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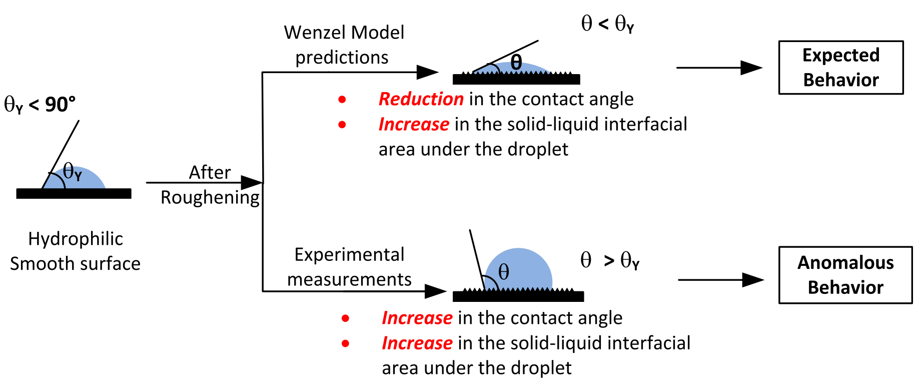
Regular Article

Understanding the wettability of rough surfaces using simultaneous optical and electrochemical analysis of sessile droplets

Beniamin Zahiri, Pradeep Kumar Sow, Chun Haow Kung, Walter Mérida *

Clean Energy Research Centre, The University of British Columbia, 6250 Applied Science Lane, Vancouver, BC V6T 1Z4, Canada

GRAPHICAL ABSTRACT



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ABSTRACT

The interaction of a droplet with a solid surface is characterized by two parameters, the contact angle and the wetted area under the droplet. The Cassie-Baxter and the Wenzel modes make predictions on the interfacial area by comparing the contact angles on smooth surfaces (the intrinsic wettability) with those on rough surfaces (the apparent wettability). In these models, the actual wetted area is used as a fitting parameter. In this work, we highlight the significance of determining the actual wetted area under the droplet and the limitation of using only the contact angle to represent the wetting behavior of a surface. Our experimental studies were performed on hydrophilic carbon surfaces where a combination of optical measurements (contact angle and hysteresis) along with an electrochemical approach was employed. An electrochemical method was used to determine the true wetted area using a droplet of aqueous electrolyte on the surface. The interfacial area was then used to correlate wetting behavior to that of the model predictions. We examined the impact of electrolyte concentration and potential sweep rate in our evaluation of the wetted area. Our results show that, for a rough hydrophilic surface, the decrease in contact angles with increasing solid-liquid interfacial areas is not always valid, as generally predicted by the Wenzel and the Cassie-Baxter models.

1. Introduction

The apparent contact angle of a droplet placed on a rough surface differs from that on a smooth surface and it depends on the type of solid-liquid (S-L) interface under the droplet. For a rough

* Corresponding author.
E-mail addresses: bzahiri@mech.ubc.ca (B. Zahiri), psow@mail.ubc.ca (P.K. Sow), chkung@chbe.ubc.ca (C.H. Kung), walter.merida@ubc.ca (W. Mérida).

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surface, the liquid can penetrate the roughness features leading to a fully wetted homogenous interface under the droplet, or the liquid phase can stay suspended on the roughness asperities leading to a composite solid-liquid-air interface. This solid-liquid interfacial interaction (induced by the roughness) determines the interfacial area under the droplet, which in turn, affects the apparent contact angle that can be described by the Cassie-Baxter or the Wenzel wetting equations.

Wenzel wetting corresponds to the homogenous interface under the droplet, mathematically represented as [1]

$$\cos\theta = r\cos\theta_Y \tag{1}$$

Conversely, for a composite interface, the Cassie-Baxter equation is used [2]:

$$\cos\theta = f_s(\cos\theta_Y + 1) - 1 \tag{2}$$

In the above equations, the apparent contact angle (CA) is denoted by θ and the Young CA is θ_Y. For the Cassie-Baxter equation, f_s is the ratio of S-L interfacial area to the total interfacial area. The parameter r in the Wenzel model corresponds to the ratio of S-L interfacial area to the projected interfacial area. Based on these equations, the contact angle is a function of the S-L interfacial area under the droplet. According to the Cassie-Baxter equation and for a hydrophilic surface with Young contact angle < 90°, the contact angle should increase with increasing surface roughness when the liquid is suspended on the roughness features. However, if the liquid penetrates the roughness features, according to the Wenzel model, the contact angle should become smaller. Recently, the dependence of the CA on the S-L interfacial area under the droplet predicted by the above equations has been the subject of intense debate [3–8], and the predictions from these equations can deviate from the experimental results [9,10]. However, determining the extent of these deviations still remains an open problem of general interest.

In the present work, we report an anomalous wetting behavior on rough hydrophilic surfaces by correlating the wetted area under the droplet to the apparent contact angle. Our results show that the Wenzel model is unable to predict either the magnitude or trend (increase or decrease) in the apparent contact angle for a rough surface. In particular, we observed an increase in the apparent contact angle along with the wetted area under the droplet for an intrinsically hydrophilic rough material. This observation contradicts the predictions from the Wenzel and the Cassie-Baxter equations. The anomaly addressed in this work is shown schematically in Fig. 1. This anomalous behavior was observed for multiple samples with irregular roughness features.

Conventionally, studies to determine the validity of the theoretical models have been performed on regularly patterned surfaces by taking advantage of the well-defined roughness features (which simplify analysis and modelling). The experimental protocol involves evaluating the dimensions of the roughness features followed by calculating the S-L interfacial area for the two conditions corresponding to the Wenzel and the Cassie-Baxter models. However, these protocols become impractical for studying the surfaces with irregular roughness due to the stochastic nature of the roughness features. In the reported literature, very few studies have focused on surfaces with irregular features, and their results are limited by the unavailability of a singular parameter to represent the surface heterogeneity and to link it to the contact angle measurements. Following these practical limitations, the effect of irregular roughness on the contact angle and its compliance with wetting models remain largely unexplored. In practice, rough and irregular surfaces are more common than patterned surfaces, and they are present on a wide range of applications such as biomimetic surfaces [11–13], tribology [14] and in-service engineering parts [15,16]. Our work presents studies on irregular roughness features where we utilize a combination of optical measurements for measuring the apparent CA, and electrochemical measurements to determine the interfacial area under the droplet. We used the proportionality between the electrochemically measured double layer capacitance and the solid-liquid interfacial area to determine the wettability of these rough surfaces. This approach enables the study of surfaces with a stochastic distribution of roughness features, circumventing the problem of determining the dimensions of the roughness features on the surface. It has been shown that the relative scale of the roughness with respect to the double layer thickness affects the capacitance measurement [17]. Moreover, the mass transport rates within nano-pores also affect the measured capacitance [18,19]. The impact of these roughness-induced phenomena on the electrochemical wettability measurement has been systematically studied in the present work. The possibility of creating rough surfaces with large contact angles while simultaneously enabling large interfacial areas observed in this study could also be particularly interesting for lab-on-a-chip applications.

2. Experimental

2.1. Materials and methods

The substrates used for the present studies were glassy carbon (GC) discs (Sigradur G from Hochtemperatur-Werkstoffe GmbH, 10 mm dia.). The samples were prepared by first polishing them to a mirror finish. One of the polished samples was used as the

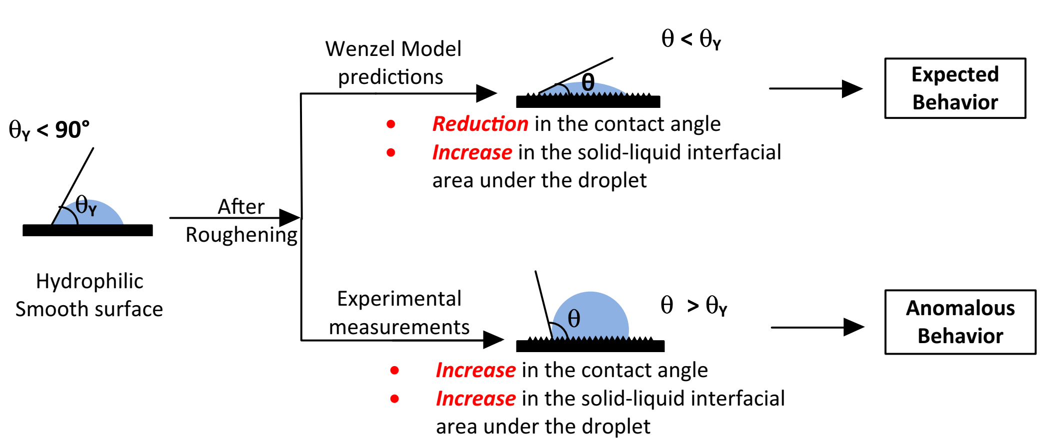

Fig. 1. The wetting anomaly on a rough hydrophilic surface presented in this study.