Chapter 1
Background

Abstract Studies of surface and liquid–solid interaction have always been an important branch of science, and its role just increases exponentially due to the expanded application of digital printing. To date, due to the on-demand nature of ink printing, it has become a manufacturing technology for many current and futuristic electronic devices, such as display, printed electronics, and wearable and flexible devices. Research on surface has always been messy, however. Debates and rigorous discussion on the Young's contact angle, measurement procedures, and data interpretation have been ongoing in the surface literature for many decades. In this chapter, the justification of writing this book is described. The shortfalls in surface science are briefly overviewed. A roadmap that systematically addresses fundamental issues on measurements, basic concepts in wetting and surface characterization, and definitions and terminologies is provided throughout this book. It is our hope that this collection of surface fundamentals will improve readers' basic understanding of all the key concepts, which will eventually enhance the quality of surface research in the future.

Keywords Surface • Young's equation • Contact angle • Wetting • Liquid–solid interaction • Young's angle • Contact angle measurement • Data interpretation

Surface is a very important branch of science that touches all facets of our lives. Fundamental understanding of the interactions between a liquid droplet and a solid surface, such as wetting, spreading, adhesion, and de-wetting, is not only crucial to the science itself, but also of tremendous values to many seemingly unrelated applications. In our daily activities such as cleaning and washing, surface active materials known as detergents are commonly used to aid detachments of dirt and stain from a solid surface initiating the cleaning process. Although we have been taken the process for granted, there is a lot of science involved in washing and cleaning, e.g., the type of detergent used, its efficiency, cost, and the impact to human and environment. Even as simple as ink writing with a fountain pen, Kim and co-workers [1] found that the line width of the ink image on paper depends on the speed of the pen as well as the physicochemical properties of both ink and paper. Controlling ink wetting and spreading is crucial in avoiding clogging and ink spreading. Similarly, mastering and controlling liquid–solid interactions have become critical skills in many industries, such as in the design and manufacturing of paints, stain/

K.-Y. Law, H. Zhao, *Surface Wetting*, DOI 10.1007/978-3-319-25214-8_1

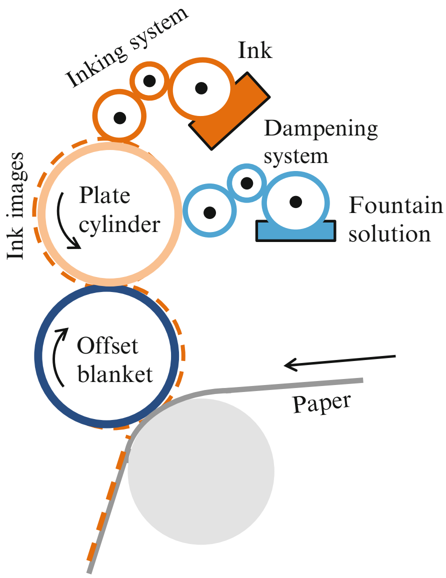

Fig. 1.1 A schematic of the offset printing process

soil-resistant textiles and clothing, anticorrosion surfaces for bridges and other metal structures, antifouling coatings for ships and marine structures, anti-icing surfaces for power line, airplane and roof-top, mining, and petroleum fracking. Whether it is surface design or process development, knowledge in manipulating liquid–surface interaction in the "right" place at the "right" time is imperative in microfluidic device [2, 3], oil/fluid transportation [4], and printing and coating [5, 6], just to name a few. In printing, understanding the wetting and de-wetting of ink on different printing surfaces is critical to the quality of the final print. As a society, we have been practicing offset printing for more than a century, and the entire print process is a good illustration on the importance of ink–surface interaction [7]. A schematic for the offset printing process is shown in Fig. 1.1.

In a very simple term, the offset printing process involves (1) wetting of the plate cylinder with a fountain solution image wise through the dampening system, followed by (2) inking the plate cylinder with the inking system, (3) transfer of the ink image from the plate cylinder to an offset blanket, and (4) fixing it on paper. In the first step, the desirable outcome is to have the fountain solution first wets and then pins on the surface of the plate cylinder. While wetting is required for the formation of the wetted images, a successful pinning of the contact line on the plate cylinder is needed to ensure image integrity and resolution control. Offset inks are acrylate materials, and they will be repelled by areas that are wetted with the fountain solution. On the other hand, ink will be attracted and adhered to the oleophilic areas on the plate cylinder surface. Controlling ink adhesion in the oleophilic region and repelling it from the fountain solution wetted areas are critical to the image quality of the output. Afterward, the transfer of the ink image to the offset blanket and then paper is more straightforward as these surfaces are selected based on their relative affinity to the ink materials. Although printing (on papers) is an industry in decline, printing has evolved and has become a manufacturing technology for printed electronics, flexible and wearable devices, ceramics, textiles, solar cells, and many others [8–20]. Arias et al. [19] showed that balance between pinning and overspreading of printed liquid ink on the solid surface is very important in defining the position, resolution, and size in the fabrication of thin-film-transistor array. Jetted ink drop is also known to form the so-called coffee ring stain due to un-optimized spreading and drying, which is detrimental to the quality of the printed image and ultimately the performance of the printed device [21]. The need of characterizing surfaces and understanding liquid–surface interaction continues to play a critical role in the modern technology arena [8].

Studies of surface and liquid–surface interaction can be traced back to Thomas Young's work two centuries ago [22]. In his legendary article entitled "An Essay on the Cohesion of Fluids," he described his study of wetting of glass by water and mercury, wetting of various metal surfaces by mercury and the capillary effect. He descriptively stated that the angle of contact between a liquid on a solid surface is the result of a mechanical equilibrium among the three surface tensions at the contact line. They are the liquid, solid and liquid–solid interfacial surface tensions. This has become the famous Young's equation in the literature. Today, surface is a multidiscipline subject and is studied by chemists, physicists, and engineers both theoretically and experimentally worldwide. Research topics range from fundamental understanding of the wetting, spreading, adhesion, and de-wetting phenomena to their applications in materials, surface coatings, and device innovations. Unfortunately, there have been continuous confusion and faulty intuition about the measurements, data interpretation, and definitions in the surface literature. One of the reasons is due to the multidiscipline nature in this field, where researchers with a very diverse background are investigating surfaces together. Another reason, which was pointed out by Gao and McCarthy, is their insufficient basic surface training in school [23, 24]. This flaw in surface science has been recognized by expert researchers. In 2009, Gao and McCarthy published an excellent article titled "Wetting 101°" where they discussed the faulty perception and used demonstrative examples to illustrate the correct basic concepts [24]. While we are certainly benefitted from the article and references therein, the faulty perception and confusion are continuing unfortunately.

Contact angle measurement is commonly used to characterize a surface and to study various wetting and de-wetting phenomena. While the measurement is simple, the interpretation is not. This point has been noted by many surface investigators in the past, e.g., Pease in 1945 [25], Morra et al. [26] in 1990, Kwok and Neumann [27] in 1999 and more recently by Marmur [28] as well as Strobel and Lyons [29]. Prior to data interpretation, one has to make sure that the measurement apparatus and procedures are impeccable. Over the years, many have voiced concerns over surface preparation and conditioning, measurement procedure and technique, and data analysis [26, 30–35]. It is therefore imperative for the community to have a set of common measurement protocol or guideline, so that inter laboratory data can be compared. Discrepancy in conclusion can be rationalized without concerns of experimental setups or procedures.

In view of the ongoing discussions on measurement procedures, data interpretation, terminologies, and definitions, the surface community would be benefitted for an overview of the past conversations and a recent account of the resolution. The objective of this book is to provide a coherent, easy to understand, fundamental picture on surface wetting and characterization. In Chap. 2, we first summarize the best practices in static and dynamic contact angle measurements. This may be served as a standard protocol for surface researchers and practitioners in the future. From there, data collected in different laboratories can be compared without casting doubt to each other. Some of the fundamental measurement issues, such as drop size, drop dispensing procedure, lab ambient condition (temperature and relative humidity), and method of calculating the contact angle will be discussed. This is followed by discussions of the concept of wetting, first on smooth surfaces in Chap. 3 and then on rough surfaces in Chap. 4. Important concepts such as (1) the Young's angle is a result of a mechanical equilibrium, not thermodynamic equilibrium, at the three phase contact line, (2) the liquid droplets are all in their metastable states in their static, advancing and receding positions, and (3) contact line, not contact area determines the contact angle, will be articulated with conclusions that are supported by both experimental and theoretical data. The rationale for the shortfall in both the Wenzel and Cassie–Baxter analysis of wetting on rough and porous surfaces is summarized. Recent results on factors that govern wettability and wetting dynamics of liquid on rough surfaces are overviewed. Visuals on the distortion of the contact line by surface roughness as well as the structure of the liquid–solid–air composite interfaces are reported. Chapter 4 also includes discussions on the design principles for superhydrophobic and superoleophobic surfaces as well as the challenges related to technology implementation.

Due to simplicity of the contact angle measurement, it has become a popular tool to characterize the property of a surface or probing liquid–solid interactions. However, the literature is full of conflicting information owing to the difficulty in correctly interpreting contact angle data. Chapter 5 is devoted to provide experimental data to shrine light into this specific issue. Evidence is provided that advancing and receding contact angles are measurement of surface wettability and adhesion, respectively. The stickiness of liquid on surface can be predicted from the sliding angle. A recommendation for surface characterization is provided. As for contact angle hysteresis, the difference between advancing and receding contact angle, it is shown to relate to adhesion and stickiness qualitatively only. More work is needed to clarify the origin of contact angle hysteresis as well as its role in surface characterization. As a fundamental book, it is hard not to discuss the "pains" we have in surface definitions and terminologies as well as early work on the use of contact angle to determine the surface energy of solid, where the practice and its usefulness have been constantly challenged. In Chaps. 6 and 7, updates on the definitions for hydrophilicity/hydrophobicity, oleophilicity/oleophobicity, and other related terminologies will be provided. The different methodologies used to determine surface energy will briefly be reviewed. Fundamental issues will be discussed, and a path to move forward is shared. We are not taking side in these discussions, rather updating the readers with the latest experimental data and the current status.

This book will conclude with a brief look back on the evolution of surface science, followed by a summary of some of the basic concepts as a reminder for new or young researchers in this field. It is our hope that surface science will prosper when researchers in the next-generation are armed with improved basic concepts and fundamentals.

References

1. Kim J, Moon MW, Lee KR, Mahadevan L, Kim HY (2011) Hydrodynamics of writing with ink. Phys Rev Lett 107:264501
2. Bruzewicz DA, Reches M, Whitesides GM (2008) Low-cost printing of PDMS barriers to define microchannels in paper. Anal Chem 80:3387–3392
3. Martinez AW, Phillips ST, Whitesides GM (2008) Three-dimensional microfluidic devices fabricated in layered paper and tape. Proc Natl Acad Sci U S A 105:19606–19611
4. Paso K, Kompalla T, Aske N, Ronningsen HD, Oye G, Sjoblom J (2009) Novel surfaces with applicability for preventing wax deposition: a review. J Dispersion Sci Technol 30:757–781
5. Katano Y, Tomono H, Nakajima T (1994) Surface property of polymer films with fluoroalkyl side chains. Macromolecules 27:2342–2344
6. 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
7. Dejidas LP Jr, Destree TM (2006) Sheetfed offset press operating, 3rd edn. PIA-GATF Press, Pittsburgh, Chapter 6
8. Perelaer J, Smith PJ, Mager D, Soltman D, Volkman SK, Subramanian V, Korvink JG, Schubert US (2010) Printed electronics: the challenges involved in printing devices, interconnects, and contacts based on inorganic materials. J Mater Chem 20:8446–8453
9. Zielke D, Hubler AC, Hahn U, Brandt N, Bartzsch M (2005) Polymer-based organic field-effect transistor using off-set printed source-drain structures. Appl Phys Lett 87:123508
10. Kang B, Lee WH, Cho K (2013) Recent advances in organic transistor printing processes. ACS Appl Mater Interfaces 5:2302–2315
11. Fukuda K, Sekine T, Kumake D, Tokito S (2013) Profile control of inkjet printed silver electrodes and their application to organic transistors. ACS Appl Mater Interfaces 5:3916–3920
12. Schuppert A, Thielen M, Reinhold J, Schmidt WA, Schoeller F, Osnabruck O (2011) Ink jet printing of conductive silver tracks from nanoparticle inks on mesoporous substrates. NIP27 and digital fabrication 2011. Technical Programs and Proceeding. pp 437–440
13. Wu Y (2011) Inkjet printed silver electrodes for organic thin film transistors. NIP27 and digital fabrication 2011. Technical Programs and Proceeding. pp 441–444
14. Zipperer D (2011) Printed electronic for flexible applications. NIP27 and digital fabrication 2011. Technical Programs and Proceeding. pp 452–453
15. Simske S, Aronoff JS, Duncan B (2011) Printed antennas for combined RFID and 2D barcodes. NIP27 and digital fabrication 2011. Technical Programs and Proceeding. pp 544–547
16. Sanz V, Bautista RY, Feliu C, Roig Y (2011) Technical evolution of ceramic tile digital decoration. NIP27 and digital fabrication 2011. Technical Programs and Proceeding. pp 532–536
17. Nossent KJ (2011) A breakthrough high speed wide format print concept for textile. NIP27 and digital fabrication 2011. Technical Programs and Proceeding. p 556
18. Huson D (2011) 3D printing of ceramics for design concept molding. NIP27 and digital fabrication 2011. Technical Programs and Proceeding. pp 815–818
19. Arias AC, Mackenzie JD, McCulloch I, Pivnay J, Salleo A (2010) Materials and applications for large area electronics: solution-based approaches. Chem Rev 110:3–24
20. Habas SE, Platt HAS, van Hest MFAM, Ginley DS (2010) Low-cost inorganic solar cells: from ink to printed devices. Chem Rev 110:6571–6594

21. Deegan RD, Bakajin O, Dupont TF, Huber G, Nagel SR, Witter TA (1997) Capillary flow as the cause of ring stains from dried liquid drops. Nature 389:827–829
22. Young T (1805) An essay on the cohesion of fluids. Phil Trans R Soc London 95:65–87
23. Gao LC, McCarthy TJ (2009) An attempt to correct the faulty intuition perpetuated by the Wenzel and Cassie "Laws". Langmuir 25:7249–7255
24. Gao LC, McCarthy TJ (2009) Wetting 101°. Langmuir 25:14105–14115
25. Pease DC (1945) The significance of the contact angle in relation to the solid surface. J Phys Chem 49:107–110
26. Morra M, Occhiello E, Garbossi F (1990) Knowledge about polymer surfaces from contact angle measurements. Adv Colloid Interface Sci 32:79–116
27. Kwok DY, Neumann AW (1999) Contact angle measurement and contact angle interpretation. Adv Colloid Interfacial Sci 81:167–249
28. Marmur A (2006) Soft contact. Measurement and interpretation of contact angles. Soft Matter 2:12–17
29. Strobel M, Lyons SL (2011) An essay on contact angle measurements. Plasma Process Polym 8:8–13
30. 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
31. Bartell FE, Hatch GB (1934) Wetting characteristics of galena. J Phys Chem 39:11–24
32. Fox HW, Zisman WA (1950) The spreading of liquids on low energy surfaces. 1. Polytetrafluoroethylene. J Colloid Sci 5:514–531
33. Good RJ (1977) Free energy of solids and liquids: thermodynamics, molecular forces, and structure. J Colloid Interface Sci 59:398–419
34. Decker EL, Frank B, Suo Y, Garoff S (1999) Physics of contact angle measurement. Colloids Surf A 156:177–189
35. Drelich J (2013) Guidelines to measurements of predictable contact angles using a sessile-drop technique. Surf Innov 1:248–254