

Wetting on Real Surfaces

Abraham Marmur
Department of Chemical Engineering,
Technion – Israel Institute of Technology
Haifa, Israel

Abstract

Recent advances regarding the measurement and theory of equilibrium contact angles on real surfaces are presented. The intrinsic contact angle is discussed in terms of the Young equation and the line tension concept. The fundamental question that is presented and discussed is the relationship between the intrinsic, actual and apparent contact angles. Apparent contact angle measurement using the Capillary Bridge System (CBS) is explained. The main advantages of this approach are the use of force measurements rather than direct optical measurements, and the ability to calculate an average apparent contact angle. The Wenzel equation for rough surfaces and the Cassie equation for heterogeneous surfaces are shown to be true only for drops that are very large compared to the scale of roughness/heterogeneity. Contact angle hysteresis is explained. Of special interest is the predicted difference between the drop and captive bubble techniques, which stems from contact angle hysteresis.

Introduction

Wetting of substrates by liquid drops is one of the key processes in non-impact printing. The mode of wetting and the force driving it depend on the nature of the substrate and the liquid. If the substrate is non-absorbing, wetting occurs on the outer surface of the substrate. If it is absorbing, like paper, for example, wetting occurs by penetration into capillary spaces. The initial phase of wetting is dynamic, eventually leading to the final equilibrium situation. The latter is an essential factor underlying print quality. In addition, wetting equilibrium measurement is a useful tool for the characterization of printing substrates.

This paper deals with recent advances in the theory and measurement of equilibrium wetting of solid surfaces by liquid drops. Emphasis is put on real surfaces, which may be rough and chemically heterogeneous. On such surfaces the drop may not possess any symmetry, therefore previous theories and measurement techniques had to be extended to three-dimensional situations. This presentation and the references cited below describe the recent work of the author and his co-workers. The important contributions of other researchers can be traced through these references.

The Intrinsic Contact Angle

The starting point of the theory of wetting equilibrium is the well-known Young equation¹ for the contact angle that a liquid forms with an ideal solid surface, when both are immersed in a fluid (Fig. 1):

$$\cos\theta_y = (\sigma_{sf} - \sigma_{sl})/\sigma_f \quad (1)$$

θ_y is the contact angle as calculated from the Young equation, σ stands for interfacial tension, and the subscripts *s, l, f* indicate the solid, liquid, and fluid phases, respectively. An ideal solid surface is a perfectly smooth, chemically homogeneous, rigid, insoluble, and nonreactive surface. The contact angle on such a solid surface is called the intrinsic contact angle. The contact angle calculated from the Young equation represents the state of minimum free energy of the drop on the surface.

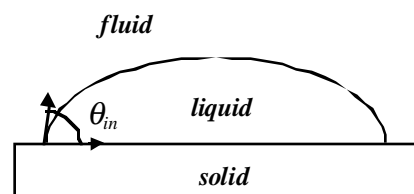


Figure 1. The intrinsic contact angle

It has been recognized for a long time that the Young equation for the intrinsic contact angle does not account for the three-phase molecular interactions at the contact line, namely the line at which the solid, liquid and fluid phases intersect. Following Gibbs, who suggested the concept of line tension as the one-dimensional analog of surface tension, the equation below was developed for the intrinsic contact angle, θ_i , that a liquid drop makes with an ideal solid surface²:

$$\cos\theta_i = \cos\theta_y - \tau/(R\sigma_f) \quad (2)$$

τ is the line tension, and R is the radius of the base of the drop. The order of magnitude of the line tension has been debated for many years. Various experiments have yielded values different by almost six orders of magnitude. Recently, theory and experiment seem to have concluded that the order of magnitude of the line tension is about 10^{-9} N.² This implies that the effect of line tension on an ideal solid surface is meaningful only for drop radii of less than about 1

micrometer. In most situations of interest the drop size is much bigger than that. However, for non-ideal surfaces (i.e. rough or heterogeneous surfaces), the effect of line tension may be meaningful, since *local* radii of curvature of less than a micrometer may exist along the contact line. This is still an open question that needs to be addressed in the future.

The Actual and Apparent Contact Angles

When real surfaces are considered, one should distinguish between two additional definitions of contact angles: the actual and the apparent [3]. The actual contact angle (Fig. 2) is the angle between the direction of the tangent to the solid surface at a given point and the direction of the tangent to the liquid-fluid (*lf*) interface at that point. The usual optical methods for measuring contact angles yield the apparent contact angle (Fig. 3). This is the angle between the direction of the tangent to the seemingly smooth solid surface, as seen by using relatively low magnification, and the direction of the tangent to the *lf* interface. On perfectly smooth solid surfaces, the apparent contact angle is identical with the actual one. On rough surfaces, they may be very different.

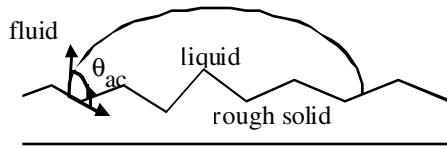


Figure 2. The actual contact angle

The fundamental question that needs to be answered is: what is the relationship between the intrinsic contact angle, which is characteristic of the material properties of the system, and the measurable contact angle? The contact angle that is currently accessible to experimental measurement is the apparent contact angle. Most of the following discussion will be devoted to describing what is known about the relationship between the apparent and intrinsic contact angles. However, it should be mentioned at this point that the relationship between the actual contact angle and the intrinsic one has been recently explained.^{4,5} It turns out that when line tension effects are negligible, the actual and intrinsic contact angles should be equal, even under the most complicated three-dimensional situations. If line tension effects are meaningful, the problem becomes much more complex. Initial attempts in this direction have been made.^{4,5}

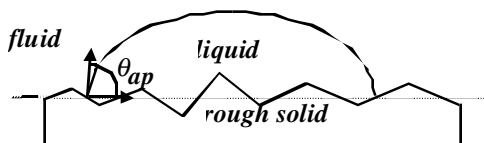


Figure 3. The apparent contact angle

If the drop is axisymmetric, the apparent contact angle has a unique value. However, on real surfaces, for which the local topography and chemical nature may vary from point to point, the apparent contact angle may also vary along the contact line. Thus, two types of problems need to be solved in order to answer the fundamental question: (a) how can the apparent contact angle be measured? and (b) how should the measurements be interpreted. The following sections summarize the current state of knowledge on these topics.

Measurement of the Apparent Contact Angle

When the apparent contact angle has a unique value, namely when the drop is axisymmetric, it can be easily measured by direct optical techniques. The classical method of using a goniometer has been replaced in recent years by video and image processing techniques. However, if the drop does not have a smooth, axisymmetric contact line, the apparent contact angle needs to be measured at each point along the contact line. In principle, this can be done by using suitable scanning techniques, however it is not simple, and has not yet been performed for practical cases.

Another approach is to measure the average apparent contact angle along the contact line. This can be done by using the Capillary Bridge System (CBS) [3]. This system (Fig. 4) uses a liquid drop in-between two surfaces (capillary bridge). The two surfaces may be identical, or one of them may be a well-characterized reference surface. During an experiment the volume of the capillary bridge, the distance between the surfaces, and the force exerted by the bridge on the lower surface are accurately measured. These data allow the calculation of the average apparent contact angle, *assuming* that the capillary bridge is axisymmetric.

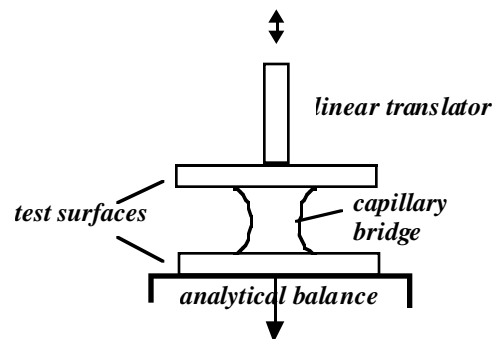


Figure 4. The Capillary Bridge System (CBS)

Interpretation of the Apparent Contact Angle

The Young equation predicts a single value for the contact angle. This is so, because the free energy curve of a system that consists of a drop on an ideal surface has a single minimum (curve a in Fig. 5). In contrast, the free energy curve for a drop on a real surface is characterized by many

minima points. For example, curve b in Fig. 5 shows the free energy calculated for a two-dimensional drop on a periodically heterogeneous surface. Each minimum corresponds to a metastable equilibrium state, so there is a multitude of possible values for the apparent contact angle. The lowest (global) minimum corresponds to the stable equilibrium state. The problem of interpretation of apparent contact angles can thus be divided into two sub-problems: (a) how can one identify the most stable contact angle that corresponds to the global minimum in the free energy, and what can one deduce from it? (b) what is the range of possible apparent contact angles? The former question was partially answered many years ago by Wenzel⁶ and Cassie.⁷ The first subsection will explain the recent understanding of these old contributions. The latter is related to the problem of contact angle hysteresis. This important topic will be discussed in the second subsection.

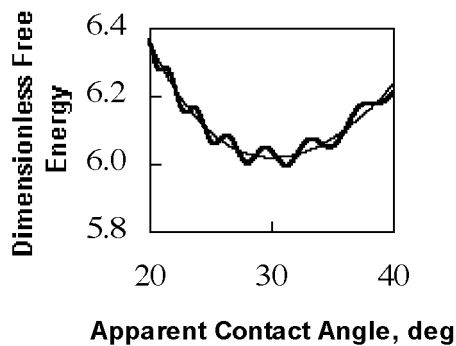


Figure 5. Free energy vs. apparent contact angle for a two-dimensional example

The Wenzel and Cassie Equations

Many years ago, Wenzel⁶ developed the following equation for the contact angle, θ_w , on rough surfaces:

$$\cos\theta_w = r\cos\theta_y \quad (3)$$

where r is the roughness ratio (the ratio of the true surface area of the solid to its nominal surface area). This equation was actually developed for an unrealistic picture of a drop sitting on an ideal surface, the surface area of which is bigger by a factor of r than that of the nominal surface area. In modern terminology, θ_w was meant to describe the apparent contact angle corresponding to the global free energy minimum.

Recent detailed analysis⁸ has shown that, in general, the Wenzel equation is not accurate. However, it has been mathematically proven that the Wenzel contact angle becomes an excellent approximation to the apparent contact angle corresponding to the global minimum in free energy when the size of the drop becomes very large compared with

the scale of roughness. Moreover, it has been shown⁸ that the drop becomes more axisymmetric as its size (normalized to the scale of roughness) increases. Thus, for a rough surface, one should use sufficiently large drops for contact angle measurements. Axisymmetry may serve as a good indication of the drop being sufficiently large. Then, if one is able to identify the most stable situation of the drop, Eq. (3) may yield the Young contact angle if the roughness ratio is known. It should be noted, however, that the problem of identifying the most stable situation is still an open question.

The Cassie equation for heterogeneous surfaces⁷ is the conceptual equivalent of the Wenzel equation. It states that the cosine of the contact angle on a heterogeneous surface is the weighted average of the cosines of the contact angles on the various heterogeneous patches on the surface. The status of the Cassie equation is similar to that of the Wenzel equation, as demonstrated below. Curve b in Fig. 5 shows an example calculated for a two dimensional case. The solid surface is assumed to be heterogeneous in a smooth periodic way, such that its intrinsic contact angle varies with the distance from the center of the drop, x , according to

$$\cos\theta_m = \cos\theta_{av} + \varphi\cos(2\pi x/l) \quad (4)$$

θ_{av} is the average contact angle, φ is the amplitude of the variation, and l is the wavelength of the heterogeneity. According to the Cassie equation the contact angle should equal θ_{av} .

It is clearly seen in Fig. 5 that the global minimum is not at the average contact angle, which was 30° in this calculation. However, for the case shown in Fig. 6 the position of the global minimum is much closer to 30°. This is so, because the drop size (compared with the wavelength of heterogeneity) in this case is bigger (by a factor of $\sqrt{10}$) than for the case shown in Fig. 5. Three dimensional calculations that are being done confirm this conclusion, thus supporting the general statement that as the drop is getting bigger compared with the scale of heterogeneity, the Cassie equation becomes a better approximation for the most stable apparent contact angle.

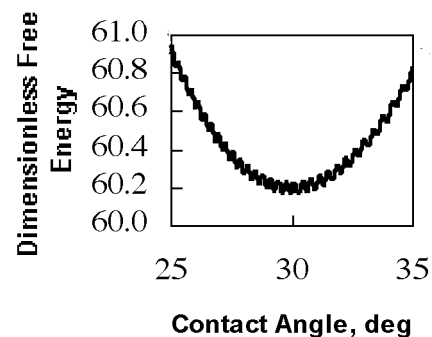


Figure 6. Free energy vs. apparent contact angle for a drop bigger than in the case presented in Fig. 5.

Therefore, if one uses a sufficiently large drop, it may, in principle, be possible to identify the most stable situation on a heterogeneous surface. The apparent contact angle corresponding to this state is the average of the intrinsic contact angles characterizing the surface. However, this information is not sufficient for elucidating the distribution of heterogeneity on the surface.

Contact Angle Hysteresis

As mentioned above, there is no unique value of the contact angle for a drop on a real surface. Rather, there is a range of possible contact angles, as demonstrated, for example, by the minima in Fig. 5. It is well known in practice that if the drop volume is increased, the apparent contact angle also increases, until a maximum value is reached. This is called the "advancing" contact angle. Similarly, when the drop volume is decreased, the apparent contact angle decreases, until a minimum is reached. This minimum contact angle is the "receding" one. The path followed by the contact angles when the volume is increased is different from that followed when the volume is decreased, hence the term contact angle hysteresis.

The reason for the existence of a finite range of contact angles (the hysteresis range) can be explained as follows. As the apparent contact angle gets further away from the global minimum, the minima become shallower. This is clearly seen in Fig. 5. Eventually, instead of a minimum there exists an inflection point. Beyond the inflection points there are no local minima any more. So the highest contact angle for which there is an inflection point is the advancing contact angle, and the lowest corresponds to the receding contact angle.

The existence of multiple minima within a finite range of contact angles explains the existence of a range of metastable contact angles. This, however, is not sufficient to explain hysteretic behavior. The sufficient condition turns out to be the dependence of the locations of the minima on the drop volume.^{9,10} An important outcome of this analysis is that contact angle measurements may strongly depend on the system used.¹¹ While the values of the advancing and receding contact angles are independent of the method of measurement, the practical possibility of reaching these values does depend on the method. The theory and calculations of hysteresis for three-dimensional situations¹² is still in its infancy. Much more is needed to be learned in order to be able to fully and correctly interpret contact angle measurements on real surfaces.

Conclusions

The following conclusions summarize the main points emphasized in this discussion:

1. Line tension is important when local radii of curvature are smaller than about 1 micrometer.
2. The CBS enables measurement of average apparent contact angles.
3. The Wenzel and Cassie equations for the most stable apparent contact angle become more accurate as the size of the drop increases compared with the scale of roughness or heterogeneity.
4. Understanding contact angle hysteresis is essential for the correct interpretation of contact angle measurements. These measurements may depend on the system that is used.

References

1. Young, T., *Phil. Trans. Roy. Soc. (London)* **95**, 65 (1805).
2. Marmur, A., *J. Coll. Int. Sci.* **186**, 462-466 (1997).
3. Marmur, A., *Colloids & Surfaces A*, **116**, 55-61 (1996).
4. Wolansky, G. and Marmur, A., *Langmuir* **14**, 5292-5297 (1998).
5. Marmur, A., *Colloids & Surfaces A* **136**, 81-88 (1997).
6. Wenzel, R.N., *Ind. & Eng. Chem.* **28**, 988 (1936).
7. Cassie, A.B.D., *Disc. Faraday Soc.* **3**, 11 (1948).
8. Wolansky, G., and Marmur, A., *Colloids & Surfaces A* (1999).
9. Marmur, A., *Adv. in Coll. & Int. Sci.* **50**, 121-141(1994).
10. Brandon, S., and Marmur, A., *J. Coll. Int. Sci.* **183**, 351-355 (1996).
11. Marmur, A., *Colloids & Surfaces A* **136**, 209-215 (1998).
12. Brandon, S., Wachs, A., and Marmur, A., *J. Coll. Int. Sci.* **191**, 110-116 (1997).

Biography

Prof. Marmur has been working in the field of interfacial phenomena and wetting for over twenty years. He has published many papers on the theory and practice of wetting processes, and has been consulting for major companies involved in the design and utilization of inkjet printing systems. He is also an editor of *Reviews in Chemical Engineering*, and was on the advisory committees of *J. of Colloid and Interface Science* and *J. of Adhesion Science and Technology*.