[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, PHOSPHATE DIVISION, MONSANTO CHEMICAL COMPANY]

A Thermodynamic Derivation of Wenzel's Modification of Young's Equation for Contact Angles; Together with a Theory of Hysteresis[1]

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Wenzel's modification of Young's equation for contact angles, equation (1), may be derived from considerations of free surface energy, though not from the assumption that surface "tensions" may be represented by vectors. A theory is presented for the hysteresis of contact angles. The "driving force" toward the attainment of an equilibrium contact angle is found to be equal to the surface tension of the liquid times the deviation of the cosine of the contact angle from its equilibrium value. It is shown that this may be equated to the "contortional energy" F_c that the drop must have in order for its edge to surmount a ridge. The result is in the same form as the equation of Adam and Jessop: $r(\gamma_1 - \gamma_2) = \gamma_2 \cos \theta_{a,r} \pm F_c$, but with a new and physically meaningful interpretation of F_c.

Introduction

Wenzel,[2,3] in 1936, proposed the following generalization of Young's[4] equation for contact angles

$$r(\gamma_{1f} - \gamma_{12}) = \gamma_2 \cos \theta \qquad (1)$$

$$r = \frac{a}{A} = \frac{da}{dA} \geqq 1$$

with

a = actual area of interface
A = "apparent" area of the "geometrical" interface
θ = contact angle (see Fig. 1)
γ = interfacial tension, or, better, free interfacial energy

The subscript 2 refers to the liquid–gas interface; 12 to the solid–liquid interface and 1f to the solid–gas interface.[5,6]

Wenzel presented data to support his equation but did not give a mathematical derivation. Cassie and Baxter[7] have attempted a derivation, but in their equation number 4 they replaced E_D, the work of spreading, by E, the work of immersion, and proceed to "define" a contact angle on a rough surface. As Bartell, *et al.*, have pointed out[8] these quantities differ by the term γ_2. When the correct substitution is made, Cassie and Baxter's derivation yields an identity.

Derivation of the Young–Wenzel Equation.—Young's equation is customarily derived by resolution of vectors (the surface tensions). Adam,[9] states that "This is legitimate, as the mathematical surface tension can always be substituted for the physical free surface energy, to obtain the conditions of equilibrium when only the consequences of this free energy are concerned." But the derivation of Wenzel's modification of Young's equation constitutes an exception to Adam's generalization. The vector derivation yields no answer as to the effects of. roughness, for the directions of the "surface tension vectors" are determined by the geometry of the three interfaces within only an infinitesimally small distance from the triple interface.

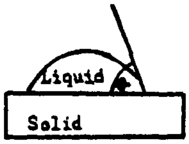

Fig. 1.

The use of the free surface energy removes this difficulty. Adam's discussion of free surface energy may be put in the form

$$\gamma_n = \partial F_n/\partial a_n \qquad (2)$$

where F is free energy, and n refers to the nth interface. The general equation for the free energy relations of the system containing three interfaces at equilibrium is

$$dF = 0 = \left(\frac{\partial F_{12}}{\partial a_{12}}\right)\left(\frac{\partial a_{12}}{\partial A_{12}}\right) dA_{12} + \left(\frac{\partial F_{1f}}{\partial a_1}\right)\left(\frac{\partial a_1}{\partial A_1}\right) dA_1 + \left(\frac{\partial F_2}{\partial a_2}\right)\left(\frac{\partial a_2}{\partial A_2}\right) dA_2 \qquad (3)$$

$$\left(\frac{\partial F}{\partial A_{12}}\right) = 0 = \left(\frac{\partial F_{12}}{\partial a_{12}}\right)\left(\frac{\partial a_{12}}{\partial A_{12}}\right) + \left(\frac{\partial F_{1f}}{\partial a_1}\right)\left(\frac{\partial a_1}{\partial A_1}\right)\left(\frac{\partial A_1}{\partial A_{12}}\right) + \left(\frac{\partial F_2}{\partial a_2}\right)\left(\frac{\partial a_2}{\partial A_2}\right)\left(\frac{\partial A_2}{\partial A_{12}}\right) \qquad (4)$$

$$= \gamma_{12}r - \gamma_{1f}r + \gamma_2 \frac{\partial A_2}{\partial A_{12}} \qquad (5)$$

Equations 3 to 5 may be conveniently interpreted, and $\partial A_2/\partial A_{12}$ evaluated, by consideration either of a small section of the triple interface, or of an entire drop that is small enough that the liquid–air interface is a segment of a sphere.[10] The former method was used by Poynting and Thompson[11] to derive Young's equation from free surface energy consideration. Their derivation evaluates $\partial A_2/\partial A_{12}$ at once as $\cos \theta$, and we have equation 1.

Alternatively, considering a droplet, a differential change in the shape of the drop (*e.g.*, flattening it out) must produce no change in free energy, though the interfacial areas do change. This is a verbal expression of equation 3. $\partial A_2/\partial A_{12}$ may be

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[1] Based on a paper presented before the Division of Colloid Chemistry at the 119th Meeting of the American Chemical Society, Boston, Mass., April 1 to 5, 1951.

[2] R. N. Wenzel, *Ind. Eng. Chem.*, **28**, 988 (1936).

[3] R. N. Wenzel, *J. Phys. Colloid Chem.*, **53**, 1466 (1949).

[4] T. Young, *Trans. Roy. Soc.* (*London*), **95**, 65 (1805).

[5] W. D. Harkins, G. Jura and E. H. Loesser, THIS JOURNAL, **68**, 559 (1946).

[6] W. D. Harkins and H. K. Livingstone, *J. Chem. Phys.*, **10**, 342 (1942). These authors pointed out that the free interfacial energy between solid and air, γ_1, should not in general be used in Young's equation because the solid surface may be covered by an adsorbed film. This does not necessarily refer to surface active agents, but to the adsorbed molecules of the substances that form the liquid phase. Harkins, *et al.*, have reported that $\gamma_1 - \gamma_{1f}$ is often far from negligible.

[7] A. B. D. Cassie and S. Baxter, *Trans. Faraday Soc.*, **40**, 546 (1944).

[8] F. E. Bartell and H. J. Osterhof, *J. Phys. Chem.*, **34**, 1399 (1930).

[9] N. K. Adam, "Physics and Chemistry of Surfaces," Third Edition, Oxford, 1941, pp. 2 and 178.

[10] G. L. Mack, *J. Phys. Chem.*, **40**, 159 (1936).

[11] J. H. Poynting and J. J. Thompson, "A Textbook of Physics; Properties of Matter," Eighth edition, Chas. Griffin and Co., Ltd., London, 1920, pp. 139–140. I am indebted to Dr. W. A. Adamson for calling this method of derivation to my attention.

evaluated by considering the analytical formulas for the areas of the base and the spherical surface of the drop. Restriction to constant drop volume makes A_2 a function of A_{12}, and differentiation at constant volume yields the result cos θ. The corresponding treatment for the case of a liquid in a capillary yields exactly the same result.

Theory of Hysteresis.—If we consider a non-equilibrium contact angle, then

$$\frac{\partial F}{\partial A_{12}} = \pm\, r(\gamma_{12} - \gamma_1) + \gamma_2 \cos \theta_{\text{obsd}}$$
$$= \pm\, \gamma_2(\cos \theta_{\text{obsd}} - \cos \theta_{\text{eq.}}) = \gamma_2\, \Delta \cos \theta \quad (6)$$

From this it may be seen that the driving force toward the attainment of the equilibrium contact angle is proportional to the surface tension of the liquid and to the deviation of the *cosine* of the contact angle from the equilibrium value.

This suggests a source of hysteresis of the contact angle on chemically homogeneous surfaces. Consider first a drop placed in the center of a system of ridges forming concentric circular rings. Bikerman[12] has given a detailed discussion of the motion of a drop front over a rough surface. He pointed out that the climbing of a drop front over a ridge requires "contortion [*i.e.*, extension] of the liquid–air interface," and consequently an increase in the energy of the system. If this additional energy is F_c, then the drop will cease to change its shape spontaneously when

$$\frac{\partial F}{\partial A_{12}} = |\gamma_2\, \Delta \cos \theta| \leqq F_c \quad (7)$$

While a system of concentric circular ridges is in principle attainable, it does not correspond to the ordinary "roughness" of a solid surface. Clearly, for a rough surface having a completely random array of hills and valleys, there will be paths by which the triple interface can move without surmounting the entire height of the energy barrier, F_c described above. But a configuration will be attainable, corresponding to a value of F_c between zero and the value for the case of concentric ridges, at which motion of the triple interface will cease. Δ cos θ will be somewhere between zero and that value corresponding to the case of concentric circular ridges.

In principle, the height of the energy barrier F_c should be calculable for certain simple configurations—*e.g.*, saw-tooth, or sinusoidal concentric ridges. But it should be far more difficult to calculate F_c for any "random" type of roughness. (Bikerman has showed that the motion of a drop-front is very different, on a ridged surface, depending on whether the motion is parallel or perpendicular to the ridges.)

Equation 7 may be put in the form of the equation of Adam and Jessop[9,13] (which was proposed without mathematical proof)

$$r(\gamma_{1f} - \gamma_{12}) = \gamma_2 \cos \theta_a + F$$
$$= \gamma_2 \cos \theta_r - F \quad (8)$$

Here θ_a is the observed advancing or contact angle and θ_r is the observed receding contact angle. F was hypothesized as a "frictional force, operating along the surface with equal intensity, when advancing and receding motions were just prevented." Adam remarks of this proposal, "This treatment is probably nothing but a formal description, however. It is very difficult to see how there can be a permanent frictional resistance to the motion of a liquid over a solid."

It is now seen that there is a valid physical meaning for F: it is the "contortional energy" that the drop must have if the drop front is to move from one favored configuration of the triple interface (more or less meandering across the "hills and valleys" of the solid surface) to another. Evidently, as roughness decreases, less "contortion" of the liquid–air interface is required in order for the drop front to advance or recede. Consequently hysteresis decreases also.

A somewhat similar treatment could be given for hysteresis on smooth but chemically inhomogeneous surfaces, having regions, *e.g.*, of polar and of non-polar molecules. A drop of, say, water would have an average free surface energy in the liquid–solid interface corresponding to the average composition of the solid surface. This (together with the other free surface energies) would determine the equilibrium contact angle. But as the drop front advances or recedes, regions must be crossed in which the energies are such that the contact angle does not correspond to the equilibrium value. Hence there must be contortion of the liquid–air interface, requiring extra energy, F_c, if the drop front is to move. The result is hysteresis, following equation 8.

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[12] J. J. Bikerman, *J. Phys. Colloid Chem.*, **54**, 653 (1950).

[13] N. K. Adam and G. Jessop, *J. Chem. Soc.*, **127**, 1863 (1925).