Advances in Colloid and Interface Science 222 (2015) 92–103

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

journal homepage: www.elsevier.com/locate/cis

Historical perspective

Progress in understanding wetting transitions on rough surfaces

Edward Bormashenko [1]

Ariel University, Physics Faculty, P.O.B. 3, Ariel 40700, Israel

ARTICLE INFO

Available online 17 February 2014

Keywords:
Rough surfaces
Apparent contact angle
Wetting states
Cassie wetting
Wenzel wetting
Superhydrophobicity
Wetting transitions

ABSTRACT

The abrupt change in the apparent contact angle occurring on a rough surface is called wetting transition. This change may be spontaneous or promoted by external stimuli such as pressure or vibration. Understanding the physical mechanism of wetting transitions is crucial for the design of highly stable superhydrophobic and omniphobic materials. Wetting regimes occurring on rough surfaces are introduced. Experimental methods of study of wetting transitions are reviewed. Physical mechanisms of wetting transitions on rough surfaces are discussed. Time and energy scaling of wetting transitions are addressed. The problem of the stability of Cassie wetting on inherently hydrophobic and hydrophilic surfaces is discussed. The origin and value of a barrier separating the Cassie and Wenzel wetting states are treated in detail. Hierarchical roughness increases the value of the energy barrier. The stability of Cassie wetting observed on re-entrant topographies is explained. The irreversibility of wetting transitions is explained, based on the asymmetry of the energy barrier, which is low from the side of the metastable (higher-energy) state and high from the side of the stable state. The critical pressure necessary for a wetting transition is introduced. The problem of "dimension" of wetting transition is discussed. Reducing the micro-structural scales enlarges the threshold pressure of a wetting transition. The roles of gravity and air compressibility in wetting transitions are treated. The dynamics of wetting transitions is reviewed. The results of molecular simulations of wetting transitions are presented. The trends of future investigations are envisaged.

Contents

1. Introduction

The discovery of natural surfaces demonstrating pronounced water repellence (the so-called "lotus effect" or superhydrophobicity) stimulated extended theoretical and experimental research of wetting

---

E-mail address: edward@ariel.ac.il.

[1] Tel.: +972 3 9066134; fax: +972 3 9066621.

http://dx.doi.org/10.1016/j.cis.2014.02.009
0001-8686/© 2014 Elsevier B.V. All rights reserved.

phenomena occurring on rough surfaces [1,2]. The group led by Professor Barthlott discovered the extreme water repellency and unusual self-cleaning properties of the “sacred lotus” (*Nelumbo nucifera*) and coined the notion of the “lotus effect”, which is now one of the most studied phenomena in surface science [1,2]. Afterwards, the same group studied a diversity of plants and revealed a deep correlation between the surface roughness of plants, their surface composition and their wetting properties (varying from superhydrophobicity to superhydrophilicity) [3].

Superhydrophobic properties demonstrate plants, birds' wings, legs of water striders and other natural objects [4–10]. It is already well understood that certain kinds of hierarchically rough reliefs supply extreme water repellency (superhydrophobicity) to interfaces [11–18]. Much experimental effort was spent in mimicking natural superhydrophobic surfaces. This effort resulted in the manufacture of superhydrophobic and superoleophobic (also called “omniphobic”) surfaces [19–27]. It is already well understood that superhydrophobicity and superoleophobicity occur when the Cassie air-trapping heterogeneous wetting regime takes place for a liquid/solid pair [28–33].

The Cassie wetting regime is characterized by high apparent contact angles (the rigorous definition of an apparent contact angle, abbreviated as APCA, will supplied in the next Section), promoting easy sliding of droplets [34,35]. However, high APCAs are not sufficient for true superhydrophobicity: low contact angle hysteresis and high stability of the Cassie wetting regime are also necessary [33,36]. When the initial Cassie wetting state is not stable, the *wetting transition* (WT), namely the transition from the Cassie heterogeneous to the Wenzel homogeneous wetting, may occur [33,37]. This review is devoted to consolidating the understanding of WTs gained in the past decade. The understanding of the physics of WTs is crucial for the design of superhydrophobic and superoleophobic self-cleaning surfaces, giving rise to broad technological implications in areas related to water, energy, and health [21,38–40].

2. Contact angles and wetting states

We start from the partial wetting of *ideal* (atomically flat, chemically homogeneous, isotropic, insoluble, non-reactive and non-deformed) solid surfaces. The natural macroscopic parameter characterizing wetting is the contact angle θ, shown in Fig. 1. Wetting of *ideal* surfaces is characterized by the equilibrium or the Young angle θ_Y given by the well-known Young Equation [31–33,41]:

$$\cos\theta_Y = \frac{\gamma_{SA} - \gamma_{SL}}{\gamma}, \tag{1}$$

where γ, γ_{SL}, γ_{SA} are the surface tensions at the liquid/air, solid/liquid, and solid/air (vapor) interfaces, respectively. The line at which solid, liquid and gaseous phases meet is called the *triple* (or three phase) *line*. The behavior of the triple line (shown in Fig. 1) plays a crucial role in wetting phenomena. Eq. (1) was not written explicitly in the famous paper by Sir Th. Young [41], but Ref. [41] contained a statement that contact angle depends unambiguously on the triad of surface tensions: γ, γ_{SL}, γ_{SA}. In spite of its two-century history, the Young Equation was rigorously derived only recently [42–44]. In particular, it was demonstrated that Eq. (1) results from the transversality condition of the appropriate variational problem of wetting [44]. The Young contact angle is insensitive to the volume of a droplet and external fields, under very broad assumptions about the nature of these fields [44].

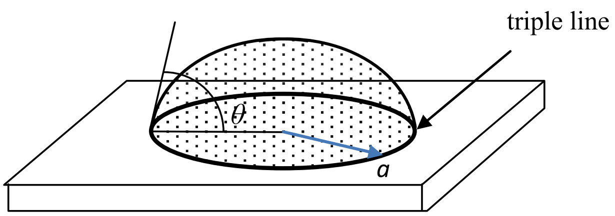

Fig. 1. A drop resting with a contact angle θ on a substrate, a is the contact radius.

When a droplet is small (typically micrometrically scaled and less) the effects of line tension become essential, and the contact angle is then given by the Neumann–Boruvka Equation:

$$\cos\theta_{NB} = \frac{\gamma_{SA} - \gamma_{SL}}{\gamma} - \frac{\Gamma}{\gamma a}, \tag{2}$$

where a is the contact radius of the droplet (see Fig. 1), and Γ is the line tension. In spite of the fact that the concept of line tension is intuitively clear, it remains one of the most obscure and disputable notions of the surface science [45]. The researchers disagree not only about the value of the line tension but also even about its sign [45]. Experimental values of a line tension Γ in the range of 10^{-5}–10^{-11} N were reported [45]. Very few methods allowing accurate experimental measurement of line tension were developed [46,47]. A. Marmur estimated a line tension as $\Gamma \cong 4 d_{\mathrm{m}} \sqrt{\gamma_{SA}\gamma}\cot\theta_Y$, where d_{m} is the molecular dimension. Marmur concluded that the magnitude of the line tension is less than $5 \cdot 10^{-9}$ N, and that it is positive for acute and negative for obtuse Young angles [48].

The contact angle of a droplet deposited on a solid surface depends on external parameters, such as temperature. Change in temperature may stimulate the transition from a partial wetting to a complete wetting of the solid substrate. In this case we observe a WT on a smooth solid surface [49,50].

The Young Equation supplies the sole value of a contact angle for a certain combination of solid, liquid and gaseous phases. Regrettably, the true experimental situation is much more complicated; even on atomically flat surfaces, a diversity of contact angles is observed. This is due to the long-range interaction between molecules forming the triple (three-phase) line of the droplet and molecules forming the solid substrate [51]. It was shown recently that the drop-surface attraction is time-dependent due to re-orientation of the molecules constituting the solid-substrate [51,52]. The phenomenon of contact angle hysteresis makes the Young angle, given by Eq. (1), an experimentally unattainable value for the majority of solid surfaces [33].

The maximal contact angle observed on a surface is called the advancing angle θ_{adv}; the minimal one is called the receding angle θ_{rec} [31–33,53–55]. The difference between advancing and receding contact angles $\theta_{\mathrm{adv}} - \theta_{\mathrm{rec}}$ is called the contact angle hysteresis [31–33,35]. A diversity of factors contributes to the contact angle hysteresis on flat surfaces, including deformation of the surfaces and water sorption [56,57]. Experimental establishment of advancing and receding angles is a challenging task, and it should be mentioned that reported contact angles are sensitive to the experimental technique used for their measurement [58–62]. The most problematic is the establishment of receding contact angles [59,62]. Actually, due to the contact angle hysteresis, we always observe the apparent and not the equilibrium (Young) contact angle [60,62,63]. And this is true even for atomically flat surfaces [62,63].

Wetting of rough and chemically heterogeneous surfaces is characterized by an apparent contact angle (APCA) which is defined as an equilibrium contact angle measured macroscopically [64]. The detailed microscopic topography of a rough or chemically heterogeneous surface cannot be viewed with regular optical means; therefore this contact angle is defined as the angle between the tangent to the liquid–vapor interface and the apparent solid surface as macroscopically observed [64].

Chemical heterogeneities and roughness strengthen the hysteresis of a contact angle [65–69]. Various models explaining the phenomenon of hysteresis were proposed [33,70–72]. The effect was related to pinning of the triple line by defects [67–70,73].

Wetting of flat, chemically heterogeneous surfaces is characterized by an APCA θ^* predicted by the Cassie–Baxter wetting model [28–33].