we obtain from (195) the corresponding criterion for the stability to aggregation and spontaneous dispersion of these emulsions:[5, 79]

$$\frac{R^2\Delta\Omega^2(H_f)}{\sigma_0} \leqslant B . \tag{197}$$

The expression (197) shows that if the isotherm $\Pi(H)$ has one coagulation minimum the coagulation tendency increases as σ_0 decreases, and that the tendency towards spontaneous dispersion of the precipitate from these emulsions decreases. The criterion (197) differs from the Lee and Tadros criterion for spontaneous emulsification,[82] given (in our symbols) by

$$\pi R^2\sigma_0 \leqslant B , \tag{198}$$

which describes the spontaneous formation of emulsions from macroscopic phases and predicts an increased propensity towards emulsification for lower values of σ_0.

Effect of the coagulation barrier on the adhesion of fluid particles. If the disjoining pressure isotherm $\Pi(H)$ has a coagulation barrier of height Π_2 (see Fig. 20*b*) the barrier can be surmounted in a fluid particle by applying the critical compressive force f_p^* (for a zero or negligibly small long-range coagulation minimum Π_1):[3, 5, 79, 83]

$$f_p^* = \nu_p \pi R \Delta\Omega(H_f^c) , \tag{199}$$

where $\Delta\Omega(H_f^c)$ is the specific free energy of the interaction for a thickness corresponding to the transition from a common black film to a Newtonian Black film or to coalescence, and $v_p = \Pi_2/P_c$ is a parameter which characterises the deformability of the particle in compression:

$$v_p \simeq \frac{1}{1-\alpha_p} \quad \text{for } P_c > \Pi_2 , \tag{200}$$

$$v_p = +\infty \quad \text{for } P_c \leqslant \Pi_2 .$$

Obviously, if the interfacial tension σ_0 is so low that the capillary tension P_c is smaller than Π_2 the coagulation barrier prevents the transition from α to β films (see Fig. 20*a*). At constant σ_0 the critical force f_p^* increases with the radius R of the particle. When $P_c > \Pi_2$ β-films are formed, and their adhesion force f_a^* is proportional to $\Delta\Omega(H_f^N)$ (see Fig. 20*a*). On the other hand if $P_c < \Pi_2$ α-films are formed, whose adhesion force f_a^* is proportional to $\Delta\Omega(H_f^c)$, i.e. it is $\sim 10^2 - 10^3$ times smaller than for β-films. During phase transitions (for example, during the melting of solid particles) we can expect a large decrease in the force of adhesion if the condition $P_c < \Pi_2$ applies to the liquid particles (assuming that compression of the solid particles invariably produces β-films).

These features of the contact interactions of liquid particles of emulsions and of the same particles with solid supports play an important role in technological processes (microencapsulation, filtration of emulsions, etc.), and also in biological processes.[27, 84–87]

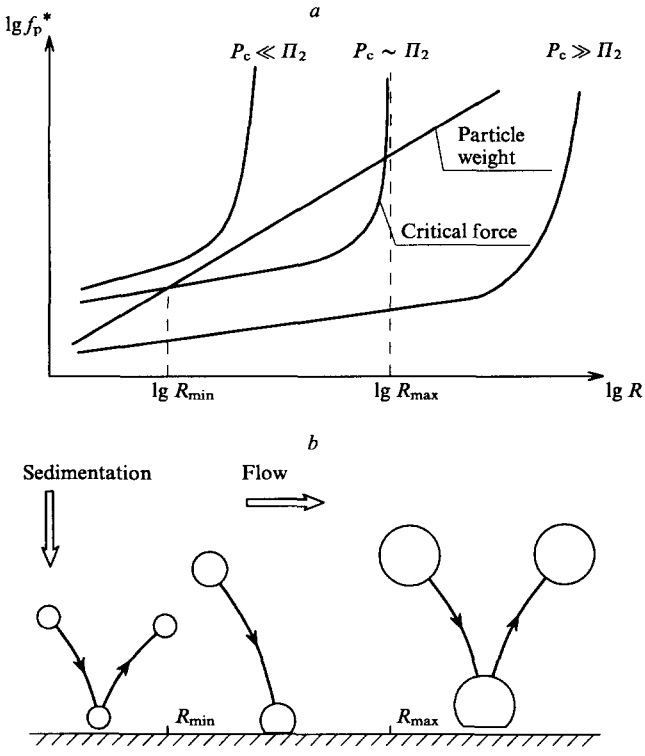


Figure 25. Effect of the radius of a liquid particle on its adhesion to a solid surface (idealised): (*a*) the dependence of the weight of a liquid particle and of the critical breaking force of the α-film for different relative values of the capillary pressure and of the height of the coagulation barrier in the disjoining pressure isotherm; (*b*) schematic illustration of the selective hetero-coagulation of the emulsion drops on the solid surface during sedimentation and flow.

The results of the theory of adhesion of solid particles are illustrated in Fig. 25*a*, which shows the dependence of the critical force f_p^* on the radius R, calculated by Eqn (199) for different heights of the coagulation barrier Π_2 in the disjoining pressure isotherm. For comparison we also show the dependence on R of the gravity force on the particles in the liquid.[3] In the case of the flow of a polydispersed emulsion with sedimentation of the liquid drops the drops accumulating at the bottom will experience the Stokes frictional force, and their weight will reflect the resultant of the force of gravity and of the repulsive force (Fig. 25*b*).

In the general case the plots of the critical force and of the weight against the radius of the particles intersect at two points, corresponding to R_{min} and R_{max}. In the region of $R < R_{min}$ the weight of the particle is insufficient to overcome the coagulation barrier Π_2, and the particles form α-films with a solid surface. They can be extracted by the flow because the force f_a^* is very small.

Similar effects are observed when $R > R_{max}$, i.e. for $P_c < \Pi_2$.

On the other hand if the condition $R_{min} < R < R_{max}$ applies the weight of the particles is insufficient to overcome the coagulation barrier and the drops form thin β-films with the surface. Under these conditions the force of adhesion may be sufficient to hold the drops on the surface during the flow of liquid. Thus we may achieve the selective heterocoagulation of fluid particles on a solid surface: only particles of a size within a fairly narrow range of radii become adsorbed.[3] The radius range corresponding to heterocoagulation can be varied by varying the physicochemical parameters of the system. For example, raising the coagulation barrier (by decreasing the concentration of electrolyte in solution) can make the $f_p^*(R)$ curve lie above the graph of the force of gravity experienced by the particles (Fig. 25*a*), and β-films will not be formed, whatever the radius of the particles. If the concentration of electrolyte is increased, i.e. if the coagulation barrier is lowered, the $f_p^*(R)$ curve will lie below the plot of the particle weight in a range of radii, and only β-films will be formed.

The radii R_{min} and R_{max} have been established experimentally[88] for a system in which gas bubbles are in contact with the phase boundary in gas–aqueous SAS solutions. The experimental values of R_{min} and R_{max} have been used[3] to calculate the parameters which characterise the coagulation barrier (Π_2 and Δ_2) of the disjoining pressure isotherm.

The work W_p^s needed to overcome the coagulation barrier at the contact of solid particles can be written as[18, 83]

$$W_p^s \simeq \pi R \frac{\Delta\Omega^2(H_f^s)}{\Pi_2}(1+\beta) , \tag{201}$$

where $\beta = \Pi_2/\Pi_3$. Under these conditions the corresponding work for liquid particles is[5, 18, 83]

$$W_p^f \simeq W_p^s \frac{1+\alpha_p}{1-\alpha_p} \quad \text{for } P_c > \Pi_2 . \tag{202}$$

The value of this work tends towards infinity for $P_c \leqslant \Pi_2$.

If the solid particle can overcome the coagulation barrier by expending an amount of work W_p^s it can be extracted (i.e. it can overcome the coagulation barrier in the reverse direction) by performing an amount of work[79]

$$W_a^s \simeq \pi R \frac{\Delta\Omega^2(H_f^N)}{\Pi_1} , \tag{203}$$

where

$$\Delta\Omega(H_f^N) \simeq \Pi_3 A_3(\alpha - 1) \quad \text{and} \quad \alpha = \frac{\Pi_2 A_2}{\Pi_3 A_3} .$$

The expression for the corresponding work in the case of a liquid particle is

$$W_a^f \simeq W_a^s(1 + \alpha_p + \alpha_a) , \tag{204}$$

where $\alpha_p = \Pi_2/P_c$ and $\alpha_a = \Pi_3/P_c$.

In conclusion we quote expressions for the aggregation stability criterion of the emulsion in the case of irreversible coagulation of the particles (for the condition $W_a^f \gg k_B T$),[83]

$$W_p^s \frac{1+\alpha_p}{1-\alpha_p} > B , \tag{205}$$

and for the spontaneous dispersion of the precipitates from the emulsion[83]

$$W_a^s(1 + \alpha_p + \alpha_a) < B . \quad (206)$$

The writer has discussed[18, 79, 83-87] the effect of σ_0 on the stability of emulsions and their propensity for spontaneous dispersion by allowing for the criteria (195), (196), (197), (205), and (206). In particular it was shown that whereas in a disjoining pressure isotherm without a coagulation barrier a decrease in the interfacial tension lowers the aggregation stability of the emulsion, in the presence of a coagulation barrier of sufficient height the effect of the surface tension on the stability of the emulsion is exactly the opposite. Therefore when examining the stability of emulsions and comparing the results of different studies of its dependence on σ_0 it is essential to allow for differences in the concentration of electrolytes and for other factors which influence the height of the coagulation barrier.

V. Conclusions

This review of studies of the thermodynamics of curved free interfacial surfaces in the region of the bulk meniscus of liquid films has identified different approaches to the determination of the interfacial tension of these surfaces.[8, 19, 21] We have shown that alternative methods of determining the interfacial tension of curved surfaces are possible, and that they lead to fundamental (Gibbs–Kelvin) equilibrium equations more convenient for practical applications in the case of objects of submicroscopic dimensions.

The thermodynamics of interacting curved interfaces (i.e. the thermodynamics of the transition region of a liquid film)[1-6, 18] are a self-consistent and closed system of concepts and of equations relating the disjoining pressure to other thermochemical parameters and functions. They reconcile the thermodynamics of free curved interfaces with those of the interacting interfaces in plane-parallel liquid films, and they reduce to the latter in the appropriate ranges.

The invariants obtained for the profiles of liquid films can be used to find all the known equations for the equilibrium of liquid films with a bulk meniscus, both in the membrane approach and in the approach based on the assumption of two dividing surfaces in the liquid film. These invariants can also be used to derive precise analytical expressions for the line tension.[3, 5, 6]

The theory of the adhesion of liquid particles developed by the writer[1, 4, 18] establishes the relationship between the adhesion forces and the parameters which characterise the disjoining pressure isotherm in the liquid film. The relationship between the force of adhesion and the specific free energy of adhesion obtained by this theory differs from the corresponding expression of the Johnson–Kendall–Roberts theory,[77] which is usually adopted to describe the adhesion of elastic solid particles and includes the Bradley–Deryagin theory[68, 69] as a limiting case (relating to liquid particles with a very large capillary pressure).

Our criterion[18, 79, 83] for the aggregation stability of emulsions can be used to explain the effect of the interfacial tension and of the shape of the disjoining pressure isotherm on the stability of emulsions towards coagulation. In particular we have shown that a decrease in σ_0 can both increase and decrease the aggregation stability of emulsions, depending on whether or not the $\Pi(H)$ isotherm includes a coagulation barrier. This large difference in the behaviour of emulsions as compared with sols under identical physicochemical conditions is attributed to the fact that in the interaction between liquid drops in emulsions the work associated with the deformation of the particle surfaces can exceed by a factor of $\sim 10^3$ the work of the disjoining pressure forces.[1, 4]

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