Journal of Engineering Physics and Thermophysics, Vol. 76, No. 3, 2003

RHEOLOGICAL ELEMENTS IN THE STATICS AND DYNAMICS OF WETTING

B. D. Summ

UDC 532.64:541.1

Consideration has been given to the possibility of applying rheological methods to description of certain problems of the theory of wetting of solid bodies — hysteresis of boundary angles in inflow and outflow, influence of the deformations of a solid surface in contact with a wetting liquid — and the dynamic problems related to spontaneous spreading of a liquid on the substrate. It has been shown that the rheological methods are quite promising for solving the enumerated problems.

The statics and dynamics of wetting represent a topical trend in the physics and chemistry of surface phenomena [1]. Modern theory possesses methods of calculation of boundary angles, adhesion work, and other parameters of wetting [1–3]. At the same time, in a number of cases one must use approaches taking into account the special properties of the line of contact of the three phases involved in wetting and deformation changes in the substrates in contact with a wetting liquid. Below, we consider the possibilities of using rheological methods for these problems.

Hysteresis of Boundary Angles. The fundamental law of wetting of solid bodies was derived nearly 200 years ago (in 1804) by Young from the condition of mechanical equilibrium of forces on the line of the three-phase contact solid body (s)–liquid (liq)–gas (g):

$$\cos\theta_0 = \frac{\sigma_{\text{s.g}} - \sigma_{\text{s.liq}}}{\sigma_{\text{liq.g}}} \,. \tag{1}$$

In 1878, Gibbs derived Eq. (1) by the thermodynamic method from the condition of the minimum free surface energy F_{sf} of the three-phase system: $F_{\text{sf}} = \sigma_{\text{s.g}}\Omega_{\text{s.g}} + \sigma_{\text{s.liq}}\Omega_{\text{s.liq}} + \sigma_{\text{liq.g}}\Omega_{\text{liq.g}}$.

In most cases, the experimental values of boundary angles correspond to the metastable equilibrium on the three-phase contact line (TCL) rather than to the thermodynamic equilibrium; therefore, they are called static angles. The value of the static angles depends not only on the three surface tensions appearing in the Young law (1) but also on the conditions of their formation. As a rule, the boundary angles θ_a formed in the case of flow of a liquid onto a "dry" solid surface differ from the angles θ_r for the reverse direction of the process — flow of the liquid from the prewetted surface. Usually we have $\theta_a > \theta_r$. The difference in the boundary angles of inflow and outflow characterizes the wetting hysteresis.

Elucidation of the factors affecting the static (metastable) boundary angles and their hysteresis is a topical problem of the physicochemistry of wetting.

In 1930, to explain the hysteresis of boundary angles P. A. Rebinder introduced the notion of the resistance force Ψ keeping the TCL from moving on a solid surface [4]. The nature of this force is different and depends on the direction of flow of a wetting liquid. In inflow, the resistance force Ψ_a is produced by friction occurring in the TCL zone; therefore, the TCL can be considered as the rheological Coulomb element. In outflow from the prewetted surface, the resistance force Ψ_r can be determined by the viscosity of the liquid η; then the TCL will represent the rheological Newton element. The resistance force on the TCL (analog of the dry friction Ψ_a) was measured for the first time in [5] for water in contact with paraffin (Ψ = 7.6 mN/m). More recently, the values of Ψ_a similar in order of magnitude were obtained for a number of other systems (water–polyethylene, water–Teflon, and formamide–Teflon) [6].

M. V. Lomonosov Moscow State University, Moscow, Russia; email: summ@colloid.chem.msu.ru. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 76, No. 3, pp. 156–158, May–June, 2003. Original article submitted November 12, 2002.

1062-0125/03/7603-0655$25.00

Physically, the dimensionless ratio Ψ_a/W_{adh} represents an analog of the coefficient of friction. With allowance for the above values of Ψ and adhesion works W_{adh} typical of water and organic liquids, the coefficient of friction is $k \approx 0.1$, which approximately corresponds to the coefficients of friction in contact of dissimilar solid bodies.

The reasons for the occurrence of the resistance force are diverse. They are frequently attributed to the inhomogeneities of the solid surface. It is common practice to subdivide them into two groups [1, 3]:

(1) geometric defects — departures of the actual (rough) microrelief of the solid surface from an ideally smooth plane;

(2) chemical defects — inhomogeneities of the composition and structure of the surface; according to their size, these defects can be molecular, mesoscopic (approximately tens of nm in size) and micron.

Under certain conditions (steepness of the microrelief, surface energy of individual portions, i.e., domains), the inhomogeneities become energy barriers that retard the movement of the TCL. A typical example is as follows: the displacement of the TCL from a domain with a relatively better wettability to a domain with a poorer wettability with a given liquid involves an increase in the surface energy. In this direction of spreading, a given boundary between neighboring domains is used as the energy barrier. On the contrary, spreading toward the domain with a better wettability is barrier-free.

Deformation of the Wetted Surface. The derivation of the fundamental law of wetting, i.e., of the Young law, involves several assumptions on the geometry (relief) and properties of the surface of a solid body. One assumption is that the solid surface is considered to be ideally rigid, i.e., not experiencing any deformations in contact with the wetting liquid. For rather strong materials with an elastic modulus of $E > 10^9$ N/m^2 (metals, glasses, minerals) this assumption always holds, in practice. However for "soft" materials with an elastic modulus of $E < 10^7$ N/m^2 (solid paraffins, rubbers, certain polymers) one observes marked changes in the shape of the wetted surface. The reason for the occurrence of deformations is as follows. The Young law reflects the equilibrium of only those forces that are directed along the solid surface. However, the substrate is also acted upon by the pressure $P = P_c + P_h$ ($P_c = 2\sigma_{liq.g}/R$ is the capillary pressure) produced by a droplet. This pressure causes a deflection of the substrate below the droplet and the formation of a hole in the shape of a spherical segment. The hole depth is in proportion to the ratio P/E; therefore, marked deformations are experienced only by the materials with a small elastic modulus E. The boundary angle of the droplet, measured by the slope of a meniscus to the horizontal surface, decreases as the hole becomes deeper.

Another type of deformation is caused by the "vertical" component of the surface tension $\sigma_{liq.g} \sin \theta$. Its action is counterbalanced by the elastic stresses developing under these deformations in a narrow annular zone near the TCL. The annular step formed can have dimensions of about 0.1 mm. The presence of this step affects the value of the measured boundary angle. The theory of calculation of boundary angles under deformations near the TCL has been developed by A. I. Rusanov [7].

Thus, in the general case the surface layer of the wetted substrate represents an elastic rheological element (Hooke element).

For experimental study of the relationship between the rheological properties of a solid surface and its wettability it is very convenient and informative to use gels. One can flexibly vary their strength in a very wide range.

Gelatin gels have been investigated in the greatest detail in this respect [8].

Noteworthy is the concentration dependence of the boundary angles of small water droplets. For low concentrations of the gelatins ($C < 0.7$ wt.%) the limit shear stress P is low; therefore, a water droplet is not kept on the gel surface and rapidly falls inside the sample. In the range of 1–2%, the strength of the gels increases to approximately 300 N/m^2; the boundary angles abruptly grow. Thereafter they remain constant, since the surface gel layer no longer experiences marked deformations. Different physical and chemical actions affecting the limit shear stress cause slope-similar changes in the boundary angles. For example, a decrease in the temperature deformation of a gelatin gel from a supersaturated solution leads to both an improvement in the gel strength and an increase in the boundary water angles. Additions of carbamide to the gel-forming solution decrease the strength of the gels; accordingly the boundary angles of water abruptly decrease upon reaching a certain threshold concentration of carbamide.

After mechanical destruction, gels are capable of restoring their structure thixotropically. The thixotropic effect is also detected in the wettability of the gels.

Dynamics of Wetting. The main problem is to find the dependence of the dynamic boundary angle on the time of spreading of a droplet on a solid surface. In inflow, we have $\theta_i > \theta_d > \theta_{st}$. Another problem is to calculate the motion of the TCL on a solid surface, i.e., the dependence $r = f(t)$. If the droplet has the shape of a spherical segment in the spreading, the TCL radius r and the dynamic boundary angle are interrelated.

Study of the dynamics of wetting is necessary for determination of the motive forces and resistance forces of this process and for many applied problems, for example, of application of thin liquid layers to a moving substrate in the production of photomaterials.

In the first approximation, we can consider the process of spontaneous spreading of a wetting liquid on a solid surface as the hydrodynamic problem. Such an approach enables us to obtain, in explicit form, the approximate relations $\theta_d = f(t)$ and $r = f(t)$ which satisfactorily describe the process of spreading of different liquids, for example, of droplets of liquid metals (mercury, gallium) on the surface of hard metals [3]. The main limitation of hydrodynamic models is that they refer to the steady-state (stationary) spreading and are not applicable to the initial stage of the process when the departure of the three-phase system from thermodynamic equilibrium is maximum.

A more general method of solution of dynamic problems is provided by rheology. The simplest model includes just two elements — those of Newton and Hooke. The Newton element is the viscosity of the wetting liquid η (similarly to hydrodynamic theory). The curved surface layer of a spreading droplet is the elastic element. Such modeling is substantiated by the initial postulate of the Laplace–Young capillariry theory. In it, the surface layer of a liquid with a thickness δ and of molecular size is likened to a thin-walled shell. This analogy underlies the derivation of the Laplace law of capillary pressure: $P_c = \sigma_{liq.g}(1/R_1 + 1/R_2)$.

In the process of spreading, the curvature of the droplet surface K changes from the maximum value $K_{max} = 2/R_i$ to the minimum value $K_{min} = 1/R_{st}$. Accordingly, the relative deformations of the surface layer change from ε_{max} at $t = 0$ (maximum compression) to ε_{min}. For the surface layer we employ the parameter $\sigma_{liq.g}/\delta$ instead of the elastic modulus E used to characterize the Hooke element.

To describe the dynamics of wetting we must first find the dependence of the relative deformations ε of the liquid surface on the time t. This problem is solved within the framework of the rheological model of parallel connection of the elastic and viscous elements (Kelvin model). From the geometric relations for a spherical segment the relative deformation is $\varepsilon = (1 - \cos\theta_d)/2$. This finally yields the rheological equation of the dynamics of boundary angles:

$$(\cos\theta_0 - \cos\theta_d)/(\cos\theta_0 - \cos\theta_i) = \exp(-t/t_{rel})\,. \qquad (2)$$

It describes the entire process of wetting from the initial instant $t = 0$ up to its completion and it also enables us to calculate the relaxation period $t_{rel} = \eta R_i/\sigma_{liq.g}$.

The correctness of the rheological method has been confirmed by a number of experiments. A characteristic example is provided by the initial stage of capillary flow at which the boundary angles decrease from the initial value θ_i to the static value θ_{st} [9].

The data presented show that it can be quite promising to apply rheology methods to some problems of the statics and dynamics of wetting.

This work was carried out with support from the Russian Foundation for Basic Research, grant No. 01-03-3218.

NOTATION

θ, boundary angle, deg; θ_0 and θ_{st}, equilibrium and static boundary angles, deg; θ_a and θ_r, boundary angles of inflow and outflow, deg; θ_i and θ_d, initial and dynamic boundary angles, deg; $\sigma_{s.g}$, $\sigma_{s.liq}$, and $\sigma_{liq.g}$, surface tensions at the boundary solid body–gas, solid body–liquid, and liquid–gas, mJ/m^2; Ψ, resistance force on the three-phase contact line, mN/m; Ψ_a and Ψ_r, resistance force in inflow and outflow of the wetting liquid, mN/m; W_{adh}, work of adhesion of the liquid to the solid surface, mJ/m^2; k, coefficient of friction; E, elastic modulus of the substrate, N/m^2; P, pressure produced by the droplet on the substrate, Pa; P_h and P_c, hydrostatic and capillary pressure, Pa; P_s, limit shear stress of the gels, Pa; R, radius of curvature of the droplet surface, m; R_1 and R_2, principal radii of curvature of the droplet surface, m; R_i, initial radius of the droplet (at the instant of application), m; R_{st}, final radius of curvature of the droplet (after completion of the spreading), m; C, concentration of the gelatin, wt.%; t, wetting time, sec; t_{rel}, period of relaxation of the wetting, sec; r, radius of the droplet base, m; K, K_{max}, and K_{min}, curvature of the liquid surface, m^{-1}, ε, relative deformation of the droplet surface; ε_{max} and ε_{min}, maximum and minimum deformations;

δ, thickness of the surface liquid layer, m; η, viscosity of the liquid, Pa·sec; $\Omega_{s.g}$, area of the solid body–gas surface, m^2; $\Omega_{s.liq}$, wetted area, m^2; $\Omega_{liq.g}$, area of the liquid–gas surface, m^2; F_{sf}, free surface area, mJ/m^2. Subscripts: st, static; a, inflow; r, outflow; i, initial; d, dynamic; s.g, solid body–gas; s.liq, solid body–liquid; liq.g, liquid–gas; adh, adhesion; h, hydrostatic; c, capillary; s, shear; rel, relaxation; sf, surface; max, maximum; min, minimum.

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