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Wetting films and wetting

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Résumé. — Une approche macroscopique des phénomènes de mouillage, basée sur les isothermes de pression de disjonction des films de mouillage en équilibre avec des ménisques concaves ou des gouttes, permet le calcul des angles de contact de divers liquides sur des substrats solides. Nous présentons les résultats de calculs utilisant la théorie des forces de surface à longue portée et nous montrons leur accord avec des données expérimentales. Nous insistons sur le rôle de la zone de transition entre le film de mouillage et le liquide en volume dans l'étude des tensions de ligne, de l'équilibre mécanique et thermodynamique et de la formation des angles de contact dynamiques. Les transitions de mouillage et de prémouillage sont discutées dans le cadre de cette théorie macroscopique.

Abstract. — Macroscopic approach to the wetting phenomena, based on the isotherms of disjoining pressure of wetting films in equilibrium with concave menisci or drops, allows one to calculate the contact angles for different liquids and solid substrates. The results of calculations are presented using the theory of long-range surface forces, and their agreement with experimental data is shown. The role of the transition zone between the wetting films and bulk liquid in the phenomena of line tension, mechanical and thermodynamical equilibrium, and the formation of dynamic contact angles, is demonstrated. Within the framework of the macroscopic approach the phenomena of prewetting and wetting transition are discussed.

1. Introduction.

The phenomenon of wetting consists in the formation of a contact angle between a liquid and a solid substrate. The equilibrium contact angle is determined by the surface forces field and depends on the energy of interaction of the liquid with a solid substrate. A weak interaction causes the partial wetting or nonwetting, whereas a strong one the spreading of the liquid over the surface, i.e. its complete wetting.

We shall consider a macroscopic approach to wetting phenomena, based on an analysis of the equilibrium of menisci or drops with wetting films. The wetting films, in distinction from adsorption ones, may be considered as a part of the liquid phase. For such films the known concept of disjoining pressure may be used. The macroscopic approach is restricted to not very large contact angles, and it is valid until the thickness of wetting films exceeds several molecular layers. This allows the wetting phenomenon to be considered within the framework of the theory of long-range surface forces [1]. Reasonable combination with another microscopic

approach taking into account the molecular structure of liquids [2-5], permits, as may be supposed, covering the whole range of possible values of contact angles.

In distinction from the microscopic approach, the macroscopic one enables one to take into account, not only the molecular forces, but also other components of disjoining pressure: for instance, the double-layer electrostatic forces and structural forces arising due to the overlapping of boundary liquid layer with modified structure.

Development of the long-range surface forces theory [1] allowed quantitative evaluations of wetting to be made depending on the physical properties of a solid substrate and the liquid interacting with the latter.

This approach was for the first time indicated by Frumkin and Derjaguin [6, 7]. They have substantiated the relationship between the value of contact angle θ_0 and the disjoining pressure isotherms of wetting films $\Pi(h)$.

That the $\Pi(h)$ isotherms had been studied but insufficiently delayed for a long time the application

of Frumkin-Derjaguin's theory. At present, a considerable progress has been achieved both in the experimental examination of the disjoining pressure isotherms of wetting films [1, 8] and in developing methods for theoretical calculation of different components of disjoining pressure, acting in films.

2. Theory of contact angles.

We begin considering the wetting theory with the definition of the concept on the contact angle θ_0 . In the equilibrium state, the contact angle is determined at the intersection point of a continuation of the drop or meniscus profile undisturbed by the surface forces with the substrate (curve 1, Fig. 1). The meniscus contacts with a wetting film, whose equilibrium thickness h_0 is determined by the equation of $\Pi(h)$ — isotherm. The value of h_0 corresponds to the disjoining pressure, which is equal to the capillary pressure of an equilibrium meniscus: $P_C = \Pi_0$. A transition zone 2 is formed between the bulk portion of the meniscus having a constant (if neglecting the gravity force) surface curvature, $K_0 = P_C/\gamma$ (where γ is the surface tension), and a flat wetting film. The capillary forces due to the curvature of the liquid layer surface, and the surface forces associated with the long-range substrate field, act simultaneously in that transition zone.

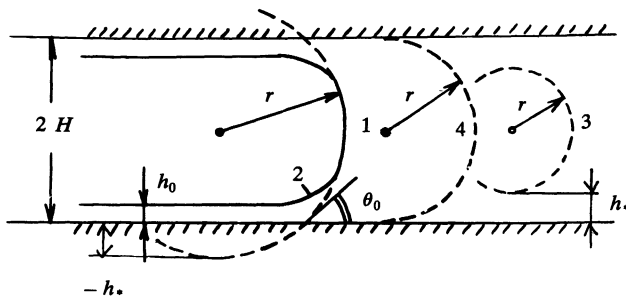


Fig. 1. — Formation of an equilibrium contact angle, θ_0 , when the liquid is in contact with the surfaces of a flat slit.

In the equilibrium state, we obtain from the condition of constancy of pressure in all the parts of the system [9]:

$$\gamma \cdot K(h) + \Pi(h) = P_C = \text{Const.}, \quad (1)$$

where h is a local thickness of the transition zone and $K(h)$ is a local curvature of its surface. This equation is valid for the gently sloping profiles of the transition zone ($\partial h/\partial x \ll 1$), when the $\Pi(h)$ isotherm of a flat film is applicable to each elementary part dx .

The extension of the transition zone is determined

by the radius of action of surface forces, usually on the order of $10^{-6} - 10^{-5}$ cm. Beyond the zone of influence of surface forces $\Pi = 0$, and equation (1) transforms into Laplace equation for an undisturbed meniscus: $\gamma \cdot K_0 = P_C$. At $h \rightarrow h_0$, the profile of the transition zone becomes all the more gentler sloping ($K \rightarrow 0$), and for a flat film, when $K = 0$, equation (1) gives the known condition of equilibrium between the flat wetting film and the meniscus $\Pi(h_0) = P_C$.

For a flat slit having the width $2H$, and in the case of the complete wetting (for instance, for the isotherms of the type $\Pi = A/h^n > 0$) the extension ℓ of the transition zone in the direction of the axis x is approximately equal to $\ell \sim (H \cdot h_0)^{1/2}$ [10, 11]. Thus, for example, for slits $H = 10 \mu\text{m}$ wide and at $h_0 = 10^{-5}$ cm, $\ell = 10^{-4}$ cm.

The aforesaid method for determination of the contact angle is inapplicable in two cases. The value of θ_0 cannot be determined in narrow slits, where the fields of surface forces overlap one another, and where the meniscus has no part of a constant curvature. Here another approach was developed to calculate the equilibrium of the capillary liquid with the wetting films [12].

Special consideration must also be paid to the cases of complete wetting, where a continuation of the meniscus profile does not intersect the substrate (curve 3, Fig. 1), and a contact angle does not form.

The macroscopic theory includes consideration of the cases of both partial ($\theta_0 > 0$) and complete wetting. Hereinbelow is given one of the derivations of the corresponding equations of the theory, based on the application of equation (1). For the meniscus in a flat slit $H \gg h_0$, the curvature of the cylindrical surface of the meniscus is equal to $K = h''[1 + (h')^2]^{-3/2}$, where h' and h'' are the first and the second derivative of the thickness h of a liquid layer with respect to the coordinate x . Substituting this value of $K(h)$ into equation (1) and using the boundary conditions: $h' = 0$ at $h = h_0$, and $h' \rightarrow \infty$ at $h = H$, we obtain the following solution of equation (1) [13]:

$$H \cdot P_C = \gamma + \Pi_0 h_0 + \int_{h_0}^{\infty} \Pi(h) dh = \gamma + \Pi_0 h_0 + \Delta, \quad (2)$$

where $\Pi_0 = \Pi(h_0)$ and Δ denotes the value of the integral.

When $\theta_0 \geq 0$, the value of P_C may be expressed through $\cos \theta_0$. In the case of a flat slit, which is here considered, $P_C = \gamma/r = \gamma \cdot \cos \theta_0/H$, where r is the radius of curvature of an undisturbed part of meniscus (Fig. 1). Then, instead of equation (2), we obtain:

$$\gamma \cdot \cos \theta_0 = \gamma + \Pi_0 h_0 + \Delta. \quad (3)$$

Now we can compare this expression with the known Young equation

$$\gamma \cdot \cos \theta_0 = \gamma_{SV} - \gamma_{SL} \quad (4)$$

To determine the contact angle θ_0 from equation (4) requires knowing the specific interphase energies of the solid substrate at the boundary with the gas phase, γ_{SV} , and the liquid, γ_{SL} . The Young equation, in distinction from equation (3), does not allow determination of the contact angle, because there are available no methods independent of equation (4), for determining either each of interphase energies or the difference between these. Now, the Young equation is usually employed for solving an inverse problem — finding a difference $\gamma_{SV} - \gamma_{SL}$ on the basis of the measured values of θ_0 .

The Frumkin-Derjaguin's theory enables one to determine the value of γ_{SV} for the solid surface coated by a wetting film. Its value is equal to a sum of the interphase energies of two surfaces of a liquid film : one, contacting gas, γ , and another, contacting the solid substrate, γ_{SL} , and variations in the free energy of the film, $\Delta G = \int_{\Pi}^{\Pi_0} h \cdot d\Pi = \Delta + \Pi_0 h_0$, when it is thinning out from ∞ to the equilibrium thickness h_0 . As a result, the difference between

$$\gamma_{SV} = \gamma + \gamma_{SL} + \Pi_0 h_0 + \Delta$$

and γ_{SL} proves to be equal simply to $\gamma + \Pi_0 h_0 + \Delta$, which just contains equation (3).

Equation (3) allows a theoretical determination of the value of θ_0 in accordance with the known $\Pi(h)$ isotherm of the wetting films of a given liquid on a given substrate. The methods for the experimental and the theoretical determination of $\Pi(h)$ isotherms are presented in reference [8].

Equation (3) has a similar form for cylindrical drops on a flat substrate [13]. This is not surprising, since at $H \gg h_0$ (in this case H denotes the drop height) the equilibrium conditions should not depend on the surface curvature sign beyond the radius of action of surface forces. A difference resides only in that the values of Π_0 are negative, because the capillary pressure of the drop having a convex surface, has another sign $\Pi_0 = P_C = -\gamma/r$, where r is the radius of curvature of an undisturbed portion of the drop. Equation (3) is also applicable at $P_C = 0$, when the surface of the bulk liquid is plane, and its profile is wedge-shaped. In such a case, the second term disappears from the right-hand side of equation (3), since $\Pi_0 = P_C = 0$.

For drops having the spherical surface the calculations are complicated in connection with a necessity of taking into account the secondary curvature of the drop surface. If we limit ourselves to the case of relatively small contact angles (when it is possible to

assume $\partial h/\partial x \ll 1$), equation (1) may be written in the following manner [14]:

$$\gamma \cdot [h'' + (h'/\rho)] + \Pi(h) = P_C = -2\gamma/r = \text{Const.}, \quad (5)$$

where $h' = dh/d\rho$, $h'' = d^2h/d\rho^2$, $r = \text{Const.}$ is the drop surface curvature radius, and ρ is the radial coordinate in the substrate plane. In the general case, nonlinear differential equation (5) may be solved only numerically. It can be linearized by using a simplified form of the disjoining pressure isotherm:

$$\Pi(h) = \begin{cases} 0, & \text{at } h > t; \\ a(t_0 - h), & \text{at } 0 \leq h \leq t, \end{cases} \quad (6)$$

where a and t are the parameters of the isotherm, which are characteristic of the slope of its stable part, where $\partial\Pi/\partial h < 0$, and the radius of action of surface forces, accordingly. The form of simplified isotherm (curve 1, Fig. 2) is similar to the real one (curve 2), when only thin wetting films are stable.

The solution of equation (5) gives the following expression for the equilibrium contact angle [14]:

$$\text{tg } \theta_0 = [t - t_0 + (P_C/a)](a/\gamma)^{1/2}, \quad (7)$$

where t_0 is the film thickness at $\Pi = 0$.

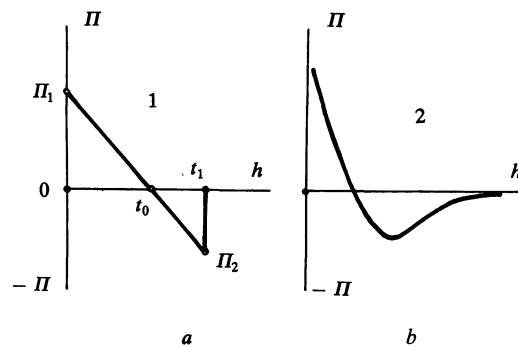


Fig. 2. — Simplified isotherm of disjoining pressure (a) and its real analogue (b).

As appears from this expression, the drop contact angle θ_0 decreases with its dimensions, which is accompanied by an increase in the negative capillary pressure P_C . Such an effect was, in particular, detected experimentally for water drops less than 3 mm in diameter [15]. Under otherwise equal conditions, an increase in the radius of action of surface forces, t , or a decrease in t_0 causes an increase in the contact angle values. This is connected with a displacement of the isotherm (6) into the region of negative values of disjoining pressure.

The range of the applicability of equation (3) is restricted by the values of $\theta_0 \geq 0$, when $\Pi_0 h_0 +$

$\Delta \leq 0$ and $\cos \theta_0 \leq 1$. In the case where the continuation of the meniscus in a flat slit does not intersect substrates (Fig. 1, curve 3) equation (3) permits determination of the capillary pressure of the meniscus in equilibrium with the film having the thickness h_0 . Taking into account that in the equilibrium state, $P_C = \Pi_0$, we obtain from equation (2) :

$$P_C = (\gamma + \Delta) / [H - h_0(P_C)]. \quad (8)$$

This equation correlates the capillary pressure of meniscus, P_C , and hence, its curvature radius, $r = \gamma / P_C$, with the slit half-width H and through Δ with the disjoining pressure isotherm. It should be taken into account, however, that h_0 is a function of P_C . The value of h_0 can be determined from the isotherm equation, $\Pi(h)$, at $\Pi_0 = \Pi(h_0) = P_C$.

Equation (8) enables one to determine, instead of the contact angle, another parameter, which may be used to characterize the complete wetting conditions; namely, — the difference $h_* = H - r$ (Fig. 1). The larger the value of h_* the smaller the meniscus curvature radius and the better the liquid wets the solid surface. Transforming equation (8), we obtain the following expression for h_* :

$$h_* = (\gamma \cdot h_0 + H \cdot \Delta) / (\gamma + \Delta). \quad (9)$$

The values of h_* are equal to 0 (curve 4, Fig. 1), when $P_C = \gamma / H$ and $\Pi_0 h_0 + \Delta = 0$. This, according to equation (3), corresponds to $\cos \theta_0 = 1$ and $\theta_0 = 0$.

At $\Delta = 0$, $h_* = h_0$. If the positive values of Δ increase, the values of h_* increase, too, exceeding the equilibrium film thickness. In the case of $H \gg h_0$ we may consider that $\gamma \gg \Delta$, and $P_C \approx \gamma / H$. Then equation (9) transforms into a simpler form :

$$h_* = h_0 + (\Delta / P_C). \quad (10)$$

Then the ratio, $S = h_* / h_0$, may be used as a unified characteristic of wetting, which is suitable in the cases of complete and partial wetting :

$$S = 1 + (\Delta / P_C h_0). \quad (11)$$

The value of $S = 0$, corresponding to $\theta_0 = 0$, separates the region of complete wetting ($S > 0$) from that of partial wetting ($S < 0$). The higher the positive values of S the better will be the wetting. Thus, in particular, for the isotherms $\Pi(h) = A/h^n > 0$, taking into account that $P_C = \Pi_0 = A/h_0^n$, instead of equation (11) we obtain the following expression :

$$S = n / (n - 1); \quad h_* = h_0 \cdot n / (n - 1). \quad (12)$$

At $n = 3$, which corresponds to the wetting films that are stable due to Lifshitz dispersion forces, $S = 1.5$, and $h_* = 1.5 h_0$. At $n = 2$, which corres-

ponds to the wetting films that are stable due to the electrostatic repulsive forces, $S = 2$, and $h_* = 2 h_0$. In general, the relationship between h_* and h_0 proves to be a function of the slit width H and the form of the $\Pi(h)$ isotherm, including the different components of disjoining pressure.

In the case of partial wetting ($\theta_0 > 0$), it is possible to establish, by using equations (3) and (11), a relatively simple functional relationship between the parameter S and the equilibrium contact angle, as formed by the meniscus in a flat slit :

$$S = - (r/h_0)(1 - \cos \theta_0). \quad (13)$$

Only the conditions of partial wetting can be realized for equilibrium drops on a solid substrate. The parameter S is here unacceptable, and the contact angle value remains the only characteristic of wetting. For drops having a small-radius base, the equilibrium contact angle is also influenced by the line tension of the wetting perimeter, which will further be considered (Sect. 8). For the films on curved surfaces, as for example, for those on filaments or in capillaries, a variation in the pressure in a film due to the curvature of its surface adjacent to the gas phase must be taken into account [8].

3. Isotherms of disjoining pressure of wetting films.

The macroscopic approach allows one to ascertain what physical phenomenon controls the wetting or the non-wetting of the surface. For this purpose, we consider, as an example the isotherms of disjoining pressure of aqueous wetting films (Fig. 3). Here, curves 1-4 represent the dependences of film thick-

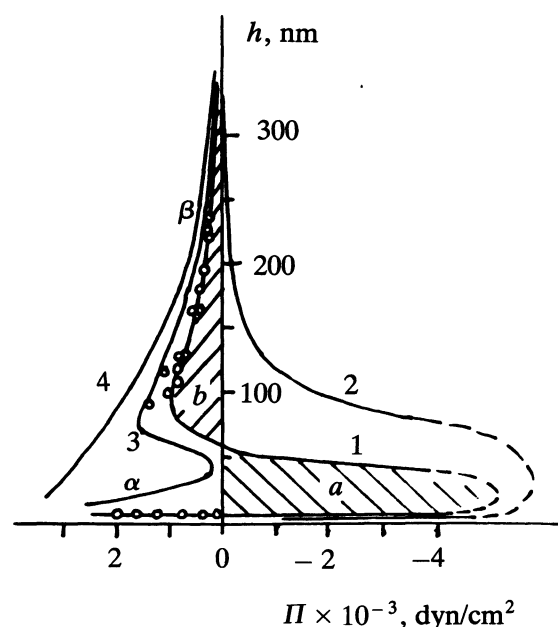


Fig. 3. — Isotherms of the disjoining pressure $\Pi(h)$ of water films on the solid surface.

ness h on disjoining pressure, or, which is the same, on the capillary pressure of a liquid in equilibrium with the film. Curve 1 relates to water films on a quartz surface. The known experimental data [8] are indicated by points, while a solid line represents a computed isotherm [16], accounting for the effect of three components of disjoining pressure in the film-molecular Π_m , electrostatic Π_e , and structural Π_s . The isotherm branches, where $\partial\Pi/\partial h < 0$, respond to the stable states of the film. The water films on quartz within the range of thicknesses of 60 to 10 nm (curve 1) are unstable, and are not realized. A metastable state of thick β -films ($h > 100$ nm) forms as a bulk water layer is thinning out. The time of their transition into a thermodynamically stable state of thin α -films ($h < 10$ nm) depends on the closeness of the capillary pressure to the critical one, P_{cr} (when $\partial\Pi/\partial h = 0$), and on the surface area of β -films. The larger the surface area the higher the probability of the formation of nuclei of the stable α -phase in metastable β -films. In the framework of the microscopic approach to the wetting theory, the $\beta \rightarrow \alpha$ transition is denominated as a pre-wetting transition [5].

The existence of thick β -films of water is conditioned by the electrostatic repulsion of charged surfaces of the films ($\Pi_e > 0$). As in this case ($\Pi_0 h_0 + \Delta) > 0$, the β films are completely wetted by water. Hereinbelow (Sect. 9) this case will be illustrated by comparison of the results of the experimental determination of the values of h_* with the theoretical ones, calculated with equation (10).

When the meniscus of bulk water is in contact with α -films, the values of Δ in equation (3) may be negative in view of the $\Pi(h)$ isotherm partly entering in the region of $\Pi < 0$. The change in the sign of the electrostatic component of disjoining pressure (curve 1) is connected with the different values of electrical potentials ψ_1 and ψ_2 of the film surfaces. The known tabulated data of electrostatic forces [17] are used to calculate the $\Pi_e(h)$ isotherms. The calculation gives that at $h < 600$ Å, the repulsive electrostatic forces transform into attraction forces: $\Pi_e < 0$. The repulsive forces do appear again as the film thickness decreases further, but these are already associated with the effect of molecular ($\Pi_m > 0$) and structural ($\Pi_s > 0$) forces. Calculations with equation (3) by using the theoretical isotherm 1 (Fig. 3) lead to the contact angle of water on quartz $\theta_0 \approx 5^\circ$ [16], which is close to the experimental data.

When the electrostatic repulsive forces are suppressed or the film surfaces have different signs of electrical potentials ψ , the β -branch of the isotherm cannot be realized. In this case, the isotherm shifts into the range of $\Pi < 0$ (curve 2, Fig. 3), which causes, in accordance with equation (3), the worsening of wetting.

On the contrary, when potentials ψ_1 and ψ_2 (of

the same sign) increase or approach each other in their values, this causes an increase in the electrostatic repulsive forces. As a result, the whole isotherm may be found within the $\Pi > 0$ region, which must lead to the complete wetting (curves 3 and 4, Fig. 3).

Thus, the conditions controlling the wetting of solid surfaces by water may be formulated as follows. Two effects — those of electrostatic (Π_e) and structural (Π_s) forces — can influence the shape of the isotherms $\Pi(h)$ of the wetting films of water. The dispersion forces depending on the spectral characteristics of water and the solid substrate, are less sensitive to the composition of an aqueous solution, temperature, and the surface charge. Three factors can influence the structural forces; namely — increasing the electrolyte concentration and raising temperature, which leads to decreasing the structural repulsion; as well as through adsorption of molecules, which changes the character of the interaction of water molecules with the solid surface.

The worsening of wetting, which is required, for example, for enhancing the flotation effectiveness, is usually attained through adsorption of ionic surfactants. In this case, it would be of importance that a surfactant would be selectively adsorbed on one of the film surfaces, imparting to it a charge, whose sign is reverse with regard to the charge of another surface. Thus the forces of electrostatic attraction arise ($\Pi_e < 0$), which shifts the isotherm into the $\Pi < 0$ region. Adsorption of surfactants may also simultaneously lead to hydrophobization of the solid substrate, which reduces the repulsive structural forces. A high degree of hydrophobization may also reverse the sign of structural forces, too ($\Pi_s < 0$) [18, 19]. At $\Pi_e < 0$ and $\Pi_s < 0$, still higher contact angle values may be attained [16].

On the contrary, all the measures causing an increase in the forces of electrostatic and structural repulsion, improve the wetting. This aim is attained either by imparting a high potential of the same sign to the film surfaces and/or through hydrophilization of the substrate, as for example, by increasing the number of centers that are able to form hydrogen bonds with water molecules. Adsorption of nonionic surfactants or polymers leads to an additional effect of the sterical repulsion of adsorption layers. Thus, in each specific case, one can choose the optimum methods for controlling the wetting.

A similar program of the theoretical calculation of contact angles on the basis of equation (3) was performed for alkanes on the Teflon surface [20]. In this simpler case, one could restrict oneself to the taking into account of only one molecular component of disjoining pressure $\Pi_m < 0$. A good agreement of the calculation results with the experimental values of θ_0 has thus been obtained.

The region of the applicability of equation (2) is

limited by such thicknesses of wetting films, when these can yet be considered as a liquid phase. With poor wetting ($\theta_0 \geq 90^\circ$), a two-dimensional adsorption phase is formed on the solid surface, and the thickness of films does not exceed a monolayer. In this case, another expression following from Gibbs equation, correlating the adsorption Γ with a change in the interphase tension γ_{sv} depending on the adsorbate vapour pressure, p , is applicable [21, 22]:

$$\gamma \cdot \cos \theta_0 = \gamma + \int_p^{p_s} \Gamma(p) d \ln p, \quad (14)$$

where p_s is the pressure of the saturated vapour.

Equation (14) transforms into equation (2) with a formal replacement $\Gamma = h_0/v_m$, where v_m is the molar volume of liquid, and with the use of a known thermodynamic relationship between the equilibrium vapour pressure over the film p and its disjoining pressure Π [1, 8]:

$$v_m \cdot \Pi = RT \cdot \ln (p_s/p), \quad (15)$$

where R is the gas constant, and T is temperature.

4. Effect of concentration of electrolyte and surfactants.

The main difficulty involved in calculating the contact angle values θ_0 from equations (2), (3), and (14) resides in that at $\theta_0 > 0$ the isotherms of disjoining pressure $\Pi(h)$ or the isotherms of adsorption $\Gamma(p/p_s)$ are partly disposed in the supersaturation region ($\Pi < 0$, $p/p_s > 1$). The values of $\cos \theta_0$ are proportional to the value of Δ — that is, to the difference between the areas a and b in figure 3 (curve 1). As it is difficult to determine experimentally the isotherms in the supersaturation region, these parts of the isotherms can be determined only theoretically. Such calculations were made on the basis on the theory of surface forces for different aqueous solutions [16, 23, 24].

In figure 4 are represented the results of calculation with equation (3) of contact angles θ_0 for the aqueous KCl solutions of different concentrations (curve 1) and different pH values (curve 2), while preserving in the latter case a constant ionic strength of the solution, $J = 10^{-2}$ mole/l [23, 24]. In carrying out calculation of $\Pi_e(h)$, the known dependences on the concentration of quartz-solution potentials ψ_1 and the aqueous solution-air interface ψ_2 were used. For the dispersion forces $\Pi_m = A/6 \pi h^3$, the value of constant $A = 7.2 \times 10^{-13}$ erg was adopted. A known exponential dependence [16] was adopted for the isotherm of structural forces $\Pi_s(h)$, whose parameters were used as adjusting ones in making the theoretical calculation of θ_0 agree with the experimental data [25]. An increase in the values of

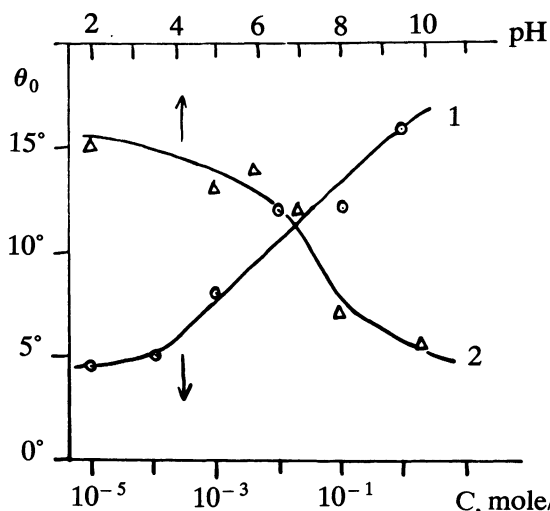


Fig. 4. — The results of calculation of contact angles θ_0 for aqueous KCl solutions of different concentrations (curve 1) and at different pH-values (curve 2).

θ_0 with the electrolyte concentration (curve 1) may be explained by two causes: i) a reduction in the thickness of the boundary layers of water, which leads to a reduction in the structural repulsive forces; ii) a decrease in the values of potentials ψ_1 and ψ_2 , which decreases the electrostatic repulsive forces.

A decrease in the contact angles as the pH value increases (curve 2), was caused mainly by an increase in the potentials ψ_1 and ψ_2 of the film surfaces as a result of adsorption of the potential-determining OH-ions. We note that at J of 10^{-2} mole/l (curve 2), the dependences of contact angles are described by using the $\Pi(h)$ isotherm, including only two components of disjoining pressure; namely — an electrostatic, and a molecular one. At such an electrolyte concentration the structural forces are small ($\Pi_s \approx 0$), and these could not be taken into account.

In figure 5 are presented the results of calculation of the isotherms of disjoining pressure of the wetting films of 10^{-3} mole/l KCl aqueous solution with additions of ionic surfactants. The isotherm indicated by curve 6, is the initial one, for KCl solution without addition of surfactants. In this case, the potentials of the quartz and film surfaces were assumed to be equal to: $\psi_1 = -100$ mV, and $\psi_2 = -25$ mV, respectively. The value of $\theta_0 = 8^\circ$ (as is also shown in Fig. 4) was obtained by calculating with equation (3). In the calculations done, the influence of surfactants was expressed as a variation in the values of potential ψ_2 due to the adsorption of surfactant on the film-gas interface. Adsorption of an anionic surfactant increases the negative values of ψ_2 and leads to an improvement in wetting. Thus, for example, at $\psi_2 = -35$ mV the calculated value of θ_0 reduces to 7° , while at $\psi_2 = -45$ mV it reduces to 5° . A further increase in the absolute values of

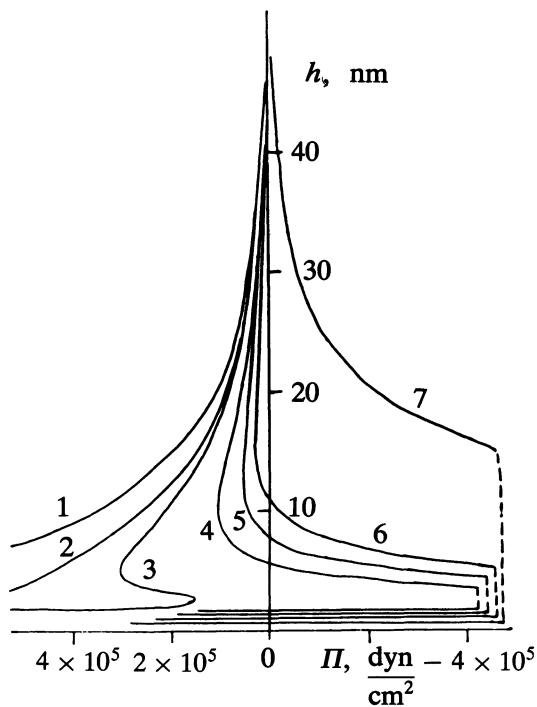


Fig. 5. — $\Pi(h)$ isotherms calculated for a 10^{-3} mole/l KCl aqueous solution with additions of surfactants at $\psi_1 = -100$ mV = Const. ; $\psi_2 = -100$ (curve 1) ; $\psi_2 = -75$ (curve 2) ; $\psi_2 = -65$ (curve 3) ; $\psi_2 = -45$ (curve 4) ; $\psi_2 = -35$ (curve 5) ; $\psi_2 = -25$ (curve 6) and $\psi_2 = +100$ mV (curve 7).

ψ_2 (curves 1-3) corresponds to the complete wetting of the quartz surface.

Adsorption of a cationic surfactant charged positively the film-gas interface ($\psi_2 = +100$ mV). When the substrate remains negatively charged (curve 7), the contact angle increases up to 28° owing to the electrostatic attraction of the film surfaces ($\Pi_e < 0$).

The calculations are in good agreement with the results of direct measurements of the contact angles of KCl solutions with additions of anionic sodium-dodecylsulfate and cationic cetyltrimethylammonium bromide [26].

5. Contact angle hysteresis.

In a number of cases to form equilibrium contact angle requires a long time. This is connected with the retarded mass exchange between the bulk liquid and the thin wetting film [27]. The kinetics of transition into the equilibrium state is controlled by the viscous resistance of films and the diffusion of the dissolved components, whose equilibrium concentrations in the bulk phase and in a thin film may be different. In view of this, at first a partial mechanical equilibrium can rapidly be established in the bulk part of a drop or meniscus in the absence of both the mechanical and the thermodynamic equilibrium with the film. A possibility of realization of a number of states of the mechanical equilibrium results in the phenomenon of the static hysteresis of the contact angle [13]. In this case the transition zone between the meniscus and the film plays a substantial role (Fig. 6). The state of its mechanical equilibrium, which is determined by fulfillment of the condition (1) breaks up at two values of the capillary pressure $P_C \geq P_A$ and $P_C \leq P_R$, and accordingly at two values of the contact angle — an advancing $\theta_A > \theta_0$, and a receding $\theta_R < \theta_0$. A plurality of the mechanical equilibrium states can be established in the whole interval between θ_A and θ_R . This interferes with determination of the equilibrium value of the contact angle [28]. The better the wetting — that is, the larger the film thickness h_0 , the quicker occurs the transition into the equilibrium state, and the smaller the difference between the values of θ_A and θ_R .

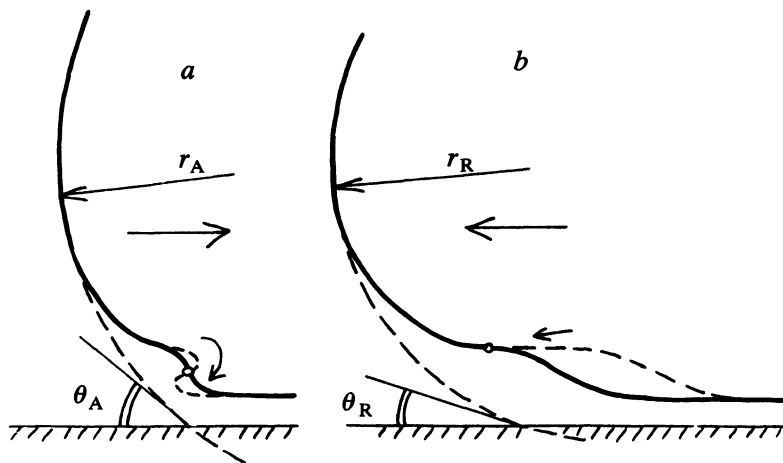


Fig. 6. — Influence of the transition zone on the static hysteresis of the contact angle in a flat slit : (a) advancing meniscus ; (b) receding meniscus.

It was considered earlier that the contact angle hysteresis is due either to the surface roughness or to its chemical heterogeneity — the presence of the areas that differ from one another in the values of equilibrium contact angles. Examination of the stability of the transition zone has demonstrated that hysteresis is possible also on a smooth, uniform surface, too. In this case, the values of θ_A and θ_R can also be determined on the basis of the isotherms of disjoining pressure, $\Pi(h)$ [13]. For the S-shaped isotherms (curves 1, Fig. 3) it was shown that the values of θ_A are within the range between θ_0 and 90° (depending in the $\Pi(h)$ Eq.), whilst the values of θ_R are close to zero, because a thick metastable β -film remains behind the retreating meniscus.

6. Wetting transition.

The macroscopic approach enables one also to examine the known phenomenon of the wetting transition, which is at present widely discussed within the framework of the microscopic approach [5, 29, 30].

An increase in temperature T influences the $\Pi(h)$ isotherms, the consequence of which is transition from the complete wetting to the partial one. For quartz and glass substrates a worsening of the wetting by water is experimentally detected, as T is raised [31-33]. In view of the $\Pi(h)$ isotherms considered in figure 3, the transition of wetting, i.e., transition from isotherms 4 and 3 to isotherms 1 and 2, can result from a number of causes. The most probable is the influence of temperature on the structure of the boundary layers of water. It has experimentally been shown that the raising of temperature from 20°C to 70°C causes gradual disintegration of the special structure of the boundary layers of water and its approach to the bulk structure [34]. A decrease in the structural repulsive forces as T is raised, can enhance the extent of isotherm 3 (Fig. 3) entering the range of $\Pi < 0$. This may cause transition from the complete wetting to the partial one. The structural mechanism of transition is confirmed by a thermal reduction in the thickness of α -films [35], as well as by the fact that the higher the substrate hydrophilicity the higher the sensitivity of contact angles to variation in temperature [31].

The cause of wetting transition is quite different for the films of nonpolar liquids on dielectric substrates, when only dispersion forces are acting. As is known [36], the disjoining pressure of such thin films ($h < 10\text{-}20\text{ nm}$) is determined by a difference in the dielectric function of the substrate 1 and the liquid 3 :

$$\Pi_m(h) = \frac{\hbar}{8\pi^2 h^3} \int_0^\infty \frac{(\varepsilon_1 - \varepsilon_3)(\varepsilon_3 - 1)}{(\varepsilon_1 + \varepsilon_3)(\varepsilon_3 + 1)} d\xi. \quad (16)$$

Here \hbar is the Planck constant, subdivided by 2π ; $\varepsilon(\omega)$ are the frequency dependences of dielectric permeability, where $\omega = i\xi$ is the circular frequency along the imaginary frequency axis.

The wetting transition corresponds to the change in the sign of the integral in equation (16). At $\varepsilon_1 > \varepsilon_3$ in the frequencies range, making the main contribution to the integral ($10^{16}\text{-}10^{17}\text{ rad/s}$), the values of $\Pi_m > 0$. This is the case of complete wetting. At $\varepsilon_1 < \varepsilon_3$, the transition to the partial wetting can occur. For the same liquid and substrate, this is possible when its temperature dependences $\varepsilon(T)$ are different. The values of ε depend on density (the number of molecules per unit volume). Then, at a higher coefficient of thermal expansion of the liquid, than that of substrate, the values of ε_3 (larger than ε_1 at a low temperature) may become less than ε_1 as temperature T is raised. In accordance with equation (16), in this case an increase in T should lead to a reversal of the disjoining pressure sign and to the wetting transition. Since in this case the film thickness changes jump-wise, the wetting transition is of the first order.

A possibility of the wetting transition due to the temperature dependence of the electric potentials of the film surfaces is also not excluded. However, this is possible at the adsorption energy values of potential - determining ions comparable to kT . In this case, as in that of structural forces, the film thickness can change gradually, and the transition may be of the second order.

7. Dynamic contact angles.

Up to now, we have considered the state of thermodynamic or mechanical equilibrium of the meniscus-film system. When drops or menisci move, the distribution of pressures throughout the transition zone and the film changes, which cause also the curvature of the meniscus to change. If we continue an undisturbed by surface forces meniscus profile until it intersects the substrate, then the contact angle values determined by that formal method will indicate the dependence on the flow rate v . The dynamic contact angles θ_d begin to differ from the static values of θ_0 and exceed these at $v > 10^{-3}\text{ cm/s}$ [37-39].

The theory of dynamic contact angles has so far been developed only for the case of complete wetting, and when the meniscus advances at a constant velocity onto an equilibrium wetting film. The numerical calculations were made on the basis of equation (1) [40]. Assuming that the condition $dh/dx \ll 1$ holds also for the flowing transition zone, the following expression for the pressure gradient can be obtained :

$$\frac{dP}{dx} = -\gamma \frac{\partial^3 h}{\partial x^3} - \frac{\partial \Pi(h)}{\partial x} = -\gamma \frac{\partial^3 h}{\partial x^3} - \frac{\partial \Pi}{\partial h} \cdot \frac{\partial h}{\partial x}, \quad (17)$$

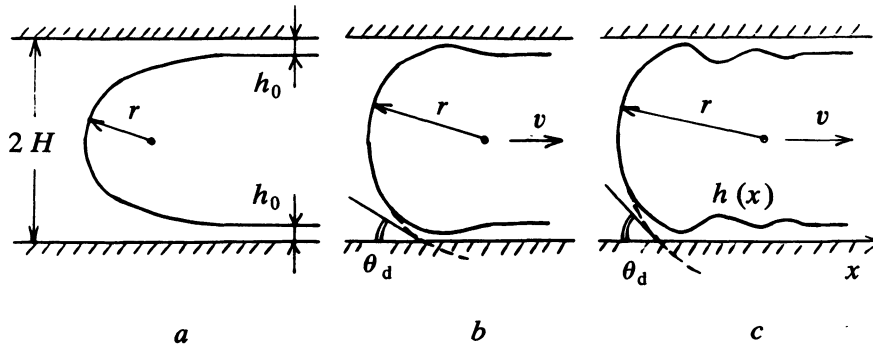


Fig. 7. — The meniscus profiles of completely wetting liquid in a flat capillary. (a) at rest ; (b) and (c) in motion at an increasing velocity, $V = \text{Const}$.

where an approximation $K = d^2h/dx^2$ is used for the surface curvature of liquid layer.

In equation (17) $P = P_0 - P_c(x) - \Pi(x)$ is the hydrodynamic pressure in a film. It is equal to the pressure in the gas phase P_0 minus the local values of the capillary and the disjoining pressure [41].

Expression (17) for dP/dx may now be substituted into the known equation of hydrodynamics of thin layers at $v = \text{Const}$. [42] :

$$\frac{h^3}{3\eta} \frac{dP}{dx} = v[h(x) - h_0], \quad (18)$$

where η is viscosity, $h(x)$ is the local thickness of liquid layer, and h_0 is the thickness of an equilibrium film. A steady-state solution of the differential equation gives the profile $h(x)$ of a flowing liquid.

In figure 7 are shown the computed profiles of a meniscus moving at different flow rates v through a flat slit [40]. For determination of θ_d , we have used a part of the profile of a constant curvature, which is directly adjacent to the flow zone, and which is therefore found still within the region of the sloping liquid layer $dh/dx \ll 1$.

In figure 8 are presented computed dependences $\cos \theta_d$ on the capillary number $Ca = v\eta/\gamma$. Calculations were made for the isotherms $\Pi(h) = A/h^3$ (with $A = 10^{-14}$ erg) and different half-widths of a slit H . As appears from figure 8, an increase in the flow rate causes an increase in the values of θ_d . Differences of θ_d from the static value of $\theta_0 = 0$, begin to show up at $Ca > 10^{-3}$. The narrower the slit and accordingly the smaller the thickness of an equilibrium wetting film h_0 — the smaller the meniscus profile is disturbed.

Experimental investigations of dynamic contact angles for water on the quartz surface had shown that the values of θ_d began to exceed the equilibrium values ($\theta_0 = 10^\circ$) at $v \geq 10^{-3}$ cm/s, thus attaining a value of 75 to 80° at $v \geq 0.1$ cm/s [39]. As appears from figure 9, these data only qualitatively agree with the theoretical ones (full line in Fig. 9). The quantitative discrepancy is associated with the fact

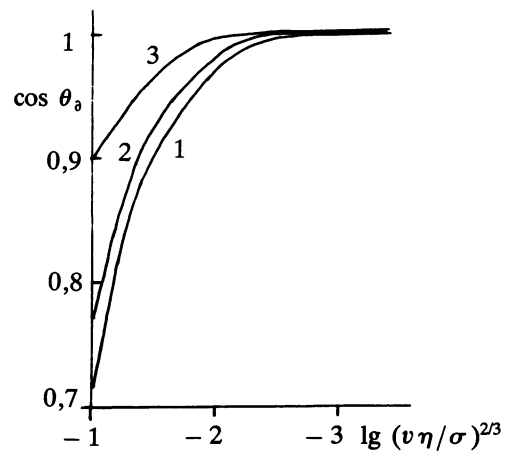


Fig. 8. — The dependences of the dynamic contact angle θ_d on the meniscus flow rate. (1) $H = 10^{-2}$ cm, $h_0 = 150 \text{ \AA}$; (2) $H = 1.25 \times 10^{-3}$ cm, $h_0 = 74 \text{ \AA}$; (3) $H = 1.25 \times 10^{-5}$ cm, $h_0 = 16 \text{ \AA}$.

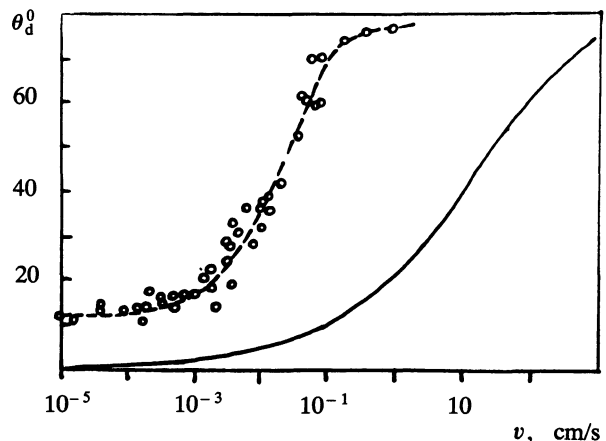


Fig. 9. — The experimental dependence $\theta_d(v)$ (shown by points) obtained for water in quartz capillaries $30 \div 35 \mu\text{m}$ in diameter. The solid line indicates the results of theoretical simulation [40].

that the theory has been developed only for the conditions of complete wetting and monotonous $\Pi(h)$ isotherms (curve 4, Fig. 3). For water on

quartz, another type of the S-shaped isotherm is characteristic (curve 1, Fig. 3), which substantially changes the shape of the transition zone, and, hence, the qualitative calculation results.

At a slow flow rate v forms the equilibrium contact angle θ_0 (Fig. 10a). For instance, the spontaneous immiscible displacement of one liquid by another, which better wets the capillary surface, occurs (at $v \leq 10^{-4}$ - 10^{-3} cm/s) at a constant value of θ_0 and a constant capillary pressure of meniscus P_C . In the case of the spontaneous displacement of tetradecane, dibutylphthalate, and toluene by water from the molecularly smooth quartz capillaries having the radii $r = 10$ - 20 μm , the values of θ_0 remained constant and equal to about 83° - 86° [43].

When displacement takes place under the applied pressure gradient ($v \geq 10^{-2}$ - 10^{-1} cm/s), the capillary pressure of the meniscus remains also constant, but equal to $P_C = 2\gamma/r$ (Fig. 10b). The capillary pressure hinders the displacement, and reduces the flow rate. The condition of the complete wetting of a capillary by the liquid being displaced is dynamic, and is associated with the formation of thick, nonequilibrium films of liquid 2, after the rapidly receding meniscus. When the liquid flow is stopped, these films are ruptured and form slugs of 2 in liquid 1. At a very high flow rate ($v \geq 1$ cm/s), the non-equilibrium films can be ruptured in the course of flow. As a result, for example, the displacing liquid disintegrates into droplets forming an emulsion.

The thickness of nonequilibrium films may be evaluated with Derjaguin's equation [44]:

$$h = 1.32 r (v\eta/\gamma)^{2/3}, \quad (19)$$

where η is the viscosity of a liquid being displaced.

Thus, in displacing dibutylphthalate by water, the values of thickness h were obtained ranging from 70 to 300 nm; whilst in displacing water by dibutylphthalate, the values of h varied from 10 to 40 nm, when the displacement rates vary from 10^{-2} to 10^{-1} cm/s, respectively.

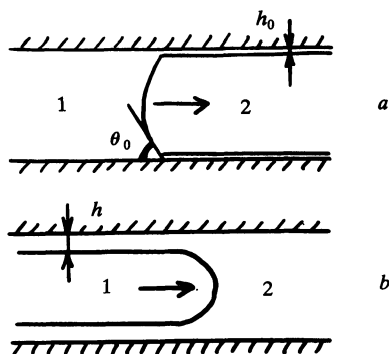


Fig. 10. — Immiscible displacement of fluid 2 by liquid 1. (a) during spontaneous imbibition; (b) rapid displacement under the effect of pressure gradient.

8. Line tension.

The existence of the transition zone between the meniscus and the film leads to one more effect, which in the general case has been predicted by Gibbs — namely; the effect of line tension κ [45]. In similarity with the surface tension γ , when the transition zone between the liquid and its vapour is replaced by a plane of tension, the transition zone between the meniscus and the film may be replaced by a three-phase contact line. In distinction from γ , the values of κ may be both positive and negative; they make the circular wetting perimeter tend to contraction in the first case, and to expansion in the second case.

When the transition zone is replaced by the three-phase contact line, an additional term, κ/r , is introduced in the Young equation:

$$\gamma \cdot \cos \theta_0 = \gamma_{SV} - \gamma_{SL} \pm (\kappa/r), \quad (20)$$

where r is the wetting perimeter radius. The line tension effect does show up the more noticeably the smaller the radius r .

In the case of drops on the flat substrate, the positive values of κ cause an increase in the values of θ_0 , whereas the negative ones their decrease. For the flat films surrounded by a concave meniscus, the influence of the sign of κ is inverse, which is just the cause of the introduction of a double sign before the last term in equation (20).

For water and aqueous solutions the values of κ are of about 10^{-6} - 10^{-5} dyne [43]. Thus, the term κ/r in the right-hand side of equation (20) becomes noticeable at $r \leq 10^{-4}$ - 10^{-5} cm — that is, for drops and films of a very small radius. The line tension may, in particular, show up to a very noticeable degree in flotation — on the initial stage of gas bubbles approaching particles [46], as well as in condensation of water on solid surfaces — on the condensate nuclei formation stage [47].

The values of the line tension κ for drops on the solid substrate were calculated as a difference between the values of $\gamma \cdot \cos \theta$, obtained while neglecting the transition zone and taking it into account [9, 14]. Since the line tension arises due to the existence of the transition zone, it is clear that this difference is just associated with the term κ/r .

The line tension depends on the curvature radius r [9, 14]. This is connected with the dependence of the transition zone profile on the value of r . However, if the influence of curvature on the surface tension γ does show up with the surface curvature radius on the order of distances between molecules, then in the case of line tension κ the influence of the wetting perimeter curvature is felt at much larger values of r — that is, on the order of the radius of action of surface forces.

An analytical expression for κ was obtained for a simplified isotherm of disjoining pressure (6) [14]:

$$\kappa = - \frac{2 \gamma t \operatorname{tg} \theta_0}{1 + (2/r)(\gamma/a)^{1/2}}, \quad (21)$$

where a and t are the parameters of a model isotherm $\Pi(h)$.

At $r \rightarrow \infty$, the values of κ tend to a constant value of $\kappa_0 = -2 \gamma t \operatorname{tg} \theta_0$. For small values of θ_0 , when a gradual profile of the transition zone is formed, the values of κ are negative, and amount to 10^{-6} dyne in their order of magnitude, which is in agreement with the experimental data for foam films [48].

9. Transition zone.

Quite recently, the profile of the transition zone between the meniscus and a film on the solid substrate has for the first time been experimentally investigated, and the correctness of equations (8) and (10) of the theory of complete wetting has been verified [49].

The wetting films were formed on a polished quartz plate 1 (Fig. 11) by making approach to it the meniscus of liquid in a tube 2 about $R = 1$ mm in radius. The liquid is sucked from the tube through slots 3. The thickness of a film h_0 in the equilibrium state with the meniscus surrounding it was obtained from the intensity of reflected light. Depending on the capillary pressure of meniscus P_C the radius of the film r_0 amounts to several scores microns. Simultaneously with measuring thickness, the interference rings from meniscus were photographed. This allowed its profile $h(r)$ to be determined, where r is the radial coordinate.

An analysis of experimentally obtained profiles of the meniscus for water and aqueous KCl solutions of low concentration has shown that their continuation does not intersect the substrate plane — that is, the complete wetting takes place. The undisturbed profile was calculated with the Laplace equation for an axisymmetrical meniscus:

$$r \cdot \sin \theta(r) = (P_C/2 \gamma)(r^2 - r_0^2), \quad (22)$$

where $\theta(r)$ is the current angle value, for which $\operatorname{tg} \theta = \partial h / \partial r$ (Fig. 11).

Solution of equation (20) allows the coordinate r_0 to be determined, at which the theoretical profile of meniscus passes through a minimum. Its position corresponds to the thickness h_* (compare Figs. 1 and 11). As has been demonstrated above, the value of $S = h_*/h_0$ is a quantitative characteristic of complete wetting.

For the aqueous KCl solutions, Z. M. Zorin has obtained the following values of h_0 and h_* ; namely — for a 10^{-4} mole/l solution $h_0 = 1025 \text{ \AA}$, and $h_* = 1450 \text{ \AA}$; for a 10^{-3} mole/l solution, $h_0 =$

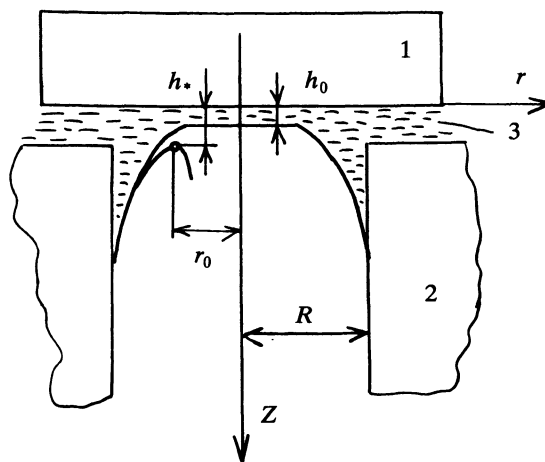


Fig. 11. — Formation of an equilibrium wetting film having the thickness h_0 and radius r_0 on the solid substrate 1 in pipe 2, when the liquid is being sucked off through slit 3 under the effect of the capillary pressure.

590 \AA , and $h_* = 710 \text{ \AA}$. This leads to the h_*/h_0 values equal to 1.41 and 1.2, respectively.

The experimental values of S may be compared with theoretical ones. Large values of the equilibrium thicknesses of films h_0 and the complete wetting indicate that the long-range electrostatic repulsion forces predominantly act there. Assuming the potentials of quartz surface ψ_1 and film surface ψ_2 , it is possible to calculate from Devereux and de Bruyn tables [17] the isotherm of electrostatic forces $\Pi_e(h)$. On the basis of references [50, 51], for 10^{-4} mole/l KCl solution, it is possible to assume that $\psi_1 = -150$ mV, and $\psi_2 = -45$ mV, while for a 10^{-3} mole/l solution, $\psi_1 = -125$ mV, and $\psi_2 = -45$ mV. Under the condition of $\psi = \text{Const.}$, the calculated isotherms $\Pi_e(h)$ are linearized in logarithmic coordinates with the correlation coefficient being equal to 0.996. This enables one to approximate the β -part of the isotherm by a power-function, $\Pi = A/h^n$. For a 10^{-4} mole/l KCl solution $n = 2.87$; and for a 10^{-3} mole/l KCl solution the value of n was obtained to be equal to 6. Substituting these values of n into equation (12), we obtain the theoretical values of the parameter S , which are equal to $S = 1.5$ for the 10^{-4} mole/l concentration, and to $S = 1.2$ for the 10^{-3} mole/l. These values satisfactorily agree with the experimental ones. Similar results were obtained for water and for a number of aqueous solutions [49].

At a low electrolyte concentration, the extension of the transition zone amounts to about 5-10 μm , which allows its investigation by means of optical methods. On the basis of a photogramme of the interference patterns, Z. M. Zorin has calculated the profile of the meniscus and that of the transition zone (curve 1, Fig. 12). Curve 2 gives the profile of the meniscus that has not been disturbed by surface

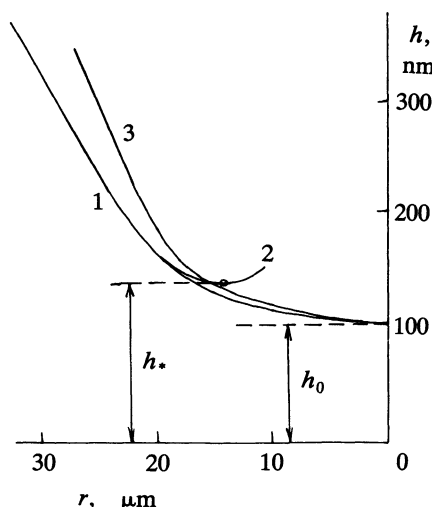


Fig. 12. — The profiles of the transition zone between the meniscus and a flat film having the radius $r = 10 \mu\text{m}$, both determined experimentally (curve 1) and calculated theoretically (curve 3). Curve 2 indicates the profile of an undisturbed meniscus (10^{-4} mole/l NaCl).

forces, as plotted with the use of equation (22). A minimum on this curve determines the layer thickness h_* .

Then the theoretical profile of the transition zone may also be attempted to be constructed. However, the theory of the transition zone has so far been developed only for a meniscus in a flat slit, and for the isotherms of the type $\Pi = A/h^n$ [11]. A corresponding equation for the profile of the transition zone $h(x)$ has the following form :

$$x = \int_h^H \left[\frac{\int_{h_0}^H (P_C - Ah^{-n}) dh}{\int_h^H (P_C - Ah^{-n}) dh} - 1 \right]^{-1/2} dh, \quad (23)$$

where x is the tangential coordinate.

The width of the slit H , which is equivalent to the round cell, was determined by equalizing the capillary pressure of the cylindrical meniscus in a flat slit (Fig. 1) and that of the meniscus in the tube (Fig. 11). This gives in both cases the equality of the disjoining pressure $\Pi_0 = P_C$ in the films. The profile of the transition zone calculated with equation (23) (at $n = 2.87$, and $A = 9.54 \times 10^{-12}$, if Π is expressed in dyne/cm², and h in cm) is indicated by curve 3 in figure 12. Agreement between the experimental and the theoretical profile is a satisfactory one.

10. Conclusion.

Thus, the review of the current state of the macroscopic theory of the wetting shows that the disjoining pressure isotherms can be successfully used for theoretical evaluation of contact angles. This approach is limited to solid surfaces which are sufficiently lyophilic that the contact angles did not exceed a value of about $30 \div 40^\circ$.

The object of further investigations will consist in the obtaining of experimental isotherms of disjoining pressure for wetting films of different liquids on different substrates. This will enable one to render more correct the values of the parameters of the isotherms, which will make the results of the calculation more reliable.

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