Thin Liquid Films

Fundamentals and Applications

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Mechanics and Thermodynamics of Curved Thin Films

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I. HYDROSTATICS OF SPHERICAL THIN FILMS

The basic idea of the micromechanical treatment of nonuniform systems is to consider the pressure as a nonisotropic tensor. Since the components of this tensor are statistically averaged quantities, they are continuous functions of [illegible] position. They vary rapidly, but smoothly, in the transition reg[illegible] between the phases which compose a given heterogeneous system. As pointed out by Irving and Kirkwood (1950) the pressure tensor can be expressed through integrals over the intermolecular potentials and the correlation functions (see, e.g., Ono and Kondo, 1960).

In the framework of the Gibbs' (1906) approach, the real nonhomogeneous system (with transition regions of finite width) can be replaced by a suitably chosen idealized system. The phases of the latter are considered as being homogeneous, the transition regions are replaced by sharp boundaries (surfaces, lines or points), and the integrals over the pressure tensor are replaced by forces acting on the surfaces (e.g., surface tension), the lines, or the points. In order to make this idealized (model) system equivalent to the real one, excesses of the system properties are also introduced. They are ascribed to the boundaries separating the respective homogeneous phases (e.g., to the surfaces separating the bulk phases). The position of the phase boundaries (surfaces, lines, and points) in the model system are fixed by the conditions for equivalence of the real and model systems, both mechanically and with respect to the extensive properties.

The well-known formula of Bakker (1928) for the surface tension of a flat interface [see Eq. (24) of Chapter 1 in this book] is a condition for equivalence between the real and idealized systems with respect to the acting forces. This approach in the theory of the surface tension was further generalized for planar interfaces by Kirkwood and Buff (1949), Buff (1952), and Triezenberg and Zwanzig (1972) (for details see Evans, 1979) and for curved interfaces by Buff (1951, 1955, 1956, 1960a,b), Buff and Saltsburg (1957), and Murphy (1966). As it will be shown below, the same approach can be extended to the mechanical theory of thin liquid films.

Let $\underset{\sim}{\mathbf{P}}$ denote the total pressure tensor, which satisifies the condition for hydrostatic equilibrium:

$$\nabla \cdot \underset{\sim}{\mathbf{P}} = 0 \tag{1}$$

The total pressure tensor equals the total momentum flux density (Landau and Lifshitz, 1973, Section 32). It can be thought of as composed of fluxes due to different sources: thermal motion, electrostatic, van der Waals and other interactions, external forces†, etc. The representation of the total pressure tensor as a sum of several terms accounting for different kind of interactions is not unique and it needs some additional model considerations. For example, in the approach of Felderhof (1968), called "body force approach," the contribution to the pressure due to the van der Waals forces is dissociated from the total pressure tensor because there is a separate expression for the van der Waals body force potential.

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†In this section, which is devoted to spherical films [illegible] neglect the action of gravity.

In this chapter we work only with the total pressure tensor without using any model considerations. This general approach in the thin film mechanics is called sometimes the "disjoining pressure approach."

A. Film Tension

When a spherical film is considered as a membrane of zero thickness the hydrostatic equations for its tension γ are the same as for the surface tension of a spherical drop. Imagine two bulk phases, α and β, separated by a spherical thin film, enveloping the phase α. Since this system is not homogeneous the force field in it is described by the pressure tensor $\underset{\sim}{\mathbf{P}}$. Due to the symmetry of the system the pressure tensor has only three nonzero components: P_{rr} and $P_{\theta\theta} = P_{\varphi\varphi}$, where r, θ, and φ are polar coordinates (r is the distance to the center of the system). The force (per unit area) acting normally to any surface r = const is P_{rr} and it is called the normal component of the pressure tensor $P_N(r)$; along the same surface acts $P_T(r) = P_{\theta\theta} = P_{\varphi\varphi}$, which is called the tangential component of the pressure tensor.

Let us consider a portion of the system, enclosed between two spheres of radii r_α and r_β. The total force acting on the surface (hatched in Fig. 1a) in a direction perpendicular to it will be

$$f\, d\theta = d\theta \int_{r_\alpha}^{r_\beta} P_T r\, dr \tag{2}$$

The respective force moment is defined by

$$M\, d\theta = d\theta \int_{r_\alpha}^{r_\beta} P_T r^2\, dr \tag{3}$$

Following Gibbs (1906) we define an idealized system by introducing two bulk phases, α and β, homogeneous up to the dividing spherical surface of radius r_0. We apply (per unit length) at r_0 a force γ (see Fig. 1b) and require that the real and the idealized systems be mechanically equivalent (in terms of force and moment). If the pressures in the homogeneous phases are P_α and P_β, respectively, from the conditions for mechanical equivalence of the two systems and Eqs. (2) and (3) it follows that

$$\gamma r_0 = \int_{r_\alpha}^{r_\beta} (P_{\alpha\beta} - P_T) r\, dr \tag{4}$$

$$\gamma r_0^2 = \int_{r_\alpha}^{r_\beta} (P_{\alpha\beta} - P_T) r^2\, dr \tag{5}$$

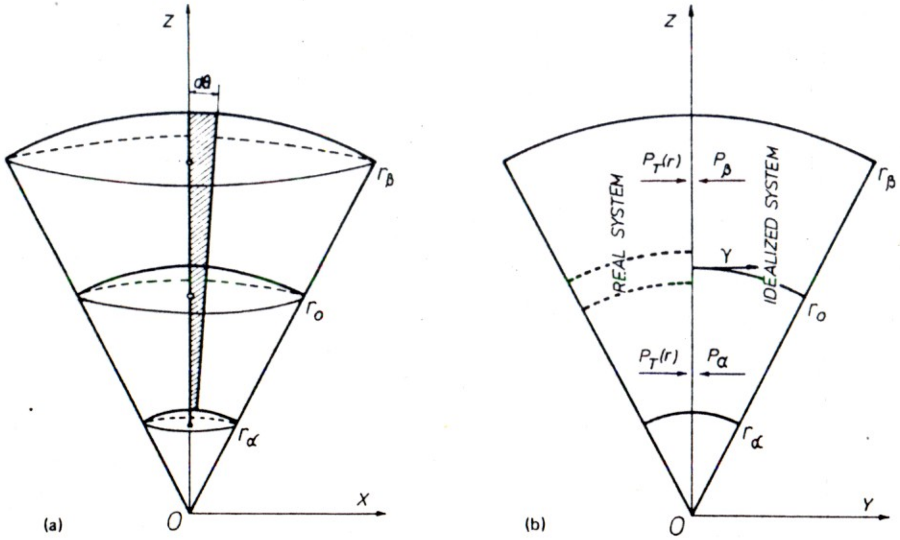


FIG. 1 Derivation of the conditions for mechanical equilibrium of a spherical film (see the text).

where

$$P_{\alpha\beta} = P_\alpha\theta(r_0 - r) + P_\beta\theta(r - r_0) \tag{6}$$

and

$$\theta(x) = \begin{cases} 1 & \text{at } x > 0 \\ 0 & \text{at } x < 0 \end{cases} \tag{7}$$

Equations (4) and (5) define the film tension γ and the radius of the dividing surface r_0 in terms of P_T, P_α, and P_β. The dividing surface defined in this way is called "the surface of tension" (Ono and Kondo, 1960; Rusanov, 1967a).

The condition for hydrostatic equilibrium (1) can be expressed by any of the following three equivalent equations (see, e.g., Kirkwood and Buff, 1949; or Ono and Kondo, 1960):

$$\frac{d(r^2P_N)}{d(r^2)} = P_T \tag{8}$$

$$\frac{dP_N}{dr} = \frac{2}{r}(P_T - P_N) \tag{9}$$

$$\frac{d(r^3P_N)}{dr} = r^2(P_N + 2P_T) \tag{10}$$

Let us assume that the pressures P_α and P_β coincide with the values of P_N at $r = r_\alpha$ and $r = r_\beta$, respectively, i.e.,

$$P_\alpha \equiv P_N(r_\alpha) \quad \text{and} \quad P_\beta \equiv P_N(r_\beta) \tag{11}$$

Then on integrating Eq. (8) we obtain

$$\frac{1}{2}(P_\beta r_\beta^{\,2} - P_\alpha r_\alpha^{\,2}) = \int_{r_\alpha}^{r_\beta} P_T r\,dr \tag{12}$$

On performing the integration in Eq. (4) and substituting the expression for the integral of P_T from Eq. (12) one easily obtains

$$\frac{2\gamma}{r_0} = P_\alpha - P_\beta \tag{13}$$

which is the familiar Laplace equation.

This result calls for some comments. It is shown in Section I.F. that Eq. (5) holds for any arbitrarily chosen position of the dividing surface, whereas Eq. (4) specifies the surface of tension. The Laplace equation [Eq. (13)] follows from Eq. (4), therefore Eq. (13) holds only for the surface of tension. When carrying out similar derivations for a spherical drop (see Ono and Kondo, 1960) one usually assumes that r_α and r_β lie in the regions where there are homogeneous fluids, so that P_α and P_β are the respective isotropic pressures. This assumption substantially simplifies the thermodynamic treatment. However, as far as the mechanical equilibrium is concerned, this assumption is not necessary. Indeed, in our derivation r_α and r_β can be arbitrary [P_α and P_β were defined by Eqs. (11)]: for example, r_α can be zero and then P_α will equal the value of P_N in the center of the inner phase α. This fact can be of importance in the treatment of very small drops, when the phase encircled by the film never becomes homogeneous.

It is pertinent to derive expressions for γ only in terms of integrals over ($P_N - P_T$). The integration of Eq. (9) along with (13) yields

$$\gamma = \int_{r_\alpha}^{r_\beta} (P_N - P_T)\frac{r_0}{r}\,dr \tag{14}$$

An alternative expression is obtained by integrating Eq. (10) and making use of Eqs [illegible]) and (13):

$$\gamma = \int_{r_\alpha}^{r_\beta} (P_N - P_T) \frac{r^2}{r_0^2}\, dr \tag{15}$$

The analogues of these equations for the surface tension of a spherical drop were first derived by Goodrich (1969) and Buff (1955). Equations (14) and (15) lead to an explicit equation for r_0:

$$r_0^3 = \left[\int_{r_\alpha}^{r_\beta} (P_N - P_T) r^2\, dr\right] \Big/ \left[\int_{r_\alpha}^{r_\beta} (P_N - P_T) \frac{dr}{r}\right] \tag{16}$$

B. Surface Tensions of the Film

In Section I.A we used the so-called "membrane approach" in which the film is treated as a membrane of zero thickness. On the other hand, the film can be considered also as a bulk phase of finite thickness h: This is the so-called "detailed approach." In this approach some other macroscopic properties of the film are introduced, e.g., disjoining pressure and surface tensions of the film. A thermodynamic definition of the film surface tensions was given by Rusanov (1967a,b), and a hydrostatic definition for flat films was given by Toshev and Ivanov (1975) [see Eq. (59) of Chapter 1 in this book]. Here we present the extension of this definition to spherical films.

Let us introduce an idealized system consisting of the bulk phase α with pressure P_α (lying within $r_\alpha < r < r_1$), bulk phase β with pressure P_β (within $r_2 < r < r_\beta$), and a reference phase R (for details see below) with pressure P_R (note that $r_1 < r_0 < r_2$) (see Fig. 2). The film is, therefore, represented as a spherical layer of thickness $h = r_2 - r_1$. The spheres of radii r_1 and r_2 are called "film surfaces" and by analogy with Eqs. (4) and (5) the respective surface tensions of the film σ_1 and σ_2 can be defined by (Kralchevsky and Ivanov, 1986):

$$\sigma_1 r_1 = \int_{r_\alpha}^{r_0} (P_{\alpha R} - P_T) r\, dr, \qquad \sigma_1 r_1^2 = \int_{r_\alpha}^{r_0} (P_{\alpha R} - P_T) r^2\, dr \tag{17}$$

$$\sigma_2 r_2 = \int_{r_0}^{r_\beta} (P_{R\beta} - P_T) r\, dr, \qquad \sigma_2 r_2^2 = \int_{r_0}^{r_\beta} (P_{R\beta} - P_T) r^2\, dr \tag{18}$$

with

$$\begin{aligned} P_{\alpha R} &= P_\alpha \theta(r_1 - r) + P_R\, \theta(r - r_1), \\ P_{R\beta} &= P_R\, \theta(r_2 - r) + P_\beta \theta(r - r_2) \end{aligned} \tag{19}$$

The radii r_1 and r_2, thus introduced, define the surface of tension for the two interfaces between the film and the adjacent phases α and β. It should be noted that the four quantities σ_1, σ_2, r_1, and r_2 depend on the reference pressure P_R. That is why different choices of P_R correspond to different model systems. When the film contacts with a bulk liquid (see Section I.D) it is convenient to use the pressure in the liquid as a reference pressure P_R. Eriksson and Toshev (1982) used the normal component of the pressure tensor P_N as a reference pressure in a flat film. The dependence of the film surface tensions on the choice of P_R is considered in Section I.E.

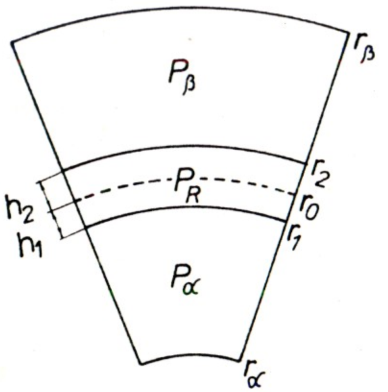


FIG. 2 Sketch of a spherical film as a layer of finite thickness $h = h_1 + h_2$ (detailed approach).

Similarly to Eq. (16) for r_0, the expressions for the radii r_1 and r_2 can be written only in terms of the components of the pressure tensor P_T and P_N and the reference pressure P_R. It follows from the definitions (17) and (18) (Kralchevsky and Ivanov, 1984) that

$$h_1^2 = \frac{2}{r_0} \frac{J_2 - (1 - h_1/r_0) J_1}{(1 - h/3r_0) P_{c1}}, \qquad h_2^2 = \frac{2}{r_0} \frac{J_4 - (1 + h_2/r_0) J_3}{(1 + h_2/r_0) P_{c2}} \tag{20}$$

where the following notation is used:

$$h_1 = r_0 - r_1, \qquad h_2 = r_2 - r_0 \tag{21}$$

$$P_{c1} = P_\alpha - P_R, \qquad P_{c2} = P_R - P_\beta; \tag{22}$$

$$J_1 = \int_{r_\alpha}^{r_0} (P_\alpha - P_T) r r_0\, dr, \qquad J_2 = \int_{r_\alpha}^{r_0} (P_\alpha - P_T) r^2\, dr$$

$$J_3 = \int_{r_0}^{r_\beta} (P_\beta - P_T) r r_0\, dr, \qquad J_4 = \int_{r_0}^{r_\beta} (P_\beta - P_T) r^2\, dr$$

One can determine h_1 and h_2 (and hence r_1 and r_2) from the cubic equations [Eq. (20)]; when $h_1, h_2 \ll r_0$ this can be done by iterations.

The surface tensions of the film, σ_1 and σ_2, can be expressed as algebraic combinations of γ, r_0, r_1, r_2, P_{c1}, and P_{c2}. These expressions, which result directly from the definitions (4), (5), (17), and (18), read

$$\sigma_1 = \frac{r_0(r_2 - r_0)\gamma + Q - qr_2}{r_1(r_2 - r_1)}$$
$$\sigma_2 = \frac{r_0(r_0 - r_1)\gamma - Q + qr_1}{r_2(r_2 - r_1)} \tag{23}$$

where

$$q = \tfrac{1}{2}[(r_0^2 - r_1^2)P_{c1} - (r_2^2 - r_0^2)P_{c2}],$$
$$Q = \tfrac{1}{3}[(r_0^3 - r_1^3)P_{c1} - (r_2^3 - r_0^3)P_{c2}]$$

C. Disjoining Pressure of a Spherical Film

The concept of disjoining pressure as an additional pressure that must be introduced in the macroscopic theory of thin liquid films was first introduced by Derjaguin and Kusakov (1936). The role of the disjoining pressure in the thermodynamics of plane-parallel films is extensively considered in Chapter 1 of this book. We continue here with the definition of the disjoining pressure of a spherical film.

To obtain an analogue (in the framework of the detailed approach) of Eq. (13) one can integrate Eq. (8) and the first of Eq. (19) (the latter multiplied by r) from r_α to r_0 and eliminate $P_\alpha r_\alpha^2$ between the resulting equations. So we obtain

$$\frac{2\sigma_1}{r_1} = P_\alpha - P_R - [P_N(r_0) - P_R]\frac{r_0^2}{r_1^2} \tag{24}$$

By analogy with the definition of the disjoining pressure Π in flat films, the quantity

$$\Pi \equiv P_N(r_0) - P_R \tag{25}$$

can be termed disjoining pressure of the spherical film (Kralchevsky and Ivanov, 1986). According to this definition the disjoining pressure Π is connected with the total pressure tensor and therefore Π accounts for all kinds of interactions in the film: van der Waals forces, electrostatic forces, etc. Equations (22), (24), and (25) lead to

$$\frac{2\sigma_1}{r_1} = P_{c1} - \Pi\frac{r_0^2}{r_1^2}, \qquad \frac{2\sigma_2}{r_2} = P_{c2} + \Pi\frac{r_0^2}{r_2^2} \tag{26}$$

Equation (26) can be interpreted as normal force balances at the two film surfaces. They show that in the pressure drops P_{c1} and P_{c2} the interaction between the film surfaces is accounted for by two terms: the curvature term $2\sigma_i/r_i$, i = 1, 2 (in which the surface tensions σ_1 and σ_2, because of the interaction between the film surfaces, will be different from the surface tensions of drops of the same radii), and the disjoining pressure terms $\Pi r_0^2/r_i^2$, i = 1, 2. In the limit $r_0 \to \infty$ (keeping h_1 and h_2 finite), Eqs. (26) lead to the known definition of Π in a flat film:

$$\Pi = P_\alpha - P_R = P_\beta - P_R \tag{27}$$

The definition (25) of the disjoining pressure and normal force balances (26) enables one to throw some light on the somewhat obscure problem about the localization of the disjoining pressure. Equation (25) shows that Π can be calculated from the value of P_N on the reference surface $r = r_0$; note that $P_N(r_0)$ can be expressed through integrals over the intermolecular potentials and the pair correlation functions [see, e.g., Ono and Kondo, 1960, Eqs. (34.6)-(34.8)]. Imagine a surface element of area ΔA on the reference surface $r = r_0$. The orthogonal projections of this element onto any of the film surfaces $r = r_i$, i = 1, 2, are of area $\Delta A r_i^2/r_0^2$. Then the disjoining pressure Π, as defined by Eq. (25), can be interpreted as an excess force per unit area of the reference surface accounting for the different pressures in the real and the idealized systems. The terms $\Pi r_0^2/r_i^2$, i = 1, 2, in Eqs. (26) are the orthogonal projections of this force per unit area of the film surfaces $r = r_i$. In order to show the direction of this force one can write a vectorial version of Eq. (25):

$$\Pi = \mathbf{n}\cdot(\underset{\sim}{\mathbf{P}} - P_R\underset{\sim}{\mathbf{U}})|_{r=r_0} \tag{28}$$

where $\underset{\sim}{\mathbf{U}}$ is the three-dimensional idemfactor and $\mathbf{n}$ is an outer unit normal with respect to the reference surface. It is important to note that the definition (28) is valid not only for a spherical film, but for any film with arbitrary curvature (see Section III for details). These considerations imply that for curved thin films Π is an excess pressure, applied at the reference surface.

Here we chose the surface of tension of the film $r = r_0$ as a reference surface dividing the film onto two parts [cf. Fig. 2 and the limits of integration in Eqs. (17) and (18)]. But, in the general case, the role of reference surface could be played by any spherical surface lying inside the film region. Hence, the disjoining pressure depends on the choice of both the reference surface and the reference pressure P_R. However, once this choice has been made, Π has well-defined values for a given physical state of the real system.

For a plane-parallel film the definition (25) and the normal force balances (26) coincide by form due to the symmetry of this system. Moreover, as pointed out by Toshev and Ivanov (1975), the normal component of the pressure tensor in the real system, P_N, suffers a jump equal to Π on the boundary between the film and the meniscus of the bulk liquid. On the other hand, de Feijter et al. (1978), who chose the pressure in the meniscus as a film reference pressure, have noted that an effective pressure jump, equal to Π, appeared over the film surfaces in the idealized system. There is no contradiction between the statements of Toshev and Ivanov (1975) and de Feijter et al. (1978), and their basic thermodynamic equations for planar thin films are completely equivalent. This problem was more recently taken up by Bisch and Wendel (1983). Unfortunately, their own work is somewhat controversial because these authors did not distinguish between the real and idealized system and did not consider the body force potential as an excess quantity, as it should be done according to Maldarelli et al. (1980).

By means of Eqs. (9) and (10) [cf. also Eq. (21)] one can derive the following expressions analogous to Eqs. (14) and (15) (Kralchevsky and Ivanov, 1986):

$$\frac{\sigma_1}{r_1} = \int_{r_\alpha}^{r_0} (P_N - P_T)\,\frac{dr}{r} - \frac{1}{2}\,\Pi\left(\frac{r_0^2}{r_1^2} - 1\right) \tag{29}$$

$$\frac{\sigma_2}{r_2} = \int_{r_0}^{r_\beta} (P_N - P_T)\,\frac{dr}{r} - \frac{1}{2}\,\Pi\left(1 - \frac{r_0^2}{r_2^2}\right) \tag{30}$$

$$\sigma_1 r_1^2 + \Pi h_1 r_0^2 = \int_{r_\alpha}^{r_0} (P_N - P_T) r^2\,dr \tag{31}$$

$$\sigma_2 r_2^2 + \Pi h_2 r_0^2 = \int_{r_0}^{r_\beta} (P_N - P_T) r^2\,dr \tag{32}$$

By summing up Eqs. (29) and (30) and keeping also in mind Eq. (14), one obtains

$$\frac{\gamma}{r_0} = \frac{\sigma_1}{r_1} + \frac{\sigma_2}{r_2} + \frac{(r_1 + r_2) r_0^2}{2 r_1^2 r_2^2}\,\Pi h \tag{33}$$

where $h = h_1 + h_2$. The limiting case of a flat film can be obtained by letting $r_0 \to \infty$ (but keeping h_1 and h_2 finite):

$$\gamma = \sigma_1 + \sigma_2 + \Pi h \tag{34}$$

[see Eq. (74) of Chapter 1 in this book, or the works of Rusanov (1966, 1967a)]. Another important relationship is obtained by summing up Eqs. (31) and (32) and taking into account Eq. (15):

$$\gamma A_0 = \sigma_1 A_1 + \sigma_2 A_2 + \Pi h A_0 \tag{35}$$

where A_0 is the area of a parcel on the reference surface $r = r_0$, and A_i $(i = 1,2)$ is the area of its orthogonal projection on the film surface $r = r_i$. In the limit $r_0 \to \infty$, Eq. (35) also leads to Eq. (34).

D. Hydrostatics of a Bubble Attached to a Liquid Surface

As an application of the above equations let us consider a system, consisting of a small bubble attached to a liquid surface and forming a thin liquid film at the top of the bubble (see Fig. 3). (Instead of gas bubble, a drop of lighter liquid could be considered.) We will assume that the bubble is sufficiently small to enable neglecting the gravity effect due to the elevation of the film over the liquid surface (the respective hydrostatic pressure is negligible with respect to Π). Let us choose the bulk liquid phase as a reference phase in the film with reference pressure $P_R = P_\gamma$. Also, $P_\gamma = P_\beta$ because the liquid surface is flat. In this case

$$P_{c1} = P_\alpha - P_\beta \equiv P_c, \qquad P_{c2} = P_\gamma - P_\beta = 0 \tag{36}$$

Then Eqs. (13) and (23) yield

$$\sigma_1 = \left(\frac{2}{3}\,\frac{r_1}{r_0} - \frac{1}{3}\,\frac{r_0^3 - r_1^2 r_2}{r_0 r_1 h}\right)\gamma, \qquad \sigma_2 = \frac{r_0^3 - r_1^3}{3 r_0 r_1 h}\,\gamma \tag{37}$$

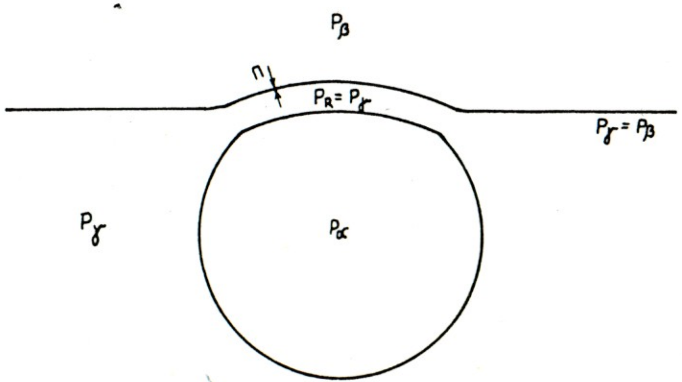


FIG. 3 Scheme of a small bubble attached to a liquid surface.

and Eqs. (26) reduce to

$$\frac{2\sigma_1}{r_1} = P_c - \Pi\frac{r_0^2}{r_1^2}, \qquad \frac{2\sigma_2}{r_2} = \Pi\frac{r_0^2}{r_2^2} \tag{38}$$

It is interesting to note that the curvature pressure drop on the upper film surface, $2\sigma_2/r_2$, is completely balanced by the disjoining pressure term. The elimination of σ_2 between Eq. (37) and (38) yields

$$\Pi = \frac{r_0^3 - r_1^3}{3r_0^2 h} P_c \tag{39}$$

where Eq. (13) was also used [the same expression for Π is obtained by elimination of σ_1 in the first equation in each of Eqs. (37) and (38)]. If $h_1 \ll r_0$, from Eq. (39) one obtains

$$\Pi \approx \frac{h_1}{h} P_c \approx \frac{1}{2} P_c \tag{40}$$

This result could seem strange, because for plane-parallel films $\Pi = P_c$ [cf. Eq. (26) of Chapter 1 in this book]. In fact, there is no contradiction. The capillary pressure in the theory of the plane-parallel films (see, e.g., Toshev and Ivanov, 1975) is the pressure drop on the meniscus surface. This quantity is different from P_c in Eq. (40), which is the pressure drop across the curved film; this drop is zero when the film is plane-parallel.

E. Choice of the Reference Pressure P_R

The surface tension of a flat interface does not depend on the location of the Gibbs' dividing surface. If the interface is spherical, there is an additional degree of freedom (the curvature) and the surface tension (e.g., of a small drop) depends on the position of the dividing surface (see Ono and Knodo, 1960; or Rusanov, 1967a). A spherical film possesses one more degree of freedom (one can choose its thickness); i.e., in comparison with a flat interface the spherical film has two additional degrees of freedom. That is why (1) at given reference pressure P_R the surface tensions of the film, σ_1 and σ_2, depend on the choice of the dividing surfaces similarly to the surface tension of a spherical drop (this problem is examined in Section I.F); and (2) if the dividing surfaces have been already chosen, σ_1 and σ_2 exhibit a dependence on the choice of the reference pressure P_R. This dependence, which is specific for thin films, is studied in the present section. It is important to note that we mean here degrees of freedom of the macroscopic model and therefore the dependences mentioned above are formal, i.e., they correspond to different choices of the model (at fixed physical state) rather than to a real process. But once the choice of the reference pressure and the dividing surfaces has been made, all parameters of the system have well-defined values that depend on the real physical state only.

The choice of the dividing surfaces and of the reference pressure is a matter of convenience and it could be done in various ways. For example, the dividing surfaces could be defined as surfaces of tension (see Section I.B), or as surfaces of the minimum tension (see Section I.F), or as equimolecular surfaces with respect to some components (whose adsorptions are supposed to be zero: cf. Chapter 1 in this book), etc. On the other hand, at any given choice of the dividing surfaces one has the freedom to select arbitrarily the reference pressures: $P_R = P_\gamma$ (see Fig. 3), or $P_R = P_T(r_0)$, or $P_R = P_N(r_0)$, or $P_R = P_\alpha$, etc.

Let us specify the dividing surfaces as surfaces of tension as described in Section I.B. Then, let us differentiate the second equation in Eqs. (17) with respect to r_1 at fixed physical state of the system. By means of Eq. (26) the result can be cast in the following form:

$$\left[\frac{d\sigma_1}{dr_1}\right] = \Pi\frac{r_0^2}{r_1^2} + \frac{r_0^3 - r_1^3}{3r_1^2}\left[\frac{dP_R}{dr_1}\right] \tag{41}$$

where the increments $d\sigma_1$ and dr_1 correspond to an increase of P_R with dP_R, and the square brackets symbolize differentiation at fixed physical state. In the same way, one finds the following from the first equation in Eqs. (17):

$$\left[\frac{d\sigma_1}{dr_1}\right] = \frac{1}{2} \quad \Pi\frac{r_0^2}{r_1^2} + P_\alpha - P_R \quad + \frac{r_0^2 - r_1^2}{2r_1}\left[\frac{dP_R}{dr_1}\right] \tag{42}$$

Besides, $dr_1 = -dh_1$ [cf. Eq. (21)]. Then, after elimination of $[d\sigma_1/dr_1]$ between Eqs. (41) and (42), one obtains a linear differential equation for P_R as a function of r_1. The other film surface can be treated in an analogous way. Thus one obtains

$$y_i(x_i) = \frac{x_{i0}^2(x_{i0} + 3\varepsilon_i)}{x_i^2(x_i + 3\varepsilon_i)}\left[1 - \frac{3(x_i - x_{i0})}{x_{i0}^2(x_{i0} + 3\varepsilon_i)}\right], \quad i = 1,2 \tag{43}$$

where $\varepsilon_i = (-1)^i$,

$$x_i = \frac{h_i}{r_0}, \qquad y_i = \frac{P_R - P_i}{P_N(r_0) - P_i}, \qquad i = 1,2 \tag{44}$$

with $P_1 = P_\alpha$ and $P_2 = P_\beta$. When deriving Eq. (43) the boundary condition $y_i(x_{i0}) =$ [illegible] was used, where x_{i0} is the value of x_i corresponding to $P_R = P_N(r_0)$. Equation (43) yields the function $h_i = h_i(P_R)$, $i = 1,2$, which shows how the film thickness depends on the choice of the reference pressure at a given physical state. On the other hand, from Eqs. (26) and (44) it follows that

$$\bar{\sigma}_i = [1 + (x_i^2 + 2\varepsilon_i x_i)y_i]/[2(1 + \varepsilon_i x_i)], \quad i = 1,2 \tag{45}$$

where

$$\bar{\sigma}_1 = \frac{\sigma_1}{[P_\alpha - P_N(r_0)]r_0}, \qquad \bar{\sigma}_2 = \frac{\sigma_2}{[P_N(r_0) - P_\beta]r_0} \tag{46}$$

Equations (45), along with Eq. (43), express the dependencies $\sigma_i(h_i)$, $i = 1,2$, or, alternatively, the dependencies $\sigma_i(P_R)$, $i = 1,2$, at constant P_α, P_β, and r_0. In the limiting case of a flat film ($r_0 \to \infty$), when P_α, $P_\beta \to P_N(r_0)$, Eq. (45) yields

$$\lim \bar{\sigma}_i = \frac{1}{2}, \qquad i = 1,2 \tag{47}$$

The numerical investigation of Eqs. (43) and (45) showed that when $x_i, x_{i0} \ll 1$ ($i = 1,2$), h_i and σ_i depend slightly on P_R. This is illustrated in Fig. 4 for Eq. (43).

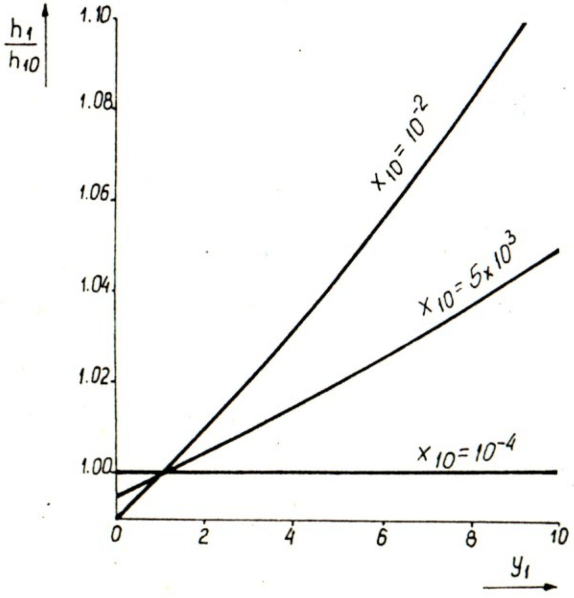


FIG. 4 The dependence of $h_1/h_{10} = x_1/x_{10}$ on $y_1 = (P_\alpha - P_R)/[P_\alpha - P_N(r_0)]$, calculated from Eq. (43) for three values of x_{10}.

We must stress again that the above considerations refer only to the dependence of the model thickness of the film (it was called thermodynamic thickness by Ivanov and Toshev, 1975) on the reference pressure P_R. They allow no calculation of the model thickness itself nor do they give its connection with the "real" thickness, the latter being the distance between the (relatively) sharp boundaries separating the film from the adjacent bulk phases α and β in the real system. These questions can be answered, at least in principle, only by a microscopic theory, based on statistical mechanics.

F. Choice of the Dividing Surfaces

The macroscopic film properties depend not only on the choice of the reference pressure P_R but also on the definitions of the dividing surfaces. In this section we first derive several general relationships and then examine some special cases.

Membrane Approach.

As mentioned above, a thin film and the interface between two bulk phases can both be treated as membranes of zero thickness. Let us consider the system depicted in Fig. 5, where r_x is the radius of an arbitrarily chosen spherical dividing surface, modeling the film as a membrane. The continuum mechanics yields the following expression for the work done by a system undergoing an elementary deformation (see, e.g., Landau and Lifshitz, 1965; or Rusanov, 1967a):

$$\delta W = -\iiint_{(V)} dV \underset{\sim}{\mathbf{P}} : \delta \underset{\sim}{\Phi} \tag{48}$$

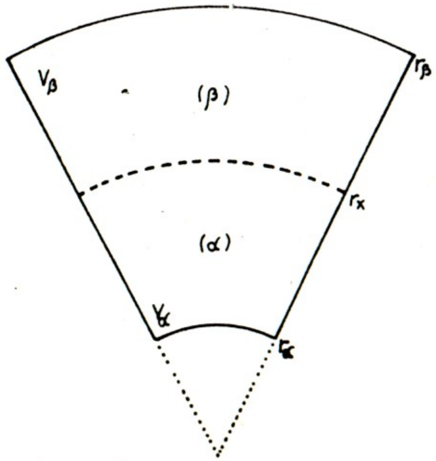


FIG. 5 Sketch of a spherical thin liquid film as a membrane of zero thickness and radius r_α (membrane approach).

where $\underset{\sim}{\mathbf{P}}$ and $\delta\underset{\sim}{\Phi}$ are the pressure tensor and the tensor of deformation in the real system of volume V; ":" denotes the double scalar product of two tensors. Rusanov (1967a) showed that when the substance deforms as a set of layers, parallel to the dividing surface, Eq. (48) can be transformed into

$$\delta W = -P_\alpha \delta V_\alpha - P_\beta \delta V_\beta + \delta W^f \tag{49}$$

with

$$\delta W^f = \gamma_x \, \delta A_x + A_x \left(\frac{\partial \gamma_x}{\partial r_x}\right)^* \delta r_x \tag{50}$$

Here A_x and γ_x are the area and the tension of the membrane (the film), and by definition

$$\gamma_x = \int_{r_\alpha}^{r_\beta} [P_{\alpha\beta}^{(x)} - P_T(r)] \, \frac{r^2}{r_x^2} \, dr \tag{51}$$

with

$$P_{\alpha\beta}^{(x)} = P_\alpha \theta(r_x - r) + P_\beta \theta(r - r_x) \tag{52}$$

[cf. also Eq. (7)]. The formal derivative $(\partial\gamma_x/\partial r_x)^*$ corresponds to a change of r_x at a fixed physical state and reference pressure. The derivatives of this kind will be denoted hereafter by *. The differentiation of Eq. (51) with respect to r_x, along with Eq. (52), yields

$$\frac{2\gamma_x}{r_x} + \left(\frac{\partial \gamma_x}{\partial r_x}\right)^* = P_\alpha - P_\beta \tag{53}$$

Equation (53) is in fact a generalization of the Laplace equation [Eq. (13)]. Equations (50) and (53) were first derived by Kondo (1956).

If one supplements the definition (51) with the condition for force balance (between the real and idealized system) (4), then he or she will obtain the usual Laplace equation [Eq. (13)], i.e., for the surface of tension:

$$\left(\frac{\partial \gamma_x}{\partial r_x}\right)^*_{r_x = r_0} = 0 \tag{54}$$

Let us introduce the dimensionless variables

$$x = \frac{r_x}{r_0}, \qquad y = \frac{\gamma_x}{\gamma} \tag{55}$$

From Eq. (13) $(P_\alpha - P_\beta)r_0/\gamma = 2$, so that Eq. (53) takes the form

$$\frac{dy}{dx} + \frac{2}{x}y - 2 = 0 \tag{56}$$

The solution of this linear differential equation, along with the boudnary condition $y(1) = 1$, reads

$$y(x) = \frac{1}{3x^2} + \frac{2}{3}x \tag{57}$$

This equation, first derived by Kondo (1956), represents the dependence of the film (or interface) tension on the choice of the dividing surface for a given physical state. It follows from Eqs. (54), (55), and (57) that the film tension γ_x takes its minimum value at the surface of tension, i.e., the surface of tension in this case coincides with the surface of minimum tension.

Equation (50) is valid only for isotropic deformations, which transform a spherical surface into a spherical one. In the general case Eq. (50) must be replaced by the following expression, proposed by Gibbs (1906):

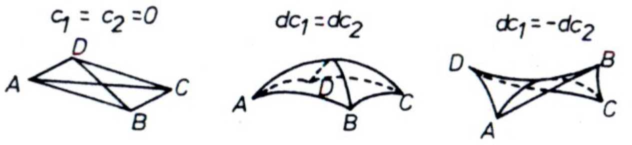
$$\delta w^f = \gamma_x \, \delta\alpha + B \, \delta H + \Theta \delta D \tag{58}$$

Here δw^f is the surface work per unit area, $\delta\alpha = \delta(\Delta A)/\Delta A$ is the relative increase of the area ΔA from the dividing surface, and

$$H = \frac{1}{2}(c_1 + c_2), \qquad D = \frac{1}{2}(c_1 - c_2) \tag{59}$$

where c_1 and c_2 are the two principal curvatures of this surface; H and D are the mean and the deviative curvatures (the latter being a measure for the local deviation of the surface from spherical shape). The sign of the curvatures is defined in the same way as in the books by McConnell (1957) and Aris (1962). Note that Eq. (58) contains only intensive quantities and therefore holds in each point of the surface. One sees from Eq. (58) that $\gamma_x \delta\alpha$ is the work for simple dilation ($\delta c_1 = \delta c_2 = 0$) of the interface, $B \delta H$ is the work for simple bending of the interface ($\delta c_1 = \delta c_2$, $\delta\alpha = 0$), and $\Theta \delta D$ is the work for simple torsion of the interface ($\delta c_1 = -\delta c_2$, $\delta\alpha = 0$) (see Fig. 6). That is why the quantities B and Θ are called bending and torsion moments, respectively (cf., e.g., Murphy, 1966). [In the works of Buff (1956) and Buff and Saltsburg (1957) the bending moment B is denoted by $-2C/s$, and the tor[illegible]n moment Θ is neglected.]

The [illegible]eneralization of Eq. (51) for arbitrarily curved interfaces reads



REFERENCE STATE SIMPLE BENDING SIMPLE TORSION

FIG. 6 Bending and torsion modes of deformation of a surface element.

$$\gamma_x = \frac{1}{2}\int_{\lambda_\alpha}^{\lambda_\beta} \underset{\sim}{U}_{II} : (\underset{\sim}{\bar{P}} - \underset{\sim}{P})(1 - 2\lambda H + \lambda^2 K)\, d\lambda \tag{60}$$

Here $K = c_1 c_2$ is the gaussian curvature, $\underset{\sim}{U}_{II}$ is the (dividing) surface idemfactor, and

$$\underset{\sim}{\bar{P}} = [P_\alpha \theta(-\lambda) + P_\beta \theta(\lambda)]\underset{\sim}{U} \tag{61}$$

is the pressure tensor in the idealized system. The value $\lambda = 0$ corresponds to the dividing surface, and $\lambda = \lambda_\alpha$, $\lambda = \lambda_\beta$ correspond to two parallel surfaces situated in the two adjacent bulk phases. Expressions analogous to Eq. (60) can be derived for the bending and torsion moments

$$B = \int_{\lambda_\alpha}^{\lambda_\beta} (\underset{\sim}{P} - \underset{\sim}{\bar{P}}) : \underset{\sim}{L}\, \lambda\, d\lambda \tag{62}$$

$$\Theta = \int_{\lambda_\alpha}^{\lambda_\beta} (\underset{\sim}{P} - \underset{\sim}{\bar{P}}) : (\underset{\sim}{L}\cdot\underset{\sim}{q})\lambda\, d\lambda \tag{63}$$

with $\underset{\sim}{L} = (1 - 2\lambda H)\underset{\sim}{U}_{II} + \lambda\underset{\sim}{b}$, $\underset{\sim}{q} = (\underset{\sim}{b} - H\underset{\sim}{U}_{II})/D$ and $\underset{\sim}{b}$ being the surface curvature tensor. For the case of a transversely isotropic (with respect to the interface) stress tensor $\underset{\sim}{P}$ Equations (60), (62) and (63) were derived by Murphy, 1966†; the derivations of these equations in the general case can be found in the work of Kralchevsky, 1987.

For spherical surfaces Eq. (60) reduces to Eq. (51); Eq. (63) yields $\Theta = 0$ and Eq. (62) transforms into

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†The definitions of the bending and torsion moments in the work of Murphy (1966) are somewhat different from the definitions of Gibbs (1906), which are used here.

$$B = 2\int_{\lambda_\alpha}^{\lambda_\beta} (P_T - \bar{P})(1 + \lambda/r_x)\,\lambda\, d\lambda \tag{64}$$

which is known as Tolman-Buff's equations—see Tolman, 1948, Buff, 1955, and Ono and Kondo, 1960. Besides, if one writes Eq. (58) for a spherical interface ($H = -1/r_x$, $D = 0$) and multiplies the result by the interfacial area A_x, one obtains

$$\delta W^f = \gamma_x\, \delta A_x + A_x(B/r_x^2)\,\delta r_x$$

Then one finds from the comparison of the last equation with Eq. (50) that

$$B = r_x^2\left(\frac{\partial \gamma_x}{\partial r_x}\right)^* \tag{65}$$

This relation reveals the physical meaning of the formal derivative $(\partial\gamma_x/\partial r_x)^*$. Equation (54) shows that $B = 0$ for the surface of tension.

The equation of Kondo [Eq. (53)] can then be rewritten into an alternative form:

$$\frac{2\gamma_x}{r_x} + \frac{B}{r_x^2} = P_\alpha - P_\beta \tag{66}$$

Similarly to the film tension, the bending moment also depends on the location of the dividing surface. This dependence can be easily obtained by differentiation of Eq. (57) with respect to x [cf. also Eqs. (55) and (65)]:

$$\frac{B}{\gamma r_0} = \frac{2}{3}\,\frac{x^3 - 1}{x} \tag{67}$$

Equation (66) can be rearranged into the alternative form

$$\frac{2\gamma_x}{r_x}(1 + \bar{B}) = P_\alpha - P_\beta \tag{68}$$

where

$$\bar{B} = B/2\,\gamma_x r_x \tag{69}$$

From Eqs. (55), (57), and (67) one finds

$$\bar{B} = \frac{x^3 - 1}{2x^3 + 1} \tag{70}$$

with

$$x = \frac{r_x}{r_0} \tag{71}$$

Equation (70) is presented graphically in Fig. 7, and it is seen that the (dimensionless) bending moment, $\bar{B}$, depends on the displacement between the surface of tension and the dividing surface ($r = r_x$), but nonetheless the values of $\bar{B}$ are limited:

$$-1 < \bar{B} < \frac{1}{2} \tag{72}$$

Hence $|\bar{B}| \le 1$ and then the absolute value of the bending term in Eqs. (66) or (68) cannot exceed the interface tension effect. This conclusion holds (1) for formal variations of x, when the position of the dividing surface, $r = r_x$, is changed at given physical state (r_0 = const), and (2) for physical processes, when the dividing surface is defined in some way, e.g., as being the equimolecular dividing surface (the latter is close to what can be called "real interface" (see Ono and Kondo, 1960). Equation (72) also means that however large the distance between the surface of tension and the equimolecular dividing surface might be, the bending moment term is limited.

As pointed out by Miller (1985) the distance between the surface of tension and the real interface can be large enough for some small systems, like microemulsion droplets, for the bending effect to become important. But not all values of $\bar{B}$ obtained in this work by means of a specified model satisfy the conditions (72). In principle, one can calculate B with the help of a microscopic theory, but the results must be consistent with the limitation imposed on the bending effect by the macroscopic theory.

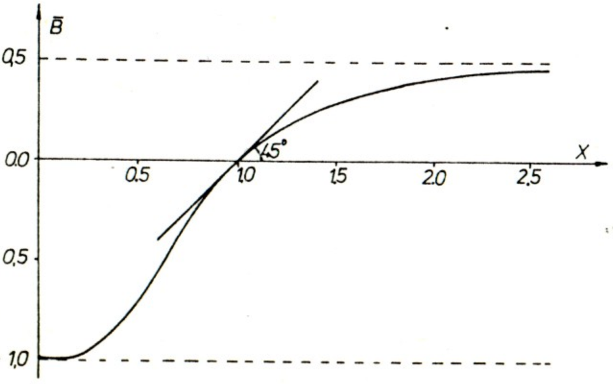

FIG. 7 Dependence of the dimensionalized bending moment, $\bar{B} = B/2\gamma_x r_x$, of a spherical film (interface) on the rat[illegible] $= r_x/r_0$; r_0 and r_x are the radii of the surface of tension and of the dividing surface.

The Detailed Model Approach.

The surface of tension $r = r_0$ divides the film into two parts: lower part of volume V_α at $r_\alpha < r < r_0$ and upper part ($r_0 < r < r_\beta$) of volume V_β (see Fig. 8). The mechanical work for deformation of the system can be split into two parts:

$$\delta W = \delta W_1 + \delta W_2 \tag{73}$$

$$\delta W_1 = -\iiint\limits_{(V_\alpha)} dV \underset{\sim}{\mathbf{P}} : \delta \underset{\sim}{\Phi}, \qquad \delta W_2 = -\iiint\limits_{(V_\beta)} dV \underset{\sim}{\mathbf{P}} : \delta \underset{\sim}{\Phi} \tag{74}$$

In the detailed model the film is considered as a homogeneous layer from a reference liquid (phase) with isotropic pressure P_R. The volume, V_f, of this layer is comprised between two spheres of radii r_{1x} and r_{2x}, and its thickness is $h = r_{2x} - r_{1x}$ (Fig. 8). The surface of tension $r = r_0$ divides the film into two parts of volumes V_{1f} and V_{2f}, respectively:

$$V_f = V_{1f} + V_{2f} \tag{75}$$

with thickness h_{1x} and h_{2x} (obviously $h = h_{1x} + h_{2x}$). We will use also the notation

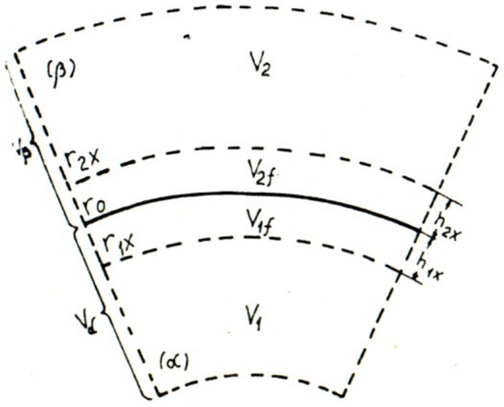

FIG. 8 Sket[illegible] of a spherical thin film as a liquid layer of volume $V_f = V_{1f} + V_{2f}$.

$$V_1 = V_\alpha - V_{1f}, \qquad V_2 = V_\beta - V_{2f} \tag{76}$$

Then, the approach used by Rusanov (1967a) to derive Eqs. (49)-(51), applied to the present case, yields (Kralchevsky and Ivanov, 1984):

$$\delta W_1 = -P_\alpha \delta V_1 - P_R \delta V_{1f} + \sigma_{1x}\,\delta A_{1x} + A_{1x}\left(\frac{\partial \sigma_{1x}}{\partial r_{1x}}\right)^* \delta r_{1x} - \Pi A_0\,\delta r_0 \tag{77}$$

$$\delta W_2 = -P_\beta \delta V_2 - P_R \delta V_{2f} + \sigma_{2x}\,\delta A_{2x} + A_{2x}\left(\frac{\partial \sigma_{2x}}{\partial r_{2x}}\right)^* \delta r_{2x} + \Pi A_0\,\delta r_0 \tag{78}$$

Here Π is the disjoining pressure, defined by Eq. (25); A_{1x} and A_{2x} are the areas of the two film surfaces, whose surface tensions are defined by

$$\sigma_{1x} = \int_{r_\alpha}^{r_0} [P_{\alpha\beta}^{(x)} - P_T(r)]\frac{r^2}{r_{1x}^2}\,dr,$$
$$\sigma_{2x} = \int_{r_0}^{r_\beta} [P_{R\beta}^{(x)} - P_T(r)]\,\frac{r^2}{r_{2x}^2}\,dr \tag{79}$$

Here $P_{\alpha R}^{(x)}$ and $P_{R\beta}^{(x)}$ are given by Eq. (19) with r_{ix} ($i = 1,2$) instead of r_i. Similar to the derivation of Eq. (53) from Eq. (51), one finds from Eq. (79) that

$$\frac{2\sigma_{1x}}{r_{1x}} + \left(\frac{\partial \sigma_{1x}}{\partial r_{1x}}\right)^* = P_\alpha - P_R, \qquad \frac{2\,\sigma_{2x}}{r_{2x}} + \left(\frac{\partial \sigma_{2x}}{\partial r_{2x}}\right)^* = P_R - P_\beta \tag{80}$$

Equations (80) were first derived by Rusanov (1967a,b) in another (thermodynamic) way. Let us substitute P_α and P_β from Eqs. (80) into Eq. (53); the result is

$$\frac{2\gamma_x}{r_x} + \left(\frac{\partial \gamma_x}{\partial r_x}\right)^* = \frac{2\,\sigma_{1x}}{r_{1x}} + \left(\frac{\partial \sigma_{1x}}{\partial r_{1x}}\right)^* + \frac{2\,\sigma_{2x}}{r_{2x}} + \left(\frac{\partial \sigma_{2x}}{\partial r_{2x}}\right)^* \tag{81}$$

On the other hand, one can substitute δW_1 and δW_2 from Eqs. (77) and (78) into Eq. (73); the result must be identical with Eq. (49). Thus one obtains another general expression connecting the same quantities:

$$\left[\frac{\gamma_x}{r_x} - \left(\frac{\partial \gamma_x}{\partial r_x}\right)^*\right] r_x^{\,3} = \left[\frac{\sigma_{1x}}{r_{1x}} - \left(\frac{\partial \sigma_{1x}}{\partial r_{1x}}\right)^*\right] r_{1x}^{\,3} + \left[\frac{\sigma_{2x}}{r_{2x}} - \left(\frac{\partial \sigma_{2x}}{\partial r_{2x}}\right)^*\right] r_{2x}^{\,3} \tag{82}$$

Below, these relations are applied to some special definitions of the dividing surfaces.

Surfaces of tension: The surfaces of tension are defined through Eqs. (17) and (18). In this case Eqs. (26) hold and their comparison with Eqs. (80) yield

$$\left(\frac{\partial \sigma_{1x}}{\partial r_{1x}}\right)^*_{r_{1x}=r_1} = \Pi\,\frac{r_0^2}{r_1^2}\,; \qquad \left(\frac{\partial \sigma_{2x}}{\partial r_{2x}}\right)^* = -\Pi\,\frac{r_0^2}{r_2^2} \tag{83}$$

If one substitutes the formal derivatives from Eqs. (54) and (83) into Eqs. (81) and (82), one will recover Eqs. (33) and (35).

The fact that the formal derivatives in Eqs. (83) are not zero, means that the surfaces of tension in the detailed approach [unlike the membrane approach; cf. Eqs. (83) and (54)] are in general different from the respective surfaces of minimum surface tensions. During the formal differentiation r_0 must be treated as a constant so that both Eqs. (83) lead to (note that $h_{1x} = r_0 - r_{1x}$ and $h_{2x} = r_{2x} - r_0$)

$$\left(\frac{\partial \sigma_{ix}}{\partial h_{ix}}\right)^*_{h_{ix}=h_i} = -\,\Pi\,\frac{r_0^2}{r_i^2}, \qquad i = 1,2 \tag{84}$$

The last equation is a generalization of the well-known equation

$$\left(\frac{\partial \sigma}{\partial (h/2)}\right)^* = -\,\Pi \tag{85}$$

which holds for plane-parallel films (Ivanov and Toshev, 1975); cf. also Eq. (96) of Chapter 1 in this book. If the reference phase is chosen to be the bulk liquid from which the film has been formed, in the limiting case of a thick film we have $\Pi = 0$ and Eqs. (83) transform into the usual relation for the surface of tension of a spherical drop (see, e.g., Ono and Kondo, 1960; or Rusanov, 1967a).

For the surface of tension, Eq. (73), along with Eqs. (77) and (78), leads to

$$\delta W = -P_\alpha \delta V_1 - P_\beta \delta V_2 - P_R\,\delta V_f + \sigma_1 \delta A_1 + \sigma_2 \delta A_2 - \Pi A_0\,\delta h \tag{86}$$

where Eqs. (83) were also used. A similar expression for the mechanical work was obtained in Rusanov's (1967a) thermodynamics of thin films.

Surfaces of minimum tension: Let us define the four quantities σ_{1x}, r_{1x}, σ_{2x}, and r_{2x} by means of the two equations (79) and the two equations

$$\left(\frac{\partial\sigma_{1x}}{\partial r_{1x}}\right)^* = 0, \qquad \left(\frac{\partial\sigma_{2x}}{\partial r_{2x}}\right)^* = 0 \tag{87}$$

Equations (87) mean that the dividing surfaces thus defined have minimum (more precisely, extremum) surface tensions with respect to a displacement of the dividing surfaces at given physical state and reference pressure. That is why the quantities referring to these two surfaces will be denoted by a subscript m: σ_{1m}, r_{1m}, σ_{2m}, r_{2m}. The comparison of Eqs. (87) and Eqs. (83) shows again that the surfaces of tension differ from the surfaces of minimum tension when a thin film is concerned.

If one replaces the formal derivatives in Eqs. (80)-(82) from Eqs. (54) and (87), one obtains

$$\frac{2\sigma_{1m}}{r_{1m}} = P_\alpha - P_R, \qquad \frac{2\,\sigma_{2m}}{r_{2m}} = P_R - P_\beta \tag{88}$$

$$\frac{\gamma}{r_0} = \frac{\sigma_{1m}}{r_{1m}} + \frac{\sigma_{2m}}{r_{2m}}, \qquad \gamma r_0^2 = \sigma_{1m}r_{1m}^2 + \sigma_{2m}r_{2m}^2 \tag{89}$$

These equations were first derived by Rusanov (1967a) for the special case $P_R = P_\gamma$ (P_γ is the isotropic pressure in the bulk liquid that is in equilibrium with the thin film).

The comparison of Eqs. (88) and (89) with the respective equations for the surface of tension [Eqs. (26), (33), and (35)] shows that the definitions (87) lead to the elimination of the disjoining pressure terms. This does not mean, however, that the disjoining pressure Π is zero, or that Π is eliminated from all hydrostatic equations: For example, the term $\Pi A_0\,\delta r_0$ remains in Eqs. (77) and (78). From Eqs. (80) and (88) it follows that

$$\left(\frac{\partial\sigma_{ix}}{\partial r_{ix}}\right)^* + \frac{2\,\sigma_{ix}}{r_{ix}} = \frac{2\sigma_{im}}{r_{im}}, \qquad i = 1,2 \tag{90}$$

In dimensionless variables

$$x = \frac{r_{ix}}{r_{im}}, \qquad y = \frac{\sigma_{ix}}{\sigma_{im}}$$

Eqs. (90) reduce to the known equation (56), whose solution [with the boundary condition y(1) = 1] is again Eq. (57), or alternatively

$$\sigma_{ix} = \sigma_{im}\left[\frac{1}{3}\,\frac{r_{im}^2}{r_{ix}^2} + \frac{2}{3}\,\frac{r_{ix}}{r_{im}}\right], \quad \sigma_{im} \neq 0;\ i = 1,2 \tag{91}$$

Equation (91), which is plotted in Fig. 9, has the same form as the equation of Kondo (1956) for the surface of a spherical drop. One can calculate from Eq. (91) the second derivative

$$\left(\frac{\partial^2\sigma_{ix}}{\partial r_{ix}^2}\right)^* = \frac{2\sigma_{im}r_{im}^2}{r_{ix}^4}, \qquad i = 1,2$$

For $\sigma_{im} > 0$ this derivative is positive and the curve $\sigma_{ix}(r_{ix})$ has a minimum at $r_{ix} = r_{im}$; for $\sigma_{im} < 0$ (such a case seems to be possible for lipid bilayers) the function $\sigma_{ix}(r_{ix})$ has a maximum at $r_{ix} = r_{im}$. Note however, that the plot in Fig. 9 includes both cases, because the ratio σ_{ix}/σ_{im} is always positive. One seems from Fig. 9 that the curve $\sigma_{ix}(r_{ix})$ does not cross the axis of the abscissa, which means that one cannot change the sign of the surface tension σ_{ix} by mere displacement of the dividing surfaces.

An analogue to Eq. (91), in which σ_{im} and r_{im} are replaced by the respective quantities σ_i and r_i referring to the surfaces of tension, $r = r_i$ ($i = 1,2$) can also be derived (Kralchevsky and Ivanov, 1984):

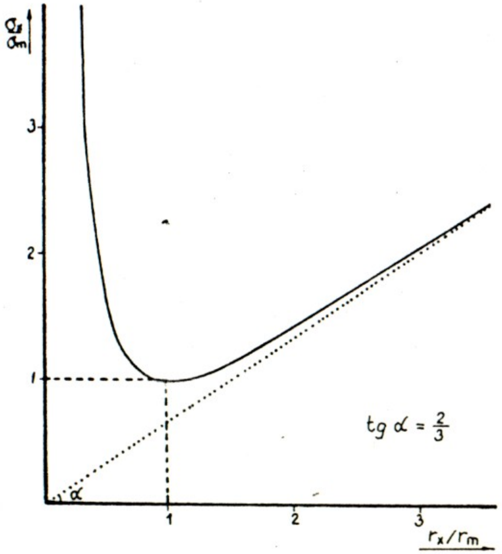

FIG. 9 Dependence of the surface tension of a spherical film on the location of dividing surface at fixed physical state.

$$\sigma_{ix} = \frac{\sigma_i}{3}\left[\frac{r_i^2}{r_{ix}^2} + 2\,\frac{r_{ix}}{r_i}\right] - (-1)^i\,\Pi\,\frac{r_0^2}{r_i^2}\left(1 - \frac{r_i^3}{r_{ix}^3}\right), \quad i = 1,2 \tag{92}$$

If one first differentiates Eq. (92) with respect to r_{ix}, and then substitutes $r_{ix} = r_{im}$, one gets

$$\left(1 - \frac{r_i^3}{r_{im}^3}\right)\frac{\sigma_i}{r_i} = (-1)^i\,\Pi\frac{r_0^2}{r_i^2}\left(\frac{1}{2} + \frac{r_i^3}{r_{im}^3}\right), \qquad i = 1,2 \tag{93}$$

Let us now consider the limiting transitions (1) from a thin spherical film to a thick spherical film, and (2) from a thin spherical film to a plane-parallel film. For the sake of simplicity let us choose, following Rusanov (1967a), $P_R = P_\gamma$. Then for the limiting transition (1), $\Pi \to 0$ and one sees from Eq. (93) that $r_{im} \to r_i$; this was to be expected, because the surface of minimum tension coincides with the surface of tension for a spherical drop.

When one deals with surfaces of tension the limiting transition (2), more precisely $r_i \to \infty$ at finite h_i ($i = 1,2$), leads to correct results (see Section I.C for details). However, when one deals with surfaces of minimum tension this limiting transition is impossible. Indeed, if one takes the limit $r_{im} \to \infty$ in Eqs. (88) with $R_R = P_\gamma$, the result will be $\sigma_{im} \to \infty$, because the differences $P_\alpha - P_\gamma$ and $P_\beta - P_\gamma$ are not equal to zero for plane-parallel films. This is due to the fact, pointed out by Rusanov (1966, 1967a), that the plane-parallel films have no surfaces of minimum tension.

Hybrid Case: The only choice of the reference pressure, for which the surfaces of tension and of minimum tension coincide, is $P_R = P_N(r_0)$. In this case, as a result of Eq. (25) Π is identically zero. It follows then from Eq. (93) that $r_i = r_{im}$ and Eq. (91) (with $r_{ix} = r_i$) yields $\sigma_i = \sigma_{im}$. In this case the limiting transition to a plane-parallel film is possible and leads to the equations for a flat film with reference pressure $P_R = P_N$; for example, one obtains $\gamma = \sigma_1 + \sigma_2$, where γ is the film tension of the flat film. Such an approach for flat films was developed by Eriksson and Toshev (1982).

In the hybrid case, i.e., with $P_R = P_N(r_0)$, all equations derived above for the surface of minimum tension remain valid and all equations for the surface of tension hold with $\Pi = 0$. In particular, Eqs. (83) and (87) coincide.

The shortcoming of the hybrid case is that, due to the special choice of the reference pressure the theory cannot be extended to dynamic systems, when there is fluid flow inside the thin film.

II. THERMODYNAMICS OF CURVED THIN FILMS

A. Basic Principles

The thin liquid film is a nonautonomous syst It is always a part of a larger thermodynamic system, and the processes in the film are governed by the processes occurring in the whole system. This fact implies that the study of the thermodynamic properties of the film should be carried out by accounting for the conditions for thermodynamic equilibrium in the whole system. A powerful method for solving this problem is the thermodynamic approach of Gibbs (1906), extended recently by Boruvka and Neumann (1977). In the framework of this method the system is considered as a set of bulk, surface, line, and (even) point phases, being in full or partial thermodynamic equilibrium.

For example, let us consider a small drop or bubble, phase α, floating on the interface between the bulk phases β and γ (see Fig. 10). We suppose that a curved thin film intervenes between the phases α and β. In the Gibbs approach this system must be considered as being composed of three bulk phases (α, β, and γ), of several surface phases (e.g., the interfaces α/β, β/γ, and α/γ), and of several line phases (e.g., the intersection line of the three interfaces enumerated above). The logical scheme of the Gibbs' approach is the following.

1. The situation of all phases and phase boundaries irrespective of their shape (the topology of the system) is believed to be known. Besides, the total amounts of all extensive parameters (internal energy V, entropy S, number of molecules N_i of the ith component, etc.) and their densities in all phases far away from the phase boundaries are regarded in principle as being known.
2. One constructs mentally an idealized system, in which all the phases (bulk, surface, or linear) are considered as being

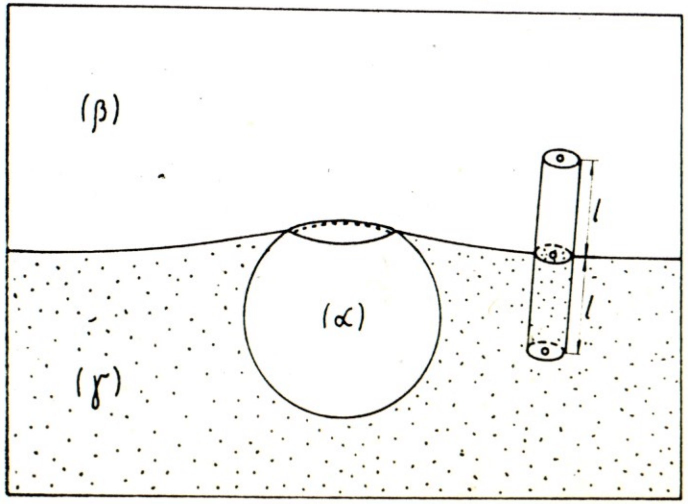

FIG. 10 An illustrative three-phase system consisting of bulk, surface, and linear ases. The schematic cylinder is used when defining surface excess quantities (see the text).

homogeneous, the transition regions between the phases in the real system are replaced by sharp boundaries, and the resulting excesses of the extensive parameters in the idealized system with respect to the real one are ascribed to these boundaries.

This procedure is illustrated in Fig. 10 for the interface β/γ. Two cylinders of macroscopic height ℓ are built on both sides of a surface element of area ΔA, which is situated far enough from the boundaries of the interface. If ΔN_i is the number of molecules of the ith component, enclosed in this cylinder, the excess of molecules ascribed to the interface in question will be

$$N_i^s = [\Delta N_i - (n_i^\beta - n_i^\gamma)\ell\,\Delta A]A/\Delta A, \qquad i = 1,2,\ldots,k$$

where n_i^β and n_i^γ are the bulk densities of the ith component in two neighboring phases, and A is the total area of the interface β/γ. The surface excesses of the internal energy U^s, entropy S^s, and of the other extensive properties can be introduced in an analogous way. The linear excesses U^L, S^L, and N_i^L, $i = 1,2,\ldots$, etc., are similarly defined. Further, if the lines intersect, point excesses can be introduced in their common points (see Boruvka and Neumann, 1977).

3. The next step is to formulate the Gibbs' fundamental equations of the various phases in the idealized system. If the internal energy does not depend on the distance between the phases or on their configuration, one assumes that for a bulk phase (superscript v) $U^v = U^v(S^v,V,N_i^v)$, where V is its volume; for a surface phase of area A there exists another function $U^s = U^s(S^s,A,N_i^s)$; and similarly for a linear phase of length L, one has $U^L = U^L(S^L,L,N_i^L)$. Then it follows that

$$dU^v = T^v\,dS^v - P\,dV + \sum_{i=1}^{k} \mu_i^v\,dN_i^v \tag{94}$$

$$dU^s = T^s\,dS^s + \sigma\,dA + \sum_{i=1}^{k} \mu_i^s\,dN_i^s \tag{95}$$

$$dU^L = T^L\,dS^L + \kappa\,dL + \sum_{i=1}^{k} \mu_i^L\,dN_i^L \tag{96}$$

where P is the pressure in the (homogeneous) bulk phase, σ is the surface tension of the interface, and κ is the line tension of the linear phase. The symbols T and μ_i (with the respective superscripts) are defined through the corresponding derivatives of the internal energy and have the meaning of temperature and chemical potentials in the phases under consideration. Note that both the temperatures, T^v, T^s, and T^L, and the chemical potentials μ_i^v, μ and μ_i^L, could in principle take different values in the different phases.

When the surface or linear phases are not defined as surfaces or lines of tension, additional terms [of the kind of the last term in Eq. (50)] appear in the fundamental equations (see the works of Ono and Kondo, 1960; Ivanov et al., 1978; Toshev and Ivanov, 1973/1974; Navascues and Tarazona, 1981). In the detailed approach the fundamental equations of the film surfaces and their boundary lines contain also a term, proportional to the differential of the film thickness dh [cf. Eqs. (134) and (135) below].

By definition dU^v, dU^s, and dU^L are total differentials and therefore a series of Maxwell's relations results from Eqs. (94)-(96). The total internal energy of the whole system, and hence its fundamental equation, is found by summing up the internal energies of all phases (bulk, surface, or linear) from which the system is built up.

The fundamental equations can be valid for not only reversible, but also for some sufficiently slow, irreversible processes.

4. The next step is to impose the general condition for the whole system to be in thermodynamic equilibrium. According to Gibbs this is tantamount to require that the appropriate thermodynamic potential of the system has a minimum value (see, e.g., Section II.C). A variety of special conditions for equilibrium follows from this general principle. The subject is examined in detail by many authors (see, e.g., Kirkwood and Oppenheim, 1961), so that we will consider here only a few special features of the capillary systems and thin films.

In a capillary system, there are usually no barriers preventing the heat transfer and because of that the condition for thermal equilibrium is trivial: $T^v = T^s = T^L = T = \text{const}$ throughout the system.

The conditions for chemical (diffusive) equilibrium could be more complicated and the equalities $\mu_i^v = \mu_i^s = \mu_i^L = \mu_i$, $i = 1,2,\ldots,k$, are not always fulfilled for the whole system. For example, the boundary between two phases could be nonpermeable for some species and their chemical potentials could in general take different values in two phases. As suggested by Gibbs (1906), in such cases these species must be treated as different components in the two phases.

The conditions for mechanical equilibria are multiform due to the variety in the geometric configurations of the capillary systems. For example, the well-known Laplace equation

$$-2H\sigma = P_c \tag{97}$$

(H is the mean curvature and P_c is the capillary pressure) expresses the mechanical equilibrium in each point of the surface of tension. Due to the connection between H and the shape of the surface, Eq. (97) is a second-order differential equation, whose solution yields the equation of the surface of tension. Another example is the Neumann-Young equation, which expresses the condition for mechanical equilibrium in each point of a three-phase contact line. In fact, the Neumann-Young equation erves as a boundary condition for the solution of the Laplace equatio Eq. (97)]. In other words, the conditions for mechanical equilibrium determine the shape of the interfaces and the angles at which they intersect (the so-called contact angles).

From another point of view the role of the conditions for thermodynamic equilibrium is the following. The number of the thermodynamic degrees of freedom of the whole system is usually less than the number of the differentials in the right-hand sides of the fundamental equations (94)-(96). Depending on the real process in the system, the conditions for equilibrium provide connections between these differentials, thus ensuring the correct number of degrees of freedom.

In Section II.B the fundamental equations of a curved film and its boundary lines are considered and some corollaries are examined. Section II.C is devoted to the equilibrium between the film and the surrounding phases. A local formulation of the capillary thermodynamics, which is of importance for films with high curvature, is presented in Section II.D.

B. Fundamental Equations

Both the membrane and the detailed approaches already used in the hydrostatics of thin films (see Section I) will be now extended to the thin film thermodynamics. In the membrane approach the film is treated merely as a surface phase. In the detailed approach the film is considered as consisting of one bulk phase (the interior of the film) and of the two surface phases (the film surfaces). Each approach requires respective description of the transition region at the film periphery: In the membrane approach the film is bound by a single contact line, but two contact lines (one for each surface) are needed in the detailed approach. The fundamental equations of these surface or line phases are discussed below.

The Film as a Single Surface Phase (The Membrane Approach).

The fundamental equation of the film in this case, written for the surface of tension, is

$$dU^f = T^f\,dS^f + \gamma\,dA_0 + \sum_{i=1}^{k} \mu_i^f\,dN_i^f \qquad (98)$$

where A_0 is the area of the surface of tension; γ is the film tension; U^f, S^f, and N_i^f ($i = 1,\dots,k$) are the Gibbs excesses of the internal energy, the entropy, and the number of molecules, ascribed to the film; and T^f and μ_i^f are the temperature and the chemical potentials of the film. The comparison with Eq. (95) shows that Eq. (98) has the usual form of a fundamental equation of a surface phase. A similar fundamental equation was used by Martynov and Derjaguin (1962) and Derjaguin et al. (1965) in their treatment of flat films. The differentials in the right-hand side of Eq. (98) are increments of the respective parameters when a thermodynamic process takes place in the system. It is often more convenient to work with the grand potential $\Omega^f = U^f - S^fT^f - \sum_i \mu_i^f N_i^f$, instead of with the internal energy. It follows from Eq. (98) that

$$d\Omega^f = -S^f\,dT^f + \gamma\,dA_0 - \sum_{i=1}^{k} N_i^f\,d\mu_i^f \qquad (99)$$

Equations (98) and (99) can be applied for the film as a whole as well as for each macroscopic part of the film. This is due to the fact that the film is considered as being a homogeneous surface phase. Let us apply Eq. (99) to a small but macroscopic part of the film. If the remaining part of the film and the surrounding phases are large, they serve as heat and matter reservoirs and the stretching of the film can be carried out at constant T^f and μ_i^f, i.e., at constant physical state. Then γ is also constant, so that Eq. (99) can be integrated to yield

$$\Omega^f = \gamma A_0 \qquad (100)$$

and

$$U^f = TS^f + \gamma A_0 + \sum_{i=1}^{k} \mu_i^f N_i^f \qquad (101)$$

Equation (100) means that the film tension equals the grand potential per unit area of the film, just as the grand potential per unit volume of a homogeneous bulk phase equals the negative pressure (see, e.g., Rusanov, 1967a). Under these conditions (constant temperature and all chemical potentials) the work γdA_0 for increasing the film area by dA_0 coincides with the work $d\Omega^f$ for creating the same new area, so that the differentials in Eq. (98) have also the meaning of internal energy dU^f, entropy dS^f, and amount of molecules dN_i^f that must be added to the considered part of the film to increase its area by dA_0. By substitution of Eq. (100) in the left-hand side of Eq. (99) one obtains the Gibbs-Duhem equation for the film:

$$d\gamma = -s^f dT^f - \sum_{i=1}^{k} \Gamma_i d\mu_i^f \qquad (102)$$

with

$$s^f = \frac{S^f}{A_0}, \qquad \Gamma_i = \frac{N_i^f}{A_0}, \qquad i = 1,2,\dots,k$$

It is important to note that all differentials in the right-hand side of Eq. (102) are independent, because the dividing surface has been already chosen (as the surface of tension). Because the considered part of the film was arbitrarily chosen, Eq. (102) holds in each point of the film.

The validity of Eq. (102) is subject to some limitations.

1. If the remaining part of the film and the surrounding phases cannot serve as reservoirs of matter and head, Equation (100) [and hence Eqs. (101) and (102)] cannot be derived for whatever part of the film. (Such is the case when the film is closed, small, and insoluble in the adjacent phases (see, e.g., Eriksson, 1971, 1981).

2. If the work performed against shearing stresses in the film substance is not negligible, the work for deformation of the film is no longer equivalent to the work for creating the same new area at constant physical state. Therefore, the integration, which leads to Eq. (100), cannot be performed and Eq. (102) cannot be deduced. This is the case of solid surfaces and biomembranes (see Shuttleworth, 1950; Herring, 1951; Benson and Yun, 1967; Eriksson, 1969; Rusanov, 1977, 1978; Evans and Skalak, 1980). We restrict our considerations below only with the cases when Eq. (102) is valid.

If the film is in thermal and chemical equilibrium with the surrounding phases

$$T^f = T^\alpha = T^\beta = T^\gamma = \cdots = T$$
$$\mu_i^f = \mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \cdots = \mu_i, \qquad i = 1,2,\ldots,k \tag{103}$$

For the density of the internal energy, $u^f = U^f/A_0$, one has from Eqs. (101) and (103):

$$u^f = Ts^f + \gamma + \sum_{i=1}^{k} \mu_i \Gamma_i \tag{104}$$

Then one finds from Eqs. (102)-(104) that

$$du^f = Tds^f + \sum_{i=1}^{k} \mu_i \, d\Gamma_i \tag{105}$$

The specific internal energy of the film, u^f, can be changed according to Eq. (105), by using heat or changing the adsorption. It does not depend on the stretching of the film, because, as shown above, the newly created area has the same intensive properties (u^f, s^f, Γ_i, etc.) as the one before stretching. We remind the reader that the above results are valid only for the surface of tension and for uniform films. A more general treatment, which will be applied also to the formulation of local film thermodynamics, is presented in Section II.D.

When the conditions (103) are fulfilled, following Gibbs (1906) one can eliminate one or more chemical potentials between the Gibbs-Duhem equation of the film [Eq. (102)] and the Gibbs-Duhem equations of the other (bulk) phases:

$$dP_\chi = S_v^\chi \, dT + \sum_{i=1}^{k} n_i^\chi \, d\mu_i, \qquad \chi = \alpha, \beta, \gamma, \cdots \tag{106}$$

Here S_v is the bulk density of the entropy and n_i is the numerical bulk density of the ith component. If the phases are situated as shown in Fig. 10, the pressure drop across the film is $P_c = P_\alpha - P_\beta$ and from Eq. (106) one obtains

$$dP_c = (S_v^\alpha - S_v^\beta)\, dT + \sum_{i=1}^{k} (n_i^\alpha - n_i^\beta)\, d\mu_i \tag{107}$$

Then the elimination of $d\mu_1$ between Eqs. (102) and (107), and also keeping in mind Eqs. (103), yields (Gibbs, 1906):

$$d\gamma = -[s^f - (s_v^\alpha - s_v^\beta)H_1]\, dT - H_1\, dP_c$$
$$- \sum_{i=\cancel{1}2}^{k} [\Gamma_i - (n_i^\alpha - n_i^\beta)H_1]\, d\mu_i \tag{108}$$

with

$$H_1 = \frac{\Gamma_1}{n_1^\alpha - n_1^\beta} \tag{109}$$

According to Gibbs the quantity H_1 can be interpreted as the distance between the surface of tension and the dividing surface, for which the adsorption of component 1 is zero. For flat films or interfaces $P_c = 0$. Therefore, the term proportional to dP_c in Eq. (108) accounts for the additional degree of freedom of the spherical film (its curvature).

In a similar way, two differentials, say $d\mu_1$ and $d\mu_2$, can be eliminated between Eqs. (102) and (106) [cf. also Eqs. (103)]. If $d\mu_1$ is expressed from Eq. (106) (applied to the phase α) and $d\mu_2$ is expressed from Eq. (106), applied to the phase γ, the result is (Rusanov, 1983)

$$d\gamma = -\bar{s}\, dT + \bar{h}_\alpha\, dP_{c1} - \bar{h}_\beta\, dP_{c2} - \sum_{i=3}^{k} \bar{\Gamma}_i\, d\mu_i \tag{110}$$

where

$$P_{c1} = P_\alpha - P_\gamma, \qquad P_{c2} = P_\gamma - P_\beta$$

and

$$\bar{h}_\alpha = [(n_1^\beta - n_1^\gamma)\Gamma_2 - (n_2^\beta - n_2^\gamma)\Gamma_1]/\Delta$$
$$\bar{h}_\beta = [(n_2^\alpha - n_2^\gamma)\Gamma_1 - (n_1^\alpha - n_1^\gamma)\Gamma_2]/\Delta \tag{111}$$

$$\Delta = (n_1^{\alpha} - n_1^{\gamma})(n_2^{\beta} - n_2^{\gamma}) - (n_1^{\beta} - n_1^{\gamma})(n_2^{\alpha} - n_2^{\gamma})$$

$$\bar{s} = s^f + (s_v^{\alpha} - s_v^{\gamma})\bar{h}_{\alpha} + (s_v^{\beta} - s_v^{\gamma})\bar{h}_{\beta} \tag{112}$$

$$\bar{\Gamma}_i = \Gamma_i + (n_i^{\alpha} - n_i^{\gamma})\bar{h}_{\alpha} + (n_i^{\beta} - n_i^{\gamma})\bar{h}_{\beta}, \qquad i = 3,\ldots,k \tag{113}$$

The quantities $\bar{h}_{\alpha}$ and $\bar{h}_{\beta}$ have dimension of length. Their physical meaning can be elucidated in the same way as it was done for flat films by Toshev and Ivanov (1975), de Feijter et al. (1978), and Rusanov (1983). Imagine two equidistant surfaces, parallel to the surface of tension of the film. The latter divides the space between them into two parts of volumes V_{1f} and V_{2f}. The layer of volume $V_{1f} + V_{2f}$ is thought to be filled in with the bulk reference phase (γ). For this model liquid layer, one can derive the following equation (Rusanov, 1983):

$$d\gamma = -\tilde{s}\, dT + h_{\alpha}\, dP_{c1} - h_{\beta}\, dP_{c2} - \sum_{i=1}^{k} \tilde{\Gamma}_i\, d\mu_i \tag{114}$$

where

$$h_{\alpha} = \frac{V_{1f}}{A_0}, \qquad h_{\beta} = \frac{V_{2f}}{A_0} \tag{115}$$

$$\tilde{s} = s^f + (s_v^{\alpha} - s_v^{\gamma})h_{\alpha} + (s_v^{\beta} - s_v^{\gamma})h_{\beta} \tag{116}$$

$$\tilde{\Gamma} = \Gamma_i + (n_i^{\alpha} - n_i^{\gamma})h_{\alpha} + (n_i^{\beta} - n_i^{\gamma})h_{\beta}, \qquad i = 1,\ldots,k \tag{117}$$

Equation (114) can be obtained quite formally: Toward this aim the expressions for dP_{c1} and dP_{c2}, analogous to Eq. (107), must be multiplied by h_{α} and $-h_{\beta}$, respectively, and then the resulting equations msut be subtracted from Eq. (102). A comparison of Eq. (114) with Eq. (110) shows that there are two additional differentials in the right-hand side of Eq. (114). They correspond to the two supplementary formal degrees of freedom connected with the choice of the two parameters h_{α} and h_{β}. That is why one needs two additional equations for determination of h_{α} and h_{β}. For example, let these equations be

$$\tilde{\Gamma}_1 = 0, \qquad \tilde{\Gamma}_2 = 0 \tag{118}$$

In view of Eq. (117), for i = 1,2, Eqs. (118) compose a set of two linear equations whose solution is $h_{\alpha} = \bar{h}_{\alpha}$, $h_{\beta} = \bar{h}_{\beta}$ [cf. Eq. (111)]. In other words the quantities $\bar{h}_{\alpha}$ and $\bar{h}_{\beta}$ in Eq. (110) are defined in such a way that the sum $\bar{h}_{\alpha} + \bar{h}_{\beta}$ equals the thickness of a liquid layer from the reference phase containing the same amount of the components 1 and 2 as the real film. This thickness is called thermodynamic thickness of the film (Ivanov and Toshev, 1975), and it would be of the order of the real thickness of the film, if the compo[illegible]ts 1 and 2 are chosen in an appropriate way.

The approach with two dividing surfaces can lead to different forms of the Gibbs-Duhem equation when, instead of Eqs. (118), other conditions are used. Note that in this heuristic approach the dividing surfaces are not treated as surface phases with their own Gibbs fundamental equations. Such equations will be introduced in the detailed approach, which is considered at the end of this section.

Dependence of the Film Tension on the Capillary Pressure.

The Gibbs-Duhem equation of a curved film [in its different forms (102), (108), or (110)] can be used for studying the variations of the film tension γ during different thermodynamic processes. The dependence of γ on the temperature and the composition of the system is investigated in the same way as for flat films [see Rusanov (1967a) and Chapter 1 of this book]. We will study here the dependence of γ on the curvature, because this effect is specific for curved films. It is tantamount to study the dependence of γ on the capillary pressure, $P_c = 2\gamma/r_0$, which is due to the curvature.

From Eqs. (108) and (109) one finds that

$$\left(\frac{\partial\gamma}{\partial P_c}\right)_{T,\mu_2,\ldots,\mu_k} = -\frac{\Gamma_1}{n_1^{\alpha} - n_1^{\beta}} \tag{119}$$

In a similar way, from Eq. (110) it follows (Rusanov, 1983):

$$\left(\frac{\partial\gamma}{\partial P_{c1}}\right)_{T,P_{c2},\mu_3,\ldots,\mu_k} = \left(\frac{\partial\gamma}{\partial P_c}\right)_{T,P_{c2},\mu_3,\ldots,\mu_k} = \bar{h}_{\alpha} \tag{120}$$

$$\left(\frac{\partial\gamma}{\partial P_{c2}}\right)_{T,P_{c1},\mu_3,\ldots,\mu_k} = \left(\frac{\partial\gamma}{\partial P_c}\right)_{T,P_{c1},\mu_3,\ldots,\mu_k} = -\bar{h}_{\beta} \tag{121}$$

$$\left(\frac{\partial\gamma}{\partial P_{c1}}\right)_{T,P_c,\mu_3,\ldots,\mu_k} = -\left(\frac{\partial\gamma}{\partial P_{c2}}\right)_{T,P_c,\mu_3,\ldots,\mu_k} = \bar{h}_{\alpha} + \bar{h}_{\beta} \tag{122}$$

where the relationship

$$P_c = P_{c1} + P_{c2} \tag{123}$$

was used. Depending on the real process under consideration, the effect of the curvature on the film tension can be more or less pronounced. As an example we will consider a system that is met very often in applications: a thin film formed from the liquid of phase γ, between two drops or bubbles, phases α and β (see Fig. 11). We will study how the film tension γ depends on the pressure in phase α. If phase β is infinitely large, the configuration of the system becomes the same as in Fig. 10. We will consider several possibilities.

The film and the bulk phase γ are in equilibrium: Let us assume that in phas[illegible] there is at least one component that is nonsoluble in phase γ, an[illegible]ence in the film. (In other words the independent

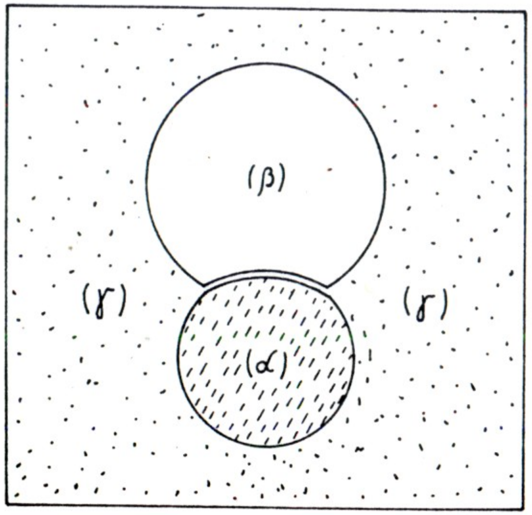

FIG. 11 A thin film formed from the liquid from the phase (γ) between two fluid particles, phases α and β.

equilibrium variation of P_α is not possible, because the value of P_α is fixed by the state in phase γ.) Let this be component 1. For example, if α and β are two attached oil drops in a water solution, one can choose the oil in phase α as component 1 (if the same substance is contained in phase β, according to Gibbs (1906) it should be considered as a separate component, because the two drops are not in diffusive equilibrium due to the nonpermeability of the film). In other words, we assume that

$$n_1^{\beta} = n_1^{\gamma} = 0 \tag{124}$$

Then from Eq. (119) one finds

$$\left(\frac{\partial\gamma}{\partial P_c}\right)_{T,\,\mu_2,\ldots,\mu_k} = -\,\frac{\Gamma_1}{n_1^{\alpha}} \tag{125}$$

If one imagines an assembly of doublets (like that in Fig. 11) with different drop size, then Eq. (125) describes the variation of the film tension due to the variation in the size of the different members of this assembly.

Let h^r be the real thickness of the film. The surface of tension of the film divides h^r into two parts, which we denote by $h_\alpha{}^r$ and $h_\beta{}^r$. In the membrane model the lower part of the film (with thickness $h_\alpha{}^r$), which does not contain component 1, is replaced by a layer from the bulk phase α, in which the density of component 1 is $n_1{}^\alpha \neq 0$. Then having Eq. (124) in mind it is not difficult to realize that the excess amount of component 1 ascribed to the membrane is $N_1{}^f = -n_1{}^\alpha h_\alpha{}^r A_0$ and hence $\Gamma_1 = -n_1{}^\alpha h_\alpha{}^r$. Then Eq. (125) takes the form

$$\left(\frac{\partial\gamma}{\partial P_c}\right)_{T,\,\mu_2,\ldots,\mu_k} = h_\alpha{}^r \tag{126}$$

Usually $h_\alpha{}^r$ is of the order of several nanometers. Hence the dependence of γ on P_c expressed through Eq. (126) can become important only for very small drops, when the radius of curvature of the film and its thickness are of the same order of magnitude. For drops α of larger size the film tension γ should be practically independent on P_α.

The film and the bulk phase γ are not in diffusive equilibrium: The size and the pressure of phase α (see Fig. 11) can change due to diffusion of some components through the boundaries of this phase. If the diffusive process is very slow, the phases α, β, and γ and the film can be considered as homogeneous bulk or surface phases at every moment. Then the Gibbs-Duhem equation of the film, Eq. (102), holds. For example, such a system could consist of two attached gas bubbles α and β, when the gas diffuses through the film from the smaller to the larger bubble. Another example are two attached liquid droplets or cells, which interchange some components through the film intervening between them. For an isothermal process Eq. (102) yields

$$\left(\frac{\partial\gamma}{\partial P_c}\right)_T = -\sum_{i=1}^{k} \Gamma_i \left(\frac{\partial\mu_i{}^f}{\partial P_c}\right)_T \tag{127}$$

The specificity of the process determines how the chemical potentials $\mu_i{}^f$ (i = 1,...,k) depend on P_c and which parameters should be kept constant when carrying out the differentiation with respect to P_c. The expression

$$\mu_i{}^f = \frac{1}{2}\,(\,\mu_i{}^\alpha + \mu_i{}^\beta) \tag{128}$$

may serve as a realistic approximation for the chemical potentials, $\mu_i{}^f$, of the diffusing components. Note that Eq. (128) reduces the derivatives $(\partial\mu_i{}^f/\partial P_c)_T$ in Eq. (127) to the respective derivatives in the bulk phases α and β.

Let us consider as an illustration the case, when phase α is a small bubble, phase β is infinitely large (see Fig. 10), and phase γ is a water solution of a surfactant. Due to the gas diffusion through the film such a bubble slowly and smoothly decreases its size up to the disappearance of the bubble. Similar systems have been studied by Princen and Mason (1965), Nikolov et al. (1986a,b), and others. The thorough analysis of the experimental data is impossible without a detailed examination of all transport processes in the system. Nevertheless, a physical insight can be gained by assuming that the path of the real process is along the trajectory of the faster decrease of the free energy. In this way and by means of some simplifications one can show that the bubble should diminish its radius at constant composition of the gas mixture inside it, i.e.,

$$x_i^\alpha = N_i^\alpha/(N_1^\alpha + N_2^\alpha) = \text{const}, \qquad i = 1,2 \tag{129}$$

where subscripts 1 and 2 refer to the gas and water vapor, respectively. Then, the equation for the chemical potentials of an ideal gas yields

$$d\,\mu_i^\alpha = kT\ d(\ln x_i^\alpha P_\alpha) = kT\ d(\ln P_\alpha), \qquad i = 1,2 \tag{130}$$

Also, for the process under consideration $d\,\mu_1^\beta = d\,\mu_2^\beta = 0$. For the sake of simplicity, let us assume that the remaining chemical potentials of the components of film, $\mu_3^f, \ldots, \mu_k^f$, do not change during that process. Then from Eqs. (127), (128), and (130) one obtains

$$\left(\frac{\partial\gamma}{\partial P_c}\right)_{T,\mu_3^f,\ldots,\mu_k^f} = -(\Gamma_1 + \Gamma_2)\,\frac{kT}{P_\beta + P_c} \tag{131}$$

Usually $\Gamma_1 \ll \Gamma_2$ and $P_c \ll P_\beta$, so that Eq. (131) acquires the following approximate form:

$$\left(\frac{\partial\gamma}{\partial P_c}\right)_{T,\mu_3^f,\ldots,\mu_k^f} = -\frac{n_2^f}{n^\beta}\,h_\alpha^r \tag{132}$$

where $n_2^f = \Gamma_2/h_\alpha^r$ is the mean density of component 2 (the water) in the film, and $n^\beta = P_\beta/kT$ is the mean density of the gas phase β. The comparison between Eqs. (126) and (132) show that the dependence of γ on P_c for shrinking bubbles should be considerably stronger than it is for equilibrium doublets of attached droplets. This is due to the factor $n_2^f/n^\beta \gg 1$ in the right-hand side of Eq. (132). It is possible that such factors appear in other cases as well, e.g., for attached droplets out of diffusive equilibrium.

However simplified the analysis of the above illustrative examples might be, it still shows that γ could depend on P_c in quite different ways, and that when interpreting the experimental data one should apply the Gibbs-Duhem equation of the film by taking care of the most important features of the real process.

Fundamental Equations in the Detailed Approach.

In the membrane approach the fundamental equation of a thin film (a couple of interfaces) is the same as the fundamental equation of a single interface [see Eq. (98) above]. The specific character of the thin film can be manifested by means of the detailed approach, when the film is considered as consisting of two surface phases and a [illegible] liquid layer between them. However, this thermodynamical extension of the detailed approach is not only more complicated than the membrane model, but it also contains some parameters connected with the separate film surfaces, which as a rule are not amenable to direct experimental determination. That is why this approach has been applied mostly for deriving the condition for mechanical equilibrium (Rusanov, 1967a; Kralchevsky and Ivanov, 1985a) rather than as a thermodynamic alternative of the membrane approach, presented above.

Let us introduce two equidistant dividing surfaces that are parallel to the surface of tension of a curved film. The surface of tension divides the space between these dividing surfaces into two layers of thicknesses h_1 and h_2. The whole layer, of thickness

$$h = h_1 + h_2 \tag{133}$$

is thought to be filled with the reference liquid phase γ. The two surfaces of this layer are interpreted as two surface phases. Their fundamental equations can be obtained by supplementing the expressions for the surface mechanical work [see Eqs. (77), (78), and (83)] with a thermal and with chemical terms. Thus, the fundamental equations for the surfaces of a spherical thin film will be

$$dU^{(j)} = T^{(j)}dS^{(j)} + \sum_{i=1}^{k} \mu_i^{(j)}dN_i^{(j)} + \sigma_j^f dA_j - \Pi A_0 dh_j, \qquad j = 1,2 \tag{134}$$

Here the superscript j denote the surfaces of the film, which are chosen to be the surfaces of tension [cf. Eq. (83)]. The quantities $U^{(j)}$, $S^{(j)}$, and $N_i^{(j)}$ ($i = 1,\ldots,k$) are surface excesses of the corresponding extensive properties, which are defined with respect to the bulk phases α and β, and the reference phase γ in the film. If both surfaces of the film are in thermal and chemical equilibrium, from Eqs. (133) and (134) one obtains (Rusanov, 1967a):

$$dU^f = T^f\,dS^f + \sum_{i=1}^{k} \mu_i^f\,dN_i^f + \sigma_1^f\,dA_1 + \sigma_2^f\,dA_2 - \Pi A_0\,dh \tag{135}$$

where

$$U^f = U^{(1)} + U^{(2)}, \qquad S^f = S^{(1)} + S^{(2)}, \qquad N_i^f = N_i^{(1)} + N_i^{(2)}$$

In comparison with Eq. (98) the fundamental equations (134) and (135) contain an additional term, proportional to the film thickness. In other words, two additional degrees of freedom (corresponding to two new parameters, h_1 and h_2) are included by means of Eqs. (134) and therefore two new conditions for equilibrium are needed: One can check that these are Eqs [illegible]26), which connect the disjoining pressure Π with the capillary pres[illegible]e drops across the film surfaces. (For flat films there is one additional parameter, h, and only one new condition for equilibrium, $\Pi = P_\alpha - P_\gamma$, appears.)

The fundamentl equations (134) can serve as starting point for the thermodynamic description of the film, just as it was done in the membrane approach. For example, the Gibbs-Duhem equations for the film surfaces read

$$d\,\sigma_j^{f} = -\frac{S^{(j)}}{A_j}\,dT^{(j)} - \sum_{i=1}^{k}\frac{N_i^{(j)}}{A_j}\,d\,\mu_i^{(j)} - \frac{A_0}{A_j}\,\Pi\,dh_j, \qquad j = 1,2 \tag{136}$$

Such equations are more suitable when making molecular model of the film, rather than when interpreting experimental data; in the latter case the membrane approach is more appropriate.

In the detailed approach the two film surfaces meet the two (extrapolated) surfaces of the liquid meniscus at two contact lines: In Fig. 12 the points where they pierce the plane of the drawing are denoted by C_1 and C_2. These contact lines can be treated as line phases; their fundamental equations (in the case when all surfaces are surfaces of tension) read

$$d\tilde{U}^{(j)} = \tilde{T}^{(j)}d\tilde{S}^{(j)} + \sum_{i=1}^{k}\tilde{\mu}_i^{(j)}\,d\tilde{N}_i^{(j)} + \tilde{\kappa}_j\,dL_j + \tau_j L_j\,dh_j, \qquad j = 1,2 \tag{137}$$

The index j denotes any of the contact lines; $\tilde{U}^{(j)}$, $\tilde{S}^{(j)}$, and $\tilde{N}_i^{(j)}$ are the linear excesses of the respective extensive properties; L_j $(j = 1,2)$ is the length of the jth contact line. The quantities $\tilde{\kappa}_j$ and τ_j $(j = 1,2)$ are the line and transversal tensions. It is shown in the next Section II.C that $\tilde{\kappa}_j$ and τ_j actually can be interpreted as mechanical tensions. The last term in Eq. (137) accounts for the dependence of the internal energy $\tilde{U}^{(j)}$ of the contact line on the thickness of the film. In the case of a flat symmetrical film Eq. (137) reduces to (Kralchevsky and Ivanov, 1985a)

$$d\tilde{U} = \tilde{T}\,d\tilde{S} + \sum_{i=1}^{k}\tilde{\mu}_i\,d\tilde{N}_i + 2\tilde{\kappa}\,dL + \tau L\,dh \tag{138}$$

where

$$\tilde{S} = \tilde{S}^{(1)} + \tilde{S}^{(2)}, \qquad \tilde{U} = \tilde{U}^{(1)} + \tilde{U}^{(2)}, \qquad \text{and} \qquad \tilde{N}_i = \tilde{N}_i^{(1)} + \tilde{N}_i^{(2)}$$

The comparison between Eqs. (134) and (137) reveals that $\tilde{\kappa}_j$ and τ_j are linear analogues of σ_j^t and Π. Note that in the corresponding fundamental equations in the membrane approach [Eqs. (95) and (96)], terms with Π and τ (i.e., the terms connected with [illegible] film thickness) do not appear. But the line tension terms, κ and $\tilde{\kappa}$, remain in both approaches; as shown by Kralchevsky and Ivanov (1985a) κ and $\tilde{\kappa}$ are simply connected.

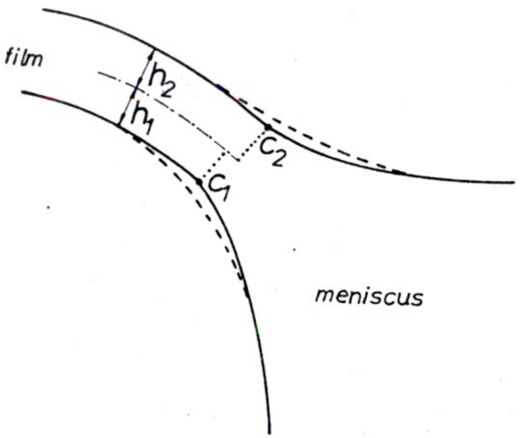

FIG. 12 A thin film and its contact with the liquid meniscus in the detailed approach. C_1 and C_2 are the pierce points of the two contact lines in the plane of the drawing. The real and extrapolated surfaces in the transiton region are shown by dashed and solid lines, respectively.

On the basis of the considered fundamental equations, the conditions for equilibrium can be derived. They are discussed in Section II.C.

C. Conditions for Mechanical Equilibrium

It was pointed out in Section II.A that the number of differentials in the fundamental equations of the constituent phases of the system is usually greater than the number of degrees of freedom of the whole system. The conditions for all parts of the system to be in thermodynamical equilibrium provide connections between the parameters of the system, thus ensuring the correct number of degrees of freedom. As mentioned earlier, the conditions for thermal and chemical equilibrium in most capillary systems are trivial: they are merely conditions for constancy of the temperature and the chemical potentials throughout the whole system. Hence, we deal here only with the conditions for mechanical equilibrium. For an isothermal system it is most convenient to derive these conditions by using the system grand thermodynamic potential Ω, which is the sum of the grand potentials of all bulk, surface, and linear phases in the system, i.e.,

$$\Omega = -\sum_i P_i V_i + \sum_j \sigma_j A_j + \sum_k \kappa_k L_k \tag{139}$$

The necessarv condition for equilibrium is that Ω be minimum, i.e., nullification [illegible] its first variation:

$$(\delta\Omega)_{T,V,\mu_1,\ldots,\mu_k} = 0 \tag{140}$$

at fixed temperature T, total volume V, and chemical potentials μ_i of all components. If the problem of interest is the equlibrium between the film and its surroundings, it is sufficient to imagine a volume V' containing the film and parts of the neighboring phases and then to apply the general principle (140) to the substance in V'. The constancy of T and μ_i ($i = 1,\ldots,k$) will be ensured if the boundaries of V' are open for transfer of heat and molecules.

When carrying out the variation in Eq. (140), both the extensive and intensive parameters in Eq. (139) are subject to variation. But when using the membrane approach, all variations of the intensive parameters identically cancel due to the fact that they are interrelated by the Gibbs-Duhem equations of the phases (see, e.g., Gibbs, 1906; or Ivanov et al., 1986). When one uses the detailed description of the film, the variations of the intensive parameters produce a term, proportional to the film thickness (see Kralchevsky and Ivanov, 1985a; in fact in this case the thickness behaves like an intensive quantity, because the state of the film depends on it). We will discuss below only the results of the variation; the reader could find the details of the variational procedure in the references cited above. As a matter of fact the conditions for mechanical equilibrium are usually force balance equations that could have been derived by purely mechanical considerations. The major advantage of the variational approach is its universality and physical transparency, which, in turn, gives answers to several somewhat obscure questions [e.g., the role of the line and transversal tensions in the Neumann-Young equations; see Eqs. (142) and (143)].

The condition for mechanical equilibrium at the surface of tension of the film (or at any surface of tension in the system) is the well-known Laplace equation [Eq. (97)]. When the interface is axisymmetric, this equation reads

$$-\frac{r''}{(1 + r'^2)^{3/2}} + \frac{1}{r(1 + r'^2)^{1/2}} = \frac{2}{b} + \frac{\Delta\rho g z}{\sigma} \tag{141}$$

where σ is the surface tension, r(z) is the generatrix of the interface, g is the acceleration due to gravity, and $\Delta\rho$ is the difference in mass densities of the lower and upper bulk phases. The z-axis coincides with the axis of symmetry, and b is the radius of curvature at the point at which this axis pierces the interface (for details, see Princen, 1969). If $\Delta\rho g \neq 0$, Eq. (141) can be solved only numerically or by means of perturbational methods. The numerical solutions are tabulated by Huh and Scriven (1969) (for the external meniscus) and by Hartland and Hartley (1976) (for sessile and pendant interfaces and the external meniscus). Perturbational solutions were published by Concus (1968) (for sessile and pendant interfaces), Lo (1983) (for external meniscus), and Kralchevsky et al. (1986a) (for sessile and pendant interfaces and external meniscus).

The conditions for equilibrium at the contact lines provide boundary conditions for the Laplace equation (141). They are so[illegible] that different

in the membrane and the detailed approaches. In the membrane approach (see Fig. 13a) the transition-region film meniscus is replaced by a single contact line, where the mechanical equilibrium is determined by the balance of four forces (Rusanov, 1967a; Torza and Mason, 1971; Pujado and Scriven, 1972; Ivanov et al., 1986):

$$\gamma + \sigma_1^{\ell} + \sigma_2^{\ell} + \sigma_\kappa = 0 \tag{142}$$

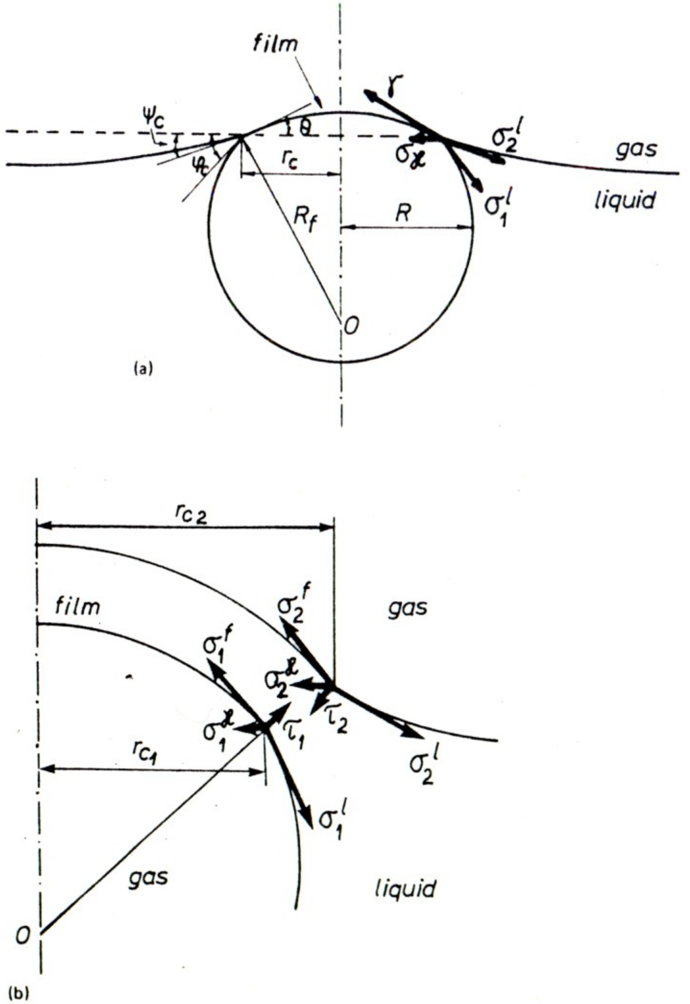

FIG. 13 The force balance in each point of the periphery of a spherical film in the membrane approach (a) and in the detailed approach (b).

Here the forces γ, σ_1^ℓ, and σ_2^ℓ act tangentially to the film and the two meniscus surfaces and are equal, in magnitude, to the film tension γ and the respective surface tensions σ_1^ℓ and σ_2^ℓ. The force σ_κ is directed toward the center of curvature (Veselovsky and Pertzov, 1936) and is determined by the line tension κ and the radius of curvature r_c of the contact line: $|\sigma_\kappa| = \kappa/r_c$. In Fig. 13a, Eq. (142) is visualized for the case of a spherical film, which can be formed, for example, by a bubble (or drop) pressed against another fluid interface by the buoyancy force F_b. Note that the three interfaces intersect into a single (contact) line. If one assumes that the three extrapolated surfaces do not intersect on a single line, there should be two contact lines of different radii of curvature. One can easily realize that if such were the case, the portion of the film lying between the two lines could not be in mechanical equilibruim; hence this possibility must be ruled out.

There are two contact lines in the detailed approach (one for each film surface) with line tensions $\tilde{\kappa}_1$ and $\tilde{\kappa}_2$, and each of the lines must be in equilibrium. Carrying out the variation in Eq. (140) with respect of the positions and radii of the two contact lines and taking into account Eqs. (134) and (137), one obtains (Kralchevsky et al., 1986c):

$$\sigma_i^f + \sigma_i^\ell + \sigma_i^\kappa + \tau_i = 0, \qquad i = 1,2 \tag{143}$$

where $|\sigma_i^\kappa| = \tilde{\kappa}_i/r_{ci}$, and the transversal tension τ_i is a force acting inwards on the contact line perpendicularly to the film surfaces (see Fig. 13b and Kralchevsky and Ivanov, 1985a).

Explicit expressions for κ, $\tilde{\kappa}$, and τ can be derived from the micromechanical conditions for equilibrium in the transition region between the film and meniscus (see Section III.A).

In the case of a floating fluid particle, like the one shown in Fig. 13, the transversal tension can be calculated with sufficient accuracy from the force balance equation (Kralchevsky et al., 1986c):

$$F_b - F_m = \pi r_c^2 \Pi - 2\pi r_c \tau_1 \cos\theta \tag{144}$$

where F_m is the weight of the particle and F_b is the buoyancy force. Equation (144) is obtained by elimination of σ_1^f between Eq. (26) and the vertical projection of Eq. (143) for i = 1; For small particles (or in a space laboratory) the left-hand side of Eq. (144) is negligible, and the two terms in the right-hand side counterbalance each other (Kralchevsky et al., 1986c). The force $F_b - F_m$ due to gravity deforms the bulk liquid interface and thus creates an external meniscus around the particle; its boundary slope angle ψ_c is connected with $F_b - F_m$:

$$F_b - F_m = 2\pi r_c \sigma_2^\ell \sin\psi_c \tag{145}$$

i.e., the knowledge of ψ_c enables one to calculate $F_b - F_m$. Alternatively, if the buoyancy force is calculated from the equation (Princen, 1969; Ivanov et al., 1986)

$$F_b = g[\rho^\gamma V_\ell + \rho^\beta V_u - (\rho^\gamma - \rho^\beta)V_c] \tag{146}$$

one can find ψ_c from Eq. (145). In (146) V_ℓ and V_u are the lower and the upper parts (with respect to the plane of the contact line) of the particle volume and V_c is the volume of a cylinder having for a base the contact circumference and whose height equals the (algebraic) value of the elevation of the contact line over the flat liquid surface away from the particle.

Equations (142)-(145) provide a suitable basis for the measurement of the film and line tensions (see, e.g., Gershfeld and Good, 1967; Torza and Mason, 1971; Kralchevsky et al., 1986b). However, we must emphasize that these equations are valid only for the true, i.e., the correctly defined, contact radius and angles. Experimentally the contact angles are usually measured by determining by some optical method the shape of the interfaces at some distance from the contact line and then by extrapolating them until they intersect.

The first problem encountered when this procedure is carried out in practice is that the minimum distance from the contact line at which one can still obtain experimental information about the shape of the interfaces is limited by the microscope resolution power (Pethica, 1977). At the same time the deformation of the interfaces caused by the gravity is much larger close to the contact line than away from it. Therefore, if this effect is not properly taken into account one will determine only an apparent contact angle and its value will depend not only on the gravity but also on the optical method used.

The second problem is related to the so-called transition region (see Section III.A). As a matter of fact the microscopic contact angle between fluid interfaces should be zero, because in the transition region, where the interfaces meet each other, they should undergo a smooth transition from the one interface to the other (see Fig. 12). Although the width of the transition region is most probably smaller [it was estimated to 1 μm by de Feijter and Vrij (1972)] than the resolution of the microscope, if some of the experimental points happen to lie there, this will again affect the extrapolation procedure and hence will affect the value of the macroscopic contact angle.

The only way to avoid these two errors is (1) to make sure that all experimental points used lie outside of the transition region and (2) to carry out the extrapolation of the surface in such a way that its shape all the time satisfies the Laplace equation with the macroscopic value of the surface tension. [In the absence of external fields the second statement means that the extrapolation must be carried out at constant capillary pressure as suggested by Ivanov et al. (1978).]

D. Local Formulation of the Capillary Thermodynamics

When previously we considered the thin film as a single membrane we assumed that the intensive properties are uniform along the membrane surface. Strictly speaking such an assumption can be valid only for spherical, cylindrical, or flat films, but in the general case of curved films it is at best a good approximation. This is due to the fact that when the film is arbitrarily curved not only the principal curvatures, but also the surface densities of the extensive parameters, can depend on the position at the interface. That is why a local thermodynamic description is needed.

The basic idea of the local description, which is due to Gibbs (1906), is to apply the fundamental equations of a uniform surface phase locally, i.e., for each elementary portion, dA, of the curved interface.

Let the internal energy, entropy, grand potential, and number of adsorbed molecules on that portion be

$$dU^f = u^f\,dA, \qquad dS^f = s^f\,dA, \qquad d\Omega^f = \omega^f\,dA, \qquad dN_i^f = \Gamma_i\,dA \tag{147}$$

where u^f, s^f, ω^f, and Γ_i are the respective surface densities. Since the latter depend on the position at the dividing surface, the total amounts, U^f, S^f, Ω^f, and N_i^f for the whole film are obtained by integrating Eqs. (147) over the film area A:

$$U^f = \int_{(A)} u^f\,dA, \qquad S^f = \int_{(A)} s^f\,dA, \qquad \Omega^f = \int_{(A)} \Omega^f\,dA,$$
$$N_i^f = \int_{(A)} \Gamma_i\,dA \tag{148}$$

Let the area dA of the portion under consideration be changed during a thermodynamic process by

$$\delta(dA) = \frac{\delta(dA)}{dA}\,dA = \delta\alpha\,dA \tag{149}$$

where $\delta\alpha = \frac{1}{2}\delta\ln a$ is the relative increase of the area and a is the determinant of the surface metrics (Eliassen, 1963). The changes of the internal energy, entropy, and number of adsorbed molecules and the grand potential during this process, according to Eqs. (147) and (149), will be

$$\delta(dU^f) = (\delta u^f + u^f\delta\alpha)\,dA, \qquad \delta(dS^f) = (\delta s^f + s^f\delta\alpha)\,dA \tag{150}$$
$$\delta(dN_i^f) = (\delta\Gamma_i + \Gamma_i\delta\alpha)\,dA, \qquad \delta(d\,\Omega^f) = (\delta\omega^f + \omega^f\delta\alpha)\,dA$$

where the first terms in parentheses are connected with the variation of state (at constant area) of the portion dA during the process and the terms proportional to $\delta\alpha$ arise because of the stretching of the area by $\delta(dA)$. These changes are related by the second law of thermodynamics:

$$\delta(dU^f) = T\delta(dS^f) + \sum_i \mu_i\,\delta(dN_i^f) + \delta W^f \tag{151}$$

where [cf. Eqs. (58) and (59)]

$$\delta W^f = (\gamma\delta\alpha + B\,\delta H + \Theta\delta D)\,dA \tag{152}$$

is the work done by the external forces and the remaining parts of the system for the deformation (stretching, bending, and torsion) of the element dA. Equation (152) was postulated by Gibbs (1906) based on considerations about the thermodynamic degrees of freedom and confirmed by Murphy (1966) by means of a quasi-thermodynamic approach. [More precisely, Murphy has used variables H and $K = H^2 - D^2$ instead of variables H and D in the Gibbs approach; the variables H and D have the advantage of providing simple geometric interpretation (cf. Fig. 6), and moreover, the bending and torsion moments B and Θ have the same physical dimension.]

To make the following treatment clearer, let us return for a moment to the case of a spherical film. We will generalize the treatment from Section II.B so that the results be valid for any dividing surface (of radius r_x and area A_x), not only the surface of tension. In this case $\Theta = 0$, and since the system is uniform, Eq. (151) becomes

$$dU^f = T\,dS^f + \sum_i \mu_i\,dN_i^f + \gamma\,dA_x + A_x B\,dH \tag{153}$$

where $H = -1/r_x$ and $B(r_x)$ is defined by Eq. (64). When the conditions (103) hold, the grand potential is [compare with Eq. (99)]

$$d\,\Omega^f = -S^f\,dT + \gamma\,dA_x + A_x B\,dH - \sum_{i=1}^{k} N_i^f\,d\mu_i \tag{154}$$

We will integrate this equation at constant values of the intensive parameters of the system. This means holding constant not only the temperature and all chemical potentials (which are prescribed by the environment) but also the radius r_x of the dividing surface. Physically, this is tantamount to increasing the area of the film by changing the body angle in Fig. 5. Then, we obtain equations analogous to Eqs. (100) and (104):

$$\Omega^f = \gamma A_x, \qquad u^f = Ts^f + \sum_i \Gamma_i\mu_i + \gamma$$

Differentiating Ω^f back and equating the result to Eq. (154) we obtain the Gibbs-Duhem equation

$$d\gamma = -s^f\,dT - \sum_i \Gamma_i\,d\mu_i + B\,dH \tag{155}$$

The last term reflects the fact that the film tension γ depends on the choice of the radius r_x of the dividing surface (see section I.F, subsection "M[illegible]rane Approach"). Equation (155), along with the expression for u^f, leads to

$$du^f = T\, ds^f + \sum_i \mu_i\, d\Gamma_i + B\, dH \tag{156}$$

The comparison of this equation with Eq. (105) shows that the specific internal energy will depend on the curvature of the dividing surface. Note hwoever, that because of the assumed thermal and chemical equilibrium with the environment, again there is no stretching term in Eq. (156).

Coming back to the case of nonuniform films and keeping Eq. (152) in mind, we can postulate, by analogy with (156), the following local fundamental equation:

$$\delta u^f = T\, \delta s^f + \sum_i \mu_i\, \delta\Gamma_i + B\delta H + \Theta\delta D \tag{157}$$

In line with our previous reasoning, we kept in Eq. (157) only those parts of the total variations of the entropy and the number of adsorbed molecules, which are connected with the variation of state [cf. Eq. (150) and the comment thereafter].

Because of the nonuniformity of the film, Eq. (151), unlike Eq. (153), cannot be integrated directly. An integral result for u^f can be obtained by substituting Eq. (150) and (152) in Eq. (151). This yields

$$\delta u^f - T\delta s^f - \sum_i \mu_i\, \delta\Gamma_i - B\,\delta H - \Theta\delta D$$

$$= -(u^f - Ts^f - \mu_i\Gamma_i - \gamma)\delta\alpha$$

Because of the fundamental equation (157) the left-hand side is zero and we obtain the local counterparts of Eqs. (104) and (100):

$$u^f = Ts^f + \mu_i\Gamma_i + \gamma, \qquad \omega^f \equiv u^f - Ts^f - \mu_i\Gamma_i = \gamma \tag{158}$$

Again the surface density of the grand potential equals the film tension. The Gibbs-Duhem equation follows from Eqs. (157) and (158):

$$\delta\gamma = -s^f\, \delta T - \sum_i \Gamma_i\, \delta\mu_i + B\delta H + \Theta\delta D \tag{159}$$

Note that this equation, as well as Eqs. (157) and (158), holds for an arbitrary dividing surface, which can be fixed by imposing additional conditions. We will find now the variation of the total surface internal energy in order to derive a generalization of the Laplace equation. Before doing that we must introduce some notation from the differential geometry of the surfaces.

Let u^α ($\alpha = 1,2$) be a set of curvilinear coordinates in [illegible]e dividing surface. They generate a local surface basis

$$\mathbf{a}_\alpha = \frac{\partial \mathbf{R}}{\partial u^\alpha}, \qquad \alpha = 1,2 \tag{160}$$

in each point of the surface; $\mathbf{R}(u^1,u^2)$ is the equation of the surface with respect to a cartesian coordinate system (for details see, e.g., McConnell, 1957; Aris, 1962; or Eliassen, 1963).

Let us first consider a pure tangential deformation (at fixed temperature and chemical potentials) of the surface, given by the variable infinitesimal surface vector $\boldsymbol{\xi} = \xi^\alpha \mathbf{a}_\alpha$; $\delta\mathbf{R} = \boldsymbol{\xi}$ (summation with respect to the repeating indices is understood). Then $\delta\gamma = \gamma_{,\alpha}\xi^\alpha$ (here $\gamma_{,\alpha}$ is the covariant derivative of γ). It follows from the Gibbs-Duhem equation (159) that under these conditions

$$\gamma_{,\alpha} = BH_{,\alpha} + \Theta D_{,\alpha}, \qquad \alpha = 1,2 \tag{161}$$

The arbitrariness of the vector $\boldsymbol{\xi}$ also being used.

Now, let us consider the whole surface (or whatever part of it) A, enclosed by a contour C. Then, let

$$\delta\mathbf{R} = \boldsymbol{\xi} + \eta\mathbf{n} \tag{162}$$

($\mathbf{n}$ is the running unit normal to the surface) be a virtual deformation of the surface A at fixed boundaries:

$$\boldsymbol{\xi} = 0, \ \eta = 0, \ \eta_{,\alpha} = 0 \qquad \text{over the contour C} \tag{163}$$

(ξ^α, $\alpha = 1,2$, and η are infinitesimal quantities). The virtual deformation (162) takes place at constant total volume, temperature, and chemical potentials. The variation of the film grand potential at these conditions, according to Eqs. (148), (149), (158), and (159), is

$$\delta\Omega^f = \int_{(A)} (\delta\omega^f + \omega^f\delta\alpha)\, dA = \int_{(A)} (B\delta H + \Theta\delta D + \gamma\delta\alpha)\, dA$$

The variation of the total grand potential of the system is

$$\delta\Omega = \delta\Omega^I + \delta\Omega^{II} + \delta\Omega^f = -P^I\,\delta V^I - P^{II}\,\delta V^{II} + \delta\Omega^f$$

and keeping in mind that $\delta(V^I + V^{II}) = 0$ one obtains

$$\delta\Omega = -(P^I - P^{II})\delta V^I + \int_{(A)} (\gamma\delta\alpha + B\,\delta H + \Theta\delta D)\, dA \tag{164}$$

where P^I and V^I are the pressure and volume on one side of the dividing surface, and P^{II} and V^{II} are the pressure and volume on the other side of the dividing surface. The variation of V^I is

$$\delta V^I = \int_{(A)} \text{[illegible]}\, dA$$

and the other variations in (164) are

$$\delta\alpha = \xi^{\alpha}_{,\alpha} - 2H\eta$$

$$\delta H = H_{,\alpha}\xi^{\alpha} + (H^2 + D^2)\eta + \frac{1}{2}a^{\alpha\beta}\eta_{,\alpha\beta}$$

(see, e.g., Murphy, 1966) and

$$\delta D = D_{,\alpha}\xi^{\alpha} + 2HD\eta + \frac{1}{2}q^{\alpha\beta}\eta_{,\alpha\beta}$$

Here $a^{\alpha\beta}$ is the surface metric tensor and $q^{\alpha\beta} = (b^{\alpha\beta} - Ha^{\alpha\beta})/D$, where $b^{\alpha\beta}$ is the symmetric surface curvature tensor. Note that $a^{\alpha\beta}$ and $q^{\alpha\beta}$ are constant tensors on the surface, i.e.,

$$a^{\alpha\beta}_{,\nu} = 0, \qquad q^{\alpha\beta}_{,\nu} = 0 \qquad (165)$$

(in the bases of the principal curvatures the tensor $\mathbf{q} = \mathbf{a}_{\alpha}\mathbf{a}_{\beta}q^{\alpha\beta}$ is diagonal with eigenvalues 1 and −1).

There are three independent variations (ξ^{α}, $\alpha = 1,2$; and η) so that the general condition for equilibrium [Eq. (140)] will produce three independent equations. [The derivatives $\xi^{\alpha}_{,\alpha}$ and $\eta_{,\alpha\beta}$ can be reduced to the variations $\boldsymbol{\xi}$ and η by means of standard integrations by parts (see, e.g., Elsgoltz, 1969) and by making use of Eqs. (163) and (165).] The first two of them, which correspond to the tangential variation $\boldsymbol{\xi}$, coincide with Eq. (161) and hence they do not yield new information with respect to the Gibbs-Duhem equation. The third one, which corresponds to the normal variation η, is a new equation, which generalizes the Laplace equation (97) for the cases when the surface is not uniform (Kralchevsky, 1987):

$$-2H\gamma + (H^2 + D^2)B + 2HD\Theta + \frac{1}{2}(a^{\alpha\beta}B_{,\alpha\beta} + q^{\alpha\beta}\Theta_{,\alpha\beta}) = P^{I} - P^{II} \qquad (166)$$

The first two terms in Eq. (166) were derived by Buff (1960a). Murphy (1966) has erroneously considered η and $\eta_{,\alpha\beta}$ as being independent variations and thus the number of equations obtained by him is greater than the number of the independent variables.

For a spherical surface, when $H = -1/r$, $D = 0$, and $B_{,\alpha\beta} = \Theta_{,\alpha\beta} = 0$, one obtains from Eq. (166) the known equation (66).

Boruvka and Neumann (1977) and Boruvka et al. (1985) follow another (slightly different but equivalent) way in the thermodynamics of curved interfaces. Instead of using Eq. (152), which for uniform surfaces (sphere, pseudosphere, cylinder, or plane) reads

$$\delta W^{f} = \gamma\delta A + BA\,\delta H + \Theta A\,\delta D$$

they used another equation of the type of

$$\delta W^{f} = \gamma^{BN}\delta A + B\delta(AH) + \Theta\delta(AD)$$

It is obvious that in fact these authors used another definition of the interfacial (film) tension:

$$\gamma^{BN} = \gamma - BH - \Theta D$$

One sees that γ^{BN} has the meaning of work (per unit area) done during an elementary deformation of the dividing surface at fixed products AH and AD. Such a deformation is a combination of dilation, bending, and torsion (cf. Fig. 6). In contrast, the usual interfacial (film) tension γ is connected only with the simple dilation of the surface area (at constant H and D). That is why, following Ono and Kondo (1960), Murphy (1966), and Rusanov (1967a), we deal with γ (instead of γ^{BN}) in the present text.

III. MECHANICS OF CURVED FILMS AND OF THE TRANSITION ZONE FILM-MENISCUS

In this section we generalize the treatment from Section I in two respects: (1) we deal with films of arbitrary (but not small) curvature and (2) we consider not only static systems, but dynamic systems as well. The mathematical apparatus of the differential geometry, which is used in the present section, is described in detail in the books of Weatherburn (1939), McConnell (1957), and Aris (1962) and in the thesis of Eliassen (1963). It is not needed only for Section III.A, which is devoted to the transition zone between a flat film and the capillary meniscus. In Sections III.B and III.C the membrane and the detailed approaches are applied to curved films. It is shown that in the general case the film stress is a tensor and the disjoining pressure is a vector. The dynamical considerations are restricted to viscous flow at low Reynolds number. The boundary conditions at the film surfaces are derived.

A. The Transition Region Film-Meniscus and Line Tension Effects

Conditions for Equilibrium of the Transition Region.

We consider a symmetrical planar thin liquid film in the absence of external fields, encircled by a capillary meniscus of the same liquid (Fig. 14). Close to the axis of symmetry Oz the film has constant thickness h (defined as the distance between the two surfaces of tension, each with film surface tension σ^{f}). Far from Oz (in the meniscus) the disjoining pressure Π equals 0, the surface tension of the meniscus is a constant, σ^{ℓ}, and the generatrix of the surface z(x) satisfies the Laplace equation (97). In the intermediate region the two surfaces interact, and since the interaction energy depends on the distance between them, the surface [illegible]sion in this region $\sigma(x)$ changes gradually from

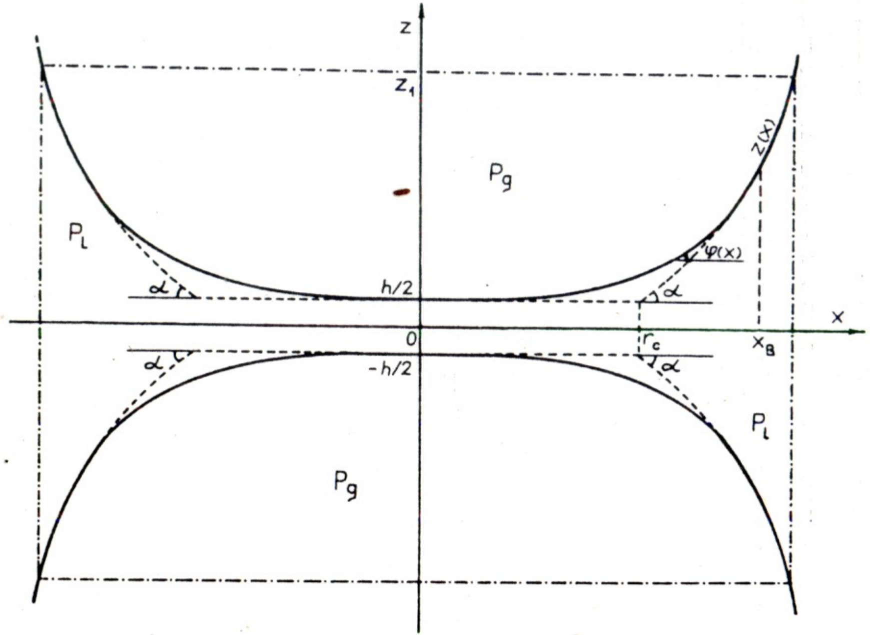

FIG. 14 The transition between a thin liquid film and the capillary meniscus is smooth. The solid and dashed lines represent the real and the extrapolated interfaces, respectively.

σ^f to σ^ℓ. The disjoining pressure Π is also a function of x in this region. This (real) system is depicted in Fig. 14 with continuous solid lines. It is customary to introduce an idealized system by extrapolating the meniscus and film surfaces [at constant surface tensions and capillary pressure, Ivanov et al. (1978)] until they intersect to form a contact angle α. The extrapolated surfaces are shown in Fig. 14 with dashed lines.

According to Derjaguin (1955), the profile of the transition region between the film and the meniscus [where $\sigma = \sigma(x)$ and $\Pi = \Pi(x)$] obeys the equation

$$-\sigma H(x) = P_c - \Pi(x) \tag{167}$$

where H(x) is the local mean curvature, P_c is the capillary pressure of the meniscus, and the surface tension σ is assumed constant [usually one assumes $\sigma \equiv \sigma^\ell$; see, e.g., Derjaguin et al. (1976), Martynov et al. (1977), Renk et al. (1978), Neimark and Heifets (1981), and Churaev et al. (1982)]. De Feijter and Vrij (1972) accounted partially for the variation of σ with x by making a local tangential (along Ox) force balance (see below), but in their calculations of the film profile they also used Eq. (167).

Our purpose now is to derive a self-consistent set of differential equations describing the hydrostatic equilibrium of the transition region. Following the detailed approach (Sections I.B and I.C) we consider the film as divided by its surface of tension (in this case the surface z = 0) into two parts and we will define the local disjoining pressure as

$$\Pi(x) = P_N{}^0(x) - P_\ell \tag{168}$$

where P_ℓ is the pressure in the meniscus and $P_N{}^0(x)$ is the value of the component P_{zz} of the pressure tensor at the surface of tension. Equation (168) connects Π directly with statistical mechanics, because P_{zz} can be expressed through integrals over the intermolecular potentials and the correlation functions. Let us consider a volume element (see Fig. 15) whose lower base of area x dx dψ (ψ is the azimuthal angle) lies on the surface of tension and where upper base is in the gas phase. According to the method of the local balance (see Martynov et al., 1976) we require that the total forces acting on this volume along the axes Ox and Oz are zero. Along the axis Oz we have

$$[P_\ell - \Pi(x)]x\,d\psi\,dx + (x + dx)\sigma(x + dx)\sin\varphi(x + dx)\,d\psi$$
$$= P_g x\,d\psi\,dx + \sigma(x)x\sin\varphi(x)\,d\psi \tag{169}$$

where P_g is the gas pressure and $\varphi(x)$ is the running slope angle:

$$\tan\varphi = \frac{dz}{dx} \tag{170}$$

By taking the limits $d\psi \to 0$ and $dx \to 0$ we thus obtain

$$\frac{d(\sigma\sin\varphi)}{dx} + \frac{\sigma(x)\sin\varphi(x)}{x} = P_c - \Pi(x) \tag{171}$$

where $P_c = P_g - P_\ell$. For the forces acting along the axis Oz we similarly obtain

$$-\frac{d(\sigma\cos\varphi)}{dz} + \frac{\sigma(x)\sin\varphi(x)}{x} = P_c \tag{172}$$

In a slightly different form Eq. (172) was first derived by de Feijter and Vrij (1972). The approximation σ = const reduces Eq. (171) to Derjaguin's equation [Eq. (167)]. When the distance between the meniscus surfaces is large ($\sigma = \sigma^\ell$ = const, $\Pi \equiv 0$), Eqs. (171) and (172) coincide and both lead to the Laplace equation in parametric form (see, e.g., Princen, 1969). However, when the meniscus surfaces interact, so that $\sigma = \sigma(x)$ and $\Pi(x) \neq 0$, Eqs. (171) and (172) are no longer equivalent and their combination leads to an interesting equation, connecting σ and Π (Kralchevsky and Ivanov, 1985b):

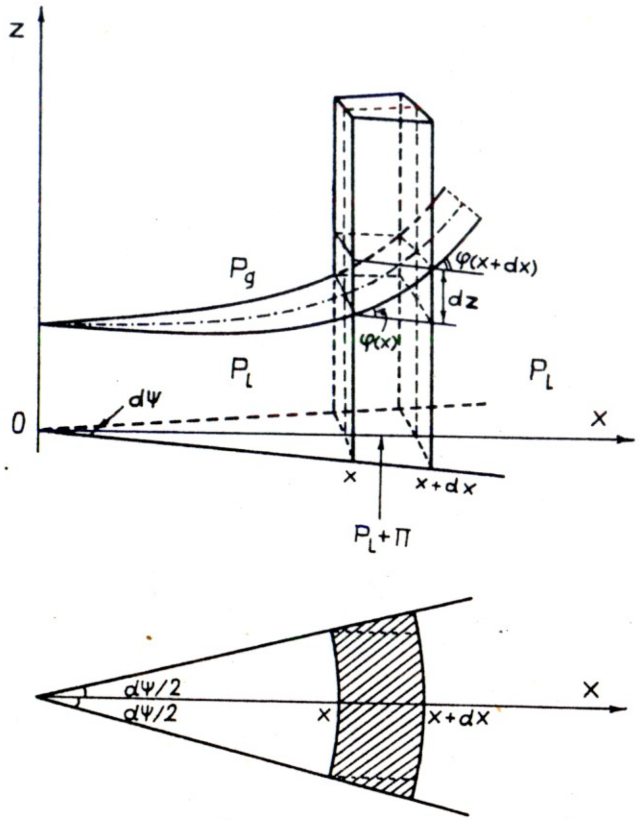

FIG. 15 A volume element in the transition region used for deriving the conditions for local mechanical equilibrium.

$$\frac{d\sigma}{dx} = -\Pi(x)\sin\varphi(x) \tag{173}$$

This result shows that the hydrostatic equilibrium in the transition region is ensured by simultaneous variation of σ and Π. In other words the assumptions $\Pi \neq 0$ and $\sigma = \text{const}$ are incompatible. Therefore, all attempts to ascribe the interaction between the meniscus surfaces solely either to $\Pi(x)$ (with $\sigma = \text{const}$) or to $\sigma(x)$ (with $\Pi = 0$) are inconsistent.

Equations (170), (171) [or (173)], and (172) form a full set, allowing the calculation of $z(x)$, $\varphi(x)$, and $\sigma(x)$, provided that $\Pi(x)$ is known from microscopic theory. Generally speaking $\Pi(x)$ is a functional of the shape $z(x)$ of the meniscus surfaces so that Eq. (171) [and (173)] is in fact an integrodifferential equation. One way to solve it is to use an iterative procedure, starting with $\Pi(x)$ for the idealized system as

zeroth approximation. Other forms of Eqs. (171) and (172) that are convenient for the calculation of the line tension are

$$d(\sigma\cos\varphi) + P_c\,dz = \frac{\sigma\sin^2\varphi}{x\cos\varphi}\,dx \tag{174}$$

$$d(x\sigma\cos\varphi) + P_c\,d(zx) = \left(\frac{\sigma}{\cos\varphi} + P_c z\right)dx \tag{175}$$

$$d(x^2\sigma\cos\varphi - xz\sin\varphi) + P_c\,d(x^2 z) = \{2\sigma\cos\varphi + [P_c + \Pi(x)]z\}x\,dx \tag{176}$$

The first two follow from Eqs. (170) and (172) and the third one follows from Eqs. (170), (171), and (172). These results are generalized in Section III.C, where equations for the surfaces of a curved film are derived.

Equations for the Line and Transversal Tensions.

The conditions for mechanical equilibrium between the film and the meniscus in the "membrane" and "detailed" approach were discussed in Section II.C [see Eqs. (142) and (143)]. The horizontal projection of Eq. (142) and the horizontal and vertical projections of Eq. (143) for a flat symmetrical film read, respectively,

$$\gamma + \frac{\kappa}{r_c} = 2\sigma^\ell\cos\alpha_0 \tag{177}$$

$$\sigma^f + \frac{\tilde{\kappa}}{r_{c1}} = \sigma^\ell\cos\alpha \tag{178}$$

$$\tau = \sigma^\ell\sin\alpha \tag{179}$$

where γ is the film (membrane) tension, κ, r_c, and α_0 (and $\tilde{\kappa}$, r_{c1}, and α) are, respectively, the line tension, the contact radius, and the contact angle in the membrane (and in the detailed approaches) (see Fig. 16); we call τ the transveral tension [see Kralchevsky and Ivanov (1985a) and Section II.B, subsection "Fundamental Equations in the Detailed Approach"]. We now derive expressions for κ, $\tilde{\kappa}$, and τ in terms of $\sigma(x)$, $\Pi(x)$, and the meniscus shape.

Let x_B be chosen in such a way that at $x \geq x_B$ the shapes of the menisci of the real and the idealized systems coincide (see Fig. 14) and $\sigma(x_B) = \sigma^\ell$. The integration of Eq. (174) from 0 to x_B yields

$$\sigma(x_B)\cos\varphi(x_B) - \sigma^f + P_c\left[z(x_B) - \frac{h}{2}\right] = \int_0^{x_B}\frac{\sigma(x)\sin^2\varphi(x)}{x\cos\varphi(x)}\,dx \tag{180}$$

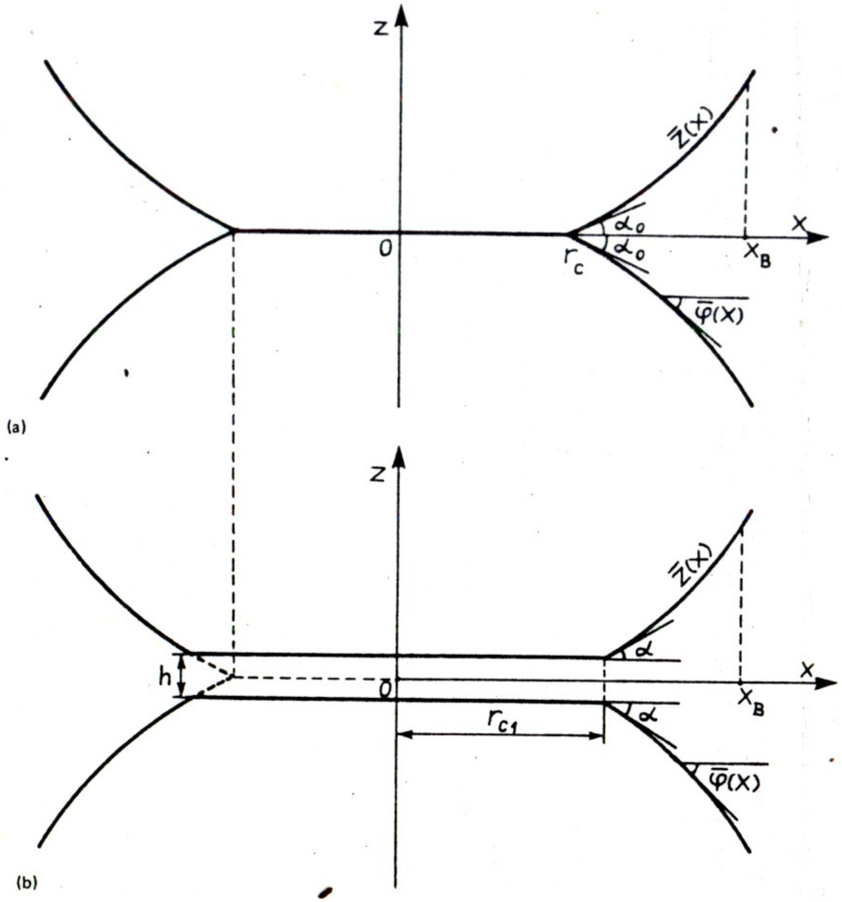

FIG. 16 The idealized system in the membrane (a) and the detailed (b) approaches.

By integrating Eq. (174) from r_c to x_B for the meniscus of the idealized system [set $\sigma \equiv \sigma^\ell$ in Eq. (174)] we obtain

$$\sigma^\ell \cos \bar{\varphi}(x_B) - \sigma^\ell \cos \alpha_0 + P_c \bar{z}(x_B)$$

$$= \int_{r_c}^{x_B} \frac{\sigma^\ell \sin^2 \bar{\varphi}(x)}{x \cos \bar{\varphi}(x)} dx \tag{181}$$

where the overbarred quantities correspond to the idealized system.

Equation (180) and (181) along with Eq. (177) and $\gamma = 2\sigma^f + P_c h$ [the latter follows from Eq. (34) for symmetrical flat films, when $\sigma_1 = \sigma_2 = \sigma^f$ and $\Pi = P_c$] lead to

$$\frac{\kappa}{r_c} = 2 \int_0^{x_B} \left[\left(\frac{\sigma \sin^2 \varphi}{x \cos \varphi} \right) - \left(\frac{\sigma \sin^2 \varphi}{x \cos \varphi} \right)_m^{id} \right] dx \tag{182}$$

where the superscript id refers to the idealized system and the subscript m denotes that the quantity in parentheses must be calculated in the membrane model (see Fig. 16a). In a similar way, from Eqs. (175) and (176) two alternative expressions for κ can be derived:

$$\frac{\kappa}{r_c} = 2 \int_0^{x_B} \left[\left(\frac{\sigma}{\cos \varphi} + P_c z \right) - \left(\frac{\sigma}{\cos \varphi} + P_c z \right)_m^{id} \right] \frac{dx}{r_c} \tag{183}$$

$$\frac{\kappa}{r_c} = 2 \int_0^{x_B} \{ [2\sigma \cos \varphi + (P_c + \Pi) z] - (2\sigma \cos \varphi + P_c z)_m^{id} \} \frac{x\, dx}{r_c^2} \tag{184}$$

The same treatment of Eqs. (174)-(176) and (178) leads to three expressions for the line tension $\tilde{\kappa}$ in the detailed model, i.e., film of finite thickness h (subscript h) (see Fig. 16b):

$$\frac{\tilde{\kappa}}{r_{c1}} = \int_0^{x_B} \left[\left(\frac{\sigma \sin^2 \varphi}{x \cos \varphi} \right) - \left(\frac{\sigma \sin^2 \varphi}{x \cos \varphi} \right)_h^{id} \right] dx \tag{185}$$

$$\frac{\tilde{\kappa}}{r_{c1}} = \int_0^{x_B} \left[\left(\frac{\sigma}{\cos \varphi} + P_c z \right) - \left(\frac{\sigma}{\cos \varphi} + P_c z \right)_h^{id} \right] \frac{dx}{r_{c1}} \tag{186}$$

$$\frac{\tilde{\kappa}}{r_{c1}} = \int_0^{x_B} \left\{ \left[2\sigma \cos \varphi + P_c z + \left(z - \frac{h}{2} \right) \Pi \right] - [2\sigma \cos \varphi + P_c z]_h^{id} \right\} \frac{x\, dx}{r_{c1}^2} \tag{187}$$

Equation (186) was first derived by de Feijter and Vrij (1972) by a different method. Equations (182)-(187) all contain the film radii and the meniscus capillary pressure so that, generally speaking, κ (and $\tilde{\kappa}$) will depend on the geometrical parameters of the system.

By multiplying Eq. (171) by x dx, integrating it, and using (179), one can derive an expression for the transversal tension τ (Kralchevsky and Ivanov, 1985b):

$$\tau = \frac{1}{r_{c1}} \int_0^{x_B} [(\Pi)^{id} - \Pi(x)] x\, dx$$

$$(\Pi)^{id} = P_c \quad \text{for } 0 < x < r_{c1}$$

$$= 0 \quad x > r_{c1} \tag{188}$$

One sees that τ is an integral effect of the difference of the disjoining pressure in the real and idealized systems whereas κ and $\tilde{\kappa}$ [see Eqs. (182) and (185)] are also integral effects but are determined by $\sigma(x)$ and the slope angle $\varphi(x)$ rather than by $\Pi(x)$. The fact that κ, $\tilde{\kappa}$, and τ are represented as integrals over small differences suggests that they should be very sensitive with respect to minor variations of the functions in the integrands. In this respect the replacement of $\sigma(x)$ in Eq. (172) by σ^{ℓ} may substantially affect the result of the calculations. Besides, the expressions (182)-(184) for the line tension at the boundary film-meniscus are much more complicated than the simple estimate $\kappa \approx \sigma\delta$, which holds for the edges of a solid (σ is the surface tension and δ is the thickness of a monolayer). That is why the applicability of this estimate to the transition zone between a thin liquid film and the capillary meniscus is questionable.

B. The Membrane Approach for Films of Arbitrary Curvature

In this section the membrane approach from Section I.A is applied to curved films (or interfaces) in the presence of a viscous flow.

Film Tension and Surface of Tension.

Let us consider a curved thin film that intervenes between two bulk fluid phases in the presence of viscous flow in the system. The total stress tensor $\underset{\sim}{\mathbf{T}}$ can be represented as a superposition of the pressure tensor $\underset{\sim}{\mathbf{P}}$ and the tensor of viscous stresses $\underset{\sim}{\mathbf{Q}}$:

$$\underset{\sim}{\mathbf{T}} = -\underset{\sim}{\mathbf{P}} + \underset{\sim}{\mathbf{Q}} \tag{189}$$

We introduce again an idealized system consisting of one dividing surface and two bulk phases, (I) and (II), which preserve their bulk properties up to the dividing surface. The quantities pertaining to the bulk phases in the idealized system will be denoted by superscripts I and II, so that instead of Eq. (189) one has

$$\underset{\sim}{\mathbf{T}}^{I} = -\underset{\sim}{\mathbf{P}}^{I} + \underset{\sim}{\mathbf{Q}}^{I}, \qquad \underset{\sim}{\mathbf{T}}^{II} = -\underset{\sim}{\mathbf{P}} + \underset{\sim}{\mathbf{Q}}^{II} \tag{190}$$

where the pressure tensors are isotropic:

$$\underset{\sim}{\mathbf{P}}^{I} = p^{I}\underset{\sim}{\mathbf{U}}, \qquad \underset{\sim}{\mathbf{P}}^{II} = p^{II}\underset{\sim}{\mathbf{U}} \tag{191}$$

However, as mentioned earlier, the real pressure tensor is not isotropic in the interfacial region. Moreover, the rheological behavior in this region is different from that in the bulk phases (see, e.g., Goodrich, 1981). In order to make up for the differences between the stresses in the real and the idealized systems one must introduce a film stress tensor $\underset{\sim}{\tau}$ in each point of the dividing surface. (It will be shown below that when the film stress tensor is tangentially isotropic, it reduces to the usual film tension.)

To define the dividing surface and the film stress tensor one must impose some conditions for equivalence between the real and the idealized systems. By analogy with the definition of the film tension of a spherical film (see Section I.A) one can introduce a sectorial strip ΔA_s for each element dl of a curve C lying on the dividing surface (see the hatched area in Fig. 17, where $\mathbf{n}$ is the running unit normal to the surface, and ν is the unit normal to the curve C). Then we impose the following two conditions defining the film stress tensor $\underset{\sim}{\tau}$ and the surface of tension of the film (Kralchevsky, 1986):

1. The real and the idealized system must be equivalent with respect to the total force and moment acting on each sectorial strip.
2. The dividing surface must be defined in such a way that the tangential part $\underset{\sim}{\tau}_{II} = \underset{\sim}{\mathbf{U}}_{II}\cdot\underset{\sim}{\tau}\cdot\underset{\sim}{\mathbf{U}}_{II}$ of the tensor $\underset{\sim}{\tau}$ be diagonal in the basis of the principal curvatures on the surface. [As pointed out by Scriven (1960) the surface tensor $\underset{\sim}{\tau}_{II}$ is symmetric due to the general condition for balance of the angular momenta (see below).]

It can be demonstrated (Kralchevsky, 1987) that these two conditions determine the film (surface) stress tensor and the surface of tension in an unique way.

In order to give mathematical form of the conditions (1) and (2) let us introduce curvilinear coordinates (u^1, u^2, λ) in the space:

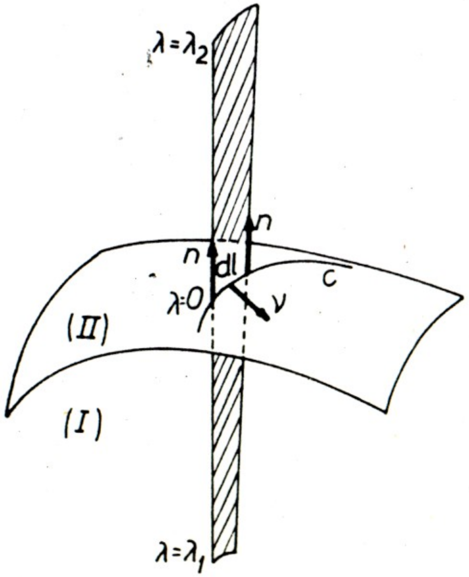

FIG. 17 A sectorial strip associated with an element dl of the curve C lying in the dividing surface. $\mathbf{n}$ is the running normal to the dividing surface.

$$\mathbf{r} = \mathbf{R}(u^1,u^2) + \lambda\mathbf{n}(u^1,u^2) \tag{192}$$

where (u^1, u^2) are curvilinear coordinates in the dividing surface, $\mathbf{R}(u^1, u^2)$ and $\mathbf{n}(u^1,u^2)$ are the equation and the running unit normal to the dividing surface, respectively, and $\mathbf{r}$ is the radius vector of a point in the space. Obviously, the surface $\lambda = 0$ is the dividing surface, and any surface with $\lambda = \text{const} \neq 0$ is parallel to it (Buff, 1956). (In contrast to Buff we do not suppose here that the surfaces $\lambda = \text{const}$ are surfaces of constant density.) Then in view of Eqs. (7) and (190) one can express the (bulk) stress tensor $\overline{\underset{\sim}{\mathbf{T}}}$ in the idealized system as follows:

$$\overline{\underset{\sim}{\mathbf{T}}} = \underset{\sim}{\mathbf{T}}^{I}\,\theta(-\lambda) + \underset{\sim}{\mathbf{T}}^{II}\,\theta(\lambda) \tag{193}$$

The force acting on a sectorial strip ΔA_s (see Fig. 17) in the <u>real</u> system is

$$\int_{\Delta A_s} d\mathbf{s} \cdot \underset{\sim}{\mathbf{T}}$$

The corresponding force in the <u>idealized</u> system is

$$\int_{\Delta A_s} d\mathbf{s} \cdot \overline{\underset{\sim}{\mathbf{T}}} + \boldsymbol{\nu} \cdot \underset{\sim}{\tau}\, dl$$

According to condition (1) these two forces must be equal:

$$\boldsymbol{\nu} \cdot \underset{\sim}{\tau} = \boldsymbol{\nu} \cdot \int_{\lambda_1}^{\lambda_2} d\lambda\, \underset{\sim}{\mathbf{L}} \cdot (\underset{\sim}{\mathbf{T}} - \overline{\underset{\sim}{\mathbf{T}}}) \tag{194}$$

where we have used Eliassen's (1963) finding, i.e., that the vectorial surface element $d\mathbf{s}$ of a sectorial strip can be expressed as

$$d\mathbf{s} = \boldsymbol{\nu} \cdot \underset{\sim}{\mathbf{L}}\, d\lambda\, dl, \qquad \underset{\sim}{\mathbf{L}} = (1 - 2\lambda H)\underset{\sim}{\mathbf{U}}_{II} + \lambda \underset{\sim}{\mathbf{b}} \tag{195}$$

Here H is the mean curvature and $\underset{\sim}{\mathbf{b}}$ is the curvature tensor

$$\underset{\sim}{\mathbf{b}} = -\nabla_{II}\mathbf{n} \tag{196}$$

with

$$\nabla_{II} = \mathbf{a}^{\alpha} \frac{\partial}{\partial u^{\alpha}} = \underset{\sim}{\mathbf{U}}_{II} \cdot \nabla \tag{197}$$

being the surface gradient operator [cf. Eq. (160) and E[illegible]ssen, 1963].

Similarly, the condition for equivalence with respect to the force moments yields

$$\boldsymbol{\nu} \cdot \underset{\sim}{\tau} \times \mathbf{R} = \boldsymbol{\nu} \cdot \int_{\lambda_1}^{\lambda_2} d\lambda\, \underset{\sim}{\mathbf{L}} \cdot (\underset{\sim}{\mathbf{T}} - \overline{\underset{\sim}{\mathbf{T}}}) \times \mathbf{r} \tag{198}$$

Because of the arbitrariness of $\boldsymbol{\nu}$, one obtains from Eqs. (194) and (198)

$$\underset{\sim}{\tau} = \int_{\lambda_1}^{\lambda_2} d\lambda\, \underset{\sim}{\mathbf{L}} \cdot (\underset{\sim}{\mathbf{T}} - \overline{\underset{\sim}{\mathbf{T}}}) \tag{199}$$

$$\underset{\sim}{\tau} \times \mathbf{R} = \int_{\lambda_1}^{\lambda_2} d\lambda\, \underset{\sim}{\mathbf{L}} \cdot (\underset{\sim}{\mathbf{T}} - \overline{\underset{\sim}{\mathbf{T}}}) \times \mathbf{r} \tag{200}$$

For a static spherical film, Eqs. (199) and (200) reduce to Eqs. (4) and (5).

Some properties of the film stress tensor $\underset{\sim}{\tau}$ can be deduced from Eqs. (199) and (200). It follows from Eq. (195) that $\underset{\sim}{\mathbf{L}}$ is a surface tensor, i.e., $\mathbf{n} \cdot \underset{\sim}{\mathbf{L}} = 0$. Then from Eq. (199) it can be implied that

$$\mathbf{n} \cdot \underset{\sim}{\tau} = 0 \tag{201}$$

but in general $\underset{\sim}{\tau} \cdot \mathbf{n} \neq 0$. Hence in the local basis formed by the vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{n}$, the matrix of the tensor $\underset{\sim}{\tau}$ is

$$(\underset{\sim}{\tau}) = \begin{pmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ 0 & 0 & 0 \end{pmatrix} \tag{202}$$

The components $\tau_{\alpha\beta}$ $(\alpha,\beta = 1,2)$ form the matrix of the surface part $\underset{\sim}{\tau}_{II}$ of the tensor $\underset{\sim}{\tau}$; it will be shown below that the components τ_{13} and τ_{23} have predominantly viscous character. It follows from Eqs. (192), (199), and (200) (the latter is valid only for the surface of tension) that

$$\int_{\lambda_1}^{\lambda_2} d\lambda\, \lambda \underset{\sim}{\mathbf{L}} \cdot (\underset{\sim}{\mathbf{T}} - \overline{\underset{\sim}{\mathbf{T}}}) \cdot \underset{\sim}{\mathbf{U}}_{II} = 0 \tag{203}$$

Let us define the quantities

$$^{k}\underset{\sim}{\mathbf{T}} \equiv \int_{\lambda_1}^{\lambda_2} d\lambda\, \lambda^{k}\, \underset{\sim}{\mathbf{U}}_{II} \cdot (\underset{\sim}{\mathbf{T}} - \overline{\underset{\sim}{\mathbf{T}}}) \cdot \underset{\sim}{\mathbf{U}}_{II}, \qquad k = 0,1,2 \tag{204}$$

Then Eqs. (199) and (203) lead to

$$\underset{\sim}{\tau}_{II} = {}^{0}\underset{\sim}{T} + (\underset{\sim}{b} - 2H\underset{\sim}{U}_{II}) \cdot {}^{1}\underset{\sim}{T} \tag{205}$$

$$0 = {}^{1}\underset{\sim}{T} + (\underset{\sim}{b} - 2H\underset{\sim}{U}_{II}) \cdot {}^{2}\underset{\sim}{T} \tag{206}$$

According to condition (2) the tensor $\underset{\sim}{\tau}_{II}$ diagonalizes together with the curvature tensor $\underset{\sim}{b}$. Since the total stress tensors $\underset{\sim}{T}$ and $\overline{\underset{\sim}{T}}$ are symmetrical, the tensors ${}^{k}\underset{\sim}{T}$ (k = 0,1,2) are symmetrical surface tensors due to Eq. (204). Then it follows from Eqs. (205) and (206) that all three tensors ${}^{k}\underset{\sim}{T}$ diagonalize together with $\underset{\sim}{b}$. This result is used below to connect the film stress tensor, the film tension, and the bending and torsion moments.

In view of Eqs. (189), (190), and (199) the film stress tensor can be represented as a sum of an elastic and a viscous parts

$$\underset{\sim}{\tau} = \underset{\sim}{\gamma} + \underset{\sim}{\tau}^{(v)} \tag{207}$$

where

$$\underset{\sim}{\gamma} = \int_{\lambda_1}^{\lambda_2} d\lambda\, \underset{\sim}{L} \cdot (\overline{\underset{\sim}{P}} - \underset{\sim}{P}), \qquad \underset{\sim}{\tau}^{(v)} = \int_{\lambda_1}^{\lambda_2} d\lambda\, \underset{\sim}{L} \cdot (\underset{\sim}{Q} - \overline{\underset{\sim}{Q}}) \tag{208}$$

($\overline{\underset{\sim}{P}}$ and $\overline{\underset{\sim}{Q}}$ are defined by Eq. (193), with $\underset{\sim}{P}$ or $\underset{\sim}{Q}$ standing for $\underset{\sim}{T}$). Here $\underset{\sim}{\gamma}$ is the tensor of the film (interfacial) tension. The usual scalar film tension γ is merely the half of the trace of $\underset{\sim}{\gamma}$ similarly to the scalar pressure P in a bulk phase, which is equal to a third of the trace of the pressure tensor $\underset{\sim}{P}$. Indeed, let us consider a static state of the system ($\underset{\sim}{Q} = 0$), let the eigenvalues of $\underset{\sim}{\gamma}_{II} = \underset{\sim}{\gamma} \cdot \underset{\sim}{U}_{II}$ be γ_1 and γ_2, and let the eigenvalues of ${}^{k}\underset{\sim}{T}$ be p_{k1} and p_{k2}, k = 0,1,2. Then Eqs. (205) and (206) read (Kralchevsky, 1987)

$$\gamma_1 = p_{01} - p_{11}c_2, \qquad \gamma_2 = p_{02} - p_{12}c_1 \tag{209}$$

$$p_{11} = p_{21}c_2, \qquad p_{12} = p_{22}c_2 \tag{210}$$

where we used also Eq. (59) and the fact that the eigenvalues of $\underset{\sim}{b}$ are the principal curvatures c_1 and c_2. On the other hand, according to Eq. (204) the definition (60), written for the surface of tension, acquires the following form:

$$\gamma = \frac{1}{2}\,({}^{0}\underset{\sim}{T} - {}^{1}\underset{\sim}{T}2H + {}^{2}\underset{\sim}{T}K) : \underset{\sim}{U}_{II} \tag{211}$$

Then by making use of Eqs. (209) and (210) one easily obtains from Eq. (211) that

$$\gamma = \frac{1}{2}\,(\gamma_1 + \gamma_2), \tag{212}$$

which was to be demonstrated. Equation (212) is in accordance with the corresponding result for solid surfaces (cf. Benson and Yun, 1967).

By analogy with Eq. (211) one can derive from (62) and (63) that

$$B = -({}^{1}\underset{\sim}{T} - {}^{2}\underset{\sim}{T}2H) : \underset{\sim}{U}_{II} - {}^{2}\underset{\sim}{T} : \underset{\sim}{b} \tag{213}$$

$$\Theta = -({}^{1}\underset{\sim}{T} - {}^{2}\underset{\sim}{T}H) : \underset{\sim}{q} - {}^{2}\underset{\sim}{T} : \underset{\sim}{U}_{II}D \tag{214}$$

where

$$\underset{\sim}{q} = (\underset{\sim}{b} - H\underset{\sim}{U}_{II})/D \tag{215}$$

is the deviatoric curvature tensor introduced in Section II.D. Equations (213) and (214) could be rewritten in terms of the eigenvalues of the corresponding tensors:

$$B = -(p_{11} - p_{21}c_2) - (p_{12} - p_{22}c_1), \tag{216}$$

$$\Theta = -(p_{11} - p_{21}c_2) + (p_{12} - p_{22}c_1). \tag{217}$$

We must emphasize again that the above treatment is valid for an arbitrary dividing surface, not necessarily the surface of tension. For the surface of tension, Eqs. (210) hold and from (216) and (217) it follows (Kralchevsky, 1987)

$$B = \Theta = 0. \tag{218}$$

In other words, for the surface of tension one again recovers Gibbs' equation (98), which does not contain bending and torsion terms. In this way we proved that Gibbs' analysis of a curved surface of tension is rigorous. Similarly, the bending and torsion terms disappear in Eq. (166) when it is applied to the surface of tension and again one obtains Laplace's equation (97).

Balances of the Linear and Angular Momenta.

The balance of linear momentum in a fluid, undergoing a slow viscous flow and in the presence of an external field with acceleration $\mathbf{f}$, reads

$$\nabla \cdot \underset{\sim}{T} + \rho\mathbf{f} = 0 \tag{219}$$

where $\rho = \rho(\mathbf{r})$ is the mass density in the system and the inertial terms were neglected. Equation (219) holds in the real system. In the idealized system there are two similar equations:

$$\nabla \cdot \underset{\sim}{T}^{I} + \rho^{I}\ \text{[illegible]} = 0 \qquad \nabla \cdot \underset{\sim}{T}^{II} + \rho^{II}\mathbf{f} = 0 \tag{220}$$

which hold in the model bulk phases (I) and (II), respectively, ρ^{I} and ρ^{II} are the mass densities in these model phases. By analogy with Eq. (193) one can express the mass density in the idealized system as

$$\bar{\rho} = \rho^{I}\theta(-\lambda) + \rho^{II}\theta(\lambda). \tag{221}$$

Our purpose here is to find the boundary conditions for Eqs. (220) at the dividing surface between the phases I and II in the idealized system. With this end in view let us consider an arbitrarily chosen parcel A of the dividing surface and a cylinder, built on it, as shown in Fig. 18. In fact, the cylindrical surface is a superposition of an infinite number of sectorial strips like the one shown in Fig. 17. The lower and upper bases, $\lambda = \lambda_1$ and $\lambda = \lambda_2$, of this cylinder are supposed to be far enough from the film (interfacial) region to satisfy the relationships

$$(\underset{\sim}{\mathbf{T}} - \overline{\underset{\sim}{\mathbf{T}}})_{\lambda=\lambda_1} = (\underset{\sim}{\mathbf{T}} - \overline{\underset{\sim}{\mathbf{T}}})_{\lambda=\lambda_2} = 0 \tag{222}$$

Then by means of the Gauss-Ostrogradsky theorem and Eqs. (193) and (221) one finds from Eqs. (219) and (220) that

$$\oint_{A_T} d\mathbf{s} \cdot (\underset{\sim}{\mathbf{T}} - \overline{\underset{\sim}{\mathbf{T}}}) - \int_A dA\mathbf{n} \cdot (\underset{\sim}{\mathbf{T}}^{I} - \underset{\sim}{\mathbf{T}}^{II})$$
$$+ \int_V dV(\rho - \bar{\rho})\mathbf{f} = 0 \tag{223}$$

where V is the volume of the cylinder and A_T is its total surface. In the curvilinear coordinates (192) the volume element dV has the form (see, e.g., Buff, 1956)

$$dV = \chi\, dA\, d\lambda, \qquad \chi = 1 - 2\lambda H + \lambda^2 K \tag{224}$$

Thus one obtains

$$\int_V dV(\rho - \bar{\rho})\mathbf{f} = \int_A dA\, \Gamma\hat{\mathbf{f}} \tag{225}$$

where by definition (Murphy, 1966)

$$\Gamma = \int_{\lambda_1}^{\lambda_2} (\rho - \bar{\rho})\chi\, d\lambda, \qquad \hat{\mathbf{f}} = \frac{1}{\Gamma}\int_{\lambda_1}^{\lambda_2} (\rho - \bar{\rho})\mathbf{f}\chi\, d\lambda \tag{226}$$

Obviously Γ has the meaning of mass adsorption at the film (interface). Besides, by means of Eqs. (222), (194), (195), and Green's theorem [see McConnell (1957), Chapter XIV] one obtains

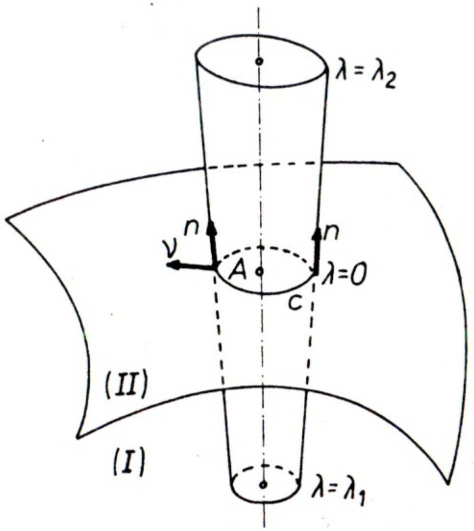

FIG. 18 Derivation of the balance of the linear momenta at the dividing surface between phases I and II. $\mathbf{n}$ and $\boldsymbol{\nu}$ are the running unit normals to the surface and to the contour C in the surface.

$$\oint_{A_T} d\mathbf{s} \cdot (\underset{\sim}{\mathbf{T}} - \overline{\underset{\sim}{\mathbf{T}}}) = \oint_C dl\boldsymbol{\nu} \cdot \underset{\sim}{\tau} = \int_A dA\, \nabla_{II} \cdot \underset{\sim}{\tau} \tag{227}$$

where C is the contour containing the area A, and ∇_{II} is the surface gradient operator (197). Then, the substitution of Eqs. (225) and (226) in Eq. (223) leads to

$$\nabla_{II} \cdot \underset{\sim}{\tau} - \mathbf{n} \cdot (\underset{\sim}{\mathbf{T}}^{I} - \underset{\sim}{\mathbf{T}}^{II})_{\lambda=0} + \Gamma\hat{\mathbf{f}} = 0 \tag{228}$$

which is the boundary condition sought for. Equation (228) (disregarding the inertial term) was derived by Scriven (1960) in a phenomenological way with purely tangential film stress tensor ($\underset{\sim}{\tau} \equiv \underset{\sim}{\tau}_{II}$).

For a static system $\underset{\sim}{\tau} = \underset{\sim}{\gamma}$ and Eq. (228) reduces to [cf. also Eq. (191)]

$$\nabla_{II} \cdot \underset{\sim}{\gamma} + (P^{I} - P^{II})\mathbf{n} + \Gamma\hat{\mathbf{f}} = 0 \tag{229}$$

Moreover, by means of Eq. (198) it can be proven that the balance of the angular momenta at the surface of tension in a static system leads to (Kralchevsky, 1987)

$$\gamma_{\alpha\beta} = \gamma_{\beta\alpha}, \qquad \alpha,\beta = 1,2 \qquad (\gamma_{\alpha\beta} = \mathbf{a}_\alpha \cdot \underset{\sim}{\gamma} \cdot \mathbf{a}_\beta) \tag{230}$$

and

$$\gamma_{\alpha 3} = \Gamma \mathbf{a}_\alpha \cdot \hat{\mathbf{f}}', \qquad \alpha = 1,2 \tag{231}$$

where

$$\hat{\mathbf{f}}' = \frac{1}{\Gamma} \int_{\lambda_1}^{\lambda_2} \mathbf{f}(\rho - \bar{\rho})\chi\lambda \, d\lambda \tag{232}$$

The absolute value of $\hat{\mathbf{f}}'$ is usually very small. Indeed, if $\mathbf{f}$ is the acceleration $\mathbf{g}$ due to gravity, then

$$\hat{\mathbf{f}}' = \mathbf{g}\delta \qquad \delta = \frac{1}{\Gamma}\int_{\lambda_1}^{\lambda_2} (\rho - \bar{\rho})\chi\lambda d\lambda \tag{233}$$

where δ is of the order of the distance between the surface of tension and the equimolecular dividing surface. For example, for the phase boundary air/water $\delta \approx 3 \times 10^{-8}$ cm, $\Gamma = \Delta\rho\delta$, $\Delta\rho = 10^3$ kg/m^3, and $|\hat{\mathbf{f}}' \Gamma| \approx 10^{-12}$ mN/m. In other words the right-hand side of Eq. (231) is usually negligible, and one can write almost exactly

$$\underset{\sim}{\boldsymbol{\gamma}} \cdot \mathbf{n} = 0 \tag{234}$$

or

$$\underset{\sim}{\boldsymbol{\gamma}} = \underset{\sim}{\boldsymbol{\gamma}}_{II} \tag{235}$$

Then from Eq. (207) one finds $\tau_{\alpha 3} \approx \tau_{\alpha 3}^{(v)}$ ($\alpha = 1,2$), i.e., these components of the surface stress tensor (202) have predominantly viscous nature. They could be due, for example, to an excess friction in the film (interfacial) region when molecules cross the film (interface).

The other condition for balance of the angular momentum (230) merely means that the tensor $\underset{\sim}{\boldsymbol{\gamma}}_{II}$ is symmetric. Its eigenvalues were denoted above by γ_1 and γ_2. Then by using Eq. (235) one can obtain the tangential and the normal projection of Eq. (229) with respect to the dividing surface:

$$\gamma_{\alpha\beta}{}^{,\beta} + \mathbf{a}_\alpha \cdot \hat{\mathbf{f}}\Gamma = 0 \tag{236}$$

$$c_1\gamma_1 + c_2\gamma_2 + (P^I - P^{II}) + \mathbf{n} \cdot \hat{\mathbf{f}}\Gamma = 0 \tag{237}$$

The latter equation is a generalized form of the Laplace equation, accounting for the weight of the film (interface). [Set $\gamma_1 = \gamma_2$ and $\Gamma = 0$ and then according to (59) the usual Laplace equation (97) is recovered from (237)].

We must emphasize that in a purely fluid interface or film there can be no shear stresses. In this case the tension γ is isotropic (i.e. $\underset{\sim}{\boldsymbol{\gamma}} = \gamma\underset{\sim}{\mathbf{U}}_{II}$ (where γ is a scalar). The tensor $\underset{\sim}{\boldsymbol{\gamma}}$ is not isotropic only when the interface has a shear elasticity ζ. This is the case of some lipid bilayers and biomembranes (Evans and Skalak, 1979). Then $\gamma_1 \neq \gamma_2 \neq \gamma$. As with the film tension γ, the shear elasticity ζ could be expressed through integrals over the components of the pressure tensor (Kralchevsky, 1987):

$$\zeta = \frac{1}{2}\int_{\lambda_1}^{\lambda_2} \underset{\sim}{\mathbf{q}} : (\underset{\sim}{\bar{\mathbf{P}}} - \underset{\sim}{\mathbf{P}})(1 - 2\lambda H + \lambda^2 K) d\lambda \tag{238}$$

cf. Eqs. (60) and (215). Then by analogy with Eq. (211) one finds

$$\zeta = \frac{1}{2}\,({}^0\underset{\sim}{\mathbf{T}} - {}^1\underset{\sim}{\mathbf{T}}\,2H + {}^2\underset{\sim}{\mathbf{T}}K) : \underset{\sim}{\mathbf{q}} \tag{239}$$

By making use of Eqs. (209) and (210) one easily obtains from Eq. (239) that at the surface of tension

$$\zeta = \frac{1}{2}(\gamma_1 - \gamma_2) \tag{240}$$

This result in conjunction with Eq. (212) shows that

$$\gamma_1 = \gamma + \zeta, \qquad \gamma_2 = \gamma - \zeta \tag{241}$$

and

$$\underset{\sim}{\boldsymbol{\gamma}}_{II} = \gamma\underset{\sim}{\mathbf{U}}_{II} + \zeta\underset{\sim}{\mathbf{q}} \tag{242}$$

(In view of Eq. (235) $\underset{\sim}{\boldsymbol{\gamma}}_{II}$ in the left hand side of Eq. (242) can be replaced by $\underset{\sim}{\boldsymbol{\gamma}}$.) Equation (242) represents the film (interfacial) tension tensor as a superposition of an isotropic and of a deviative part. When the deviative curvature D is zero, due to the symmetry of the system the deviative part of $\underset{\sim}{\boldsymbol{\gamma}}_{II}$ is also zero. If the film is not spherical (D is not identically zero), the film tension tensor can be considered (approximately) as isotropic only when $\zeta \ll \gamma$.

Equation (242) along with Eq. (235), is in fact a constitutive relation for the film tension tensor. The only restrictions used when deriving this relation are the conditions (1) and (2), which defining the film stress tensor and the surface of tension (see the beginning of this subsection).

It is important to note that up to here we did not use any assumptions about the form of the pressure tensor $\underset{\sim}{\mathbf{P}}$ in the <u>real</u> system. However, this does not mean that the behavior of the pressure tensor in the film (interfacial) region can be arbitrary. Indeed, the general condition (231) f balance of the angular momenta in the real and idealized systems and hence, its (approximate) corollary, Eq. (234), impose some restrictions on $\underset{\sim}{\mathbf{P}}$. By means of Eqs. (191), (208) and (234), the (approximate) necessary condition which must obey $\underset{\sim}{\mathbf{P}}$ can be written in the form

$$\int_{\lambda_1}^{\lambda_2} d\lambda\, \underset{\sim}{\mathbf{L}} \cdot \underset{\sim}{\mathbf{P}} \cdot \mathbf{n} = 0. \tag{243}$$

Some previous workers, e.g. Buff (1956), Buff and Saltsburg (1957), Buff (1960), and Murphy (1966), have used the representation

$$\underset{\sim}{\mathbf{P}} = \underset{\sim}{\mathbf{P}}_T + P_N \mathbf{n}\mathbf{n} \tag{244}$$

In Eq. (244) $\underset{\sim}{\mathbf{P}}_T$ is a surface tensor† ($\underset{\sim}{\mathbf{P}}_T \cdot \mathbf{n} = 0$) that has nonzero components only along each member of the family of parallel surfaces λ = const produced by Eq. (192). In fact, Eq. (244) is a model, which seems reasonable for an interface or when the film surfaces are parallel. Although Eq. (244) satisfies the condition (243), it cannot be applied when the film surfaces are not parallel, for example, when one deals with the transition region film-meniscus (Fig. 14) or when the so-called squeezing mode in the theory of the capillary waves (Chapter 8) is considered. In this respect Eq. (243) must be looked at as a generalization of Eq. (244).

C. The Detailed Approach for Films of Arbitrary Curvature

Equations of Motion and Boundary Conditions.

We will generalize here the equations derived in Section III.A by means of the method used in Section III.B. However, in contrast with Section III.B we will follow here the detailed approach, i.e., we will consider the film (in the idealized system) as a (curved) liquid layer with finite and variable thickness; the transition region film-meniscus is obviously a special case (see Fig. 14).

Let $\mathbf{R} = \mathbf{R}(u^1, u^2)$ be the equation of a reference surface, located somewhere inside the film; e.g., the surface of tension of the film could serve as a reference surface. Then let us introduce curvilinear coordinates in the space by means of Eq. (192). Further, let the equations of the dividing surfaces, which represent the film surfaces in the idealized system, be

$$\lambda = \bar{\zeta}(u^1,u^2) \qquad \text{and} \qquad \lambda = \tilde{\zeta}(u^1,u^2)$$

Here and hereafter the overbar and tilde denote quantities connected, respectively, with the lower and the upper film surface (Fig. 19). There must be three model bulk phases in the detailed approach and therefore one can express the mass density profile and the stress tensor in the idealized system as

$$\bar{\rho} = \begin{cases} \rho^I & \text{for } \lambda_1 < \lambda < \bar{\zeta}, \\ \rho^R & \text{for } \bar{\zeta} < \lambda < \tilde{\zeta}, \\ \rho^{II} & \text{for } \tilde{\zeta} < \lambda < \lambda_2, \end{cases} \qquad \overline{\underset{\sim}{\mathbf{T}}} = \begin{cases} \underset{\sim}{\mathbf{T}}^I & \text{for } \lambda_1 < \lambda < \bar{\zeta} \\ \underset{\sim}{\mathbf{T}}^R & \text{for } \bar{\zeta} < \lambda < \tilde{\zeta} \\ \underset{\sim}{\mathbf{T}}^{II} & \text{for } \tilde{\zeta} < \lambda < \lambda_2 \end{cases} \tag{245}$$

where the superscript R refers to the bulk (reference) phase inside the film. Equations (190) and (191) hold again, and they must be supplemented by analogous relationships for the reference phase:

$$\underset{\sim}{\mathbf{T}}^R = -\underset{\sim}{\mathbf{P}}^R + \underset{\sim}{\mathbf{Q}}, \qquad \underset{\sim}{\mathbf{P}}^R = P^R \underset{\sim}{\mathbf{U}} \tag{246}$$

where $\underset{\sim}{\mathbf{P}}^R$ and $\underset{\sim}{\mathbf{Q}}$ are the pressure and the viscous stress tensors in the reference phase.

The curvilinear coordinates (u^1,u^2) on the reference surface along with Eq. (192) generate curvilinear coordinates on the two film surfaces with basis vectors

$$\bar{\mathbf{a}}_\alpha = \frac{\partial}{\partial u^\alpha} \mathbf{r}[u^1,u^2, \bar{\zeta}(u^1,u^2)] \qquad \tilde{\mathbf{a}}_\alpha = \frac{\partial}{\partial u^\alpha} \mathbf{r}[u^1,u^2,\tilde{\zeta}(u^1,u^2)],$$
$$\alpha = 1,2 \tag{247}$$

Let us consider an elementary arc [illegible] ference surface and let ΔA_s be the corresponding sectorial [illegible] (see Fig. 19). The condition for equivalence between the real and idealized systems with respect to the force acting on the sectorial strip, applied to the lower ($\lambda_1 < \lambda < 0$) and to the upper ($0 < \lambda < \lambda_2$) parts of the system separately, provides the following equations, analogous to Eq. (194):

$$d\bar{l}\,\bar{\boldsymbol{\nu}} \cdot \bar{\underset{\sim}{\tau}} = dl\,\boldsymbol{\nu} \cdot \int_{\lambda_1}^{0} d\lambda\, \underset{\sim}{\mathbf{L}} \cdot (\underset{\sim}{\mathbf{T}} - \overline{\underset{\sim}{\mathbf{T}}}) \tag{248}$$

$$d\tilde{l}\,\tilde{\boldsymbol{\nu}} \cdot \tilde{\underset{\sim}{\tau}} = dl\,\boldsymbol{\nu} \cdot \int_{0}^{\lambda_2} d\lambda\, \underset{\sim}{\mathbf{L}}\, (\underset{\sim}{\mathbf{T}} - \overline{\underset{\sim}{\mathbf{T}}}) \tag{249}$$

where $d\bar{l}$ ($d\tilde{l}$) is the common arc of the lower (upper) film surface and the sectorial strip, and $\bar{\boldsymbol{\nu}}$ ($\tilde{\boldsymbol{\nu}}$) is the normal to this arc lying in the respective film surface. Equations (248) and (249) are definitions of the tensors of the film surface stress $\bar{\underset{\sim}{\tau}}$ and $\tilde{\underset{\sim}{\tau}}$, which, similarly to Eq. (207), can be represented as sums of an elastic and a viscous part.

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†The simplest case of transversally isotropic pressure tensor, $\underset{\sim}{\mathbf{P}}_T = P_T \underset{\sim}{\mathbf{U}}_{II}$, used by Buff (1956), Murphy (1966), and other authors, is possible only when the interface is spherical. Indeed, the transversal isotropy implies $p_{k1} = p_{k2}$ ($k = 1,2$) and thus one finds from Eq. (210) that $c_1 = c_2$.

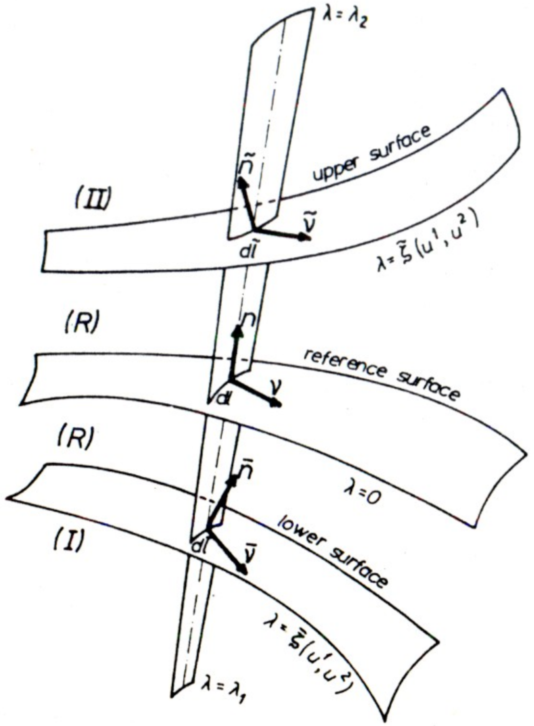

FIG. 19 A sectorial strip associated with a length element dl in the reference surface. $d\bar{l}$ and $d\tilde{l}$ are the common length elements of the sectorial strip with dividing surfaces representing the lower and upper film surfaces. $\mathbf{n}$, $\bar{\mathbf{n}}$, $\tilde{\mathbf{n}}$ and ν, $\bar{\nu}$, $\tilde{\nu}$ are unit normals to the corresponding surfaces or line elements.

If the inertial terms are negligible, the balances of the linear momenta in the real system and in the model bulk phases (I) and (II) are again given by Eqs. (219) and (220). The respective equation for the (reference) model bulk phase inside the film is

$$\nabla \cdot \underset{\sim}{\mathbf{T}}^R + \rho^R \mathbf{f} = 0 \tag{250}$$

Our purpose now is to find the boundary conditions that the solutions of Eqs. (220) and (250) must obey at the film surfaces $\lambda = \bar{\zeta}(u^1,u^2)$ (between the phases I and R) and $\lambda = \tilde{\zeta}(u^1,u^2)$ (between the phases R and II) in the idealized system. Then let A be an arbitrary parcel from the reference surface and let us consider a cylinder built on A, as shown in Fig. 20. The cylindrical surface, which is a superposition of sectorial strips like the one in Fig. 19, cuts two parcels, $\bar{A}$ and $\tilde{A}$, from the lower and the upper film surfaces. The bases $\lambda = \lambda_1$ and $\lambda = \lambda_2$ of the cylinder are thought to be far enough from the film for Eq. (222) to be satisfied. However, if the thickness of the film is small enough, the stress tensor in the real system $\underset{\sim}{\mathbf{T}}$ at $\lambda = 0$ will be different from the reference stress tensor $\underset{\sim}{\mathbf{T}}^R$, just like the normal component of the pressure tensor P_N does not coincide with the reference pressure at the surface of tension $r = r_0$ (see Section I.C). Therefore, in the general case at the dividing surface $\lambda = 0$ we have

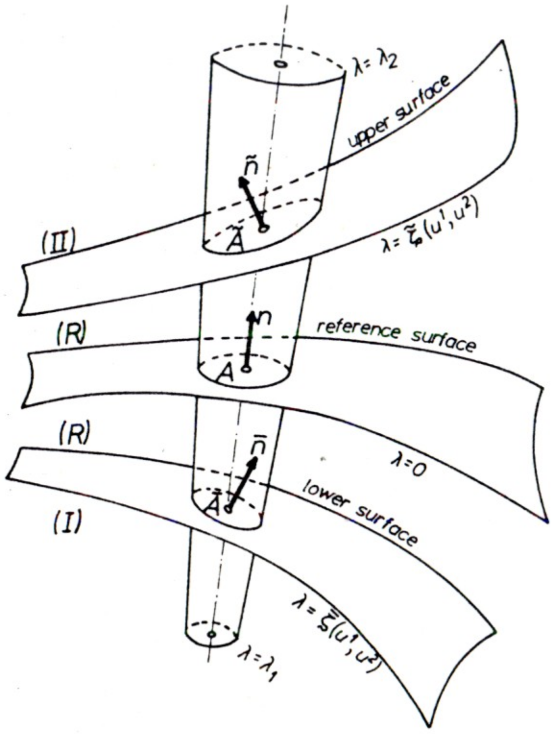

FIG. 20 A cylinder associated with the area A on the reference surface used for deriving the balances of momenta at the film surfaces (see the text). $\mathbf{n}$, $\bar{\mathbf{n}}$, and $\tilde{\mathbf{n}}$ are unit normals to the respective surfaces.

$$(\underset{\sim}{\mathbf{T}} - \overline{\underset{\sim}{\mathbf{T}}})_{\lambda=0} \neq 0 \tag{251}$$

Then using Eqs. (248) and (249) one can derive an analogue of Eq. (228) for each film surface by considering the lower ($\lambda_1 < \lambda < 0$) and the upper ($0 < \lambda < \lambda_2$) parts of the cylinder separately (Kralchevsky and Ivanov, 1987):

$$\bar{\nabla}_{II} \cdot \overline{\underset{\sim}{\tau}} - \bar{\mathbf{n}} \cdot (\underset{\sim}{\mathbf{T}}^I - \underset{\sim}{\mathbf{T}}^R)_{\lambda=\bar{\zeta}} - \Pi\sqrt{\frac{a}{\bar{a}}} + \bar{\Gamma}\bar{\mathbf{f}} = 0 \tag{252}$$

$$\tilde{\nabla}_{II} \cdot \tilde{\underset{\sim}{\tau}} \quad \tilde{\mathbf{n}} \cdot (\underset{\sim}{\mathbf{T}}^R - \underset{\sim}{\mathbf{T}}^{II})_{\lambda=\tilde{\zeta}} + \Pi\sqrt{\frac{a}{\tilde{a}}} + \tilde{\Gamma}\tilde{\mathbf{f}} = 0 \tag{253}$$

where $\bar{\mathbf{n}}$ and $\tilde{\mathbf{n}}$ are the unit normals and $\bar{\nabla}_{II}$ and $\tilde{\nabla}_{II}$ are the surface gradient operators for the lower and upper film surfaces:

$$\bar{\nabla}_{II} = \bar{\mathbf{a}}^{\alpha} \frac{\partial}{\partial u^{\alpha}}, \qquad \tilde{\nabla}_{II} = \tilde{\mathbf{a}}^{\alpha} \frac{\partial}{\partial u^{\alpha}} \tag{254}$$

[cf. Eqs. (197) and (247)]; also, similarly to Eq. (226)

$$\bar{\Gamma} = \sqrt{\frac{a}{\bar{a}}} \int_{\lambda_1}^{0} (\rho - \bar{\rho})\chi \, d\lambda, \qquad \bar{\mathbf{f}} = \frac{1}{\bar{\Gamma}} \sqrt{\frac{a}{\bar{a}}} \int_{\lambda_1}^{0} \mathbf{f}(\rho - \bar{\rho})\chi \, d\lambda$$

$$\tilde{\Gamma} = \sqrt{\frac{a}{\tilde{a}}} \int_{0}^{\lambda_2} (\rho - \bar{\rho})\chi \, d\lambda, \qquad \tilde{\mathbf{f}} = \frac{1}{\tilde{\Gamma}} \sqrt{\frac{a}{\tilde{a}}} \int_{0}^{\lambda_2} \mathbf{f}(\rho - \bar{\rho})\chi \, d\lambda$$

where a, $\bar{a}$, and $\tilde{a}$ are the determinants of the surface metrics at the reference, lower, and upper surfaces, respectively. The term with

$$\boldsymbol{\Pi} = \mathbf{n} \cdot (\bar{\underset{\sim}{\mathbf{T}}} - \underset{\sim}{\mathbf{T}})_{\lambda=0} \tag{255}$$

which is a consequence from the relationship Eq. (251), is the only term in Eq. (252) or (253) which has no analogue in Eq. (228). In fact, Eq. (255) is the most general definition of the disjoining pressure, which reveals the vectorial excess nature of this quantity. By means of Eqs. (189) and (246) it can be splitted into a hydrostatic $\boldsymbol{\Pi}^{s}$ and a viscous part, $\boldsymbol{\Pi}^{v}$:

$$\boldsymbol{\Pi} = \boldsymbol{\Pi}^{s} + \boldsymbol{\Pi}^{v}$$

$$\boldsymbol{\Pi}^{s} = \mathbf{n} \cdot (\underset{\sim}{\mathbf{P}} - P^{R}\underset{\sim}{\mathbf{U}})_{\lambda=0}, \quad \boldsymbol{\Pi}^{v} = \mathbf{n} \cdot (\bar{\underset{\sim}{\mathbf{Q}}} - \underset{\sim}{\mathbf{Q}})_{\lambda=0} \tag{256}$$

Obviously the disjoining pressure defined for a static system by Eq. (28) or by Eq. (168) coincides with Π^{s}.

Let us now consider some corollaries from Eqs. (252) and (253). For simplicity we will deal only with one of these equations, say Eq. (253). If the surface viscosity and the deviative part of $\tilde{\underset{\sim}{\tau}}$ are negligible (i.e., if the effect of the surface viscosity is not important), one can write approximately

$$\tilde{\underset{\sim}{\tau}} = \tilde{\sigma}\underset{\sim}{\mathbf{U}}_{II} \tag{257}$$

Then Eq. (253) reduces to

$$\tilde{\sigma}_{,\alpha} = -\tilde{\mathbf{a}}_{\alpha} \cdot \boldsymbol{\Pi} \sqrt{\frac{a}{\tilde{a}}} + \tilde{\mathbf{a}}_{\alpha} \cdot [(\underset{\sim}{\mathbf{Q}}^{R} - \underset{\sim}{\mathbf{Q}}^{II})_{\lambda=\tilde{\zeta}}] \cdot \tilde{\mathbf{n}} \tag{258}$$

(tangential projection)

$$2\tilde{H}\tilde{\sigma} - \tilde{\mathbf{n}} \cdot [(\underset{\sim}{\mathbf{Q}}^{R} - \underset{\sim}{\mathbf{Q}}^{II})_{\lambda=\tilde{\zeta}}] \cdot \tilde{\mathbf{n}} + (P^{R} - P^{II})_{\lambda=\tilde{\zeta}} + \tilde{\mathbf{n}} \cdot \boldsymbol{\Pi} \sqrt{\frac{a}{\tilde{a}}}$$

(normal projection) (259)

where the term proportional to the body force $\tilde{\mathbf{f}}$ was also neglected. For example, Eqs. (258) and (259) can be applied as boundary conditions for the surface of a spreading drop. In addition, one can prove (Kralchevsky, 1987) that

$$\sqrt{\frac{a}{\tilde{a}}} = \frac{(\mathbf{n} \cdot \tilde{\mathbf{n}})}{\chi(\tilde{\zeta})} \tag{260}$$

where $\chi(\lambda)$ is defined by Eq. (224).

For the transition region between a flat symmetrical film and the capillary meniscus (see Section III.A), the reference surface is the plane $z = 0$ in Fig. 14. Then $\chi \equiv 1$, $\sqrt{a/\tilde{a}} = \cos\varphi$, $\boldsymbol{\Pi} = \mathbf{n}\,\Pi$, and hence Eqs. (258) and (259) reduce to

$$\frac{d\tilde{\sigma}}{dx} = -\Pi \sin\varphi \cos\varphi + \tilde{\mathbf{a}}_{x} \cdot [(\underset{\sim}{\mathbf{Q}}^{R} - \underset{\sim}{\mathbf{Q}}^{II})_{z=z(x)}] \cdot \tilde{\mathbf{n}} \tag{261}$$

$$2\tilde{H}\tilde{\sigma} = P^{II} - P^{R} - \Pi \cos^{2}\varphi + \tilde{\mathbf{n}} \cdot [(\underset{\sim}{\mathbf{Q}}^{R} - \underset{\sim}{\mathbf{Q}}^{II})_{z=z(x)} \cdot \tilde{\mathbf{n}} \tag{262}$$

Having in mind that $2\tilde{H} = [\partial(x \sin\varphi)/\partial x]/x$ one can easily check that under static conditions, i.e., with $\underset{\sim}{\mathbf{Q}} \equiv 0$, Eqs. (261) and (262) are equivalent to Eqs. (171) and (172). More precisely, Eqs. (261) and (262) are the tangential and normal projections with respect to the film surface whereas Eqs. (172) and (171) are the horizontal and vertical projections of same vectorial equation.

In the case of a static spherical film (considered in Sections I.B and I.C), $\boldsymbol{\Pi}$ acts normally to the film surfaces and both sides of Eq. (258) are identically zero. The factor $\sqrt{a/\tilde{a}}$ is equal to r_0^2/r_2^2 [cf. Eq. (260)] and $\tilde{H} = 1/r_2$. Then Eq. (259) reduces to the second Eq. (26); the first Eq. (26) follows from Eq. (252).

In summary, the equations for mechanical equilibrium of a spherical film or of the transition-region film meniscus follow from Eqs. (252) and (253). These equations serve as boundary conditions at the film surfaces in the case of slow viscous flow.

By the end of this section we will discuss the connection between the approach described above, namely, the disjoining pressure approach, and the alternative body force approach (see, e.g., Felderhof (1968), Maldarelli et al. (1980), or Chapter 8 in this book). The difference between these two approaches lies in the choice of the idealized system modeling the same real system. In the body force approach another scalar pressure is introduced in the model bulk phases:

$$P_b^{k} = P^{k} - \rho^{k}W^{k}, \qquad k = I, II, R \tag{263}$$

where P^k (k = I,II,R) is the pressure in the disjoining pressure approach [cf. Eqs. (191) and (246)], ρ^k is the mass density, and W^k is the excess van der Waals potential in the respective bulk phases, also known as the body force potential. Then from Eqs. (190), (220), (250), and (263) one obtains the balance of the linear momenta in the following form:

$$\nabla P_b{}^k = \nabla \cdot \underset{\sim}{\mathbf{Q}}^k + \rho^k \mathbf{f} - \rho^k \nabla W^k, \qquad k = \mathrm{I,II,R} \tag{264}$$

One sees that in Eqs. (263) and (264) the contribution of the van der Waals interaction due to the presence of a thin film in the system is considered separately as an additional body force. The subtraction of Eq. (264) from Eq. (219), in view of Eq. (189), leads to the equation

$$\rho^k \nabla W^k = \nabla \cdot [(\underset{\sim}{\mathbf{P}} - P_b{}^k \underset{\sim}{\mathbf{U}}) - (\underset{\sim}{\mathbf{Q}} - \underset{\sim}{\mathbf{Q}}^k)] + (\rho - \rho^k)\mathbf{f},$$
$$k = \mathrm{I,II,R}$$

which reveals the excess nature of the body force potential W^k. The following model expression for W^k is used in practice (Maldarelli et al., 1980):

$$W^k(\mathbf{r},t) = \int_{\substack{\text{real}\\ \text{system}}} w(|\mathbf{r} - \mathbf{r}'|^{1/2})\rho(\mathbf{r}',t)\, d\mathbf{r}' - \int_{\substack{\text{infinite}\\ \text{phase (k)}}} w(|\mathbf{r} - \mathbf{r}'|^{1/2})\rho^k(\mathbf{r}',t)\, d\mathbf{r}', \qquad k = \mathrm{I,II,R} \tag{265}$$

where the radius vector $\mathbf{r}$ is located in the phase (k) of the idealized system, t represents time, $\rho(\mathbf{r}',t)$ is the mass density at the source point $\mathbf{r}'$, and $w(r)$ is the intermolecular potential divided by the masses (per molecule) of the molecules located at $\mathbf{r}$ and $\mathbf{r}'$. It is clear that Eq. (265) defines three different functions, W^{I}, W^{II}, and W^{R}, which are not bound to match at the dividing surfaces. The boundary conditions at these surfaces, say the upper film surface, can be obtained from Eqs. (259) and (263). Thus, for a flat reference surface one obtains

$$2\tilde{H}\tilde{\sigma} - \tilde{\mathbf{n}} \cdot [(\underset{\sim}{\mathbf{Q}}^{\mathrm{R}} - \underset{\sim}{\mathbf{Q}}^{\mathrm{II}})_{\lambda=\tilde{\zeta}}] \cdot \tilde{\mathbf{n}} + (P_b{}^{\mathrm{R}} - P_b{}^{\mathrm{II}})_{\lambda=\tilde{\zeta}}$$
$$+ (\rho^{\mathrm{R}}W^{\mathrm{R}} - \rho^{\mathrm{II}}W^{\mathrm{II}})_{\lambda=\tilde{\zeta}} + \tilde{\mathbf{n}} \cdot \Pi = 0 \tag{266}$$

For a static flat thin film Eq. (266) reduces to

$$(P_b{}^{\mathrm{II}} - P_b{}^{\mathrm{R}})_{\lambda=\tilde{\zeta}} = \Pi - (\rho^{\mathrm{II}}W^{\mathrm{II}} - \rho^{\mathrm{R}}W^{\mathrm{R}})_{\lambda=\tilde{\zeta}} \tag{267}$$

As pointed out by Maldarelli et al. (1980) the equation

$$\Pi = (\rho^{\mathrm{II}}W^{\mathrm{II}} - \rho^{\mathrm{R}}W^{\mathrm{R}})_{\lambda=\tilde{\zeta}} \tag{268}$$

according to Eq. (265) can serve as a model expression for the disjoining pressure Π. Then Eq. (267) leads to the following simple boundary condition for the pressure in the body force approach (Maldarelli et al. 1980):

$$P_b{}^{\mathrm{II}} = P_b{}^{\mathrm{R}} \qquad \text{(upper film surface)} \tag{269}$$

the boundary condition at the lower film surface is analogous. In return, the balance of momenta (264) is more complicated in the body force approach than in the disjoining pressure approach. Besides, when the film surfaces are not parallel, the boundary conditions in the body force approach [cf. Eq. (266)] are more complicated. This is probably due to the fact that the single scalar parameter W^k can hardly make up for the tensorial pressure around the film in the real system.

In conclusion, there is no contradiction between the disjoining pressure and the body force approach. The disjoining pressure approach has the advantage of enabling us to derive the macroscopic theory of the curved thin films in a general form without making any model assumptions or simplifications from the very beginning, which is unavoidable in the body force approach.

NOTATION

$a_{\alpha\beta}$	surface metric tensor
$\mathbf{a}_\alpha$	vector of the local surface basis, Eq. (160)
A	area of a surface
A_0	area of the surface of tension
$\underset{\sim}{\mathbf{b}}, b_{\alpha\beta}$	curvature tensor and its components
B	bending moment, Eq. (58)
$\bar{B}$	dimensionless bending moment, Eq. (69)
c_1, c_2	principal curvatures of surface
D	deviative curvature, Eq. (59)
$\mathbf{f}$	external force per unit mass, Eq. (219)
F_m	see Eq. (144)
F_b	buoyancy force, Eq. (144)
$\mathbf{g}$	acceleration due to gravity

h	film thickness
H	mean curvature, Eq. (59)
k	Boltzmann's constant
K	gaussian curvature
$\underset{\sim}{\mathbf{L}}$	tensor defined by Eq. (195)
L	length of a line phase, Eq. (96)
n_i	numerical density of the ith component
$\mathbf{n}$	unit normal to a surface
N_i	number of the molecules of the ith component
p_{k1}, p_{k2}	eigenvalues of the tensors ${}^k\underset{\sim}{\mathbf{T}}$, Eq. (204)
$\underset{\sim}{\mathbf{P}}$	pressure tensor
P	isotropic pressure in a bulk phase
P_c	capillary pressure
P_N, P_T	eigenvalues of the pressure tensor
$\underset{\sim}{\mathbf{q}}, q_{\alpha\beta}$	curvature deviatoric tensor, Eq. (215), and its components
$\underset{\sim}{\mathbf{Q}}$	tensor of viscous stress, Eq. (189)
$\mathbf{r}$	radius vector of a point in space
r_0	radius of the surface of tension
r_1, r_2	radii of the surfaces of tension for the film surfaces
r_{1m}, r_{2m}	radii of the surfaces of minimum tension
r_c	radius of a contact line
r_x	radius of an arbitrarily chosen dividing surface
r_{1x}, r_{2x}	radii of arbitrarily chosen dividing surfaces in the detailed approach
$\mathbf{R}$	radius vector of a point of the dividing surface
s^f	surface excess entropy per unit area of the film
s_v	bulk density of the entropy
S	entropy
T	temperature
$\underset{\sim}{\mathbf{T}}$	total stress tensor
${}^k\underset{\sim}{\mathbf{T}}$	tensors, defined by means of Eq. (204)
u^1, u^2	surface curvilinear coordinates
u^f	surface excess internal energy per unit area of the film
U	internal energy
$\underset{\sim}{\mathbf{U}}_{II}$	surface idemfactor
V	volume
w^f	mechanical work per unit area of the film, Eq. (58)
W	mechanical work, Eq. (48)
W^f	mechanical work for deformation of the film, Eqs. (50) and (154)

α	dilation parameter, Eqs. (58) and (151)
γ	scalar film (interfacial) tension [see Eq. (212)]
$\underset{\sim}{\boldsymbol{\gamma}}$	tensor of the film (interfacial) tension, Eq. (208)
$\underset{\sim}{\boldsymbol{\gamma}}_{II}$	tangential part, $\underset{\sim}{\boldsymbol{\gamma}} \cdot \underset{\sim}{\mathbf{U}}_{II}$, of the tensor $\underset{\sim}{\boldsymbol{\gamma}}$
γ_1, γ_2	eigenvalues of $\underset{\sim}{\boldsymbol{\gamma}}_{II}$
Γ_i	adsorption of the ith component, Eq. (103)
Γ	total mass adsorption, Eq. (226)
δ	see Eq. (233)
ζ	deviative coefficient of $\underset{\sim}{\boldsymbol{\gamma}}_{II}$
η	infinitesimal normal displacement of a surface, Eq. (162)
$\theta(x)$	stepwise function of Heaviside, Eq. (7)
Θ	torsion moment
κ	line tension, Eq. (96)
$\tilde{\kappa}_1, \tilde{\kappa}_2$	line tensions in the detailed approach, Eq. (137)
λ	distance parameter along the normal to a surface, Eq. (192)
μ_i	chemical potential of the ith component
$\boldsymbol{\nu}$	unit normal to a curve in a surface; $\boldsymbol{\nu}$ is tangential to the surface
$\boldsymbol{\xi}$	infinitesimal tangential displacement of a surface, Eq. (162)
Π	disjoining pressure, Eq. (25)
$\boldsymbol{\Pi}$	vector of disjoining pressure, Eqs. (28) and (255)
$\boldsymbol{\Pi}^s$	hydrostatic part of the disjoining pressure, Eq. (256)
$\boldsymbol{\Pi}^v$	viscous part of the disjoining pressure, Eq. (256)
ρ	mass density, Eq. (219)
σ	surface tension
σ_1, σ_2	surface tensions of film surfaces
τ	transversal tension, Eqs. (137) and (188)
$\underset{\sim}{\boldsymbol{\tau}}$	film stress tensor, Eq. (199)
$\underset{\sim}{\boldsymbol{\tau}}_{II}$	tangential part, $\underset{\sim}{\boldsymbol{\tau}} \cdot \underset{\sim}{\mathbf{U}}_{II}$, of the tensor $\underset{\sim}{\boldsymbol{\tau}}$
$\underset{\sim}{\boldsymbol{\tau}}^{(v)}$	viscous part of $\underset{\sim}{\boldsymbol{\tau}}$, Eq. (208)
$\varphi(x)$	running slope angle, Eq. (170)
$\underset{\sim}{\boldsymbol{\Phi}}$	tensor of deformation, Eq. (48)
χ	scaling factor, Eq. (224)
ψ	azimuthal angle, Eq. (169)
ψ_c	boundary slope angle, Eq. (145)
ω^f	film excess grand potential per unit area, Eq. (149)
Ω	grand thermodynamical potential, Eq. (139)
Ω^f	grand potential of the film, Eq. (150)
∇	space gradient operator
∇_{II}	surface gradient operator, Eq. (197)

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