Numerical Simulation of Droplet Shapes on Rough Surfaces

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ABSTRACT

It has been demonstrated that surface roughness causes superhydrophobicity. Our objective is to develop a numerical tool and study the relationship between the roughness characteristics and the apparent contact angle and motion of liquid drops on rough surfaces.

As a first step we consider a stationary drop on a substrate with a simple geometry of horizontal grooves. A public domain software is modified to numerically investigate the 3D equilibrium drop shapes on a rough surface. We observe that a drop of given volume and actual contact angle attains different equilibrium positions on a rough substrate. The energies and the apparent contact angles of each equilibrium state are different. The actual contact angle in our simulations was $\geq 90^o$. It was also seen that for higher values of actual contact angles the liquid tends to move out of the grooves thus leading to the formation of a composite surface of contact on the substrate.

Keywords: Superhydrophobicity, contact angle, roughness, drop, numerical simulation.

1 INTRODUCTION

It is known that the wettability of a surface is a function of its roughness (Figure 1). Non-wetting liquids exhibit superhydrophobicity on a rough surface. It has been demonstrated that surfaces with micromachined structures can have similar effects [1]. This phenomenon has many applications.

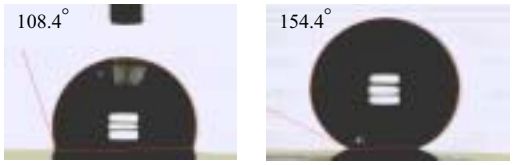

Figure 1: Wettability shift due to surface roughness (courtesy B. He & J. Lee).

Our goal is to develop a numerical tool and study the relationship between the roughness characteristics and the apparent contact angle and motion of liquid drops on rough surfaces. This investigation focuses on stationary drops on rough substrates. It is a critical step to develop numerical models for drops moving on rough surfaces.

The earliest work on this problem can be attributed to Wenzel [2] and Cassie [3]. They provided expressions for the apparent contact angle based on certain average characteristics of the roughness. Their formulas suggest a single equilibrium shape for a sessile drop on a given substrate. This is not necessarily true. Indeed, it has been observed that the apparent contact angle of a stationary drop need not be single valued. There can be multiple equilibrium drop shapes for a given rough surface depending on how the drop was formed or on the motion of the drop in response to some external forcing.

In this work, a public domain software is used to numerically investigate the 3D equilibrium drop shapes and the apparent contact angles on a rough surface. Similar investigation of drop shapes on a chemically heterogeneous surface has been reported by Brandon *et al.* [4].

We consider a simple geometry of horizontal grooves for the substrate. Gravity is neglected. Comparison with experiments will be done in the subsequent stages of our research.

2 NUMERICAL PROCEDURE

We have used a public domain "Surface Evolver" software by Ken Brakke [5] with suitable modifications. The numerical procedure is based on minimizing the free energy of the system to obtain the equilibrium drop shape. The free energy G of the system is given by

$$G / \sigma_{lf} = S_{lf} - \iint_{S_{sl}} \cos\theta_a \, dA \ , \qquad (1)$$

where l denotes the liquid that makes the drop, f denotes the fluid surrounding the drop, s denotes the solid surface, S_{lf} and S_{sl} are the liquid-fluid and the solid-liquid interfacial areas of contact and σ_{lf} is the liquid-fluid interfacial tension (or surface energy density). σ_{lf} is assumed to be constant. The local actual (or intrinsic) contact angle θ_a is defined by Young's equation:

$$\cos\theta_a = \frac{\sigma_{sf} - \sigma_{sl}}{\sigma_{lf}}, \qquad (2)$$

where σ_{sl} and σ_{sf} are the local solid-liquid and solid-fluid interfacial tensions, respectively. $\theta_a > 90^0$ represents a non-wetting contact. The expression for the free energy can be appropriately modified to account for gravity. Minimizing the free energy G (Equation 1) with respect to the liquid-fluid interface shape, while constraining the drop volume to a fixed value, gives the equilibrium drop shape. In the solution procedure, G/σ_{lf} is minimized. Hence for a given problem, the only material parameter we need to specify is the actual contact angle.

It can be shown [6] using variational principles that the constrained minimization procedure, above, is equivalent to solving the Laplace equation for the pressure drop at each point on the liquid-fluid interface:

$$\frac{2\sigma_{lf}}{R_m} = \Delta p \,, \tag{3}$$

along with Young's equation (Equation 2) on the solid-liquid-fluid contact line as the boundary condition. R_m is the mean radius of curvature and Δp is the pressure drop, at a point on the drop surface. A stationary drop on a substrate, in constant ambient pressure, will have a constant pressure drop at each point on the liquid-fluid interface (gravity neglected). Hence, it follows directly from Equation 3 that a sessile drop should have a constant mean curvature surface. In two-dimensions the arc of a circle is the only constant mean curvature curve. In three-dimensions, the spherical surface is one of the many possible constant mean curvature surfaces.

Detailed information about the numerical methodology to solve the constrained minimization problem (Equation 1) is available in the Surface Evolver manual [5]. A brief description is given here.

The equilibrium drop shape is obtained iteratively from the initial shape. At each iteration the vertices on the liquid-fluid interface are moved in order to reduce the energy of the system while adhering to the constant volume constraint and the constraint that the contact line remains on the solid surface. Iterations are repeated until the system's energy does not change significantly.

3 RESULTS

The geometry of problem being considered is shown in Figure 2. Suitable modifications were done to the software to handle a rough substrate. We consider a drop of a given volume placed on the rough substrate. We start with an initial drop shape. The intrinsic or the actual contact angle of the drop with the solid surface is specified. The Surface Evolver is used evolve the initial drop shape to the final equilibrium shape. During a given run we fixed the number of grooves on which a drop sits. The volume of the drop is 1 unit (of volume) and the size of groove is 0.1 unit × 0.1 unit.

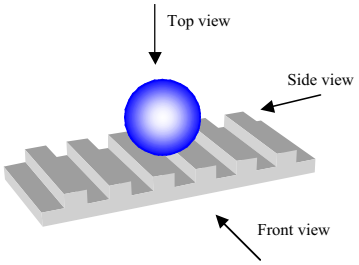

Figure 2: Schematic of a sessile drop on a substrate with horizontal grooves.

Figure 3 shows the initial shape (which is arbitrary) and the final equilibrium shape when the drop resides on five grooves, i.e. the left and the right edges of the drop are constrained to move on the horizontal pillars adjacent to the first and the fifth grooves, respectively (see Figure 3). Gravity is neglected. Clearly, the equilibrium shape thus obtained represents the local minimum or a metastable state of the free energy. The resultant equilibrium shape satisfies the condition that the mean curvature of the surface is constant. The local contact angle along the solid-liquid-fluid contact line is equal to the actual contact angle (= 90^0 in this case).

Figure 4 shows the various views of the drop in Figure 3. We see that the fluid tends to 'anchor' on the corner of the horizontal pillars. For an actual contact angle of 90^o, the apparent contact angle on the corner can vary between 90^o and 180^o (see Oliver *et al.* [7]). This plays a significant role in determining the equilibrium drop shape and the apparent contact angle. Since we have horizontal grooves the apparent contact angles in directions parallel and perpendicular to the grooves are different (Figure 4).

Figure 5 shows the effect of the number of grooves on which the drop is constrained to reside. All the other parameters i.e. the drop volume, the liquid-fluid surface tension and the actual contact angle are the same as in Figure 3. The shape of the drop becomes longer as the number of grooves are reduced. The apparent contact angle increases in the front view as the number of grooves are reduced. In each case the left and the right edges get anchored on the corner of the horizontal pillars. Of the three cases considered here, the free energy of the drop sitting on five grooves (Figure 3) is minimum.

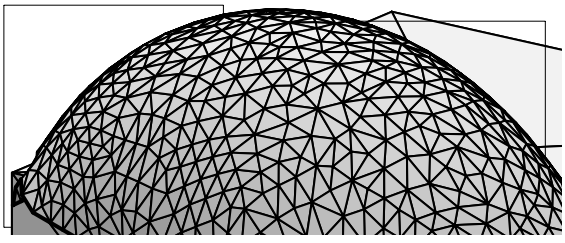

Figure 3: Initial and equilibrium configurations of a drop on five grooves. Actual contact angle is 90^0.

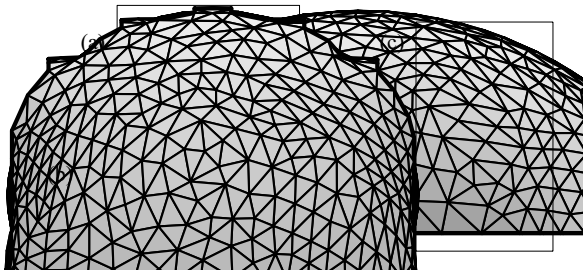

Figure 4: (a) Front, (b) side and (c) top views of the drop in Figure 3.

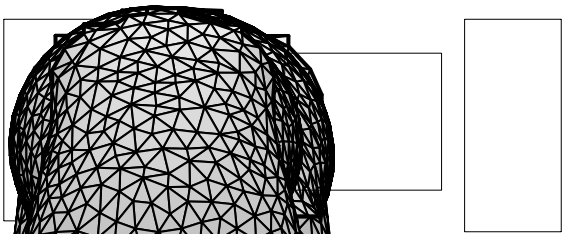

Figure 5: The equilibrium drop shapes as a function of the number of grooves on which it settles. Two figures on the left are for four grooves and the two on the right are for three grooves (figures for the two cases are not drawn to the same scale).

The drop can acquire any of the configurations above depending on how they were formed. Longer drops can help in diffusive mixing in the transverse direction since the length scale over which the diffusion has to occur is reduced.

The effect of changing the actual contact angle is depicted in Figure 6. All the parameters are the same as that in Figure 3 except that the actual contact angle is now changed to 120^0. It is seen that the liquid in the grooves moves 'in' and 'up' i.e. it is moving out of the grooves. Since the solid-liquid contact is non-wetting, this reduces the free energy of the system. Figure 6 is not the equilibrium shape but it indicates that a composite surface is being formed where the liquid is in contact with the solid only on the horizontal pillars (Figure 7).

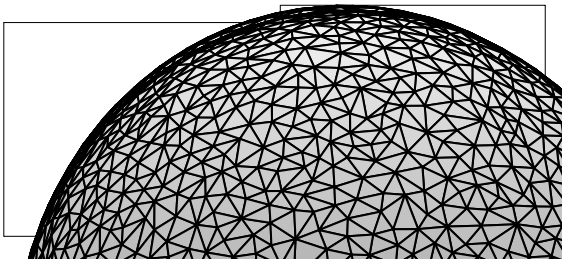

Figure 6: The (non-equilibrium) drop shape for an actual contact angle of 120^0 (other parameters are the same as in Figure 3). The liquid tends to move out of the grooves.

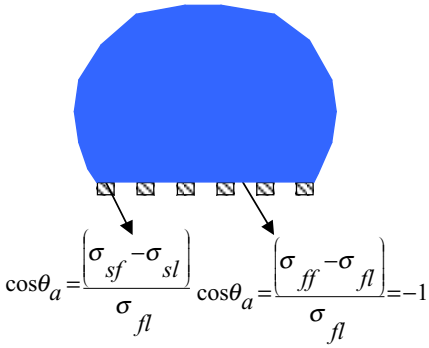

Figure 7: A cartoon of the front view of a drop with a composite surface on a rough substrate with horizontal grooves.

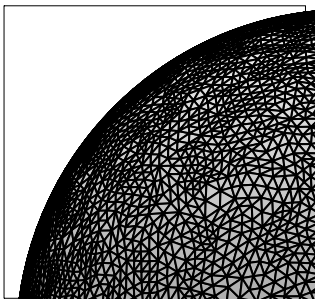

Figure 8: The drop shape on a rough substrate obtained by the composite surface approach for the case depicted in Figure 6.

Figure 7 shows a cartoon of the front view of a drop on five grooves with a composite surface on the rough substrate. The assumptions involved are that the liquid moves out of the groove completely and that the liquid-fluid interface on the empty grooves is almost flat. The first assumption is reasonable for a non-wetting liquid-solid contact under certain conditions (Equation 4). The second assumption of a flat interface is reasonable when the drop size is large so that the mean radius of curvature is large compared to size of the roughness features.

The above assumptions lead to a simplified approach to model the rough substrate. One can imagine a drop on a flat surface with varying contact angle. On the horizontal pillars the contact angle is θ_a and at the location of the grooves the contact angle is 180^0 (Figure 7). Figure 8 shows the drop shape obtained by this approach for the same case as that in Figure 6. The shapes in Figures 8 and 6 are in qualitative agreement.

4 DISCUSSION AND CONCLUSION

The approach based on a composite surface described above, is computationally less expensive and more suitable to use for moving drop simulations with viscous effects. Solution of full Navier-Stokes equations for a moving drop with complete resolution of the surface roughness features

is extremely difficult. A simplified approach, where a varying contact angle on a flat projected surface models the effect of the surface roughness, is more desirable.

Cassie [3] first used the concept of a composite surface to obtain the apparent contact angle of a drop on a rough substrate. We apply the same concept at the 'microscopic' level where the details of the roughness pattern is preserved. This enables us to generate information about multiple equilibrium drop shapes not accessible by the analysis of Cassie [3].

Improvements to the composite surface approach are necessary. It is desirable to have a model or criterion to determine when a composite surface will be formed. We have considered the following simple criterion for the horizontal groove geometry. If we assume *two-dimensionality* and that the energy principles can be applied *locally* at a groove then for a non-wetting θ_a we have:

$$\sigma_{lf} W < (\sigma_{sl} - \sigma_{sf})(2H + W),$$
$$\Rightarrow H/W > -(1+\cos\theta_a)/2\cos\theta_a, \qquad (4)$$

where H is the height and W is the width of the groove. Equation 4 states that the surface energy of an empty groove should be less than the surface energy of the wetted groove. For a given θ_a this leads to a condition on the aspect ratio. The critical aspect ratio is plotted as a function of θ_a in Figure 9. If the actual aspect ratio is less than the critical value for a given contact angle then the liquid will not move out of the groove. Similar conclusions were reported by Johnson and Dettre [8].

The aspect ratio in the geometry we have considered here is 1. From Figure 9 we expect the formation of a composite surface for $\theta_a \geq 110^0$. Our observation, based on the full simulations like those in Figures 3-6, agrees with this prediction. We obtained an equilibrium drop shape for $\theta_a = 105^0$ (Figure 10) but for higher contact angles we ran into situations similar to Figure 6, where the liquid in the groove kept moving out. We could not obtain a minimum energy state even after large numbers of iterations.

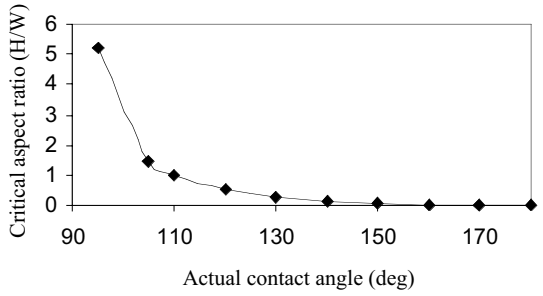

Figure 9: Critical aspect ratio to form a composite surface on a substrate with horizontal grooves.

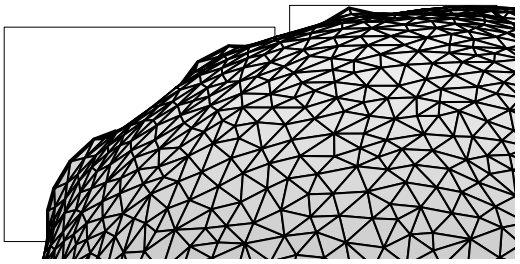

Figure 10: Equilibrium drop shape for $\theta_a = 105^0$. All other parameters are the same as the case in Figure 3.

The criterion in Equation 4 is subject to assumptions. We are further investigating the validity such simplified criteria. If a composite surface is not formed i.e. the liquid fully wets the solid in the grooves, then ideas of Wenzel [2] may have to be used to obtain a distribution of the contact angle on a flat projected surface. Similarly, for rounded roughness features, unlike the current case where we have sharp corners, it may be necessary to use the ideas of both Cassie [3] and Wenzel [2], in combination, to get the contact angle distribution on the projected surface.

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