Wetting and Superhydrophobicity†

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Received August 15, 2009. Revised Manuscript Received August 27, 2009

This article is written to serve as an introduction to the topic of “Wetting and Superhydrophobicity” and to give some perspective for the papers that follow. This area of research that impacts and overlaps many fields of science and technology has been identifiable for centuries, but has gained considerable traction in the past decade.

The field of science known as “wetting” (limiting it to the wetting of solids by liquids) is central to innumerable natural processes as well as many human-derived (invented, caused, manufactured) technologies. These could be put into an endless list that would include life-essential, useful, beautiful, exciting, and even dangerous items. This list could include the growing number of studies of solid life forms (examples are beautiful insect wings and plant leaves) that evolved on earth both requiring and needing protection from the earth’s liquid (water). It could also include intricate fluidics devices, efficient condensers, photoresists on silicon, house paint, nonfogging bathroom mirrors, biomimetic models of various body parts, lethal solutions that can penetrate the protective layers of pests, and treated surfaces of heat-seeking missile optics. This field overlaps, intersects or impacts in some way, every field of science and every technology.

Over the past decade, the field of wetting has gained renewed interest in large part due to what has become known as superhydrophobicity. We leave the definition of this term for discussion by others; however, extreme water repellency is a sufficient description for these introductory remarks. Evidence for this renewed interest is shown in Figure 1, which plots annual citations of the two seminal publications on extreme hydrophobicity: the 1936 paper1 of Wenzel that explains how roughness can contribute to hydrophobicity, and the 1944 paper2 of Cassie and Baxter that shows that porous surfaces (functioning as surface mixtures of solid and air) can impart superhydrophobicity. The impressive increase in citation rates of these two papers over the past 10 years is due to numerous key reports during this period that helped accelerate interest, but two early reports stand out as being particularly influential. The 1996 Langmuir paper3 by Onda et al. (this issue of the journal featured a cover showing a photograph of a surface supporting a near-180° sessile water drop) and the 1997 Planta paper4 by Barthlott and Neinhuis that coined the term “lotus effect” should be acknowledged for activating much of the interest in wetting demonstrated by Figure 1. Studies on what now would be called superhydrophobicity were carried out prior to the mid-1990s and, indeed, prior to the Wenzel and Cassie & Baxter reports, but, relative to now and the recent years indicated in Figure 1, this area of research received only limited attention.5 6

To introduce the papers on wetting and superhydrophobicity that follow this article and as well to contribute to the perspective that this group of papers gives to this field of research in 2009, we have one goal in particular: to refer the reader to several perspectives of this field that others have had at certain points in time over the past ~200 years and trace a line of history that begins in 1804 and is ongoing today. The particular points in time and the papers we reference here were chosen to lead the post-2009 reader to these sources for appreciation of additional and different perspectives.

1804. Quoting Good,7 “most surface and colloid chemists think of Thomas Young as the father of scientific research on contact angles and wetting.” Good briefly reviews earlier contributions to wetting mentioning Aristotle, Archimedes, and Galileo. Young was a genius and polymath who lived at the turn of the 18th to the 19th century.8 He was a physician who made major contributions to vision, physiology, sound, light, language, solid mechanics, and Egyptology. He also dabbled in many things, and, one of these, the cohesion of fluids, led to research and analysis that was presented in an essay read to the Royal Society in 1804 and published in 1805.9

In the second paragraph of his essay, Young makes the following comment:

“But it is necessary to premise one observation, which appears to be new, and which is equally consistent with theory and experiment; that is, that for each combination of a solid and a fluid, there is an appropriate angle of contact between the surfaces of the fluid, exposed to the air, and to the solid.”

†Part of the “Langmuir 25th Year: Wetting and superhydrophobicity” special issue.
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(7) This quotation is taken from Good, R. J. J. Adhes. Sci. Technol. 1992, 6, 1269.
(9) Young, T. Philos. Trans. R. Soc. London 1805, 95, 65. This essay has been digitized and is available at www.google.com/books.
This was the first description of what we now refer to as contact angle. He goes on in his essay to examine this observation in incredible (even for today) detail and makes his genius obvious. Young did not know about atomic or molecular structure, chemical bonding, dipoles, molecular interactions, or thermodynamics. Gibbs, Helmholtz, and van der Waals were not yet born. Young viewed a liquid as a collection of particles that attract one another giving rise to a “uniform tension of the surface.” What is now understood as surface tension was known to Young and he attributes it to Segner (1751) in his essay and makes the point, “Since the time of Segner, little has been done in investigating accurately and in detail the various consequences of the principle.” Young’s perspective involving particles with short-range attractive forces is shown in Figure 2. The nature of the cohesive forces between particles (molecules) would not be known until the next century, but Young understood that the “cohesion of superficial particles” at the surfaces of the liquid (Figure 2a) and solid (Figure 2b), and the common surface of the solid and liquid (Figure 2c) give rise to forces that balance to give an “appropriate angle of contact” between the liquid and solid. Young did not write an equation, but states clearly, using the word “force”, what others have expressed in equation form (eq 1) as the balance of forces due to the cohesion of superficial particles

\[ F_{SV} = F_{LV} \cos \theta + F_{SL} \]  

(1)

at the three interfaces \((F_{SV}, F_{LV}, \text{and} F_{SL})\). Young also made the following statement in the second-to-last paragraph of his essay:

“it may be assumed as consonant both to theory and to observation, that the contractile force of the common surface of two substances, is proportional, other things being equal, to the difference of their densities.”

Equating surface forces with density shows the depth of Young’s instinct. He did not know of nuclei, protons, neutrons, or atomic weight and of course he did not know about low surface tension perfluoroalkanes, silicones, or polar interactions between liquids and solids. He assumed that dense substances must have very strong attractive forces between their particles. This simple and naive (three-dimensional (3D) density) perspective of Young is worth considering today and leads to obvious suggestions that are worthy of consideration for experiment: When contacting air, a water drop makes a contact angle of 180°. Young’s perspective would lead to the belief that a solid with a density the same as that of air would also exhibit a contact angle of 180°. With the right surface chemistry, this is likely very close to the truth. This suggests that hydrophobic aerogels (that can have densities of a few milligrams per cubic centimeter) should be superhydrophobic (air has a density of ~1 mg/cm³). If Young’s perspective is focused to a surface region, we can make statements such as “Water repellency is inversely proportional to the density of the outermost nanometer of a solid.” This focused Young’s perspective may be more useful to some than modern theories (it is certainly simpler).

Young has often been criticized for his lack of detailed experimentation, and it is often unclear from his writing whether or not an experiment had actually been performed. We note that he does not mention anything concerning reproducibility, error, or method of measurement of “an appropriate angle of contact” for any solid/liquid pair, and he certainly did not observe that static contact angles are irreproducible while advancing and receding contact angles can be measured precisely and reproducibly. His tacit assumption that there is no contact angle hysteresis suggests that he did not make many measurements. Independent of any experiments that he may or may not have carried out, however, his insight into wetting is clear and still applicable after more than 200 years. The qualifications that he makes in his writing (that “cover” his claims - even to readers two centuries later) are worthy of note and we have given two examples in the indented statements above: In the first he says with regard to an appropriate angle of contact, “equally consistent with theory and experiment.” He does not state that it is consistent with either or that no theory or experiment had yet been reported. In the second he says with regard to density differences, “other things being equal,” when he could not have known what these other things were. It is important to realize that the perspective of wetting that
Young had was many decades before the development of thermodynamics. The concepts of energy and work were not available; Carnot was 8 years old.

1948. This year was chosen because a Faraday Discussion on “Interaction of Water and Porous Materials” was held from 31 March to 2 April of that year at University College in Southampton. This discussion is recorded as Volume 3 of the Discussions of the Faraday Society. These 294 pages, which are not available digitally, offer a broad, deep, and scholarly perspective on wetting. Papers were submitted for sessions on Fundamental Aspects, Botanical Aspects, Zoological Aspects, and Textiles and Fibrous Materials. There was even a discussion on Oleophobic Surfaces, although no papers were submitted for discussion. The reading of this volume is an advisable prerequisite to working in the field of wetting and superhydrophobicity.

Much had happened between 1804 and 1948; in particular, Helmholtz (1821–1894) and Gibbs (1839–1903) both were born and died, thermodynamics was invented, and wetting was viewed from the perspective of surface and interface energy (areas: two-dimensional (2D)) rather than from the perspectives of density (3D) and particle cohesion that Young had. The first industrial scientist (Langmuir) received a Nobel Prize in Chemistry in 1932 for “Surface Chemistry”, and his work supported this 2D perspective. Professor N.K. Adam, the author of the then well-known textbook, The Physics and Chemistry of Surfaces, presented the Introductory Paper titled Contact Angles. These papers review capillarity and wetting and the contributions that Wenzel1 and Cassie and Baxter2 made to the understanding of rough and composite surface wetting. Cassie expresses Young’s statement with respect to contact angle in equation form (eq 2) and makes the following statement:

“Eqn (2) shows that the cosine of the contact angle gives the ratio of the energy gained in forming unit area of the solid–liquid interface to that required to form unit area of the liquid–air interface. It should be emphasized that (2) is a geometrical relation, and the unit areas are plane geometrical areas.”

Cassie goes on to discuss Wenzel’s and Cassie and Baxter’s extensions of eq 2 in terms of area and energy. This 2D perspective, that interfacial free energies control contact angle, is abundantly demonstrated throughout the 1948 Faraday Discussion. Indeed, the citations indicated in Figure 1 show that this perspective has had a powerful influence on recent researchers. Noticeably absent (at least in retrospect) from this discussion is the 1945 paper by Pease3 that suggests that contact angle is determined by structure and events at the contact line. In Pease’s summary, he states, “It is emphasized that the junction of the air–liquid interface with the solid surface is fundamentally a one-dimensional system.” Pease’s paper was not cited until 1964. Gao and McCarthy address the issue of one-dimensional (1D) versus 2D perspectives in their contribution to this Special Edition.

\[ \cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \] (2)

Unlike Young’s perspective, researchers in 1948 were well aware of contact angle hysteresis and receding contact angles and much general discussion is recorded.16 Their confusion is demonstrated in a section of Cassie’s paper titled “The Problem of Receding Contact Angles” in which he states:

“The instability of receding contact angles is the real bar to progress in the theory of water repellency, and it may be worthwhile discussing once again the problem of the difference between the advancing and receding angles.”

In a paper presented in the Textiles and Fibrous Materials section, Robinson reports using a method (on leather) recommended by Baxter and Cassie17 to test water repellency of yarns that involves measuring the “rate of fall of the apparent receding contact angle with time.”

A significant depth of scholarship is apparent in the 1948 perspective on wetting, as evidenced by the presentations in the Botanical and Zoological Aspects sessions. The trademarked “lotus effect” that we refer to today was understood in detail in 1948. Fogg19 presented advancing contact angle data on four different plant leaves before and after benzene or ether extraction and on cast films of the extracted substances. Crisp and Thorpe20 presented a detailed view of the physics of surface respiratory systems of numerous underwater insects. They show that the stability of the plastron (air layer) depends on the quantity, distribution, shape, and strength of hairs. They also demonstrate that the plastron can withstand greater hydrostatic pressure when the hairs are bent near their tips. Figure 3 that is taken from their paper is indicative of the detail of their studies.

1953. This date was chosen because of three papers published by Bartell this year. To appreciate the perspective and insight that Bartell had in 1953 to wetting...
superhydrophobicity requires reading a few more of Bartell’s papers. He published 94 papers from 1909 to 1957, and the majority of them would have been appropriate for Langmuir. Eighty-seven of his papers are in American Chemical Society journals, and we note that eight of them appeared in The Journal of Physical and Colloid Chemistry during the 4 years (1947–1950) that this was the name for The Journal of Physical Chemistry. To show that his insight into wetting was profound and that he had this insight long before 1953 and indeed before Wenzel’s publication, we quote from his 1932 paper,24 which discusses work he published in 1927:25

“The existence of advancing and of receding angles was well known, but it was assumed, at least by us, that either an advancing or a receding angle would, within a short time, so adjust itself as to give finally a definite equilibrium angle which would be the same whether approached from the advancing or the receding angle. We have since obtained good evidence that advancing angles and receding angles may each exist as definite, but different, equilibrium angles.”

The three 1953 papers21–23 are titled “Surface Roughness as Related to Hysteresis of Contact Angle” (Parts I, II and III). These papers are well written, straightforward accounts of careful contact angle measurements made on paraffin surfaces that were machined to have pyramid-shaped asperities with different sizes, separations, and angles of inclination. The contact angle and hysteresis values measured are discussed using simple geometric analysis of contact line motion. Bartell saw no need to use Cassie’s analysis, no need to invoke thermodynamics or equilibrium, and disproved Wenzel’s theory by measuring contact angles of a puddle that was over a patch of pyramids. He states:

“The results of this experiment indicate that the contact angle and resultant drop shape are determined at the solid–liquid–air interface and that increasing the surface area beneath the drop by roughening does not alter the contact angle. One must conclude, therefore, that Wenzel’s modification of the Young Equation is not justified for roughness of a microscopic or macroscopic magnitude.”

Two of the surfaces that Bartell prepared (with 60° sloped pyramids) exhibited water contact angles of θA/θR = 158°/125° and θA/θR = 163°/122° and were described as follows:21 “On these surfaces water drops were exceptionally mobile and rolled freely over the surface on slight tilting.” Figure 4 is from the first of these three papers. The caption is identical to the one used in 1953; ϕ refers to the angle of inclination of the pyramid features that they studied.

1963–1968. This period of time was chosen because four monographs are available that are based on international symposia held during this timespan. The Kendall Award Symposium, sponsored by the Division of Colloid and Surface Chemistry and honoring W. A. Zisman, was held at the Los Angeles National ACS Meeting in April, 1963, and a monograph, Contact Angle, Wettability and Adhesion26 was published. The Division of Industrial and Engineering Chemistry held symposia at National ACS meetings in Washington, DC, in June 1964 and June 1968. Two monographs, Chemistry and Physics of Interfaces27 and Chemistry and Physics of Interfaces II,28 were published. A meeting of the Society of Chemical Industry at the University of

Figure 4. On a fibrillar surface, ϕ would have a value of 90°, and, if the stable contact angle were 90° or greater, one would observe an apparent contact angle of approximately 180°. As a result, the water would not penetrate beneath the exterior surface, and air would be entrapped beneath the drop. Reprinted with permission from ref 21.

Bristol in September 1966 led to the monograph Wetting.29 These books show that the perspective of the field of wetting at that time was very mathematical and that contact angle measurements were primarily being used to derive thermodynamic information about solids. A single, “surface energy” parameter was desired. Zisman developed an empirical wetting parameter, critical surface energy (γc), and Good and Fowkes proposed that interfacial tension could be broken into components such as polar and dispersive or dispersive and acid–base. There are multiple papers by these authors in these monographs. In a paper by Adamson and Ling in ref 26 titled “The Status of Contact Angle as a Thermodynamic Property”, an interesting, important, and most often ignored conclusion was made: “In the usual circumstance of solids not near their melting point, these interfaces will not be equilibrium ones, so it appears operationally meaningless even to apply the term of surface free energy to them.”

During this period there was little interest in superhydrophobicity, with the exception of a five-part series of papers by Johnson and Dettre. Parts I and II are in ref 26, Part V is in ref 29, and Parts III and IV were published as journal articles.30,31 They performed calculations on surfaces with idealized roughness and showed that energy barriers between metastable drop states determine the magnitude of contact angle hysteresis. They also reported experimental data on both randomly rough surfaces and patterned surfaces. Figure 5 shows a figure reproduced from Part V of the series of papers. Fluoropolymer surfaces of the structures indicated as E and F in the figure exhibited advancing and receding contact angles over 160°. It is clear from this figure that Johnson and Dettre, in 1965, were wrestling with issues of superhydrophobicity that are being readressed after more than 40 years.

1992. This date is included because another monograph32 was published based on a Symposium honoring R. J. Good.

sponsored by the Division of Colloid and Surface Chemistry, at the National ACS meeting in San Francisco in April, 1992. This symposium and monograph have the same title, Contact Angle, Wettability and Adhesion, that was used in 1963 to honor W. A. Zisman. There is much to contrast between 1963 and 1992 and between these two volumes with the same name. We make only three related points: (1) During these 29 years, X-ray photoelectron spectroscopy became the quantitative technique to assess surfaces and contact angle measurements were down-played. (2) Good, in the first paper7 of this symposium (and on page 10 of the monograph), urges investigators of contact angles to measure both advancing and receding angles. He says with regard to a sessile drop measurement, “Obviously, such an angle will be of a lower degree of scientific usefulness than will a true $\theta_A$ or $\theta_R$.” There are numerous examples in this monograph of where receding contact angles were not measured and where data were just identified as “contact angles.” (3) During the 1980s, self-assembled monolayers (SAMs), very similar to those prepared by Zisman in the 1950s, were developed by Sagiv,33 Nuzzo,34 and Whitesides,35 and these developments have had a profound impact on surface chemistry and indeed the content of Langmuir. Zisman developed methods for careful advancing and receding contact angle analysis of SAMs because this was the only technique he had at his disposal. The 1980s groups had more sophisticated analytical methods and did not choose to measure receding contact angles.

1996–2009. There are recent reviews5,36–40 on wetting and superhydrophobicity that indicate that this field is alive, healthy, and growing. We have chosen to outline historical perspectives to be tactily self-critical of our “field” that has developed since refs 3 and 4 catalyzed renewed interest in wetting. We note that neither ref 3 nor ref 4 report advancing or receding contact angles. Our critical tone should not be confused with a lack of optimism. The growth indicated by Figure 1 has been and is exciting, even if the theories in these papers cited are fundamentally flawed. The field has grown so fast that it will take time for it to catch up with all the things that happened before it began, but it will. Even the terminology has moved too fast to keep up with. Reference 37 states “At this stage there are many reports using whatever terminology comes to mind, making it unclear exactly what kind of surface is being dealt with,” and “There are therefore many categories of surface where roughness enhances contact angle and not enough official names to define them.” This certainly sounds like an exciting and dynamic area of research, and it is. The papers that follow this one are only “snapshots” of a broad, interdisciplinary, and worldwide field that spans fundamental theoretical and experimental physics (see the papers of McCarthy, Neumann, Amirfazli, Erbil, and Bhushan), many disciplines of chemistry (see the papers of Theato and Matar), biology (botany and zoology; see the papers of Koch and Shirtcliffe), and materials science (see the papers of Jiang, Chen, Han, and Nakajima).

Acknowledgment. L.G. and T.J.M. thank the NSF-sponsored Center for Hierarchical Manufacturing (CMMI-0531171) and Materials Research Science and Engineering Center (DMR-0213695) at the University of Massachusetts. X.Z. thanks the National Basic Research Program (2007CB808000) for financial support.

Figure 5. Surface configurations for several porous surfaces. Reprinted with permission from ref 29.

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<td>1989</td>
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<td>2006</td>
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<td>Capillary and Wetting Phenomena</td>
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