Is the Cassie–Baxter Formula Relevant?

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The utility of the Cassie–Baxter formula to predict the apparent contact angle of a drop on rough hydrophobic surfaces has been questioned recently. To resolve this issue, experimental and numerical data for advancing and receding contact angles are reported. In all cases considered it is seen that contact angles follow the overall trend of the Cassie–Baxter formula, except for the advancing front on pillar type roughness. It is shown that deviations from the Cassie–Baxter angle have a one-to-one correlation with microscopic distortions of the contact line with respect to its configuration in the Cassie–Baxter state.

1. Introduction

Two approaches to understand the state of a drop on rough surfaces, in particular hydrophobic surfaces, have been discussed in the literature. The first approach is considered to be based on the interfacial energy minimization technique that, after homogenization approximation, leads to Cassie–Baxter formulas (depending on the wetting configuration) for the apparent contact angle of a drop. While these formulas provide useful guidance to design rough superhydrophobic surfaces, they do not capture the interfacial energy minimization approximation, leading to Cassie-Baxter configurations in the Cassie–Baxter case. Provided equivalent approximations are used, the energy-based and contact-line-based approaches are in fact equivalent.

Minimization of the interfacial energy leads to the equation of force balance at the contact line. The apparent contact angles, according to Cassie–Baxter (C–B) and Wenzel formulas, represent an average (or homogenized) measure of the minimum-energy state experienced by a contact line. While these formulas provide useful guidance to design rough superhydrophobic surfaces, they do not capture hysteresis. It has been proposed that the degree of deviation of the advancing or receding contact angles from the C–B formula is a measure of the additional energy associated with pinning/depinning events of the contact line. Motivated by some experimental data, one view is to propose that the deviation of contact angles, from the prediction based on the C–B formula, is so substantial that using such homogenized interfacial-energy-based models is not practically meaningful. There have been many insightful discussions in the literature but with incomplete resolution of this critically important and fundamental issue in this field.

This paper addresses the above issue by enquiring if the C–B formula is practically relevant. Two sets of experimental data and one set of numerical data for advancing and receding contact angles are reported and compared to predictions from the C–B formula. Pillar and hole type rough surfaces are considered in the experiments, whereas a flat checkerboard pattern with different contact angles is considered in numerical simulations. Section 2 briefly describes the experimental and numerical methods and presents the key results. Discussion are presented in section 3, and conclusions are summarized in section 4.

2. Methods and Results

2.1. Experimental Section. Square (24 μm × 24 μm) pillar and hole arrays (Figure 1) were fabricated on a silicon surface by using deep reactive ion etching (RIE). A range of roughness geometries were fabricated by varying the spacing between the pillars and holes in the respective cases. The height and depth of the pillars and holes were typically 56 μm. The silicon surface was coated with HDFS (heptadecafluorooctafluorotetradecyltri-chlorosilane, Gelest #SIH5841.0). The advancing and receding angles, on a flat surface of this silanized monolayer, were 111° and 97°, respectively. A water droplet of 10 μL was gently placed on the fabricated sample. The droplet, in a C–B state, was then forced to slide on the rough surface by using a probe tip (Figure 2). Contact angles at advancing and receding fronts in the state of impending motion were measured from video images (Figure 2) and compared with predictions from the C–B formula (Figure 3). The C–B angles were calculated as follows. The area fraction φ of the solid at the liquid—solid contact underneath the droplet was calculated according to the following equations:

\[ \phi = \frac{a^2}{(a + b)^2}, \quad \text{for pillar geometry} \]

\[ = 1 - \frac{a^2}{(a + b)^2}, \quad \text{for hole geometry} \]

where a and b are as defined in Figure 2. For geometries considered here, a = 24 μm and b is varied as shown in Figure 1.

The values of $\phi$ are listed in Figure 2. The $C-B$ angles are predicted and plotted in Figure 3 according to the following equation:

$$\cos \theta_{\text{Cass}} = \phi \cos \theta_{\text{adv/rec}} + \phi - 1$$  \hspace{1cm} (2)

where $\theta_{\text{Cass}}$ is the predicted $C-B$ angle, $\theta_{\text{adv}} = 111^\circ$ is the advancing angle on the flat surface that is used if it is an advancing front, and $\theta_{\text{rec}} = 97^\circ$ is the receding angle on the flat surface that is used if it is a receding front.

2.2. **Numerical.** Numerical simulations of advancing and receding fronts on a flat checkerboard patterned surface were done (Figure 4). Each square in the pattern was 1 cm $\times$ 1 cm. The advancing/receding angles were $145^\circ/125^\circ$ and $135^\circ/115^\circ$ for the two domains on the patterned surface. The simulations were based on a novel technique that couples Surface Evolver$^{12}$ with a phase-field model for contact line motion.$^{13}$ The method is briefly described below.

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Figure 1. SEM images of surfaces with pillar and hole geometries. The pillar and hole spacings are in increasing order from left to right.

Figure 2. Snapshots of droplets being dragged to the left or to the right on surfaces with pillar and hole geometries. The inset in each snapshot shows the measured angles at the left and right fronts of the droplet, respectively. Depending on which way the droplet is being dragged, these angles are the advancing or receding angles.

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Figure 3. Comparison between experimentally measured advancing and receding contact angles, for the pillar (a) and hole (b) type surface roughness, with predictions based on the $C-B$ formula. Lines joining the experimental data points are for visual aid only.

Figure 4. Schematic of the numerical simulation setup. The liquid–vapor interface is moved as shown by the arrow. One edge of the interface moves on a flat surface with checkerboard pattern of surface wettability (darker shade is more hydrophobic).

deviation of the observed contact angle with respect to the C–B formula (section 3.2).

3.1. Evidence of Relevance of the Cassie–Baxter Formula. We compare the predictions for the apparent contact angle with respect to the area fraction of the solid to experimental observations. Two fundamentally different kinds of roughness features, a pillar type geometry, which results in a discontinuous contact line, and a hole type roughness, which results in a continuous contact line, are considered. Figure 3 shows that in all cases considered, except for the advancing front on pillar type roughness which has strong pinning and therefore a constant contact angle, the apparent contact angles follow the overall trend of the C–B formula. Replotting past data for pillar type geometry in the same way leads to similar conclusions.2 (Note: it was not always possible to get the entire range of area fraction from prior data,8 no systematic data were available for hole type roughness.) Deviations from the C–B formula do not significantly compromise the primary trend, except for one case among those considered by us. Thus, disregarding the C–B formula as irrelevant is not warranted in general.

3.2. Contact Line Distortion and the Cassie–Baxter Angle. The goal of this section is twofold. First is to emphasize that the C–B angle in general corresponds to a “microscopic” state, to be referred to as the C–B state of the contact line. The second goal is to correlate deviations of the observed angle, with respect to the C–B angle, to distortions of the contact line away from its C–B state. To this end, numerical simulations were performed, as explained in section 2.2 (Figure 4). A checkerboard pattern was chosen because it is an ideal case to illustrate the two points listed above.

It is seen from Figure 5 that in each of the advancing and receding cases the contact line configurations A and E correspond to the C–B state where the apparent contact angle is in reasonable agreement with the C–B angle. When the advancing front pins at the edge of the more hydrophobic patch on the checkerboard pattern, the microscopic state of the contact line changes (see contact lines B and C in Figure 5a) from the C–B state to a pinned state. Correspondingly, the apparent angle deviates away from the C–B angle. When the contact line depins (transition of the contact line from C to D to E in Figure 5a), the C–B state of the contact line is recovered and the apparent contact angle drops back to the C–B angle within the margin of the numerical error. Similar behavior is observed in case of the receding front in Figure 5b. The presence of the “ideal” C–B state of the contact line, which results in an apparent angle nearly equal to the C–B angle, is also seen in prior experimental results (see Figure 2 in ref 15). Thus, the C–B formula is not divorced from the configuration of the contact line.

The C–B state of the contact line can, thus, be described as a state where the microscopic deformation of the contact line remains unchanged during the advancing or receding process in the absence of pinning. In this scenario the contact line only undergoes a general translational transformation. However, when pinning/depinning occurs, the shape of the contact line undergoes a change. This causes energy to be stored during the pinning process and dissipated during the depinning process. These pinning/depinning processes are the root cause of deviations from the C–B state and therefore hysteresis. As long as such pinning/depinning processes can be avoided, it is expected that the C–B formula will be obeyed. This argument is also consistent with that set forth originally by Cassie and Baxter themselves.1

Figure 5. Deviation of the numerically calculated values of advancing (a) and receding (b) angles compared to the C–B angles correlate with pinning/depinning events as shown in the inset. The simulation setup is as shown in Figure 2. In this case the C–B formula is \( \cos \theta_{\text{C-B}} = \cos \theta_{\text{adv}} + \cos \theta_{\text{rec}} \), where subscripts 1 and 2 denote the respective wetting domains on the checkerboard pattern.

Surface Evolver (SE)12 is an interactive program for the study of surfaces shaped by surface tension and other energies. The user specifies an initial surface, the constraints that the surface should satisfy throughout the evolution, and an energy function that depends on the surface. SE then modifies the surface, subject to the given constraints, so as to minimize the energy. This minimization of energy is performed through a gradient descent method. The numerical results are based on an approach that constitutively incorporates contact angle hysteresis. Therefore, the advancing and receding angles of the two materials that make up the chessboard are all inputs to the model.

In the current problem, the geometry is as shown in Figure 4. For a given volume \( V \) of the liquid, the liquid–air surface is evolved until the total energy, with surface tension and gravitational energies being two components, is minimized. On the contact line (see Figure 4) the local contact angle is satisfied at each point. This is ensured by using a phase-field model for contact line motion.13 The advancing front scenario is emulated by increasing the liquid volume \( V \) in steps and calculating the minimum-energy state at each volume. Similarly, the receding front is emulated by decreasing the liquid volume \( V \) in steps. More details of the simulation technique can be found elsewhere.13,14 The apparent contact angle is calculated by averaging the local contact angle (which is calculated from the local meniscus shape obtained from the simulation solution) along the contact line on the checkerboard surface. This is done at each liquid volume during advancing and receding simulations. The calculated contact angles are plotted in Figure 5 where the inset shows the shapes of the contact line. The calculated apparent contact angle is compared with the C–B formula in Figure 5.

3. Discussion

Two issues are discussed. First is whether the C–B formula is relevant at all to model the apparent contact angles of drops on rough hydrophobic surfaces (section 3.1). Second pertains to the

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The corresponding mathematical derivation relies on the assumption that each infinitesimal (advancing or receding) motion of the triple line causes the same area fraction to be wetted or dewetted. This is possible if the microscopic shape of the contact line is preserved. Thus, a surface material that is devoid of pinning sites will show no hysteresis and will be in agreement with the C–B formula. Joanny and deGennes\textsuperscript{10} show that surfaces will be devoid of pinning if the heterogeneities are weak/small for pinning to happen. It has also been demonstrated computationally and theoretically that if the size of a droplet is large relative to the heterogeneity size on the surface, then the agreement with Cassie–Baxter and Wenzel formulas is improved due to weak pinning.\textsuperscript{16,17}

4. Conclusions

In summary, the C–B formula is found to be relevant in general to model the apparent contact angle on rough surfaces. The actual

\begin{itemize}
  \item Deviations of the apparent contact angle from the C–B angle directly correlate with distortions of the actual contact line, due to pinning, from its C–B state.
\end{itemize}

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\textsuperscript{17} Wolansky, G.; Marmur, A. Apparent contact angles on rough surfaces: the Wenzel equation revisited. \textit{Colloids Surf., A} \textbf{1999}, \textit{156}(1–3), 381–388.