Liquid interface on a structured surface and apparent contact angle

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Abstract

This experimental and theoretical study is devoted to the description of the wettability of structured surfaces. The method is based on the assumption that an air layer under the liquid at the structured surface exists. The three-dimensional shape of the liquid interface on the substrate is calculated numerically, accounting for the topography of the rigid substrate and the average local pressure. These numerical predictions are validated by the experimental data. The results of computations are then used for the estimation of the apparent contact angle. We demonstrate that the well-known Wenzel and Cassie-Baxter cannot reliably predict this angle.

Key words: Structured surface, contact angle, surface evolver, μ-g, microgravity, wettability

Introduction

Numerous studies on the wettability of structured surfaces have been performed in recent years and the present state-of-the-art and can be found in the comprehensive reviews [1-4]. The aim of many of these studies is to control and modify the wettability, as represented by the effective or apparent contact angle. One application, among many others, is to mimic the surface of a lotus leaf, i.e. a hydrophobic surface with self-cleaning properties. For such purposes, a contact angle close to 180° is desirable [5-6], as this is one of the pre-requisites for the self-cleaning feature. However there are also other interesting, new application areas of high contact angle surfaces e.g. in underwater breathing [7].

Most of these efforts are directed either towards achieving a high or low apparent contact angle. But there are some new applications which actually need to control the apparent contact angle at intermediate values. One example is the manipulation of a drop flow using contact angle gradients [8-10]. Applications can also be found in the area of spray cooling.

In the field of wettability on structured surfaces models for two extreme states are well established: completely wetted rough surface described by Wenzel [11] and the partially wetted structured surface described by Cassie-Baxter [12]. These models have been discussed widely with over 600 references between 1996 and 2005 [13] and with no apparent loss of controversy [14-19]. Important for the present discussion is to continually be aware of the assumptions made in deriving each of these models.

If the substrate material is hydrophobic, the liquid spreading on a structured surface leads to the appearance of an air layer or air bubbles on the surface. If the structure is two-dimensional (if it consists of grooves of various shapes) the shape of the liquid-air interface is cylindrical since it has to satisfy the condition of the constant pressure at the interface. In this case the apparent contact angle can be easily estimated using the Cassie-Baxter Model. If the structure or the liquid interface is three-dimensional, the analysis becomes much more complicated. In some cases the solution is not unique. The sessile drop on the same structured surface can take various shapes, even not necessarily axisymmetric. In more complicated cases, if the structure or the substrate wettability is not uniform, it is not immediately clear how to use the existing analytical models for determining the apparent contact angle. Difficulties also arise in the case of super-hydrophobic surfaces. In this case the size of the wetted spot is comparable with the typical structure length scale. In this case averaging methods for determining apparent contact angle [11, 12] are not accurate.

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A sketch showing the wetting of an arbitrary structured surface is given in Fig. 1. In the physical model the contact line is a surface line and not necessarily continuous. For example it is discontinuous in the case of the "fakir" state when the drop is supported by an array of long micro-rods. The wetted region includes a gas layer (or gas bubbles). The liquid-gas interface near the contact region is a complex three-dimensional surface which, remote enough from the contact line, can be approximated by a plane surface. The angle of inclination of this asymptotic plane to the average median substrate plane can be defined as an apparent contact angle. This angle is shown in the sketch in Fig. 1, representing the engineering model of wettability. In the case of an ideally smooth substrate the contact angle is determined by the interfacial forces following the well-known Young equation [20]

$$\sigma_{lg} \cos\Theta_e + \sigma_{sl} - \sigma_{sg} = 0 \tag{1}$$

where σ_{lg}, σ_{gs} and σ_{sl} are the surface tensions liquid-gas, gas-substrate and substrate-gas respectively.

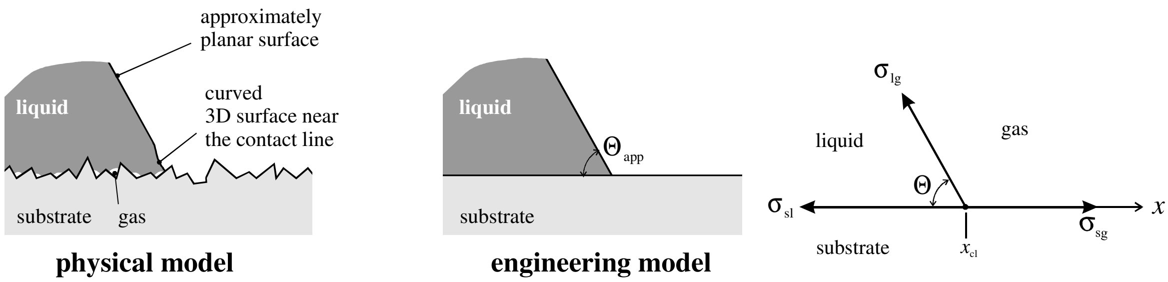

Figure 1. Left and middle: Wetting of a hydrophobic structured substrate: physical and engineering models. Right: Force balance at the contact line

In the case of the structured surface we can use for an estimation of the apparent contact angle Θ_{app} the effective surface forces in the wetted and dry regions of the substrate

$$\sigma_{lg} \cos\Theta_{\text{app}} + \sigma_{sl}^{\text{eff}} - \sigma_{sg}^{\text{eff}} = 0 \tag{2}$$

The effective internal forces can be evaluated as the derivatives of the surface energies in the corresponding regions of the substrate with respect to the coordinate x of the effective contact line. The final expression for the apparent contact angle in the Cassie-Baxter case is

$$\cos\Theta_{app} = \cos\Theta_e \Phi_{sl} - \Phi_{lg} \tag{3}$$

Where Φ_{sl} and Φ_{lg} are the projected effective areas of the solid-liquid and liquid-gas surfaces in the wetted region in the neighborhood of the contact line. Note that the expression for the apparent contact angle (3) is obtained using the assumption that the average local normal to the surface is normal also to the median surface. This means that this expression cannot be applicable to chiral surfaces. The question now arises whether this well-known expression for the apparent contact angle can be blindly used for the design and analysis of structured substrates in relation to their wettability? Recently some doubts appeared about the reliability of this expression, since it is not able to always predict the experimental data well [21]. The reason is not completely clear.

The aim of the present study is to investigate of the shape of the liquid interface on a structured substrate in order to develop a model for the apparent contact angle on such structures. We show that the Cassie-Baxter prediction is not applicable to our structures since it produces no real solution for Θ_{app}.

Experimental simulation of a structured hydrophobic surface

The problem is that it is not easy to visualize and to analyze the shape of the liquid-gas interface on a structured substrate when the shape is three-dimensional, possibly periodic, but has a constant curvature. It does not depend on the material properties of the liquid and gas. It depends only on the substrate geometry and wettability.

In the following experiments the gas layer trapped below the liquid layer on a hydrophobic surface is investigated by inverting the phases and examining the shape of a liquid on a hydrophilic structured substrate. It is assumed that the shape of this liquid layer is equivalent to the liquid-gas interface on a hydrophobic substrate. In order to avoid the effect of gravity (which is negligibly small in the case of micro- or nano-structured surfaces) the experiments have been performed under microgravity conditions during the 46$^{\text{th}}$ ESA parabolic flight campaign.

The experimental setup is shown schematically in Fig. 2. The shape of the liquid layer is captured using two digital photo cameras at various liquid heights.

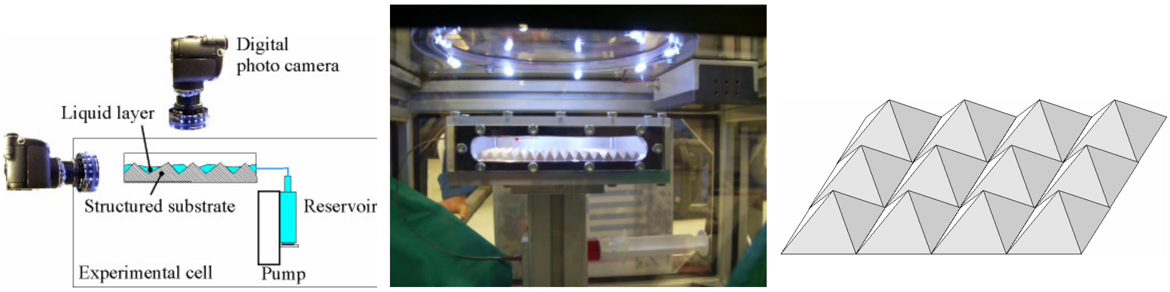

Figure 2. Experimental setup: Left: schematic diagram, Middle: side view of experimental cell, Right: the pyramid structured substrate

A periodic liquid layer exists on the substrate and moreover, this layer was observed to be very stable, which is actually a non-trivial result. The experimental results for the shape of this liquid layer have been used for the validation of the numerical simulations of this layer shape.

Numerical simulations of a structured hydrophobic surface

The numerical simulations have been performed using Surface Evolver [22, 23]. It is an open source code that can be used for the calculation of a static liquid interface based on the minimization of the surface energy. The equilibrium contact angle and gravity effects have been taken into account. In this investigation a pyramid surface has been studied (see Figs. 2 and 3). Only a segment of the surface is considered taking advantage of the structure's symmetry and assuming periodicity.

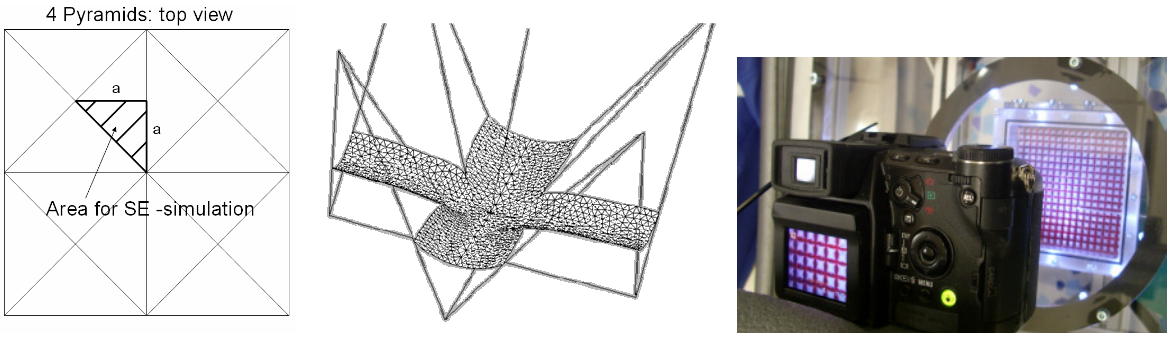

Figure 3. Left and middle: Surface Evolver simulation of the liquid-gas interface. For this middle visualization eight computational domains have been combined. Right: the upper view on the wetted structure under μg conditions.

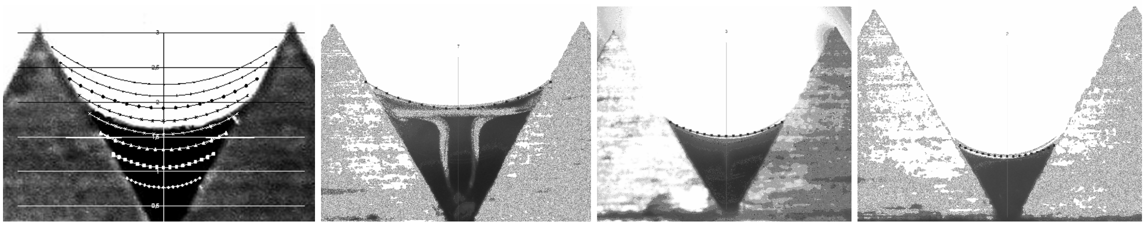

Figure 4. Comparison of the numerical simulations of the liquid-gas interface with the experimental data under μg (left photo) and under the terrestrial conditions (three photos on the right).

One example of the predicted liquid-gas interface on the pyramid surface is shown in Fig. 3. This interface is periodic, symmetric and has a constant radius of curvature and contact angle with the rigid surface. For a given surface topography and wettability several solutions can be found depending on the level of the liquid layer in the experiments (or the average height of the gas layer in calculations). In Fig. 4 the predicted contour of the gas-liquid interface at various gas heights is compared with the experimental data. The predictions agree well with the experimental film profile.

Approximate solution

The contact line can be approximated by the intersection of a pyramid with a horizontal plane. In this case the analysis of the geometry of the liquid on the surface can be significantly simplified.

Consider a structured substrate shown schematically in Fig. 5. Denote α as the base angle of the pyramid and h is the penetration depth of the liquid into the structure. The angle γ and the total length of the contact line, L_{cl} can be estimated using

$$\gamma = \alpha + \Theta_e - \pi , \qquad L_{cl} = \frac{8h}{\tan\alpha} \tag{4}$$

The total vertical force applied to the liquid interface at the contact angle is $F_z = \sigma L_{cl} \sin\gamma$. Therefore, the average pressure $p = \sigma\kappa$ applied to the liquid-gas interface can be obtained dividing F_z with the corresponding projected area and κ being the surface double average curvature. An expression for the constant curvature of the gas-liquid interface is expressed in dimensionless form using L as the length scale:

$$\bar{\kappa} = \kappa L = \frac{F_z}{\sigma(L^2 - L_{cl}^2/16)} L = -\frac{8\bar{h}\cot\alpha\sin(\alpha+\Theta_e)}{1-4\bar{h}^2\cot^2\alpha} \tag{5}$$

All variables in this expression are dimensionless. Now, since the geometry of the liquid wetting of the structure is known, the parameters of equation (3) can be easily determined

$$\Phi_{sl} = \frac{L_{cl}^2}{16L^2\cos\alpha}, \qquad \Phi_{lg} = \frac{1}{L^2}\left[L^2 - \frac{L_{cl}^2}{16}\right]\frac{\gamma}{\sin\gamma} \tag{6}$$

Finally, the value of the apparent contact angle can be estimated using (3) as

$$\cos\Theta_{app} = \frac{4\bar{h}^2\cos\alpha}{\sin^2\alpha}\cos\Theta_e - (1-4\bar{h}^2\cot^2\alpha)\frac{\gamma}{\sin\gamma} \tag{7}$$

In our analysis the value of the apparent contact angle depends on the curvature κ through the depth of penetration h. The value of the curvature is determined by the local pressure in the liquid at the substrate. In the absence of gravity (or if the drop size is much smaller than the capillary length) the pressure in the drop is uniform and the curvature can be then estimated as $\kappa = 2/R$, where R is the radius of the drop surface. The volume of such a drop is

$$V = \frac{\pi R^3}{3}(3-\cos\Theta_{app})\cos^2\Theta_{app} \tag{8}$$

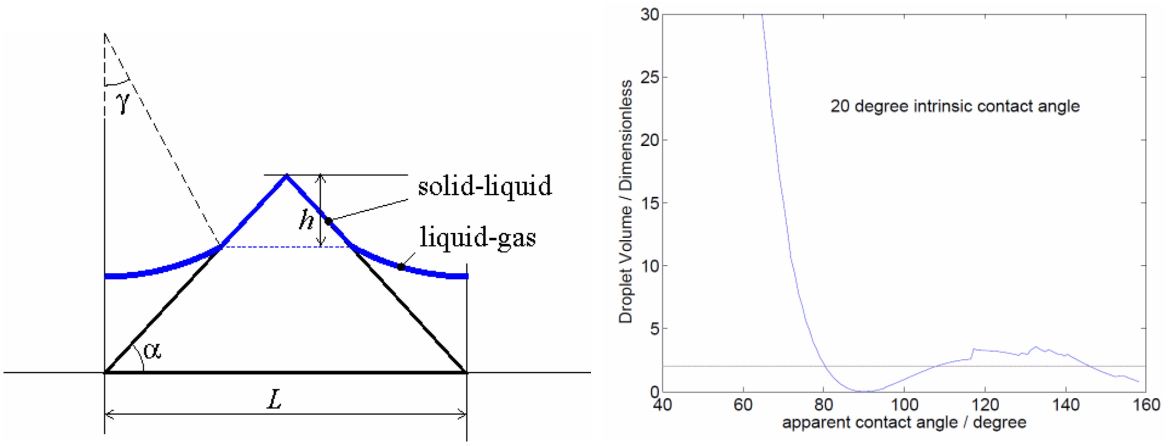

Figure 5. Left: Geometrical parameters of the pyramid structures. **Right:** Drop volume as a function of the predicted apparent contact angle for a constant intrinsic contact angle of 20°

Apparent contact angle: Results and discussion

The initial idea of this study was to elegantly relate the internal pressure inside the drop with the local curvature of the liquid-gas interface at the structured substrate, and then also with the apparent contact angle. The base angle in our pyramid structures is $\alpha = 67^\circ$. In this case the expression (7) can be rewritten as

$$\cos\Theta_{app} \approx -1 + (0.720 + 1.845\cos\Theta_e)\bar{h}^2 \qquad (9)$$

This means that if the equilibrium contact angle of the material of the substrate is $\Theta_e = 113^\circ$, the predicted apparent contact angle is 180° independent of the penetration depth *h*. There is no real solution for the apparent contact angle if $\Theta_e > 113^\circ$.

In Fig. 5 on the right, the predicted value of the apparent contact angle is plotted as a function of the dimensionless drop volume. It can be seen that in this case, for a fixed drop volume the contact angle problem can have three possible solutions. This plot is a detail of the plot in Fig. 6 on the right.

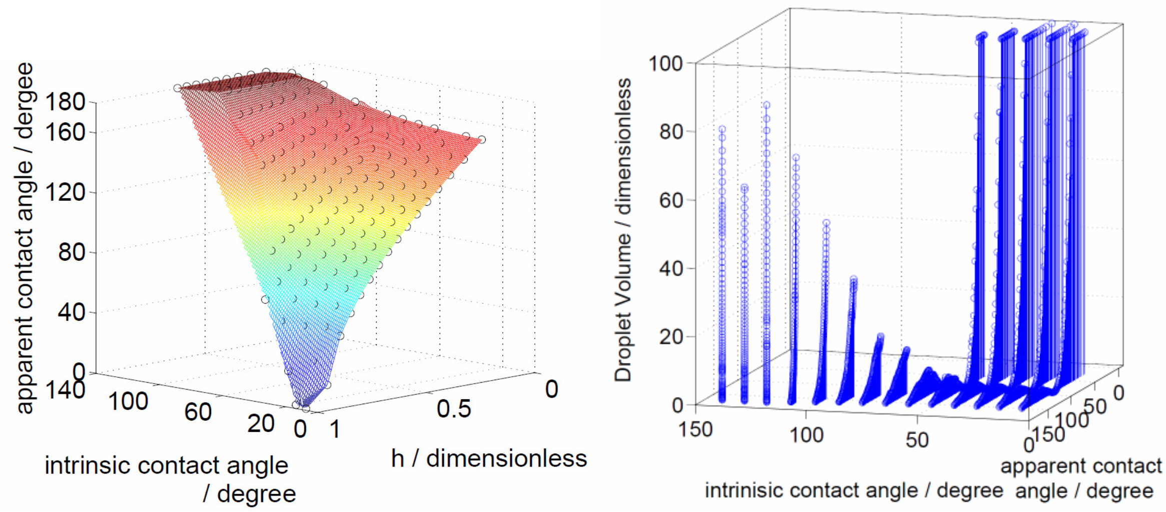

Figure 6. Surface Evolver simulation for the pyramid structure: Left: Apparent contact angle plotted over intrinsic contact angle and penetration depth *h*. Right: Droplet volume plotted over intrinsic and apparent contact angle

In Fig. 6 the left graph is a plot of the apparent contact angle over the intrinsic contact angle and the height *h*. For intrinsic contact angles above 113° the apparent contact angle is always 180° for this structure. For the other data points a clear dependence is found: lower intrinsic contact angles result in lower apparent contact angles and lower *h* values, corresponding to less penetration of the structure by the droplet and higher apparent contact angle values.

The right graph in Fig. 6 is a plot of the droplet volume over the intrinsic and apparent contact angle. The simulation links the apparent contact angle, calculated using Eq. (9), with the curvature of the surfaces. With this link the volume can be calculated, using expression (8). Again the intrinsic contact angle limit of 113° is visible. For values from 70° to 110° the relation of volume to apparent contact angle is straight-forward. A droplet of a certain volume will have a certain apparent contact angle on the structured surface. The smaller the droplet volume is, the bigger is the apparent contact angle. That also implies that structured surfaces can have droplets on it with different apparent contact angles.

For values from 0° to 60° there are droplet volumes with 3 possible apparent contact angles, as also shown in Fig. 5. But some predictions of the apparent contact angle less than 90° are not relevant, because in combination with the low intrinsic contact angle these solutions refer to a super-wetting behavior. The liquid is most probably between the structures and does not form a droplet shape. These cases have to be considered in a different numerical approach in a future study.

The two remaining possible solutions for a certain droplet volume can indicate a contact angle hysteresis. The inclusion of a contact angle hysteresis would be an obvious next step for the present model.

Although the results and conclusions of this study are brief, they are rather significant. The well-known and widely used Cassie-Baxter relation is not applicable to our structures if the intrinsic, equilibrium contact angle is higher than some critical value. This conclusion can easily be generalized to other surface topologies. We can give a clear explanation for this. The problem is that the Eq. (3) is developed from energy considerations. Mechanically it can represent an average over all possible realizations of the apparent contact angle and positions of the contact line. But some of these mathematical solutions are not physical:

- some are not stable;
- some correspond to the gas-liquid interface intersecting with itself;
- some correspond to the gas-liquid interface intersecting with the solid structure.

Therefore, the correct solution for the apparent contact angle of the liquid on a structured surface has to be obtained using a completely different approach which accurately accounts for the possible non-physical solutions. One of the potentially useful instruments is using Surface Evolver for accurate prediction of the real drop shape on a structured surface.

Conclusions

We have shown experimentally and numerically that the gas-liquid interface on a structured surface exists and is stable. It is also known that any structure on a substrate modifies the apparent contact angle. This angle has a physical value. The well-known Cassie-Baxter expression for the apparent contact angle is not applicable to the description of the apparent contact angle on a structured surface. The numerical predictions using Surface Evolver can be a useful tool for prediction of the apparent contact angle and drop shape.

Acknowledgements

The parabolic flight opportunity was provided by the European Space Agency und Topical Team Grant HSF-U/2009-161.

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