PHYSICAL MECHANISM OF THE WETTING OF SOLID SURFACES

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This article examines physical principles in the theory of wetting. Wetting angles are calculated by using isotherms of the disjoining pressure of wetting liquid films on solid substrates.

The phenomenon of wetting, consisting of the formation of the contact angle between a liquid and a solid substrate, is the basis of many mass-transfer processes in porous bodies and capillaries, processes involving the spreading of liquids, and the application of films and liquid coatings. Analysis of this phenomenon is also important for the study of the equilibrium states of a liquid in porous bodies, determining the degree of their saturation by the liquid at different capillary pressures, and determining the mechanism by which the liquid moves under the influence of difference external physical fields.

The quantity θ_0 is used as a wetting characteristic. This quantity is usually determined experimentally, and different methods and apparatuses have been developed for this purpose. However, this approach does not offer insight into the mechanism of the phenomenon, and it does not allow prediction of wetting conditions on the basis of the physical properties of the solid surface and the liquid interacting with it.

The principles of the thermodynamic theory of wetting were developed by Frumkin [1] and Deryagin [2]. These principles were briefly described in the well-known monograph by Landau and Lifshitz [3], but practical application of the theory has come only recently. This was made possible by the development of methods of calculating the surface forces acting in thin wetting films [4] with which the meniscus of the bulk liquid (and not the "dry" surface) is in equilibrium (Fig. 1).

We will begin our discussion of modern methods of wetting theory by refining the notion of the wetting angle θ_0. It is defined as the angle between the substrate and a continuation of the profile of the meniscus undisturbed by surface forces (curve 1, Fig. 1). For a miniscus in a plane slit, $R = H/\cos\theta_0$ and $P_C = \sigma/R = \sigma\cos\theta_0/H$. For a cylindrical capillary: $R = r/\cos\theta_0$ and $P_C = \sigma/R = 2\sigma\cos\theta_0/r$. The meniscus is in equilibrium with the wetting film, the thickness of which h_0 is determined by the action of the field of surface forces and which decreases with an increase in P_C. A transitional zone 2 is formed between the meniscus and the film, and both capillary and surfaces forces act simultaneously within this zone. The dimensions of the transitional zone are limited by the radius of action of the surface forces: 10^{-6}-10^{-5} cm [5].

The above definition of the wetting angle becomes meaningless in the case of very narrow slits ($H \leq 10^{-6}$-10^{-5} cm), when the field of surface forces is overlapped. Calculations of the equilibrium of a capillary liquid should be based on another thermodynamic approach in this case [6]. Special study is also required by the case of complete wetting, when the extension of the meniscus does not intersect the substrate (curve 3 in Fig. 1) and no wetting angle is formed. Another limit of the applicability of the concept θ_0 is the situation when the continuation of the meniscus profile touches the substrate. Here, $\theta_0 = 0$ (curve 4, Fig. 1).

The Frumkin–Deryagin theory includes examination of both the cases of incomplete ($\theta_0 > 0$) and complete wetting. Below we examine one of the derivations of the main equation of the theory, based on study of the equilibrium conditions of the film, transitional zone, and meniscus [4]. In the equilibrium state, the pressure in all parts of this system is the same and is equal to the capillary pressure of the meniscus:

$$\sigma K(h) + \Pi(h) = P_c = \mathrm{const}. \tag{1}$$

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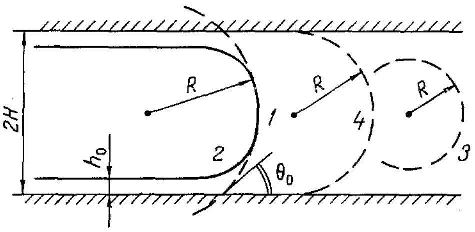

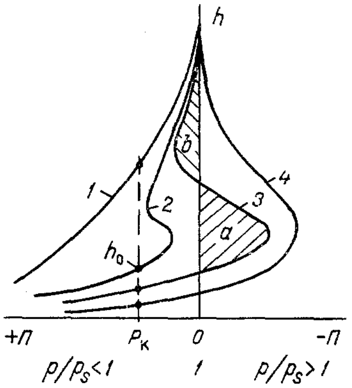

Fig. 1 Fig. 2

Fig. 1. Formation of the equilibrium wetting angle θ_0 in the contact of a liquid with the surfaces of a plane slit.

Fig. 2. Different forms of isotherms of the disjoining pressure of wetting films on a solid substrate.

At $h \to h_0$, $K \to 0$ and $\Pi(h_0) = P_c$, which determines the thickness of the film. At a given pressure P_c, the thickness h_0 depends on the form of the isotherm $\Pi(h)$, i.e., on the different components of the surface forces acting in the given system. At $h \to \infty$, $\Pi(h) \to 0$ and $K \to (1/R) = \text{const}$; Eq. (1) becomes the Laplace equation in this case. Introducing the well-known expression for the curvature of a cylindrical surface $K = h''[1 + (h')^2]^{-3/2}$ and solving differential equation (1), we obtain

$$\sigma \cos \theta_0 = \sigma + P_c h_0 + \int_{h_0}^{\infty} \Pi(h)\, dh. \qquad (2)$$

Comparison of this equation and the Young equation shows that its right side is equal to the difference $\sigma_{SV} - \sigma_{SL}$. Here, σ_{SV} pertains to a solid surface covered by a thin wetting film. Wetting theory defines σ_{SV} as the sum of the free energies of the two surfaces of the film $\sigma + \sigma_{SL}$ and the isothermal work Δ done in thinning the film from ∞ to the finite thickness h_0. Values of Δ are determined by the last two terms of the right side of Eq. (2).

Equation (2) makes it possible to calculate values of θ_0 on the basis of the known isotherm $\Pi(h)$ for the given system, which expresses the dependence of the film thickness on the capillary pressure of the meniscus, $P_c = \Pi$, or on the relative vapor pressure p/p_s (Fig. 2). Methods of experimentally and theoretically determining isotherms are presented in [4].

The range of application of Eq. (2) is limited to the values $\Delta \leq 0$ if $\Delta_0 \geq 0$. With complete wetting, when no wetting angles are formed, $\Delta > 0$. In this case, the isotherms $\Pi(h)$ are located in the region of positive values of Π (curves 1 and 2, Fig. 2). For these isotherms, Eq. (1) makes it possible to determine the value of the ratio

$$H/R = 1 + (1/\sigma) \int_{h_0}^{\infty} \Pi(h)\, dh. \qquad (3)$$

The greater this ratio, the better the liquid wets the surface of the slit and the greater the capillary pressure of the meniscus $P_c = \sigma/R$, other conditions being equal.

The applicable range of Eq. (2) is also limited by the thickness of the film – thin films cannot be considered part of the refined liquid phase. This case exists with poor wetting when a two-dimensional phase – adsorption layers several molecules thick – is formed on the solid surface. Here, it is possible to use another expression obtained from the Gibbs adsorption equation [5]:

$$\sigma \cos \theta_0 = \sigma + \int_{p}^{p_s} \Gamma(p)\, d \ln p. \qquad (4)$$

It should be noted that this equation becomes Eq. (2) with the substitution $\Gamma = h_0/v_m$ and with the use of the well-known thermodynamic relation between p and Π: $v_m\Pi = R_0T \ln(p_s/p)$.

The main difficulty in calculating θ_0 on the basis of Eqs. (2) and (4) is that at $\theta_0 \geq 0$ the isotherms $\Pi(h)$ or $\Gamma(p/p_s)$ are located partly in the region $\Pi < 0$. This corresponds to the supersaturation region $p/p_s > 1$ (curves 3 and 4, Fig. 2). In this case, the values of

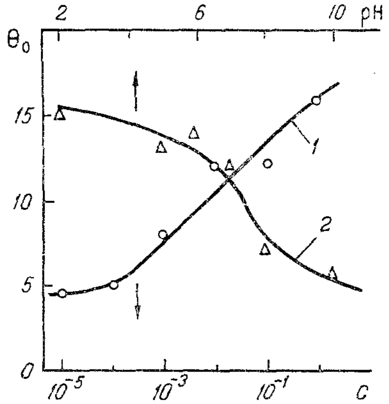

Fig. 3

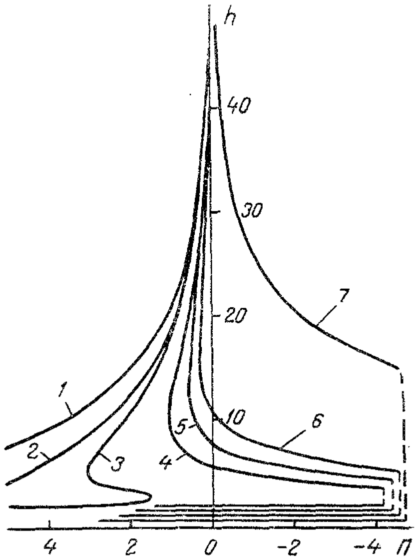

Fig. 4

Fig. 3. Results of calculations of the wetting angles θ_0 (degrees) for KCl solutions of different concentration C and with different values of pH on a quartz surface.

Fig. 4. Isotherms $\Pi(h)$ calculated on the basis of the theory of surface forces for KCl solutions with $I = 10^{-3}$ moles/liter at $\psi_1 = -100$ mV = const and $\psi_2 = -100$ (1); -75 (2); -65 (3); -45 (4); -35 (5); -25 (6); and + 100 mV (7). $\Pi \cdot 10^{-5}$; dyn/cm²; h, nm.

cos θ_0 are proportional to the difference of the areas a and b of the isotherm graphs. The deeper the isotherm penetrates the supersaturation region, the higher the value of θ_0 and the worse the wetting. The physical reason for the poor wetting, thus, is the action of forces of attraction of the film surfaces exceeding the forces of repulsion in the existing thickness region. However, isotherms cannot be successfully studied experimentally with supersaturation, so that isotherms calculated on the basis of the theory of surface forces [4, 5] should be used to calculate θ_0.

Such an approach was taken in [7, 8] for aqueous solutions and in [9] for the simpler case of nonpolar liquids. Only molecular forces act in films of nonpolar liquids, which facilitates the calculations. In this case, the isotherm $\Pi(h)$ has the following form: $\Pi_m(h) = -A/6\pi h^3$. In the case of nonpolar wetting, $A > 0$, and the entire isotherm lies in the region $\Pi < 0$. To obtain finite values of the integral in Eq. (2), this isotherm is cut off at a value of h_0 on the order of molecular dimensions, when discrete effects begin to be manifest. This value determines the lower limit of the integral in (2). The method just described was used successfully to obtain good agreement between theoretical values of θ_0 and experimental data for liquid alkanes on Teflon [9]. In accordance with the theory of molecular forces, the wetting angles increased from $\theta_0 = 0°$ for pentane to $\theta_0 = 46°$ for hexadecane.

The calculations are more complicated for films of aqueous solutions, since the effect of Π_m is augmented by electrostatic forces Π_e, connected with the charge of the surface film, and structural forces Π_s, due to the change in the structure of the boundary layers of water [5]. Nevertheless, since the theory of these surface-force components is fairly well-developed, it is possible to calculate θ_0 in this case as well. Here, Eq. (2) includes the algebraic sum of the components: $\Pi(h) = \Pi_m + \Pi_e + \Pi_s$. For water on the surface of quartz, calculations lead to values $\theta_0 \approx 5°$, which are close to the experimental values [7]. As the initial parameters to perform such calculations, we use the value $A = -7.2 \cdot 10^{-14}$ erg, the potentials ψ_1 and ψ_2, and parameters of the structural-force isotherm. The parameter values were used to refine calculations for electrolyte solutions.

Figure 3 shows the dependence of θ_0 on the concentration (curve 1) and the pH of a KCl solution at $I = 10^{-2}$ moles/liter (curve 2) as calculated from Eq. (2). These results agree with direct interference measurements of θ_0 on a quartz surface [10] (see points in Fig. 3).

The increase in θ_0 with an increase in C is due to two factors: a reduction in the thickness of the water boundary layers, which leads to weakening of the forces of structural repulsion; a reduction in the potentials ψ_1 and ψ_2. The improvement in wetting which takes place with the transition to the alkali region is due to the increase in the potentials ψ_1 and ψ_2 as a result of adsorption of the potential-determining ions OH^-. The reduction in the forces of structural repulsion as a result of destruction of the special structure of the water boundary layers also explains the increase in the wetting angles with an increase in temperature.

Making the surface hydrophobic may lead to a change in the sign of the structural forces. At $\Pi_s < 0$, the complete isotherm is shifted farther into the region $\Pi < 0$ (isotherm 4 in Fig. 2 is an example). This leads to an increase in θ_0. Here, calculations show an increase in the wetting angles for water on quartz from 5° (at $\Pi_s > 0$) to 60-80° (at $\Pi_s < 0$). The change in the sign of Π_s is connected with the fact that structural changes of water near hydrophobic surfaces are sharply different from the angles near hydrophilic surfaces [11]. Overlapping of the structurally-altered boundary layers as the films become thinner leads to the creation of forces of attraction between the surfaces in the first case ($\Pi_s < 0$) and to forces of repulsion in the second case ($\Pi_s > 0$). Both of these effects have been observed experimentally [5]. For the surface to be made hydrophobic, it should be free of centers which can form hydrogen bonds with water molecules.

In the absence of structural forces, the main contribution to the isotherm $\Pi(h)$ is made by electrostatic forces. This fact is the basis of well-known methods of controlling wetting by using ionogenic surfactants. Selectively adsorbed on the surfaces of the film, these materials change the potentials ψ_1 and ψ_2. Figure 4 shows theoretical isotherms $\Pi(h)$ for a KCl solution at $I = 10^{-3}$ moles/liter with an addition of a cation-active surfactant (CASF) and an anion-active surfactant (AASF). The initial solution, without the surfactant, is isotherm 6. According to Eq. (2), $\theta_0 = 8°$ in this case. In constructing the isotherms, we considered the contributions of Π_e and Π_m and the short-range structural forces Π_s. It is assumed that the surfactant is adsorbed only on the film surface in this case, altering the potential ψ_2 of the film. The potential ψ_1 remains constant and equal to -100 mV.

It can be seen from Fig. 4 that adsorption of the CASF, by increasing the negative potential ψ_2, leads to shifting of the isotherms (curves 5-1) to the region $\Pi > 0$ as a result of an increase in the forces of electrostatic repulsion. Accordingly, the wetting angles calculated from Eq. (2) decrease to 7° (isotherm 5) and 5° (isotherm 4), while complete wetting occurs for isotherms 3-1. In the case being considered, complete wetting is achieved due to charge effects, not structural effects.

Overcharging of the film surface as a result of surfactant adsorption ($\psi_2 = +100$ mV, curve 7) leads to the attraction of differently-charged film surfaces ($\Pi_e < 0$) and an increase in the wetting angle to $\theta_0 = 28°$. All these conclusions of the theory are well-supported by data from experiments in which θ_0 was measured for aqueous solutions with additions of a surfactant [12].

The existence of a transitional zone results in yet another effect, an effect predicted by Gibbs but first studied only recently – the effect of linear tension [13]. By analogy with σ, when the transitional zone between the liquid and vapor is replaced by a plane of tension, the transitional zone between the meniscus and the film can be replaced by a three-phase contact line associated with a certain linear tension $\varkappa$. In contrast to σ, values of $\varkappa$ can be both positive and negative, causing a circular wetting perimeter to constrict in the first case or expand in the second case. Investigators for the first time recently successfully used interference methods to study the profile of the transitional zone and confirm the validity of Eqs. (1) and (3) [14].

If we replace the transitional zone by a three-phase contact line, we should also introduce the term $\varkappa/r_0$ into the Young equation [13]. Its value can be found from the difference between the values of $\sigma\cos\theta_0$ calculated with allowance for the transitional zone and with its replacement by the three-phase contact line [15]. As surface tension, linear tension depends on curvature – in the present case, the curvature of the contact line. This dependence is due to the change in the profile of the transitional zone with a change in r_0. As was shown in [15, 16]:

$$\varkappa = -\frac{\varkappa_0}{1 + (2/r_0)(\sigma/a)^{1/2}}. \tag{5}$$

At $r_0 \to \infty$, $\varkappa \to \varkappa_0 = 2\sigma t \tan \theta_0$. The values of $\varkappa$ are negative for relatively low values of θ_0 and are on the order of 10^{-6} dyn. This result, as was shown in [16], is consistent with experimental values of $\varkappa$. It follows from the data obtained here that the effect of linear tension begins to be manifest appreciably and influence equilibrium conditions at $r_0 \leq 0.1$ μm. It was shown in [17] that $\varkappa$ plays the decisive role in heterogeneous condensation, affecting the work of formation of a nucleus of the new phase. The role of linear tension is also important in the initial stage of contact of gas bubbles with surfaces and particles, such as in flotation.

Here, we examined questions relating to the statics of wetting and the formation of equilibrium wetting angles. The pressure distribution in the film and the transitional region changes with the motion of drops or menisci. The wetting angle becomes dependent on the rate of displacement of the wetting line v. These problems require the simultaneous application of hydrodynamics and the theory of surface forces. Solutions have been obtained thus far only by numerical methods. Experiments show, however, that at $v \leq 10^{-3}$ cm/sec, the wetting angles are nearly independent of v [18]. This also determines the range of application of the above-examined equilibrium theory of wetting. The dynamic wetting angle exceeds θ_0 at higher values of v and approaches 90° in the limit. Conversely, in the case of the absence of menisci, an increase in the rate of displacement of the wetting line leads to the formation of thicker ($h > h_0$) nonequilibrium films behind the meniscus and, thus, to an improvement in wetting. The theory of this effect developed in [19] has found application in calculations of the application of films on a moving substrate [20]. The films remaining on the surface behind the rapidly receding meniscus change to the equilibrium state and form local thick regions. These regions connect with each other and in turn form capillary bridges.

Along with dynamic hysteresis, static hysteresis may play a significant role in the motion of liquids in porous bodies. At $\theta_0 < 90°$, $\theta_A > \theta_0$. This means that additional pressure must be applied for motion of the liquid to begin. The theory of static hysteresis on smooth surfaces, based on examination of the conditions whereby the mechanical equilibrium of the transitional zone is disturbed [21], also links the values of θ_A with the parameters of the isotherm $\Pi(h)$.

Thus, use of the theory of surface forces makes it possible to predict wetting and equilibrium conditions for a capillary liquid in porous bodies on the basis of physical characteristics of the solid substrate and the liquid interacting with it.

NOTATION

θ_0, equilibrium wetting angle; R, radius of curvature of the undisturbed meniscus; H, half-width of the plane slit; P_c, capillary pressure of the meniscus; r, radius of the capillary; σ, surface tension of the liquid; h_0, equilibrium thickness of the wetting film; K, local curvature of the liquid surface; h, thickness of the liquid layer; $\Pi(h)$, isotherm of the disjoining pressure of the wetting films; σ_{SV} and σ_{SL}, solid–gas and solid–liquid interfacial energies; Γ, adsorption, moles/cm²; p, vapor pressure; p_s, saturation vapor pressure; v_m, molecular volume of the liquid; R_0, gas constant; T, temperature, °K; A, Hamaker's constant, ergs; ψ_1 and ψ_2, electric potentials of the surfaces of the substrate and film; I, ionic strength of the solution; C, concentration of the solution, moles/liter; Π_m, Π_e, and Π_s, molecular, electrostatic, and structural components of the surface forces; r_0, radius of the base of the drop; t and a, parameters of the isotherm $\Pi(h)$ [15]; v, rate of displacement of the meniscus; θ_A, advancing wetting angle.

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FORMATION OF HETEROGENEOUS REACTION REGIMES UNDER THE ACTION OF MULTIPLICATIVE NOISE

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It is shown that transitions from the diffusion regime to the kinetic regime are possible when the fluctuations of the heat transfer from the zone of an exothermic reaction exceed a certain critical value, and the diffusion regime of the reaction can be suppressed when they exceed a second, higher level.

The occurrence of fluctuations of the properties of nonlinear dynamical and physicochemical systems and of the parameters of external fields interacting with those systems can radically influence the behavior of the systems. The systems are no longer described by deterministic equations in this case, but by stochastic equations of the Langevin type with the inclusion of additive and multiplicative noise. The existence of the latter cannot only alter the characteristics of the steady-state regimes in the quantitative respect, but also lead to a qualitative reorganization of these regimes, along with their stability domains and the condition underlying their occurrence (see, e.g., [1]).

The action of "white" noise (delta-correlated Gaussian stochastic processes) on the formation of the regimes of lumped-parameter physicochemical systems was first investigated [2-4] by analyzing the steady-state solutions of the Fokker–Planck equations corresponding to the stochastic equations for these systems. The influence of "colored" noise, i.e., situations in which the correlation time of the stochastic processes is commensurate with the time scale of the mean characteristics of the system, has been investigated [5-7]. Some of the authors [4-7] have reported the observation of transitions to bistable behavior. A certain classification of such transitions and a survey of research in the indicated direction may be found in [8]. Analogous phenomena in distributed systems appear to have been treated for the first time [9] on the basis of an analog of the Ginzburg–Landau equation in the theory of second-order phase transitions.

In the present article we investigate the influence of fluctuations of the heat- and mass-transfer coefficients on the process of a heterogeneous exothermic reaction (combustion) described by the system of nonlinear equations [10]

$$\begin{gathered}\varepsilon dc/dt = \beta(c_0 - c) - k(T)c,\\ c_p dT/dt = Qk(T)c - \alpha(T - T_0),\\ k(T) = z\exp(-E/RT).\end{gathered} \tag{1}$$

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