SLIP OR NOT SLIP? A COMPARISON OF THE INTERFACE FORMATION MODEL WITH CONVENTIONAL THEORIES

David N. Sibley[a)], Nikos Savva & Serafim Kalliadasis
Department of Chemical Engineering, Imperial College London, London, SW7 2AZ

Summary We consider the spreading of a thin two-dimensional droplet on a planar substrate as a prototype system to compare a contemporary model for contact line motion based on interface formation to more prevalent models in the literature. Quasistatic evolution of the droplet radius using the interface formation model is found to reduce to an equivalent expression for a slip model when the prescribed dynamic contact angle has velocity dependent correction to its static value.

PROBLEM DESCRIPTION

The wetting of a solid by a liquid occurs via a moving contact line in a gas/liquid/solid system, and is a crucial part of many natural and technological processes, [1]. The *interface formation model* developed by Shikhmurzaev [2] using thermodynamic principles is one of many put forward to understand this situation. For all models considered here, the bulk liquid is taken as a viscous incompressible Newtonian fluid, governed by the usual Navier–Stokes equations. $\mathbf{u}$, ρ and μ are the bulk fluid velocity, density and viscosity, and p is the pressure. Interfaces have unit normal and tangent vectors $\mathbf{n}$, $\mathbf{t}$, with subscript S and G for solid and gas respectively. Classical conditions on a flat solid boundary are no-slip, $\mathbf{u}\cdot\mathbf{t}_S = 0$, and no-penetration, $\mathbf{u}\cdot\mathbf{n}_S = 0$, and on the free surface between a liquid and a gas

$$\frac{\partial f}{\partial t} + \mathbf{u}\cdot\boldsymbol{\nabla} f = 0, \quad \mu\mathbf{n}_G\cdot\left[\boldsymbol{\nabla}\mathbf{u} + (\boldsymbol{\nabla}\mathbf{u})^{\mathrm{T}}\right]\cdot\mathbf{t}_G = -\boldsymbol{\nabla}_s\sigma_{NS}\cdot\mathbf{t}_G, \quad -p + \mu\mathbf{n}_G\cdot\left[\boldsymbol{\nabla}\mathbf{u} + (\boldsymbol{\nabla}\mathbf{u})^{\mathrm{T}}\right]\cdot\mathbf{n}_G = \sigma_{NS}\boldsymbol{\nabla}_s\cdot\mathbf{n}_G,$$

which are the kinematic condition, the tangential stress equation, and the normal stress equation, where σ_{NS} is the surface tension on the liquid-gas interface $f = 0$, and the atmospheric pressure has been normalised to zero. Application of these classical boundary conditions to the moving contact line leads to the nonexistence of a solution, often seen as a nonintegrable shear-stress singularity, [3]. To alleviate this problem, a variety of models and associated contributing phenomena have been proposed. These include allowing slip to occur at the solid surface, such as in the popular Navier-slip condition $\mathbf{u}\cdot\mathbf{t}_S = \mu^{-1}\beta_{NS}\mathbf{n}_S\cdot\boldsymbol{\sigma}\cdot\mathbf{t}_S$, where β_{NS} is the coefficient of slip. Other models include accounting for the existence of a precursor film ahead of the contact line, incorporating intermolecular forces, considering the interface to be diffuse, and accounting for evaporation. An equivalence between slip and precursor film models has been recently demonstrated in spreading situations, [4], so we draw a comparison with the Navier-slip model primarily.

The interface formation model

The interface formation model is motivated through two key mechanisms. (i) surface layers exist in regions near the interfaces, where the density differs from the bulk due to the unfavourable energy state of the molecules near the interface. This density variation appears as the surface tension in a macroscopic description. The surface layer at a solid surface allows a generalised slip condition to be applied between the bulk and surface layer, but with no-slip between the surface layer and the wall, see Fig. 1(a). (ii) surface tension relaxation, which through the assumption that Young equation $\sigma_{12}\cos\theta_s + \sigma_{1S} = \sigma_{2S}$, see Fig. 1(b), holds true for dynamic processes, suggests that the surface tension varies as a fluid particle moves through the contact line, taking a finite time τ to relax to equilibrium. For the full details of the governing equations, see [2].

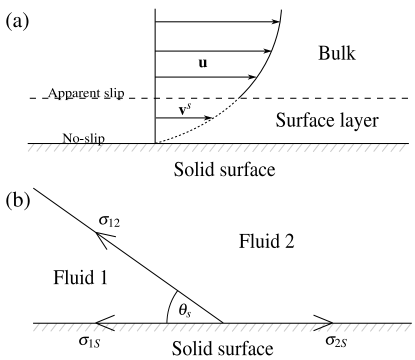

Figure 1. (a) A solid-surface layer with surface velocity $\mathbf{v}^s$. (b) A Young's force diagram.

Droplet spreading

Considering droplet spreading as a prototype system, then after a process of nondimensionalisation and neglecting small terms in a long-wave expansion, we have a system including an evolution equation for the interface coupled to two ODEs, and supplemented by four boundary conditions at the contact line, three at the droplet centre-line and a conservation of mass constraint:

$$\partial_t h + \partial_x\left[-\frac{1}{2}h^3\partial_x^3 h + \frac{3}{2}Ah^2 + Bh\right] = \bar{R}_0\mathcal{D}, \qquad \bar{\beta}B - A = \bar{\tau}\breve{\rho}\,\partial_x^2\left[\frac{1+4\bar{\alpha}}{4}B - \frac{\bar{\alpha}}{\bar{\beta}}A\right],$$

$$h\partial_x^3 h - A = \bar{\tau}\partial_x^2\left[\frac{3}{2}h^2\partial_x^3 h - 3Ah - B + \frac{1+4\bar{\alpha}}{4\bar{\beta}}\left(h\partial_x^3 h - A\right)\right],$$

where $h(x,t)$ is the droplet height, $A(x,t)$ and $B(x,t)$ are unknown variables related to the shear stress and slip velocity at the solid surface, and $\bar{\alpha}$, $\bar{\beta}$, $\bar{\tau}$, $\breve{\rho}$ and $\bar{R}_0$ are nondimensional model parameters. At the contact line, $x = a(t)$, we have

$$h = h\partial_x^3 h = 0, \quad 1 - (\partial_x h)^2 = 2\mathcal{D}, \quad 2(2+\breve{\rho})\bar{\beta}B - 4\bar{\beta}U_{CL}\left(1+\breve{\rho}\right) - 8\breve{\rho}\bar{\alpha}(A - \bar{\beta}B) = (1+4\bar{\alpha})\left[h\partial_x^3 h - A\right],$$

[a)] Corresponding author. E-mail: d.sibley@imperial.ac.uk

where $U_{CL} = B - \bar{R}_0 \left(\partial_x h\right)^{-1} \mathcal{D}$ is the contact line velocity, and the second condition $h\partial_x^3 h = 0$ arises from the requirement of finite pressure at the contact line. The droplet centre-line conditions and volume constraint are

$$\partial_x h|_{x=0} = A|_{x=0} = B|_{x=0} = 0, \quad \int_0^a h dx = 1 - \bar{R}_0 \bar{\tau}(1+\breve{\rho})(a - a(\infty)),$$

and for simplicity in the above we have

$$4\bar{\beta}\mathcal{D} = \bar{\tau}\, \partial_x[(1+4\bar{\alpha})(h\partial_x^3 h - A - 2\breve{\rho}\bar{\beta}B) + 8\breve{\rho}\bar{\alpha}A + 6\bar{\beta}h^2\partial_x^3 h - 4\bar{\beta}(3Ah+B)].$$

Noting that typical parameter values, [5], suggest the nondimensional slip and relaxation time satisfy $\bar{\beta} \gg 1$ and $\bar{\tau} \ll 1$, then following studies with slip models [6] by assuming quasistatic spreading ($\dot{a} \ll 1$), we find through a process of matched asymptotic expansions that the free surface slope and contact line velocity have behaviours

$$-\partial_x h \sim 1 + \dot{a}\ln\left[\mathrm{e}^{1+c_0}\bar{\beta}(a-x)\right], \qquad 3\dot{a}a^6 \ln\left[\frac{\mathrm{e}^{2-c_0}}{2a\bar{\beta}}\right] = a^6 - 27, \quad (1)$$

where c_0 is an unknown parameter arising in the matching behaviour from the inner region near the contact lines. This parameter c_0 is zero for slip models when the dynamic contact angle is prescribed to be equal to its static value, but for the interface formation model it is a function of the model parameters, obtained through the solution of a coupled seventh order system of two ODEs. A comparison between this asymptotic result and a solution of the full PDE system is given in Fig. 2.

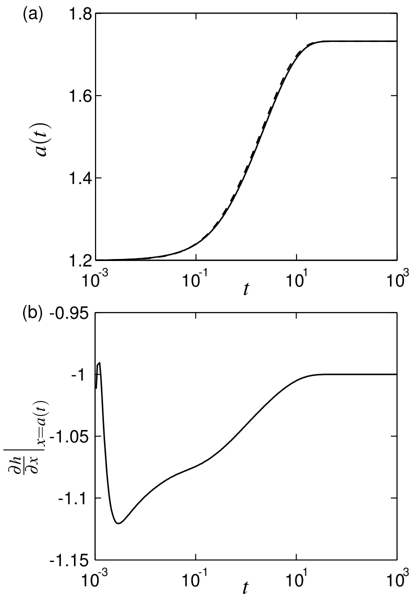

Figure 2. (a) Droplet front evolution for initial droplet radius $a(0) = 1.2$ and parameter values $\bar{\beta} = 10^3$, $\bar{\beta}\bar{\tau} = 1$, $\bar{\alpha} = 1/12$, $\breve{\rho} = 0.1$, $\bar{R}_0 = 1/3$. Dashed lines use the asymptotic result in (1), with $c_0 = 0.12$, and solid lines from the full numerical solution. (b) the contact angle variation from the PDE solution.

Comparison to conventional models

Given that the interface formation model predicts a velocity dependent contact angle, it is of interest to see how similar behaviour would affect the Navier-slip model. As an example, we consider the contact line condition $[\partial_x h(a)]^2 = 1 + 2\dot{a}\bar{c}_0$, giving the free surface slope and spreading rate behaviours

$$-\partial_x h \sim 1 + \dot{a}\ln\left[\mathrm{e}^{1+\bar{c}_0}\bar{\beta}(a-x)\right], \quad 3\dot{a}a^6 \ln\left[\frac{\beta_{NS}\,\mathrm{e}^{2-\bar{c}_0}}{2a}\right] = a^6 - 27, \quad (2)$$

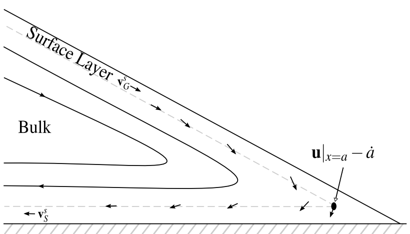

Figure 3. Rolling motion in the moving frame of reference, with interfaces shown schematically as layers of finite thickness.

showing that the variation of θ_d with contact line velocity impacts the spreading rate in the same way as found for the interface formation model, see (1). A similar slip model of Ruckenstein and Dunn [7] yields $u = (\beta_{RD}^2/h)\partial_z u$, at the solid surface in the long-wave approximation, [4], and we find that (2) holds also for this model. Two features of the interface formation model are that it predicts finite pressure at the contact line, seen through the asymptotic procedure used to obtain (1) and that rolling motion can occur as the effective contact line for the bulk is not a stagnation point in the moving frame of reference ($U_{CL} = \dot{a} \neq \mathbf{u}|_{x=a}$, see Fig. 3), although we find this second feature only in the modern version of the model, where $\bar{R}_0 \neq 0$. We note that Navier-slip predicts logarithmically singular pressure at the contact line, whereas the Ruckenstein and Dunn model is able to predict finite pressure. Slip models are not able to predict rolling motion through the contact line.

Through investigation of a variety of model equations, it may be seen that the removal of the stagnation point at the contact line is only possible if mass transfer from the bulk is allowed, either across either gas or solid interface (e.g. via diffusion, evaporation or with a porous solid surface) or into a surface layer such as that in the interface formation model. Consequently, a suitably chosen slip model with empirical relations for the dynamic variation of the contact angle and mass transfer across the liquid-gas interface related to the pressure difference, for instance, will be able to remove the stagnation point, predict finite pressure and stresses at the contact line, and display the same spreading behaviour as the interface formation model.

References

[1] P. G. de Gennes. *Rev. Mod. Phys.* **57**, 827–863 (1985); T.D. Blake. *J. Colloid Interface Sci.* **299**, 1–13 (2006); D. Bonn, J. Eggers, J. Indekeu, J. Meunier, and E. Rolley. *Rev. Mod. Phys.* **81**, 739–805, (2009).
[2] Y. D. Shikhmurzaev. *Int. J. Multiphas. Flow* **19**:589–610, 1993; Y. D. Shikhmurzaev. Taylor & Francis, London 2008.
[3] H. K. Moffatt, *J. Fluid Mech.* **18**, 1–18 (1964); C. Huh and L. E. Scriven. *J. Colloid Interface Sci.* **35**, 85–101 (1971).
[4] N. Savva and S. Kalliadasis, *Europhys. Lett.* **94**, 64004 (2011).
[5] T. D. Blake and Y. D. Shikhmurzaev *J. Colloid Interface Sci.* **253**, 196–202 (2002); J. Billingham *Eur. J. Appl. Math.* **17**, 347–382 (2006).
[6] L. M. Hocking *Q. J. Mech. Appl. Math.* **36**, 55–69 (1983); N. Savva and S. Kalliadasis *Phys. Fluids* **21**, 092102 (2009).
[7] E. Ruckenstein and C. S. Dunn, *J. Colloid Interface Sci.* **59**, 135–138 (1977).