Moving Contact Lines on Rough Surfaces*

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Abstract
A simple explanation for moving contact lines based on surface irregularities has been proposed by L.M. Hocking. His thesis is that fluid slip at a solid boundary cannot occur at microscopic scales, but surface irregularities with microscopic scales can induce flow structures that may be interpreted as slip from a macroscopic point of view. The principal deficiency of Hocking's proposal is that there is no direct evidence to support it. In this paper we use computational fluid dynamics simulations to show in detail how a contact line can move over or get stuck on a rough surface.

1. Introduction

At a liquid/air interface moving over a solid surface there should be no velocity slip. However, it is well known [1,2] that flow at a contact line, when modeled using a continuum description, exhibits singularities. The singularities are associated with the use of continuum flow equations (i.e., the Navier-Stokes equations) together with the no-slip boundary condition [2]. Having said this, it is important to recognize that this difficulty with singularities is confined to a region about the contact line of molecular scale where there is no reason to expect a continuum model to be valid.

In most numerical treatments of flows involving moving contact lines a finite-element-based technique is used in which a computational grid node must be placed at the location of a contact line. Placing a node at a point known to have singularities is not a good idea. It necessitates the introduction of ad hoc assumptions, e.g., specifying some amount of slip on the solid surface or specifying the location and/or dynamic contact angle.

In this paper we use a finite-control-volume technique, which does not require the introduction of ad hoc assumptions. The finite-control-volume method does not attempt to assign specific values to quantities at the location of a control line, instead it simply keeps track of the mass, momentum, and energy in the control volume element. With this approach we focus on modeling the basic fluid-dynamic conservation processes.
The locations of contact lines, and for that matter the location of fluid surfaces or interfaces are tracked by a volume-of-fluid (VOF) method in which the fraction of liquid in each computational grid element is recorded. Using the fluid fraction value in an element together with the fractional values in neighboring elements one can easily locate surfaces and even compute surface slopes and curvatures [3].

At a contact line the only additional consideration needed beyond the standard dynamic processes contained in the Navier-Stokes equations is a mechanism to describe the adhesion between liquid and a solid substrate. This is done by assuming that the adhesion force, which arises from molecular interactions between solid and liquid, can be characterized by a static

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contact angle. In any grid element containing a contact line (i.e., a fluid interface and a solid surface) there is an additional adhesion force computed and added to the other forces acting on the element (e.g., pressures, body forces, viscous stresses, advective processes, etc.). The additional force is computed from the slope of the fluid surface with respect to the solid surface and assuming that Young's equation describes the proper balance of forces under static conditions [4].

In dynamic situations involving moving contact lines, we continue to compute adhesion forces using the static contact angle, a physical quantity that can be easily measured. This is justified because the molecular processes responsible for adhesion forces occur on space and time scales that are orders of magnitude smaller and faster, respectively, than those of macroscopic flow processes. Because of this macroscopic processes cannot have any significant influence on the molecular level.

Dynamic contact angles are not specified but computed as part of the solution in the finite-control-volume method using the VOF technique. They arise automatically from the basic balance of forces on which the numerical method is built. This is one of the several practical advantages of this modelling approach.

All the simulations presented in this paper were performed using this combined control-volume-VOF approach as it has been implemented in the commercial software program FLOW-3D® developed by Flow Science, Inc. located in Santa Fe, New Mexico, USA. Reference [5] may be consulted for additional information about this program.

2. Demonstration Application

Before proceeding with the main topic of the paper, we present a demonstration of the utility and viability of our modeling approach. In particular, the modeling of dynamic contact lines with static contact angles characterizing liquid-solid adhesive forces. The application is that of the fingering observed in liquid films flowing down an inclined surface [6,7]. Experimental observations show that two distinct patterns of fingering occur. One pattern, corresponding to small contact angles (i.e., highly wetting), exhibits wedge shaped fingers whose top and bottom limits both move downward. The second pattern, corresponding to large contact angles (i.e., poorly wetting), is characterized by long fingers of nearly uniform width whose top most limits are not moving downward.

In Fig. 1 we show the results of two simulations using the numerical approach described earlier, except in this case a further assumption of depth-averaged flow has been made [8], which is justified because of the thinness of the liquid films. The only difference between the two simulations is the value of the static contact angle (0° versus 70°).

Experimental results reproduced from [6] are shown for comparison, although they do not directly correspond to the conditions in the simulations. The simulations have wavelengths within experimentally observed limits and exhibit the qualitative features seen in the experimental results.

While a more detailed investigation of fingering would be interesting, the purpose of presenting these results here is only to show that a static contact angle describing liquid-solid adhesion has validity.

3. A Little Problem

Many useful simulations have been performed with the modeling approach described here showing good agreement with observations. However, there is one everyday observation that appears not to be modeled. After a rainstorm the water on our windows mostly runs down the window in rivulets, but some small drops appear stuck in place. How can this be?

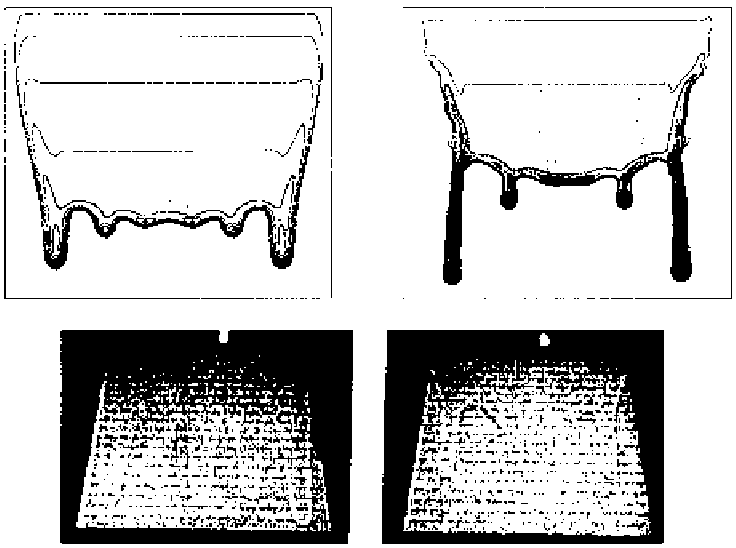

Figure 1: Fingering of liquid sheets. Zero contact angle on left and 70° contact angle on right. Experimental results for similar, but not exactly the same, cases below (from Ref.6).

According to our model the only force between the water and the window glass is an adhesion described by a static contact angle. This is a constant force normal to the contact line. When integrated around a closed contact line, such as that surrounding a droplet, the force must integrate to zero. Computations confirm this. Droplets might move slowly because of viscous stresses, but they still move down under the action of gravity. How is it, then, that small drops are observed to be stationary?

4. Little-Problem Solutions

Of course, one explanation is that the window surface may be dirty and change the local value of contact angle, but observations show that even well cleaned glass exhibits this behavior. Another possibility, that has attracted the interest of manufacturers of products such as paint and fabrics, is the roughness of solid surfaces. In these cases the object is usually to produce the opposite of struck drops, that is, how to make surfaces more waterproof by reducing their wettability [10].

L.M. Hocking has proposed [9] that contact lines move over a solid surface because microscopic irregularities induce flow structures that may be interpreted as "velocity slip" from a macroscopic point of view.

In the remainder of this paper we shall look into the issue of microscopic roughness and show how it can change dynamic contact angles, approximate slip conditions, reduce wettability, and even prevent small drops from flowing down a vertical surface.

5. Flow over a Rough Surface

It is instructive to see how a contact line moves over a rough surface consisting of transverse, regularly spaced, rectangular slots. For our test case the slots are 2μm deep and 10μm wide, and spaced to have 10μm wide solid pieces between them. The static contact angle with the solid was chosen to be 120°. Water is the working fluid. The test consisted of driving water at 30cm/s through a two-dimensional channel of height 15μm, having a free-slip top boundary.

In the first test, used as a control, the "roughness" slots along the bottom of the channel were omitted. The contact line moves smoothly over the solid surface with a dynamic contact angle of about 115°, see Fig. 2a. One would have expected that the advancing contact angle would have been larger, not smaller, than the static contact angle. In this case, however, the top boundary symmetry plane imposes a 90° contact angle on the liquid surface, which contributes to a straightening of the curvature at the bottom boundary and results in a lower advancing contact angle. The proximity of the top boundary will not affect the conclusions to be drawn from the remaining test cases.

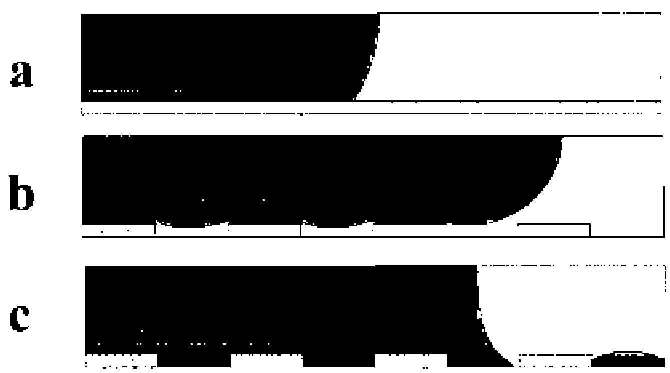

Figure 2: Flow of liquid with static contact angle 120° over (a) smooth surface, (b) rough surface, and (c) liquid filled rough surface.

Repeating the simulation with the rough boundary, it is immediately evident that the water surface gets attached to the edge of a slot and remains there until the surface becomes horizontal and makes contact with the next, downstream portion of the boundary, see Fig.2b. The liquid cannot fill in the slots because of the non-wetting static contact angle. The good way to think of this is that any adhesive force existing along the sides of a slot would be directed upward into the fluid.

An effective, advancing contact angle for this case is a mixture of the 115° angle when the contact line moves across the solid portions of the boundary and 180° while the liquid surface is pulled out flat from the edges of the slots. If β is the fractional area, per unit area, of solid surface then the effective advancing contact angle θ_a is approximated by $\theta_a=120\beta+180(1-\beta)$.

This result is basically the same as that found for flow over fabric surfaces, which consist of parallel rows of circular cylinders instead of rectangles [10].

Finally, we repeat the simulation once again, but this time with the slots initially filled with water, Fig.2c. When the liquid contact line reaches the beginning of a slot, instead of being held back at the corner as in the empty slot case, it shoots rapidly across the surface of the liquid in the slot approximating zero contact angle behavior. Actually, in our example the zero angle concept is not fully realized because the liquid in the slot is pulled into the main body of fluid leaving a small portion of the slot dry ahead of the contact line. This result is partly due to the limited resolution used in the simulation. In reality there would probably be a thin viscous layer of water in the slot that would prevent water in the slot from being completely pulled out to form a dry region. The effective advancing contact angle in this, pre-wetted, situation is $\theta_a=120\beta+0(1-\beta)=120\beta$.

Hocking's assertion that micro-scale disturbances can be interpreted as a kind of velocity slip when looked at from the point of larger scales is supported by the computed velocity field. Vertical velocity disturbances introduced by the roughness slots are confined to a height above the solid surface comparable to the depth/width of the slots. That is, to microscopic depths for microscopic roughness elements. This is shown graphically in Fig.3, which gives the horizontal velocity distribution in the layer of control volumes immediately above the surface. With further grid refinement, the velocity above the solid portions of the surface would tend to zero, but above the slots the velocity remains non-zero. Averaging over many roughness elements for a macroscopic view results in a non-zero horizontal velocity that could be interpreted as an effective slip.

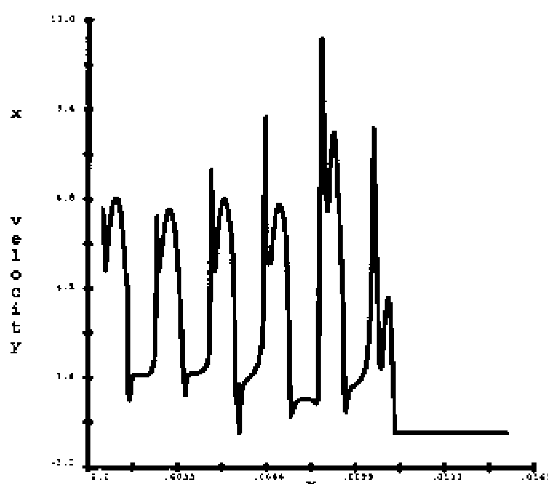

Figure 3: Horizontal velocity profile immediately above solid surface. Horizontal line segment at right side is zero level.

6. How do Drops Get Stuck?

To see how roughness can hold a droplet on the surface of a vertical plate, consider an example of a hemispherical droplet having a static contact angle of 90°. This contact angle implies an adhesion force normal to the solid surface. A drop on a smooth surface would then be expected to run off a tilted surface, its motion being retarded only by viscous shear stresses. On the other hand, we have also seen that on rough surfaces contact lines are caught at roughness edges. On a rough surface there must be regions having a surface normal with components parallel with the macroscopically smooth surface. At these locations adhesion forces can act counter to gravity.

The gravitational force pulling a drop down is proportional to its size (mass). A simple upper bound for a net adhesion force would be to have it acting on roughness surfaces with a total width equal to the diameter of the droplet (i.e., no net restraining forces along the sides of the drop). Equating this adhesion force, $4R\sigma$, to that of gravity, $(2\pi/3)\rho g R^3$, gives the maximum droplet radius that could be held stationary on a vertical wall. For water this value is R=0.38cm. This estimate is surely an upper bound, but it offers a reasonable estimate of the size of drops observed to remain at rest (e.g., about R=0.3cm on our office windows).

Figure 4 shows simulations that illustrate the effect of roughness. A cylindrical cap of fluid with a 60° static contact angle has been initialized on a vertical surface such that is makes a 60° angle with the solid, Fig.4a. The maximum height of the drop above the surface is 0.5mm. After some time the drop on the rough surface (60μm groves), Fig.4b, has only adjusted its contact lines to the edges of the groves and has no net vertical motion. In contrast, the same drop on a smooth surface, Fig.4c, is sliding downwards.

7. Summary

A numerical simulation method has been used to investigate the microscopic behavior of a moving contact line in the presence of roughness elements. The qualitative, macroscopic results agree with observations, but the details of the local flow behavior, which has never been directly observed, is found to be quite complex. It has been argued that roughness is one way for small droplets to remain at rest on a tilted surface. Computational examples clearly exhibit this behavior.

These results demonstrate how a continuum model based on conservation laws applied to finite control volumes can be used for detailed investigations of wetting and drying phenomena on non-uniform surfaces. Because the model approach described here exists in a commercial software product [5], it is available for immediate application to the investigation of stability and quality issues associated with many types of coating processes.

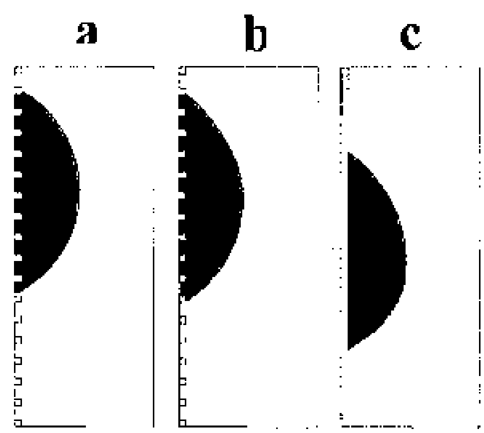

Figure 4: Droplet on a vertical wall. (a) initial condition, (b) stuck on roughness elements, and (c) sliding down smooth wall.

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