
On the Relation between Surface Forces and Wetting

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Structural forces play a dominant role in the range of contact angles $\theta < 15^\circ$ (hydrophilic repulsion) and $\theta > 40^\circ$ (hydrophobic attraction); the intermediate region corresponds to the field of application of the DLVO (Derjaguin–Landau–Verwey–Overbeek) theory. The short-range hydrophobic forces in the wetting films of water seem to be the same as in colloids; this can be explained by assuming an unstable wetting film to be disposed between two hydrophobic surfaces: the hydrophobic solid substrate and the water–air interface.

Thin wetting films, like thin liquid interlayers between solids, are systems subjected to the action of a field of surface forces. However, a wetting film as distinct from a colloidal system represents a non-symmetrical case. The film is bounded by two different phases: a solid and a gaseous one, so long-range surface forces manifest themselves in films and interlayers in very different ways.

Molecular forces in colloidal systems are always attractive and are responsible for the aggregation of particles. Molecular forces in wetting films are attractive only when the liquid is more polar than the substrate. This takes place, for instance, in the case of low-energetic solids. As distinct from colloids, the molecular forces are positive and stabilize the wetting films of organic liquids and aqueous solutions on dielectrics and metals.^{1,2}

Electrostatic repulsion takes place between identical colloidal particles immersed in an aqueous solution. The strength of the interaction depends on the magnitude of the surface potential ψ . Electrostatic forces in wetting films depend on the values of the electrical potentials of both solid–liquid ψ_1 and liquid–gas ψ_2 interfaces, which are seldom

equal to each other. When ψ_1 and ψ_2 potentials have the same sign, but are different in magnitude, the electrostatic forces change from repulsion to attraction at some critical film thickness $h^* = (1/\kappa) \ln(\psi_1/\psi_2)$, where $1/\kappa$ is the Debye length. When ψ_1 and ψ_2 potentials are different in sign, the electrostatic forces are only attractive.

Structural forces are now being intensively studied both experimentally and theoretically.^{2,3} Experiments include direct force–distance measurements between macroscopic bodies of different shape simulating a point contact of colloidal particles. The structural forces arise as a result of the overlapping of the structured boundary layers of polar liquids. Hydrophilic repulsion forces are expected to be the principal forces in wetting films of water on silica at $\theta_a < 20^\circ$. In the case of aqueous films on hydrophobic substrates one needs also to take into account, besides molecular and electrostatic forces, the force of hydrophobic attraction.

Hydrophilic and hydrophobic forces influence the contact angles. To take these effects into account, we have used the Frumkin–Derjaguin approach^{4,5} to derive the relation

between a contact angle and the disjoining pressure isotherm $\Pi(h)$ of wetting films:^{1,2}

$$\cos \theta_0 = 1 + (1/\gamma_{lv}) \int_{h_0}^{\infty} \Pi(h) dh = 1 + [G(h_0)/\gamma_{lv}] \quad (1)$$

where θ_0 is the equilibrium contact angle; h_0 is the film thickness in equilibrium with a droplet, and γ_{lv} is the surface tension.

Equation (1) allows us to calculate the value of the equilibrium contact angle θ_0 based on the $\Pi(h)$ isotherm and the surface force theory.^{2,3} Such a program was partly realized earlier.⁶⁻⁸ We now intend to include in our consideration a new kind of force, namely, the force of hydrophobic attraction. In the case of large contact angles we can neglect other components of the surface forces, and use for the excess free energy $G(h_0)$ the expression:

$$G(h_0) = K\lambda \exp(-h_0/\lambda) < 0 \quad (2)$$

where λ is the decay length (of the order of bulk correlation length of the liquid) and the parameter K depends on boundary conditions.

Aqueous films are unstable on hydrophobic substrates simply due to a strong hydrophobic attraction of the film interfaces. It is known that two hydrophobic surfaces in water "jump in" to contact under the action of hydrophobic attraction forces.⁹⁻¹⁴ Similarly, water films on hydrophobic surfaces rupture under the action of the same forces. Taking into account that in this case $h_0 \rightarrow 0$, it is possible to simplify equation (1):

$$\cos \theta_0 \simeq 1 + (K\lambda/\gamma_{lv}) \quad (3)$$

where $K < 0$.

Fig. 1 (curve 1) shows the dependence of the product $K\lambda$ on θ_0 calculated using equation (3) with $\gamma_{lv} = 72 \text{ dyn cm}^{-1}$ for water. Let us compare the calculated dependence with the results of an estimation of parameters K and λ from direct measurements of the hydrophobic attraction forces between the hydrophobized surfaces of mica⁶⁻¹³ and glass¹⁴ in water. The $K\lambda$ data obtained vs. the θ_a values for the hydrophobized surfaces are shown by open circles in Fig. 1. The data are in reasonable agreement with the calculated values using equation (3) and shown by curve 1. This means that the constants that characterize hydrophobic forces in water interlayers are almost the same as in water films on hydrophobic substrates. The short-range hydrophobic forces seem to be the same in colloids and in wetting films. This may be explained by considering the unstable wetting films of water to be disposed between two hydrophobic surfaces: the hydrophobic solid substrate and the water-air interface.

The square point in Fig. 1 shows the result of a calculation of the values of $K\lambda$ when hydrophilic repulsion forces act in wetting films. In this case $K\lambda = 20 > 0$, and the contact angle is small, $\theta_a \approx 15^\circ$. Consideration of the data shown in Fig. 1 leads to the conclusion that in the range of contact angles from $20-40^\circ$ the structural forces change from attraction ($K < 0$) to repulsion ($K > 0$). In this intermediate region the structure of the boundary layers of water is only slightly changed as compared with that in the bulk. The molecular and electrostatic forces are the dominant forces in this case. This is the only region of application of the DLVO theory.^{2,3}

In Fig. 1 are shown by dotted lines the possible levels of $G(h_0)$ values for molecular forces (lines 2 and 3) and for electrostatic ones (lines 4, 5 and 6). The excess free energy of the molecular interaction was calculated using equation (4),

$$G_m = A_{slv}/12\pi h_0^2 \quad (4)$$

where A_{slv} is the Hamaker constant. In the case of water on low

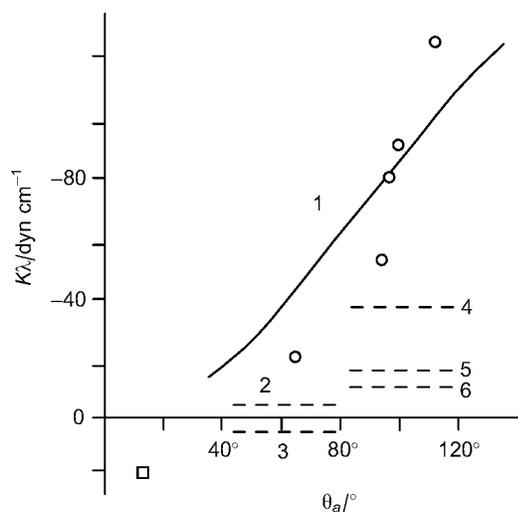


Fig. 1 Dependence of the $K\lambda = G(h_0)$ values on the contact angles θ calculated from equation (3) (curve 1). Curves 2, 3 and 4-6 show the levels of the free energy of molecular $G_m(h_0)$ and electrostatic $G_e(h_0)$ interaction in aqueous wetting films, respectively.

energetic surfaces $A_{slv} \approx -10^{-13} \text{ erg}$ (line 2). In the case of water on methylated silica $A_{slv} \approx +10^{-13} \text{ erg}$ (line 3).

The excess free energy of electrostatic attraction between the film interfaces was calculated from equation (5):^{2,8}

$$G_e = \varepsilon(\psi_1 - \psi_2)^2/8\pi h_0 < 0 \quad (5)$$

where ε is the relative permittivity of water.

For hydrophobic surfaces the value of h_0 was taken as the thickness of a monolayer, 0.2 nm. The G_e values are high enough in the case of aqueous solutions of cationic surfactants, when ψ_1 and ψ_2 potentials may be different in sign. The result of the G_e calculation at $\psi = \psi_1 - \psi_2 = 150 \text{ mV}$ is shown by line 4, whereas line 5 corresponds to $\Delta\psi = 90 \text{ mV}$, and line 6 to $\Delta\psi = 40 \text{ mV}$.

From Fig. 1 it follows that large contact angles of water on hydrophobic surfaces ($\theta_a > 40^\circ$) are formed as a result of the action of hydrophobic attraction forces. The only exceptions are solutions of cationic surfactants when contact angles up to 60° may be caused by strong electrostatic forces of attraction (line 4). In the region of $\theta_a < 40^\circ$ many components of the disjoining pressure give a contribution to the free energy of wetting films. For an assessment of contact angles in this case, one needs to know the Hamaker constant, potentials ψ_1 and ψ_2 , and parameters K and λ . Unfortunately, the latter are not well known for surfaces of moderate hydrophobicity.

It should be noted that in the range of contact angles $40^\circ > \theta_a > 15^\circ$ the predominant role is played by molecular and electrostatic forces. The results obtained show that it is possible in a similar manner, using the theory of surface forces, to describe both the colloid stability and wetting phenomena.

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