# THE FREE ENERGY OF WETTING

WILLIAM G. PITT
*Brigham Young University*
*Provo, UT 84602*

The wetting and spreading of liquids on solids is frequently encountered in the chemical industry. Examples include the application of herbicides, adhesives, inks, paints and other coatings, flotation of minerals, containing and cleaning chemical spills, waterproofing, cloud seeding, lubrication, corrosion protection, enhanced oil recovery, and more. Despite its importance, however, wetting and spreading in the chemical process industries is often without a home in most undergraduate chemical engineering curricula.

The subject could be taught in classes on engineering materials, plant design, or separations. An informal survey of nine undergraduate texts[1-9] on engineering materials found that six of them mentioned the concept of surface energy, but only in the context of nucleation[1-5] and fracture propagation.[5,6] Only one of these texts introduced the concept of contact angle and presented Young's equation in a discussion of heterogeneous nucleation,[1] and none discussed wetting or spreading of liquids on other liquids or solids. Unfortunately, the only text on engineering materials that discussed contact angle, spreading, and wetting is no longer in print.[10]

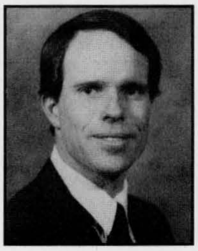
This paper will present some simple but powerful thermodynamic concepts that can be taught in a 1-hour lecture on wetting and spreading. We approach the subject through the theme of the minimization of free energy—a concept with which chemical engineering students are well acquainted.

## TO SPREAD OR NOT TO SPREAD

The two practical questions about spreading and wetting which an engineer usually addresses are:

- *Does the liquid spread completely or only partially on the solid surface?*
- *If partial spreading occurs, what is the contact angle of the drop on the surface?*

To address these questions we begin with the definition of the surface energy, γ, which is defined as the change in free energy as new surface area is created. If new surface is created under reversible conditions at constant pressure, temperature, and number of molecules, this surface energy is the change in Gibbs free energy[11]



***William G. Pitt*** *is an associate professor in the Chemical Engineering Department at Brigham Young University. He is active in AIChE as the student chapter advisor at Brigham Young University and as chair of the National Student Paper Competition. He obtained his BS from Brigham Young University and his PhD from the University of Wisconsin, Madison. His research activities deal with adhesion phenomena on biomedical polymers and in polymer composites.*

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{P,T,n} \tag{1}$$

where G is Gibbs free energy and A is the surface area. If the surface is created at constant volume, temperature, and number of molecules, this surface energy is the change in Helmholtz free energy

$$\gamma = \left(\frac{\partial F}{\partial A}\right)_{V,T,n} \tag{2}$$

Because pressure is generally a more constant parameter than volume, Eq. (1) is sometimes (but not always) preferred. In this paper, the term *free energy* can refer to either of these definitions, depending on whether the wetting and spreading occurs under constant pressure or volume. Thus, the free energy associated with the surfaces of a system is simply the surface area of each phase boundary multiplied by γ for that boundary. Subscripts of γ refer to the surface free energy of the interface between the liquid, solid, and vapor phases.

Next let us perform a thought experiment suggested by Figure 1 in which we force a small drop to spread over a large surface. Before a drop of liquid contacts the surface, the surface free energy of the system is the solid-vapor surface free energy, $\gamma_{sv}$, multiplied by the solid area (assuming the original area of the drop is much smaller than the solid area). When the liquid is spread completely on the solid, the system now consists of two interfaces (the solid-liquid and the liquid-vapor interfaces), and the surface energy of the system is $\gamma_{lv} + \gamma_{sl}$ multiplied by the solid area. One may now ask the question, "Does the system attain the lowest free energy when the drop is spread completely on the solid?" If so, complete spreading will occur. We can see that if the $\gamma_{sv}$ is larger than the sum of $\gamma_{lv} + \gamma_{sl}$, the reduction in free energy will drive the drop to spread completely over the surface. Thus, spreading occurs if

$$\gamma_{sv} > \gamma_{lv} + \gamma_{sl} \quad \text{or} \quad 0 < \gamma_{sv} - (\gamma_{lv} + \gamma_{sl}) \tag{3}$$

Complete spreading will also occur if

$$\gamma_{sv} = \gamma_{lv} + \gamma_{sl}$$

because the drop will flatten out until it has a contact angle of zero (as will be shown in the next section).

In the early 1920s, Harkins and Feldman[12] studied the spreading of organic liquids on a number of solid and liquid substrates. They defined a "spreading coefficient," S, as the difference between the work of adhesion, $W_a$, and the work of cohesion $W_c$. The work of adhesion is the work per interfacial area needed to separate two adjacent (solid and liquid) phases:

$$W_a = \gamma_{lv} + \gamma_{sv} - \gamma_{sl}$$

The work of cohesion is the work per area needed to separate a single liquid phase:

$$W_c = 2\,\gamma_{sv}$$

Therefore, the spreading coefficient becomes

$$S = W_a - W_c \tag{4}$$

$$S = \gamma_{sv} - (\gamma_{lv} + \gamma_{sl}) \tag{5}$$

Harkins and Feldman observed that liquids spread completely when $S \geq 0$, which is consistent with Eqs. (3) and (5).

One final note on spreading concerns the rate or kinetics of spreading. The velocity of the moving three-phase contact line at the edge of the drop can be as high as 30 cm/s and is dependent upon the viscosity and surface energy of the spreading liquid.[11] Brochard and deGennes show that the change in the drop radius, R, with time (the velocity) is proportional to $R^{-9}$.[13] Thus the latter stages of spreading can be a slow process.

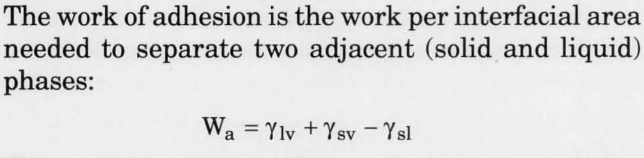


***Figure 1.*** *Process of complete spreading of a liquid drop on a solid substrate.*

***This paper presents some simple but powerful thermodynamic concepts that can be taught in a 1-hour lecture on wetting and spreading. We approach the subject through the theme of the minimization of free energy...***

If the spreading occurs on a liquid instead of a solid, the velocity varies inversely with the substrate viscosity.[14] The viscosity of the surrounding fluid also plays a role, especially if the fluid is a liquid (instead of a gas). The spreading velocity increases as the viscosity of the displaced liquid decreases. More importantly, a stable liquid film separating the drop from the substrate prevents the initial formation of the three-phase contact line, and in most practical cases, the stability of this liquid film controls spreading. Thus, spreading entails multifarious phenomena, and its complexity should not be underestimated by the simplicity of the thermodynamic statement of Eq. (3).

## PARTIAL SPREADING

We will now examine the case in which the solid surface energy is less than $\gamma_{lv} + \gamma_{sl}$, or in which S is negative and the spreading is not complete. In this case the drop forms a sphere or spherical cap on the solid as long as the drop is small enough that gravitational distortion of the shape is negligible. The contact angle is defined as the angle between the solid-liquid interface and the liquid-gas interface at the edge of the drop. In 1805, Thomas Young stated (without proof) that the equilibrium among the attractive forces between particles of fluid and particles of solid will cause the fluid to form a certain angle with the solid.[16] This angle was defined by

$$F_s = F_{sl} + F_l \cos\theta \tag{6}$$

where the $F_s$, $F_{sl}$, and $F_l$ refer to the forces of the solid, the common surface, and the liquid, respectively. This was the genesis of Young's equation, a mechanical balance of rather ill-defined forces. In introductory texts, Young's equation is often taught as a force balance at the edge of the drop. While this model of a force balance is convenient and easy to teach, many students find it unsettling. They see little logic in a force balance in the horizontal direction, but not in the vertical direction. They may also have trouble conceiving surface energy as a force per linear distance because most chemistry courses introduce $\gamma$ as an energy per surface area.

Of course, both of these apparent inconsistencies can be adequately addressed.[17,18] There is a force balance in the vertical direction: just as students learn in their introductory physics course, *when you push against an immovable wall, the wall exerts an equal force in the opposite direction,* so the solid substrate exerts an equal force in the downward direction at the three-phase boundary. Interesting experimental evidence of this vertical force is shown by drops of liquids on elastic hydrogels—the drops actually pull the hydrogel upward at the periphery of the drop.[19]

Unlike Young, Willard Gibbs related the contact angle to the more familiar concept of surface energy. He proposed that the three-phase boundary line (between an insoluble solid and two fluids) would displace along the solid surface until it reached a point at which any further displacement of the line would create an increase in the free energy associated with the three-phase boundary line.[20] This condition of equilibrium reduces to

$$\gamma_{lv} \cos\theta = \gamma_{sv} - \gamma_{sl} \qquad (7)$$

which has the same form as Young's equation, but which employs surface energies instead of surface forces. While the student may feel more familiar with the language of surface energy, Gibb's derivation is usually not intuitively obvious. It also has the drawback (as does Young's derivation) that the derivation is done in two-dimensional space. Most classical textbooks on colloidal and surface chemistry derive Young's equation using free energy concepts and a differential change in contact area.[11,15]

## A CONCEPTUALLY STRAIGHTFORWARD APPROACH

A straightforward approach to teaching the concept of contact angle and incomplete wetting is to combine the familiar rule that "a system moves to its state of lowest free energy" with a simple model of a liquid drop contacting a solid surface. Referring to the discussion of the spreading coefficient, we see that if

$$\gamma_{sv} < \gamma_{lv} + \gamma_{sl}$$

then the free energy of the system is not minimized at a state of complete spreading, and so the drop will not spread completely. The question now becomes, "How far must the drop spread to minimize the free energy of the system?" The answer is given by formulating the equation that describes the change in free energy: we simply subtract the energy "before" from the energy "after" the drop wets the surface. The surface energy before the drop contacts the surface is

$$\text{Total surface energy before} = S_T\gamma_{sv} + 4\pi r_d^2\gamma_{lv} \qquad (8)$$

where $S_T$ is the total area of the solid surface and $r_d$ is the radius of the drop. After the drop has contacted the surface, it spreads to form a spherical cap with a contact angle $\theta$ as shown in Figure 2. The total surface energy after the wetting of the drop is

$$\text{Total surface energy after} = (S_T - A_I)\gamma_{sv} + A_c\gamma_{lv} + A_I\gamma_{sl} \qquad (9)$$

where $A_I$ is the area of the interface between liquid and solid, and $A_c$ is the liquid-vapor interfacial area of the spherical cap of liquid. $A_I$ and $A_c$ are given by

$$A_I = \pi r_c^2\left(1-\cos^2\theta\right) \qquad (10)$$

and

$$A_c = 2\pi r_c^2(1-\cos\theta) \qquad (11)$$

where $r_c$ is the radius of curvature of the spherical cap. The change in free energy of the system is found by subtracting Eq. (8) and Eq. (9)

$$\Delta G = 2\pi\gamma_{lv}\left(r_c^2(1-\cos\theta) - 2r_d^2\right) + \pi r_c^2\left(1-\cos^2\theta\right)(\gamma_{sl} - \gamma_{sv}) \qquad (12)$$

The minimum in free energy is found by equating to zero the derivative of Eq. (12) with respect to cos $\theta$, and then solving for cos $\theta$

$$\frac{d\Delta G}{d(\cos\theta)} = 0 = \pi\left\{2\gamma_{lv}\left[(1-\sigma)\frac{dr_c^2}{d\sigma} - r_c^2\right] - 2\sigma r_c^2(\gamma_{sl}-\gamma_{sv}) + \left(1-\sigma^2\right)(\gamma_{sl}-\gamma_{sv})\frac{dr_c^2}{d\sigma}\right\} \qquad (13)$$

where $\sigma$ is a shorthand notation for cos $\theta$. The spherical cap has constant volume

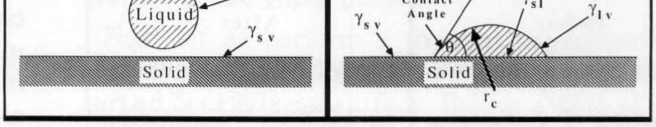


***Figure 2.*** *Process of partial spreading of a liquid drop to form a spherical cap with radius $r_c$ and contact angle $\theta$ on the solid.*

$$V = \pi r_c^3\left(\frac{2}{3} - \sigma + \frac{\sigma^3}{3}\right)$$

so we can use implicit differentiation under conditions of constant volume to derive that

$$\frac{dr_c^2}{d\sigma} = \frac{2r_c^2(1-\sigma)^2}{2-3\sigma+\sigma^3} \tag{14}$$

Combining Eqs. (13) and (14) and solving for σ gives

$$\sigma = \cos\theta = \frac{(\gamma_{sv} - \gamma_{sl})}{\gamma_{lv}} \tag{15}$$

which is identical to Eq. (7).

## DISCUSSION

This derivation contains several important points that the students should understand about wetting and contact angles. On the practical side, nearly all liquids partially or completely spread on solid surfaces. It is very rare to have a contact angle of 180° (no wetting). Equation (15) indicates that an angle of 180° would require $\gamma_{sl} = \gamma_{sv} + \gamma_{lv}$. This is rarely the case for aqueous solutions or organic liquids because the interfacial free energy usually has a value that is less than $\gamma_{lv}$. In the case of liquid metals (such as mercury) on organic solids, $\gamma_{lv}$ and $\gamma_{sl}$ are both so high that $\gamma_{sv}$ becomes negligible and a contact angle of 180° is approached. This does not mean that "waterproofing" a porous surface is impossible. If the contact angle is greater than 90°, capillary pressure will resist the penetration of a liquid into a porous solid.

Another point on the practical side is that this derivation employed an ideal system that assumed the absence of gravity, surface roughness, surface contamination, surface chemical heterogeneity, surface mobility, liquid viscosity, line tension, or other real effects that often cause contact angles to depart from the contact angle predicted by Eq. (15).[21] These real complications and departures from the ideal case can often aid in understanding the nature of complex surfaces, but they are not the focus of this discussion. (More information on these topics can be found in references 17 and 21.) In some very clean and specialized experiments, all of these complications can be eliminated with the exception of gravity and line tension.

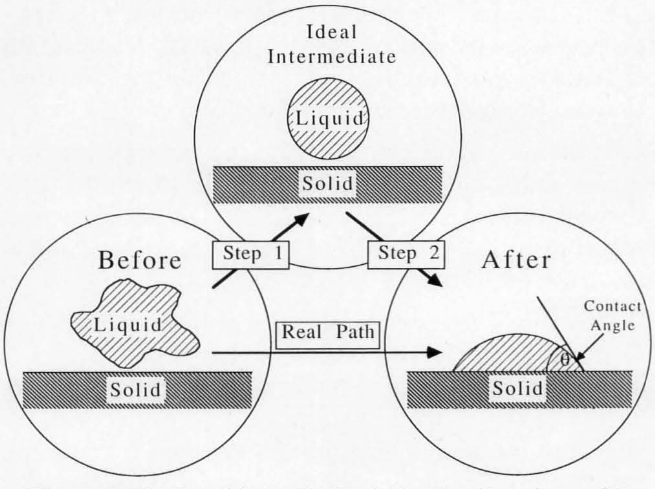


***Figure 3.*** *Real and hypothetical ideal paths of an arbitrarily shaped liquid forming a spherical cap on a solid.*

If one cannot eliminate gravity and line tension effects in real measurements, one should at least understand what perturbations they may impose upon the theoretical contact angle. Gravity always distorts the drop shape from a spherical cap to an oblate spheroidal cap, but this distortion is negligible for sufficiently small drops. For example, with water on polyethylene, gravity distortion becomes noticeable if the drop volume is greater than about 2μl. This distortion causes the surface area of the cap ($A_c$) and the interface area ($A_I$) to increase over that of the ideal case.

Line tension is the one-dimensional analog to surface tension and can be defined as the excess free energy per distance at the three-phase boundary line between the liquid, solid, and vapor at the perimeter of the cap. Assuming that the free energy contribution from line tension is positive, a drop will not spread as far (compared to the case without line tension) before it reaches the minimum in free energy, and thus it will have a larger contact angle than predicted by Eq. (15). Both gravity and line tension contribute to the free energy of the system, and the net result upon equilibrium contact angle is still a subject of controversy.[22]

In the ideal case neglecting gravity and line tension, the contact angle is independent of the initial spherical drop size. The following argument also shows that contact angle is independent of initial drop shape; *i.e.*, a volume of liquid or arbitrary initial shape will form a spherical cap having Young's contact angle. Given that the resultant drop shape and contact angle is only a function of the free energy state, we can break the pathway of going from initial to final energy state into two hypothetical paths, neither of which may have actually occurred, but which represent the change in free energy states of the system (see Figure 3). The first path minimizes the free energy of the liquid shape by forming a sphere not yet in contact with the surface. The second step minimizes the free energy after the liquid sphere contacts the surface and results in a Young's contact angle according to the derivation presented above. Since both steps are minimizations

*Continued on Page 193.*

# FREE ENERGY OF WETTING

*Continued from page 187.*

in free energy, the total path represents a minimum in free energy, and Young's angle is the result.

In summary, when a liquid contacts a solid, either partial or complete wetting occurs. The extent of wetting is determined by a simple thermodynamic rule familiar to all students: the system will move to the state of lowest free energy. Although the rules are simple, the implications of the rules are profound and can have important consequences in many areas of applied chemistry.

## ACKNOWLEDGMENTS

The author would like to thank the Exxon Education Foundation for a grant supporting education and research associated with this study.

## REFERENCES

1. Smith, William F., *Principles of Materials Science and Engineering,* 2nd ed., McGraw-Hill, Inc., New York, NY (1990)
2. Shackelford, James F., *Introduction to Materials Science for Engineers,* 3rd ed., Macmillan Publishing, New York, NY (1992)
3. Askeland, Donald R., *The Science and Engineering of Materials,* 2nd ed., PWS-KENT Publishing, Boston, MA (1989)
4. VanVlack, Lawrence H., *Elements of Materials Science and Engineering,* 6th ed., Addison-Wesley Publishing, New York, NY (1989)
5. Flinn, Richard A., and Paul K. Trojan, *Engineering Materials and Their Applications,* 3rd ed., Houghton Mifflin Co., Boston, MA (1990)
6. Callister, William D., *Materials Science and Engineering,* 2nd ed., John Wiley and Sons, New York, NY (1991)
7. Budinski, Kenneth G., *Engineering Materials,* 4th ed., Prentice Hall, New Jersey (1992)
8. Newey, Charles, and Graham Weaver, *Materials Principles and Practice,* The Open University, England (1990)
9. Keyser, Carl A., *Materials Science in Engineering,* 4th ed., Charles Merrill Publishing Company, Ohio (1986)
10. Jastrzebski, Zbigniew D., *The Nature and Properties of Engineering Materials,* 3rd ed., John Wiley & Sons, New York, NY (1987)
11. Adamson, A.W., *Physical Chemistry of Surfaces,* 4th ed., John Wiley & Sons, New York, NY (1982)
12. Harkins, W.D., and A. Feldman, *J. Amer. Chem. Soc.,* **44**, 2665 (1922)
13. Brochard, F., and P.G. deGennes, *J. Physique Lett.,* **45**, L-597 (1984)
14. Ahmad, J., and R.S. Hansen, *J. Colloid Interface Sci.,* 601 (1972)
15. Ross, S., and I.D. Morrison, *Colloidal Systems and Interfaces,* John Wiley and Sons, New York, NY; p. 87 (1988)
16. Young, T., *Miscellaneous Works,* G. Peacock, Ed., Murray, London, England; Vol. 1, 432 (1855)
17. Andrade, J.D., L.M. Smith, and D.E. Gregonis, *Surface and Interfacial Aspects of Biomedical Polymers,* J.D. Andrade, Ed., Plenum Publishing Co., New York, NY; Vol. 1, 260 (1985)
18. Pirie, B.J.S., and D.W. Gregory, *J. Chem. Educ.,* **50**, 682 (1973)
19. Andrade, J.D., R.N. King, D.E. Gregonis, and D.L. Coleman, *J. Polym. Sci. Symp.,* **66**, 313 (1979)
20. Gibbs, J.W., *The Scientific Papers of J. Willard Gibbs,* Dover, New York, NY; Vol. 1, 326 (1961)
21. Morra, M., E. Occhiello, and F. Garbassi, *Adv. Colloid Interface Sci.,* **32**, 79 (1990)
22. Gaydos, J., and A.W. Neumann, *J. Colloid Interface Sci.,* **120**, 76 (1987) ❐

---

# REVIEW: HAZOP and HAZAN

*Continued from page 167.*

tive risk assessment" (QRA) or "probabilistic risk assessment" (PRA). This chapter includes very introductory material on calculating human risks and equipment reliability. There is an interesting section on calculating the cost of saving a life, demonstrating a huge range of cost values for various activities.

Chapter 4 is a manager's guide to hazard analysis and discusses the problems associated with hazard analysis in a managerial environment.

Chapter 5 discusses the most common objections raised against HAZOP and HAZAN, and the author provides a convincing case for applying these techniques.

Chapter 6 is a very short chapter which discusses sources of data and confidence limits, and Chapter 7 presents an interesting history of HAZOP and HAZAN.

I am a considerable fan of the author, Trevor Kletz, and buy all of his books as soon as they are published. He uses a powerful technique of mixing case histories with discussion to provide convincing cases for his material. Furthermore, he has a unique way of looking at things and often arrives at an "obvious" result that no one else even thought of.

The content of this book is introductory in nature and would be suitable for anyone with an interest in learning about basic HAZOP and HAZAN methods. It does not discuss techniques for decomposing large process units into suitable subunits for HAZOP analysis, a major problem for industrial practitioners, nor does it include some of the more recent organizational methods for managing a large HAZOP. There are some simple calculations related to equipment reliability, but nothing particularly difficult for chemical engineering students.

This book, along with Trevor's other books, would be a suitable reference or supplemental material for a chemical engineering design course or a course in chemical process safety. The students would be most responsive to the case histories and examples that are provided. ❐