Not even Hercules : the moving contact line problem

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Abstract

The problem of the moving contact line is described and the singularity that arises after application of the classic hydrodynamic model is discussed. The central experimental observation that the motion is rolling is confirmed by a simple experiment. Subsequently, some of the various methods that have been developed to resolve the difficulty are briefly described. In addition, the lubrication equation for thin films is derived for the linear slip-shear boundary condition and Van Der Waal force potential that depends on the height of the thin film. This associated partial differential equation serves as the starting point for many numerical and analytical studies of the moving contact line problem.

1 Introduction

In our daily experience, the motion of fluids is a familiar event. Specifically the motion of fluids upon solid objects i.e. honey flowing down onto our breakfast, or droplets of water moving around the windshield as we drive. There is nothing obviously remarkable about this motion in our daily lives. However, the mechanisms responsible for this motion are not as simple as we could expect. Removed from everyday experience, controlling this mechanism has applications to industrial processes like oil extraction, de-icing of airplanes or spin coating of microchips [3].

The motion of the fluid outlined above seems innocent enough to be sure. However, it is a example of the breakdown of the classical theory of continuum fluid dynamics. Scientists have known about such exceptions before, for example in the case of high speed flows where gas intermolecular dynamics become more and more important. These kinds of problems arise as a result of the breakdown of the continuum assumption of fluids and it should not be surprising for the continuum theory to fail. However, in the case of viscous flow over a solid, no such violation can be readily detected. Where does the breakdown occur and why does it arise?

To understand this fundamental source of the problem it is first necessary to describe the classical theory. The Navier-Stokes equations are based on a macroscopic, continuum model of fluids (and not by definition molecular). Classically, the governing boundary condition for a viscous fluid at a solid boundary is that of continuity of the velocity [2]. In particular the condition can be mathematically realized by imposing that the velocity field $\mathbf{u}$ be continuous across any two media. In particular, for a solid boundary the tangential velocity must be zero since there clearly is not any velocity in the solid. The following is the no-slip boundary condition at the intersection between

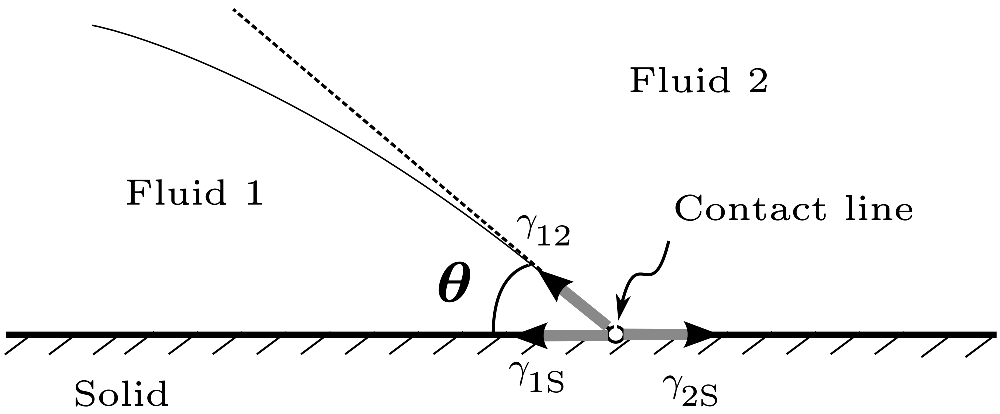

Figure 1: The contact line is the intersection of the three media. In our case we have a solid wall as a third medium.

the solid and fluid:

$$\begin{aligned}
&\mathbf{u}_+ \cdot \mathbf{t} = \mathbf{u}_- \cdot \mathbf{t} \\
&\mathbf{t} : \text{tangential vector at the solid} \\
&\mathbf{u}_+ : \text{velocity vector vector in the fluid} \\
&\mathbf{u}_- : \text{velocity vector at the solid}
\end{aligned} \tag{1}$$

The basis for such a boundary condition comes from a microscopic argument. It is argued that if there exists slip between the two media. This slip gives rise to a stress that tends to force the system to equilibrate, i.e. the momentum gets dissipated to a mean level that causes the velocities to be equal on both sides of said interface. The Navier-Stokes equations along with the no-slip condition at the boundary are referred to as the classical theory.

We are interested in application of this hydrodynamic framework to the motion of fluids along solid boundaries. Referring to Figure. 1, in the static case of a bounded fluid it is well known that the interface between the fluids makes a characteristic angle θ with the solid boundary. The intersection of the interface and the boundary is known as a contact line. The balancing of interfacial surface tension energies γ_{1S}, γ_{2S} and γ_{12} produces the equilibrium or static case. The subscripts refer to the materials in contact at the interface. Using simple geometry it leads to the Young-Dupree equation:

$$\gamma_{2S} - \gamma_{1S} - \gamma_{12} \cos\theta = 0 \tag{2}$$

The static contact line is well documented empirically through the measurement of the contact angle and certain interfacial energies for different fluid and solid configurations. In the moving contact line (MCL) problem, the interface between the two immiscible fluids is in steady motion upon a solid substrate. In nature we can readily observe contact lines in motion. For example as temperature rises so does mercury in the thermometer due to pressure differences and capillarity. Such a simple motion exceeds the scope of the classic hydrodynamic theory described above as it predicts infinite forces and energies. As Huh and Scriven write:

Not even Herakles could sink a solid if the physical model [no-slip] were entirely valid [20]

How and why can Hercules be brought so low by a MCL? What can be done about it? The infamous MCL problem is the primary focus of this review.

Briefly, the structure of this paper is as follows: first, the specific origin of the infinite force is discussed and defined along with experimental conclusions drawn about the nature of a MCL. Then, several of the various methods to reconcile the apparent paradox are introduced. In section 3, we introduce the slip boundary condition, section 4 deals with the concept of a precursor film. Finally in section 5, the application of variational principles to the MCL problem is reviewed. Additionally, the lubrication equation for thin films is derived since it is known to capture the physics of the MCL while vastly simplifying the daunting Navier Stokes equations. A discussion summarizes the findings in this work.

2 The apparent paradox

2.1 Experimental observations

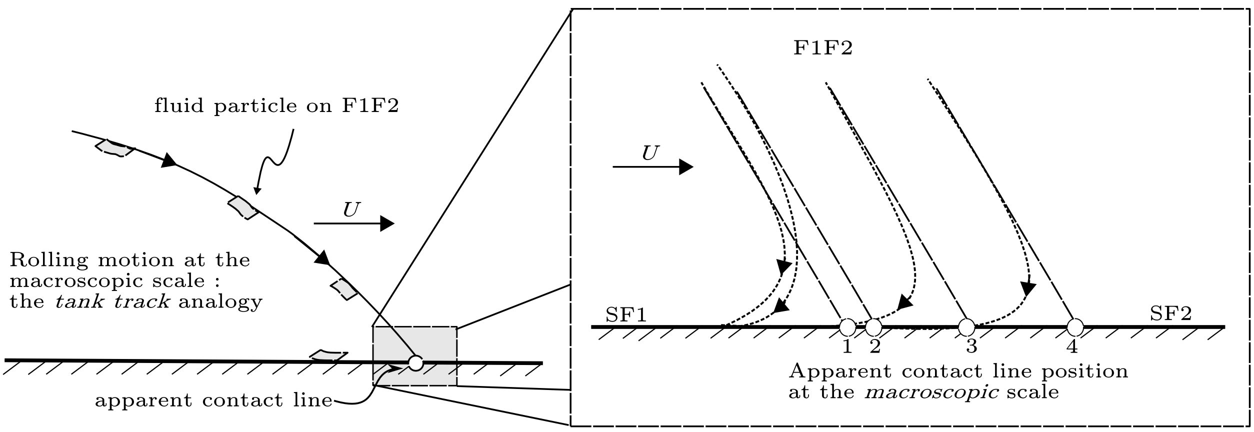

Figure 2: The rolling motion may have an analogy to the motion of tank tracks. The interface between the fluids is not a material line, i.e. different fluid particle become *part* of the interface over time. For consistency with no slip, the actual contact angle would tend to zero as shown on the right.

Much effort has been spent over the years to try to understand the dynamics of the advancing contact line. It is helpful to first describe the empirical observations that characterize the MCL problem.

- The motion is *rolling* more akin to a rigid body than a fluid [12, 18]. Figure 2 shows the motion at the macroscopic and microscopic length scales. The interface relaxes onto the solid and the interface clearly does not *slide* along the surface. The description of rolling is meant to signify material fluid points that make up the interface between the two fluids reach the contact line in finite time as the fluid moves and this points are deposited onto the solid fluid interface. An apt analogy is the motion of the tracks of a tank.

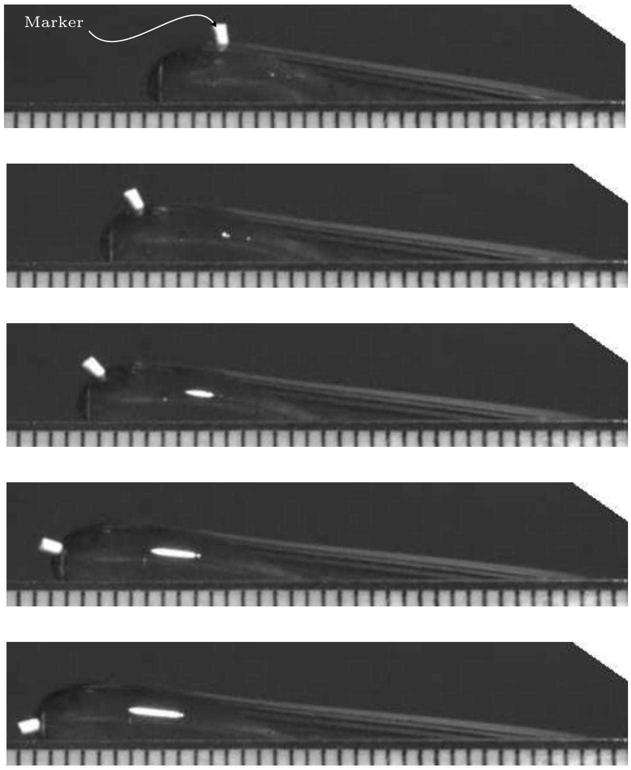

Figure 3: The motion of the marker is clearly rolling. Assuming that the velocity field can be inferred from the position of the marker, then it is clear that the motion is as described in Ref. [12].

To confirm this we conducted an experiment at the Applied Math laboratory at the University of Arizona. A drop of honey was placed on an inclined plate of plexiglass at 35 degrees. The subsequent motion driven by gravity clearly shows the rolling motion that was originally observed by Dussan and Davis [12]. The motion was observed with a high-speed camera and recorded as shown in Figure 3. A marker was placed on the drop as it moved and was observed to follow a rolling motion as the drop moved down the incline.

- The equilibrium contact angle of the fluid-solid interface evolves during motion to a so-called dynamic contact angle that depends on the velocity of the contact line [24]. Also, the value of the dynamic contact angle has a limit that depends on the media that are involved in the motion.

- An instability caused by increasing the speed of propagation can cause a *sawtooth* profile of the advancing front as well [4].

Our main concern in this review is to explore the consequences of the first point. As found by Dussan and Davis in Ref. [12], the rolling assumption together with the no-slip boundary condition causes an unacceptable result: the stress on the solid walls of an advancing contact line is infinite for normal Newtonian fluids.

2.2 The classic model

As mentioned, we are interested in the application of the classical theory in the context of the moving interface between three different media. In our macroscopic model the interface of different media are realized as infinitely thin surfaces in three or two dimensions. For completeness we present the full Navier-Stokes (NS) equation of motion for incompressible flow and the continuity equation:

$$\nabla \cdot \mathbf{u} = 0 \tag{3a}$$

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla)\mathbf{u} = -\nabla p + \rho \mathbf{f} + \mu \nabla^2 \mathbf{u} \tag{3b}$$

where $\mathbf{u}$ is the velocity vector, p is pressure, and $\mathbf{f}$ is the body force on the fluid. In this case the parameter ρ is the density of the fluid, and μ is the dynamic viscosity.

Applying the classical machinery to describe the flow runs into a brick wall as described in the next section. The problem arises when the mechanism used to describe such flows includes the so-called no-slip condition in the context of the NS equations. This condition has been known to be consistent with situations where non-continuum effects in the fluid under study are negligible, i.e. when the mean free path scale is far smaller than that of the geometric scale of the flow. Nevertheless the moving contact line eludes easy description within this framework even though the continuum assumption of the fluid seems entirely reasonable.

2.3 The multivaluedness

The underlying difficulty originates from a fundamental failure of the the no-slip condition [Eq. (1)] at the solid boundary to hold while maintaining a properly defined velocity field near the MCL [12]. Specifically, if we impose the no-slip condition, the velocity field at the MCL is discontinuous, i.e. we can show that the velocity is dependent on the direction in which we approach the MCL be it along the wall or along a material particle surface ending in the MCL.

Following Dussan and Davis [12], consider a moving contact line between fluid 1 and 2 ($F1$ and $F2$) at a uniform speed U over the solid denoted by S as shown in Figure 4. If we attach the coordinates of the system to the contact line locus, then the solid wall appears to be moving toward the contact line at a speed U. The interface between the solid and fluid 2 is abbreviated by $SF2$, and likewise the same follows for $SF1$ and $F1F2$.

Since we consider a no-slip condition the fluid particles in $F2$ that are adjacent to the wall *adhere*, i.e. cannot drift away from the corresponding material point on the wall since this would imply slip. Therefore a pair of fluid and solid material points (denoted $\mathbf{x}_{F2}$ and $\mathbf{x}_S$ respectively) reach the contact line at the same finite time interval t_1 and are in contact (for $t < t_1$). It is clear that the solid material point becomes part of the $SF1$ interface after passing through the contact line. However, where does $\mathbf{x}_{F2}$ go after meeting the CL? We make the following assumptions about the system:

- From experiment [12], the interface between $F1F2$ is not a material surface, different material points make up the interface and are mapped onto the CL, i.e. there is motion into the CL from the right if the motion of the CL is to the right. (This is the forward assumption).
- The interface between $SF1$ is made up of only $F1$ and solid material points.

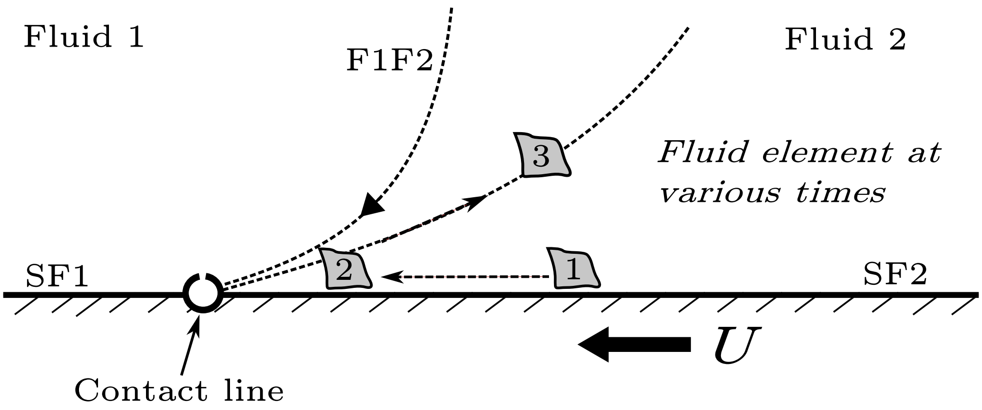

Figure 4: The region near the contact line (coordinates attached to the MCL). The wall has velocity U in this frame of reference. Material points on $F1F2$ reach the contact line in a finite time in the direction noted. A material surface must exit from the MCL as well.

- The density has no singularities, i.e. $\rho \neq 0, \infty$.
- The no-slip condition holds at the boundary.

We note that these assumptions do not hold for all possible fluid configurations. We are concerned with fluids that form well defined interfaces both dynamically and statically. There are four possibilities for the trajectory of the $\mathbf{x}_{F2}$ material point:

1. $\mathbf{x}_{F2}$ remains attached to the solid boundary material point $\mathbf{x}_S$.
2. The fluid particle is mapped onto the $F1F2$ fluid interface.
3. $\mathbf{x}_{F2}$ remains on the CL.
4. Finally, the fluid particle is mapped into $F2$.

We treat the viability of each of these outcomes in turn. **Alternative 1** is impossible since the $F2S$ interface is composed of solid and $F2$ material points. If $\mathbf{x}_{F2}$ is mapped into this interface it is implied that its volume has been shrunk to zero and since we must have conservation of mass this implies that the density has gone to ∞. This is not possible so we discard this possibility.

Alternative 2 is likewise impossible, simply because the the material points on the interface are in a rolling motion that deposits them in a finite time into the CL. Therefore to maintain a continuous velocity we cannot allow points to move in the opposite direction along the interface. Therefore $\mathbf{x}_{F2}$ cannot be mapped onto the interface.

Alternative 3 is also impossible since this would violate no-slip, i.e. $\mathbf{x}_{F2}$ is then attached to a different material point on the solid for $t > t_1$.

Alternative 4 is therefore the only choice left. It implies that the material point on the $SF1$ interface are *ejected* onto $F2$ after reaching the CL. So along the surface the tangential velocity at the CL must be opposite that of the motion of the solid. This is a result of the no-slip condition imposition.

This ejected surface is the source of the discontinuity. As mentioned, the velocity along the ejected surface must be opposite in direction to that along the surface. This causes the discontinuity of the velocity field near the CL. The multivaluedness of the velocity field is evident. Since the tangential stress felt by the wall for a large set of fluids like honey or water goes like the gradient of the velocity, the no-slip condition precipitates an infinite stress under these circumstances. If the stress is then integrated, the singularity will cause an *infinite* force which is profoundly unrealistic. Note: this is a product of the underlying model, it is not due to a shortcoming in a solution found by approximate means. This is a more general treatment than that given by Huh and Scriven [20] who make a Stokes approximation to the NS equations and eventually encounter the discontinuity using the no-slip condition for a moving contact line system.

As noted in Ref. [3], we should not expect our macroscopic hydrodynamics model to hold in all situations. It is recognized that the mechanism at work must be acting at a molecular scale [20] and can possibly be very complicated. The challenge is to reconcile this divergence with our hydrodynamic model to produce a physically realistic idea of the underlying molecular mechanism.

3 The slip boundary condition

One the first methods that was proposed to relieve the force singularity at the CL was to simply relax the no-slip condition in the region of the contact line. For example, Huh and Scriven suggest just that in Ref. [20]. The relaxation of the no-slip condition near the contact line eliminates the discontinuity of the velocity by allowing slip, or a relative fluid velocity at the wall.

Mathematically, the most popular form of the condition is to assume that the velocity at the wall is proportional to the normal velocity gradient [21], and is referred to as the linear slip-shear relation. The constant of proportionality has units of length and is referred to as the slip length. If u is the tangential velocity component at the surface and z is the normal coordinate, it is written as

$$u|_{z=0} = \beta \frac{\partial u}{\partial z}\bigg|_{z=0} \tag{4}$$

In the case that the β coefficient is simply zero then it is clear that the no-slip condition is recovered, i.e. if the slip length is zero, then naturally, there is no slipping. The specific form that β takes varies according to the physical setting of the problem. The discontinuity in the velocity is removed since the fluid is allowed to slip near the MCL. Since the material fluid particles in front of the MCL are no longer required to reach the CL in a finite time, then the material surface in Figure 4 does not originate in the MCL. This allows the velocity to be single-valued at the contact line.

The slip model was applied by Hocking in Ref. [19] to the problem of MCL between a gas and fluid and to the normal contact between two fluids in a pipe. Using the technique of matched asymptotic expansions, Hocking calculates the *finite* force imparted on the solid boundary by the slip flow. Under the Stokes approximation, Hocking found a solution in the vicinity of the contact line that was calculated using the slip condition and matched it to a second solution calculated using no-slip model. Dussan showed that the particular form of the relaxation had little effect on the macroscopic picture although it naturally did have an impact for scales very close to the CL [10]. The particular form of the slip condition used in Ref. [10] allows slip near the CL but with varying degrees decays to the no-slip condition far from the CL. However beyond the solving of specific problems using the slip-condition, there was no initial rational basis for the new boundary condition as readily accepted in these two investigations.

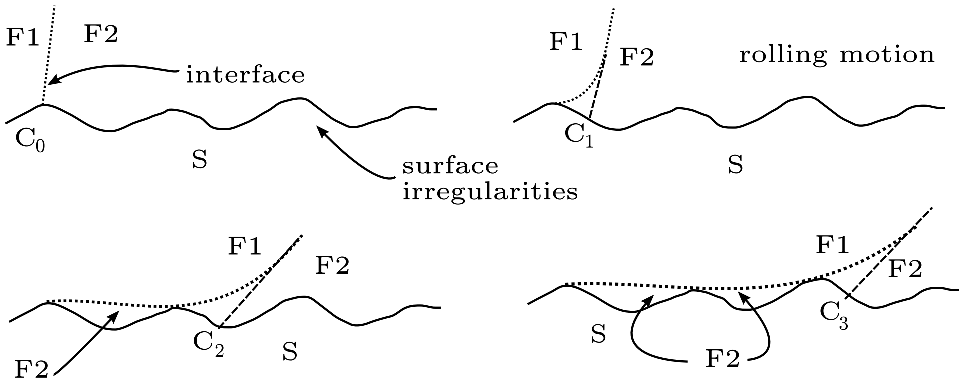

Figure 5: The figure shows the rolling motion that would be observed at the scale of surface roughness. The apparent contact line would be the position C_i in each snapshot of the motion as shown. It is clear that pockets of fluid 2 would lubricate the motion of the interface above thereby causing an apparent slip, while the no-slip condition would in fact hold for the fluid in the pockets.

As mentioned, the physical justification was not clear in the initial attempts to solve well-posed boundary value problem with slip. Hocking in Ref. [18] theorized that the slip condition was the result of surface irregularities which he shows in a figure similar to Figure 5. Hocking argues then, that we can model the result of the microscopic process in Figure 5 by allowing a slip-boundary condition over a ideally smooth surface in the macroscopic scale. Using particular simplifications for the seemingly random irregularities in the physical world, Hocking derives theoretical values for the slip coefficient within this framework.

The slip boundary condition can be used in the Stokes flow approximation which leads to the biharmonic equation

$$\nabla^4 \psi = 0 \tag{5}$$

where ψ is a streamfunction that satisfies the continuity equation [19, 10]. These class of solutions we important for testing the consequences of allowing slip at the boundary. They have the added benefit that the unknown pressure field is not explicitly formulated.

There are other physical justifications that have been proposed over the years and these led to more sophisticated boundary conditions than the simple linear slip relation. Among these, it has been proposed that by Shikhmurzaev [25] that a surface-tension gradient caused by the *rolling* motion of the interface between $F1F2$ is responsible for the slip boundary condition. It relates the difference in tangential velocities to a expression relating forces acting at the boundary surface. As Shikhmurzaev describes in Refs. [26, 25], the generalized Navier slip boundary condition is in reasonable agreement with experimental data. It is derived from the physical ideas expressed previously, in contrast with the initial lack of physical justification offered for the Navier slip condition [10, 20].

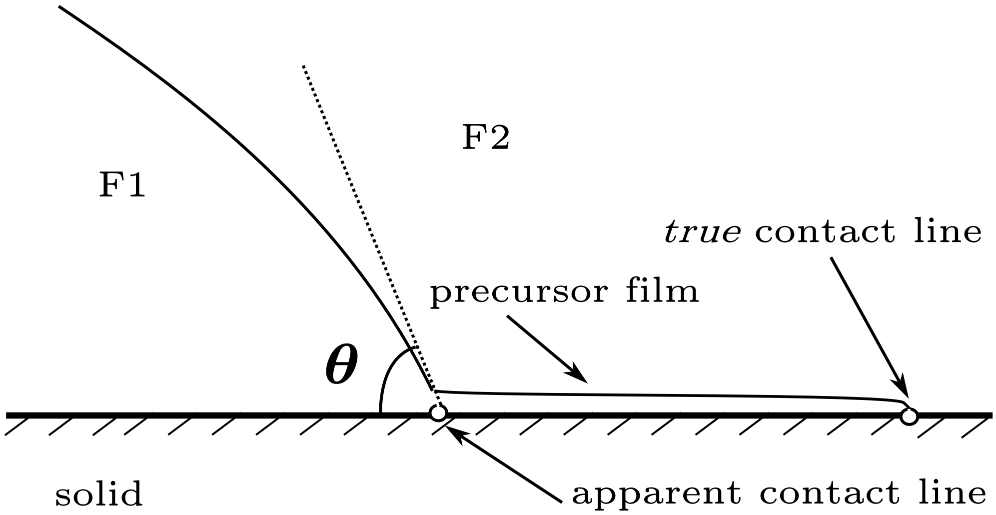

Figure 6: The precursor film advances ahead of the primary part of the interface.

4 The precursor film

Another attempt at resolving the present difficulty that arises with the no-slip condition was to simply propose that there is a *foot* or very thin layer of fluid that lubricates the advance of the now *apparent* contact line. This idea has a broad basis in the study of wetting, i.e. the spread of drops or droplets on solid surfaces. Clearly, moving contact line dynamics are involved in the description of the wetting phenomena. This advancing thin film is usually considered to be less than a micrometer thick. Bascom et al. found precursor films of a few hundred angstroms in thickness [1]. Given this thickness falls within the effective range of Van Der Waals interaction with the molecules that make up the surface of the solid, Van der Waals forces (VW) are thought to generate the precursor film [7]. Broadly, the VW forces are microscopic scale forces between the solid and liquid substances in question[3]. The mechanism for the formation of said films is the disjoining pressure near the contact line caused by the VW forces [7].

In Figure 6, the main idea is presented. The precursor film announces the arrival of the apparent contact line $\mathcal{L}_a$. However, the *true* contact line $\mathcal{L}_r$ is now displaced a finite distance ahead of $\mathcal{L}_a$. This alleviates the requirement that material points from the displaced liquid reach $\mathcal{L}_a$ and thus there is no multivaluedness as described previously. However, an obvious question arises: if the contact line is simply displaced forward, is not the singularity present there?

The precursor film eliminates the discontinuity and thus the singularity associated with the moving contact line [6]. According to de Gennes [7]: ”All the excess free energy is burned in the film” and so the total energy dissipated from the apparent contact line motion is finite which eliminates the MCL singularity.

The applicability of the precursor film model is not universal. For instance in partial wetting situations (the contact angle in equilibrium is finite), the precursor film does not exist [8]. Additionally, the thin film cannot be treated solely within the hydrodynamic framework since intermolecular forces may play a dominant role [5]. Its role in wetting dynamics however cannot be ignored as a way to explain the energy dissipation and the MCL dynamics.

5 Variational approach

Variational principles are an important concept in physics and more specifically mechanics. In Ref. [15], the principles are described within the context of fluid flow as

- *the free energy in the flow decreases as fast as possible* and
- *changes in configuration cause the fluid flow to choose the configuration that minimizes the energy dissipation*.

or in a more general setting, the system's configuration *chooses* that which minimizes energy dissipation.

The application of variational principles to the contact line problem has some history. In de Gennes' work on wetting [7], the author resolves the MCL singularity with the use of the precursor film using arguments based on energy dissipation. In wetting flows for example, Otto and Giacomelli used variational arguments to obtain analytic bounds for droplet spread in slip models of contact line motion [13]. Similar arguments were also used by Glasner in Ref. [14] in the context of lubrication equation with intermolecular forces. These tools have been mainly used for the mathematical analysis of the problem.

The use of variational calculus can be extended. In [15], Glasner uses variational principles in actual modeling of the contact line evolution. The salient point made in [15] is to recognize that the microscopic mechanism that describes the motion near the contact line may not be resolvable in the macroscopic flow. The argument is that any method that relieves the infinite energy dissipation at the contact line is characterized by the rate of energy dissipation and not the actual microscopic mechanism be it slip, VW forces or precursor films.

In Ref. [22], Qian et al use variational methods and the idea of minimizing energy dissipation to derive the generalized Navier slip condition outlined in section 3. Within this framework, it is shown that the hydrodynamic flow generated by the generalized Navier slip is in qualitative agreement with molecular dynamics simulations. These simulations involve modeling of force interactions with elements on the scale of molecules and atoms. These lead to so-called *virtual* experiments.

6 Derivation of lubrication equation

Many studies involving the moving contact line problem are investigated within the framework of the lubrication approximation including models using slip, variational and precursor film ideas [9, 15, 29]. This framework is a convenient setting to test the consequences of the specific mechanism used to remove the MCL singularity since it captures the underlying physics of the MCL. Solving the Navier-Stokes equations in the presence of fluids of different physical characteristics and varying interface location is extremely difficult. Fortunately, flow near a contact line can be considered within the framework of the so-called lubrication approximation. This reduces the Navier-Stokes equations to a more tractable *single* PDE with the height of the thin film as the sole dependent variable. The specific form of the equation can be made quite general but we focus on the equation resulting from the linear slip-shear boundary condition as in [16] and simple Van Der Waal (VW) type forces that act as a function of the film height. The lubrication approximation has the defining characteristics:

- The pressure is independent of the height of the thin film,
- the temporal and convective accelerations are negligible, and
- therefore the predominant forces are the viscous and pressure forces and their balance gives the approximate momentum equation. The viscous force in the horizontal direction is dominant as well.
- Also, we consider a height-averaged equation of continuity.

We consider a thin film of very viscous liquid above a planar solid substrate as in Figure 7. Define the following variables: $\mathbf{u}_H = u\mathbf{e}_x + v\mathbf{e}_y$ (horizontal part of the velocity vector), $p = p(x, y, t)$ is the modified pressure, i.e. the sum of mechanical pressure p' and body force potential ϕ. The terms relating pressure and body forces can then be combined in the momentum equation (3), i.e.

$$\begin{aligned} \rho \frac{D\mathbf{u}_H}{Dt} &= -\nabla_H p' + \mathbf{f} + \mu \nabla_H^2 \mathbf{u}_H = -\nabla_H (p' + \psi) + \mu \nabla_H^2 \mathbf{u}_H \\ &= -\nabla_H p + \mu \nabla_H^2 \mathbf{u}_H. \end{aligned} \tag{6}$$

since $\mathbf{f} = -\nabla\phi$ and where $\nabla_H = \frac{\partial}{\partial x}\mathbf{e}_x + \frac{\partial}{\partial y}\mathbf{e}_y$, i.e. only the horizontal projection. In the lubrication approximation, the pressure is independent of height z, and we write the approximate momentum equations (ignoring the acceleration terms, i.e. $\partial \mathbf{u}_H / \partial t$ and $\mathbf{u}_H \cdot \nabla_H \mathbf{u}_H$) and since the vertical scale is considered much smaller, then derivatives in this variable will be more significant than those in the dominant horizontal scales,

$$\frac{\partial^2 \mathbf{u}_H}{\partial z^2} \gg \frac{\partial^2 \mathbf{u}_H}{\partial x^2} + \frac{\partial^2 \mathbf{u}_H}{\partial y^2} \tag{7}$$

so we obtain that

$$\nabla_H p = \mu \frac{\partial^2 \mathbf{u}_H}{\partial z^2} \tag{8}$$

As we hypothesized, the pressure is independent of z and therefore the above equation can be integrated twice exactly for $\mathbf{u}_H$,

$$\mathbf{u}_H = \frac{\nabla_H p}{\mu}\left(z^2/2 + C_1 z + C_2\right) \tag{9}$$

The constants above can be eliminated with the help of the following boundary condition:

- vanishing shear stress at the free surface i.e.

$$\frac{\partial \mathbf{u}_H}{\partial z} = \mathbf{0}, \; z = h(x, y, t) \tag{10}$$

- and also introduction of the linear slip-shear condition,

$$\kappa(h) \frac{\partial \mathbf{u}_H}{\partial z} = \mathbf{u}_H, \; z = 0 \tag{11}$$

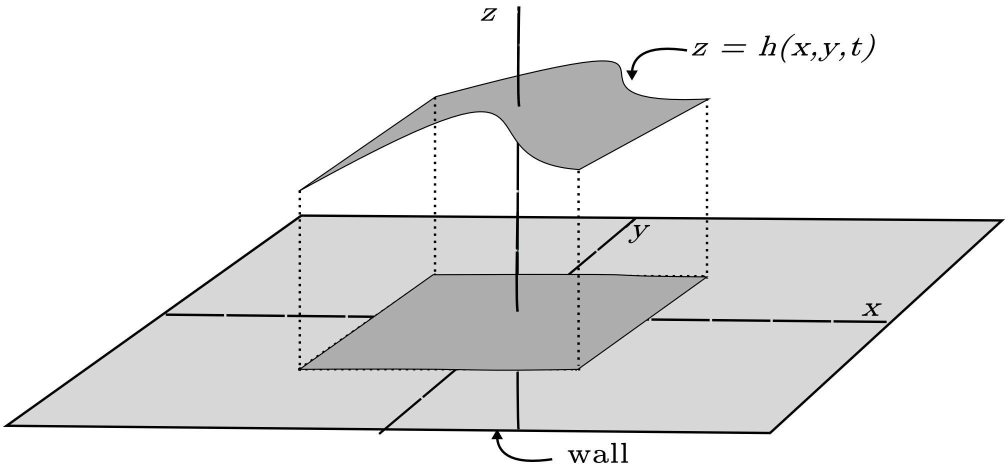

Figure 7: The height of the film depends on x, y and projects onto the z axis.

where $\kappa(h)$ is a function of h and called the slip coefficient. Generally, this slip coefficient should vanish far from the contact line which in the lubrication approximation implies that κ is important only when $h \to 0$. Typically forms for $\kappa(h)$ that are chosen are α/h^n for $n = 0, 1, 2$ etc. The imposition of the above gives that

$$C_1 = -h, \; C_2 = -h\kappa(h)$$

and so we write the full expression for the horizontal velocity in terms of the yet unknown p,

$$\mathbf{u}_H = \frac{\nabla_H p}{\mu}\big(z^2/2 - hz - h\kappa(h)\big) \tag{12}$$

Introducing the depth averaged velocity $\mathbf{Q}$,

$$\mathbf{Q} = \frac{1}{h}\int_0^h \mathbf{u}_H dz \tag{13}$$

we can produce the depth-averaged conservation of mass equation in terms of h and $\mathbf{Q}$ by considering a small volume element bounded by a rectangle in the wall (size $\Delta x \times \Delta y$) and the height $h(x, z, t)$ as in Figure 7.

Taking the limit as $\Delta x, \Delta y \to 0$, the equation reads

$$\frac{\partial h}{\partial t} + \nabla_H \cdot (h\mathbf{Q}) = 0 \tag{14}$$

Now we must say a word about the modified pressure p. The mechanical pressure p' is assumed to depend on the curvature of the interface via the relation due to surface tension i.e.

$$p' - p_0 = -\gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = -\frac{\gamma\nabla_H^2 h}{(1 + (\nabla_H h)\cdot(\nabla_H h))^{3/2}}, \tag{15}$$

p_0 : ambient pressure above the fluid interface

$R_1, \; R_2$: mean radii of curvature of the free surface in 2D for fairly flat geometries we can ignore the contribution from the denominator and we simply hold that $p' - p_0 = -\gamma \nabla_H^2 h$, i.e. $\nabla_H h \approx 0$. In general, so-called long-range Van Der Waals forces which arise from the interaction of particles near the wall and the thin film can be introduced into the thin film equation via the imposition of a specific form of the potential term ϕ in p. These Van Der Waals forces are modeled in the following form:

$$\phi(h) = A_D h^{D-5} \tag{16}$$

where A_D is a particular constant that depends on the dimension of the substrate [3, 23, 28]. Then we have an explicit expression for the modified pressure,

$$p' = p_0 - \gamma \nabla_H^2 h + \phi(h), \tag{17}$$

Using these definitions, we can write the full dimensional equation governing the film height

$$\begin{aligned} &\frac{\partial h}{\partial t} + \frac{1}{\mu} \nabla \cdot \Big(f(h)(\gamma \nabla \nabla^2 h - \nabla \phi(h)) \Big) = 0 \\ &f(h) = h^3/3 + \kappa(h) h^2, \; \phi(h) = A_D h^{D-5} \end{aligned} \tag{18}$$

We note that the equation is ultimately fourth order in spatial derivatives of h whether or not slip and Van Der Waal's forces are included. This leads to so-called fourth order degenerate diffusion [3]. The boundary conditions, initial condition and constraints of the above equation are as follows:

- The film is bounded by a contour delineated by two functions of time $x_e(t)$ and $y_e(t)$, the *edge* values. Specifically it means that at $(x_e(t), y_e(t))$ the height of the film is zero i.e. $\Gamma = h(x_e(t), y_e(t), t) = 0$,

  $$h(x, y, t) = 0 \text{ on } x = x_e(t), y = y_e(t) \tag{19}$$

  The evolution of the contact line is governed by its velocity or time derivative of the above quantities,

  $$\mathbf{u}_e = \left(\frac{dx_e}{dt}, \frac{dy_e}{dt} \right)^T = \mathbf{Q}(x, y, t) \Big|_{h=0} \tag{20}$$

  where $\mathbf{u}_e$ is the edge velocity or the velocity of the contact line. This condition follows that from Greenspan in Ref. [16]. There is physical evidence that suggests that the contact line velocity is tied to the apparent contact angle θ the film makes with the solid [11] near the CL. In Ref. [17], the case of an axisymmetric one-dimensional surface in polar coordinates (r, ϕ, z) is treated. The contact line therefore lays on a spreading circle of radius $R_e(t)$, and its evolution is related to the height of the film by a relation of the sort

  $$U_s = \frac{dR_e}{dt} \propto f(\theta), U_s : \text{slip velocity} \tag{21}$$

  The angle θ can be related to the height profile at the CL in the following way

  $$\frac{\partial h}{\partial r}\Big|_{r=R_e(t)} = -\tan\theta$$

However, the particular form of $f(\theta)$ is not definite. In particular there seems to be experimental evidence showing that $U_s \propto \theta^3$ and this empirical *law* was introduced by Tanner [27]. Subsequently, theoretical arguments have derived this relationship as well [11].

There is also some question about the additional boundary conditions that must be furnished to develop a well-posed problem based on the lubrication equation for thin films, Eq. 18 [3]. Haley and Miksis note that since the coefficient of the highest order goes to zero as $h \to 0$ an additional boundary condition may not be necessary [17]. The authors appeal to the smoothness and symmetry of the drop setting the first and third derivative of the film height to be zero at its center.

- The system has some initial shape at the initial time $t = 0$,

$$h(x, y, 0) = h_0(x, y) \tag{22}$$

- The constancy of mass and the incompressible assumption gives conservation of volume,

$$\int_{\mathcal{A}} h(x, y, t)dxdy = V_0. \tag{23}$$

This constraint is actually no constraint at all, since the lubrication equation is volume preserving by construction. However, it serves as a check that the numerical scheme used for solving the equation is physically consistent.

7 Discussion

In Ref. [10], it was shown that the no-slip boundary condition is *kinematically* compatible with the MCL. However, dynamic considerations i.e. where material fluid points are mapped to after reaching the CL, produce a multivalued velocity field. For Newtonian fluids under incompressible conditions, this implies that the stress at the wall or boundary is unbounded. It should be emphasized this singularity is a result of the no-slip condition and not a product of an approximation to the governing equations such as assuming Stokes or creeping flow. Therefore, it becomes clear that the no-slip condition is incompatible with a MCL and a mechanism for the elimination of unbounded force that results must be found. This gives rise to the various methods that have been proposed over the 30 years since its formal formulation.

After the initial problem was recognized formally for example in Refs. [20, 10], the correct approach to the modeling of the MCL problem was not clear. As Dussan notes in Ref. [11]:

> It is difficult to model a phenomenon for which there has been very little direct experimental measurement. It also seems naive to expect one model to cover all situations.

Dussan then discusses the relative merits of the removal of the singularity by the linear slip-shear relation and the precursor film. Initially, the natural solution seemed to be to simply relax the canonical no-slip condition even though it had no physical basis. Over the years, different physical justifications were proposed as experimental data increased. In addition, molecular dynamics (MD) simulations have solidified the idea that slip exists near the moving contact line.

One can ask the million dollar question: which method is the *correct* approach? The persistence of the various solutions that have been proposed over the year seems to imply that there is no correct solution. Consider that in Ref. [9], the authors solve the lubrication equation numerically using the linear slip relation and the precursor film approach. They report similar results for the profiles resulting from the different models. This lends support to the supposition that the particular microscopic mechanism to resolve the contact line singularity is effectively minimal when one considers the macroscopic picture. As noted by Glasner in Ref. [15], the key aspect may be simply that the energy be minimized. To infer which method is correct then, it is not enough to simply choose the one that produces the macroscopic flow since more than one method can serve. In Ref. [10], Dussan V. chooses three different functional forms for the slip parameter β such that the stress on the wall takes the values $0, 1$ and ∞ and yet finds little difference when considering the resulting flows in the macroscopic scale.

Recently MD simulations have been found to obey a differential boundary condition known as the generalized Navier slip boundary condition [22]. Additionally the boundary condition in question can be derived from energy minimization principles. Now, it is possible to perform numerical experiments through MD simulations that show agreement with theoretical considerations explaining the origin of slip at the MCL through force based descriptions [25] and energy minimization principles [22]. However, different schemes have physical basis and perform well when compared to experiments: both numerical and physical. As more experimental data is amassed perhaps the *correct* model for the MCL problem will gain focus.

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