Contact line motion enabled by piezoviscosity

J. Eggers[1], M. A. Fontelos[2] and H. A. Stone[3]
School of Mathematics, University of Bristol, Fry Building, Woodland Road, Bristol BS8 1UG, United Kingdom [2] *Instituto de Ciencias Matemáticas, (ICMAT, CSIC-UAM-UCM-UC3M), C/ Serrano 123, 28006 Madrid, Spain*
[3] *Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544, USA.*

We consider the contact line motion of a liquid over a solid, allowing the viscosity of the liquid to increase exponentially with the pressure (piezoviscosity). Using the lubrication approximation, we show that the viscous contact line singularity is regularized, and the contact line can move. In the limit of small speeds, the piezoviscous model is equivalent to a slip model, whose slip length increases linearly with speed. We confirm our theory by comparing to a numerical calculation of the intrinsic length scale of a moving contact line, and illustrate our result using the example of a spreading drop.

I. INTRODUCTION

The motion of a three-phase contact line, for example at the border of a drop spreading over a solid substrate (see Fig. 1), or dipping a solid plate into a container of liquid, is a common occurrence in nature or industry. However it was first pointed out by Huh and Scriven [1] that, in a continuum description of a viscous fluid, a diverging force would be required to move the contact line [2–4]. This so-called contact line singularity can be alleviated in many different ways [5, 6], for example by allowing the fluid to slip partially over the solid, or by assuming a shear-thinning rheology [7]. Somewhat surprisingly, here we show that the contact line singularity can also be regularized by taking into account the *increase* of viscosity at high pressures.

In the field of elasto-hydrodynamic lubrication, as well as geology, the effective viscosity is seen to rise steeply at elevated pressures [8, 9], an effect know as piezoviscosity. Most often, one uses the Barus equation [10], which assumes an exponential pressure dependence of the form

$$\eta = \eta_0 e^{\alpha p}. \tag{1}$$

Typical values are $\alpha = 2 \cdot 10^{-8}\mathrm{m}^2/\mathrm{N}$; together with the coefficient of surface tension with the outer atmosphere, γ, this defines a typical length scale $\ell_p = \gamma\alpha$, which is of microscopic size, $O(1\mathrm{nm})$.

We next analyze the film flow near the contact line in Section II. The equation including piezoviscous effects is solved numerically, and studied asymptotically for large distances from the contact line, where it is characterized by a single intrinsic length scale L. In the following subsection, we calculate the intrinsic length analytically by mapping the equations onto a slip model, valid for asymptotically small speeds. We also consider more general piezoviscous models, and show that all that is required for the contact line to move is that the viscosity continues to increase with pressure. We conclude with an application to drop spreading.

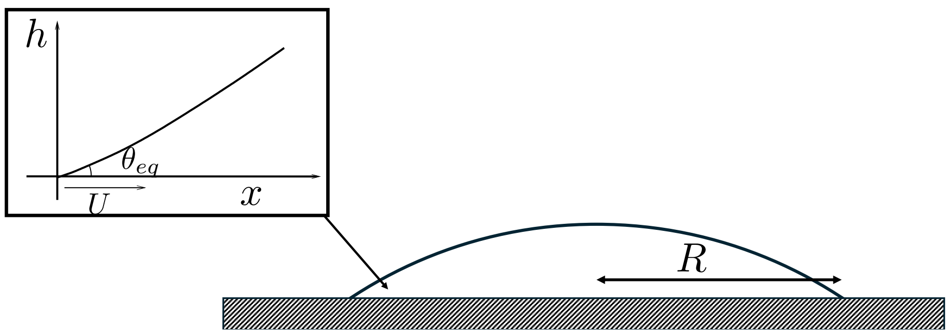

FIG. 1: Schematic of a drop of radius R, spreading on a solid surface, with detail of the corner. In a frame of reference in which the contact line is stationary, the solid moves at a speed U, with $U = \dot{R}$; $h(x)$ is the stationary profile near the contact line, and $\theta_{eq} \equiv h'(0)$ the contact angle.

II. LUBRICATION APPROXIMATION OF THE PIEZOVISCOUS MODEL

We consider the motion of a thin layer of viscous fluid on a flat, horizontal substrate. For simplicity, we work in the lubrication approximation, which assumes horizontal length scales to be large compared to the thickness of the layer, and characteristic speeds of the motion to be small compared to the intrinsic capillary velocity γ/η_0. The liquid-air interface is assumed stress free. In this approximation, the pressure can be considered constant across the liquid layer, and the velocity profile becomes semi-parabolic. As a result, the profile in the vertical dimension can be integrated out, and one arrives at an equation for the thickness profile $h(x, y, t)$ as a function of the horizontal coordinates (x, y) and time only:

$$\frac{\partial h}{\partial t} = \boldsymbol{\nabla} \cdot \left(\frac{h^3}{3\eta} \boldsymbol{\nabla} p \right), \text{ where } \quad p = -\gamma \triangle h. \tag{2}$$

Here $-h^3/(3\eta)\boldsymbol{\nabla} p$ is the horizontal flux, driven by gradients of the capillary pressure; we disregard gravitational effects. The friction factor $3\eta/h^3$ expresses the fact that viscous resistance increases rapidly with decreasing film thickness.

At a contact line, where h vanishes, the flux goes to zero rapidly, which for a constant viscosity results in a paradox: the contact line cannot move [1, 4]. To analyze this situation, we consider two-dimensional motion, where the contact line is straight in the y direction, and the motion is in the x-direction only. In order to study the motion of the contact line, we assume that the flow near the contact line is quasi-steady, so in a frame of reference in which the contact line is stationary, the substrate moves at speed U to the right, see Fig. 1. As a result, we can write $h = h(x + Ut)$ as a traveling wave solution, and $\partial_t h = U h_x$, where the subscript denotes the derivative. Defining the capillary number $\mathcal{C} = \eta_0 U/\gamma$, a traveling wave solution of (2) becomes

$$\frac{3\mathcal{C}}{h^2} = -e^{\ell_p h_{xx}} h_{xxx}, \tag{3}$$

having integrated once. The boundary conditions at the contact line are $h(0) = 0$ and $h_x(0) = \theta_{eq}$, where θ_{eq} is the equilibrium contact angle. We ignore possible deviations between the equilibrium angle θ_{eq} and a microscopic angle, imposed at the origin [2]. We will see below that a necessary third boundary condition, away from the contact line, can be found by interpreting (3) as the inner problem in a matched asymptotic expansion [3, 11]. In the example of Fig. 1, the outer problem is that of a circular drop, described on the scale of its radius R.

In the Newtonian case of constant viscosity, we have $\ell_p = 0$, and (3) becomes (up to a trivial rescaling, and an inversion): $h_{xxx}h^2 = 1$. This equation has a complete, exact solution in terms of Airy functions [12], so all solutions can be classified. Thus it is seen that all solutions that end at a point with $h = 0$ have a logarithmically diverging slope, and so the contact angle condition cannot be satisfied. This is one way to demonstrate the contact angle paradox. We will see now that, surprisingly, taking into account the dependence of the viscosity on h_{xx}, a solution with finite contact angle becomes possible.

To that end it is useful to think of the solution of (3) as the inner solution of a contact line problem, whose outer solution depends on the geometry at hand [3, 13]. For example, in the case of a drop spreading on a substrate, to leading order the outer problem is a spherical cap. In the case of a contact line on a moving plate, the outer solution is a static capillary meniscus [2, 14]. Since the outer problem is characterized by a length scale (such as the drop radius R) much larger than the intrinsic length scale near the contact line (which is ℓ_p in the present case), solutions of (3) extrapolate to a profile whose curvature is of order $1/R$. Thus, in the limit of $\ell_p/R \to 0$, for the inner problem we can solve (3) with the boundary condition $h_{xx}(\infty) = 0$. This supplies the missing third condition for the solution of (3). The same inner solution is matchable to any outer problem characterized by a length scale much larger than ℓ_p (and the capillary number being low). In the final discussion we will make the matching explicit for the case of a spreading drop.

Far from contact line, the curvature becomes small, and hence the exponential factor in (3) is unity. Thus the universal form of the equation becomes $3\mathcal{C}/h^2 = -h_{xxx}$, with asymptotic solution (for $x \gg \ell_p$) [3]

$$h_x^3(x) = \theta_{eq}^3 + 9\mathcal{C} \ln \frac{x}{L}, \tag{4}$$

written as a perturbation to the equilibrium angle. The goal of our calculation is to identify the length L. The universal form (4) can then be matched to an outer solution, describing for example a spreading drop. Introducing the similarity variables

$$h(x) = \ell_p \theta_{eq}^2 H(\xi), \quad \xi = \frac{x}{\ell_p \theta_{eq}}, \tag{5}$$

(3) turns into

$$\frac{\delta}{H^2} = -e^{H''} H''' = -\left(e^{H''}\right)', \quad H(0) = 0,\ H'(0) = 1,\ H''(\infty) = 0, \tag{6}$$

with a single speed parameter $\delta = 3\mathcal{C}/\theta_{eq}^3$; the prime denotes the derivative with respect to the argument.

A. Numerical

To solve (6) numerically, we need an expansion of $H(\xi)$ for small ξ, since the behavior is expected to be singular. Indeed, from the boundary condition $H'(0) = 1$ with $H(0) = 0$, we have $H \approx \xi$ for small ξ, so we can approximate (6) by

$$\frac{\delta}{\xi^2} \approx \left(e^{H''}\right)'. \tag{7}$$

Integrating, we find $H''(\xi) = -\ln(\xi/\delta)$ to leading order. This equation suggests a double expansion in ξ and $\ln(\xi/\delta)$ of the form

$$H(\xi) = \xi + \sum_{j=2}^{\infty} \sum_{i=0}^{j} a_{ji} \xi^j (\ln \xi/\delta)^i. \tag{8}$$

At the first three orders, one finds that $a_{22} = a_{33} = 0$, and the expansion begins as

$$H = \xi + \xi^2 \left(\frac{3}{4} - \frac{1}{2}\ln(\xi/\delta)\right) + \xi^3 \left(f + \frac{7}{18}\ln(\xi/\delta) - \frac{1}{12}\ln^2(\xi/\delta)\right) + O(\xi^4), \tag{9}$$

where f is a free parameter, to be adjusted in order for the solution to satisfy $H''(\infty) = 0$. At any higher order, $a_{j0}, \ldots a_{jj}$ can be found in terms of the free parameter f.

For large ξ, $e^{H''} \approx 1$, and (6) turns into $\delta/H^2 = H'''$, which has asymptotic solutions of the form

$$H'^3(\xi) = 3\delta \ln(\xi/\xi_0) + O((\ln \xi)^{-1}). \tag{10}$$

We are interested in finding ξ_0, which in general is a function of δ. In order to accelerate convergence, we compare the numerical solution for $H'^3(\xi)$ at some large value of ξ to (10) with an expansion to 7th order in $(\ln \xi)^{-1}$ included, treating $\ln \xi_0$ as a fit parameter. To compare to (4), we separate out the angle at the contact line by writing

$$H'^3(\xi) = 1 + 3\delta \ln(\xi/\xi_l), \quad \ln \xi_l = \ln \xi_0 + \frac{1}{3\delta}. \tag{11}$$

Using that $h_x(x) = \theta_{eq} H'(\xi)$, we then find

$$L = \ell_p \theta_{eq} \xi_l = \ell_p \theta_{eq} e^{1/(3\delta)} \xi_0, \tag{12}$$

for the intrinsic length scale defined by (4).

Now for any given δ, ξ_0 can be calculated by integrating (6) with initial condition (9). The free parameter f is adjusted such that $H''(\xi) = 0$ for a very large value of ξ, e.g. $\xi = 10^{25}$. Using this solution, and evaluating $H'(\xi)$ for an intermediate but still very large value of ξ, we can use (11) to find ξ_0; here higher-order corrections in $(\ln \xi)^{-1}$ are included. In Fig. 2, we show the numerical result for the characteristic length scale L, using (12), as the solid line. Next we compute L analytically in an expansion valid for small speeds.

B. Small-speed expansion

Since $e^{H''} H''' = \left(e^{H''}\right)'$, and using the boundary condition for large ξ, we can integrate (6) to find

$$H''(\xi) = \ln\left(1 + \delta \int_{\xi}^{\infty} \frac{1}{H^2} d\xi\right). \tag{13}$$

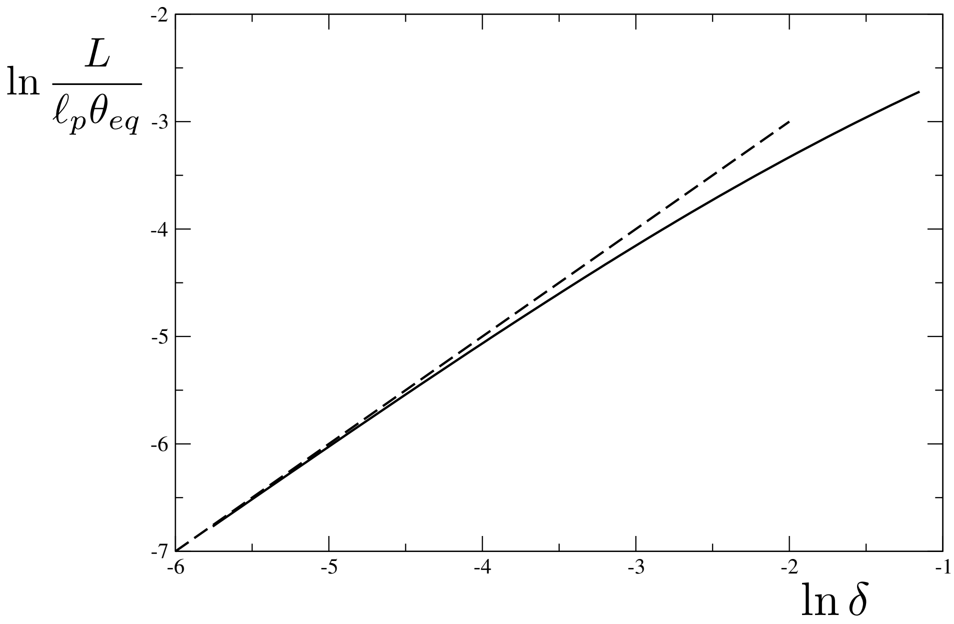

FIG. 2: Characteristic length scale of the local solution, as defined by (4), as a function of the logarithm of the dimensionless speed $\ln \delta$. The low-speed asymptotics (20) corresponds to $\ln \delta - 1$, which is shown as the dashed line.

Differentiating, this gives

$$H'''(\xi) = -\frac{\delta}{H^2 + H^2 \int_\xi^\infty \frac{\delta}{H^2} d\xi}; \tag{14}$$

but in the limit of small speeds, $H' = 1 + O(\delta)$, so that

$$\int_\xi^\infty \frac{1}{H^2} d\xi = \int_\xi^\infty \frac{H'}{H'H^2} d\xi = \int_\xi^\infty \frac{H'}{H^2} \left(1 + O(\delta)\right) d\xi = \frac{1}{H(\xi)} \left(1 + O(\delta)\right). \tag{15}$$

In other words, up to corrections of order δ^2, we obtain

$$H''' = -\frac{\delta}{H^2 + \delta H}, \tag{16}$$

which is exactly the lubrication description for a conventional slip model [3], but with the slip length proportional to the speed δ. This situation bears some resemblance to perfect wetting, in that in that case the inner length scale also has a power-law dependence on the speed [15, 16].

C. Slip model

Using the transformation $H(\xi) = \delta \bar{H}(\xi/\delta)$, (16) turns into

$$\bar{H}''' = -\frac{\delta}{\bar{H}^2 + \bar{H}}, \tag{17}$$

which can be solved approximately using perturbation theory in δ [3]. Writing $\zeta \equiv \xi/\delta$ and $\bar{H}(\zeta) = \zeta + \delta \bar{H}_1(\zeta) + O(\delta^2)$, one finds

$$\bar{H}'(\zeta) = 1 + \delta(\ln \zeta + 1), \tag{18}$$

which satisfies the boundary condition at infinity ($\bar{H}'' \to 0$ as $\zeta \to \infty$). As a result, we have

$$H'^3(\xi) = 1 + 3\delta \ln\left(\frac{\xi e}{\delta}\right), \tag{19}$$

or $\xi_l = \delta/e$, which in view of (12) implies

$$L = \frac{\delta \ell_p \theta_{eq}}{e} = \frac{3\mathcal{C}\ell_p}{e\theta_{eq}^2}. \tag{20}$$

This leading-order result is shown as the dashed line in Fig. 2, compared to the full numerical result as described in Subsection II A (solid line). According to (12), this amounts to calculating the effective inner length scale $\ln \xi_0 + 1/(3\delta)$, plotted as a function of $\ln \delta$. The result is seen to work well for reduced speeds up to about $\delta \approx 0.1$, which is approximately the range over which the lubrication approximation works [3].

D. Dependence on the functional form of piezoviscosity

Since the dependence of viscosity on pressure cannot always considered to be exponential [9], it is of interest to consider other laws. To this end we assume that the exponential e^s in (6) is replaced by a function $f(s)$, and we arrive at

$$\frac{\delta}{H^2} = -f(H'')H'''; \tag{21}$$

we assume without loss of generality that $f(0) = 1$, and that we can expand in the form $f(s) = 1 + f'(0)s + O(s^2)$. Now if we define

$$F(s) = 1 + \int_0^s f(s')ds', \tag{22}$$

and following the same steps as in the derivation of (14), we arrive at

$$H'''(\xi) = -\frac{\delta}{H^2 f\left[F^{-1}\left(\int_\xi^\infty \frac{\delta}{H^2} d\xi\right)\right]}, \tag{23}$$

where F^{-1} is the inverse of F.

On the one hand, this confirms that for $\xi \to \infty$, $H'''(\xi)$ behaves like $1/H^2(\xi)$, and in particular the solution will again be (4) for large arguments. However, the approximation (16) will in general have to be modified. On the other hand, in the limit $\xi \to 0$, $H \approx \xi$, and the integral in (23) diverges like ξ^{-1}. Now assuming that $f(s)$ behaves like s^q for large arguments, we find that $f\left[F^{-1}(s)\right] \propto s^{q/(1+q)}$. As a result, near the contact line

$$H''' \propto \frac{\xi^{q/(1+q)}}{H^2}; \tag{24}$$

this result means that as soon as $q > 0$, the contact line singularity is alleviated, and a local solution consistent with the boundary conditions $H(0) = 0$, $H'(0) = 1$ can be found [3]. In other words, as soon as there is an unbounded increase of the viscosity under pressure, the contact line is able to move. In fact, putting $\beta = q/(1+q)$, the expansion of H' is of the form

$$H'(\xi) = 1 + 2A\xi + \frac{\xi^\beta}{\beta(\beta-1)} - 2\sum_{n=1}^{\infty} \frac{a_n}{(\beta+n\beta)(\beta+n\beta-1)}\xi^{n\beta+\beta}, \tag{25}$$

instead of (9). The coefficients a_n satisfy the system (for suitable Q_n):

$$(1+n\beta)a_n = \frac{a_{n-1}}{n\beta(n\beta-1)} + Q_n(a_1, ..., a_{n-2}), \tag{26}$$

which allows to compute all a_n provided that $\beta \neq 1/m$, $m = 1, 2, 3, ...$ In this case, the coefficient A is free. Otherwise, the free coefficient only appears at order ξ^3 in the expansion of $H(\xi)$, as is the case for (9).

III. DISCUSSION

To illustrate the significance of our results, let us apply them to the classical problem of a circular drop spreading on a solid substrate. At small speeds, the shape of the drop is described by an equilibrium surface, which for a small drop (neglecting gravity), is a spherical cap, or in the approximation of small slopes, a parabola (see Fig. 1). Then, if V is the volume of the drop, and R the radius, this static shape makes an angle (or equivalently for small slope, a slope)

$$\theta_{ap} = \frac{4V}{\pi R^3} \tag{27}$$

with the substrate. This angle, measured as extrapolated from the static shape of the drop, is known as the *apparent* contact angle.

To match to the inner solution (4), one must capture the logarithmic behavior of the slope, by expanding around the static shape to first order in the capillary number [3]:

$$-h_x^3(x) = \theta_{ap}^3 + 9\mathcal{C} \ln \frac{2e^2 x}{R}; \tag{28}$$

the capillary number $\mathcal{C} = U\eta_0/\gamma = \dot{R}\eta_0/\gamma$ can be found in terms of the time derivative of the drop radius. In (28), x is the distance to the contact line, and hence the slope h_x is negative going toward the edge of the drop. Allowing for this change in sign, thus equating $-h_x(x)$ in (28) with $h_x(x)$ in (4), we obtain the apparent contact angle

$$\theta_{ap}^3 = \theta_{eq}^3 + 9\mathcal{C} \ln \frac{R}{2e^2 L}. \tag{29}$$

Together with the approximate result (20) for L, this results in an ordinary differential equation for the radius R of the drop:

$$\left(\frac{4V}{\pi}\right)^3 R^{-9} = \theta_{eq}^3 + 9\frac{\dot{R}\eta_0}{\gamma} \ln \left(\frac{\theta_{eq}^2}{6e} \frac{\gamma}{\eta_0 \dot{R}} \frac{R}{\ell_p}\right), \tag{30}$$

which is an implicit equation for $\dot{R}$ in terms of R. One can observe that for small angles much greater than θ_{eq}^3 the spreading law is approximately $R(t) \propto t^{1/10}$ (Tanner's law) with a prefactor that depends on the logarithm of speed and the piezoviscous length ℓ_p. The same idea is adapted easily for other geometries, such as a plate dipped into a bath, or fluid driven through a capillary [2].

[1] C. Huh and L. E. Scriven. Hydrodynamic model of steady movement of a solid/liquid/fluid contact line. *J. Coll. Int. Sci.*, 35:85–101, 1971.
[2] D. Bonn, J. Eggers, J. Indekeu, J. Meunier, and E. Rolley. Wetting and spreading. *Rev. Mod. Phys.*, 81:739–805, 2009.
[3] J. Eggers and M. A. Fontelos. *Singularities: Formation, Structure, and Propagation.* Cambridge University Press, Cambridge, 2015.
[4] J. Eggers and M. A. Fontelos. Dynamics of a film bounded by a pinned contact line. *J. Fluid Mech.*, 1008:A47, 2025.
[5] N. Savva and S. Kalliadasis. Dynamics of moving contact lines: A comparison between slip and precursor film models. *Europhys. Lett.*, 94:64004, 2011.
[6] A. M. Karim. A review of physics of moving contact line dynamics models and its applications in interfacial science. *J. Appl. Phys.*, 132:080701, 2022.
[7] D. E. Weidner and L. W. Schwartz. Contact-line motion of shear-thinning liquids. *Phys. Fluids*, 6:3535–3538, 1994.
[8] C. A. Herbst, R. L. Cook, and H. E. King Jr. High-pressure viscosity of glycerol measured by centrifugal-force viscometry. *Nature*, 361:518, 1993.
[9] S. Bair. The unresolved definition of the pressure-viscosity coefficient. *Scientific Reports*, 12:3422, 2022.
[10] C. Barus. Isothermals, isopiestics and isometrics relative to viscosity. *Am. J. Sci.*, 45:87, 1893.
[11] E. J. Hinch. *Perturbation Methods.* Cambridge University Press, Cambridge, 1991.
[12] B. R. Duffy and S. K. Wilson. A third-order differential equation arising in thin-film flows and relevant to Tanner's law. *Appl. Math. Lett.*, 10:63, 1997.
[13] L. M. Hocking. The spreading of a thin drop by gravity and capillarity. *Q. J. Mech. Appl. Math.*, 36:55–69, 1983.
[14] J. Eggers. Existence of receding and advancing contact lines. *Phys. Fluids*, 17:082106, 2005.
[15] P.-G. de Gennes. Wetting: statics and dynamics. *Rev. Mod. Phys.*, 57:827–863, 1985.
[16] J. Eggers and H. A. Stone. Characteristic lengths at moving contact lines for a perfectly wetting fluid: the influence of speed on the dynamic contact angle. *J. Fluid Mech.*, 505:309–321, 2004.