Young–Dupre Revisited

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The Young–Dupre equation for the work of adhesion of a liquid drop to a solid surface, where the solid surface is in equilibrium with the vapor of the liquid, is given as $W = \gamma_L(1 + \cos\theta)$, where γ_L is the surface tension of the liquid and θ the contact angle. This work (W) has generally been identified with the free energy of adhesion. It is shown here that it constitutes the total work of adhesion only under the artificial condition that the sessile drop retains its shape after detaching from the solid surface. Under "real" conditions, W represents only one component of the total free-energy change taking place when a drop is separated from, or attached to, a vapor-equilibrated smooth solid surface. In the present work, a Net Free Energy of Adhesion, ΔF_N, is derived which gives the total free energy necessary to separate a sessile drop from a smooth solid surface to form a free sphere (its negative, of course, is the free energy of attachment of the sphere). It is given by $\Delta F_N = \pi r^2 \gamma_L[(2a/\sin\theta)^{2/3} - a]$, where r is the radius of the solid–liquid interface and a, called the "effective area", is $[2/(1 + \cos\theta)] - \cos\theta$. The Net Free Energy of Adhesion and Young–Dupre work of adhesion are compared as functions of the contact angle. This is done for systems of constant solid–liquid interfacial area and for systems of constant drop volume.

Introduction

The Young–Dupre Equation. Using words, Young[1] described the trigonometric relations between the contact angle and the forces acting on a liquid drop in mechanical equilibrium on a solid surface. This relationship between the surface tensions of the solid, the liquid, the solid–liquid interface, and the contact angle was subsequently expressed in mathematical form as

$$\gamma_s - \gamma_{sl} = \gamma_l \cos\theta \tag{1}$$

where γ_s is the surface tension of the solid, γ_l the surface tension of the liquid, γ_{sl} the solid–liquid interfacial tension, and θ the contact angle. Adam[2] points out that another equation, describing the relative adhesion of the liquid to itself as compared to the solid, can be extracted from Young's words, in the form of

$$W_A = \gamma_l(1 + \cos\theta) \tag{2}$$

where W_A is the work of adhesion of the liquid to the solid.

The history of this equation includes the definition by Athanase Dupre[3] in 1869 of a work of adhesion for two immiscible liquids in contact

$$W_{ab} = \gamma_a + \gamma_b - \gamma_{ab} \tag{3}$$

where the subscripts a and b designate the two condensed phases. This work of adhesion can then be calculated from measurements of the surface tensions of a and b and the interfacial tension at the interface ab. When a or b is a solid, its surface tension cannot be measured directly. However, W_{ab} can then be determined by substituting (1), the Young equation, into (3), to obtain

$$W_{ab} = \gamma_l(1 + \cos\theta) \tag{4}$$

where, if a is the solid, θ is the contact angle of b on a. Equation 4 is known as the Young–Dupre equation. According to Adam and Jessop,[4] it was first deduced in this form by Pockels.[5] Adam and Jessop, without explanation,[4] designated the surface tension of the solid as γ_{sv}, presumably indicating that it referred to the solid in equilibrium with the vapor of the liquid.

In 1937, Bangham and Razouk[6] pointed out that for thermodynamic validity, (1) should be written as

$$\gamma_L \cos\theta = \gamma_{SV} - \gamma_{SL} \tag{1a}$$

where the surface tension of the solid is written as γ_{SV} to specify that it refers to the state of the solid surface in equilibrium with the vapor of the liquid at saturation pressure. On substituting (1a) into (3), therefore, the equation

$$W_{AB} = \gamma_L(1 + \cos\theta) \tag{4a}$$

was obtained, which refers to the work required to separate the drop from the solid surface while leaving behind on that solid surface the adlayer adsorbed from equilibration with the vapor of the liquid at saturation pressure. They pointed out that while (4a) (or (4)) was commonly used for the work of adhesion, it was generally supposed that the work of adhesion referred to the separation of the drop from the solid, leaving behind a clean solid surface. They therefore designated W_{AB} in (4a) as the work of adhesion as "generally defined" and the work required to separate the drop leaving a clean solid surface as the work of adhesion as "generally understood". Neither Adam nor Bangham attempted to provide an equation for the latter, i.e., for the clean–solid work of adhesion. Harkins and Livingston,[7] in 1942, proposed such an equation, which has since gained considerable acceptance. The Harkins equation will not be used in the present paper. All work, or free energy, of adhesion here refers to the work as "generally defined", where the final state for separation (or initial state for attachment) is the solid surface in equilibrium with the vapor of the liquid at saturation vapor pressure.

Total Free Energy of Formation of the Sessile Drop. The difference in the free energy of the initial and final states during formation (or evaporation) of a sessile drop in equilibrium with its vapor at p^0, can be obtained by considering separately the free energy of formation of each of the liquid states from their vapor at p^0. The free energy of formation of the sessile drop has previously,[8,9]

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(1) Young, T. *Philos. Trans. R. Soc. London* **1805,** *95,* 65.
(2) Adam, N. K. *Nature* **1957,** *180,* 809.
(3) Dupre, A. *Theorie Mechanique de la Chaleur*; Gauthier-Villars: Paris, 1869; pp 369ff.
(4) Adam, N. K.; Jessop, G. *J. Chem. Soc.* **1925,** 1865.
(5) Pockels, A. *Phys. Z.* **1914,** *15,* 39.
(6) Bangham, D. H.; Razouk, R. I. *Trans. Faraday Soc.* **1937,** *33,* 1459.
(7) Harkins, W. D.; Livingston, H. K. *J. Chem. Phys.* **1942,** *10,* 342.

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been treated by considering the total adsorption isotherm of the vapor of the liquid onto a fixed area of the solid surface in question. Starting from the evacuated surface, increasing amounts of vapor are adsorbed as the vapor pressure above the surface is increased toward p^0. At p^0, a film of the liquid builds up on solid surfaces whose contact angle with the liquid is 0°. For those surfaces yielding greater than zero contact angles with the liquid, the surface establishes equilibrium with the vapor at p^0 and further adsorption ceases. The surface thus equilibrated will contain an adlayer of vapor molecules which may range in size from a minute fraction of a monolayer to a thin multilayer. It cannot, however, possess the characteristics of the liquid. Liquid will form on this surface only from supersaturated vapor, i.e., when the pressure is raised above p^0, and then only as sessile drops. Sessile drop formation on a given segment of surface area then requires an increase of the surface free energy from its minimum at equilibrium at p^0. The amount of this increase is given by

$$F = \pi r^2 \gamma_l[(2/(1 + \cos\theta)) - \cos\theta] \quad (5)$$

The first term on the right-hand side represents the free energy (increase) necessary for creation of the curved liquid–vapor interface of the sessile drop, while the second term represents the free energy of formation of the liquid–solid interface from the previous liquid–vapor interface.

The first thing we may observe here is that it may be strange to speak at all of a work of adhesion of this drop to the adlayer-covered solid. With respect to the solid surface equilibrated with vapor at p^0, F to form the sessile drop is always positive; therefore, the adhesion is always negative. The drop will spontaneously evaporate at p^0, the saturation vapor pressure of the liquid. However, as pointed out above, the free-energy changes here may be divided into components. The term containing $2/(1 + \cos\theta)$ in eq 5 represents the free energy of formation of the sessile drop due to the creation of the curved liquid–vapor interface of the drop, while $-\cos\theta$ results from the replacement of a solid–vapor interface by the solid–liquid interface. The latter component should be related to W, the work of adhesion of Bangham and Razouk of the liquid to the adlayer-covered solid surface

$$-W_{S(V)L} = -\gamma_{S(V)} - \gamma_L + \gamma_{S(V)L} \quad (6)$$

(In eq 6 and subsequently in this paper, the revised notation[10] recently proposed for the Young equation is used, with capital subscripts indicating the new notation. The term $\gamma_{S(V)}$ is the same as γ_{sv} of the old notation, while $\gamma_{S(V)L}$ is used for the soild–liquid interface as a reminder that the "solid" component of that interface consists of a solid surface that has been completely equilibrated with the vapor of the liquid.) Substituting (6) and (1a) into (5), we have, where the superscript u indicates unit area,

$$F^u_{S(V),D} = \gamma_L(2/(1 + \cos\theta)) - W_{S(V)L} + \gamma_L \quad (7)$$

so that the free energy of adhesion, $-W_{S(V)L}$, is associated exclusively with the solid–liquid interface.

Results and Discussion

Net Free Energy of Adhesion of the Free Sphere to the Solid Surface. Equation 4a gives W_{AB}, which according to Adam[11] is the "work necessary to separate the liquid from the solid by separating them perpendicularly from each other, against the adhesive forces between them". Equation 4a works if there are no changes in the system other than separation of the solid and liquid (in an atmosphere of saturated vapor of the liquid) at the solid–liquid interface. That restriction, however, requires that the sessile drop separate from the surface without having changed its shape; i.e., it must exist in the strange form of a free spherical section. In that case, i.e., if we detach the sessile drop without any change in shape (Figure 1a), we have, for the initial state, the free energy of formation (per unit area) of the sessile drop from vapor at p^0,

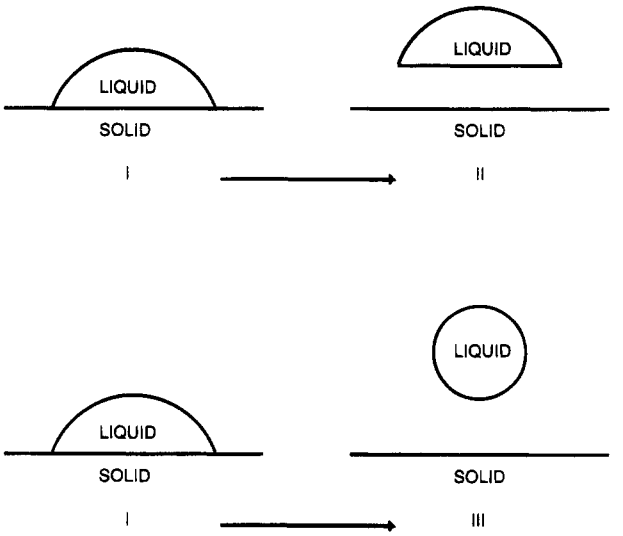


Figure 1. Models for the free energy of adhesion: (a) Young–Dupre work of adhesion ($W_{S(V)L}$); (b) net free energy of adhesion (ΔF_N).

$$F_{SV,D} = \gamma_L[(2/(1 + \cos\theta)) - \cos\theta] \quad (8)$$

and for the final state, the free energy of a strained drop with the shape of a free spherical section,

$$F_{V,StD} = \gamma_L[(2/(1 + \cos\theta)) + 1) \quad (9)$$

where $2/(1 + \cos\theta)$ is the area of the liquid–vapor interface and 1 is the area of the solid–liquid interface. Then

$$\Delta F = F_{V,StD} - F_{SV,D} \quad (10)$$

and

$$F = \gamma_L(1 + \cos\theta) \quad (11)$$

As expected, if the final state of the detached drop could have the same shape as the sessile drop, ΔF_N would reduce to the classical Young–Dupre.

Of course, a free drop with this shape is not in mechanical equilibrium. It would seem that the most convenient equilibrium configuration for the sessile drop, when separate from the surface, would be its equilibrium shape when free, i.e., a sphere (Figure 1b). A free-energy difference for the initial (bonded) state of sessile drop and final (separated) state of spherical drop can then be obtained from the surface free energy of the sphere and that of the sessile drop. This is defined as the Net Free Energy of Adhesion, ΔF_N, and is given by

$$\Delta F_N = F_{V,D} - F_{SV,D} \quad (12)$$

where $F_{V,D}$ is the free energy of formation of the free spherical drop from its saturated vapor and $F_{SV,D}$ is the free energy of formation of the sessile drop on a surface previously equilibrated with the vapor of the drop at p^0.

(8) Schrader, M. E.; Weiss, G. H. *J. Phys. Chem.* **1987**, *91*, 353.
(9) Schrader, M. E. *J. Adhesion Sci. Technol.* **1992**, *6*, 969.
(10) Schrader, M. E. *Langmuir* **1993**, *9*, 1959.
(11) Adam, N. K. *The Physics and Chemistry of Surfaces*, 3rd ed.; Oxford University: London, 1941.

Now,

$$F_{V,D} = 4\pi r_0^2 \gamma_L \tag{13}$$

where r_0 is the radius of the sphere. Writing this in terms of r and θ, where r is the basal plane radius and θ the contact angle of a sessile drop of equal volume,

$$F_{V,D} = 4^{1/3}\pi r^2 \gamma_L (2 - 3\cos\theta + \cos^3\theta)^{2/3}/\sin^2\theta \tag{14}$$

This can be written as

$$F_{V,D} = 4^{1/3}\pi r^2 \gamma_L [[(2/(1 + \cos\theta)) - \cos\theta]/\sin\theta]^{2/3} \tag{15}$$

Defining[12]

$$a = [2/(1 + \cos\theta)] - \cos\theta$$

we have

$$F_{V,D} = \pi r^2 \gamma_L (2a/\sin\theta)^{2/3} \tag{16}$$

and

$$\Delta F_N = \pi r^2 \gamma_L [(2a/\sin\theta)^{2/3} - a] \tag{17}$$

For unit area of the basal plane (designated by superscript u),

$$\Delta F_N^u = \gamma_L [(2a/\sin\theta)^{2/3} - a] \tag{18}$$

Tracing a pathway from a sessile drop to a free drop, rather than to vapor at p^0, the overall process is no longer spontaneous. Now there is always an overall increase in free energy due to that required to create the surface area of the free drop. In other words, while removal of a sessile drop to form vapor at p^0 has a negative free energy and is spontaneous, its removal to form a free drop has a positive free energy and is not spontaneous. Conversely, while formation of a sessile drop from vapor at p^0 has a positive free energy and is not spontaneous, formation of a sessile drop from a free drop in an environment of p^0 has a negative free energy and is spontaneous.

In Figure 2, the Net Free Energy of Adhesion per unit area of solid–liquid interface, ΔF_N^u, is plotted vs the contact angle. Since the curves in this figure are for constant liquid–solid interfacial area, the volume of the drop must decrease as the contact angle decreases. For the dashed line, which depicts the classical Young–Dupre representation, the sessile drop is imagined to lift off the surface without any change in shape. As can be seen from eqs 8–11 (also see eq 7), as we progress from a contact angle of 180° toward 0°, it is the increasing interaction (more negative free energy) occurring along the solid–liquid interface which lowers the contact angle. This is represented in a straightforward manner by an increase in $\cos\theta$ and therefore, of course, an increase in $\gamma_L(1 + \cos\theta)$ which is the Young–Dupre work of adhesion. The dotted curve, therefore, rises continuously as it approaches $\theta = 0°$, where the maximum interaction takes place. At $\theta = 0°$, the value is twice the surface tension of water, the energy necessary to cleave a film of liquid water. This is so since the work of adhesion is defined for a liquid and solid where the solid remains in equilibrium with the vapor of the liquid. For zero contact angles, that equilibrium produces a film of bulk water.

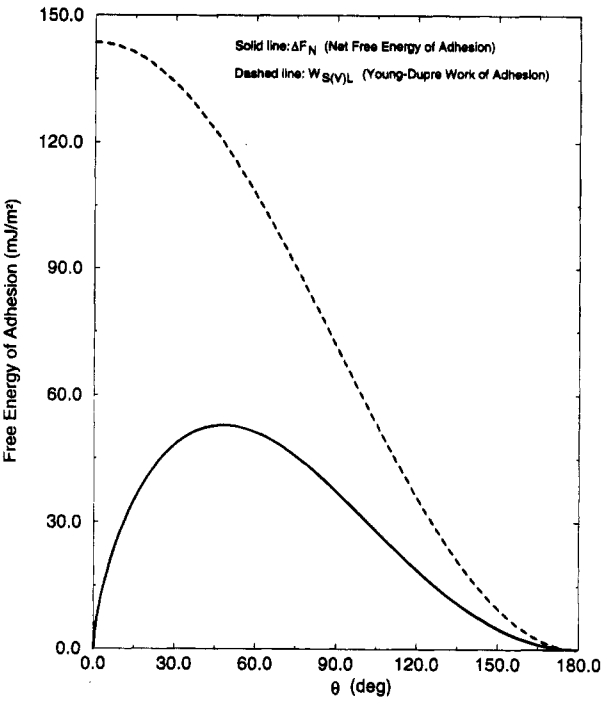


Figure 2. Comparison of the net free energy of adhesion with the Young–Dupre work of adhesion: variable contact angle with fixed solid–liquid interfacial area (unit area). Numbers on the ordinate are for water as the liquid.

For the case of the solid line in the graph, a more realistic situation is depicted. Here, the drop separating from the solid surface does not maintain its original shape but detaches to form a free sphere (or, in reverse, a free sphere deposits on a solid surface to form a sessile drop). Starting from 180°, the curve rises as the solid–liquid adhesion increases from the original near-zero value. Now, however, the detached drop has a lower free-energy state than previously, since the sphere has a lower surface energy than the distorted free drop. Since less free energy is required to reach the final (detached) state, the solid line in the figure is always below the dashed line.

As the contact angle decreases, this trend in the net free energy of adhesion (solid line) continues. However, there is another variable involved. As mentioned above, since the area of the solid–liquid interface is fixed, the volume of the drop must decrease with lower contact angle. The detached spherical drop will then have lower surface area with corresponding lower surface energy. This carries the Net Free Energy of Adhesion through a maximum and then a decline. The maximum occurs at $\theta = 48°$ since it is at this angle that the difference between the surface area of the sphere and the "effective area" of the sessile drop is greatest.[13] As the angle approaches 0°, the sessile drop approaches the shape of a flat film, its volume approaches zero, and the surface area of the detached sphere approaches 0 with the $^2/_3$ power of the volume. Its final state, a sphere with zero volume and zero surface free energy, then occurs at the contact angle of 0°. This is $F_{V,D}$ in eq 12. The initial state, $F_{SV,D}$ in (12), is also equal to 0 at $\theta = 0°$; see eq 5. Therefore, ΔF_N approaches 0° as the contact angle θ approaches 0°.

This rather large difference between W (of Young–Dupre) and ΔF_N at 0° contact angle can probably be

(12) The quantity $\gamma_L a$ was derived in ref 8 as the free-energy input required to form a sessile drop on unit area of solid surface from the initial state of equilibrium of the surface with liquid vapor at $p = p^0$ to the final state at $p = p'$, where p' is the Kelvin pressure of the drop. The quantity a was previously used as an "effective area" to provide the conditions for mechanical equilibrium of a liquid in various flow systems. See the following: Sewell, E. C.; Watson, E. W. *Bull. RILEM (Reunion Int. Lab. Essais Rech. Mater. Constr.)* **1965** (Dec), *29*, 125. Everett, D. H.; Haynes, J. M. *J. Colloid Interface Sci.* **1972**, *38*, 125.

(13) The angle 48° also appears in the vapor pressure phenomena of sessile drops restrained by contact angle hysteresis. See: Schrader, M. E.; Weiss, G. H. *J. Colloid Interface Sci.* **1990**, *135*, 586.

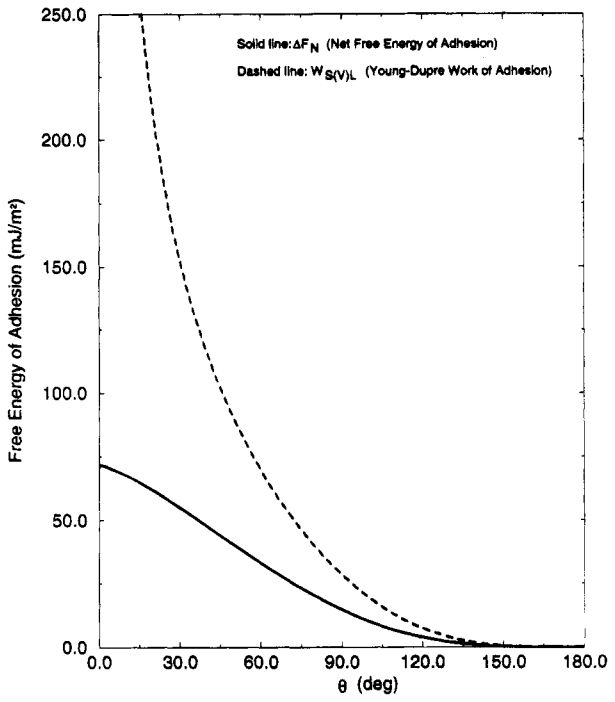


Figure 3. Comparison of net free energy of adhesion with the Young–Dupre work of adhesion: variable contact angle with fixed liquid–volume (the free liquid–sphere has unit surface area). Numbers on the ordinate are for water as the liquid.

described in words as follows: Young–Dupre tells us that if there were a way to forcibly tear the film off the surface (at p^0) while keeping the detached liquid in its previous shape of a flat film, the free-energy cost per unit area would be twice the surface tension of the liquid. The figures here are for water, so the value is 143.6 mJ/m^2. On the other hand, the net free energy of adhesion calculation informs us that if we remove the drop to assume its lowest free-energy shape, that is, a sphere of zero volume and zero surface area, which is, under our conditions, vapor at p^0, there is no free-energy change.

Variations in the Net Free Energies of Adhesion for Spherical Drops of Constant Volume. Equation 12 can also be written in terms of r_0, the radius of the free sphere. In that case, we have $F_{V,D}$ as in (13), and $F_{SV,D}$ is given by

$$F_{SV,D} = 4\pi r_0^2 \gamma_L (\sin\theta)^{2/3}(a/4)^{1/3} \qquad (19)$$

Therefore, since $\Delta F_N = F_{V,D} - F_{SV,D}$,

$$\Delta F_{N,r_0} = 4\pi r_0^2 \gamma_L [1 - (\sin\theta)^{2/3}(a/4)^{1/3}] \qquad (20)$$

where $\Delta F_{N,r_0}$ is ΔF_N expressed as a function of r_0. For unit area of the free spherical drop,

$$F^u_{N,r_0} = \gamma_L [1 - (\sin\theta)^{2/3}(a/4)^{1/3}] \qquad (21)$$

The Young–Dupre equation, (4a), is, of course, understood as being for unit area. For any area, using the recent notation,[10] it is

$$W_{S(V)L} = \pi r^2 (1 + \cos\theta) \qquad (22)$$

Writing it in terms of the radius r_0 of the free sphere,

$$W_{S(V)L,r0} = 4\pi r_0^2 (\sin\theta/2a)^{2/3} \gamma_L (1 + \cos\theta) \qquad (23)$$

In Figure 3, $\Delta F_{N,r_0}$ is compared with $W_{S(V)L,r_0}$ as a function of the contact angle. Since all the drops have the same volume, the basal plane surface area increases with decreasing contact angle. This graph describes what happens when drops of a liquid of equal volume are deposited on different types of surfaces. It also approximates what takes place when the sessile drop method for contact angle measurement is used as a probe for solid-surface characterization.

The volume chosen is such as to yield unit surface area for the free sphere. For the dotted line in Figure 3, i.e., the case of the Young–Dupre energy of adhesion, the energy is of course 0° at 180° contact angle. As the angle decreases, the interaction increases, increasing the value for the adhesion energy given by the Young–Dupre equation. At the same time, the drop spreads indefinitely in area over the solid surface, thus increasing the total solid–liquid interaction energy depicted. Since the liquid is treated as a continuum, there is no limit to its expansion over the surface as it approaches zero contact angle, and the total energy of interaction of this drop of fixed volume rises indefinitely as the solid area it covers rises indefinitely. (Per unit solid–liquid interfacial area, of course, it approaches $2\gamma_L$, as in Figure 2.) In Figure 2, at $\theta = 0°$, a solid–liquid interface of unit area was cleaved to yield $2\gamma_L$. Here at $\theta = 0°$, a solid–liquid interface of infinite area is cleaved to yield $2\gamma_L$ times infinity. Taken in reverse, i.e., attachment rather than detachment of the sessile drop, as the contact angle approaches 0°, this Young–Dupre energy depicted in the dotted line curves of Figures 2 and 3 measures the free energy of adhesion of a nearly flat filmlike drop, existing freely in space, to a solid surface. The usefulness of this concept to the experimentalist who is using a device that deposits nearly spherical drops on a series of solid surfaces is obviously problematical. Also, the perception that the total free energy of adhesion of a drop of fixed size can approach infinity as the contact angle approaches zero is not quite realistic, as will be seen below.

The solid line depicts the Net Free Energy of Adhesion for this series of drops of fixed volume. Once again, at 180°, the free energy is 0 where there is no adhesion. As the contact angle decreases, the positive free energy of the sessile drop (the initial state of the detachment process) per unit area of the solid–liquid interface decreases. At the same time, the area increases. The former effect predominates so that the free energy of the sessile drop decreases toward zero. However, the energy of the final state, that of the surface of the free sphere per unit area, remains constant. Thus, the difference between the two states increases as the energy of the sessile drop decreases and reaches a maximum at zero contact angle where the free energy of the sessile drop is zero. The maximum is then equal to the total free energy of the detached state, which is the surface free energy of the water per unit area, 71.8 mJ/m^2.

Conditions for the Validity of the Equations for the Energy of Adhesion as Functions of Contact Angle and Liquid Surface Tension. In view of the relatively natural initial or final conditions assumed in the net-free-energy calculations, it may be asked whether there is ever any significant advantage to using classical Young–Dupre. With the prevalent electronic hand calculators, the difference in calculation time between (4a) and the more complicated (18) can be a matter of seconds. Before addressing this question, however, it may be worthwhile to consider a broader one. That is, what is the usefulness of, and what are the limitations on, any equation which gives the energy of adhesion as a function of contact angle, be it Young–Dupre or the net free energy.

In this connection, an important thing to keep in mind is that these equations rely on the reversible, generally physical, interfacial interactions which combine to establish the equilibrium contact angle. For example,

suppose one places a drop of a pure single-liquid resin, at zero time of the beginning of a slow cure process, on a smooth solid surface. Suppose that all adsorption of the resin molecules to the solid surface is rapidly reversible (these conditions are, of course, hypothetical and not necessarily likely of realization) and furthermore that the viscosity is sufficiently low so that the resin immediately establishes an equilibrium contact angle. The calculated free energy of adhesion, be it a component as in (4a) or the total as in (18), will be that which exists at zero time. Once the cure has started, of course, many things can occur. For example, the resin may bond chemically to the surface, with the resulting chemical bonding largely determining the average adhesive bond energy and durability. If so, the physical forces which established the contact angle no longer exclusively, or even predominantly, determine the bond energy. Another, in an opposite sense, possibility is that the resin bonding to itself may cause it to abhere, i.e., withdraw from the previous extent of molecular contact with the surface. Once again, the original energy of adhesion will have changed drastically, and none of the contact angle equations apply to the interfacial bond formed by a solidified, or partially solidified, drop.

If a drop of liquid, say water, is placed on a smooth solid surface and is then frozen, there is, once again, no reason to assume that the nature and/or extent of molecular interaction at the solid–liquid interface will not have changed. The contact angle of the ice on the solid can then not be used to calculate a free energy of adhesion without the introduction of extrathermodynamic assumptions.

For accurate application of the classical Young–Dupre, either one should have a situation where the liquid, when detached from the surface, maintains the sessile drop shape (Figure 1a) or one should be interested only in the solid–liquid component of the total free energy. Referring to the above discussion on cured resins or frozen liquids, it is clear that ordinary situations where maintenance of sessile drop shape can actually occur, do not allow use of any contact angle function to determine the energies of adhesion. However, accurate use of the classical Young–Dupre can occur, of course, in theoretical calculations which only involve the solid–liquid interaction component of the total free energy.

Conclusions

1. The presently used formula for the work of adhesion of a liquid drop to a solid surface (in the presence of the vapor of the liquid at saturation), $W = \gamma_L(1 + \cos\theta)$, where γ_L is the surface tension of the liquid and θ the equilibrium contact angle is valid as a total free energy of adhesion only in the hypothetical circumstance that the drop retains its shape as a section of a sphere (Figure 1a) when detached from the surface. When the drop detaches to, or attaches from, a normal equilibrium shape, W represents only one component of the total free energy of adhesion.

2. An alternative formulation, the Net Free Energy of Adhesion, ΔF_N, is defined to describe the reversible work required to separate a sessile drop from a smooth solid surface (in the presence of the vapor of the liquid at p^0), to form a free sphere. Its negative gives the energy of attachment, due to surface forces, which causes a spherical liquid drop to adhere to a smooth solid surface.

3. The Net Free Energy of Adhesion is given by

$$\Delta F_N = \pi r^2 \gamma_L[(2a/\sin\theta)^{2/3} - a]$$

where r is the radius of the solid–liquid interface and a, called the "effective area", is $(2/(1 + \cos\theta)) - \cos\theta$.

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