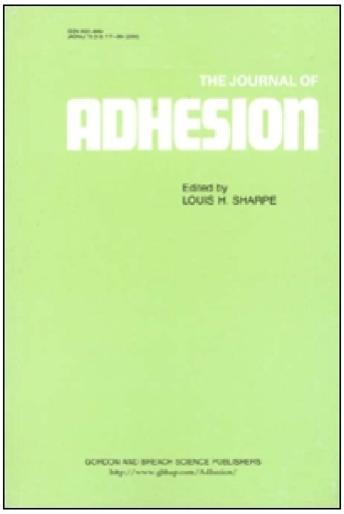

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STABILITY OF THE LENSLIKE LIQUID THICKENING (THE DROP) ON A SOLID SUBSTRATE

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The quasi equilibrium of a liquid lens or a liquid drop on a solid substrate is considered on the basis of the thermodynamics of microscopic thin liquid films. Both contact angles, corresponding to the membrane model and to the finite thickness layer convention of the film, have been derived as a function of the disjoining pressure isotherm. The analytical expressions for the line tension terms have been obtained, and the criterion for the stability of a liquid drop on a solid substrate has been proposed.

Keywords: Contact angle; Contact line; Line tension; Wetting; Spreading

INTRODUCTION

The thermodynamics of the three-phase system consisting of a small wetting liquid drop (phase α) in contact with a solid substrate inside a fluid phase β (Figure 1) represents the background for the description of wetting phenomena. The mechanical equilibrium of this system is commonly described by the modified Young equation,

$$\gamma_{\alpha\beta}\cos\theta = \gamma_{s\alpha} - \gamma_{s\beta} + \frac{\kappa}{r_d}, \tag{1}$$

where $\gamma_{\alpha\beta}, \gamma_{s\alpha},$ and $\gamma_{s\beta}$ are the interfacial tensions of the corresponding interfaces; r_d is the radius of the three phase contact line; θ is the contact angle; and κ is the tension acting along the contact line.

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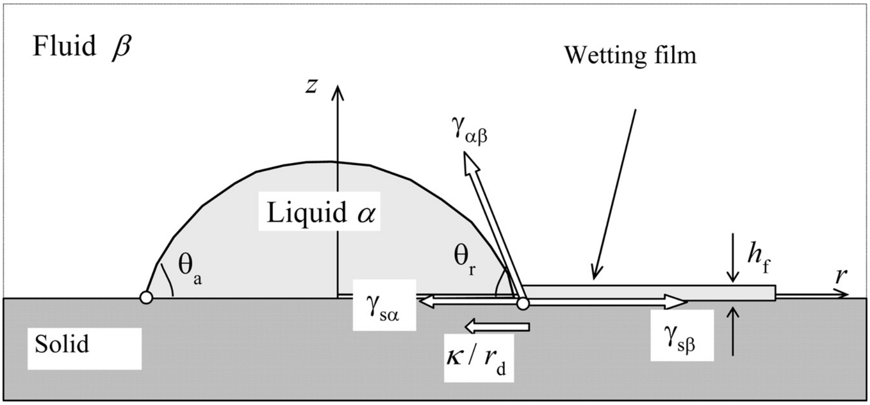

FIGURE 1 The closed thermodynamic system, including a wetting liquid drop (the phase α) on a solid substrate inside a fluid phase β (for explanation see the text).

The experimental estimation of the line tension term, κ, may be obtained from the dependence of the contact angle, θ, on the radius, r_d, of the contact line [1–6]. The contact angle θ depends on the thickness, h_f, of the wetting layer in the vicinity of the drop that is used to describe the adsorption effects on solid substrates and to characterize the surface forces (disjoining pressure) acting between solid and liquid phases (Figure 2) [7]. In two extreme wetting–dewetting experimental situations represented schematically as the left and the right sides of the drop, these contact angles are designated as advancing θ_a and

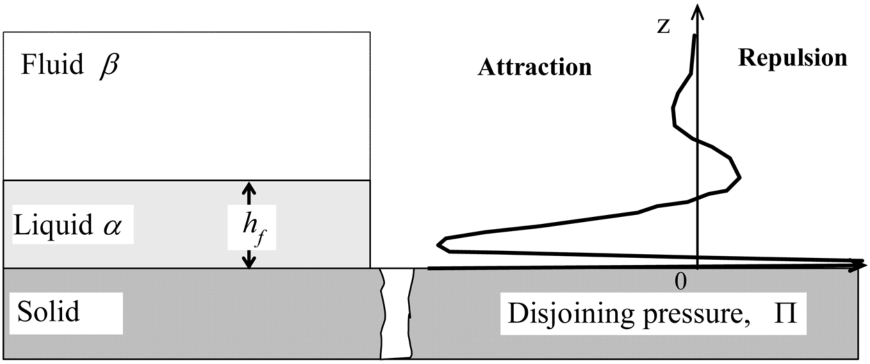

FIGURE 2 Wetting liquid layer thickness in comparison with the shape of the disjoining pressure isotherm, $\Pi(h)$.

receding θ_r contact angles. So, the contact angle measurements provide us with precious information concerning the surface forces and the structure of wetting layers. The contribution of Prof. A. W. Neumann and coworkers to the development of the experimental methods of contact angle and interfacial tension measurements, as well as to the theory of the wetting phenomena, is well known and appreciated by colloid scientists [8–13].

A rigorous thermodynamic description of the equilibrium of a wetting drop at a solid substrate supposes that the parameters of Equation (1) such as θ, κ, and $\Delta\gamma_s = \gamma_{s\alpha} - \gamma_{s\beta}$ could be unambiguously and simultaneously expressed as a function of the disjoining pressure, $\Pi(h)$, acting in a thin liquid layer between the solid and the fluid phase β (Figure 2). This approach was applied for the first time by de Feijter and Vrij to the case of symmetrical circular liquid (foam) films [14] and later on was developed and generalized to the case of microscopic thin liquid films and layers in [15–19]. The originality of this approach consists of constructing the liquid drop profile, $z(r)$, on the basis of the system of equations thats consists of the fundamental thermodynamic equation and the Gibbs-Duhem equation for the liquid films, which leads to the equation [14, 20–22]

$$\Delta\Omega(h_f) = \gamma_{\alpha\beta}(\cos\theta - 1) - \frac{\kappa}{r_d}, \tag{2}$$

where

$$\Delta\Omega(\mathrm{h}) = \int_h^\infty \Pi(z)dz \tag{3}$$

is the interaction free energy (the interaction grand thermodynamic potential) of a thin liquid layer of thickness h, and $\Pi(h)$ is the disjoining pressure isotherm. As has been shown in Babak [18, 19, 23], the line tension κ value and sign contain information about the shape of the disjoining pressure isotherm $\Pi(h)$. In its turn, the value of the $\Delta\Omega(h)$ may be negative, positive or zero depending on the profile of the isotherm $\Pi(h)$. For the simplified isotherm $\Pi(h)$ represented in Figure 2, the value $\Delta\Omega(h)$ is negative, which corresponds to finite contact angles θ. The contact angle θ, being a function of $\Delta\Omega(h_f)$, contains the information of this integral function of the interfacial forces.

It should be pointed out that, in the frame of this approach, the difference of interfacial tensions,

$$\Delta\gamma_s = \gamma_{s\alpha} - \gamma_{s\beta} = \Delta\Omega(h_f) + \gamma_{\alpha\beta} - \frac{\kappa}{r_d}, \tag{4}$$

is considered as the tension of the liquid layer $(s - \alpha - \beta)$ [24] by analogy with the tension of symmetrical thin liquid films (membranes) [25]. Remember that the modified Young Dupré equation is presented now as

$$W_a = \gamma_{\alpha\beta} + \gamma_{s\alpha} - \gamma_{s\beta} = \gamma_{\alpha\beta}(1 + \cos\theta) - \frac{\kappa}{r_d}, \tag{5}$$

where W_a is the work of adhesion of the liquid phase α to the solid substrate in the fluid medium β. This work relates to the interaction grand thermodynamic potential $\Delta\Omega(h_f)$ by the equation

$$W_a = 2\gamma_{\alpha\beta} + \Delta\Omega(h_f). \tag{6}$$

It must be pointed out that the wetting drop at a solid substrate is principally a nonequilibrium thermodynamic system (Figure 3). In the simplest case of a two-component system, *e.g.*, water (component 1) and oil (component 2), where the components are mutually nonsoluble or poorly soluble and constitute the phases α and β, respectively, the energy of adsorption of water molecules to a solid surface will be greater than that of the oil molecules. According to Rowlinson and Widom [26], the formation of a thin layer of component 1 on the solid surface is thermodynamically favorable and inevitable in the long time. Moreover, because of the capillary effect, the chemical potential of water molecules inside the drop will always be greater with regard to that of the water molecules localized in the flat layer. According to the

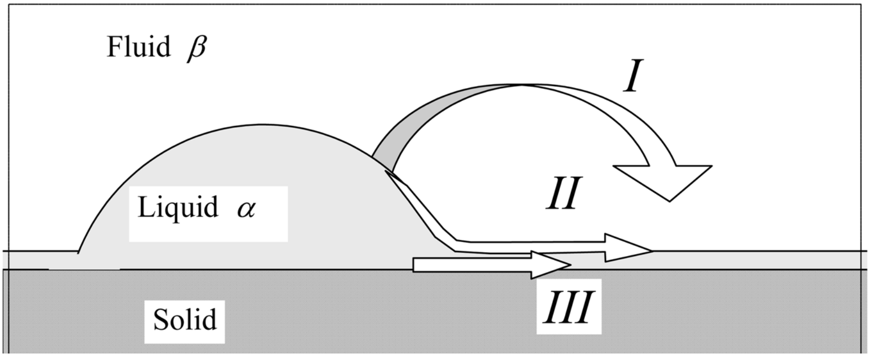

FIGURE 3 The system of a liquid drop with its thin wetting layer on a solid substrate is thermodynamically unstable. The mass transfer of the drop is realized by three possible paths: (I) dissolution (evaporation) and adsorption (condensation), (II) interfacial diffusion or flow, and (III) hydrodynamic flow.

Gibbs-Kelvin effect, the mass of the drop has the tendency to diminish and disappear by transforming into a flat layer (Figure 4).

Three main paths of the mass transport from the water drop are schematically shown in Figure 3. The first possible path (I) consists of the dissolution (evaporation) of water molecules and in the consequent adsorption (condensation) into the flat solid surface by the mechanism of bulk diffusion. The second way (II) is interfacial diffusion or interfacial flow. The third path (III) could be hydrodynamic flow or bulk diffusion inside the water layer. The relative contributions of different paths to the rate of disappearing of the drop depend on the characteristic times, τ_I, of these mechanisms, depending on the physico-chemical parameters. In the case of insoluble components we may neglect the first path (I) with regard to other ones. In their turns, the times τ_{II} and τ_{III} will decrease with decreasing contact angle, θ, *i.e.*, with increasing the difference between the energies of adsorption of water and oil molecules at the solid substrate.

For the so-called thin (Newtonian) layers, the rate of hydrodynamic and diffusion processes is very slow, and all these times τ_i will be much higher than the laboratory time, τ_{lab}. For this reason, the drop may be considered as being in quasi equilibrium with the thin liquid layer at the solid surface. This corresponds to mechanical and thermal equilibria of the drop, excepting for the chemical equilibrium, which is not established and justifies the application of the classical thermodynamics to this system. Otherwise, in the case where $\tau_i \sim \tau_{lab}$, one must

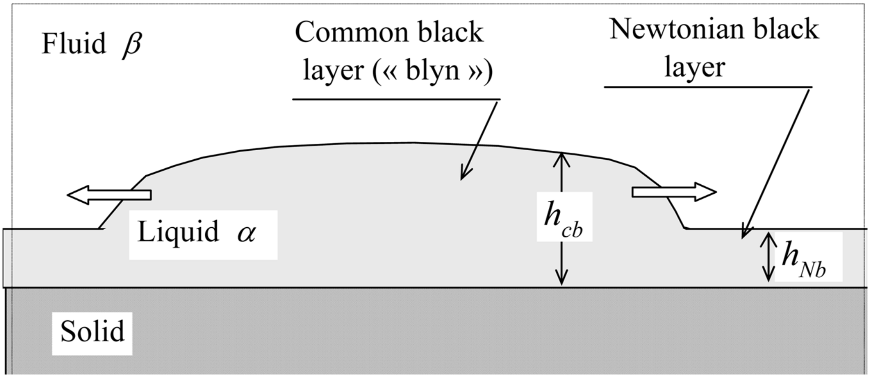

FIGURE 4 The wetting drop, after having been diminished down to its critical volume, spontaneously transforms into a thin liquid layer (the common black layer) having the form of a "blyn" (a "pancake") and a thickness, h_{cb}, that spreads over the Newtonian black layer of thickness h_{Nb}.

apply the methods of nonequilibrium thermodynamics [27], which are not considered in this article.

The final act of the diffusion scenario of the liquid drop disappearing process is its spontaneous transformation into some thicker thin liquid layer (the so-called common black film) after having achieved some critical volume (Figure 4). The possibility of the formation of this thicker layer (designated as "blyn" or "pancake" [28, 29] being in quasi equilibrium with an already formed thin wetting layer (Newtonian black film) was considered by us earlier [21]. In this article this mechanism is discussed in more detail.

The aim of this article is to give more insight into the thermodynamics of the equilibrium of a wetting liquid drop at a solid substrate.

THE INVARIANT FOR CIRCULAR LIQUID FILMS AND LAYERS

Consider a closed thermodynamic system (Figure 5a) consisting of a wetting liquid drop (the phase α) in quasi equilibrium with a liquid layer at an infinite solid surface inside a fluid medium (the phase β). For example, this could be a sessile water drop deposited on a hydrophilic surface (*e.g.*, quartz, mica sheet, *etc.*) inside an organic liquid (heptane, dichloromethane, *etc.*). Assume that the rates of the mass transports indicated in Figure 3 are so slow that they allows us to consider the system as being in mechanical and thermal equilibrium.

We must admit that the flagrant similarity exists between this system and another thermodynamic system (Figure 5b) which is formed by a big drop (the fluid phase β) brought into contact with a solid substrate and capturing a small lenslike thickening (the dimple) of the liquid phase α in contact with this solid surface. The thermodynamic

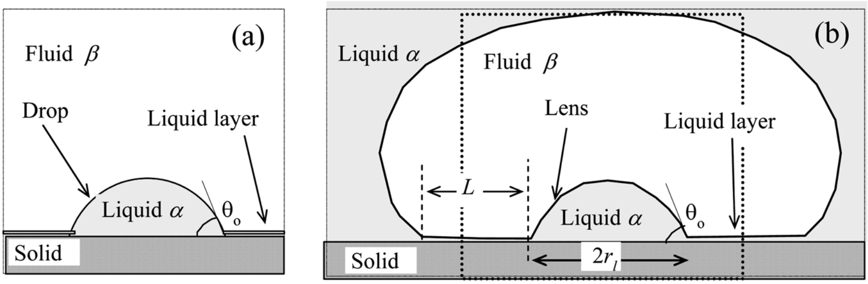

FIGURE 5 Scheme illustrating the similarity between the equilibrium conditions of (a) a liquid drop and (b) a dimple (a lenslike thickening) formed between a big fluid drop (phase β) and a solid substrate.

equivalence between these systems is accentuated when the size of the big fluid drop β tends to be much higher than that of the dimple ($L \gg r_l$) and the time of the observation tends to infinity for the drop in Figure 5a. In both cases, the liquid drop and the liquid lens form the contact angle θ_o with the solid plane.

Taking into account this geometrical and thermodynamic equivalence between the drop and the lens, we move our attention to the lens and consider in more detail the region adjacent to the three-phase contact line of the lens (Figure 6a). We always assume that $L \gg r_l$, although for the sake of commodity of the exposition this scale is not respected in Figure 6a. The surface forces acting inside the transition region of the lens (or the drop) may be characterized by the disjoining pressure isotherm $\Pi(z)$ (Figure 6b). For simplicity consider only the molecular (Van der Waals) attractive (negative) component (without DL electrical repulsion), which is characterized by only one deep coagulation minimum $-\Pi_{\min}$. The thickness of the thin liquid layer designated as h_f in the general case depends on the coordinate r. The steric repulsion due to hydration or surfactant adsorption layers of thickness h_f is responsible for the positive branch of the isotherm $\Pi(z)$ appearing when $z \to h_f$.

The real profile of the lens (the drop) z(r) (Figure 1a) is smooth without any inflections, which could be identified as the contact line or the contact angle. In the region distant from the transition zone inside the lens, where the surface forces are zero, the shape of the lens is spherical of radius R_l (for simplicity we neglect the exterior gravity force, or consider the special case $R_l \operatorname{tg} \theta_0 \ll a_c$, where $a_c = \sqrt{\Delta\rho g/\sigma_0}$ is the characteristic capillary length (the capillary constant), $\Delta\rho$ is the density difference of the phases α and β, g is the gravity constant, and σ_0 is the interfacial (surface) tension of a free (noninteracting dividing surface). We assume that the general curvature $k_l^o = -2/R_l$ of the lens, as well as the interfacial tension, σ_0, may be measured experimentally with a sufficient precision. The general curvature of the lens, k_l^o, is conventionally considered as negative in accordance with the chosen system of coordinates and the definition of the slope angle, φ (Figure 1a),

$$\frac{dz}{dr} = -\tan\varphi. \tag{7}$$

In the transition zone, the general curvature of the lens, $k_l = k_1 + k_2$ ceases to be constant. The first k_1 and the second k_2 main curvatures of the lens are equal, respectively, to

$$k_1 = \frac{d\sin\varphi}{dr} \quad \text{and} \quad k_2 = \frac{\sin\varphi}{r}. \tag{8}$$

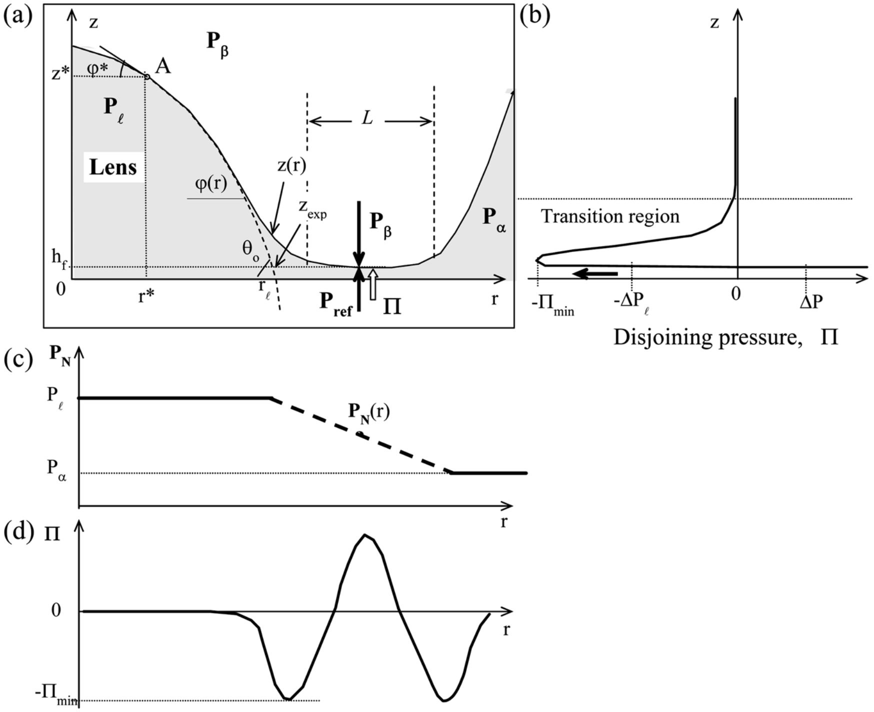

FIGURE 6 The profile, z(r), of a liquid lens (drop) in comparison with the disjoining pressure isotherm. (a) The profile, z(r), of a liquid lens differs from the experimental profile, $z_{exp}(r)$, which intersects the plane $z = 0$ at $r = r_l$ (the radius of the so-called contact line) under the contact angle, θ_o. (b) The profile of the disjoining pressure, $\Pi(z)$, in the transition region of the film (for simplicity, the repulsive DL component of the disjoining pressure is not considered). (c) The hydrostatic pressure inside the lens, P_l, is greater than P_α of the exterior phase, α; the normal component of the hydrostatic pressure inside the liquid film, P_N, is unknown (the same uncertainty exists in the case of the precursor wetting film). One may try to present this pressure as some monotonically decreasing function, $P_f(r)$. (d) The disjoining pressure, $\Pi(r)$, inside the film is characterized by two minima and a maximum, being zero inside the lens and in the exterior phase, α.

With increasing r, the second main curvature k_2 always remains positive and decreasing by its absolute value, whereas the first main curvature, k_1 changes sign from positive to negative to vanish in the "flat" region of the film.

The main difficulty in the thermodynamic description of the system lens–liquid–layer is the lack of an unambiguous definition (in terms of the two–dividing–surfaces convention of thin liquid films) of the reference system and the reference hydrostatic pressure for the layer according to the Gibbs method of excesses. This means that to make it possible to define the disjoining pressure inside the thin liquid layer one needs the reference phase and the reference pressure for the liquid layer [14, 21, 30].

In the case of circular liquid layers, for example, that formed by a big fluid drop of the phase β in contact with a flat solid surface and in the absence of the lens (Figure 6a), the reference pressure, P_{ref}, for this liquid layer is usually chosen as the constant hydrostatic pressure, P_α, of the liquid phase α outside of the big drop from which this liquid layer is made. So, by this convention, the disjoining pressure, Π, inside the flat film equilibrates the difference between the pressures P_β (inside the big drop) and P_α (outside of the big drop), according to the well-known Derjaguin mechanical equilibrium equation for thin liquid films and layers [25],

$$\Pi(h_f) = P_\beta - P_\alpha. \tag{9}$$

We should point out that the hydrostatic pressure inside the liquid layer is understood as the normal component, P_N, of the hydrostatic pressure acting on the flat dividing surface of the layer. Remember that the tangential component, $P_T(\mathrm{z})$, of the hydrostatic pressure inside the liquid layer is used to define the interfacial tension, σ_f, of the liquid layer of thickness, h_f [17, 22]:

$$\sigma_f = \int_0^{h_f} [P_\alpha - P_T(z)]dz + \int_{h_f}^{\infty} [P_\beta - P_T(z)]dz. \tag{10}$$

However, this method cannot be applied to the case of the liquid lens (the drop) existing in the center of the contact area of the big drop with the solid surface. The convention that the reference pressure is constant and equal to P_α is not productive, as it contradicts the fact that inside the lens the hydrostatic pressure is equal to P_l, which is obviously greater than the hydrostatic pressure, P_ℓ. So, the definition of the disjoining pressure according to Equation (9) is not valid to describe the equilibrium of the liquid layer in the vicinity of the lens. The same problem arises for the liquid drop in equilibrium with a wetting precursor film or without this film. One needs another definition of the disjoining pressure which would be more convenient to our case.

One possible way to the thermodynamic description of the transition region of the liquid layer at the boundary with the lens has been suggested in Babak [21]. According to this method, the reference pressure, P_{ref}, which one needs to describe the equilibrium of the liquid layer, is assumed to be not constant but varies from the minimal value, P_α, outside of the big fluid drop to the maximal value, P_l, inside the lens. The simplest function, $P_{ref}(\mathrm{r})$, which one can use for this purpose, is the linear function (Figure 6c)

$$P_{ref}(\mathrm{r}) \equiv P_l + (r - r_l)\nabla_r P_N. \tag{11}$$

The disjoining pressure inside the liquid layer now may be defined as

$$\Pi(r) = P_\beta - P_{ref}(\mathrm{r}) \cong P_\beta - P_l + (r - r_l)\nabla_r P_N, \tag{12}$$

where $\nabla_r P_N = dP_N(r)/dr \cong \left(P_\alpha - P_\beta\right)/(L - r_l) < 0$ is the gradient of the normal component of the hydrostatic pressure inside the whole liquid layer. The component $\mathrm{P_N}$ is understood as the local hydrostatic pressure, which acts in the liquid layer in the direction of the normal to the dividing surface. The graphic of the disjoining pressure $\Pi(r)$ inside the liquid layer is schematically represented in Figure 6d.

We should point out that in the case when the radius r_l of the lens is much less than the radius of the liquid layer, L, *i.e.*, $r_l \ll L$, one can neglect the gradient $\nabla_r P_N$ that allows us to use the hydrostatic pressure, P_l, inside the lens (the drop) as the reference pressure for the liquid layer,

$$P_{ref} \cong P_l, \tag{13}$$

$$\Pi(r) \cong P_\beta - P_l. \tag{14}$$

The real profile of the layer $\mathrm{z(r) = h(r)}$, including the profile of the lens itself (Figure 1a), can be described by the system of equations [17–19], consisting of the geometrical one Equation (7); the Gibbs-Duhem equation,

$$\Pi(\mathrm{z}) = -\left.\frac{\partial \sigma(z)}{\partial z}\right|_{T,\mu_i,A}, \tag{15}$$

where $\sigma(\mathrm{z})$ is the interfacial tension of the liquid layer surface; and the mechanical equilibrium equation

$$\sigma(z)\left[\frac{d \sin\varphi(z)}{dr} + \frac{\sin\varphi(z)}{r}\right] - \Pi(z)\cos\varphi(z) - \Delta \mathrm{P}_f(\mathrm{r}) = 0, \tag{16}$$

where

$$\Delta P_f(\mathrm{r}) = P_{ref}(\mathrm{r}) - P_\beta. \tag{17}$$

In spite of the ambiguity of the definition of the reference pressure inside the liquid layer, it seems possible to draw some conclusions concerning the profile z(r) of the lens in the transition region of the liquid layer. Let us simplify the equilibrium Equation (16) in different characteristic regions of the *lens–layer* system.

Relatively far away from the lens the liquid layer is almost flat and has the local contact angle $\varphi \cong 0$. This allows us to neglect the first term in Equation (16) and to put $\cos\varphi \cong 1$,

$$\Pi(\mathrm{z}) + \Delta \mathrm{P}_f(\mathrm{r}) = 0. \tag{18}$$

This means that in the vicinity of the lens the disjoining pressure inside the liquid layer is negative, while $\Delta \mathrm{P}_f(\mathrm{r}) \cong P_l - P_\beta > 0$ and (Figure 6d).

$$\Pi = P_\beta - P_l < 0. \tag{19}$$

Remember that the negative sign for the disjoining pressure denotes mutual attraction of the dividing surfaces in the layer.

On the other hand, in the bulk of the lens the disjoining pressure becomes, obviously, zero, the interfacial tension acquires its constant value σ_o, and the reference pressure is equal to P_l. The mechanical equilibrium Equation (16) in this region acquires the form

$$\sigma_o\left[\frac{d\sin\varphi(z)}{dr} + \frac{\sin\varphi(z)}{r}\right] - \Delta \mathrm{P}_l = 0, \tag{20}$$

where

$$\Delta \mathrm{P}_l = \mathrm{P}_l - P_\beta. \tag{21}$$

We point out that the experimental profile, $z_{exp}(\mathrm{r})$, of the lens is measured by shadow or light interference techniques [31–33] using the portion of the lens shape of the constant general curvature, k_l^o, which is situated far away from the transition region. On account of the relatively small thickness, δ, of this transition zone (which is of the order of the correlation length for the molecular forces, *i.e.*, $\delta \sim 10\,\mathrm{nm} \ll \lambda/4$), it is impossible to determine with sufficient precision the shape of the real profile in this transition region of the lens (or of the drop). On account of this difficulty, it is convenient to extrapolate the experimental profile, $z_{exp}(\mathrm{r})$, to the transition region without taking into account the attractive surface forces (*i.e.*, by making this profile insensitive to the disjoining pressure). Using this procedure, the extrapolated experimental profile, $z_{exp}(\mathrm{r})$, intersects the solid plane $\mathrm{z} = 0$ at the contact $r = r_l$ (which is considered as the radius of the lens) under the contact angle θ_o. We point out that the radius of the contact line may be defined as the intersection between the extrapolated experimental profile, $z_{exp}(\mathrm{r})$, and the plane $\mathrm{z} = h_f$: in this convention another contact angle, θ_f, must be taken into consideration, which differs from the contact angle θ_o. The first definition of the contact line and the contact angle refers to the so-called membrane approach of the liquid film [25], whereas the second definition is known as the two interacting dividing surfaces model of the film [21].

Integrating the equilibrium Equation (20) of the experimental profile $z_{exp}(\mathrm{r})$ within the limits z^* and some variable z, one obtains

$$\sigma_o \cos\varphi_{\exp}(z) - \Delta \mathrm{P}_l \mathrm{z}_{\exp} - \int\limits_{z}^{z^*} \frac{\sigma_o \sin\varphi_{\exp}}{r} d\,z_{\exp} = \sigma_o \cos\varphi^* - \Delta \mathrm{P}_l \mathrm{z}^*, \quad (22)$$

where the right side of the equation is constant for the fixed location of the point A on the experimental profile $z_{exp}(\mathrm{r})$. Applying the same procedure of the integration to the equilibrium equation relating to the real profile Equation (16), one obtains

$$\sigma \cos\varphi(z) + \left[\int\limits_{z}^{z^*} \Delta P_f(r) dz - \Delta P_l z^*\right] - \int\limits_{z}^{z^*} \frac{\sigma \sin\varphi}{r} d\,z = \sigma_o \cos\varphi^* - \Delta P_l \mathrm{z}^*. \quad (23)$$

The obtained result is based on Equation (7) $\mathrm{dz} = -\tan\varphi\, dr$, the Gibbs-Duhem Equation (15) written in the form $\mathrm{d}\sigma = -\Pi\, \mathrm{dz}$, and the following obvious relationship:

$$\int\limits_{z}^{z^*} \sigma(z) \frac{d \sin\varphi(z)}{dr} d\,z - \int\limits_{z}^{z^*} \Pi \cos\varphi\, dz = \int\limits_{z}^{z^*} \sigma(z) d\cos\varphi + \int\limits_{z}^{z^*} \cos\varphi\, d\sigma$$
$$= \sigma \cos\varphi(z).$$

While the left sides of Equations (22) and (23) are equal to the same value $\sigma_o \cos\varphi^* - \Delta \mathrm{P}_l \mathrm{z}^*$, one can write the general equation,

$$\sigma \cos\varphi(z) + \left[\int\limits_{z}^{z^*} \Delta P_f(r) dz - \Delta P_l z^*\right] - \int\limits_{z}^{z^*} \frac{\sigma \sin\varphi}{r} dz$$
$$= \sigma_o \cos\varphi_{\exp}(z) - \Delta \mathrm{P}_l z_{exp} - \int\limits_{z}^{z^*} \frac{\sigma_o \sin\varphi_{\exp}}{r} d\,z_{\exp}, \quad (24)$$

which is independent on the choice of the variable z.

The difference inside the brackets in the left side of Equation (24) may be expressed in the approximate form. Expanding $\Delta \mathrm{P}_f(\mathrm{r})$ in series, $\Delta \mathrm{P}_f(\mathrm{r}) \cong \Delta \mathrm{P}_l + \frac{1}{2}\left(d\Delta P_f(r)/dr\right)(r - r_l) + \cdots$, one can write $\left[\int_z^{z^*} \Delta P_f(r)dz - \Delta P_l z^*\right] \cong -\Delta \mathrm{P}_l \mathrm{z} + \frac{1}{2}\int_z^{\infty}\left[d\Delta P_f(r)/dr\right](r - r_l)dz + \cdots$, which allows us to rewrite Equation (24) as

$$\sigma \cos\varphi(z) - \Delta \mathrm{P}_l \mathrm{z} + \mathrm{I}(\mathrm{r}) - \int_z^{z^*} \frac{\sigma \sin\varphi}{r} dz$$

$$= \sigma_o \cos\varphi_{\exp}(z) - \Delta \mathrm{P}_l \mathrm{z}_{\exp} - \int_z^{z^*} \frac{\sigma_o \sin\varphi_{\exp}}{r} dz_{\exp}, \tag{25}$$

where I(r) may be expressed in the approximate form

$$\mathrm{I}(\mathrm{r}) \cong -\frac{1}{2}\int_z^{\infty} (r - r_l) tg\,\varphi\, d\Delta P_f \cong -\frac{1}{2}\int_z^{\infty} \Delta h_f d\Delta P_f, \tag{26}$$

where Δh_f is a very small variation of the thickness of the liquid film in its flat region, and the upper limit, ∞, is justified by the fact that $\Delta \mathrm{P}_f(\mathrm{r})$ is constant in the bulk of the lens.

Now we can use Equation (25) to obtain the fundamental relationships of thin liquid layer thermodynamics. Consider once more the profile of the lens in the vicinity of the contact line (Figure 7a). The experimental profile $\mathrm{z}_{exp}(\mathrm{r})$ intersects the plane $\mathrm{z} = 0$ at the radius r_l under the contact angle θ_o, whereas with the plane $\mathrm{z} = h_f$ this profile forms the contact angle θ_f at r_f. Remember [23] that the contact line with the radius r_l is used in the membrane model of liquid films (Figure 7b). In the convention of the layer with a finite thickness one uses the contact line with the radius r_f (Figure 7c).

MEMBRANE MODEL OF THE FILM

In the range of this convention, the liquid film is imagined as a membrane of zero thickness (Figure 7b). In accordance with this presentation, and taking into account that the experimental profile, $\mathrm{z}_{exp}(\mathrm{r})$, intersects the membrane at r_l under the angle θ_o, let us make the following substitutions in the right side of Equation (25): $\mathrm{z}_{exp} = 0$, $\varphi_{exp} = \theta_o$, and $r = r_l$. The real profile, z(r), transforms smoothly to the flat plane at $z = h_f$, which allows us to put the following values in the right side of Equation (25): $\mathrm{z} = h_f, \varphi = 0$, and $r = r^*$, where $r^* \gg r_l$ is situated somewhere in the flat region of the film far away

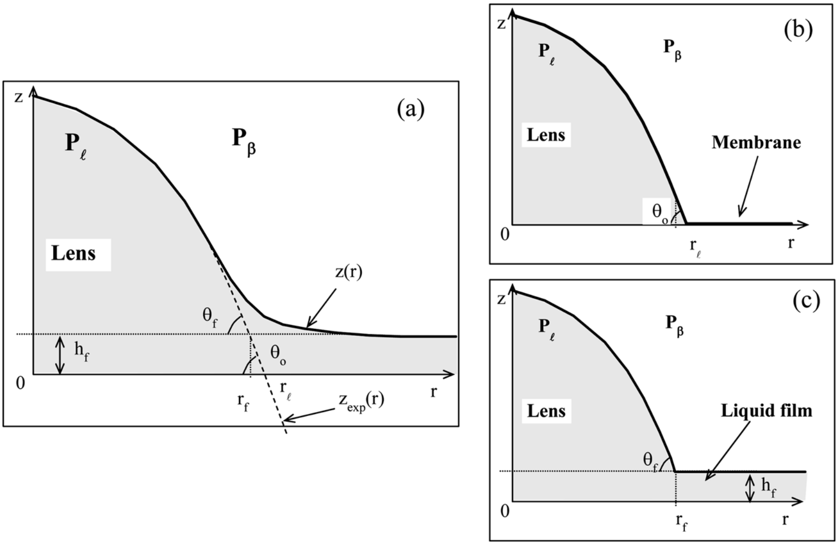

FIGURE 7 (a) The presentation of the three-phase contact region, (b) in the membrane model of the film, and (c) in the layer of the finite thickness convention.

from the meniscus. The interfacial tension of the film with the thickness h_f is denoted as $\sigma(h_f) = \sigma_f$. These substitutions lead to the expression

$$\sigma_f - \Delta \mathrm{P}_l \mathrm{h}_f + \mathrm{I}(r) - \int_{h_f}^{\infty} \frac{\sigma \sin\varphi}{r} dz$$

$$= \sigma_o \cos\theta_o - \int_{h_f}^{\infty} \frac{\sigma_o \sin\varphi_{\mathrm{exp}}}{r} dz_{\mathrm{exp}}.$$

Neglecting the term $\mathrm{I}(r^*)$ on account of the condition $\delta \ll 1$ (see Equation (26)), one can finally write

$$\sigma_f - \Delta \mathrm{P}_l \mathrm{h}_f - \frac{æ}{r_l} = \sigma_o \cos\theta_o, \tag{27}$$

where æ is the so-called line tension in the membrane convention [34, 35] defined as [17–19, 23]

$$\frac{æ}{r_l} = \int_{h_f}^{\infty} \frac{\sigma \sin\varphi}{r} dz - \int_{0}^{\infty} \frac{\sigma_o \sin\varphi_{\mathrm{exp}}}{r} dz_{\mathrm{exp}}. \tag{28}$$

In the membrane convention of the film one uses the notion of the membrane (film) tension, γ_f, which differs from the interfacial tension, σ_f:

$$\gamma_f = \sigma_f - \Delta \mathrm{P}_l \mathrm{h}_f. \tag{29}$$

This transforms Equation (27) into

$$\gamma_f - \frac{æ}{r_l} = \sigma_o \cos\theta_o. \tag{30}$$

Believing that the membrane tension could be presented as the difference

$$\gamma_f = \sigma_{s\alpha} - \sigma_{s\beta}, \tag{31}$$

where $\sigma_{s\alpha}$ and $\sigma_{s\beta}$ are interfacial tensions at the boundaries (solid phase α) and (solid phase β), respectively, and $\sigma_o = \sigma_{\alpha\beta}$, one may present Equation (30) in the more habitual form of the Young equation,

$$\sigma_{s\alpha} - \sigma_{s\beta} - \frac{æ}{r_l} = \sigma_o \cos\theta_o. \tag{32}$$

FINITE THICKNESS LAYER MODEL

This model of the film may be used when the film thickness, h_f, is a measurable parameter (Figure 7c). Because the experimental profile $\mathrm{z}_{exp}(\mathrm{r})$ intersects the plane $\mathrm{z} = h_f$ at $\mathrm{r} = r_f$ under the contact angle θ_f, one makes the following substitutions in the right side of Equation (25): $\mathrm{z}_{exp} = h_f$, $\varphi_{exp} = \theta_r$, and $r = r_f$. The substitutions concerning the real profile remain the same as has been made previously: $\mathrm{z} = h_f, \varphi = 0$, and $\sigma(h_f) = \sigma_f$. One obtains the expression

$$\sigma_f - \Delta \mathrm{P}_l \mathrm{h}_f - \int_{h_f}^{\infty} \frac{\sigma \sin\varphi}{r} dz = \sigma_o \cos\theta_f - \Delta \mathrm{P}_l \mathrm{h}_f - \int_{h_f}^{\infty} \frac{\sigma_o \sin\varphi_{\mathrm{exp}}}{r} dz_{\mathrm{exp}},$$

which may be finally rewritten in the form

$$\sigma_f - \frac{\tau}{r_f} = \sigma_o \cos\theta_f, \tag{33}$$

where τ is the so-called line tension in the finite thickness layer convention of the film defined as [14, 17–19, 23]

$$\frac{\tau}{r_f} = \int_{h_f}^{\infty} \frac{\sigma \sin\varphi}{r} dz - \int_{h_f}^{\infty} \frac{\sigma_o \sin\varphi_{\mathrm{exp}}}{r} dz_{\mathrm{exp}}. \tag{34}$$

Using the definition of the interaction free energy (the grand thermodynamic potential) for the plane-parallel liquid film (layer) of thickness h_f [18],

$$\Delta\Omega(h_f) = \int_{h_f}^{\infty} \Pi(z)dz = \sigma_f - \sigma_o,$$

one can rewrite Equation (23) in the usual form [14, 17–19, 23],

$$\Delta\Omega(h_f) - \frac{\tau}{r_f} = \sigma_o(\cos\theta_o - 1).$$

LINE TENSION

Equations (29) and (33) are used to determine the line tenstion, æ or τ, from the experimental dependence of the contact angle, θ_o or θ_f, of the lens (or drop) radius, r_l or r_f, on a solid or a liquid support [18, 19]. In these measurements it is usually assumed that the tensions, γ_f or σ_f, stay constant when the size of the drop or the lens is changed, and the Equations (29) and (33) are used in the form

$$\cos\theta_o = \cos\theta_o(\infty) - \frac{æ}{\sigma_o r_l}, \tag{35}$$

$$\cos\theta_f = \cos\theta_f(\infty) - \frac{\tau}{\sigma_o r_f}, \tag{36}$$

where $\theta_o(\infty)$ and $\theta_f(\infty)$ are the contact angles corresponding to the limits $r_l \to \infty$(or $r_f \to \infty$).

If one takes into account that, for example, the film tension could vary when the size of the lens or of the drop varies, then the more general equation must be written instead of Equation (35):

$$\cos\theta_o = \cos\theta_o(\infty) - \frac{æ}{\sigma_o r_l} + \Delta\gamma_f(r_l), \tag{37}$$

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

We note that according to the generalized theory [18, 19] of the line tension, the value of æ can only be negative for systems characterized by finite values of the contact angle. Numerical estimates of the line tension as a function of the physico-chemical parameters (shape of the profile of the disjoining pressure isotherm, contact angle value, capillary pressure, and film size) have been recently reviewed [18, 19].

STABILITY OF THE LENS (THE DROP) ON A SOLID SUPPORT

Imagine a lens or a drop formed on a solid substrate and surrounded by a thin liquid layer (Figure 8a). In the process of the ageing of the drop, when its mass gradually decreases by a different mechanism, which was discussed in the introduction (Figure 3), the hydrostatic pressure inside the drop P_l gradually increases as well. The figurative point a in Figure 8b represents the initial moment when the drop is large (position 1 in Figure 8a). This position of the figurative point a corresponds to the difference of the hydrostatic pressure $\Delta P_l = P_l - P_\beta$. This hydrostatic pressure difference, ΔP_l, is smaller than the absolute value of the attractive disjoining pressure $-\Pi_{min}$, *i.e.*, $|\Pi_{min}| \gg \Delta P_l$. The latter inequality is the condition of the stability of the lens (the drop) on the solid substrate and of the existence of the finite contact angle θ_o.

With decreasing lens (the drop) size (position 2 in Figure 8a), the figurative point a moves to the left because of increasing the difference $\Delta P_l = P_l - P_\beta$ up to the moment (position 3 in Figure 8a) when $\Delta P_l = |\Pi_{min}|$. At this moment which corresponds to the so-called wetting–spreading transfer, the drop becomes unstable, spreading as a more thick film (*e.g.*, a common black film) over the solid substrate surface. The contact angle becomes smaller, corresponding to the equilibrium between the drop and the common black film. Finally, the liquid phase of the drop may transform wholly to the layer (position 4 in Figure 8a and Figure 4).

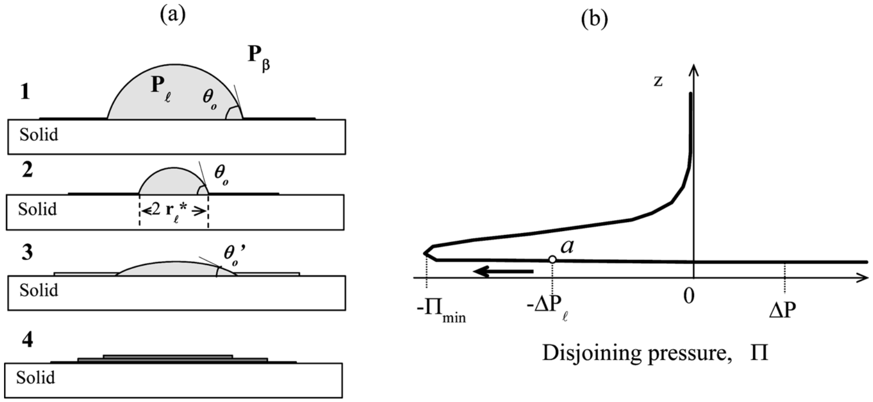

FIGURE 8 (a) Evolution of the drop on a solid substrate, (b) with regard to the disjoining pressure isotherm (for explanation see the text).

The critical radius, r_l^*, which corresponds to the instability of the lens (the drop), may be estimated by taking into account that at this moment the capillary pressure, $2\sigma_o/R = 2\sigma_o \sin\theta_o/r_l^*$, reaches the maximum value, $|\Pi_{min}|$, *i.e.*,

$$r_l^* = \frac{2\sigma_o \sin\theta_o}{\Pi_{max}}. \tag{38}$$

CONCLUSION

The thermodynamics of interacting curved interfaces (*i.e.*, the thermodynamics of the transition region of liquid films) [17, 20–22, 31] is a self-consistent and closed system of concepts and equations relating the disjoining pressure to other thermodynamic parameters and functions. This thermodynamics may be considered as the generalization of both the thermodynamics of plane-parallel thin liquid films and the thermodynamics of noninteracting curved interfaces in the appropriate region of definition.

This thermodynamics is applied to the case of a liquid lens or a drop wetting the solid substrate and forming a finite contact angle with it. The analytical expressions relating the contact angles to the thermodynamic parameters and the line tension for both the membrane and the finite thickness layer models have been obtained. The criterion of the stability of a liquid drop on a solid substrate has been formulated [21]. The latter criterion explains the transfer from the wetting to the spreading of a drop over the solid surface by the interplay between the capillary pressure inside the drop and the disjoining pressure shape.

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