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Surface forces and wetting phenomena

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Abstract

Conditions for thermodynamic equilibrium of liquid drops on solid substrates are presented. It is shown that if surface force (disjoining/conjoining Derjaguin pressure) action in a vicinity of the three-phase contact line is taken into account the condition of thermodynamic equilibrium is duly satisfied. Then the thermodynamic expressions for equilibrium contact angles of drops on solid substrates and menisci in thin capillaries are expressed in terms of the corresponding Derjaguin isotherm. It is shown that equilibrium contact angles of drops vary significantly depending on the vapour pressure in the ambient atmosphere, while there is a single, unique equilibrium contact angle in thin capillaries. It is also shown that the static advancing contact angle of a drop depends on its volume, in agreement with experimental data. In the case of menisci in capillaries, the expression for the receding contact angle is deduced, with results that are also in agreement with known experimental data.

1. Thermodynamic equilibrium of drops on solid substrates

Let us consider the equilibrium of liquid drops on homogeneous perfectly flat solid substrates. Two cases are of interest: the partial wetting case (e.g. water and aqueous electrolyte solutions on glass, mica and silicon wafers), and the complete wetting case (e.g. oils on the same solid substrates as above). Let us focus attention on the case of partial wetting. For thermodynamic equilibrium the following condition must be satisfied: the chemical potential of liquid molecules in the whole system should be equal. The latter results in the following three equilibrium conditions: (a) liquid–vapour equilibrium, (b) vapour–solid equilibrium, and (c) liquid–solid equilibrium.

Requirement a

The first requirement demands the equality of chemical potentials of the liquid molecules in the ambient vapour phase and the liquid phase inside the drop. The latter results in Kelvin's equation for the excess pressure inside the drop:

$$P_e = \frac{RT}{v_m} \ln \frac{p_s}{p}, \quad (1)$$

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with $P_e = P_v - P_l$, where P_v and P_l are the pressures in the vapour and the liquid phase, respectively; v_m is the molar volume of the liquid; p_s is the pressure of the saturated vapour at temperature T (value for a flat solid surface); R is the gas universal constant; p is the vapour pressure, which is at equilibrium with the liquid drop. Equation (1) determines a single equilibrium excess pressure P_e for a given radius of the drop, ρ_e . Hence, the equilibrium drop size depends on the vapour pressure: if the vapour pressure p in the ambient air is varied, then the size of an equilibrium drop will vary accordingly. Thus there is an infinite number of equilibrium drops on a solid substrate corresponding to the infinitely many possible different values of p . Note that the 'excess' pressure inside the drop, P_e , is negative, as the pressure inside the drop is higher than the pressure in the ambient air (Laplace's law, that we shall recover below) expressing such overpressure in terms of the surface tension of the liquid. Accordingly, the right-hand side in equation (1) should be negative, but the latter is possible only if $p > p_s$; that is, drops can be at equilibrium only with over-saturated vapour.

Requirement b

The vapour molecules tend to adsorb on the solid surface. Then thermodynamic equilibrium requires equality of chemical potentials of molecules in the vapour phase and in the adsorbed

state. Let h_e be the equilibrium thickness of the adsorbed layer at the vapour pressure p . Let us consider that the adsorption is determined by the action of some ‘surface forces’. Let $f_D(h_e)$ be the potential of these adsorption forces. The excess free energy per unit area of a flat equilibrium liquid film of thickness h_e on a solid substrate at equilibrium with the vapour in the surrounding air is given by

$$\Phi_f = [\gamma + P_e h_e + f_D(h_e) + \gamma_{sl} - \gamma_{sv}]S, \quad (2)$$

where S is the surface covered by the liquid film; γ , γ_{sl} , γ_{sv} are liquid–vapour/air, solid–liquid and solid–vapour interfacial tensions, respectively. Indeed, a bare solid substrate without an adsorbed liquid layer cannot be at thermodynamic equilibrium.

Rather than using the potential of surface forces, $f_D(h_e)$, let us use the disjoining or conjoining pressure, $\Pi(h_e)$, as defined by Derjaguin [1], with $\Pi(h) = -[\frac{df_D(h)}{dh}]_T$. Hence,

$$f_D(h_e) = \int_{h_e}^{\infty} \Pi(h) dh. \quad (3)$$

This Derjaguin pressure can be experimentally measured in the range of surface force action, $h \leq h_s \sim 100$ nm [1–3].

Requirement c

The excess free energy of the liquid drop must be a minimum. To simplify let us consider a two-dimensional (cylindrical) drop. Then the excess free energy, Φ , of such a liquid drop on a solid substrate is

$$\Phi = \gamma S_e + P_e V_e + \Phi_D + (\gamma_{sl} - \gamma_{sv})S - \Phi_f, \quad (4)$$

where S_e , V_e , and $\Phi_D = \int_S f_D(h) dx$ are excesses of the vapour–liquid interfacial area, the excess volume, and the excess energy associated with the surface force action, respectively; Φ_f (2) is the excess free energy of a reference state.

Let $h(x)$ be the unknown profile of the cylindrical liquid drop, then equation (4) can be rewritten as

$$\Phi = \int \left\{ \gamma(\sqrt{1+h'^2} - 1) + P_e(h - h_e) + \int_{h_e}^{\infty} \Pi(h) dh - \int_{h_e}^{\infty} \Pi(h) \right\} dx, \quad (5)$$

where x is the tangential coordinate and the integration is taken over the whole space occupied by the system. Under equilibrium conditions the excess free energy, Φ , should reach its minimum value. As the problem is posed in functional space, then the following conditions must be satisfied [4, 5].

- (A) The first variation of the free energy, $\delta\Phi$, should be zero.
- (B) The second variation, $\delta^2\Phi$, should be positive.
- (C) Transversality condition at the three-phase contact line: the drop edge can move only along the surface of a thin equilibrium film in front, that is along the surface $h = h_e$. This is a condition of swift matching between the drop at its perimeter with the thin flat liquid film ahead of it: $h'(h = h_e) = 0$; or $h' \rightarrow 0$ as $x \rightarrow \infty$.

- (D) With $f = \gamma(\sqrt{1+h'^2} - 1) + P_e(h - h_e) + \int_{h_e}^{\infty} \Pi(h) dh - \int_{h_e}^{\infty} \Pi(h)$, the solution, u , of the Jacobi equation

$$\left[\frac{\partial^2 f}{\partial h^2} - \frac{d}{dx} \left(\frac{\partial^2 f}{\partial h \partial h'} \right) \right] u - \frac{d}{dx} \left(\frac{\partial^2 f}{\partial h'^2} u' \right) = 0, \quad (6)$$

is to vanish at no position inside the area of integration save at its boundaries. Jacobi’s equation determines one among the otherwise infinite solutions of the functional variation problem providing a sufficient condition of minimum. We have below restricted consideration to the Π function of h and not of h' or other higher derivatives.

Condition (A) yields an Euler equation, which gives an equation for the drop profile:

$$\frac{\partial f}{\partial h} - \frac{d}{dx} \frac{\partial f}{\partial h'} = 0 \quad (\text{Euler equation}),$$

or

$$\frac{\gamma h''}{(1+h'^2)^{3/2}} + \Pi(h) = P_e \quad (\text{Laplace–Derjaguin equation}), \quad (7)$$

which is the earlier mentioned Laplace equation (except a factor of 2 missing here due to the cylindrical approximation) augmented with the Derjaguin surface force contribution.

Far from the apparent three-phase contact line, that is for $h \gg 100$ nm, the action of the Derjaguin pressure can be neglected in equation (7): $\frac{\gamma h''}{(1+h'^2)^{3/2}} = P_e$. The solution of this equation is a part of a circumference of radius $\rho = -\frac{\gamma}{P_e}$ (recall that for a drop P_e is negative). The second condition, (B), demands $\frac{\partial^2 f}{\partial h'^2} > 0$, or $\frac{\gamma}{(1+h'^2)^{3/2}} > 0$, which is always satisfied. The Jacobi equation (6) reduces to

$$\frac{d}{dx} \frac{u'}{(1+h'^2)^{3/2}} + \Pi'(h)u = 0. \quad (8)$$

Differentiating equation (7) once yields $\frac{d}{dx} \frac{h''}{[1+(h')^2]^{3/2}} + \Pi'(h) \cdot h' = 0$. Comparison of the latter equation and the Jacobi equation (8) shows that $u(x) = Ch'(x)$. Thus equation (7) really gives a minimum value to the excess free energy (5) if the first derivative vanishes nowhere inside the drop (except for $x = 0$ and ∞).

The transversality condition (C) gives $[f - h' \frac{\partial f}{\partial h'}]_{x=\mathfrak{R}} = 0$, where \mathfrak{R} identifies a microscopic drop edge. The latter condition can be rewritten as $[(\sqrt{1+h'^2} - 1) - \frac{h'^2}{\sqrt{1+h'^2}}]_{x=\mathfrak{R}} = 0$, or $[\frac{1}{\sqrt{1+h'^2}}]_{x=\mathfrak{R}} = 1$, which is satisfied only if $(h')_{x=\mathfrak{R}} = 0$, or $h'(h_e) = 0$.

Let us assume that the liquid profile does not tend asymptotically to the equilibrium thickness h_e but meets the film at a ‘final point’ $x = x_0$. Then in a vicinity of this point we can approximate the Derjaguin pressure by a linear term $\Pi(h) \approx \Pi(h_e) - a(h - h_e)$, where $a = -\Pi'(h_e)$ is a positive value, h_e is a stable flat liquid film, the derivative of the Derjaguin pressure must be negative and $\Pi(h_e) = P_e$. The liquid profile in this region has a low slope, hence equation (7) can be rewritten as $\gamma h'' - a(h - h_e) = 0$, whose solution is $h(x) = h_e + C_1 \exp(\alpha x) + C_2 \exp(-\alpha x)$, where $\alpha = \sqrt{\frac{a}{\gamma}}$,

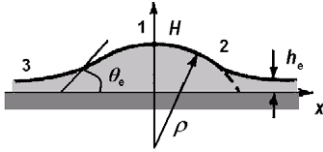


Figure 1. Equilibrium drop. 1—Circular cap (radius ρ), where capillary Laplace force dominates; 2—transition zone, where both capillary Laplace and disjoining/conjoining Derjaguin pressures are equally important; and 3—flat equilibrium film in front of the drop.

and C_1 and C_2 are two integration constants. At $x = x_0$ we have $h(x_0) = h_e$, and $h'(x_0) = 0$. These two boundary conditions yield two algebraic equations for the determination of C_1 and C_2 : $C_1 \exp(\alpha x_0) + C_2 \exp(-\alpha x_0) = 0$, and $C_1 \exp(\alpha x_0) - C_2 \exp(-\alpha x_0) = 0$. The solution $C_1 = C_2 = 0$ is unacceptable. Hence, if $h \rightarrow h_e$ the only possibility is that $C_1 = 0$ and the liquid profile has the following form $h(x) = h_e + C_2 \exp(-\alpha x)$. Accordingly, the liquid profile in the transition zone tends asymptotically to the equilibrium thickness h_e and does not meet the equilibrium flat film in any ‘final’ point x_0 contrary to what was earlier assumed.

2. Equilibrium contact angle and surface forces (Derjaguin pressure)

According to the Laplace–Derjaguin equation (7) the overall profile of a drop can be subdivided into three parts (figure 1): a spherical cap (using this part a macroscopic contact angle can be determined), a transition zone, where both capillary Laplace pressure and disjoining/conjoining Derjaguin pressure are equally important, and a flat equilibrium liquid film region ahead of the drop.

The second order differential equation (7) can be integrated once, which gives $\frac{1}{\sqrt{1+h'^2}} = \frac{C - P_e h - \int_h^\infty \Pi(h) dh}{\gamma}$, where C is an integration constant to be determined. As due to the transversality condition $h'(h_e) = 0$, then $C = \gamma + P_e h_e + \int_{h_e}^\infty \Pi(h) dh$. Hence, the drop profile is described by the following equation:

$$h' = - \left(\frac{\gamma^2}{[\gamma - L(h)]^2} - 1 \right)^{1/2}, \tag{9}$$

where $L(h) = P_e(h - h_e) - \int_{h_e}^h \Pi(h) dh$. As the expression under the square root in equation (9) must be positive, it demands that

$$0 \leq L(h) \leq \gamma, \tag{10}$$

where the first equality corresponds to a zero derivative, and the second one corresponds to a diverging (infinite) value.

On the other hand at the drop apex, H , the derivative vanishes, $h'(H) = 0$. Consequently, $C = \gamma + P_e H + \int_H^\infty \Pi(h) dh$, can be determined too. Note that the two definitions of C are identical. Hence,

$$\frac{1}{\sqrt{1+h'^2}} = \frac{\gamma + P_e(H - h) - \int_h^H \Pi(h) dh}{\gamma}. \tag{11}$$

Outside the range of the disjoining pressure action, equation (11) reduces to

$$\frac{1}{\sqrt{1+h'^2}} = \frac{\gamma + P_e(H - h)}{\gamma}, \tag{12}$$

which describes the circular cap of the drop in figure 1. Intersection of the latter profile with the thin equilibrium film of thickness h_e defines an apparent three-phase contact line and the macroscopic equilibrium contact angle: $h'(h_e) = -\tan \theta_e$. Then equation (12) can be rewritten as $P_e = -\frac{\gamma(1-\cos \theta_e)}{H}$. Casting this expression into equation (11) at $h = h_e$ results in the following expression for the contact angle in the case of sessile drops on a flat substrate:

$$\begin{aligned} \cos \theta_e &= 1 + \frac{\frac{1}{\gamma} \int_{h_e}^H \Pi(h) dh}{1 - \frac{h_e}{H}} \\ &\approx 1 + \frac{1}{\gamma} \int_{h_e}^\infty \Pi(h) dh, \quad \text{for } h_s \ll H. \end{aligned} \tag{13}$$

Equation (13) shows that for the partial wetting case

$$\int_{h_e}^\infty \Pi(h) dh < 0, \tag{14}$$

otherwise equation (13) is meaningless if θ_e is to have a finite non-zero value.

Note that the equilibrium contact angle defined by equation (13) is not completely determined by the shape of the Derjaguin pressure isotherm: it also depends on the lower limit of integration, h_e , which is determined by the equilibrium excess pressure P_e . In other words, the equilibrium contact angle of drops depends on the equilibrium volume of the drop, which can vary from ‘infinity’ (at $P_e = 0$) to a minimum value at $P_e = \Pi_{\min}$.

An interesting point is that, if for the Derjaguin pressure we take $\Pi(h) = \frac{A}{h^3} > 0$ (LVdW only), substitution of this expression into equation (13) yields $\cos \theta_e \approx 1 + \frac{1}{\gamma} \int_{h_e}^\infty \frac{A}{h^3} dh = 1 + \frac{A}{2\gamma h_e^2} > 1$, which corresponds to complete wetting [5, 6]. This latter condition implies that no solution exists for an equilibrium liquid film thickness, h_e , coexisting outside with the drop at oversaturation. And hence this corresponds to the complete wetting case [5]. If, on the other hand, we consider $A < 0$, then there is a solution for an equilibrium film thickness, h_e , but as for this value $[d\Pi(h_e)/dh] > 0$ such an equilibrium value is unstable [5] and hence not observable. Any finite value h_e being unstable, this corresponds to the non-wetting case. In view of the above, it is concluded that in order to explicitly account for partial wetting we must have a more complete expression for the Derjaguin pressure than those given by the LVdW component only. This can be achieved by considering the various electro-physical–chemical phenomena involved in the three-phase contact region (figure 2).

3. Derjaguin pressure isotherm and significant components of the surface forces

The above used expression for $\Pi(h)$ is historically called the molecular or dispersion component of the Derjaguin pressure,

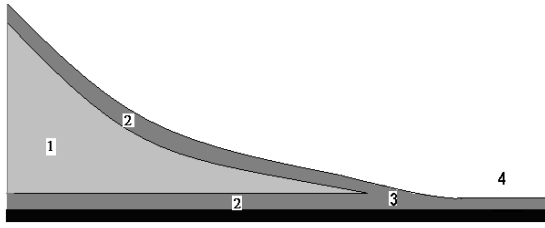


Figure 2. Equilibrium drop and the liquid profile in a vicinity of the apparent three-phase contact line. 1—Bulk liquid, where boundary layers do not overlap; 2—boundary layer in the vicinity of liquid–air and liquid–solid interfaces; 3—a region where boundary layers overlap, 4—flat thin equilibrium film. The latter two are the regions where Derjaguin pressure acts.

typical for non-polar liquid films (it is also denoted as the London–Van der Waals component) [3]. In general terms one can write

$$\Pi_{L-vdW}(h) = \begin{cases} \frac{A}{h^3}, & h < \lambda \\ \frac{B}{h^4}, & h > \lambda \end{cases} \quad (15)$$

where λ is a characteristic wavelength and A is the Hamaker constant. This Hamaker constant can be either positive or negative and, consequently, the LVdW interaction may be repulsive or attractive. Typical positive values are $A \sim 10^{-14}$ erg for oil films on glass, quartz or mica surfaces. Thus, for a liquid layer of thickness $h \sim 10^{-7}$ cm, such a Derjaguin pressure component is $\Pi_{L-vdW} \sim 10^7$ dyn cm $^{-2}$. For comparison, consider an oil drop of radius $\rho \sim 0.1$ cm sessile on a solid substrate; at standard laboratory conditions the surface tension of oils is about $\gamma \cong 30$ dyn cm $^{-1}$. Then the capillary pressure inside the spherical part of the drop is $\frac{2\gamma}{\rho} \sim \frac{2 \cdot 30}{0.1} = 6 \times 10^2$ dyn cm $^{-2}$. Accordingly, in the vicinity of the three-phase contact line the Laplace pressure is much smaller than the Derjaguin pressure. This justifies why the latter distorts significantly the spherical shape of drops in the vicinity of the three-phase contact line and hence drops cannot remain spherical up to the contact line!

Another item to include in the Derjaguin pressure originates in electric double layers (EDLs). There are a number of approximate expressions for such an electrostatic component [1, 2]. For example, in the case of an electrolyte solution (polar liquid), the EDL interaction decays exponentially with a characteristic Debye screening length, $1/\kappa \sim 1\text{--}100$ nm. This EDL force can be either repulsive or attractive. For a liquid enclosed between two semi-infinite plates it is

$$\Pi_{EDL}(h) = D \exp(-\kappa h), \quad (16)$$

where h denotes distance and D is a characteristic parameter of the system, which can be either positive or negative. Other more complete expressions than (16) have been obtained for various other systems [1, 2]. It is noteworthy that the EDL component of the Derjaguin pressure does not vanish even when only one of the two surfaces is charged. The physical reason for this phenomenon is the deformation of the EDL if

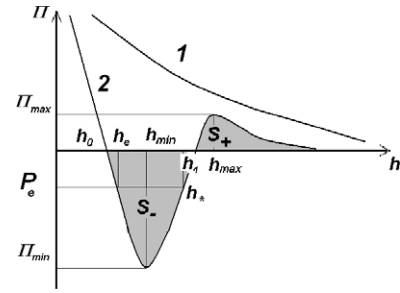


Figure 3. Derjaguin isotherms: 1—complete wetting; 2—partial wetting. The value h_e defines the equilibrium thickness of coexisting equilibrium flat films with drops.

the distance between the surfaces is smaller than the Debye length.

Incidentally, considering that $\Pi(h) = \Pi_{LVdW}(h) + \Pi_e(h)$ corresponds to the original DLVO theory [1, 2, 7] that made possible the explanation of the stability of colloidal suspensions/emulsions, as well as the static and the kinetics of wetting [5] (N.B. As might have been noticed, we denote by Derjaguin pressure (or isotherm) all possible forms of disjoining or conjoining pressure components (or isotherms)).

Yet another component of the Derjaguin pressure is the so-called structural component caused by e.g. orientation of water molecules (electric dipoles) in the vicinity of the solid surface or at the aqueous solution–air interface. Only a semi-empirical relationship exists, providing the dependence of such structural force on the thickness of the liquid film,

$$\Pi_S(h) = K e^{-\nu h}, \quad (17)$$

where K and ν are constants. For illustration $1/\nu \sim 10\text{--}15$ Å, which is the characteristic thickness of the so-called hydration layer. The understanding of the pre-exponential factor K is at present far from being complete, and it can be extracted only from experimental measurements of the Derjaguin pressure. It can be either positive or negative.

Adding the three components mentioned above (there are more than these three already established in the literature), we have

$$\Pi(h) = \Pi_{L-vdW}(h) + \Pi_{EDL}(h) + \Pi_S(h). \quad (18)$$

Figure 3 illustrates the dependence of the Derjaguin pressure on the thickness of a flat liquid film for the cases of complete wetting (curve 1, which corresponds to just $\Pi_{L-vdW}(h)$ and is typical for oil drops on a glass substrates) and partial wetting (curve 2, which corresponds to equation (18), and it is typical for aqueous electrolyte solutions on glass substrates).

In view of equation (13) and figure 3 we can write

$$\cos \theta_e \approx 1 + \frac{1}{\gamma} \int_{h_e}^{\infty} \Pi(h) dh \approx 1 - \frac{S_- - S_+}{\gamma}. \quad (19)$$

Thus partial wetting is possible only if $S_- > S_+$. Note that there are two solutions of the equation $\Pi(h_e) = P_e$ (figure 3). However, only one of them satisfies the thermodynamic stability condition $\frac{d\Pi(h_e)}{dh} < 0$. For a thorough discussion of this question see [5].

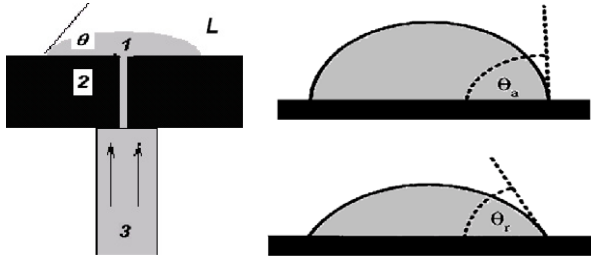


Figure 4. Left: schematic illustration of the formation of a drop by appropriate liquid pumping. L —radius of the drop base; θ —contact angle. 1—Liquid drop, 2—solid substrate with a small orifice; 3—liquid source (syringe). Right: static advancing and receding contact angles.

4. Static hysteresis of the contact angle of a sessile drop on homogeneous perfectly flat solid substrates

The derivation of equation (13) shows that it determines a single, unique equilibrium contact angle (at fixed external conditions). Experiments, however, show contact angle hysteresis with an infinite number of apparent ‘equilibrium positions’ and ‘equilibrium contact angles’ of a sessile drop on a solid surface such that $\theta_r < \theta < \theta_a$, where θ_r and θ_a denote static receding and advancing contact angles. Indeed, let us consider a liquid drop on a horizontal substrate, which is slowly growing by pumping through an orifice in the substrate (figure 4). If we stop pumping liquid an equilibrium contact angle of the drop may be established. However, if we continue carefully and slowly pumping liquid in through the orifice in the centre, the contact angle grows correspondingly. Experimental observation shows that the radius of the drop base does not change until a critical value of the static advancing contact angle, θ_a , is reached. Further pumping results in subsequent drop spreading. In the reverse experiment, if we start from the static advancing contact angle, θ_a , and slowly suck liquid through the same orifice, then the contact angle will decrease without the drop base shrinking until another critical static receding contact angle, θ_r , is reached, after which the drop starts to recede and eventually collapses. For water drops on homogeneous perfectly flat glass surfaces, $\theta_r \sim 0^\circ\text{--}5^\circ$, while θ_a is in the range of $40^\circ\text{--}60^\circ$.

It is widely accepted that contact angle hysteresis follows from imperfections like surface roughness and mechanical or chemical heterogeneity of the solid substrate. This is indeed true but our view is that hysteresis could be found even on homogeneous perfectly flat solid surfaces as a consequence of the peculiar shape of the Derjaguin isotherm in the partial wetting case (figure 3). Already it is known that contact angle hysteresis is present on surfaces which are clearly molecularly smooth as with free liquid films [8, 9]. As thermodynamics requires a single, unique equilibrium contact angle, θ_e , any other contact angle, θ , in the range $\theta_r < \theta < \theta_a$ means that the liquid drop is not at equilibrium, but presumably there is a very slow ‘microscopic’ motion in a tiny vicinity of the apparent three-phase contact line. Such a motion abruptly becomes ‘macroscopic motion’ after the critical contact angles, θ_a or θ_r , are reached.

Let us assume that a sessile drop with the equilibrium contact angle θ_e is on a homogeneous perfectly flat solid substrate where the liquid profile depends on only one variable x , thus again, for simplicity, assuming a cylindrical drop. We have to solve the Laplace–Derjaguin equation (7) with the following boundary conditions $x = 0, h = H, h' = 0$, where H is the maximum height of the drop (apex) over the surface. We shall further assume that $h_e \ll H$. By integration of equation (7) we obtain for the derivative of the liquid profile, h' , the same expression (11), which we rewrite as

$$\frac{1}{\sqrt{1+h'^2}} = \frac{\gamma - \varphi(h, P_e)}{\gamma}, \quad (20)$$

where $\varphi(h, P_e) = -P_e(H - h) + \int_{h_e}^{\infty} \Pi dh$. Then the condition for equilibrium of a drop with an equilibrium flat film of thickness $h_e, h' \rightarrow 0$ at $h \rightarrow h_e$, becomes $\varphi = 0$, hence

$$P_e(H - h_e) - \int_{h_e}^{\infty} \Pi dh = 0, \quad (21)$$

where $P_e = -\gamma/\rho_e$, with ρ_e the radius of curvature of the circular part of the surface of the drop (figure 1), and hence $\cos \theta_e = (\rho_e - H)/\rho_e$.

By differentiating equation (21) with respect to P_e and bearing in mind that $P_e < 0$, we obtain

$$\frac{\partial H}{\partial P_e} = -\frac{H - h_e}{P_e} > 0. \quad (22)$$

Equation (22) shows that the apex height of equilibrium drops, H , decreases with increasing oversaturation, when the value of P_e diminishes, as equation (1) indicates ($P_e = P_v - P_l$). However, this decrease has certain limits, since drops can be at equilibrium with flat films only if $P_e > \Pi_{\min}$ (figure 5). For $P_e < \Pi_{\min}$ there is neither a liquid film nor a drop on the solid surface at equilibrium. When P_e decreases and approaches Π_{\min} , drops whose size diminishes should be ‘torn’ off the surface and pass into the vapour phase.

Maintaining the external conditions, we consider now non-equilibrium profiles of a drop when its volume is changed by pumping in liquid (see figure 4) and the excess pressure $P = P_v - P_l$ is different from the equilibrium value. Non-equilibrium contact angles are formed if $P < P_e$. The condition for the existence of a solution for equation (20) is $\gamma \geq \varphi(h, P) \geq 0$, where now the function $\varphi(h, P)$ is given by

$$\varphi(h, P) = -P(H - h) + \int_h^{\infty} \Pi(h) dh. \quad (23)$$

Examples of the form of the function $\varphi(h, P)$ (curves 2–3) are shown in the lower part of figure 5. The extrema of $\varphi(h, P)$ are found from the condition $P = \Pi(h)$, just as in the case of equilibrium, i.e. from the points of intersection of the Derjaguin isotherm with the straight line $P = \text{const}$. It follows from equation (20) that for a drop equilibrium profile, i.e. for $P = P_e$, the function $\varphi(h, P_e)$ vanishes at $h = h_e$. On the other hand, $\varphi(h, P_e)$ also vanishes at $h = H$. Since $\varphi(h, P_e) > 0$, the function $\varphi(h, P_e)$ has a maximum for $h = h_2$ (figure 5, curve 2).

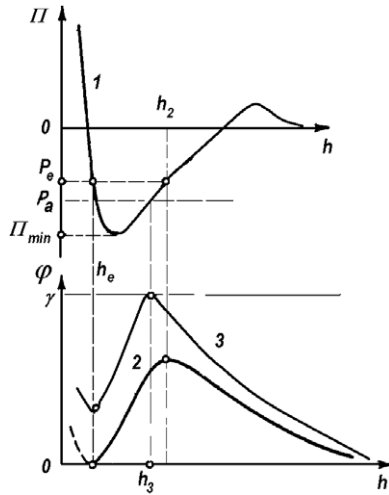


Figure 5. Sessile drop on a solid substrate. Upper figure: Derjaguin isotherm $\Pi(h)$ in the case of partial wetting (curve 1). Lower figure: corresponding curves (2, 3) of the functions φ (23) determining the conditions of equilibrium (curve 2) or quasi-equilibrium of a drop before the advancing starts (curve 3).

At lower pressures, i.e. for $P < P_e$, when the drop surface becomes more convex (from above), the line $\varphi(h, P)$ (figure 5, curve 3) is located above that of the equilibrium curve 2. The condition of quasi-equilibrium is violated and the perimeter of the drop starts to advance after the maximum of $\varphi(h, P)$ reaches the dashed line $\gamma = \text{const}$ (curve 3). This condition corresponds to the appearance of a thickness, $h = h_3$, with a vertical tangent $h' = \infty$ on the profile of the drop. Then liquid flows from the drop to the film by the so-called Frenkel’s caterpillar track (or unrolling carpet) mechanism at $\varphi(h, P) > \gamma$. This shows that the static advancing contact angle does not depend on the roughness of the solid substrate if size roughness is below the value of $h_3 \sim 10\text{--}30$ nm.

To calculate the value of the static advancing contact angle θ_a , we use the condition $\varphi(h, P) = \gamma$:

$$-P_a(H_a - h_3) + \int_{h_3}^{\infty} \Pi(h) dh = \gamma. \quad (24)$$

Keeping in mind that $P_a = \gamma(\cos \theta_a - 1)/H_a$, it follows that

$$\cos \theta_a = P_a h_3 + \frac{1}{\gamma} \int_{h_3}^{\infty} \Pi(h) dh \approx \frac{1}{\gamma} \int_{h_3}^{\infty} \Pi(h) dh. \quad (25)$$

Then, using (13) we obtain

$$\cos \theta_e - \cos \theta_a \approx 1 + \frac{1}{\gamma} \int_{h_e}^{h_3} \Pi(h) dh > 0, \quad (26)$$

which shows that $\cos \theta_e > \cos \theta_a$ and $\theta_a > \theta_e$. Thus, in the case of a drop, the advancing angle is always larger than the equilibrium angle.

Let us we now assume that the Derjaguin pressure changes very abruptly between h_{\min} and h_1 (figure 3), then $h_3 \approx h_{\min} \approx h_1 = \text{const}$ (figure 5). In this case equation (25) reduces to

$$\cos \theta_a \approx \frac{S_+}{\gamma}, \quad (27)$$

to be compared to (19). Equation (19) can be rewritten as $\cos \theta_e \approx 1 - \frac{S_-}{\gamma} + \frac{S_+}{\gamma}$ and hence $\cos \theta_e = 1 - \frac{S_-}{\gamma} + \cos \theta_a$. Thus $\cos \theta_e - \cos \theta_a \approx 1 - \frac{S_-}{\gamma} > 0$, as expected. Note that S_+ is significantly smaller than S_- , thus justifying equation (27).

In general, the advancing contact angle can be determined in the following way. From equation $P_a = \Pi(h_3)$ we get P_a as a function of the thickness h_3 . But the second, not the first, solution of the latter equation should be selected (figure 5, curve 3). Using such a solution in equation (24) yields $-\Pi(h_3)(H_a - h_3) + \int_{h_3}^{\infty} \Pi(h) dh = \gamma$, that provides the sought height of the drop H_a as a function of h_3 : $H_a = h_3 + \frac{\gamma - \int_{h_3}^{\infty} \Pi(h) dh}{-\Pi(h_3)}$, where $P_a = \Pi(h_3) < 0$ and $\gamma - \int_{h_3}^{\infty} \Pi(h) dh > 0$, so that indeed $H_a > h_3$. Note that, during the process of pumping liquid into the drop (figure 4) starting from the equilibrium position, the radius of the drop base contact line, L , remains constant and equal to the initial equilibrium value L_e . Let ρ_a be the radius of curvature of the drop at the moment of advancing. From figure 1 we have in this case

$$\begin{aligned} L_e &= \rho_a \sin \theta_a = -\frac{\gamma}{\Pi(h_3)} \sqrt{1 - \cos^2 \theta_a} \\ &= -\frac{\gamma}{\Pi(h_3)} \sqrt{1 - \left(\int_{h_3}^{\infty} \Pi(h) dh \right)^2}, \end{aligned} \quad (28)$$

where we have used equation (25). Then equation (28) determines the thickness h_3 as a function of the initial value of the equilibrium radius of the drop base. The volume (here in the two-dimensional case it is the area of the corresponding circular segment) of the drop at the moment of advancing, V_a , can be expressed as

$$V_a = \frac{L_e^2}{\sin^2 \theta_a} (\theta_a - \sin \theta_a \cos \theta_a). \quad (29)$$

Accordingly, using the relationship of θ_a and V_a , we can write $\theta_a = f(V_a)$ thus showing that the advancing contact angle is a function of the drop ‘volume’ at the moment of the advancing. As a matter of fact, it is possible to show that the advancing contact angle increases with the decrease of the drop volume. In [10] it is reported that the drop advancing contact angle increases as the volume of the drop decreases. In [11] the advancing contact angle of bubbles was considered, with a similar conclusion. We should have foreseen such a result, as the equilibrium contact angle (13) is also a function of the drop volume. Thus the static advancing contact angle in the case of drops is not a unique characteristic of solid substrates, but is also determined by the external conditions. Furthermore, evaporation, which takes place more intensively in the neighbourhood of the three-phase contact line [12], makes the measurements of both advancing and equilibrium contact angles of drops not so straightforward and unambiguous in the case of volatile liquids. This is the reason why a number of experiments on wetting/spreading of liquids have been performed in thin capillaries, where evaporation can be significantly diminished, if not ruled out. So let us consider for completeness the case of a meniscus advancing and receding inside a capillary.

5. Advancing and receding contact angles in capillaries

Let us now consider the equilibrium state of the wetting liquid meniscus ($0^\circ \leq \theta_e < 90^\circ$) in a capillary with a flat slit of breadth $H \gg h_e$, where h_e is the thickness of the equilibrium wetting film covering the surface of the capillary walls. Then the liquid in the central part of the slit is outside the range of the surface force action. Neglecting, as in the case of the drop studied above, the effect of gravitational forces, the radius of curvature of the surface of the meniscus in the central part of the slot, ρ_e , is constant. Let h be the distance along the normal between the substrate and the surface of the liquid. Then $h(x)$ defines the profile of the liquid layer, where x is the coordinate along the significant direction in the plane of symmetry of the capillary.

Between the meniscus of constant curvature ρ_e and the flat film of thickness $h_e = \text{const}$ there is the transition zone. Only capillary Laplace forces act in the region of the unperturbed meniscus, and only surface forces act in the flat film. However, both these forces act simultaneously within the transition zone as in the case of drops. Then the equilibrium profile of the meniscus is described by the Laplace–Derjaguin equation (7). Here, however, the equilibrium pressure P_e is positive because there is concavity from the liquid side. On the other hand, such equilibrium pressure is unique and completely determined by the capillary size H . This is easy to understand, because the equilibrium height of the drop apex, H , was determined by the vapour pressure $p > p_s$ (oversaturation), but in the case of the capillary the corresponding H value is fixed, hence there is only one vapour pressure $p < p_s$ (undersaturation), which corresponds to the equilibrium.

Because of the symmetry of the meniscus, it suffices to consider the equilibrium of a liquid layer $h(x)$ over the thickness range from $h = h_e$ at $x = \infty$ to $h = H$ at $x = 0$. The solution of equation (7) includes three constants, namely the excess pressure $P_e = \text{const} > 0$, and two integration constants. To determine these constants, we have three boundary conditions: two at the centre of the meniscus $h = H, h' = -\infty, x = 0$, and the condition of swift matching of the meniscus with the flat liquid film $h = h_e, h' = 0, x \rightarrow \infty$.

Multiplying both sides of equation (7) by h' and integrating it with respect to x from 0 to x , we obtain

$$\frac{\gamma}{\sqrt{1+h'^2}} = \psi(h, P_e), \tag{30}$$

where

$$\psi(h, P_e) = P_e(H - h) - \int_h^\infty \Pi dh. \tag{31}$$

By solving equation (30) with respect to h' , we obtain $h' = -[\frac{\gamma^2}{\psi^2(h, P_e)} - 1]^{1/2}$. Then using the above given boundary conditions and equations (30) and (31) we get

$$\gamma = \psi(h_e, P_e) = P_e(H - h_e) - \int_{h_e}^\infty \Pi dh. \tag{32}$$

This equation (32), together with the expression of $P_e > 0$, allows expression of the equilibrium contact angle, θ_e , in a

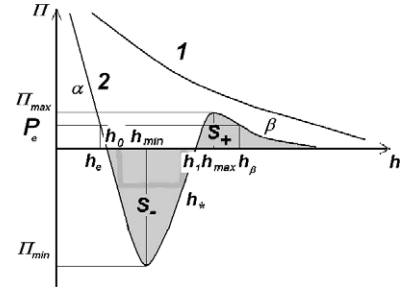


Figure 6. Derjaguin isotherms, $\Pi(h)$: 1—complete wetting, 2—partial wetting, where here h_e is the equilibrium thickness of an equilibrium flat film along the capillary, coexisting ahead of the meniscus.

form similar to equation (13). We have for the capillary meniscus

$$\cos \theta_e \approx 1 + \frac{1}{\gamma} \int_{h_e}^\infty \Pi(h) dh, \quad \text{for } h_s \ll H. \tag{33}$$

There are three solutions of equation $\Pi(h_e) = P_e > 0$ (figure 6). Only the thinnest one satisfies the thermodynamic stability condition $\frac{d\Pi(h_e)}{dh} < 0$. It belongs to the so-called α -branch of the Derjaguin isotherm. The other metastable solution, h_β , belongs to the β -branch. For a more detailed discussion of this question see [5]. Note that h_* corresponds to an unstable equilibrium flat film (figure 6).

It is noteworthy that the lower limit of integration, h_e , in equation (13) for the drop and equation (33) for the meniscus in a capillary are very different, as illustrated in figures 3 and 6, respectively. On the other hand, another difference is that there are an infinite number of equilibrium contact angles for a drop on a solid substrate (each of them corresponds to a value of the oversaturated vapour pressure in the surrounding air), but there is a single, uniquely defined equilibrium contact angle of the liquid meniscus in a capillary.

Only equilibrium α -films are observed on the surface of thin capillaries if $P_e > \Pi_{\max}$, where Π_{\max} is the stability limit of β -films (figure 6). This is the case for narrow enough capillaries. But if $P_e < \Pi_{\max}$, the formation of metastable β -films is possible, and it has been observed experimentally [13, 14].

To obtain the equilibrium profile of a liquid in a flat capillary, we rewrite the Laplace–Derjaguin equation (7) in the following form:

$$h'' = \frac{1}{\gamma} [1 + (h')^2]^{3/2} [P_e - \Pi(h)], \tag{34}$$

where it appears that the sign of h'' , and therefore the curvature of the surface, is determined by the sign of the difference $[P_e - \Pi(h)]$. In this case $P_e = \text{const} > 0$, but the value of $\Pi(h)$ varies from $\Pi(h_e) = P_e$ to $\Pi = 0$ for $h \rightarrow H$. If $P_e > \Pi_{\max}$, the bracketed difference is always positive and the liquid profile inside the transition zone is (from the liquid side) concave everywhere ($h'' > 0$). However, in thick enough capillaries $P_e < \Pi_{\max}$ (figure 6). Then $h'' < 0$ and the surface of the liquid should possess a locally convex cap (from the

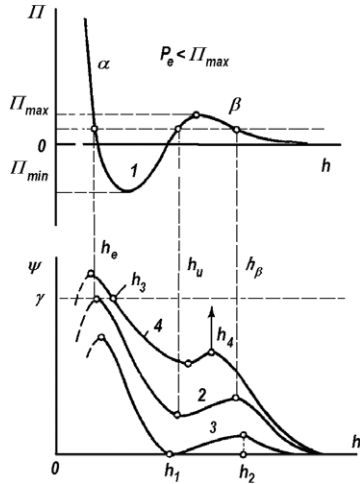


Figure 7. Meniscus in a capillary. Upper figure: Derjaguin isotherm, $\Pi(h)$ in the case of partial wetting (curve 1). The lower figure illustrates the corresponding curves, 2–4, of the function $\psi(h, P)$ (31), determining the conditions of local equilibrium of the meniscus, 3–4, and equilibrium, 2.

liquid side). Below we consider just this case of relatively thick capillaries, $r > r_{cr}$. If $\Pi_{max} \sim 10^5 \text{ cm}^{-2} \text{ dyne}$, then $\frac{\gamma}{r_{cr}} \sim 10^5 \text{ dyne}$ and in the case of water $\gamma \sim 72 \text{ dyne cm}^{-1}$: $r_{cr} \sim 7.2 \times 10^{-4} \text{ cm} \sim 7 \mu\text{m}$.

According to equations (30) and (31) the function $\psi(h, P_e)$ should be such that $0 \leq \psi(h, P_e) \leq \gamma$. As $\psi(h, P_e) = 0$, the derivative h' diverges to infinity at the thickness corresponding to the centre of the capillary, $h = H$. When $\psi(h, P_e) = \gamma$, there is zero derivative, which is satisfied for $h = h_e$. As an illustration of the equilibrium function $\psi(h, P_e)$, curve 2 is shown in figure 7. The positions of the extrema of curve 2 can be found by differentiation of equation (31) with respect to h , which results in

$$\frac{d\psi(h, P_e)}{dh} = -P_e + \Pi(h). \quad (35)$$

Hence, as the liquid thickness varies in the range $h_e < h < H$, the positions of the maximum and minimum on curve 2 correspond to the thicknesses h_u and h_β , where the straight line $P_e = \text{const}$ intersects the Derjaguin isotherm 1 and $P_e = \Pi(h)$ (figure 7).

Let us consider that the pressure behind the meniscus is changed by a value ΔP relative to its equilibrium value P_e , while the film in front and the vapour maintain their initial equilibrium state. For $\Delta P \neq 0$, i.e. in a non-equilibrium system, we can subdivide the overall system into the following regions (figure 8): a region 1 in a state of quasi-equilibrium where the hydrodynamic pressure $P = P_e + \Delta P$ is constant everywhere; a transport region 2 where viscous liquid flow occurs with the pressure gradually changing from P to P_e , and a region 3 of thin flat film, where the pressure equals the initial equilibrium P_e . Since the highest pressure difference in the transition region occurs in the thinnest part 2, it is clear that region 2 covers part of the transition region which immediately adjoins the equilibrium film h_e in region 3.

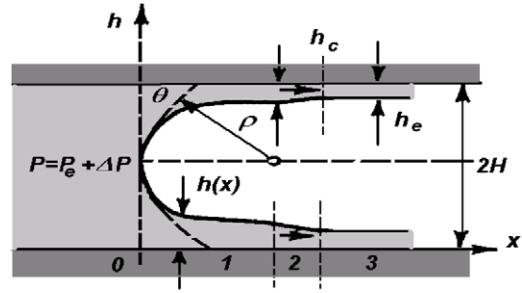


Figure 8. Profile of the meniscus in a flat capillary of thickness $2H$ indicating the various zones discussed in the main text.

Flow starts at once under the action of the pressure difference thus created, which can be separated provisionally into a rapid and a slow one. Since the resistance of the liquid–vapour phase boundary to changes in its form is small at low capillary numbers, $Ca = U\eta/\gamma \ll 1$, the fastest change is that of the curvature of the meniscus; U is the velocity of the receding/advancing meniscus, and η is the shear/dynamic viscosity. Hence, a new quasi-equilibrium state of the meniscus occurs with the pressure change, so that

$$P = P_e + \Delta P = \frac{\gamma h''}{(1 + h'^2)^{3/2}} = \frac{\gamma}{\rho} = \text{const}. \quad (36)$$

This is outside the zone of action of surface forces, where $\rho = \cos\theta/H$ is the radius of curvature of the main part of the meniscus and θ is a new value of the contact angle, corresponding to the local equilibrium state, which cannot be a true equilibrium any more. Then the change in the curvature of the meniscus causes a change in the vapour pressure over it, and hence the liquid starts to transfer by evaporation/condensation from the surface of the meniscus to the surface of the equilibrium film in front (zone 3 in figure 8). Besides, the increase in pressure inside the liquid causes it to flow to those parts of the film where the initial equilibrium pressure $\Pi(h_e) = P_e$ is still maintained. Note that the argument applies equally well to the case when the sign of ΔP is opposite, with the corresponding direction of the transfer processes inverted.

To simplify matters in the following we limit the discussion to liquids with a low volatility, whose rates of evaporation and condensation are small. The main assumption is that the liquid flow from the quasi-equilibrium meniscus to the equilibrium film in front is very slow until some critical pressure difference, ΔP_a (in the case of an advancing meniscus) or ΔP_r (in the case of a receding meniscus), is reached. These conditions may not exist in the case of complete wetting, when the equilibrium film is sufficiently thick. However, static hysteresis is usually observed in cases of partial wetting (at $0 < \theta$), when the surface of the solid body is covered with significantly thinner films, where the viscous flow resistance is very high.

We write the conditions of quasi-equilibrium of the meniscus in region 1, in the boundaries of which fluxes can be neglected and where the excess pressure can be considered to be constant at all points and equal to $P = P_e + \Delta P =$

const. We assume that equation (36) still describes the quasi-equilibrium profile of the liquid, $h(x)$, in region 1 in the absence of true thermodynamic equilibrium in the whole system. That is, we assume that

$$\frac{\gamma h''}{(1+h'^2)^{3/2}} + \Pi(h) = P. \quad (37)$$

The earlier mentioned two boundary conditions at the centre of the meniscus are maintained. However, since region 1 cannot be now connected by an equilibrium or quasi-equilibrium liquid profile with the flat equilibrium film in front, we must here assume that there is a flow zone 2 in between (figure 8). The third condition is $P = \text{const}$, since the value of the excess pressure P is now fixed independently and is not determined by the thickness of the slit and the Derjaguin pressure, as in the equilibrium case.

The solution range of equation (37) is limited from below by a certain thickness $h_c \geq h_e$, corresponding to the beginning of the flow zone (figure 8). The condition $h' = 0$ is not fulfilled at $h = h_c$ and a micro-contact angle is formed there, $\tan \theta \approx \theta = h'(h_e)$, whose value can be found by solving equation (37).

By integrating equation (37) once, we obtain again equations (30) and (31), but now we have

$$\psi(h, P) = P(H - h) - \int_h^\infty \Pi dh, \quad (38)$$

where the equilibrium pressure, P_e , is replaced by the new non-equilibrium pressure, P . The region where a solution of equation (37) exists is determined by the real values of h' , which exist only under the same conditions as in the case of equilibrium; that is,

$$0 \leq \psi(h, P) \leq \gamma. \quad (39)$$

There is no solution if $\psi > \gamma$ or $\psi < 0$. If any of these conditions is violated then the boundary of the flow zone, h_c , and the centre of the meniscus cannot be connected by a continuous profile. Accordingly, quasi-equilibrium becomes impossible, i.e., the meniscus cannot be at rest and must start moving. As will be shown below, the violation of one of the inequalities in (39) determines the static advancing contact angle, θ_a , and the violation of the other condition the static receding contact angle, θ_r .

Let us first determine the value of the static advancing contact angle, θ_a . For the motion of the meniscus to the front of the capillary, the pressure in the liquid must increase, which diminishes the Laplace pressure jump at the meniscus–vapour interface. Consequently, in this case $P < P_e$ and $\Delta P < 0$. This means that $\psi(h, P)$ (curve 3) is located below $\psi(h, P_e)$ (curve 2) in figure 7. Since $P < P_e$, the thickness interval between the positions of the minimum and the maximum broadens for the Derjaguin pressure in the case of partial wetting (curve 1, figure 7). With $P < \Pi_{\text{max}}$ we have $h_1 < h_u$ and $h_2 > h_\beta$.

When the absolute value of ΔP increases to a certain critical value ΔP_a , the curve $\psi(h, P)$ can touch at its minimum the abscissa axis h , as shown by curve 3 in figure 7. This

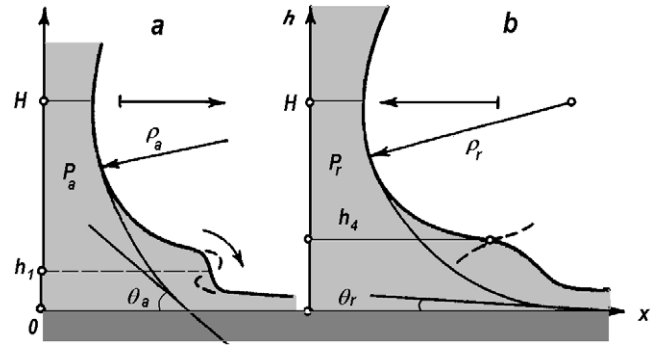


Figure 9. Meniscus on a capillary (see also figure 7). Critical profiles and a —static advancing contact angle with a vertical tangent for the thickness h_1 ; b —static receding contact angle with violation of the quasi-equilibrium condition in the region of thick β -film, h_4 .

means that a point with vertical tangent appears on the profile for $h = h_1$, where $h' = -\infty$ (figure 9).

For $|\Delta P| > \Delta P_a$ the curve $\psi(h, P)$ intersects the axis h and the value of ψ becomes negative for a certain range of thicknesses. Vertical tangents appear at the upper and lower parts of the profile, which becomes discontinuous (dashed lines in figure 9(a)). Note that, in the region of the profile marked by the dashed line, different Derjaguin pressures act, corresponding always to attraction between identical phases. Thus the dashed part of the profile is unstable; the profile loses stability and a ‘transfer’ of liquid starts towards the front of the spreading film. Note that equation (37) does not give the profile of the flowing film, but only determines the limiting positions of the static profile before the flow has set in. We see how complex the flow picture is after the advancing started.

Although the mechanism of violation of the equilibrium is understood physically, the value of the static advancing contact angle, θ_a , cannot be calculated exactly, since the point $h = h_1$ belongs to a region where the condition $h'^2 \ll 1$ is violated and the flat film Derjaguin pressure, $\Pi(h)$, cannot be used. We therefore limit ourselves to an approximate estimation of θ_a . For $\theta = \theta_a$ and $P = P_a$ the function $\psi = 0$ at $h = h_1$ (figure 7). Hence, from equation (38) it follows that

$$P_a(H - h_1) = \int_{h_1}^\infty \Pi(h) dh. \quad (40)$$

As the pressure P_a and contact angle θ_a are connected by the general relationship $P_a = \gamma \cos \theta_a / H$, we get

$$\cos \theta_a = \frac{1}{\gamma(1 - \frac{h_1}{H})} \int_{h_1}^\infty \Pi(h) dh \approx \frac{1}{\gamma} \int_{h_1}^\infty \Pi(h) dh. \quad (41)$$

It appears that the functional dependence (41) coincides with the corresponding expression for the static advancing contact angle in the case of drops (25). However, now the contact angle obtained has a unique value. Note that the integration in equation (41) (advancing contact angle in the meniscus case) and in equation (23) (advancing contact angle for the case of a drop) is to be done over quite very different regions. We solve the equation $\Pi(h_1) = \gamma \cos \theta_a / H$, using the second of its three solutions, that gives $h_1 = F(\gamma \cos \theta_a / H)$. Substitution

of the latter expression into equation (41) gives a non-linear equation to determine $\cos\theta_a$. This permits us to conclude that the Derjaguin isotherm determines uniquely not only the equilibrium value of the contact angle but also the static advancing contact angle, θ_a .

Let us now consider the static receding contact angle, θ_r . In this case, the value $\Delta P > 0$, since the curvature of the meniscus increases with decreasing pressure in the liquid phase. It follows from equation (38) that for $P > P_e$ the line $\psi(h, P)$ should be everywhere above the equilibrium curve $\psi(h, P_e)$. Its shape is shown by curve 4 in figure 7. Violation of the conditions of quasi-equilibrium occurs in this case if $\psi(h, P) = \gamma$; i.e., an increase in ΔP to such a critical value ΔP_r makes the curve $\psi(h, P_r)$ intersect the dashed line $\gamma = \text{const}$.

Consider only the case of quasi-equilibrium with receding meniscus in thick enough capillaries, when $P_e < \Pi_{\text{max}}$. Under certain conditions, which are determined by the actual form of the Derjaguin isotherm, $\Pi(h)$, with increasing ΔP , the curve $\psi(h, P)$ can touch the straight line $\gamma = \text{const}$ with the right-hand rising maximum (at $h = h_4$) earlier than thickness h_3 comes out of the transfer zone ($h_3 < h_c$) (figure 7, curve 4). Then a point with horizontal tangent $h' = 0$ appears on the convex part of the meniscus. Violation of the quasi-equilibrium occurs at $h = h_4$ and then the earlier mentioned stability condition D is violated. The quasi-equilibrium liquid profile becomes unstable and flow has to set in.

For $P > P_r$, the part of the profile indicated in figure 9(b) by dashed lines starts sliding. It can be seen from figure 7 that the thickness h_4 belongs to the β part of the Derjaguin isotherm 1. Thus, when the meniscus is displaced from it, a thick metastable β -film should remain behind, a prediction that has been confirmed experimentally [13–15].

Since the profile of the receding meniscus in the transition zone has a low slope, the value of the static receding contact angle, θ_r , in the case of sufficiently thick capillaries, that is, for $P_e < \Pi_{\text{max}}$, can be determined exactly. For this purpose we use the following system of equations:

$$P_r(H - h_4) - \int_{h_4}^{\infty} \Pi(h) dh = \gamma, \quad (42)$$

$$P_r = \Pi(h_4), \quad (43)$$

where the first equation was derived from expression (38), with $\psi = \gamma$, for $P = P_r$ and $h = h_4$. The second equation results from the fact that h_4 is an inflection point at which $h'' = 0$. Then from equation (37) follows that $\Pi(h_4) = P_r$.

For the solution of the systems of equations (42) and (43), we must know the form of the Derjaguin isotherm $\Pi(h)$. If we choose for its β branch a behaviour like $\Pi = B/h^2$, valid for β -films of water, we obtain, after integration in equation (42),

$$h_4 = \frac{B}{\gamma} \left(\sqrt{1 + \frac{\gamma H}{B}} - 1 \right) \quad \text{and} \quad P_r = \frac{B}{h_4^2}, \quad (44)$$

where B is a parameter of the surface forces. If $h_4 \ll H$, these expressions (44) reduce to $h_4 \approx \sqrt{BH/\gamma}$ and $P_r \approx \gamma/H$, respectively. Hence, $\theta_r \approx 0$. Thus, if thick β -films are formed

behind the receding meniscus, the static receding contact angle, θ_r , should be close to zero, a prediction in good agreement with experimental observations [15–17]. This solution is valid also for the case of contact of two immiscible liquids in a capillary (for example, water–oil). The only difference is that instead of the isotherm of a wetting film the theory should include in this case the Derjaguin pressure of thin layers of wetting liquids enclosed between a solid substrate and the other liquid.

6. Conclusion

In view of the results found we can conclude by emphasizing that the static contact angle hysteresis on homogeneous, perfectly flat solid surfaces is directly related to the peculiar form of the Derjaguin isotherm. Needless to say, in reality with heterogeneous surfaces the possibility of the simultaneous appearance of static hysteresis phenomena of different nature must be taken into consideration.

It would be of interest to observe the behaviour of deformed menisci in a capillary or a drop for $\theta_e < \theta < \theta_a$ and for $\theta_e > \theta > \theta_r$. If static hysteresis is related to the conditions of quasi-equilibrium, a slow motion of the position of the apparent three-phase contact line wetting perimeter should be observed. The latter slow motion should change dramatically upon attaining the static advancing or receding contact angles, θ_s and θ_r , respectively. Contact line stability and line tension are also interesting problems of ongoing research [18].

Acknowledgments

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