Toward a description of contact line motion at higher capillary numbers

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The surface of a liquid near a moving contact line is highly curved owing to diverging viscous forces. Thus, microscopic physics must be invoked at the contact line and matched to the hydrodynamic solution farther away. This matching has already been done for a variety of models, but always assuming the limit of vanishing speed. This excludes phenomena of the greatest current interest, in particular the stability of contact lines. Here we extend perturbation theory to arbitrary order and compute finite speed corrections to existing results. We also investigate the impact of different contact line models on the large-scale shape of the interface. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1776071]

The moving contact line problem is a famous example of hydrodynamics failing to describe a macroscopic flow phenomenon. But it was only in 1971 that Huh and Scriven[1] discovered that the viscous dissipation in the fluid wedge bordered by a solid and a fluid–gas interface is logarithmically infinite if the standard no-slip boundary condition[2] is applied at the solid surface. Thus infinite force would be required to submerge a solid body, and a drop could never spread on a table.

This result is of course contradicted by observation, and physical effects that relieve the singularity have to be invoked near the contact line, which go beyond the standard description. A great variety of possible mechanisms have been proposed, and indeed there is no reason to believe that for different solid–fluid–gas systems always the same mechanism is involved. However, a question rarely considered is whether the choice of different microscopic mechanisms would make a great difference when looked at macroscopically.

In a recent paper[3] we compared various microscopic models in the case of perfect wetting (see also Ref. 4). We found that the length scale that appears in the expression for the interface shape is *strongly* speed dependent, in a fashion that depends on the model. Here we are going to show that this dependence is much weaker in the case of partial wetting, and differences only come in at higher order in an expansion in capillary number $\mathrm{Ca}=U\eta/\gamma$, where η is the viscosity of the fluid and γ is the surface tension between liquid and gas. Finite capillary number corrections are of interest for various situations of "forced" wetting, in which Ca is no longer asymptotically small, and previous theories for the dynamic interface angle break down.[5]

For simplicity, we perform our calculations within the framework of lubrication theory, thus limiting ourselves to the case of small contact angles, but without altering the essential structure of the problem. We consider the neighborhood of a contact line moving with speed U across a solid in a frame of reference in which the contact line is fixed at the origin of the coordinate system (see Fig. 1). To relieve the corner singularity, we allow the fluid to slide across the solid surface, following the generalized Navier slip law[6–8]

$$u|_{y=0} - U = \lambda^{2-\alpha} h^{\alpha-1} \left.\frac{\partial u}{\partial y}\right|_{y=0} \tag{1}$$

at the plate, where $h(x)$ is the thickness of the fluid layer, and λ is taken as a constant rather than a speed dependent quantity. The case $\alpha=1$ corresponds to the usual Navier slip, and Eq. (1) is a simple generalization involving only a single length scale λ. The resulting lubrication equation is[7]

$$\frac{3\mathrm{Ca}}{h^2 + 3\lambda^{2-\alpha}h^{\alpha}} = -h'''. \tag{2}$$

The left-hand side corresponds to viscous forces, diverging as the contact line position $h(0)=0$ is approached, but weakened by the presence of slip. Viscous forces are balanced by surface tension forces on the right, resulting in a highly curved interface near the contact line. In comparison, other forces like gravity have been neglected. This restricts the validity of (2) to a distance from the contact line below the capillary length $\ell_c=\sqrt{\gamma/(\rho g)}$. We also assume that the angle at the contact line $h'(0)=\theta_e$ is constant, independent of speed. Hence it has to coincide with the equilibrium contact angle, in order to give the right result at vanishing speed.

Since we want to investigate the neighborhood of the contact line, it is convenient to introduce the scaled variables

$$h(x) = 3^{1/(2-\alpha)}\lambda H(\xi), \quad \xi = x\theta_e/[3^{1/(2-\alpha)}\lambda], \tag{3}$$

which leads to

$$\frac{\delta}{H^2 + H^{\alpha}} = -H''', \tag{4}$$

where $\delta=3Ca/\theta_e^3$ is the rescaled capillary number.

From the scaling (3) it is evident that the curvature of the interface $h''(x)$ scales like λ^{-1}, where λ is in the order of nanometers.[3] Thus, in order to match the local solution near the contact line to an outer profile with a curvature of order $1/\ell_c$, the curvature $H''(\xi)$ has to vanish for large ξ. This means the boundary conditions for the solution of (4) are

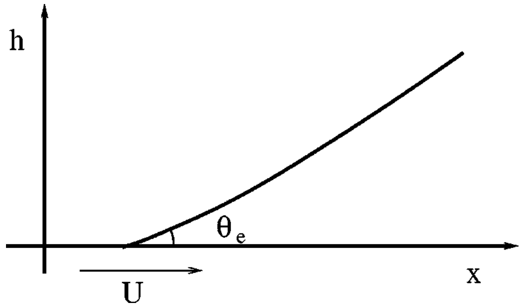

FIG. 1. A schematic of the interface near the contact line. In the frame of reference in which the contact line is stationary, the solid moves to the right in the case of an advancing contact angle, considered here. At the contact line, $h(0)=0$, the slope of the interface is θ_e.

$$H(0)=0, \quad H'(0)=1, \quad H''(\infty)=0. \tag{5}$$

The only parameter now appearing in the problem is the rescaled capillary number δ.

For $\delta>0$, Eqs. (4) and (5) have a unique asymptotic solution, proposed by Voinov,[9] for which the slope behaves like

$$H'(\xi)=[3\delta\ln(\xi/\xi_0)]^{1/3}, \quad \xi \gg 1. \tag{6}$$

This solution has vanishing curvature at infinity and only contains a single free parameter ξ_0, to be determined by matching to the contact line. In the present paper, we are going to deal exclusively with this case of an advancing contact angle. If $\delta<0$, the mathematical structure of (4) changes completely. This can be seen from considering the simpler equation $\delta/H^2=-H'''$, valid for large H. Namely, it follows from an exact solution[10] to this equation, that for $\delta<0$ all solutions have strictly positive curvature at infinity. The consequences of this observation for the stability of contact lines are explored in our forthcoming paper, "Hydrodynamic theory of forced dewetting." For $\delta>0$, (6) is recovered from the exact solution.[10]

The mathematical problem to be tackled in this paper consists in computing ξ_0 as a function of δ. Our procedure to do so can be outlined as follows. First, we obtain a solution of the full problem (4),(5) as a perturbation expansion in the small parameter δ. Second, we compute an asymptotic expansion of $H(\xi)$ in the limit of $\xi\to\infty$, which contains ξ_0 as its only adjustable parameter. By comparing the two representations of $H(\xi)$ for large ξ, we find ξ_0 as an expansion in δ. As was done in previous works,[7,11–13] we proceed by expanding around the trivial solution at zero speed $\delta=0$. In this case, the solution of (4) and (5) is evidently given by $H(\xi)=\xi$. Hence the perturbation expansion we seek looks like

$$H'(\xi)=1+\delta H_1'(\xi)+\delta^2 H_2'(\xi)+\cdots \tag{7}$$

for the slope.

This is to be compared to the full asymptotic expansion of $\delta/H^2=-H'''$ in $[\ln(\xi)]^{-1}$, p. 158 of Ref. 14

$$H(\xi)=\xi\,[3\delta\ln(\xi)]^{1/3}\left\{1+\frac{A}{\ln(\xi)}-\frac{A^2+10/27}{\ln(\xi)^2}+\cdots\right\}, \tag{8}$$

which contains exactly one free parameter A. Once the structure (8) of the expansion is known, it is easy to substitute it into the differential equation and to compute the coefficients. Note that the same expansion is valid for the full equation (4), since the two equations differ only by terms of order $1/\xi$, which is *beyond all orders*[14] in an expansion in $[\ln(\xi)]^{-1}$. We now write the derivative of (8) in a form corresponding to Voinov's solution (6),

$$H'(\xi)=[3\delta\ln(\xi/\xi_0)]^{1/3}\left\{1+\sum_{i=2}^{\infty}\frac{b_i}{[\ln(\xi/\xi_0)]^i}\right\}, \tag{9}$$

where the one-parameter freedom is now contained in ξ_0. Notice that the sub-leading term $b_1/\ln(\xi/\xi_0)$ is missing from the sum, because in a $[\ln(\xi)]^{-1}$ expansion it would simply contribute to ξ_0.

All coefficients $b_2=-7/27, b_3=-10/9\ldots$ are readily computable, using, e.g., Maple. Expanding (9) in δ and comparing to (7) leads to the following structure of the expansion of $\ln(\xi_0)$:

$$-3\ln(\xi_0)=\frac{1}{\delta}+\sum_{i=0}^{\infty}c_{i+1}\delta^i. \tag{10}$$

Substituting this back into (9), the large-ξ behavior of the $H_i(\xi)$ in (7) is given in terms of the coefficients c_i:

$$\left.\begin{aligned} H_1'(\xi)&=\ln(\xi)+c_1/3,\\ H_2'(\xi)&=-\ln^2(\xi)-2c_1/3\ln(\xi)\\ &\quad+c_2/3-c_1^2/9-7/3,\end{aligned}\right\}\xi\to\infty. \tag{11}$$

To compute c_1 we have to solve (4) to first order in δ,

$$H_1'''=-\frac{1}{\xi^2+\xi^\alpha}\equiv r(\xi) \tag{12}$$

with boundary conditions $H_1(0)=0, H_1'(0)=1$, and $H_0''(\infty)=0$. According to (11), the constant c_1 is given by

$$c_1/3=\lim_{\xi\to\infty}H_1'(\xi)-\ln(\xi+1). \tag{13}$$

Integrating (12) twice, we can thus write

$$\begin{aligned} c_1/3&=\int_0^\infty\int_\infty^{\tilde\xi}\left[r(\bar\xi)+\frac{1}{(\bar\xi+1)^2}\right]d\bar\xi d\tilde\xi\\ &=-\int_0^\infty\int_0^{\bar\xi}\left[r(\bar\xi)+\frac{1}{(\bar\xi+1)^2}\right]d\tilde\xi d\bar\xi\\ &=\int_0^\infty\left[\frac{\xi^{1-\alpha}}{\xi^{2-\alpha}+1}-\frac{\xi}{(\xi+1)^2}\right]d\xi\\ &=\left[\frac{1}{2-\alpha}\ln(\xi^{2-\alpha}+1)-\ln(1+\xi)-\frac{1}{1+\xi}\right]_\infty^0=1\end{aligned}$$

independent of α. We thus find $c_1=3$ for the first-order correction to ξ_0, regardless of how the length scale λ is introduced near the contact line.

The problem at second order can be tackled in precisely the same manner, using the equation for the second-order problem

$$H_2''' = H_1(\xi)\frac{2\xi+1}{\xi^2(\xi+1)^2}, \tag{14}$$

where we have specialized to the standard case $\alpha=1$ for simplicity. The case $\alpha=0$ can be treated analogously. Integrating the first order equation (12) three times gives

$$H_1 = [\ln(\xi+1)(\xi+1)^2 - \xi - \xi^2\ln(\xi)]/2,$$

thus specifying the right-hand side of Eq. (14). The trick used to calculate c_1 at first order can be repeated at the next order, using the second equation of (11) and $c_1=3$. Simplifying the resulting double integral as before, we find

$$\begin{aligned} c_2/3 - 10/3 &= \lim_{\xi\to\infty} H_2'(\xi) + \ln^2(\xi+1) + 2\ \ln(\xi+1) \\ &= \int_0^\infty \left[\frac{-\xi H_1(\xi)(2\xi+1) + 2\xi^3\ln(\xi+1)}{\xi^2(\xi+1)^2}\right] d\xi \\ &= \pi^2/6 - 7/2. \end{aligned}$$

In summary, we thus have $c_2=(\pi^2-1)/2$ for $\alpha=1$ and $c_2=(3\pi^2-4)/8$ for $\alpha=0$, which follows from a very similar calculation. It is evident that the same procedure can be repeated at arbitrary order, although the calculation rapidly becomes analytically intractable.

Rewriting the rescaled solution $H(\xi)$ in terms of the physical profile $h(x)$, in the limit of large arguments x we find the slope of the interface to be

$$h'^3(x) - \theta_e^3 = 9\text{Ca}\ \ln(x/L) \tag{15}$$

for any capillary number. This is the form originally proposed by Voinov,[9] using more qualitative arguments. The length L appearing inside the logarithm can be computed by comparing (15) to $H'(\xi)=[3\delta\ln(\xi/\xi_0)]^{1/3}$ in the limit of large ξ. The perturbation calculation presented above directly leads to an expansion of L in the capillary number,

$$L = \frac{3^{1/(2-\alpha)}\lambda}{e\theta_e}\left[1 - \frac{c_2\text{Ca}}{\theta_e^3} + O(\text{Ca}^2)\right]. \tag{16}$$

Integrating Eq. (2) numerically, a comparison with (15) can be made, giving L as function of capillary number. In Fig. 2 it is clearly seen that our expansion (16) describes the initial departure from the leading order result quite well. However, when the corrections amount to about 10% of the leading order, higher-order terms become important. Thus as a rough estimate, the present approach can be trusted if $\delta=\text{Ca}/\theta_e^3\lesssim 0.05$. It would be interesting to systematically investigate the dependence of L on the capillary number beyond that value.

In Ref. 15 de Gennes used a free energy balance to arrive at an expression for the interface angle $h'(x)$. In the present notation, this balance reads

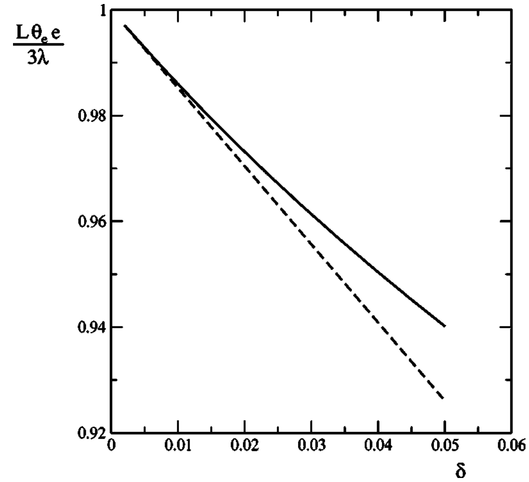

FIG. 2. A comparison of Eq. (16) with the numerical result for the characteristic length L, using numerical integration of (2) for $\alpha=1$.

$$h'^2(x) = \theta_e^2 + 6\text{Ca}\int_\lambda^z \frac{dz'}{h}. \tag{17}$$

Using the simple approximation $h(x)=\theta x$ for the interface profile, one obtains[15]

$$[h'^2(x) - \theta_e^2]h'(x) = 6\text{Ca}\ \ln(x/\lambda), \tag{18}$$

which agrees with (15) if the departure of $h'(x)$ from θ_e is small.

Beyond linear order in $h'(x)-\theta_e$, however, (18) and (15) are different. This difference can be traced back to the approximation $h(x)=\theta x$ being used to evaluate the integral in (17). Namely, differentiating (17) one finds $h''h'=3\text{Ca}/h$. Using the transformation $u(h)=h'(x)$, this can be integrated to give

$$u^3 - [u(h_0)]^3 = 9\text{Ca}\ \ln(h/h_0). \tag{19}$$

To leading order in Ca, $h(x)=\theta_e x$, so using the boundary condition $h'(\lambda)=\theta_e$, which follows from (17), we finally have

$$h'^3 - \theta_e^3 = 9\text{Ca}\ \ln(x/\lambda), \tag{20}$$

which is consistent with (15) and (16) to within the approximations considered. This also calls into question de Gennes' theory[15] of contact line instability, which crucially uses (18).

Many contact line models other than the slip law (1), combined with $h'(0)=\theta_e$, have been discussed in the literature. For example, in the case of van der Waals forces being dominant near the contact line,[12] one finds $L\propto\theta_e^{-2}$ to leading order instead of $L\propto\theta_e^{-1}$, as given by the present calculation [cf. Eq. (16)]. If other sources of dissipation become relevant near the contact line, they will appear as additional speed-dependent terms on the right-hand side of (17).[9,16,17] This will effectively lead to a speed dependence of the microscopic contact angle, taken as constant in the present treatment.

Finally, we reiterate that our analysis did not include the influence of an outer length scale, always present in real physical situations. Such a scale would be the capillary length ℓ_c in the case of a liquid meniscus climbing up a solid wall, the radius R of a spreading drop,[7,9] or the radius R_c of a capillary[9] into which a fluid is pushed. To investigate how the profile $h(x)$ depends on any of these lengths, a local solution governed by Eq. (2) has to be matched to an outer profile. This has been done[7,9,11] to leading order in Ca, but not taking into account higher-order corrections as we do here. Investigating the interplay between external scales and the local dynamics near the contact line remains a challenging open problem.

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