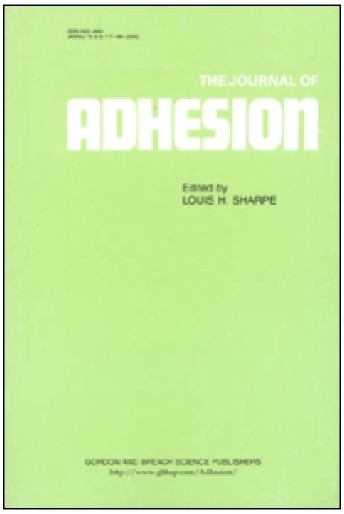

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Capillary Attraction and Hysteresis of Wetting

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Capillary attraction between two parallel plates partly immersed in a liquid is calculated, using changes in free energy as criterions. Because, when the equilibrium contact angles are different from 0°, hysteresis of wetting occurs as a rule, it is supposed that the 3-phase lines are not shifted when the plates move (for a small distance) apart or toward each other. When the two plates are identical and their mutual distance δ is small, they should attract each other. When they are different and the equilibrium contact angle is obtuse at one, and acute at the other plate, then, at small δ, repulsion is expected.

INTRODUCTION

Capillary attraction often occurs when two floating bodies are placed near each other in the surface of a liquid. Thus the two plates indicated in Figure 1 tend to come together. To render the sketch more realistic, the plates (following Laplace's suggestion) are shown hollow and provided with a load ("keel") at the bottom, to preclude significant tilts.

The forces operating in capillary attraction act parallel to the vapor/liquid interface, and the motion of the plates also is in a horizontal direction. Thus the system is quite different from those in which two solids with a "pendulous" drop between them are pulled apart; see, e.g. ref. [1-6]; there the movement and the force measured are perpendicular to the liquid film so that the phenomenon belongs to capillary pull[7] rather than to capillary attraction. This distinction (well understood by earlier investigators) must be mentioned because several modern students of *pull* believed to be studying *attraction*.

The two earliest quantitative theories of capillary attraction (Laplace 1805, Poisson 1831) were based on the consideration of forces or pressures acting on the plates; thus they may be classified as static. A theory of capillarity in which processes were considered has been formulated by Gauss

(1829), who calculated the work spent on, or by, the system during capillary rise and related phenomena. His method was extended to capillary attraction by Neumann.[8]

Using modern nomenclature, Neumann's approach may be summarized as follows: if the change in free energy dF occurs when the distance between the plates increases by $d\delta$ cm, then attraction must be expected when $dF/d\delta$ is positive, and repulsion would take place whenever $dF/d\delta$ is negative. The free energy F was treated as the sum of 3 energy kinds, namely energy of the vapor/liquid interface, energy of the liquid/solid interface, and gravitational energy. It may be noticed that the interface of vapor and solid was left out. This oversight can be corrected by re-defining Neumann's liquid/solid energy as the difference between the energies of liquid/solid and vapor/solid interfaces; no further alteration of the mathematical expressions is needed.

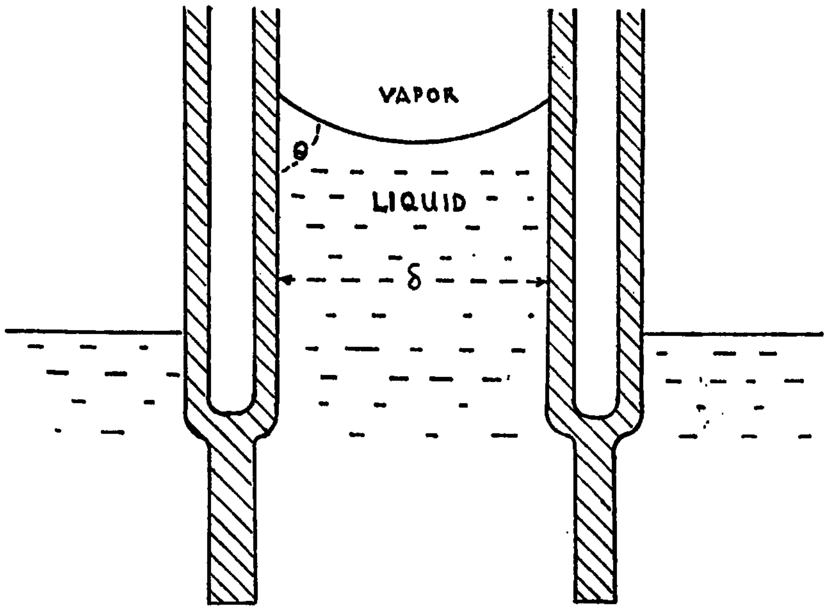

FIGURE 1 Two identical parallel plates partly immersed in a liquid. Inside contact angle is θ, the distance between the plates is δ.

More important is that all contact angles were supposed to be determined only by the invariable molecular forces of the components of the system. Thus, in agreement with Gauss, for every contact angle θ the equation

$$\cos\theta = (2\beta^2 - \alpha^2)/\alpha^2 \tag{1}$$

was assumed; α^2 (g/sec^2) is the force (per unit length) between the molecules of the liquid, and β^2 is the analogous force between the liquid and the adjacent solid. In reality, contact angles usually are not constant because of the hysteresis of wetting. As long as (a) θ is neither 0° nor 180° and (b) the change in the distance δ is small, it will be commonly observed that the 3-phase line (in which vapor, liquid, and solid meet) will not be shifted. Thus the macroscopic contact angle, on which the shape of the liquid meniscus depends, will vary with δ instead of being independent of it.

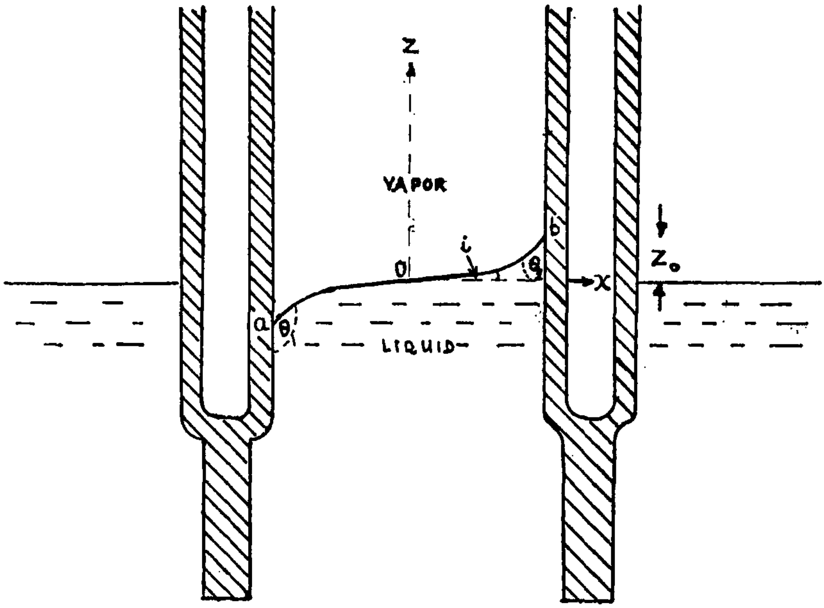

FIGURE 2 Two different parallel plates partly immersed in a liquid. θ_1 and θ_2 are the contact angles at the walls. The meniscus profile is a0b; it has an inflexion point at 0, and the acute angle (at this point) between the profile and the horizontal abscissa x is i. The ordinate of point b is z_0.

Hence, in the following calculation, only two kinds of energy are considered: that of the vapor/liquid interface and that of gravitation. The energies of the vapor/solid and the liquid/solid interfaces do not change because the 3-phase line does not move; and the energy associated with capillary pressure P_c (which is decisive in Laplace's theory) is not needed here because in this system P_c is a unique function of the meniscus profile, i.e. also of the area S of the vapor/liquid interface. An example in which consideration of S to the exclusion of P_c leads to correct results can be found in a memoir by Plateau.[9]

Two systems are treated in this note. In one, the two plates are identical (Figure 1); the contact angles along the inside faces are each equal to θ. The two angles along the outside faces are drawn as being $\pi/2$ (90°) each; their actual value should have no effect on the experimental attraction or repulsion. In the other system (Figure 2) the inside contact angles are different. At the left-hand plate, θ_1 is obtuse, and the angle θ_2 at the right-hand plate is acute; all angles are measured in the liquid, not in the vapor. The width of the plates in the direction normal to the plane of the drawing is supposed to be so great that the disturbances of the meniscus next to the ends of the plates may be disregarded.

In all instances, the alteration dS of the area S is proportional to the alteration dl of the length l of the meniscus profile inside the slit minus the simultaneous change $d\delta$ in the length of the meniscus profile outside the slit: it is clear that, when the distance between the plates rises by $d\delta$ cm, the distance between the moving plate and the nearer wall of the vessel (in which the plates float) diminishes by $d\delta$. When δ is varied, the volume of liquid in the slit usually also varies; it is assumed that the vessel is so wide that this variation of the volume in the slit has no effect on the liquid level outside the plates.

Symmetric systems

In this section the profile of the inside meniscus is approximated as a circular arc, that is, the distortion of the profile by gravitation is supposed to be very small. This approximation is more exact the smaller δ, that is, the greater the attractive (or repulsive) force between the plates; in other words, it is admissible just when the effect is particularly easy to measure. If R is the radius of the above mentioned circle, then $l = (\pi - 2\theta)R$. Since $\delta = 2R \cos \theta$,

$$l = \frac{\pi - 2\theta}{2 \cos \theta} \delta \tag{2}$$

The increase in the free surface energy F_s (per unit width) on an increase in l is $dF_s = \gamma\ (dl - d\delta)$, γ being the surface tension of the liquid.

When θ varies with δ, but the 3-phase line does not shift, the relation between dl and $d\delta$ is readily obtained from the condition that hydrostatic equilibrium must prevail. As long as the height of the 3-phase lines above the horizontal expanse of liquid is constant, also the height h of any point on the meniscus may be treated as constant. Thus the hydrostatic pressure of the liquid layer raised between the plates is practically independent of δ. Consequently also the capillary pressure $-\gamma/R$ does not vary, that is R is constant during the process. Since $dl = -2R\,.\,d\theta$ and $d\delta = -2R\,.\,\sin\theta\,.\,d\theta$, it follows that

$$dl = \frac{d\delta}{\sin \theta} \tag{3}$$

It is clear from (3) that $dl - d\delta$ is always positive, except when $\theta = 0.5\pi$ (90°C); hence dF_s increases with $d\delta$ and surface energy tends to cause attraction. The value of gravitational energy (per unit width) is approximately $0.5\,\delta h^2 g\rho$; g is the acceleration due to gravity, and ρ is the difference between the densities of the liquid and the vapor; $\delta hg\rho$ is the weight (per unit width of the liquid slab) and $0.5h$ is the height of the center of gravity. Since g and ρ are constant, and h is practically constant, $dF_g = 0.5\,h^2 g\rho\,.\,d\delta$, that is increases with the distance. Thus also gravitation causes attraction at all values of δ (compatible with the approximation of a circular meniscus).

Asymmetric systems

To simplify the calculation, θ_1 is set to be equal to $\pi - \theta_2$, Figure 2. With this condition, the meniscus profile a, b has an inflexion point at 0 which is equidistant from both plates and situated in the plane of the main outside liquid surface. If point 0 is made the origin of Cartesian coordinates, of which x is in the just mentioned plane and perpendicular to the plates while z is perpendicular to that plane, then the half-width of the slit is [10]

$$0.5\delta = \frac{a}{\sqrt{2}}\int_0^{\Phi}\frac{d\phi}{(1-c^2\sin^2\phi)^{0.5}} - \sqrt{2}\,a\int_0^{\Phi}(1-c^2\sin^2\phi)^{0.5}\,d\phi + \sqrt{2}\,ac^2\frac{\sin\phi\,.\cos\phi}{(1-c^2\sin^2\phi)^{0.5}} \tag{4}$$

The symbols φ and c are defined by the equations

$$Z^2 = \frac{2c^2(1-c^2)\sin^2\phi}{1-c^2\sin^2\phi} \tag{5}$$

and

$$2c^2 = 1 + \cos i; \tag{6}$$

Φ is the value of φ at the left-hand plate, Z is the ratio z/a at any point of the meniscus curve, a is Laplace's capillary constant equal to $(2\gamma/g\rho)^{0.5}$, and i is the acute angle between the meniscus profile and the axis of x.

For the length l, the following equation can be derived:

$$0.5l = \frac{a}{\sqrt{2}}\int_0^{\Phi}\frac{d\phi}{(1-c^2\sin^2\phi)^{0.5}} \tag{7}$$

When the plates move apart but the 3-phase lines are not shifted, the obtuse angle θ_1 (at the left-hand plate) decreases and the acute angle θ_2 increases. Table I indicates this rise of θ_2 (in the range 10°–40°) on an increase in δ, and compares some representative values of length l and distance δ. To render the results independent of the nature of the liquid, the ratios

$L = l/2a$ and $\Delta = \delta/2a$ are calculated instead of l and δ themselves. The invariable greatest height of the meniscus (at the right-hand plate) is $0.5a$ in the example chosen, so that $Z_0 = 0.5$; Z_0 is the greatest value of Z. It is seen that, as long as δ is smaller than about 0.5a (i.e. $\Delta < 0.5$), the difference $dL - d\Delta$ is negative (e.g. $0.0511 - 0.1169 = -0.0658$), so that repulsion would be expected; and at greater distances or greater angles θ_2 there is an attraction because $dL - d\Delta > 0$.

TABLE I

Increase of the meniscus length ($2L$) and the contact angle θ_2 on an increase of the distance (2Δ) between the plates.

$Z_0 = 0.5$							
Δ 0.1830		0.2999		0.4482		0.7357	
diff.	0.1169		0.1483		0.2875		
θ_2 10°		20°		30°		40°	
L 0.5339		0.5850		0.6815		0.8963	
diff.	0.0511		0.0965		0.3148		

As identical plates should attract each other also in the absence of hysteresis of wetting, this hysteresis alters only the magnitude of the attraction but does not change the direction of the force. The situation is different for asymmetric systems. According to Laplace, attraction should take place whenever the 3-phase lines inside the slit are further from the main liquid surface than are the 3-phase lines along the outside of the plates; thus the plates of Figure 2 would attract each other at all mutual distances. The above "energy treatment" leads to the conclusion that attraction would be observed only at $\delta > 0.5a$, whereas, at closer approach, it would change to repulsion. It is hoped that careful measurements will decide which of the theories, if any, is correct.

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