ON THE SEARCH OF NUMERICAL BOUNDARY CONDITIONS FOR THE COMPUTATION OF DYNAMIC CONTACT LINES

M. Delia Giavedoni (*), Diego Campana (*), Fernando Saita (*) and <u>Ramon L. Cerro</u> (**)

(*) Instituto de Desarrollo Tecnológico para la Industria Química (INTEC), Universidad Nacional del Litoral, CONICET, Guemes 3450 (3000), Santa Fe, Argentina.

(**) Chemical and Materials Engineering, University of Alabama in Huntsville
Huntsville, AL, 35899

1. **Introduction.**

   Theoretical understanding of the combined effect of different forces on the movement of dynamic contac lines is one of the outstanding problems in fluid mechanics. Much research has been done to understand this problem since the pioner work of Huh and Scriven (JCIS, 1971). Although flawless from a mathematical point of view, Huh and Scriven solution configures a modern fluid dynamics paradox (Fuentes and Cerro, 2005). Unlike most physical phenomena where small causes result in small effects and large causes result in large effects, static and dynamic contact lines are macroscopic phenomena but depend (for small Capillary numbers) strongly on short and long-range molecular forces, of sub-micrometer range. Molecular, electrostatic and structural forces near a triple, fluid-liquid-solid contact line are responsible for static configurations and static contact angles and also for macroscopic flow patterns in the vicinity of dynamic contact lines at small Capillary numbers.

   Consider a pool of fluid where a flat solid slab, perfectly smooth and homogeneous, is partially immersed in the liquid. The solid is at rest and the liquid partially wets the solid determining a static contact line with a static contact angle. The solid slab is in a vertical position and because

Figure 1: Schematic setup of a flat solid slab rising from a pool of liquid.

$$\frac{dy}{dx} = \frac{dy}{dh} = \tan\left(\frac{\pi}{2} - \theta\right)$$

---
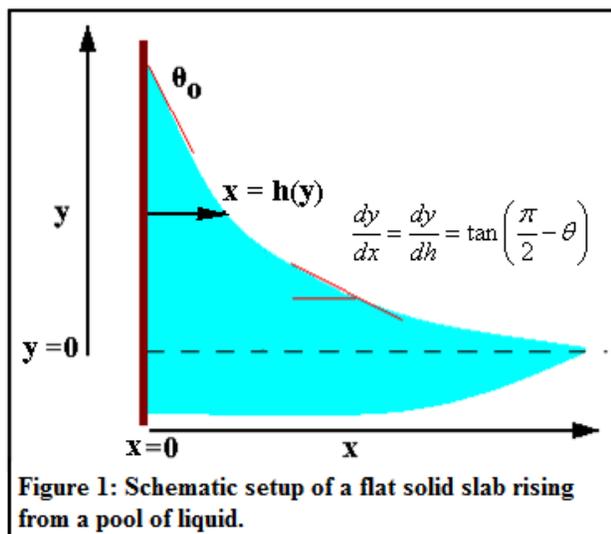
[1] Unpublished. ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.

of symmetry we only need to analyze one of the sides, as shown in Figure 1. We assume that the pool of liquid is semi-infinite and the solid slab is infinite for $y \to \pm\infty$. At some point in time, t = 0, the solid slab starts moving up at constant velocity U. If the velocity of the fluid is small and steady, we reach a regime described as dynamic dewetting (Sedev and Petrov 1991) where a dynamic contact angle is a function of the solid speed and it becomes increasingly smaller as the solid speed increases.

Above a certain critical speed [Vasilchina et al, (2004)] the dynamic contact angle vanishes and a macroscopic continuous liquid film is deposited on the solid surface. This is the dip-coating or drag-out regime, first analyzed by Landau and Levich (1941), later formalized by Wilson (1982) A variation of the dip-coating regime are Langmuir-Blodgett depositions where insoluble films of amphiphilic compounds are deposited continuously on a solid substrate while leaving most of the supporting liquid in the liquid pool (Cerro, 2003).

2. **Main theoretical and computational problems in dynamic contact line computation**.

To properly introduce molecular forces in a macroscopic computation using finite elements, we must introduce elements of nanometer size. Elements of nanometer size (10^{-9} m) within a macroscopic field of say 1 mm (10^{-3}m) characteristic size are comparable to using elements of 1 cm size (10^{-2}m) to model a hurricane that is 10 km (10^4 m) characteristic size. This *tyranny of scales* prevents the use of a straightforward approach in the computation of moving contact lines. In addition, one must have a reliable model to predict dynamic contact angles based on hydrodynamic as well as molecular level forces. Finally, the issue of slip or no-slip at the contact line, and the ensuing stress singularity (Huh and Scriven, 1971) must be resolved in a fashion that is satisfactory to a continuum mechanics approach. We will address these three aspects of the numerical computation of moving contact lines, separately.

2.1 **Slip versus no-slip.**

In static capillary rise, there is usually an adsorbed film of molecular thickness in the immediate vicinity of the contact line. This film is formed by a process combining evaporation of molecules of the liquid and successive adsorption of some of these molecules on the solid surface (Diaz et al. 2010A). The adsorbed film is not necessarily a continuous film, but depending on the liquid/solid system it may be formed by molecules of liquid adsorbed in isolated sites over the solid surface. Thus, the thickness of the film, on the average, may be smaller than a molecular diameter. The presence of adsorbed molecules of the liquid phase alters

Low N$_{Ca}$

Figure 2: Schematic view of a moving contact line leaving behind a film of molecular size.
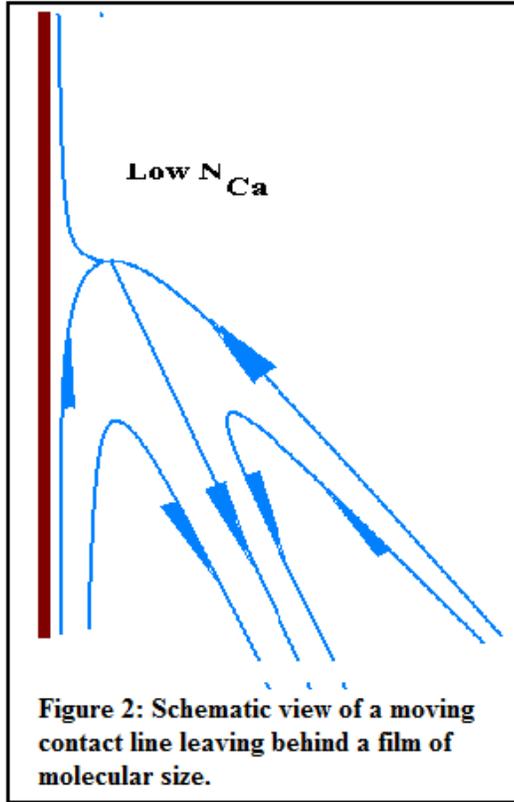
the equilibrium of molecular forces and determines the magnitude of the static contact angle (Diaz et al., 2010). As a consequence of the new equilibrium, the larger the thickness of the adsorbed film, the smaller the contact angle.

At low removal speeds, within the dynamic dewetting regime, the evaporation/adsorption process is aided by a hydrodynamic/capillary process very much like the drag-out process but with inclusion of molecular forces and disjoining pressure. Thus, there is always a film of liquid left on the solid surface as indicated qualitatively in Figure 2. The presence of this entrained film voids the no-slip problem because the moving contact line moves over a film of liquid. This model for the movement of a contact line was proposed first by Miyamoto and Scriven (1982) for an advancing contact line and later by Diaz and Cerro (2003) for a receding contact line.

2.2 **A model for dynamic contact angles**.

The thickness of a film entrained by a moving solid was analyzed by Landau and Levich (1942) including hydrodynamic and capillary forces. A similar analysis, including disjoining pressure and molecular level forces, can be used to develop a relationship between capillary and molecular forces with the flow rate or thickness of the film left behind by the movement of the contact line.

$$q = \frac{1.31\ N_{Ca}^{2/3}\ U_W}{\left(\sqrt{2} \left(\dfrac{\rho g}{\sigma} \right)^{1/2} - \dfrac{h_m^2}{h_\infty^3} \right)} \qquad ; \qquad h_m^2 = \left(\frac{A_{LL}^{[6]} - A_{SL}^{[6]}}{6 \pi \sigma} \right) \qquad (1)$$

Once the film thickness downstream is known, h_∞, we can use it to compute the dynamic contact angle using the relationship between the film thickness and the contact angle (Diaz et al. 2010). The presence of molecular forces creates three different effects. First, molecular forces result in the presence of disjoining pressure. Thus there is an additional pressure field that must be added to the existing hydrostatic pressure and normal viscous stresses. The second effect of

molecular forces is to create a tangential force along the air/liquid interface (Miller and Ruckenstein, 1974). Third, in a region very close to the contact line, interfacial tension varies due to molecular forces and creates a surface tension gradient. The second and third effect are very similar, although of a very different nature, to the additional shear stresses introduced by non-soluble surfactants.

2.3 Effect of molecular forces on elements near the solid surface.

In order to keep the number of elements within the reach of modern computational facilities one has to use small elements but of a size that is very large compared with the range of molecular forces. Even if the characteristic size of a finite element is a micrometer (10^{-6} m), it is well beyond the range of London-van der Waals non-polar forces.

There are two ways to deal with this intrinsic computational limitation, none of them completely satisfactory. One procedure consists on defining artificial boundary elements where molecular forces are computed using a weighted average of the finite element thickness. The second procedure consists on increasing the range of molecular forces by increasing molecular interation parameters or using long-range formulations, i.e. different inverse powers of the film thickness. This is still a work in progress where some encouraging results have been obtained but still without universal and reliable tools for the numerical simulation of dynamic contact angles.

References

J. Fuentes and R. L. Cerro, Experiments in Fluids, 38 (2005) 503-510.

C. Huh and L. E. Scriven, J. Colloid Interf. Sci., 35 (1971) 85-101.

L. D. Landau and V. G. Levich, Acta Physic.(USSR), 17 (1942) 42-54

K. Miyamoto and L. E. Scriven, 1st ISCST, Orlando, FL. 1982.

Diaz, M. E. and Cerro, R. L., AIChE Annual, San Francisco, CA, 2003.

Sedev, R. V. and Petrov, J. G.Coll. & Surfaces, 53 (1991) 147

Vasilchina, H., Tzonova, I. and Petrov, J., Coll. & Surf. A: Phys. And Eng.Aspects 250 (2004) 317.

Diaz, M. E, Fuentes, J., Cerro, R. L. and Savage, M., J. Colloid Int. Sci., 343 (2010), 574

Wilson, S. D. R., J. Eng. Mathematics, 16 (1982) 209.

Cerro, R. L., J. Colloid Int. Sci., 257 (2003) 276.