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Wetting phenomena and nano forces

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Wetting phenomena and nano forces

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Introduction

Why do droplets of different liquids deposited on the identical solid substrate behave so differently? Why identical droplets, for example, aqueous droplets, deposited on different substrates behave also differently?

A mercury droplet does not spread on a glass substrate. It rather forms a spherical cap with the contact angle bigger than $\pi/2$ (Fig. 1a). An aqueous droplet deposited on the same glass substrate spreads only partially down to some contact angle, θ , which is in between 0 and $\pi/2$ (Fig. 1b). However, an oil droplet (hexane or decane) deposited on the same glass substrate spreads out completely (Fig.1c), and the contact angle decreases with time down to the zero value.

By convention, the contact angle is measured inside the liquid phase Figs. 1a, 1b, 1c).

Fig.1a. Non-wetting case: contact angle is bigger than $\pi/2$. Examples: a mercury droplet on a glass surface, or a water droplet on Teflon surface.

Fig.1b. Partial wetting case: the contact angle is in between 0 and $\pi/2$. Examples: a water droplet on a glass, mica, silicon wafer surfaces.

Fig.1c. Complete wetting case: the droplet spreads out completely and the dynamic contact angle tends to zero with time. Example: an oil droplet on a glass surface.

These three cases (Figs. 1a, 1b, and 1c) are referred to as: non-wetting, partial wetting and complete wetting, respectively. In all three cases mentioned above a *three-phase contact line* (solid-liquid-vapour) is formed by a liquid drop deposited on a solid surface when we approach a solid surface.

Needless to say, wettability (complete, partial or none) is determined by the nature of both the liquid and the solid substrate and their interactions.

Below we consider as an example a behaviour of two the most important liquids in contact with solid substrates: water and aqueous solution (polar liquids) and oils (non polar liquids).

Water is essential for our life. It may very well be that without water, life would have not started on Earth. The important observation is that in the case of water and aqueous solutions the behaviour of thin liquid layers in a vicinity of the three phase contact line is a very peculiar one and differs substantially from other liquids. There is no need to mention that our life is very much adjusted to all even a very minute properties of water. The special behaviour of thin water layers tells us some very important message, which we currently are unable to decode.

Contact angle and adsorption on solid substrates

Before going further we consider a consequence of vapour adsorption on solid substrates.

It is well known from the theory of adsorption that vapours adsorb on solid substrates. Amount of adsorbed molecules or adsorption layers on the solid surfaces is determined by the vapour pressure in the ambient air.

Let us consider a solid plane in a contact with a vapour in the ambient air. As we already mentioned the liquid vapour was adsorbed on the surface of a solid plane. In the case of low adsorption (no polymolecular adsorption) the dependency of the adsorption on the vapour pressure in the ambient air p is described by the Langmuir isotherm. The latter is written below in the following form:

$$\Theta = \frac{(p/p^*)\exp\left(-\frac{\Delta U}{kT}\right)}{1 + (p/p^*)\exp\left(-\frac{\Delta U}{kT}\right)}, \quad (1)$$

where Θ is the fraction of solid substrate covered by adsorbed vapour molecules; k and T are the Boltzmann constant and absolute temperature in Kelvin; p^* is a characteristic vapour pressure and ΔU is the difference between free energy of vapour molecules in adsorbed state and in the vapour (see [1] for example). If $\Delta U/kT \gg 1$, that is the energy of adsorbed molecules is much higher than the energy of free vapour molecules (or interaction between water molecules is much stronger than the interaction of water molecules with the solid substrate), then $\Theta \approx 0$, no adsorption takes place. In this and only this particular case the water droplet forms 180° contact angle with the solid substrate (see Fig. 2a). We refer to this case as the ideal complete non-wetting case.

Fig. 2a. Water droplet on ideal complete non-wetting solid substrate, contact angle is equal to 180° : interaction between water molecules is much stronger than interaction between water molecules and the solid substrate. No adsorption of water molecules on the solid substrate.

Surprisingly there is no surfaces in the nature, which are completely non-wet by water. Even on the most hydrophobic solid, Teflon, water droplets form the contact angle in the range of 120° . The latter means that the condition $\Delta U/kT \gg 1$ is not satisfied and adsorption of water molecules on even Teflon substrate is unavoidable.

The latter means that we came to a very interesting conclusion: there is a strong link between adsorption of water molecules on solid substrates and the contact angles. Hence, the real picture should include adsorption of water vapour on non-wettable solids (Fig. 2b)!

Fig. 2b. Water droplet on a real non-wettable substrate. Contact angle, θ , is less than 180° , and, hence, adsorption of water molecules on the solid substrate is unavoidable!

Now let us look on the adsorption of water molecules from a different point of view. Let the original interfacial tension of bare solid substrate be γ_{sv}^0 . After adsorption of water molecules the new interfacial tension becomes γ_{sv}^a , which can be either higher or lower than the original interfacial tension γ_{sv}^0 . After the fraction Θ of the solid substrate is covered by adsorbed molecules the new interfacial tension, γ_{sv} , can be presented in the following form:

$$\gamma_{sv} = \gamma_{sv}^0(1 - \Theta) + \gamma_{sv}^a\Theta. \quad (2)$$

Comparison of the latter equation and Langmuir Eq. (1) shows that the solid liquid interfacial tension, γ_{sv} , is not a unique property of the solid substrate but depends on the vapour pressure in the ambient air, p , that is, $\gamma_{sv}(p)$.

Above we considered only the case of non-wetting substrates, where adsorption of water molecules is small because the interaction between water molecules is substantially stronger than the interaction between water molecules and the solid substrate. Such surfaces are referred to as “low energy surfaces”. In this case adsorption of water molecules on the solid substrates is small because adsorption results in a higher

interfacial tension γ_{sv} as compared with the initial interfacial tension γ_{sv}^0 . However, still the adsorption is unavoidable even in this extreme case!

In the case of partial or complete wetting the situation is very much different. In this case adsorption of water molecules on the solid substrate results in lowering of the solid-vapour interfacial tension and even more than that, the adsorption results in a polymolecular adsorption, that is in a formation of thin adsorption water films on the solid substrate. There is no need to say that the interfacial tension can not be referred to any more as solid-vapour interfacial tension in this case but rather solid–liquid film–vapour interfacial tension.

We have to remind that there is no experimental way to determine independently the solid – vapour interfacial tension and the latter becomes even more sophisticated in the case of the presence of adsorbed films on the solid substrate. Fortunately, there is a completely different way of thinking, which allows us to do so!

Equilibrium conditions

When we reach the range of 10^2 nm thickness inside droplet what is needed for a complete description of a fluid in the equilibrium with a solid (Fig. 3)?

Fig. 3. Liquid in contact with solid, vapour and liquid films in front. θ is the macroscopic contact angle (measured inside the liquid).

At the equilibrium the following three equilibria should hold:

- (a) the liquid in the droplet must be at the equilibrium with its own vapour;
- (b) the liquid in the droplet must be at the equilibrium with the solid;
- (c) the vapour must be at the equilibrium with the solid substrate. The latter as we already showed above results in the formation of adsorption layers on the solid surface.

The first requirement (a) results in the equality of chemical potentials of the liquid molecules in the vapour and inside the droplet. The latter gives the following expression of the excess pressure, P_e , according to well-known Kelvin equation:

$$P_e = \frac{RT}{v_m} \ln \frac{p_s}{p}, \quad (3)$$

where v_m is the molar volume of the liquid, p_s is the pressure of the saturated vapour at the temperature T , R is the gas constant, p is the vapour pressure which is at the equilibrium with the liquid droplet, the excess pressure $P_e = P_a - P_l$, where P_l is the pressure inside the liquid and P_a is the pressure in the ambient air. The latter equation determines the unique equilibrium excess pressure P_e and, hence, the unique radius of the droplet,

$$\Re = -\frac{2\gamma}{P_e}. \quad (4)$$

We remind now that the excess pressure inside the drop, P_e , should be negative (pressure inside the droplet is bigger than the pressure in the ambient air). That means that the right hand side in Eq. (3) should be negative also. The latter is negative only if $p > p_s$, that is, the droplets can be at the equilibrium only with oversaturated vapour! Note, the equilibration process goes for sufficiently long time (hours) and it is necessary to keep oversaturated vapour over a solid substrate under investigation until the equilibrium is reached. To the best of our knowledge nobody can do that. The latter means that it is difficult to investigate experimentally equilibrium droplets on the solid substrate. There is a flood of investigations published in the literature of the equilibrium contact angles of droplets on solid substrate. The previous consideration shows that contact angles measured are mostly not at the equilibrium at all.

Now we consider requirements of the equilibrium (b) and (c). Let us assume that we can create at least theoretically an oversaturated vapour over the solid substrate and wait long enough until the equilibrium is reached. Now the liquid molecules in the vapour are at the equilibrium with the liquid molecules in the droplet. The presence of adsorbed liquid layers on the solid substrate results in the case of partial or complete wetting in lower surface tension as compared with the surface tension of the bare solid surface, γ_{sv}^0 , because the presence of liquid molecules on the surface changes the initial surface tension. The presence of adsorbed liquid films results in the formation of a new interfacial tension, γ_{svh_e} , where h_e is the thickness of the adsorbed layer.

In Fig. 4 an equilibrium liquid droplet is presented in the contact with an equilibrium adsorbed liquid film on the solid surface. What happens in a vicinity of the line where they meet?

Fig. 4. Cross section of an equilibrium liquid droplet (at oversaturation) in the contact with an equilibrium adsorbed liquid film on the solid substrate. What happens on the line (shown by an arrow) where they meet?

Is the situation presented in Fig. 4 possible? Answer is obvious, such sharp transition from the liquid droplet to the liquid film is impossible: on the line shown by the arrow the capillary pressure will be infinite. Hence, it should be a smooth transition from the flat equilibrium liquid film on the solid surfaces to the spherical droplet, as shown in Fig. 5, where such smooth transition is shown.

Fig. 5. Transition zone from the flat equilibrium liquid film on a solid surface to the liquid droplet. The arrow shows the point where to the left the liquid profile is concave and to the right the profile is convex.

Fig. 6. Transition from macroscopic droplet to thin film in front via intermediate (transition) region.

Let us call this region, where transition from a flat film to the droplet takes place, a transition zone (Fig. 6). The presence of the transition zone shows that pure capillary forces can not keep the liquid in this zone at the equilibrium: the liquid profile is convex (hence, the capillary pressure under the liquid surface is higher than in the ambient air) to the right from the arrow in Fig. 5, and the liquid profile is concave (hence, the capillary pressure under the liquid surface is lower than in the ambient air) to the left from the arrow in Fig. 5. The shape of the profile inside the transition zone is determined by the nano (surface) forces action [2].

The surface forces were introduced step-by-step by a number of scientists (see [3] for more details). The most famous theory of surface forces was independently published by Derjaguin and Landau and then Verwey and Overbeek in the thirties of XXth century and referred to as DLVO theory [4, 5].

Before considering the surface forces action in a vicinity of the three phase contact line let us consider what should happen in the case of non-volatile liquid, when the formation of adsorbed layers is slow. Usually low volatility means liquids with big molecules, the latter means high viscosity and correspondingly higher time scale of equilibration process with the oversaturated vapour. In spite of that let us assume that the liquid is non-volatile. In the case of partial wetting, as we already saw, at equilibrium liquid droplets can not be at equilibrium with a bare solid surface but at the equilibrium with an adsorption layer of the liquid molecules on the solid substrate in front of the droplet. If the liquid is volatile then this layer is created by means of evaporation-adsorption. However, if the liquid is non-volatile the same layer should be created by means of flow from the droplet edge onto the solid substrate. As a result the

solid substrate is covered at the equilibrium by an equilibrium liquid layer of thickness h_e . The thickness of the equilibrium liquid film, h_e , is determined (as we see below) by the potential of surface forces action. Characteristic time scale of this process is hours, because it is determined by the flow in the thinnest part in the vicinity of the apparent three phase contact line, where the viscous resistance is very high. During these hours evaporation of the liquid from the droplet can not be ignored and we go back to the problem of volatility.

Let us assume, however, that the equilibrium film after all forms in front of the liquid droplet and we waited enough for the equilibrium. Now we have again three following interfacial tensions: γ , γ_{sl} and γ_{svh_e} , which are interfacial tensions of the following interfaces liquid -vapour, solid – liquid and solid substrate covered with the liquid film of thickness h_e - vapour. We came back to the same interfacial tensions as in the case of volatile liquid. We can not measure the interfacial tension, γ_{svh_e} . However, there is an answer to this problem and the answer is given below.

Thin liquid films on the solid substrate and solid-liquid interfacial tension

The excess free energy, Φ , per unit area of a flat equilibrium liquid film of thickness h_e on a solid substrate at the equilibrium with the vapour in the surrounding air is equal to

$$\Phi = \gamma + P_e h_e + f_D(h_e) + \gamma_{sl} - \gamma_{sv}^0, \quad (5)$$

where $f_D(h_e)$ is the excess free energy due to the action of surface forces. Note, according to the spontaneous adsorption of liquid molecules in the case of partial or complete wetting the latter excess free energy should be negative: otherwise the liquid molecules would not adsorb at all.

Because of the equilibrium of the liquid film with the vapour the excess pressure, P_e , can not be left as an arbitrary constant: it is determined by the equality of chemical potentials of liquid molecules in the film and in the vapour. The latter requirement results in the well-known Kelvin's equation (3).

The excess free energy (5) is a function of one variable, h_e , which is the thickness of the equilibrium film. Hence, the usual conditions of the thermodynamic equilibrium should hold, which give a minimum to the excess free energy (5). Those

conditions are as follows $\frac{d\Phi}{dh_e} = 0$, $\frac{d^2\Phi}{dh_e^2} > 0$. The first requirement results in

$$P_e = \Pi(h_e), \quad (6)$$

and the second requirement yields

$$\frac{d\Pi(h_e)}{dh_e} < 0, \quad (7)$$

where $\Pi(h) = -\frac{df_D(h)}{dh}$ is referred to as the disjoining pressure [4]. The disjoining pressure, $\Pi(h)$, is the physical property, which can be experimentally measured (see for example [3], [4], [5]). Using the latter definition we can rewrite the excess energy $f_D(h)$ as: $f_D(h) = \int_h^\infty \Pi(h)dh$.

Eq. (6) determines the thickness of the equilibrium liquid film, h_e , via disjoining pressure isotherm. Eq. (7) gives the well-known stability condition of flat equilibrium liquid films [4].

According to the modern theory of surface forces the following types of disjoining pressure are known and presented in Fig. 7 [2,4].

Fig. 7. Types of isotherms of disjoining pressure: 1 – complete wetting, observed for oil films on quartz, glass, metal surfaces; 2 – partial wetting, observed for aqueous films on quartz, glass, metal surfaces; 3 – non-wetting case.

According to the stability condition (7) all flat equilibrium films are stable in the case of complete wetting (curve 1, Fig. 7) and only films are stable in the range of thickness from 0 to t_{min} (these films are referred below as α -films, which are absolutely

stable, see below) and at $h > t_{max}$ (the latter films are referred below as β -films and it is shown below that they are meta-stable) in the case of partial wetting (curve 2 in Fig. 7). Hence, only those - α - and β - films can exist as flat films.

Note again, s-shaped disjoining pressure isotherms (curve 2 in Fig. 7) are characteristic shapes in the case of water and aqueous solutions thin films. All properties of water and aqueous solutions are vitally important for our life. The latter means that the peculiar shape of disjoining pressure of water and aqueous solutions, presented in Fig. 7 curve 2 in some way determines the existence of life. At the moment we do not know in which way it does but the peculiar shape of curve 2 in Fig. 7 tell us something what we are unable to decode.

Now we can rewrite the expression for the excess free energy of the film (5) using the disjoining pressure in the following way:

$$\Phi = \gamma + P_e h_e + \int_{h_e}^{\infty} \Pi(h) dh + \gamma_{sl} - \gamma_{sv}^0. \quad (8)$$

The latter expression gives the excess free energy via a measurable physical dependency, $\Pi(h)$, which is the disjoining pressure isotherm.

We can rewrite the latter expression (8) of the excess free energy of thin liquid films as

$$\Phi = \gamma_{svh_e} - \gamma_{sv}^0, \quad (9)$$

where

$$\gamma_{svh_e} = \gamma + P_e h_e + \int_{h_e}^{\infty} \Pi(h) dh + \gamma_{sl}, \quad (10)$$

is the “interfacial tension” (actually the excess free energy) of the solid substrate covered with the liquid film of thickness h_e .

The latter expression determines the unknown value of γ_{svh_e} in the Young’s equation:

$$\cos \theta_e = \frac{\gamma_{svh_e} - \gamma_{sl}}{\gamma}. \quad (11)$$

Combination of Eqs. (10) and Eq. (11) results in

$$\cos \theta_e = \frac{\gamma + P_e h_e + \int_{h_e}^{\infty} \Pi(h) dh}{\gamma} \approx 1 + \frac{1}{\gamma} \int_{h_e}^{\infty} \Pi(h) dh, \quad (12)$$

because the term $\frac{P_e h_e}{\gamma}$ is usually small as compared with other terms in Eq. (12).

The latter equation is a well-known Frumkin-Derjaguin equation for the equilibrium contact angle, which has been deduced using a different thermodynamic consideration [4] and later was deduced from the more rigorous consideration of equilibrium conditions [2].

In the case of partial wetting (water and aqueous solutions) $-1 < \cos \theta_e < 1$. From that condition we conclude that the integral in the right hand side of Eq. (12) should be negative. The latter requirement is satisfied in the case of partial wetting (see curve 2 in Fig. 7) if

$$\int_{h_e}^{\infty} \Pi(h) dh < 0 . \quad (13)$$

The latter inequality is satisfied if

$$S_- > S_+ , \quad (14)$$

see Fig. 7 curve 2.

Equilibrium droplets on the solid substrate under oversaturation

As we already noticed the excess pressure, P_e , is negative at oversaturation according to Eq. (3). The equilibrium film/films are determined according to Eq. (6) at both at under - and oversaturation.

Fig. 8. Two equilibrium flat films on the solid substrate under oversaturation: a stable film of thickness h_e and an unstable film of thickness h_u .

Fig. 8 shows, that in the case of complete wetting there is not equilibrium flat film on solid substrates under oversaturation, because the line $P_e < 0$ does not intersect curve 1 in Fig. 8. Hence, there are not equilibrium droplets on a completely wettable solids at oversaturation: they are in the surrounding air.

However, in the case of partial wetting Eq. (6) has two solutions (Fig. 8). According to the stability condition of flat films (7) one of them corresponds to the stable equilibrium film of thickness h_e and the second one corresponds to the unstable film of thickness h_u (Fig. 8). The latter means that equilibrium droplets in the case of partial wetting are “sitting” on the stable equilibrium film of thickness h_e .

However, even in the case of partial wetting equilibrium droplets can exist on the solid substrate only in a limited interval of oversaturation, which is determined by $0 < P_e < \Pi_{\min}$ (Fig. 8), or using Eq. (3) in the following range of oversaturated pressure, p , over the solid substrate

$$1 < \frac{p}{p_s} < \exp\left(\frac{v_m \Pi_{\min}}{RT}\right). \quad (15)$$

If $\Pi_{\min}$ is in the range 10^6 - 10^7 dyn/cm², then the latter inequality takes the following form $1 < \frac{p}{p_s} < 1 + \frac{v_m \Pi_{\min}}{RT} \approx 1.001 - 1.01$, that is the equilibrium droplets in the case of partial wetting exist only in a very limited interval of oversaturation on the solid substrates. Beyond this interval, at higher oversaturation neither equilibrium liquid films nor droplets exist on the solid substrate as in the case of complete wetting. Probably the critical oversaturation $p_{cr} : \frac{p_{cr}}{p_s} = \exp\left(\frac{v_m \Pi_{\min}}{RT}\right)$ determined from Eq. (15) corresponds to the beginning of homogeneous nucleation and at higher oversaturation the homogeneous nucleation is more favourable.

Let $\mathfrak{R}$ be the radius of the equilibrium droplet. According to the definition of the capillary pressure: $P_e = -\frac{2\gamma}{\mathfrak{R}}$. Hence, the radius of equilibrium drops is given by Eq.

(4). In the mentioned above narrow interval of the oversaturation the radius of equilibrium drops changes from infinity at $p \rightarrow p_s$ to $\mathfrak{R}_{cr} = \frac{2\gamma}{\Pi_{\min}}$ at $p = p_{cr}$. If

$\Pi_{\min} \approx 10^6$ dyn/cm² and $\gamma \approx 72$ dyn/cm then $\mathfrak{R}_{cr} \approx \frac{144}{10^6} = 1.44 \mu\text{m}$, that is the critical size is out of the range of the surface forces action and the droplet size is sufficiently big. However, if $\Pi_{\min} \approx 10^7$ dyn/cm² then $\mathfrak{R}_{cr} \approx \frac{144}{10^7} = 0.144 \mu\text{m} = 1440 \text{ \AA}$ and the whole droplet is in the range of the surface forces action. In the latter case the drop is so

small that it does not have anywhere (even on the very top) a spherical part, which is not disturbed by surface forces.

Flat films at the equilibrium with menisci

Fig. 9. Disjoining pressure isotherm in the case of complete wetting 1, and partial wetting 2. In thick capillaries ($H > \frac{\gamma}{\Pi_{\max}}$) there are three solutions of Eq. (6) in the case of partial wetting.

Eq. (6) and Fig. 9 show that in the case of complete wetting there is only one equilibrium flat film, h_c , which is stable according to the stability condition (7).

In the case of partial wetting (Fig. 9) solution of Eq. (6) is different in the case of $P_e > \Pi_{\max}$ and $P_e < \Pi_{\max}$. If $P_e > \Pi_{\max}$ Eq. (6) has only one solution, which is stable (according to the stability condition (7)) and referred to as α -film. In the second case, $P_e < \Pi_{\max}$, (Fig. 9) Eq. (6) has three solutions one of them corresponds to the stable equilibrium α -film with thickness h_e . The second solution of Eq. (6), h_u , is unstable according to the stability condition (7), and the third solution, h_β , is stable again according to the same stability condition (7). The latter films are referred to as β -films.

Let us compare the excess free energy of flat α - and β -films, h_e and h_β . According to the definition of the excess free energy (8) this difference is equal to

$$\Delta_{\alpha\beta} = [\Phi(h_\beta) - \Phi(h_\alpha)] = P_e(h_\beta - h_e) - \int_{h_e}^{h_\beta} \Pi(h) dh. \quad (16)$$

The difference $h_\beta - h_e$ is always positive (Fig. 9). In the case of partial wetting, $S > S_+$, according to (13, 14). Hence, the integral in the right hand side of Eq. (16) is negative. Hence, the excess free energy of β -films is higher than the excess free energy of α -films. The latter means that β -films are less stable than α -films, that is why β -films are referred to as meta-stable films and α -films are referred to as absolutely stable films.

It is necessary to make additional comments on α -films and β -films in the case of partial wetting. If we increase the vapour pressure over partially wettable surface from $p=0$ to the saturation pressure, p_s , then on the solid substrate one can observe formation of α -films only, whose thickness changes correspondingly (according to Eq. (6) and Fig. 9) from zero at $p=0$ to $t_0 \approx 70 \text{ \AA}$ at $p=p_s$ (curve 2 in Fig. 9) [4]. The latter is drastically different from the case of complete wetting: the thickness of the wetting film tends to infinity at $p=p_s$. However, β -films can not be obtained in the course of adsorption process in the case of partial wetting: they can be obtained only by decreasing thickness of very thick films down to the equilibrium thickness of the β -film. It is the reason why α -films are referred to as adsorption films (because they can be obtained in the course of adsorption) and β -films are referred to as wetting films.

Let ρ be a radius of the curvature of a meniscus in a flat capillary (a meniscus between two parallel plates): $\rho = \frac{R}{\cos \theta}$, where R is the half distance between plates (the “radius” of the flat capillary). According to the definition of the capillary pressure $P_e = \frac{\gamma}{\rho}$. Let us introduce $\rho_{\max} = \frac{\gamma}{\Pi_{\max}}$ (Fig. 9), and consider $P_e > \Pi_{\max}$ (Fig. 9). We define a capillary as a “thin” capillary if $R < R_{\max}$. In such capillary only thin α -films can be at equilibrium with the meniscus and equilibrium β -films do not exist in such thin capillaries. If, however, the capillary is “thick”, that is, $R > R_{\max}$, then in such capillaries both α - and β -films can be at equilibrium with the meniscus. However, β -films are meta-stable.

If we adopt $\gamma \sim 70 \text{ dyn/cm}$ and $\Pi_{\max} \sim 10^4 \text{ dyn/cm}^2$ for estimations then $R_{\max} \sim 7 \cdot 10^{-3} \text{ cm}$.

Hysteresis of contact angle on smooth homogeneous solid substrates

This problem is probably the most controversial in the area of wetting and spreading. However, the way forward in wetting phenomena is impossible without proper understanding of the phenomenon.

Let us explain the meaning of static advancing and receding contact angles. For that purpose let us consider a liquid droplet on a horizontal substrate, which is slowly pumped in or out through an orifice in the solid substrate (Fig. 10). Let us assume that in some way an initial contact angle of the droplet was equal to the equilibrium one. Let us start carefully and slowly pump the liquid in through an orifice 1. Contact angle will grow, however, the radius of the drop base will not change until a critical value on the contact angle, θ_a , is reached. Further pumping will result in a drop spreading.

Fig. 10. Schematic presentation of a liquid droplet on a horizontal solid substrate, which is slowly pumped in/out through the liquid source in the drop centre. R radius of the drop base; θ contact angle; 1 - liquid drop, 2 - solid substrate with a small orifice in the centre, 3 - liquid source (syringe).

If we start from the same equilibrium contact angle and pump out the liquid through the same orifice 1, then again the contact angle will decrease but the droplet will not shrink until the critical contact angle, θ_r , is reached. After that the droplet will start to recede.

For example, in the case of water droplets on a smooth homogeneous specially treated for purity glass surface: $\theta_r \sim 0^\circ - 5^\circ$, while θ_a is in the range of $40^\circ - 60^\circ$.

Traditional point of view (see for example [6, 7]) connects the contact angle hysteresis with a roughness–heterogeneity of the solid substrate (see Fig. 11).

Fig. 11. θ_{ef} is the effective apparent contact angle. a – an idealised picture of the apparent three phase contact line of a droplet on a solid rough substrate, b – a real picture of the three phase contact zone with the rough surface covered by the liquid film, which flows out from the droplet. In the region ABC a microscopic flow occurs.

Fig. 11a present an idealised picture of the apparent three phase contact line of a droplet on a solid rough substrate, when the action of surface forces is ignored. Fig. 11b presents a real picture of the three phase contact zone with the rough surface covered by the liquid film, which flows our from the droplet. In the region ABC a microscopic flow occurs.

The latter picture shows that the formation and flow of thin liquid films in a vicinity of the three phase contact line is unavoidable and influences substantially the contact angle hysteresis. Formation of such “precursor” films was both numerically simulated [8]and experimentally observed [9,10].

Fig. 11a gives a qualitative explanation of the phenomenon of the static hysteresis of contact angle traditionally adopted in the literature [6,7]: the static hysteresis of contact angle is connected with multiple equilibrium positions on the drop edge on a rough surface. No double that a roughness and/or a chemical heterogeneity of the solid substrate contribute substantially to the contact angle hysteresis.

In this case it is assumed that at each point of the surface the equilibrium value of the contact angle of that point is established, depending only on the local properties

of the substrate. As a result, a whole series of local thermodynamic equilibrium states can be realized, corresponding to a certain interval of values of the angle. The maximum value corresponds to the value of the advancing contact angle, θ_a , and the minimum value to of the receding contact angle, θ_r .

According to such model the dependency of contact angle on velocity of motion should be as presented in Fig. 12.

Fig. 12. Idealised dependency of the contact angle on the velocity of advancing ($v>0$) or receding ($v<0$) if the hysteresis is determined solely by roughness/heterogeneity of the solid substrate.

There is no doubt that heterogeneity effects the wetting process. However, it is not the only reason. It is well known if the surface roughness is less than 100 nm it can not be the reason for the contact angle hysteresis [26]. There are numerous well documented experimental confirmation of the existence of the hysteresis of contact angle on smooth enough and homogeneous surfaces [11-28]. Even more than that, the static hysteresis of contact angle is present even on surfaces which are definitely molecularly smooth: free liquid films [29-30].

Unfortunately those evidences of the presence of contact angle hysteresis on smooth homogeneous surfaces are usually ignored in the literature.

Before going further we present in Fig. 13 the equilibrium liquid profile inside the transition zone from the liquid meniscus to the equilibrium flat liquid film in front in the case of partial wetting.

Fig. 13. Partial wetting. Magnification of the liquid profile inside the transition zone in “thick capillaries”. S-shaped disjoining pressure isotherm (left side, **a**) and the liquid profile in the transition zone (right side, **b**).

From the above consideration follows that in the case of equilibrium liquid drops/menisci they should be always at the equilibrium with flat films in front, which they are in contact with. Only the capillary pressure acts inside the spherical parts of drops/menisci and only the disjoining pressure acts inside thin flat films. However, there is a transition zone between the bulk liquid (drops or menisci) and the thin flat film in front of them. In this transition zone both the capillary pressure and the disjoining pressure act simultaneously [2]. A profile of the transition zone between a meniscus in a flat capillary and a thin α -film in front of it in the case of partial wetting is presented in Fig 13. The latter figure shows that the liquid profile is not always concave, but changes its curvature inside the transition zone. Just this peculiar liquid shape in the transition zone determines the static hysteresis of contact angle (see below).

In the transition zone (Fig. 13) all thickness are presented from very thick outside the range of the disjoining pressure action to thin α -films. The latter means that the stability condition of flat films Eq. (7) can not be used any more because the latter condition is valid only in the case of flat films. More sophisticated Jacoby's condition [2] should be used instead, which shows that transition zone is stable if $h'(x)$ does not vanish anywhere inside the transition zone.

Evidently only a single unique value of the equilibrium contact angle, θ_e , is possible on a smooth, homogeneous surface. Hence, the static hysteresis contact angles $\theta_a \neq \theta_e$, $\theta_r \neq \theta_e$ and all contact angles in between, which observed experimentally on

such surfaces can correspond only to a non-equilibrium or quasi-equilibrium states of the system.

If the relaxation time of the system is long enough, a local equilibrium which is not in equilibrium with the surrounding medium can be established at the meniscus or droplet. It is shown in [2] that there are certain critical values of contact angles beyond which such local equilibrium is not possible, because the relaxation time becomes very small. These critical values of the angles were related to static advancing, θ_a , and static receding, θ_r , contact angles [2]. Thus the discussion of the static hysteresis phenomenon in the present section is based on the analysis of non-equilibrium states of a system and conditions of violation of local equilibrium of menisci or drops. Explanation of the dependence presented in Fig. 14 is based on s-shaped isotherm of disjoining pressure in the case of partial wetting.

Fig. 14. Hysteresis of contact angle in capillaries in the case of partial wetting (s-shaped isotherm of disjoining pressure).

a advancing contact angle. 1- a spherical meniscus of radius ρ_a , 2 - transition zone with a “dangerous” marked point (see explanation in the text) , 3 - zone of flow, 4 – initial flat films. Close to the marked point a dashed line shows the profile of the transition zone just after the contact angle reaches the critical value θ_a , a beginning of the “caterpillar motion”.

b receding contact angle. 1- a spherical meniscus of radius $\rho_r < \rho_a$, 2 - transition zone with a “dangerous” marked point (see explanation in the text), 3 - zone of flow, 4 – initial flat films. Close to the marked point a dashed lines show the profile of the transition zone just after the contact angle reaches the critical value θ_a .

This shape of the disjoining pressure determines a very special shape of the transition zone in the case of equilibrium meniscus (see Fig. 13). In the case of increasing of the pressure behind the meniscus (Fig. 14a) a detailed consideration of the transition zone shows [2]: close to the “dangerous” point marked in Fig. 14a, the slope of the profile becomes steeper with increasing pressure. In the range of very thin films (region 3 in Fig. 14) there is a zone of flow. Viscous resistance in this region is very high, that is why the advancing of the meniscus proceeds very slowly (with a “microscopic velocity”). After some critical pressure behind the meniscus is reached then the slope at the “dangerous” point reaches $\pi/2$, after that the flow step-wisely occupies the region of thick films the fast “macroscopic caterpillar” motion starts as shown in Fig.14a.

In the case of decreasing the pressure behind the meniscus the event proceed according to Fig. 14b. In this case again up to some critical pressure the slope in the transition zone close to the “dangerous” marked point becomes more and more flat. In the range of very thin films (region 3 in Fig. 14b) there is a zone of flow. Viscous resistance in this region again is very high, that is why the receding of the meniscus proceeds very slowly with a “microscopic velocity”. After some critical pressure behind the meniscus is reached then the profile in the vicinity of the “dangerous” point shows the discontinuous behaviour, which is obviously impossible. That means, the meniscus will start to slide along thick β -film. That is, the meniscus will move relatively fast leaving behind the thick β -film. The latter phenomenon (the presence of a thick β -film behind the receding meniscus of aqueous solutions in quartz capillaries) has been discovered experimentally [31-33]. Unfortunately, those experimental investigations were published mostly in Russian Journals (mostly Colloid Journal, Russian (USSR) Academy of Sciences) and mostly unknown for the western scientists. However, those experimental observations [31-33] provide a direct proof of the presented above qualitative picture.

Hence, the picture presented in Fig. 12 can not be true and should be replaced by a more complicated but realistic dependency as shown in Fig. 15.

Fig. 15. At any deviation from the equilibrium contact angle θ_e , the liquid drop is in the state of a slow “microscopic motion”, which abruptly transforms in the state of “a macroscopic motion” after critical contact angles θ_a or θ_r are reached.

Kinetics of spreading in the case of complete wetting

It is obvious that the same surface forces (disjoining pressure) are equally important for the kinetics of spreading. In this section we consider only the case of complete wetting. The consideration presented in [2] shows that in the case of spreading the whole drop profile should be sub divided in a number of regions, which are briefly discussed below.

We consider below a spreading of “small drops” as compared with the capillary length $a = \sqrt{\frac{\gamma}{\rho g}}$. That is the gravity action is neglected.

There are two important parameters, which are the Reynolds number and the capillary number. To deduce the relevant expression for the Reynolds number let us consider a spreading of a two dimensional (i.e. cylindrical) droplet over a solid surface (gravity action is neglected). In this case Navier-Stokes equations with the incompressibility condition in Cartesian coordinates (x, y) take the following form

$$\rho \left(u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right) = - \frac{\partial p}{\partial x} + \eta \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right)$$

$$\rho \left(u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} \right) = - \frac{\partial p}{\partial y} + \eta \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) ,$$

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0$$

where $\vec{v} = (u, v)$ is the velocity vector; ρ and η are the liquid density and viscosity. Let U_* and v_* are scales of the velocity components in the tangential and the vertical directions, respectively. Using the incompressibility condition we conclude

$$\frac{U_*}{r_*} = \frac{v_*}{h_*}, \text{ or } v_* = \varepsilon U_*, \quad \varepsilon = \frac{h_*}{r_*}, \text{ where } h_*, r_* \text{ are characteristic length scales of the}$$

thickness and the radius of the droplet base, respectively. If the droplet has a low slope, then $\varepsilon \ll 1$ and, hence, the velocity scale in the vertical direction is much smaller than the velocity scale in the tangential direction. Now using the first Navier-Stokes equation

we can estimate

$$\rho u \frac{\partial u}{\partial x} \sim \rho v \frac{\partial u}{\partial y} \sim \frac{\rho U_*^2}{r_*}, \quad \eta \frac{\partial^2 u}{\partial x^2} \sim \varepsilon^2 \eta \frac{\partial^2 u}{\partial y^2} \ll \eta \frac{\partial^2 u}{\partial y^2}, \quad \eta \frac{\partial^2 u}{\partial y^2} \sim \frac{\eta U_*}{h_*^2},$$

hence, all derivatives in the low slope approximation in x direction can be neglected as compared with derivatives in the axial direction y . Now we can estimate the Reynolds number as

$$Re \sim \frac{\rho u \frac{\partial u}{\partial x}}{\eta \frac{\partial^2 u}{\partial y^2}} \sim \frac{\frac{\rho U_*^2}{r_*}}{\frac{\eta U_*}{h_*^2}} = \frac{\rho U_* h_*^2}{\eta r_*} = \varepsilon^2 \frac{\rho U_* r_*}{\eta}$$

or

$$Re = \varepsilon^2 \frac{\rho U_* r_*}{\eta} \quad (15)$$

The latter expression shows, that the Reynolds number under the low slope approximation is proportional to ε^2 . Hence, during the initial stage of spreading, when $\varepsilon \sim 1$, the Reynolds number is not small, but as soon as the low slope approximation is valid Re becomes small even if $\frac{\rho U_* r_*}{\eta}$ is not small enough. The latter means, during

the short initial stage of spreading both the low slope approximation and low Reynolds number approximations are not valid. However, we are interested only in the main part of the spreading process when the short initial stage is over. Below we see that Re number should be calculated only in the close vicinity of the moving contact line, where the low slope approximation is valid, because in the main part of the spreading droplet the liquid is moving much slower than close to the edges. Hence, the inertial terms in

Navier-Stokes equations can be safely omitted and only Stokes equations should be used instead

$$0 = -\frac{\partial p}{\partial x} + \eta \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right)$$

$$0 = -\frac{\partial p}{\partial y} + \eta \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) .$$

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0$$

The tangential stress on the free drop surface at $y = h(x)$ is

$$\eta \left[h'^2 \left\{ h' \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \right\} + 2h'^2 \left(\frac{\partial u}{\partial x} - \frac{\partial v}{\partial y} \right) + h' \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \right] = 0$$

Under the low slope approximation, $\varepsilon \ll 1$, we can easily check that $h' \ll 1$. Using this estimation the latter condition can be rewritten as

$$\eta \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) = 0$$

Using the previous estimations we conclude

$$\frac{\partial u}{\partial y} \sim \frac{U_*}{h_*}; \quad \frac{\partial v}{\partial x} \sim \frac{\varepsilon U_*}{r_*} = \varepsilon^2 \frac{U_*}{h_*} \ll \frac{\partial u}{\partial y}$$

The latter estimation shows that under the low slope approximation the tangential stress on the free liquid interface is $\eta \frac{\partial u}{\partial y} = 0$.

The capillary number, $Ca = \frac{U_* \eta}{\gamma}$, characterises the relative influence of the

viscous forces as compared with the capillary force. Let us estimate the possible values of the Ca . Let $r_* \sim 0.1$ cm, $\gamma \sim 30$ dyn/cm and $\eta \sim 10^{-2}$ P (oils). Let the droplet edge moves on the distance equal to its radius over 1 sec, which can be considered as a very high velocity of spreading. The latter gives the following estimation $Ca \sim 3 \cdot 10^{-5} \ll 1$. That means, we should expect Ca even less than 10^{-5} over duration of spreading. According to the previous consideration we assume below that both the capillary and Reynolds numbers are very small except for a very short initial stage of spreading. Estimations of

the duration of the initial stage of spreading immediately after the deposition of the droplet onto the solid substrate were given in [34].

Let us consider the consequence of the smallness of the capillary number, $Ca \ll 1$ using again the simplest possible example of spreading of two-dimensional (cylindrical) droplets. Let the length scales in both tangential, x , and vertical, y , directions in the main part of the spreading drop be r_* , then the pressure inside the main part of the droplet has the order of magnitude of the capillary pressure, that is $p \sim \frac{\gamma}{r_*}$.

Using the incompressibility condition we immediately conclude that velocity in both directions, u and v , have the same order of magnitude U_* . Let us introduce the following dimensionless variables, which are marked by an over-bar

$$\bar{p} = \frac{p}{\gamma/r_*}, \quad \bar{x} = \frac{x}{r_*}, \quad \bar{y} = \frac{y}{r_*}, \quad \bar{u} = \frac{u}{U_*}, \quad \bar{v} = \frac{v}{U_*}$$

Using these variable the Stokes equations can be rewritten as

$$\frac{\partial \bar{p}}{\partial \bar{x}} = Ca \left(\frac{\partial^2 \bar{u}}{\partial \bar{x}^2} + \frac{\partial^2 \bar{u}}{\partial \bar{y}^2} \right)$$

$$\frac{\partial \bar{p}}{\partial \bar{y}} = Ca \left(\frac{\partial^2 \bar{v}}{\partial \bar{x}^2} + \frac{\partial^2 \bar{v}}{\partial \bar{y}^2} \right)$$

We already concluded that $Ca \ll 1$, that means the right hand side of both latter equations is very small. Hence, the latter equations can be rewritten as

$$\begin{aligned} \frac{\partial \bar{p}}{\partial \bar{x}} &= 0 \\ \frac{\partial \bar{p}}{\partial \bar{y}} &= 0 \end{aligned},$$

which means that the pressure remains constant inside the main part of the spreading droplet. If we now right down the normal stress balance on the main part of the spreading droplet we get

$$\bar{p} = \frac{\bar{h}''}{(1 + \bar{h}'^2)^{3/2}} + Ca \left[-\frac{2}{(1 + \bar{h}'^2)} \left\{ -\bar{h}' \left(\frac{\partial \bar{u}}{\partial \bar{y}} + \frac{\partial \bar{v}}{\partial \bar{x}} \right) - \frac{\partial \bar{v}}{\partial \bar{y}} - \bar{h}'^2 \frac{\partial \bar{u}}{\partial \bar{x}} \right\} \right].$$

Using the condition $Ca \ll 1$ we conclude from the latter equation

$$\bar{p} = \frac{\bar{h}''}{(1 + \bar{h}'^2)^{3/2}} = const,$$

even in the case when the droplet profile does not satisfy the low slope approximation, that is, even if $\bar{h}'^2 \sim 1$ not small. The latter shows that the spreading droplet remains its spherical shape over the main part of the droplet. Note, that the radius of the droplet base, $R(t)$, changes over time, and this change results in a quasi-steady changes of the droplet profile in the main part of the droplet.

In the case of moving meniscus in a capillary similar estimation shows that $Ca \ll 1$ results in a spherical shape of the meniscus in the main part of the capillary.

Note, the smallness of the Ca means that the surface tension is much more powerful over the most part of the droplet/meniscus and, hence, the droplet/meniscus has a spherical shape everywhere except for a vicinity of the apparent three phase contact line. A size of this region, l_* , is estimated in [2]. It is shown that the following inequality is satisfied:

$h_* \ll l_* \ll r_*$. Hence, $\delta = \frac{h_*}{l_*} \ll 1$ is a small parameter inside the vicinity of the moving contact line. The latter means that the curvature of the liquid interface inside the vicinity of the moving contact line can be estimated as

$$\frac{\gamma h''}{(1 + h'^2)^{3/2}} \sim \frac{\gamma \frac{h_*}{l_*^2} \bar{h}''}{\left(1 + \frac{h_*^2}{l_*^2} \bar{h}'^2\right)^{3/2}} = \frac{\gamma \frac{h_*}{l_*^2} \bar{h}''}{(1 + \delta^2 \bar{h}'^2)^{3/2}} \approx \gamma \frac{h_*}{l_*^2} \bar{h}''.$$

The latter gives a very important conclusion: the low slope approximation is valid inside the vicinity of the moving contact line even if the drop profile is not very low, that is, even if $\bar{h}'^2 \sim 1$ is not small. Hence, we can always use the low slope approximation inside the vicinity of the moving contact line except for the case when the slope is close to $\pi/2$.

Let us estimate a possible range of capillary numbers. If $Ca \sim 1$ then in the case of water we conclude $Ca \sim \frac{U_* \eta}{\gamma} \sim \frac{U \cdot 10^{-2} P}{72 \text{ dyn/cm}} \sim 1$. The latter results in $U_* \sim 72 \text{ m/sec}$. The

latter velocity is so high that probably can be achieved only under very special conditions. In the case of $r_* \sim 0.1 - 1 \text{ cm}$, the latter velocity results in $Re \sim 7.2 \cdot 10^4 - 7.2 \cdot 10^5$, that is a turbulent flow, which is beyond the scope of this section. The latter means that the possible range of Ca is in between 0 and $\sim 10^{-5}$. Low $Ca \ll 1$ means a relatively low rate of spreading, while $Ca \sim 1$ means a very high

velocity of motion. However, the mentioned above range of Ca , 0 and $\sim 10^5$, still include “a high capillary number limit”. The latter means that the case of low capillary numbers, $Ca \ll 1$, and intermediate capillary numbers, $Ca \sim 1$, should be considered in a completely different way. The situation is similar to the case of Reynolds number: consideration of flows at low Reynolds numbers is very much different from the consideration of flows at high Reynolds numbers.

Now we are prepared to consider in more details the vicinity of the moving contact line, which is magnified in Fig. 16.

Fig. 16. A magnification of the vicinity of the moving apparent three phase contact line in the case of complete wetting:

- 1 spherical part of the drop, which forms a dynamic contact angle, θ , with the solid substrate;
- 2 a region, where a spherical shape is distorted by the hydrodynamic force;
- 3 a region, where disjoining pressure comes into play and become increasingly important towards the end of the region 3;
- 4 a region, where a macroscopic description is not valid any more and surface diffusion takes place.

The whole vicinity of the three phase contact line can be subdivided into four regions (Fig. 16). The region 1 is a spherical meniscus in the main part of the spreading droplet. This region is included to show the dynamic contact angle, $\theta(t)$, which is defined at the intersection of the tangent to the spherical part of the droplet with the solid substrate. The dynamic contact angle is unknown and should be determined by matching of all regions presented in Fig. 16. Inside the next region, 2, the spherical shape is distorted by the hydrodynamic flow. This region is followed by region 3, where

disjoining pressure comes into play. Over the region 3 disjoining pressure action becoming increasingly important as compared with the capillary force. Towards the end of the region 3 the disjoining pressure overcomes the capillary force and becomes the only driving force of the spreading process. The region 3 is followed by region 4. In this region a macroscopic description of the spreading process becomes impossible because the characteristic scale in the vertical direction is of the order of the molecular size. We refer to region 4 as the region of surface diffusion.

The picture of a spreading drop profile in a vicinity of the three phase contact line, presented in Fig. 16 has been understood only recently [2]. A number of a simplified physical mechanisms has been introduced previously based on a simplification of the above picture.

For a long time so called “singularity on a three phase contact line” [35] has been considered as a major obstacle in the kinetics of spreading. We explain below the source of this singularity and why it is removed by the disjoining pressure acting in a vicinity of the apparent three phase contact line.

The viscous stress in the tangential direction close to the three phase contact line (Fig. 16) diverges: $\eta \frac{\partial v_r}{\partial y} \sim \frac{\eta U_*}{h} \rightarrow \infty$, as $h \rightarrow 0$. The latter means that the drop can not spread out because the friction force at the moving front becomes infinite. A possible way to overcome this problem has been suggested in [36]. Idea is as follows. The very first layer of the liquid molecules on the liquid-solid interface is attached to the solid substrate by a force of adhesion. However, the adhesion force is not infinite but finite. If the tangential stress is becoming big enough then the first layer of the liquid molecules is swept away by the tangential stress. The result is “a slippage velocity”. The slippage velocity is introduced as follows

$$\left[\eta \frac{\partial v_r}{\partial y} \right]_{y=0} = [\alpha v_r]_{y=0},$$

where α is a proportionality coefficient. That is, the slippage velocity is proportional to the applied shear stress on the solid substrate. The latter definition can be rewritten as

$$\left[\frac{\partial v_r}{\partial y} \right]_{y=0} = \left[\frac{v_r}{\lambda} \right]_{y=0}, \quad \lambda = \frac{\eta}{\alpha}, \quad (16)$$

where λ has a dimension of a length and can be refereed to as a slippage length. However, it turns out [37] that $\lambda \sim 10^{-6}$ cm, that is located just in the range where surface

forces are the most powerful. The latter means that condition (16) can not be used as a macroscopic condition because it should be used in the region of surface forces action. Note, that in the case of complete wetting the disjoining pressure is equal to $\Pi(h) = \frac{A}{h^3} \rightarrow \infty$ as $h \rightarrow 0$, that is, even faster than the tangential stress. Hence, the disjoining pressure is the driving force of spreading in a vicinity of the three phase contact line. Let us estimate the thickness where disjoining pressure overcomes the increasing tangential stress:

$$\frac{\eta U_*}{h} < \frac{A}{h^3}, \text{ or } h < \left(\frac{A}{\eta U_*} \right)^{1/2} = h_t. \text{ That is, the lower velocity of spreading } U \text{ the higher}$$

thickness below which the disjoining pressure overcomes the tangential stress. If as before we adopt at the initial stage of spreading a very high spreading velocity $U_* \sim 10^{-1}$ cm/sec, $A \sim 10^{-14}$ erg, $\eta \sim 10^{-2}$ P, then $h_t \sim 3 \cdot 10^{-6}$ cm. That is, in the range where disjoining pressure is the most powerful.

A simple way to overcome the problem of “singularity on the moving contact line” has been suggested in [38]: a cutting length was introduced in a vicinity of the three phase moving contact line. Note, the introduction of the cutting length is similar to the introduction of the slippage velocity.

A simplifying approach has been suggested in [40]. According to this approach the hydrodynamic flow in regions 2 and 3 is ignored as well as the disjoining pressure action in region 3 (Fig. 16). According to this approach a spherical meniscus is followed directly by region 4, where surface diffusion takes place. This approach results in the following equation for the velocity of spreading:

$$\dot{\mathfrak{R}} = \text{const} \cdot [\cos \theta_e - \cos \theta(t)],$$

that is the velocity of spreading is proportional to the difference between the $\cos \theta_e$, where θ_e is the equilibrium contact angle (θ_e is a fitting parameter in the theory [40]) and $\cos \theta(t)$, where $\theta(t)$ is the instantaneous dynamic contact angle. The latter equation results in the case of complete wetting, that is if $\cos \theta_e = 1$ in

$$\dot{\mathfrak{R}} = \text{const} \cdot \theta^2(t)$$

It is well established (both theoretically and experimentally [39]) that in the case of the complete wetting the latter law is

$$\dot{\mathfrak{R}} = \text{const} \cdot \theta^3(t).$$

Comparison of the latter two equations shows that the approach suggested in [40] does not agree with well-established theoretical predictions. However, the approach suggested in [40] emphasises the importance of surface diffusion though overestimate its contribution.

The next approach to be mentioned was tried long ago and based on the consideration of the surface tension of in the vicinity of the apparent moving three phase contact line. It has been assumed that the surface tension of “the fresh interface” (which appears close to the apparent three phase contact line) is higher than the surface tension behind the apparent three phase contact line on “the old interface”. The latter surface difference could be the driving force of spreading. However, both experimental investigations [41] and theoretical estimations [42] showed that the relaxation time of the surface tension on “a fresh” liquid–air interface of pure liquids is too small and, hence, can not influence the spreading process, which proceeds on much large time scales. However, recently an attempt has been made to revive the same idea of a high surface tension on “a fresh liquid-air” interface [43]. The approach suggested in [43] also completely ignore the disjoining pressure action in a vicinity of the moving three phase contact line. This approach was criticized in [42].

Surface diffusion (region 4 in Fig. 16) results in an effective slippage [44]. The first attempt to introduce the surface slippage base on the consideration of surface diffusion was undertaken in [44]. This approach is to be developed further.

Below we consider the spreading of an axi-symmetric liquid drop on a plane solid substrate in the case of complete wetting. Both capillary and disjoining pressure are taken into account [39]. As we already concluded above neglecting of the disjoining pressure in the vicinity of the moving apparent three phase contact line results in a contradiction: the disjoining pressure action removes the singularity on the moving contact line.

Inside the same vicinity of the moving contact line both the capillary and disjoining pressure should be taken into account. In the case of complete wetting, which is under consideration in this section, the disjoining pressure isotherm, $\Pi(h)$, is $\Pi(h) = \frac{A}{h^n}$, with $A > 0$ is a generalized Hamaker constant and $n=2$ or 3 . The latter constant A coincides with the real Hamaker constant only at $n=3$ [24]. Derivations give the following equation, which describes the evolution in time and space of the drop profile $h(t,r)$ [39]:

$$\frac{\partial h}{\partial t} = -\frac{\gamma}{3\eta} \frac{1}{r} \frac{\partial}{\partial r} \left[rh^3 \left[\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial h}{\partial r} \right) \right) \right] - \frac{nA}{\gamma h^{n+1}} \frac{\partial h}{\partial r} \right]. \quad (17)$$

The latter equation was solved and power laws for the following three dependencies on time: radius of the droplet base $\mathfrak{R}(t)$, height of the droplet apex $H(t)$ and the dynamic contact angle $\theta(t)$. Figs. 17 shows the comparison of the deduced theoretical dependences and the experimental data. The dimensionless time t_* was calculated in [39]. Note, the theoretical dependences plotted in Fig. 17 do not include any fitting parameters. Those theoretical dependences give the excellent agreement not only for exponents but for all three pre-exponential constants via Hamaker constant A and other measurable physicochemical parameters [39].

Fig. 17. Experimental dependencies of radius of spreading, dynamic contact angle and the drop apex height on time, lines according to the theoretical predictions [39].

Conclusions

Surface forces act in a vicinity of the three phase contact line at contact of liquids with solid substrates. Their action determines all equilibrium properties of liquids on solid substrates: complete wetting, partial wetting, non-wetting. Action of surface forces

determines also the kinetics of wetting/spreading. The action of surface forces remove well known paradox of infinite friction on the moving three phase contact line.

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