Chapter 8
Summary and Final Remarks

Abstract Many believe that the concept of wetting begins with the Young's equation. Although the Young's equation is very simple, it has been a source of arguments over the last two centuries because the equation comprises four quantities of which two of them cannot be measured reliably. Moreover, researchers did express frustration in their inability to measure the Young's angle consistently, at least a century ago. This chapter provides a brief overview of the history and the source of some of the misconceptions. Fundamental concepts that have been clarified in recent years, including (1) the recognition of the fact that it is the contact line, not the contact area, that determines the contact angle; (2) advancing and receding contact angles are the most important contact angles, and they measure wettability and adhesion respectively, and surface stickiness can be predicted from the sliding angle; and (3) hydrophilicity and hydrophobicity should be defined by the receding contact angle, not the static contact angle. In answering Good's calling for standardization of measurement protocols for contact angle measurements, a set of guidelines for determining static contact angle, advancing/receding contact angle, and sliding angle are provided. We hope that these guidelines will benefit the community in the near term and serve as a springboard for the development of standardized procedures by the "authority" or leaders in this field in the near future.

Keywords Young's equation • Misconceptions • Mechanical equilibrium • Young's angle • Advancing contact angle • Receding contact angle • Contact angle hysteresis • Ideal surface • Real surface • Contact line • Contact area • Surface characterization • Measurement protocols • Guidelines and best practices

8.1 Misconceptions in the Young's Equation

Most researchers would agree that surface science started with Thomas Young when he published his legendary article in 1805 entitled "An Essay on the Cohesion of Fluids" [1]. Young did not write any equation in his paper, but he descriptively stated that an angle is formed when liquid wets a solid surface. He wrote: *We may therefore inquire into the conditions of equilibrium of the forces acting on the angular particles, one in the direction of the surface of the fluid only, a second in that of the common surface of the solid and fluid, and the third in that of the exposed surface of the solid.* This is essentially the Young's equation we know to date.

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Young clearly stated that the angle of contact is a result of the mechanical equilibrium among the three surface tensions (γ_{LV}, γ_{SL}, and γ_{SV}) at the three-phase contact line. However, it is somewhat a mystery that there are still misquotations in recent years, either by implying or directly stating, that the contact angle is from a thermodynamically equilibrium wetting state. Such a quotation is not correct.

The Young's equation is deceptively simple, but it is problematic multidimensionally. First, two out of four quantities in the equation, γ_{SV} and γ_{SL}, cannot be measured reliably. According to Zisman [2], researchers in the nineteenth century, notably Dupre [3] and Gibbs [4], had resorted to thermodynamics to solve the Young's equation. Due to the lack of available documents in this period, we are unable to map out the evolution of the history of surface research in that era. It is however likely that our bias toward thermodynamics may be a result of our basic science training in school. As discussed in Chaps. 3 and 4, although the process of wetting is driven by thermodynamics, the way the wetting liquid reaches its final static state is controlled by kinetics. In other words, the Young's angle is from a metastable wetting state. Most static contact angles on flat surfaces and rough surfaces, including the Wenzel angle and the Cassie-Baxter angle, are all from the metastable wetting states. This has been one of the reasons for the continuous argument as researchers had a hard time to measure the Young's angle on a consistent basis.

The second issue around the Young's equation is the Young's angle itself. Researcher as early as 1890 [5] had reported the existence of multiple angles between the advancing and receding angles, which could be reliably measured. The Young's angle is just one of the angles between advancing and receding and was known to be a metastable state for some time [6–9]. Bartell and Wooley even suggested that the receding angle may be the most important angle among the three angles they measured [9]. In his 1959 paper, Johnson pointed out that researchers during that time had serious reservation about the validity of the Young's equation [10]. Experimental evidence in the last couple of decades, which is summarized in Chap. 3, shows that there indeed exist multiple metastable wetting states between the advancing and receding angles. They can be populated by carefully exciting the sessile droplet with vibration noise (Fig. 3.11). A key message from these studies is that, all the metastable wetting states can be driven to a thermodynamically most stable wetting states with optimal vibration excitation [11–14].

The third issue derived from the Young's equation is contact angle hysteresis (CAH), the difference between advancing and receding contact angle. Some early researchers thought CAH originated from microscopic heterogeneity on the surface, particularly roughness. Some thought the Young's equation would only be applicable to homogeneous, smooth, and rigid surfaces, and the term ideal surface was created. To date, we know this is not true. Both roughness [15–17] and molecular interactions between liquid and the solid surface [18, 19] are contributors to CAH, and an update was provided in Chap. 5 in this book. Undoubtedly, more work is needed to thoroughly understand the mechanism that leads to hysteresis and the role it may play in surface science in general.

8.2 Concepts that Are Turning the Corners

The pioneering thermodynamic analyses of the wetting process by Dupre [3] and Gibbs [4], coupled with our basic science training in school, seem to create a strong bias in solving scientific problem based on thermodynamic principles. The successful work by Wenzel [20] to explain the enhancement of wettability for rough hydrophilic surface and increase of resistance to wet for hydrophobic surface, coupled with the work by Cassie and Baxter [21] on porous surfaces, further solidified our bias. Although Pease [6] and Johnson [10], in the same era, had voiced the importance of the contact line, rather than the wetted area dictates the contact angle, their messages had been largely ignored for decades. On the other hand, mounting results in the last two decades, both experimental and theoretical, show convincingly that *contact angle is a one-dimensional*, *not two-dimensional problem. Contact angle is dictated by the locality of the three-phase contact line*, *not the area underneath the liquid droplet*. While disagreements between the calculated Wenzel and Cassie angles with the experimentally observed angles are often found, the discrepancy can be resolved when the classic roughness factors are modified with correction factors that include the geometry of the rough contact line [22–24]. It is important to point out that agreements between the calculated Wenzel and Cassie-Baxter angles with the observed angles are possible. This can occur when the roughness is microscopic and homogeneous such that the roughness factor calculated from the wetted area is comparable to that at the three-phase contact line [25].

Many leading researchers had advocated the importance of $\boldsymbol{\theta}_{\mathrm{A}}$ and $\boldsymbol{\theta}_{\mathrm{R}}$ in surface study, the fundamental reason was never offered clearly or convincingly. It was either because of the CAH or the surface is not *real*. Using the microbalance technique, Samuel et al. [26] reported the measure of the wetting force and the adhesion force between water and 20 surfaces of varying wettability. Good correlations were found between the wetting force and $\boldsymbol{\theta}_{\mathrm{A}}$ and the adhesion force and $\boldsymbol{\theta}_{\mathrm{R}}$. This work establishes a clear connection between contact angles and liquid–solid interactions. The study led to the recommendation that $\boldsymbol{\theta}_{\mathrm{A}}$ is a measure of surface wettability, the smaller the $\boldsymbol{\theta}_{\mathrm{A}}$, the higher the wettability. Similarly $\boldsymbol{\theta}_{\mathrm{R}}$ can be used to predict surface adhesion, the smaller the $\boldsymbol{\theta}_{\mathrm{R}}$, the stronger the surface adhesion. Sliding angle α determines the mobility of the drop or the stickiness of the surface. Evidence is provided that CAH is neither correlating to wettability nor adhesion and stickiness (Figs. 5.2, 5.7 and 5.14).

Hydrophilicity and hydrophobicity are the most recognized terms in surface science. Using them as adjectives and comparing affinity is all right. However, the science community has generally accepted that a surface is hydrophilic when its water contact angle is <90°, and it is hydrophobic when the water contact angle is >90°. There is little technical evidence to support this definition. Worse yet, the 90° cutoff has been extended to define the philicity/phobicity boundaries of other liquids. Bad definition does have unwanted consequences. For example, after defining $\boldsymbol{\theta} > 90°$ as hydrophobic, researchers further come to the consensus arbitrarily that superhydrophobicity is defined for surfaces having a contact angle >150° [27].

The inaccuracy of these definitions has led to confusing terminologies, such as sticky superhydrophobicity, oleophobic wettability, and so on. A surface is defined as superhydrophobic when it exhibits high water repellency. Can a sticky surface exhibit high repellency at the same time? Sticky superhydrophobicity seems novel, but the two components in the terminology are actually contradicting to each other. After a very careful analysis of a series of water contact angle data along with the correlations with the wetting force and adhesion force, Law [28, 29] showed that hydrophilicity and hydrophobicity should be defined by the receding contact angle. The cutoff is at water $\boldsymbol{\theta}_{\mathrm{R}}$ 90°. More importantly, the fundamental reason why the surface changes its character, from hydrophilic to hydrophobic, is a result of the stronger cohesion force within the liquid droplet versus the wetting force due to wetting. For hydrophobic surface, the water drop prefers to be in the droplet state than wetting a hydrophobic surface due to the weak wetting interaction. Since Samuel et al. also showed that there is negligible attraction between water and surfaces with $\boldsymbol{\theta}_{\mathrm{A}} \geq 145°$, a surface can further be defined as superhydrophobic when its $\boldsymbol{\theta}_{\mathrm{R}}$ is >90° and $\boldsymbol{\theta}_{\mathrm{A}} \geq 145°$. In this definition, a superhydrophobic surface will have no affinity with water. It will never be sticky as its $\boldsymbol{\theta}_{\mathrm{R}}$ has to be >90°.

This methodology has been extended to define oleophilicity/oleophobicity for hexadecane. A surface can be defined as oleophilic when its hexadecane $\boldsymbol{\theta}_{\mathrm{R}}$ is <124° and oleophobic when the hexadecane $\boldsymbol{\theta}_{\mathrm{R}}$ is >124°. The finding clearly demonstrates the incorrect presumption that the 90° cutoff is universal for all liquids. Essentially, the philicity/phobicity cutoff is dependent of the surface tension of the liquid, the lower the surface tension, the larger the $\boldsymbol{\theta}_{\mathrm{R}}$ cutoff.

8.3 Outlook and Recommendations

8.3.1 Surface Characterization

One key weakness in surface science is the correct interpretation of contact angle data. This is partly due to the absence of any standardized protocol where reliable, high-quality data can be produced and partly due to our insufficient understanding of the interactions between liquids and solid surfaces. By correlating the wetting force and adhesion force with contact angle data, the connections between wettability and adhesion with the advancing and receding contact angle are established. Based on these correlations, we recommend that surface should be characterized by its wettability, adhesion, and stickiness. Wettability is measured by the advancing contact angle. Adhesion is governed by the receding contact angle. As for surface stickiness, it can be predicted from the sliding angle; the larger the sliding angle, the stickier the surface [26]. It is important to point out that this recommendation gets its origin from the movement of the contact line during liquid–solid interaction. For wettability and adhesion, there is only one moving contact line. They are the advancing and receding contact line, respectively. An interface is formed when wetting occurs and that interface is eliminated when the liquid is fully receded. In the case of lateral mobility or sliding, both advancing and receding contact lines are moving simultaneously, and the wettability (or contact area) of the drop remains unchanged.

Contrast to the common belief, both static contact angle and CAH are not in the recommendation list. We however feel that static contact angle will still be the most measured contact angle in the future owing to its simple measurement procedure. It can be used as a surrogate for the advancing contact angle to predict wettability as the two angles usually track very well. Very likely it will be used as a screening or quality-control tool in the surface development labs. Advancing, receding, and sliding angles will play a larger role in the future for in-depth surface characterization and wetting study.

As for CAH, it is neither predicting wettability nor adhesion and stickiness. Although the mechanism for CAH is better understood, significant work remains particularly its role in surface characterization and wetting.

8.3.2 Guidelines for Best Practices

Many pioneering surface researchers were aware of the importance of surface cleanliness and liquid purification to the quality of the contact angle data they were generating. Before the design of the first goniometer in 1960, many different apparatuses were used to measure the different contact angles. While instrumentation has continued to improve, the desire to improve the consistency and reliability of contact angle measurement continues. About 40 years ago, Good [30] called for the establishment of standardized protocols for contact angle measurements, and the call was not answered. In the following, a set of general guidelines are provided. We hope that this will stimulate a more serious conversation in the research community as well as the authority or leader(s) to answer Good's calling.

Static contact angle. We recommend the use of a 5-μL droplet for general routine testing. Goniometer should be placed on a vibration-free table in a temperature/humidity-controlled lab. The deposit of the liquid droplet should be as gentle as possible and allows time for the drop to reach the static state before drop profile is captured and analyzed. If necessary, video can be used to record the wetting process and confirm the waiting time. The entire measurement procedure should be repeated 5–10 times in fresh area each time to ensure procedural consistency and sample homogeneity.

If a volatile liquid is used, the measurement should be carried out in a close chamber. Smaller drop size may be required when testing with low surface tension, high-density liquids, or on super repellent surfaces, where drop shape distortion by gravity is known to occur.

Advancing/receding contact angle. Advancing and receding contact angle should be determined with the drop expansion/contraction method. Typically, the measurement starts with a small sessile droplet (~2 μL), and small amount of test liquid is added at a very slow rate, e.g., ~0.2 μL/s. The drop profile is captured as the drop is expanded up to ~20 μL. The flow of the test liquid is then reversed, and small amount of liquid is withdrawn through the needle at the same, slow rate (~0.2 μL/s). The contact angle during receding is captured and analyzed.

The use of the titling plate method to determine advancing and receding contact angle is not recommended. The technique is known to have a limited range and measurement with large hysteresis sample is erratic [31, 32].

Sliding angle. Sliding angle is determined by first placing a sessile droplet on a horizontal surface followed by tilting the surface very slowly (~1°μL/s) till the drop starts to slide. The driving force for drop sliding is gravity, and the measured angle is strongly dependent on the drop mass. Based on available literature data, we recommend sliding angle to be performed with drop volume ranging between 5 and 10 μL. This range appears to be the most sensitive region to acquire drop mobility information. It would be a misleading conclusion if one claims a surface sticky when a small drop, e.g., 1 μL, is used to determine the sliding angle. The same would be true if one claims a surface slippery when a very large drop is used to determine the sliding angle.

Documentation. We highly recommend authors to provide the following information when publishing their contact angle results in the literature: apparatus, drop volume, dispense procedure, ambient condition, and drop profile curve fitting software. For super repellent surfaces, sticky droplets or super slippery surfaces, it does not hurt to report the sessile drop images or supply videos in the supplemental information section. Transparency would provide a trustworthy environment, which should facilitate data exchange, stimulating communications and collaboration.

References

1. Young T (1805) An essay on the cohesion of fluids. Philos Trans R Soc Lond 95:65–87
2. Zisman WA (1964) Relation of the equilibrium contact angle to liquid and solid constitution. In: Fowkes F (ed) Contact angle, wettability, and adhesion, advances in chemistry. American Chemical Society, Washington, DC, pp 1–51
3. Dupre A (1869) Theorie Mechanique de la Chaleur. Gauthier-Villars, Pairs, p 369
4. Gibbs JW (1928) Trans Connecticut Acad Arts Sci 1876–1878, 3; “Collected Works”, vol. 1. Longmans, Green, New York
5. Rayleigh L (1890) On the tension of water surfaces, clean and contaminated, investigated by the method of ripples. Lond Edinb Dublin Philos Mag J Sci 30:386–400
6. Pease DC (1945) The significance of the contact angle in relation to the solid surface. J Phys Chem 49:107–110
7. Macdougall G, Ockrent C (1942) Surface energy relations in liquid/solid systems. 1. The adhesion of liquids to solids and a new method of determining the surface tension of liquids. Proc R Soc Lond A 180:151–173
8. Bartell FE, Hatch GB (1934) Wetting characteristics of galena. J Phys Chem 39:11–24
9. Bartell FE, Wooley AD (1933) Solid-liquid-air contact angles and their dependence upon the surface condition of the solid. J Am Chem Soc 55:3518–3527
10. Johnson RE (1959) Conflicts between Gibbsian thermodynamics and recent treatments of interfacial energies in solid-liquid-vapor systems. J Phys Chem 63:1655–1658

11. Cwikel D, Zhao Q, Liu C, Su X, Marmur A (2010) Comparing contact angle measurements and surface tension assessments of solid surfaces. Langmuir 26:15289–15294
12. Meiron TS, Marmur A, Saguy IS (2004) Contact angle measurement on rough surfaces. J Colloid Interface Sci 274:637–644
13. Della Volpe C, Maniglio D, Morra M, Siboni S (2002) The determination of a 'stable-equilibrium' contact angle on a heterogeneous and rough surfaces. Colloid Surf A Physicochem Eng Asp 206:47–67
14. Mettu S, Chaudhury MK (2010) Stochastic relaxation of the contact line of a water droplet on a solid substrate subjected to white noise vibration: role of hysteresis. Langmuir 26:8131–8140
15. Joanny JF, de Gennes PG (1984) A model for contact angle hysteresis. J Chem Phys 81:552–561
16. Johnson RE, Dettre RH (1964) Contact angle hysteresis 1. Study of an idealized rough surfaces. In: Fowkes F (ed) Contact angle, wettability, and adhesion, advances in chemistry. American Chemical Society, Washington, DC, pp 112–135
17. Neumann AW, Good RJ (1972) Thermodynamic of contact angles 1. Heterogeneous solid surfaces. J Colloid Interface Sci 38:341–358
18. Chen YL, Helm CA, Israelachville JN (1991) Molecular mechanisms associated with adhesion and contact angle hysteresis of monolayer surfaces. J Phys Chem 95:10736–10747
19. Extrand CW, Kumagai Y (1997) An experimental study of contact angle hysteresis. J Colloid Interface Sci 191:378–383
20. Wenzel RN (1936) Resistance of solid surfaces to wetting by water. Ind Eng Chem 28:988–994
21. Cassie ABD, Baxter S (1944) Wettability of porous surfaces. Trans Faraday Soc 40:546–551
22. Forsberg PSH, Priest C, Brinkmann M, Sedev R, Ralston J (2010) Contact line pinning on microstructured surfaces for liquids in the Wenzel state. Langmuir 26:860–865
23. Kanungo M, Mettu S, Law KY, Daniel S (2014) Effect of roughness geometry on wetting and dewetting of rough PDMS surfaces. Langmuir 30:7358–7368
24. Choi W, Tuteja A, Mabry JM, Cohen RE, McKinley GH (2009) A modified Cassie-Baxter relationship to explain contact angle hysteresis and anisotropy on non-wetting surfaces. J Colloid Interface Sci 339:208–216
25. Nosonovsky M (2007) On the range of applicability of the Wenzel and Cassie equations. Langmuir 23:9919–9920
26. Samuel B, Zhao H, Law KY (2011) Study of wetting and adhesion interactions between water and various polymer and superhydrophobic surfaces. J Phys Chem C 115:14852–14861
27. Roach P, Shirtcliffe NJ, Newton MI (2008) Progress in superhydrophobic surface development. Soft Matter 4:224–240
28. Law KY (2014) Definitions for hydrophilicity, hydrophobicity, and superhydrophobicity: getting the basic right. J Phys Chem Lett 5:686–688
29. Law KY (2015) Water interactions and definitions for hydrophilicity, hydrophobicity, and superhydrophobicity. Pure Appl Chem 87(8):759–765
30. Good RJ (1977) Surface free energy of solids and liquids. Thermodynamics, molecular forces, and structures. J Colloid Interface Sci 59:398–419
31. Krasovitski B, Marmur A (2005) Drops down the hill. Theoretical study of limiting contact angles and the hysteresis range on a tilted plate. Langmuir 21:3881–3885
32. Pierce E, Carmona FJ, Amirfazli A (2008) Understanding of sliding and contact angle results in tilted plate experiments. Colloids Surf A Physicochem Eng Asp 323:73–82