Predicting Contact Angles for Regular Surfaces

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ABSTRACT

Surface wettability behavior and its applications have garnered great interest in the past decade. Numerous studies have been conducted to model and characterize the surface wettability behavior through the static and dynamic contact angles. The two most common models used to predict the contact angles of superhydrophobic surfaces are the Wenzel (W) and Cassie-Baxter (CB) models. Although these models were developed for static contact angles, they have been used for dynamic contact angles. In this paper we have shown that these models work for most angles but not the receding contact angle.

Keywords: regular surface, contact angle, static, dynamic, roughness

1 INTRODUCTION

1.1 Motivation

Numerous research has been conducted in modeling the antiwetting behavior of a surface based on its geometric properties. Through the use of the model, the physics of antiwetting could be well understood and therefore antiwetting surfaces with better performance could be prepared. The antiwetting behavior is typically characterized through static and dynamic contact angles. Two most common models that are used to predict the contact angles are the Wenzel (W) and Cassie-Baxter (CB) models. These models were developed for static contact angles, although they have been used for dynamic contact angles. Also, the applicability of each model for a given surface is limited (i.e the transition could not be accurately predicted). For certain gometric surfaces, the models predict two very different contact angles and the transition state could not be predicted from the model alone.

1.2 Objective

The work presented here is to investigate the performance of the aforementioned models across different surfaces. The models have been shown to work individually to corresponding surfaces. However, the universal applicability of the models is explored in this paper. The models are evaluated for the static, advancing and receding contact angles in this regard. Also, the Wenzel to Cassie state transition criterion is not well understood yet, although there is a lot of ongoing work. If the transition could be predicted accurately, this would eliminate a lot of guesswork in surface or substrate preparation as the Cassie state would result in a higher contact angle.

2 THEORY AND MODELS

The antiwetting behavior is typically characterized through the static contact angle (θ_{st}), dynamic contact angles: i) advancing contact angle (θ_{adv}) and receding contact angles (θ_{rec}).

The static contact angle (θ_{smooth}) of a liquid on a flat smooth solid surface is given by Young's equation[1]:

$$\cos\theta_{smooth} = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \qquad (1)$$

where γ_{SG}, γ_{SL} and γ_{LG} are the interfacial free energies per unit area of the solid-gas, solid-liquid and liquid-gas respectively. This equation only applies to a flat or smooth surface.

When the roughness of the surface is considered two different models were proposed.

2.1 Wenzel Model

When the surface roughness exists, Wenzel assumed that the liquid penetrates the asperities of the region where it is in contact with the surface.[2] Due to this definition, the surface that is in Wenzel state is often referred to as the "wetted surface". This model was proposed for the static contact angle.

$$\cos\theta^{w} = r\cos\theta_{smooth} \qquad (2)$$

where r is the ratio of the actual area of the rough surface to the projected area.

2.2 Cassie-Baxter Model

The other model commonly used in the literature is the Cassie-Baxter model which assumes a composite surface is formed when a droplet comes in contact with a rough surface which makes the liquid droplet to be lifted up the roughness features.[3] The contact angle is predicted by:

$$\cos\theta^{CB} = \phi_s(\cos\theta_{smooth}) - (1-\phi_s) \quad (3)$$

where ϕ_s is the solid-liquid contact fraction of the surface. The observed equilibrium contact angle falls between the advancing contact angle and the receding contact angle.

From the two models above, there exists a a transition between Wenzel and Cassi-Baxter state. The transition roughness, r_{trans} can be determined by combining eqns. (2) and (3):

$$r_{trans} = \phi_s - \frac{1-\phi_s}{\cos\theta_{smooth}} \quad (4)$$

If the r < r_{trans}, then the liquid penetrates the pillars and therefore is in the Wenzel state. If the r > r_{trans}, then the liquid suspends on a com;osite surface and is in the Cassie state.

3 RESULTS AND DISCUSSION

Analyzing the available data in the literature for contact angles for a regular surface interesting trends were observed. The Wenzel model performs well in predicting the receding contact angle as shown in Fig. 1. Also, a shift in contact angle is observed when the droplet transitions from the “Wenzel” state to “Cassie” state. It is interesting to note that the transition occurs around roughness ratio, r, of around 1.3-1.4 for the different surfaces shown.

Figure 2 shows the receding contact angles plotted as a function of the solid fraction for superhydrophobic and superoleophobic surfaces. There is a general qualitative agreement between data and the CB theory. However, a better quantititative agreement is desired. Also, some experiments might have a bigger error margin in the measurement of contact angles and could be reason for the deviation from the model. Isotropy could also impart an effect on the contact angles as shown in Fig. 8. [4]

Similar to Fig. 1, Fig. 3 shows the plot of advacing contact angle as a function of roughness ratio, r. Analagous to the trend with receding contact angle, the contact angle is well predicted till the onset of transition, which is clearly seen by the shift in contact angle. It is also interesting to note that the transition occurs at the same roughness ratio range of 1.3-1.4 compared to the receding contact angles.

Figure 4, however shows a different trend. While one would expect a similar trend as seen on Fig. 2 (i.e an increasing trend commenstruating with increasing surface texturing), the contact angle is independent of the solid fraction. Despite that, the model predicts an accurate receding contact angle given high enough texturing. However, the trend is not well predicted and this leads to the conclusion that the receding contact angle is independent of the solid fraction. It could be possible that a different surface goemetry parameter that governs the receding contact angle for a droplet in “Cassie” state.

Figure 5 shows the static contact angle as a function of roughness ratio, *r*. A similar trend (i.e as *r* increases the contact angle increases) as the advancing contact angle is observed. It has been suggested that the advancing contact angle behaves similar to the static contact angle.[5] Also it is interesting to note that the transition occurs in the range of 1.2 to 1.5. The range is similar to the range observed for advancing and receding angles earlier, albeit a wider range.

In Fig. 6, the static contact angles were plotted against the solid fraction. A qualitative agreement is observed with the CB model. However, a few outliers are also noticed. It could not be identified whether the droplets were in “Wenzel” or “Cassie” state. It could be possible some of those droplets could be in Wenzel mode. It has been suggested in the literature that through vibrations and other methods the droplet can transition from “Cassie” to “Wenzel” mode as the “Wenzel” mode is a more stable state in terms of surface energy. [10] [13]

Figure 7 shows the transition roughness of the samples predicted by eqn.(4), which is derived from both the Wenzel and Cassie-Baxter model. It is interesting to note that this model predicts a decreasing trend of transition roughness, r_{trans}, compared to the experimental data that suggests that for a given surface, the transition roughness, r_{trans} is independent of the solid fraction. It is also important to note that the r_{trans} falls between the range of 1.2 to 1.4. This result could be important in terms surface preparation in specifying and dimensionlizing the surface geometry to get a high antiwetting behavior through high contact angles.

4 CONCLUSIONS

The Wenzel and CB models are generally universally applicable for most cases with the exception of some cases. The CB model has very strong qualitative agreement with regards to the receding contact angle. The CB model does not accurately predict the advancing contact angle. Both models are inconsistent in terms of predicting the onset of transition from Wenzel to Cassie state. Additional data is needed to quantify the controlling parameters of the transition.

5 FIGURES

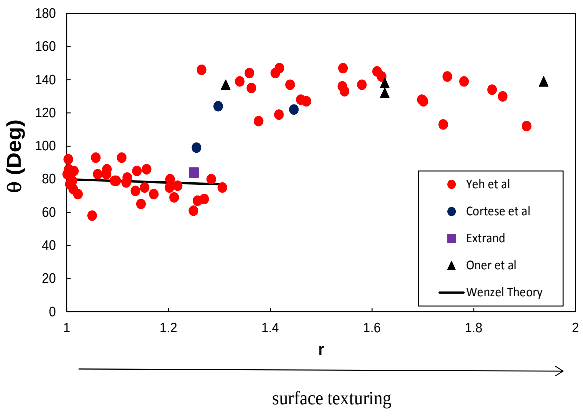

Figure 1 Receding contact angle as a function of roughness ratio

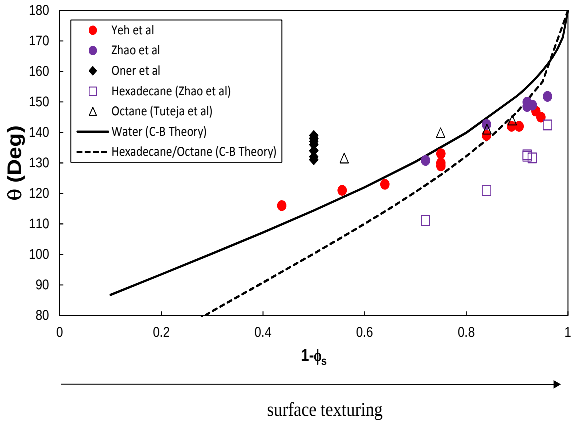

Figure 2 Receding contact angle as a function of solid fraction

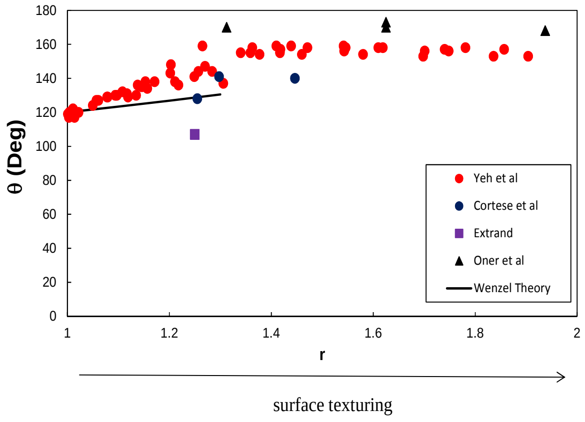

Figure 3 Advancing contact angle as a function of roughness ratio

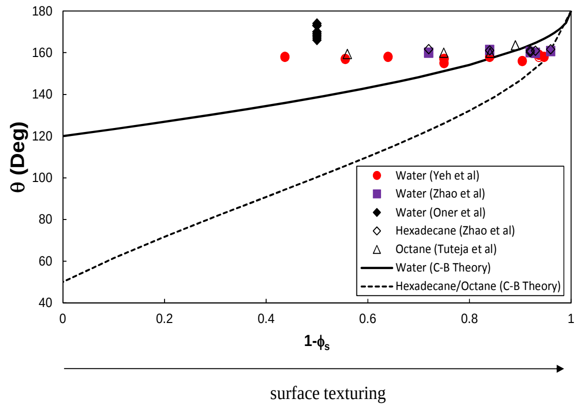

Figure 4 Advancing contact angle as a function of solid fraction

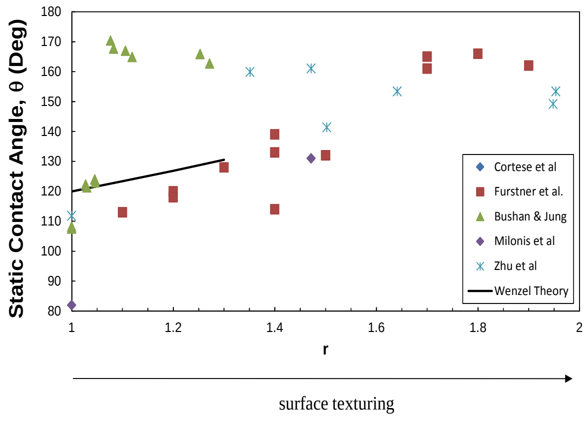

Figure 5 Static contact angle as a function of roughness ratio

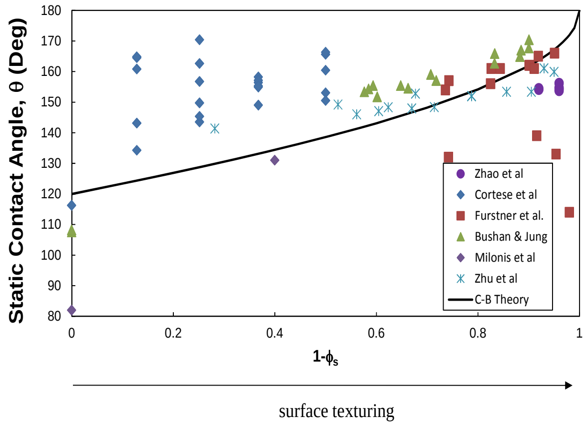

Figure 6 Static contact angle as a function of solid fraction

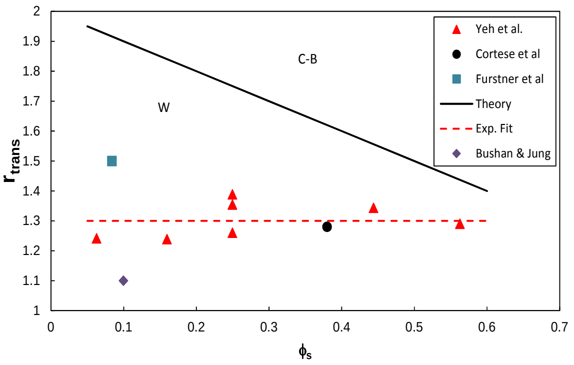

Figure 7 Transition roughness as a function of solid fraction

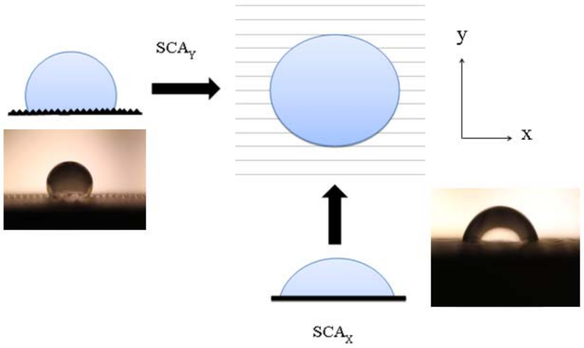

Figure 8 Different static contact angle behavior is seen with different orientation for a regular surface

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