A reappraisal of a model for the motion of a contact line on a smooth solid surface

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In this paper we investigate the model for the motion of a contact line over a smooth solid surface developed by Shikhmurzaev, [18]. We show that the formulation is incomplete as it stands, since the mathematical structure of the model indicates that an additional condition is required at the contact line. Recent work by Bedeaux, [4], provides this missing condition, and we examine the consequences of this for the relationship between the contact angle and contact line speed for Stokes flow, using asymptotic methods to investigate the case of small capillary number, and a boundary integral method to find the solution for general capillary number, which allows us to include the effect of viscous bending. We compare the theory with experimental data from a plunging tape experiment with water/glycerol mixtures of varying viscosities, [9]. We find that we are able to obtain a reasonable fit using Shikhmurzaev’s model, but that it remains unclear whether the linearized surface thermodynamics that underlies the theory provide an adequate description for the motion of a contact line.

1 Introduction

More than ten years ago, Shikhmurzaev introduced a theory that provides a model for the motion of a contact line over a smooth solid surface, [18]. The model has a number of attractive features:

1. Since the theory is based on a simple model for the thermodynamics of the fluid close to interfaces, its main components can be derived without any reference to contact lines, and indeed has proved to be of use in situations where no contact line is present, for example, in modelling cusps, the coalescence of liquid droplets and the break up of liquid threads, [22], [23], [26].

2. The dynamic contact angle is determined as part of the solution. No empirical correlation is needed.

3. The stress singularity at the contact line that arises as a result of the usual no slip boundary condition, [11], is eliminated by introducing slip, not in an ad hoc manner, but as a consequence of the thermodynamics of the fluid/solid interface.

4. The theory leads naturally to a flux of fluid through the contact line, as is observed experimentally, [11]. Most other models lead to a sliding motion.
The theory has the potential to explain the phenomenon of 'hydrodynamic assist of wetting’ whereby the dynamic contact angle is a function of both the contact line velocity and the flow field, [7], [8].

Results derived using the theory are in good agreement with experimental results for steady Stokes flow, [18], [21].

In this paper, we will demonstrate that, in spite of these features, the theory is incomplete as it stands.

It is not our intention either to give a complete defence of the assumptions that underlie Shikhmurzaev’s theory, which have proved to be controversial, [12], or to give an overview of the other theories that have been put forward as models for the motion of contact lines, for example, [15]. These issues have been addressed at length in a series of papers by Shikhmurzaev over the past ten years, and we refer the reader in particular to [21] and [28].

We begin in section 2 by informally discussing some of the key features of Shikhmurzaev’s theory and writing down the governing equations. We then eliminate all of the surface variables except for the surface density and bulk fluid velocity. This allows us to see that the surface density satisfies a nonlinear diffusion equation forced by the flow. It then becomes clear that, in order to determine the contact angle and provide connection conditions for the two nonlinear, second order equations for the surface densities at the free surface and the solid surface, three conditions are required at the contact line, not just the two proposed by Shikhmurzaev. The appropriate additional condition was recently derived by Bedeaux, [4]. In section 3 we consider how the theory works for the case of Stokes flow in a wedge with strong surface tension (small capillary number), and show how Shikhmurzaev’s original analysis, [18], [20], overlooks a one parameter family of solutions, which exists in the absence of the third condition at the contact line. In section 4 we solve the full equations numerically using a boundary integral method, so that we can assess the additional effect of viscous bending on the free surface. This also allows us to confirm that the asymptotic solution that we developed in section 3 is consistent with numerical solutions when the capillary number, Ca, is sufficiently small. In section 5, we compare the relationship between the contact angle and contact line speed implied by this new condition with some experimental data. It is worth noting that, of the six features of the theory listed above, only number 6 needs to be reconsidered in the light of this new development. We will find that by including the missing boundary condition at the contact line and the effect of viscous bending of the free surface, we are able to fit the model to the experimental data and estimate the material parameters associated with the surface layers.

2 An overview of Shikhmurzaev’s theory

Consider a static contact line, as shown in figure 1. If the surface tensions associated with the interfaces between fluids 1 and 2 and the solid surface are \(\sigma_{12}, \sigma_{1S}\) and \(\sigma_{2S}\), the horizontal force balance is given by the Young–Laplace equation,

\[
\sigma_{12} \cos \theta_c + \sigma_{1S} = \sigma_{2S}.
\]
Since the surface tension forces act upon a line, which has no mass, and because the flux of momentum at the contact line is negligible, (2.1) also holds when the contact line is moving, [4], [18], [29]. Bending of the interface by viscous forces very close to the contact line leads to a difference between the apparent contact angle, $\theta_{app}$, which can be measured experimentally, and the actual, or microscopic, contact angle, $\theta_c$. However, $\theta_c$ must be a function of the velocity of the contact line in order to account for experimental observations, [10]. This means that at least one of $\sigma_{12}$, $\sigma_{1S}$ and $\sigma_{2S}$ must deviate from its static value when the contact line is moving.

An examination of the flow field close to a moving contact line gives a straightforward explanation of this phenomenon, [11]. Fluid molecules are advected along the free surface, where they are in a thermodynamic state associated with the surface tension $\sigma_{12}$, through the contact line and into the interface between the fluid and the solid surface, where their equilibrium thermodynamic state is associated with the surface tension $\sigma_{1S}$. However, the fluid molecules take a finite time to relax from the state associated with $\sigma_{12}$ to that associated with $\sigma_{1S}$. The surface tension of the interface between the fluid and the solid surface will therefore be different from the static value, $\sigma_{1S}$, in some neighbourhood of the contact line and, in particular, the value at the contact line, which we must use in (2.1), will be different from $\sigma_{1S}$. This leads to a dynamic contact angle different from the static value. This simple idea is the basis of Shikhmurzaev’s theory.

A consequence of the gradient in surface tension close to the contact line is that the classical no slip boundary condition is modified so that there is an apparent slip between the bulk fluid and the solid surface, in a sense that we shall discuss more fully below. Shikhmurzaev claims that, as a result, the force on the solid surface is bounded, [18]. The two major modelling difficulties associated with moving contact lines, namely the specification of $\theta_c$ as a function of the velocity of the contact line, and the modification of the no slip boundary condition, are thereby overcome simultaneously in a simple, consistent theory derived from first principles. However, we shall see later that, although the force on the solid surface certainly is bounded, the singularity is not relieved in quite the manner that Shikhmurzaev suggests.

We now need to examine some of the details of the theory. Consider the interface between a liquid and either another, immiscible liquid, a gas or a solid surface. The liquid molecules close to the interface experience an asymmetric force due to the presence of the other material. This results in a slightly different liquid density in a thin surface layer,
typically \( h \approx 10^{-10} \) m thick. This gives rise to a surface tension, \( \sigma \). Note that, although this is a consistent way of defining the surface layer density, it is not the conventional way, which uses the equimolar surface as the dividing surface between the two phases (see [17], [28]).

We can now treat the surface tension as a function of the local surface density, and also define the surface pressure, \( p_s \equiv -\sigma(\rho_s) \). Since we do not expect very large changes in surface density, it is simplest to assume that the surface pressure varies linearly with the surface density, so that

\[
p_s = \gamma(\rho_s - \rho_{0s}).
\]

(2.2)

Both \( \gamma \) and \( \rho_{0s} \) are constants that must be determined experimentally. In principle, this could be an experiment that has nothing to do with contact lines. We are not, however, completely in the dark about the magnitude of these constants. The surface layer density is close to the bulk density. For water, where \( \rho \approx 1000 \) kg m\(^{-3}\), this means that \( \rho_{0s} \approx h\rho \approx 10^{-7} \) kg m\(^{-2}\). The compressibility of the surface layer will be similar to that of the bulk fluid, and for water, \( \gamma \approx 2 \times 10^6 \) m\(^2\) s\(^{-2}\).

The next step is to consider the dynamics of the liquid that forms the surface layer. We can define a surface layer velocity, \( v_s \), so that conservation of mass in the surface layer is

\[
\frac{\partial \rho_s}{\partial t} + \nabla \cdot (\rho_s v_s) = -\rho_s - \rho_{es} \tau.
\]

(2.3)

Note that in any equation involving surface variables, \( \nabla \) is the gradient operator restricted to the surface. If the right hand side of this equation were equal to zero, this would be the usual equation for conservation of mass. The actual right hand side represents a source of fluid that tends to drive the surface density towards its equilibrium value, \( \rho_{es} \), over a time scale \( \tau \). This source of fluid consists of a flow of molecules from the bulk that is too weak to significantly affect the bulk fluid velocity\(^1\), but which does affect the surface density. Note that if \( \sigma_e \) is the equilibrium, static surface tension, then (2.2) and (2.3) show that \( -\sigma_e = \gamma(\rho_{es} - \rho_{0s}) \).

Having written down equations for what goes on in the surface layer, we can now consider how this affects the bulk flow. This is governed by the usual Navier–Stokes equations for an incompressible, Newtonian fluid,

\[
\nabla \cdot \mathbf{u} = 0, \quad \rho \left( \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \mu \nabla^2 \mathbf{u},
\]

(2.4)

where \( \mathbf{u} \) is the bulk velocity field and \( \mu \) the bulk viscosity. We have assumed that the effect of gravity is negligible. The behaviour of the surface layer only affects the bulk flow through appropriate boundary conditions, the first of which is

\[
2\mu \mathbf{n} \cdot \mathbf{e} (\mathbf{I} - \mathbf{nn}) - \frac{1}{2} \nabla p_s = \beta (\mathbf{u} - \mathbf{U}) \cdot (\mathbf{I} - \mathbf{nn}),
\]

(2.5)

where \( \mathbf{n} \) is the outward unit normal, \( \mathbf{I} \) is the unit tensor, \( \mathbf{e} = \frac{1}{2} \left( \nabla \mathbf{u} + (\nabla \mathbf{u})^T \right) \) is the rate of strain tensor and \( \mathbf{U} \) is the velocity of the interface. Note that \( 2\mu \mathbf{n} \cdot \mathbf{e} (\mathbf{I} - \mathbf{nn}) \)

\(^1\) See [25] for a modification of the theory that takes into account the effect of this flux on the normal velocity.
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Figure 2. The velocity at various points in the surface layer at a fluid/solid interface.

is the shear stress exerted on the interface by the bulk fluid and \((u - U) \cdot (I - nn)\) is the tangential component of the difference between the bulk velocity and the interfacial velocity. This, and the other boundary conditions that we shall discuss, was derived by Shikhmurzaev by considering the equation for conservation of energy in the surface layer, applying the principles of near equilibrium thermodynamics, and seeking conditions that minimise the rate of production of entropy, [3]. Focussing for the moment on a fluid/solid interface, for which \(U\) is the velocity of the solid surface, this means that if the right hand side of (2.5) is nonzero, there appears to be slip between the bulk fluid and the solid. The left hand side shows that both the shear stress exerted by the bulk fluid and a gradient in surface pressure, and hence surface tension, can cause this apparent slip. The coefficient of sliding friction, \(\beta\), is a constant with dimensions of viscosity divided by length, and has typical magnitude \(\mu/h\).

We can clarify why the slip between a solid surface and the bulk fluid inherent in a nonzero value of \((u - U) \cdot (I - nn)\) is only apparent with reference to figure 2. The surface layer sees the limiting value of the bulk velocity, \(u\), on the side facing the bulk fluid. The velocity at the solid surface is \(U\) and there is no slip between the fluid and the solid surface. The surface velocity, \(v_s\), can be thought of as the velocity at the midpoint of the layer. Although there may be a significant difference between these three velocities, there is no actual slip between the fluid and the solid.

Four more boundary conditions are needed to complete the model for the surface layer. Firstly,

\[ v_s \cdot n = u \cdot n = U \cdot n, \]  

which simply states that the normal components of all three velocities are equal at the surface, and secondly,

\[ v_s \cdot (I - nn) = \frac{1}{2} (u + U) \cdot (I - nn) - \alpha \nabla p_s. \]  

If there were no surface pressure gradient term in this equation, it would simply state that the tangential component of the surface layer velocity is the average of the tangential components of the bulk and interfacial velocities, consistent with a velocity profile that varies linearly across the layer. The pressure gradient term modifies this velocity profile in a manner analogous to ordinary fluid flow in a channel. The final constant, \(\alpha\), has dimensions of length divided by viscosity, and has a typical magnitude \(h/\mu\). Finally, we have the usual conditions of continuity of normal and tangential stress at the free surface, taking into account the fact that the surface tension may vary along the interface. These
are
\[ -p + 2\mu\mathbf{n.e.n} = -p_s\kappa, \quad (2.8) \]
where \( \kappa = \nabla \cdot \mathbf{n} \) is the curvature of the interface, and
\[ 2\mu\mathbf{n.e.}(\mathbf{I} - \mathbf{nn}) = \nabla p_s. \quad (2.9) \]
Equation (2.9) states that gradients in surface tension cause a shear stress (a Marangoni stress) on the interface. For a liquid/gas interface, it is convenient to eliminate the tangential component of the interfacial velocity, \( \mathbf{U}(\mathbf{I} - \mathbf{nn}) \) between (2.5) and (2.7), making use of (2.9), to arrive at
\[ \nabla p_s = \frac{4\beta}{1 + 4\alpha\beta} (\mathbf{u} - \mathbf{v}_s) \cdot (\mathbf{I} - \mathbf{nn}). \quad (2.10) \]
This completes the model for the surface layers. Note that we have yet to mention contact lines in the formulation. Shikhmurzaev postulates two further conditions at the contact line: firstly, conservation of mass, so that the amount of fluid that flows into the contact line from one layer flows out in the other layer, and secondly, conservation of momentum, which is just the horizontal force balance given by the Young–Laplace equation, (2.1).

When a liquid moves across a solid surface displacing a gas (which we shall initially treat as a void), a free surface and a liquid/solid surface, characterized by the above equations, meet at a contact line. From this point onwards, we will assume steady, two-dimensional flow in a frame of reference where the contact line is stationary, in which case the surface gradient operators above can be replaced with \( d/ds \) or \( d/ds_i \), where \( s \) and \( s_i \) are arc length along the solid and free surfaces respectively. We also add a superscript \( i \) to free surface quantities and write \( u_s = \mathbf{u} \cdot (\mathbf{I} - \mathbf{nn}) \) and \( v_s = \mathbf{v}_s \cdot (\mathbf{I} - \mathbf{nn}) \). In this manner, conservation of mass at the contact line, \( s = s_i = 0 \), is
\[ \rho_s^i v_s^i + \rho_x v_s = 0, \quad (2.11) \]
and the Young-Laplace equation is
\[ (\rho_s^i - \rho_{0s}^i) \cos \theta_s = (\rho_{cs}^i - \rho_{0s}^i) \cos \theta_s + \rho_{cs} - \rho_s. \quad (2.12) \]
In order to clarify the structure of the model, we now eliminate the surface velocities and surface tensions, so that only the surface densities appear. Recall that these are assumed to be linearly related to the surface tensions through (2.2). On the free surface,
\[ \frac{\gamma \alpha (1 + 4A)}{4A} \frac{d}{ds_i} \left( \rho_s^i \frac{dp_s^i}{ds_i} \right) - \frac{d}{ds_i} (\rho_s^i u_s^i) - \frac{\rho_s^i - \rho_{cs}^i}{\tau} = 0, \quad (2.13) \]
\[ 2\mu\mathbf{n.e.}(\mathbf{I} - \mathbf{nn}) = \gamma \frac{d\rho_s^i}{ds_i}, \quad (2.14) \]
\[ -p + 2\mu\mathbf{n.e.n} = -\gamma (\rho_s^i - \rho_{0s}^i) \kappa, \quad (2.15) \]
\[ \mathbf{u}^i \cdot \mathbf{n} = 0, \quad (2.16) \]
\[ \rho_s^i \rightarrow \rho_{cs}^i \text{ as } s_i \rightarrow \infty, \quad (2.17) \]
where $A = \alpha\beta$ is a dimensionless constant. On the solid surface,

$$
\gamma \alpha \frac{d}{ds} \left( \rho_s \frac{d\rho_s}{ds} \right) - \frac{1}{2} \frac{d}{ds} \left\{ \rho_s (u_s + U) \right\} - \frac{\rho_s - \rho_{es}}{\tau} = 0,
$$

(2.18)

$$
\beta (u_s - U) = 2\mu \mathbf{e} \cdot (\mathbf{I} - \mathbf{n} \mathbf{n}) - \frac{1}{2} \gamma \frac{d\rho_s}{ds},
$$

(2.19)

$$
\mathbf{u} \cdot \mathbf{n} = 0,
$$

(2.20)

$$
\rho_s \to \rho_{es} \quad \text{as} \quad s \to \infty,
$$

(2.21)

where $U$ is the velocity of the contact line. At the contact line, $s = s_i = 0$, we have

$$
-\rho_s \left\{ u_s^i - \frac{\gamma \alpha (1 + 4A)}{4A} \frac{d\rho_s^i}{ds_i} \right\} = \rho_s \left\{ \frac{1}{2} (u_s + U) - \gamma \alpha \frac{d\rho_s}{ds} \right\},
$$

(2.22)

and the force balance, (2.12).

We can now see that we have steady nonlinear diffusion equations for the surface densities, (2.13) and (2.18)$^2$, coupled to the flow through the forcing terms and the remaining equations. There are two conditions at infinity, (2.17) and (2.21), and two conditions at the contact line, (2.12) and (2.22). However, the Young-Laplace equation, (2.12), determines the contact angle, and cannot be counted as a connection condition for these two second order differential equations. Another condition is required at the contact line to close the system.

Shikhmurzaev derived the equations that govern the surface layer variables by considering the nonequilibrium thermodynamics of the surface, based upon the theory of Bedeaux, Albano and Mazur, [3]. In particular, conservation of mass gives (2.3), whilst conservation of momentum gives that the normal component of the surface stress is zero, along with a generalized equation of capillarity. Conservation of energy can be used to derive the rate at which entropy is produced, which then leads to (2.5) and (2.7). Bedeaux has used this approach to consider the thermodynamics of the contact line, [4]. He also found that conservation of mass and momentum simply lead to the force balance and flux continuity at the contact line, (2.12) and (2.22). However, by considering the rate at which entropy is produced at the contact line, a third condition emerges, namely

$$
\rho_s(0) v_s(0) = k \left\{ \mu_s^i(0) - \mu_s(0) \right\},
$$

(2.23)

where $\mu_s$ is the chemical potential and $k$ is a constant. This says that the flow through the contact line is driven by a difference in the chemical potentials of the interfaces at the contact line. One assumption that underlies Shikhmurzaev’s theory is that deviations from equilibrium are small enough that the chemical potential is linearly related to changes in surface density, so that

$$
\mu_s = \mu_{es} + \frac{d\mu_s}{d\rho_s} \bigg|_{\rho_s = \rho_{es}} (\rho_s - \rho_{es}).
$$

In addition, since there is no flow through a static contact line, we must have $\mu_{es} = \mu_{es}^i$.

$^2$ Note that, in an unsteady flow, $\partial \rho_s^i / \partial t$ and $\partial \rho_s / \partial t$ would appear on the right hand sides of (2.13) and (2.18) respectively.
and hence
\[
\rho_s(0)u_s(0) = \rho_s(0) \left\{ \frac{1}{2} (u_s + U) - \gamma \alpha \frac{d\rho_s}{ds} \right\} = U_0^i \left( \rho_s'(0) - \rho_{es}' \right) - U_0 (\rho_s(0) - \rho_{es}),
\]
where the material parameters \( U_0^i \) and \( U_0 \) are
\[
U_0^i = k \frac{d\mu_s}{d\rho_s} \bigg|_{\rho_s = \rho_{es}}, \quad U_0 = k \frac{d\mu_s}{d\rho_s} \bigg|_{\rho_s = \rho_{es}},
\]
and have the dimensions of velocity. We would expect that an order of magnitude estimate of \( U_0 \) and \( U_0^i \) is \( h/\tau \).

There are now two obvious questions. Firstly, how was Shikhmurzaev able to solve for steady Stokes flow in a wedge at low capillary number when the system of governing equations was incomplete, and secondly, how does this new boundary condition affect the solution of the problem.

3 Asymptotic solution for steady Stokes flow in a wedge at low capillary number

As we have seen, Shikhmurzaev’s theory leads to the coupling of the usual bulk fluid flow to a set of equations for surface layer quantities through the boundary conditions (2.2) to (2.10). Rather than tackle this daunting problem in its full generality, Shikhmurzaev made the sensible decision to start with a simple, but nontrivial, flow, namely steady Stokes flow with strong surface tension. Apart from the linearization of the Navier-Stokes equations, the main advantage of this is that the free surface is flat at leading order, so that the flow domain is a simple wedge. As we shall see, asymptotic methods can then be used to drastically simplify the problem.

We work in terms of polar coordinates, \((r, \theta)\), with origin at the contact line and \( u = (u_r, u_\theta) \). If we define a stream function using
\[
u_r = \frac{1}{r} \frac{\partial \psi}{\partial \theta}, \quad u_\theta = - \frac{\partial \psi}{\partial r},
\]
then in Stokes flow we need to solve the biharmonic equation
\[
\nabla^4 \psi = 0,
\]
in the bulk of the fluid. In order to consider what happens in the far field, we need to think of the flow as being driven by some prescribed outer flow with the surface variables in equilibrium. As \( r \to \infty \), we therefore use
\[
u \sim \nu_\infty(r, \theta), \quad p \sim p_\infty(r, \theta).
\]
We note that as \( r \to \infty \) we recover the usual boundary conditions of no slip at the solid surface and no tangential stress at the free surface. We must therefore solve (3.2) subject to
\[
\psi = 0, \quad \frac{\partial^2 \psi}{\partial \theta^2} = 0 \quad \text{at} \quad \theta = \theta_\infty, \quad \text{and} \quad \theta = 0,
\]
and
\[
\psi = 0, \quad \frac{1}{r} \frac{\partial \psi}{\partial \theta} = 1 \quad \text{at} \quad \theta = 0.
\]
This gives

$$\psi = \psi_\infty \equiv r \frac{(\theta - \theta_\infty) \sin \theta - \theta \cos \theta_\infty \sin(\theta - \theta_\infty)}{\sin \theta_\infty \cos \theta_\infty - \theta_\infty} \equiv rf(\theta; \theta_\infty), \quad (3.6)$$

a streamfunction that was first written down by Moffatt, [14]. We conclude that

$$\mathbf{u}_\infty = \left( \frac{df}{d\theta}(\theta; \theta_\infty), -f(\theta; \theta_\infty) \right), \quad p_\infty = \frac{-1}{r} \left\{ \frac{d^2f}{d\theta^2}(\theta; \theta_\infty) + \frac{df}{d\theta}(\theta_\infty) \right\}, \quad (3.7)$$

Before proceeding, we should note that there is a slight difficulty here, since the normal stress at, and hence the curvature of, the free surface is $O(1/r)$, which suggests that the slope grows like $\log r$ as $r \to \infty$, instead of tending to the constant $\tan \theta_\infty$. Physically, viscous bending causes the free surface to deform slowly as $r \to \infty$. However, for $Ca \ll 1$ the deformation of the free surface is small, provided that $\log r \ll Ca^{-1}$, [10], a point that we shall return to later. We can therefore think of the far field flow given by $\psi_\infty$ as being driven by the outer flow at some large distance $r = r_\infty$ away from the contact line.

### 3.1 Lengthscales and dimensionless variables

In Shikhmurzaev’s analysis of this problem, [18], [20], an uncomfortable triple limiting procedure was used, taking, using his notation, $Ca \to 0$, $\lambda \to \infty$ and, implicitly, $V \to 0$. We will proceed differently here.

Turning our attention to the free surface, we note that the shear rate, $\mathbf{n.e.} (\mathbf{I} - \mathbf{nn})$, in (2.14) has dimensions of velocity over length. This means that an appropriate scale for the spatially-varying part of $\rho_s$ is $\mu U/\gamma$, since we should scale velocities with the velocity of the solid surface, which drives the flow. We therefore define dimensionless variables

$$\rho_s' = \rho_{sI} + \frac{\mu U}{\gamma} \hat{\rho}_s, \quad d_s = \frac{U_s}{U}, \quad \hat{d}_s = \frac{ds}{L_i},$$

where $L_i$ is a lengthscale that we wish to determine. In terms of these variables, (2.13) becomes

$$\frac{\mu \alpha (1 + 4A)}{4AL_i} \frac{d}{ds} \left\{ \left( 1 + \frac{Ca}{\lambda} \hat{\rho}_s \right) \frac{d\hat{\rho}_s}{ds} \right\} = \frac{d}{ds} \left\{ \left( 1 + \frac{Ca}{\lambda} \hat{\rho}_s \right) \hat{u}_s \right\} - \frac{\mu L_i}{\tau \gamma \rho_{sI}} \hat{\rho}_s = 0, \quad (3.8)$$

where $Ca = \mu U/\sigma_c^0$ is 1 is the capillary number, $\sigma_c^0$ is the equilibrium surface tension at the free surface and $\lambda = \gamma \rho_{sI}/\sigma_c^0$. Using $\gamma \approx 2 \times 10^6$ m$^2$s$^{-2}$, $\rho_{sI} \approx 10^{-7}$ kgm$^{-2}$ and $\sigma_c^0 \approx 0.07$ kgs$^{-2}$, we find that $\lambda \approx 2.5$. Since $Ca/\lambda \ll 1$, (2.14) tells us that the driving velocity is small enough that the associated surface shear rate can produce only a small deviation of the surface density from its equilibrium value. Shikhmurzaev proceeds by assuming that $\lambda \gg 1$, [19], so that a small change in the surface density leads to a large change in the surface tension (an almost incompressible surface layer). We will use this assumption here, but relax it later when we find that it does not lead to physically realistic results.

We must now choose $L_i$ to balance terms in (3.8). Balancing the second and third terms gives

$$L_i = L_{iI} \equiv \tau \gamma \rho_{sI}/\mu.$$

Using the estimate $\tau \approx 10^{-5} \mu$ made by Blake and Shikhmurzaev, [9], $L_{iI} \approx 10^{-6}$m. Note,
however, that we will revise this estimate later when we compare the model to the same experimental data set, but take into account the modified boundary condition (2.24) and the effect of viscous bending. With \( L_i = L_{i1} \), (3.8) becomes

\[
K \frac{1 + 4A}{4A} \frac{d}{ds_i} \left( 1 + \frac{Ca}{\lambda} \hat{\rho}_s \right) \frac{d\hat{\rho}_s}{ds_i} - \frac{d}{ds_i} \left( 1 + \frac{Ca}{\lambda} \hat{\rho}_s \right) \hat{u}_s^i - \hat{\rho}_s = 0,
\]

(3.9)

where \( K = \mu^2 \alpha/\tau \gamma \rho_{es} \approx 10^{-4} \ll 1 \), using the estimate \( \alpha = h/\mu \). Recall that \( h \approx 10^{-10} \text{m} \) is the thickness of the interfacial layer. Since \( K \ll 1 \), we expect that the solution on this lengthscale will be an outer solution, and that the second derivative term will come into play on a smaller, inner lengthscale. We also have

\[
2 \mathbf{n} \cdot (\mathbf{I} - \mathbf{nn}) = \frac{d\hat{\rho}_s}{d\hat{s}_i},
\]

(3.10)

\[
Ca (-\hat{p} + 2 \mathbf{n} \cdot \mathbf{e} \cdot \mathbf{n}) = - (1 - Ca \hat{\rho}_s) \hat{k},
\]

(3.11)

\[
\hat{\rho}_s \rightarrow 0 \quad \text{as} \quad \hat{s}_i \rightarrow \infty.
\]

(3.12)

Note that, since \( Ca \ll 1 \), we have \( \hat{k} \ll 1 \), so that, at leading order, the free surface is a straight line, with \( \theta = \theta_c \). This remains true for all of the scalings that we consider in this section, and, at leading order, the domain of solution is therefore the wedge \( 0 < \theta < \theta_c \), and we need not consider the normal stress balance further. Since the free surface is flat at leading order, we can now write \( r = s = s_i \).

We can now see that we cannot balance the first and third terms in (3.8) on a length-scale smaller that \( L_{i1} \), but that by taking \( L_i = L_{i2} \equiv KL_{i1} = \mu \alpha \approx h \), we obtain

\[
\frac{1 + 4A}{4A} \frac{d}{d\hat{r}} \left( 1 + \frac{Ca}{\lambda} \hat{\rho}_s \right) \frac{d\hat{\rho}_s}{d\hat{r}} - \frac{d}{d\hat{r}} \left( 1 + \frac{Ca}{\lambda} \hat{\rho}_s \right) \hat{u}_s^i - K \hat{\rho}_s^i = 0,
\]

(3.13)

\[
2 \mathbf{n} \cdot (\mathbf{I} - \mathbf{nn}) = \frac{d\hat{\rho}_s}{d\hat{r}},
\]

(3.14)

where \( \hat{r} = r/L_{i2} \). We will also see below that it is the flow in the solid surface layer that drives the bulk flow and the flow in the free surface layer, so that the details of the flow in this inner region are not important, at least when \( Ca \ll 1 \). Therefore, although this lengthscale is roughly that of the surface layer, and hence the continuum approximation starts to break down, we should not be unduly concerned.

On the solid surface, (2.19) does not suggest any restriction on changes in \( \hat{\rho}_s \). This means that there is only one possible choice of lengthscale, \( L \equiv \sqrt{\pi \gamma \rho_{es} \hat{r}} = K^{1/2} \hat{L}_{i1} = K^{-1/2} L_{i2} \approx 10^{-8} \text{m} \). We refer to this as the slip region. We define dimensionless variables

\[
\hat{\rho}_s = \frac{\rho_s}{\rho_{es}^s}, \quad \hat{u}_s = \frac{u_s}{U}, \quad \hat{r} = \frac{r}{L},
\]

in terms of which (2.18) and (2.19) become

\[
\frac{d}{d\hat{r}} \left( \hat{\rho}_s \frac{d\hat{\rho}_s}{d\hat{r}} \right) - \frac{Ca}{2\lambda K^{1/2}} \frac{d}{d\hat{r}} \{ \hat{\rho}_s (\hat{u}_s + 1) \} - (\hat{\rho}_s - \hat{\rho}_{es}) = 0,
\]

(3.15)

\[
ACa (\hat{u}_s - 1) = K^{1/2} \left\{ 2Ca \mathbf{n} \cdot (\mathbf{I} - \mathbf{nn}) - \frac{1}{2} \lambda \frac{d\hat{\rho}_s}{d\hat{r}} \right\},
\]

(3.16)

where \( \hat{\rho}_{es} = \rho_{es}/\rho_{es}^s \).
inner, outer and slip regions. We assume that and \( \lambda \).

We therefore define

\[
\frac{1}{2} \left( \tilde{u}_s + 1 \right) - \frac{\lambda K^{1/2} d\tilde{p}_s}{d\tilde{r}} \right) \rightangle = \tilde{p}_s \left( \frac{1}{2} \left( \tilde{u}_s + 1 \right) - \frac{\lambda K^{1/2} d\tilde{p}_s}{d\tilde{r}} \right) \]

so that

\[
\lambda \left( \tilde{u}_s - \tilde{p}_s \right) \] \( \rho \)

and (3.15) and (3.16) become

\[
\frac{d}{d\tilde{r}} \left( \tilde{p}_\mathrm{es} + \frac{\rho_\lambda}{\lambda} \frac{d\tilde{p}_s}{d\tilde{r}} \right) - \frac{C_a}{2 K^{1/2} d\tilde{r}} \left( \tilde{p}_\mathrm{es} + \frac{\rho_\lambda}{\lambda} \right) \left( \tilde{u}_s + 1 \right) \right\} - \tilde{p}_s = 0, \]

\[
ACa \left( \tilde{u}_s - 1 \right) = K^{1/2} \left\{ 2Ca n \cdot (I - nn) - \frac{1}{2} \frac{d\rho_s}{d\tilde{r}} \right\}. \]

We can now pull all of this together and consider the leading order solutions in the inner, outer and slip regions. We assume that \( \lambda \gg 1, K \ll 1, Ca \ll 1 \) with \( \lambda K^{1/2} = O(1) \) and \( \lambda Ca = O(1) \), since this is a distinguished limit. Note that for \( \lambda \gg 1 \), \( \tilde{p}_\mathrm{es} = 1 + O(\lambda^{-1}) \).
3.1.1 Slip region: $r = O(L)$

In this region, at leading order, (3.22) and (3.23) become

$$\frac{d^2 \tilde{\rho}_s}{dr^2} - \frac{Ca}{2K^{1/2}} \frac{d\tilde{u}_s}{dr} - \tilde{\rho}_s = 0,$$

and hence

$$1 + 4A \frac{d^2 \tilde{\rho}_s}{dr^2} - \tilde{\rho}_s = 0.$$

The solution that satisfies $\tilde{\rho}_s \to 0$ as $\tilde{r} \to \infty$ is

$$\tilde{\rho}_s = \tilde{\rho}_s(0) \exp \left(-\sqrt{\frac{4A}{1 + 4A}} \tilde{r} \right).$$

Equations (3.18) and (3.20) give

$$\cos \theta_c - \cos \theta_s = \tilde{\rho}_s(0),$$

$$\frac{1}{2} (\bar{u}_s(0) + 1) - \frac{K^{1/2}}{Ca} \frac{d\tilde{\rho}_s}{dr}(0) = -\frac{Ca_0}{\lambda Ca} \tilde{\rho}_s,$$

assuming that $Ca_0$ and $Ca_i$ are of $O(1)$. Using the solution (3.27), we find that

$$\cos \theta_c - \cos \theta_s = \tilde{\rho}_s(0) = -\frac{U}{U_c},$$

where

$$U_c = \frac{1}{\lambda} \left\{ U_0 + \sqrt{\frac{\gamma \alpha \rho e_s (1 + 4A)}{4A \tau}} \right\}.$$

Equation (3.30) says that the theory predicts a linear variation of the cosine of the actual contact angle with contact line velocity. Since this is not a good model for the observed variation of the contact angle, we will consider the solution when $\lambda = O(1)$ and $Ca = O(1)$ in section 4.

Note that we have been able to determine the surface density distribution on the solid surface without having to solve on either the free surface or in the bulk. We can see that the solid surface drives the bulk flow through the boundary condition

$$\bar{u}_s = 1 - \frac{1}{Ca_e} \sqrt{\frac{K}{A(1 + 4A)}} \exp \left(-\sqrt{\frac{4A}{1 + 4A}} \bar{r} \right),$$

where $Ca_e = \mu U_c/\sigma e$. As we shall see below, this also drives the behaviour of the free surface density.

3.1.2 Outer region: $r = O(L_1)$

At leading order, the solid surface variables take their equilibrium values, with $\tilde{\rho}_s = 1$, $\tilde{u}_\theta = 0$ and $\tilde{u}_s = \tilde{u}_r = 1$ at $\theta = 0$. On the free surface, (3.9) and (3.10) become, at leading
order
\begin{align}
\frac{du_r}{dr} &= -\dot{\rho}_s, \tag{3.33} \\
\frac{d\dot{\rho}_s}{dr} &= -\frac{1}{\hat{r}} \frac{\partial u_r}{\partial \theta}. \tag{3.34}
\end{align}

If we eliminate \( \dot{\rho}_s \) between these equations, we arrive at the boundary value problem
\begin{equation}
\nabla^4 \psi = 0 \quad \text{for} \quad \hat{r} > 0, \quad 0 < \theta < \theta_c, \tag{3.35}
\end{equation}
to be solved subject to
\begin{align}
\psi &= 0, \quad \frac{1}{r} \frac{\partial \psi}{\partial \theta} = 1 \quad \text{at} \quad \theta = 0, \tag{3.36} \\
\psi &= 0, \quad \frac{d^2}{dr^2} \left\{ \frac{1}{r} \frac{\partial \psi}{\partial \theta} \right\} = \frac{1}{r^2} \frac{\partial^2 \psi}{\partial \theta^2} \quad \text{at} \quad \theta = \theta_c, \tag{3.37} \\
\psi &\sim \psi_\infty \quad \text{as} \quad \hat{r} \to \infty. \tag{3.38}
\end{align}

Of course, one solution of this boundary value problem is \( \psi = \psi_\infty \). In other words, there is a solution available where the far field is attained with \( \hat{r} = o(1) \), and effectively this asymptotic region is not needed. This is precisely the solution used by Shikhmurzaev in his analysis, [18]. However, we will now show that this solution is not unique. It is easy to miss this possibility, and the present author made the same mistake as Shikhmurzaev in an earlier publication, [5].

We begin by defining
\begin{equation}
\psi = \psi_\infty + \Psi. \tag{3.43}
\end{equation}

Because the far field stream function, \( \psi_\infty \), is a solution of the boundary value problem given by (3.35) to (3.38), in particular, since it corresponds to a constant velocity and no shear stress at the free surface, we arrive at the boundary value problem
\begin{equation}
\nabla^4 \Psi = 0, \tag{3.39}
\end{equation}
subject to
\begin{align}
\Psi &= 0, \quad \frac{\partial \Psi}{\partial \theta} = 0 \quad \text{at} \quad \theta = 0, \tag{3.40} \\
\Psi &= 0, \quad \frac{d^2}{dr^2} \left\{ \frac{1}{r} \frac{\partial \Psi}{\partial \theta} \right\} = \frac{1}{r^2} \frac{\partial^2 \Psi}{\partial \theta^2} \quad \text{at} \quad \theta = \theta_c, \tag{3.41} \\
\Psi &\to 0 \quad \text{as} \quad \hat{r} \to \infty. \tag{3.42}
\end{align}

The eigenvalue problem given by (3.39) to (3.42) has a one-parameter family of nontrivial solutions. Details are given in appendix A, where we construct the eigensolutions using Mellin integral transforms.

The solution we have constructed in this region will become nonuniform as \( \hat{r} \to 0 \) and we enter the inner region. As \( \hat{r} \to 0 \), we find that
\begin{align}
\psi &\sim \hat{r} f(\theta; \theta_c) - \hat{r} u_\infty \frac{\theta_c \sin \theta_c}{\sin^2 \theta_c - \theta_c^2} \left\{ \left( 1 - \frac{\theta}{\theta_c} \right) \sin \theta + \frac{\theta \sin(\theta - \theta_c)}{\sin \theta_c} \right\}, \tag{3.43} \\
u_r |_{\theta = \theta_c} &\to u_0(\theta_c) + u_\infty, \tag{3.44}
\end{align}
where \( u_\infty \) is the undetermined parameter that multiplies the eigensolution and
\[
u_0(\theta_c) = \frac{\sin \theta_c - \theta_c \cos \theta_c}{\sin \theta_c \cos \theta_c - \theta_c}
\]
is the velocity at the free surface in the far field.

### 3.1.3 Inner region : \( r = O(L_{i2}) \)
In this region, the bulk velocity adjusts to be equal to the contact line velocity at the contact line. The leading order versions of (3.10) and (3.13) show that
\[
\frac{1}{r} \frac{\partial \hat{u}_r}{\partial \theta} = \frac{\partial \hat{\rho}_s}{\partial \hat{r}} = \frac{4 A}{1 + 4 A} \left\{ \hat{u}_r - u_\infty - u_0(\theta_c) \right\}, \quad \hat{u}_\theta = 0 \quad \text{at} \quad \theta = \theta_c.
\]
(3.45)

On the solid surface, making use of the solution (3.27), we find that
\[
\hat{u}_r - 1 = \frac{2}{A} \frac{\partial \hat{u}_r}{\partial \theta} = \frac{K^{1/2}}{C \alpha \sqrt{A(1 + 4A)}} \quad \text{at} \quad \theta = 0.
\]
(3.46)

The boundary conditions (3.45) and (3.46) allow the radial velocities at the two bounding surfaces to undergo apparent slip, and thereby avoid a singularity in the force at the contact line. Once the solution of the bulk problem is known, we can, in principle, solve (3.45) for \( \hat{\rho}_s \), making use of the boundary condition (3.21) at \( \hat{r} = 0 \). This determines the constant \( u_\infty \), which multiplies the eigensolution in the outer region. In other words, the strength of the flow given by the eigensolution is determined by conservation of mass at the contact line. In Shikhmurzaev’s original analysis, [18], [20], the boundary condition (2.23) at the contact line was effectively replaced by the condition \( u_\infty = 0 \).

### 4 Numerical solutions for \( Ca = O(1) \)
Since we have carefully chosen the dimensionless parameters so that the contact line speed, \( U \), only appears in the capillary number, we can consider the effect of viscous bending at sufficiently high contact line speeds by taking \( Ca = O(1) \), but with \( \lambda \) still large and \( \lambda K^{1/2} = O(1) \). We find that, on both surfaces, as above for \( Ca \ll 1 \), the surface density is an \( O(\lambda^{-1}) \) correction to its equilibrium value. This means that the surface problems can be linearized. However, the solid surface density is now coupled to both the bulk flow and the flow on the free surface. Moreover, the normal stress balance on the free surface now gives an \( O(1) \) deformation, so we are faced with a nonlinear free boundary problem, even though all the other equations can be linearized. For these reasons, and also because we would like to investigate what happens when \( \lambda = O(1) \), we will solve the full nonlinear problem numerically, treating all parameters as \( O(1) \).

We will use the slip lengthscale \( L = \sqrt{\alpha \gamma \rho_e \tau} \) to nondimensionalise the equations. In addition, since it is convenient to be able to set \( Ca = 0 \) and obtain the static solution, we will not nondimensionalise velocities and stresses using the contact line speed \( U \), but use \( \sigma_e / \mu \) instead. The full dimensionless problem is then
\[
\nabla \cdot \mathbf{u} = 0, \quad 0 = -\nabla p + \nabla^2 \mathbf{u} \quad \text{in} \ D,
\]
(4.1)
where $D$ is the region occupied by the bulk fluid,
\[
\frac{d}{dr} \left( \rho_s \frac{d\rho_s}{dr} \right) - \frac{1}{2\lambda K} \frac{d}{dr} \left\{ \rho_s (u_s + Ca) \right\} - \left( \rho_s - \bar{\rho}_{es} \right) = 0 \quad \text{on } \partial D_1, \tag{4.2}
\]
\[
A (u_s - Ca) = 2K^{1/2} f_1, \quad (I - \mathbf{mm}) - \frac{1}{2} \lambda K^{1/2} \frac{d\rho_s}{dr} \quad \text{on } \partial D_1, \tag{4.3}
\]
where $\partial D_1$ is the solid surface and $f_1$ the force exerted on the solid surface by the fluid,
\[
\frac{1 + 4A}{4A} \frac{d}{ds} \left( \rho_s \frac{d\rho_s}{ds} \right) - \frac{1}{\lambda K} \frac{d}{ds} \left( \rho_s^2 u_s^i \right) - (\rho_s^i - 1) = 0 \quad \text{on } \partial D_2, \tag{4.4}
\]
\[
f_2. (I - \mathbf{mm}) = \lambda \frac{d\rho_s}{ds} \quad \text{on } \partial D_2, \tag{4.5}
\]
\[
f_2. \mathbf{n} = (\lambda + 1 - \lambda \rho_s^i) \kappa \quad \text{on } \partial D_2, \tag{4.6}
\]
where $\partial D_2$ is the free surface and $f_2$ the force exerted on the free surface by the fluid.

At the contact line, $s = r = 0$,
\[
\cos \theta_c = \frac{\cos \theta_s - \lambda (\bar{\rho}_{es} - \rho_s(0))}{1 - \lambda (\rho_s^i(0) - 1)}, \tag{4.7}
\]
\[
-\rho_s \left\{ u_s^i - \frac{1 + 4A}{4A} \lambda K^{1/2} \frac{d\rho_s}{ds} \right\} = \rho_s \left\{ \frac{1}{2} (u_s + Ca) - \lambda K^{1/2} \frac{d\rho_s}{dr} \right\}
\]
\[
= Ca_0 (\rho_s^i - 1) - Ca_0 (\rho_s - \bar{\rho}_{es}). \tag{4.8}
\]

We treat the far field conditions by assuming that the flow a distance $s_\infty$ away from the contact line along the free surface takes the form given by (3.6) and (3.7).

The Stokes equations, (4.1), can be rewritten in boundary integral form as
\[
u(x_0) = \frac{1}{2\pi} \int_B \left\{ -f(x) \log \hat{r} + \frac{\hat{x} \cdot (f \cdot \hat{x})}{\hat{r}^2} + \frac{4 (u(x) \cdot \hat{x}) (n(x) \cdot \hat{x})}{\hat{r}^4} \right\} ds(x), \tag{4.9}
\]
where $B$ is the boundary of the domain of solution, $x_0$ is a point on $B$, but not a corner point, $\hat{x} = x - x_0$ and $\hat{r} = |\hat{x}|$, [16]. This is an extremely convenient way of treating this problem, since the boundary conditions can all be written in terms of $f$ and $u$. We truncate the infinite domain using the arc of a circle, and assume that $f$ and $u$ are given there by the far field solution, (3.6) and (3.7).

We discretize the free and solid surfaces at $N$ points, using a nonuniform grid spacing in order to capture the three natural length scales of the problem ($O(K^{1/2})$, $O(1)$ and $O(K^{-1/2})$), typically with $N = 500$. On every boundary element we assume that each of $\rho_s$, $u_s$ and $f_s$ is constant. Since we know that the normal component of the fluid velocity is zero at each surface, there are four unknowns on each element. We discretize the derivatives in the boundary conditions using finite differences, and evaluate the boundary integral equation (4.9) using two point Gaussian quadrature, collocating at the midpoint of each linear element. We solve the problem in an iterative manner. Starting from an initial guess of the position of the free surface, we solve the discrete version of the boundary value problem without (4.6) and (4.7), using Newton’s method. We then obtain an updated position of the free surface by solving (4.6) using (4.7) as the initial condition. We repeat these two procedures until the position of the free surface has converged.
4.1 A Typical Solution

We begin by showing that our numerical solutions are in agreement with the asymptotic solution that we developed in the previous section. We take \( K = 10^{-4} \) and \( \lambda = 100 \), so that \( \lambda K^{1/2} = 1 \), and use \( \theta_s = 60^\circ \) as a convenient value for the static contact angle. We then take all of the other parameters to be unity: \( A = \tilde{\rho}_x = \tilde{\rho}_s = C_0 = C_{0s} = 1 \). In this, and the other numerical solutions that we present, we take \( s_{\infty} = 25K^{-1/2} \) to ensure that the solution in the outer asymptotic region has converged.

Figure 3 shows the variation of the contact angle with \( Ca \). We have plotted \( \theta_c \), the microscopic contact angle where the free surface meets the solid surface, \( \theta_{app} \), the angle that the free surface makes with the \( x \)-axis at \( s = s_{app} = 1000 \) and \( \theta_{as} \), the contact angle given by the asymptotic solution (3.30). If the slip lengthscale is approximately \( 10^{-8} \)m, as discussed above, then the angle that the free surface makes with the solid surface at \( s = s_{app} \) corresponds to the apparent contact angle measured \( 10^{-5} \)m from the contact line. We can see that the asymptotic prediction of \( \theta_c \) is almost indistinguishable from the numerical solution, and that there is a little viscous bending. Also shown is \( \theta_{cox} \), the value of the apparent contact angle predicted by the asymptotic solution derived by Cox (1986), assuming a slip length firstly \( 10^3 \) and secondly \( 10^5 \) times smaller than the lengthscale upon which the apparent contact angle is measured, with the actual contact angle given by \( \theta_c \). It is clear that the asymptotic solution with a slip length \( 10^5 \) times smaller than the lengthscale of the measurement of \( \theta_{app} \) is in good agreement with the numerical solution. This exposes a misconception in [21]. The lengthscale over which the singularity in the shear stress is relieved is the inner length scale of \( O(K^{1/2}) \ll 1 \), not the \( O(1) \) slip lengthscale. Although there is slip between the solid surface and the fluid on the slip lengthscale due to the surface tension gradient, it is only in the inner region that slip is driven by the shear stress, and the fluid velocities tend to zero. This leads Shikhmurzaev to consistently underestimate the amount of viscous bending that arises when using his theory; a point that we shall return to later.

In order to give us more confidence in our numerical solutions, we also calculated the deformation of the free surface with Shikhmurzaev’s boundary conditions replaced by no shear on the free surface and Navier slip on a dimensionless lengthscale of unity; a simpler problem, to which Cox’s analysis is also applicable. Figure 4 shows the behaviour of the apparent contact angle when the actual contact angle is fixed at \( \theta_c = 60^\circ \). We were able to calculate the position of the free surface up to \( Ca \approx 0.5 \) before the rate of convergence of our iterative procedure became unacceptably slow. There is excellent agreement between the numerical solution and Cox’s asymptotic solution, even when \( Ca \) is not very small. Note also that viscous bending is certainly not negligible for capillary numbers greater than about 0.01.

Figures 5 and 6 show the variations of the surface densities and velocities when \( Ca = 10^{-3} \). The change in the free surface density is much smaller than that in the solid surface density, as predicted by the asymptotic theory. It is also clear that the free surface density varies over a much longer lengthscale than the solid surface density, of \( O(K^{-1/2}) \approx 10^2 \), as predicted again by the asymptotic theory. Also shown is the asymptotic solution for the solid surface density. As we would expect, there is good agreement over \( O(1) \) lengthscales, but some variation on the shorter, inner lengthscale, \( s = O(K^{1/2}) \approx 10^{-2} \).
A reappraisal of a model for the motion of a contact line

The actual contact angle, $\theta_c$, apparent contact angle, $\theta_{app}$, asymptotic prediction of the actual contact angle, $\theta_{as}$, and the apparent contact angle, $\theta_{cox}$, predicted by Cox’s analysis for two different slip lengths for the typical case described in section 4.1.

The solid surface layer velocity, shown in figure 6, similarly is in good agreement over $O(1)$ length scales, but then changes significantly over the inner length scale. The free surface layer velocity clearly shows the type of behaviour predicted by the small Ca asymptotic solution. Over an $O(1)$ length scale, the velocity is almost constant at around $-3 \times 10^{-4}$, but then asymptotes to the far field velocity over the longer, outer length scale.

It has been suggested that there is a flaw in the asymptotic analysis presented in section 3, [27]. Specifically, the ansatz $\rho_{i}^s = \rho_{i}^{cs} + \mu U \dot{\rho}_{i}^s / \gamma$, is claimed not to be consistent with a formal asymptotic solution procedure, since the variable $\dot{\rho}_{i}^s$ does not appear at leading order in the mass flux boundary condition at the contact line, (3.21), and also that the length scale that characterizes the outer region is conjured up from nowhere, and has no relevance to the problem at hand. This objection to linearization about the equilibrium free surface density remains mysterious to me, and the outer length scale, $L_{i1} = \tau \gamma \rho_{i}^{cs} / \mu$, is a material parameter, which appears naturally using the scaling arguments presented in section 3.1. Moreover, the numerical results presented above show, firstly good agreement
Figure 4. The apparent contact angle measured at $s = s_{app} = 1000$, with $\theta_c = \theta_s = 60^\circ$ and Navier slip, calculated both numerically and using Cox’s asymptotic analysis.

Figure 5. The surface densities when $Ca = 0.001$ for the typical case described in section 4.1. Also shown is the asymptotic solution on the solid surface.
A reappraisal of a model for the motion of a contact line

between numerical and asymptotic solutions, and secondly, that the outer lengthscale does indeed govern the outer solution (see figure 6).

By varying the parameters in the problem, we find that the solution is most sensitive to changes in \( \lambda \), which characterizes the compressibility of the surface layers. Figure 7 shows how the actual and apparent contact angles change as \( \lambda \) decreases. We can see that these contact angles remain below 180° for a greater range of values of \( \text{Ca} \) the lower \( \lambda \) becomes, and that, for sufficiently low values of \( \lambda \), the actual, but not the apparent, contact angle starts to decrease as \( \text{Ca} \) increases. This is because the surface layer density at the liquid/vapour interface starts to increase significantly as \( \text{Ca} \) increases, which implies a reduction in surface tension there, and hence a decrease in the contact angle. These results emphasize, firstly, that the effect of viscous bending, which leads to the difference between the actual and apparent contact angles, becomes more important as \( \lambda \) decreases, and secondly, that the results start to look more like real experimental data for lower values of \( \lambda \). Indeed, we note that our earlier estimate of the size of \( \lambda \) was 2.5.

Figures 8 to 10 show the effect of varying the dimensionless parameters, \( \rho_{ex} \), \( K \) and \( \text{Ca}_0 \), with \( \lambda = 1 \) in each case. The solution is less sensitive to changes in \( A \) and \( \text{Ca}_0 \). The ratio of the equilibrium surface densities, \( \rho_{ex} \), strongly affects the behaviour of the microscopic contact angle, \( \theta_c \). For low values of \( \rho_{ex} \), \( \theta_c \) decreases rapidly, and we were unable to obtain a converged solution for relatively small values of \( \text{Ca} \). The parameter \( K \), which affects the separation of scales between inner, slip and outer regions, modifies the rate at which \( \theta_c \) changes with \( \text{Ca} \). The parameter \( \text{Ca}_0 \), which determines the strength of the flow through the contact line, also affects the behaviour of \( \theta_c \). Note that the apparent contact angle is rather insensitive to changes in any parameter other than \( \lambda \), which suggests that this particular flow is well-suited neither to the task of distinguishing between Shikhmurzaev’s theory and others, nor to extracting estimates of the physical
Figure 7. The effect of varying $\lambda$ on the microscopic and apparent contact angles. In each case, the apparent contact angle is larger than the microscopic contact angle.

Figure 8. The effect of varying $\tilde{\rho}_{es}$ on the microscopic and apparent contact angles. In each case, the apparent contact angle is larger than the microscopic contact angle.

parameters needed for Shikhmurzaev’s theory. Nonetheless, we will soldier on, and make a comparison with some experimental data.
Figure 9. The effect of varying $K$ on the microscopic and apparent contact angles. In each case, the apparent contact angle is larger than the microscopic contact angle.

Figure 10. The effect of varying $Ca_0^i$ on the microscopic and apparent contact angles. In each case, the apparent contact angle is larger than the microscopic contact angle.
Table 1. The viscosity of the 9 different glycerol/water solutions.

<table>
<thead>
<tr>
<th>Percentage of glycerol</th>
<th>95%</th>
<th>86%</th>
<th>80%</th>
<th>72%</th>
<th>68%</th>
<th>59%</th>
<th>43%</th>
<th>16%</th>
<th>0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (mPa s)</td>
<td>672</td>
<td>104</td>
<td>58</td>
<td>23</td>
<td>19</td>
<td>10</td>
<td>4.2</td>
<td>1.5</td>
<td>1</td>
</tr>
</tbody>
</table>

5 Comparison with experiment

We will now consider how our modified version of the theory compares with the experimental data presented by Blake and Shikhmurzaev, [9]. This data relates to 9 sets of experiments that measured the variation of dynamic contact angle with contact line speed for a smooth polyethyleneterephthalate (PET) tape plunging into a container that held water/glycerol solutions of various concentrations. Each of these fluids had roughly the same surface tension and static contact angle, but varied over three orders of magnitude in viscosity (see table 5). For more details on these data sets and the experimental set up, see [9]. These data sets contains many more points than those of most other investigators, for example [30], and also covers the variation of the apparent contact angle up to 180°, when air is entrained into the liquid. We should also note that when the static contact angle is sufficiently small, we were unable to obtain a converged numerical solution, which rules out, for now, several other available data sets. The problem of thin film flow using Shikhmurzaev’s theory is currently under investigation by the author.

Blake and Shikhmurzaev were able to fit Shikhmurzaev’s analysis of his theory to their experimental data, neglecting the effect of viscous bending, using a single set of parameters for all 9 fluids, with the differences in the values of Ca at which the measured contact angle reaches 180° due solely to the difference in relative viscosity between the fluid and the surrounding air.

As discussed in [9], the flow at small capillary number, less than around $1.5 \times 10^{-3}$, was unsteady, and it seems likely that some additional physics needs to be invoked at the contact line, [24]. We therefore concentrate on the data for Ca $> 1.5 \times 10^{-3}$. Figure 11 shows the measured (apparent) contact angle as a function of Ca for each of the 9 data sets, labelled by the percentage of glycerol present in the fluid. For each of these fluids, the static contact angle was close to 65°, so the data shows that the apparent contact angle varies significantly from the static value even at very low capillary numbers. The apparent contact angles lie close to each other until this angle becomes close enough to 180° that the viscosity of the air becomes significant, when there is a rapid increase in contact angle with Ca, and eventual air entrainment. The lower the viscosity of the fluid (the lower the concentration of glycerol), the smaller the value of Ca at which this occurs.

We began our analysis by fitting a curve of the convenient form

$$\theta_{app} = 180° - k_2 e^{-k_1 Ca} - (180° - \theta_s) e^{-k_3 Ca}$$

to all of the data points that were unaffected by the viscosity of the surrounding air. There is an element of subjectivity in the choice of data points that are fitted, but the resulting curve, which has $k_1 = 6.60$, $k_2 = 91.7°$ and $k_3 = 864$, and is shown in figure 11, clearly provides a reasonable fit to the data. Next, we fitted Shikhmurzaev’s theory to this curve. For any given set of the 7 dimensionless parameters, $\rho_{es}$, $A$, $s_{app}$, $\lambda$, $K$, $C_{a0}$
and $Ca_0^i$, we can generate a quick prediction of the variation of the apparent contact angle with $Ca$ using our boundary integral solver for the single fluid problem with just 25 elements on each surface. Using these quick predictions we performed a least squares fit to the synthetic curve shown in 11. The best fit occurs for $\tilde{\rho}_{es} = 3.10$, $A = 0.092$, $s_{app} = 130$, $\lambda = 0.12$, $K^{1/2} = 4.7 \times 10^{-3}$, $Ca_0 = 0^3$ and $Ca_0^i = 0.19$. We then increased the number of boundary elements to 500 and confirmed that this remains a good fit, as

3 The best fit produced a very small value of $Ca_0$, and the resulting curve was indistinguishable from that with $Ca_0 = 0$, so we take $Ca_0 = 0$ here.
shown in figure 12. Note that the value of $A$ determined by fitting is close to the value $1/12 \approx 0.083$ suggested in [18], based upon an analogy with channel flow. The value of $\lambda$ is somewhat lower than we suggested earlier, a point that we shall return to below. The value of $Ca_0$ is significantly larger than we predicted on the basis of the estimate $U_0^3 = O(h/\tau)$, which remains to be explained.

Also shown in figure 12 is the theoretical prediction of the actual contact angle, which varies rapidly for $Ca = O(\lambda K^{1/2})$, and then slowly decreases. As discussed earlier, when $Ca \ll \lambda K^{1/2}$, the behaviour at the solid surface is dominated by the diffusive relaxation of the surface density, whilst for $Ca \gg \lambda K^{1/2}$, the action of the moving solid surface determines the behaviour of the surface density. It is clear that the majority of the
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variation in apparent contact angle is provided by viscous bending, which, in contrast to the analysis of [9], cannot be neglected.

In order to study the individual data sets, we need to modify our model and numerical solution method to take into account the effect of the air outside the fluid. The modifications needed are discussed in appendix B. For each data set, we used the best fit parameters calculated above, along with the known fluid/air viscosity ratio. The results are shown in figure 13. Whilst not perfect, the trend in the value of Ca at which the surrounding air starts to affect the solution is correctly predicted. As we noted earlier, our numerical method does not cope well with thin layers of fluid, and therefore does not provide us with a solution for values of \( \theta_{\text{app}} \) close to 180°. However, the value of Ca at which the theoretical predictions end in figure 13 indicates where the air begins to have a significant effect.

Using the known values of the surface tension, viscosity and density of the fluid, along with the fact that the apparent contact angle was measured a distance \( 2 \times 10^{-5} \) m from the contact line, we can deduce the values of the physical parameters. In particular, \( \tau/\mu \approx 4.2 \times 10^{-3} \text{kg}^{-1} \text{m}^{-1} \text{s}^{-2} \), which the theory predicts to be independent of \( \mu \). This is significantly larger than the prediction made in [9], of \( 3.7 \times 10^{-6} \text{kg}^{-1} \text{m}^{-1} \text{s}^{-2} < \tau/\mu < 1.3 \times 10^{-5} \text{kg}^{-1} \text{m}^{-1} \text{s}^{-2} \). Also, \( \gamma \approx 7.8 \times 10^{4} \text{m}^{2} \text{s}^{-2} \), rather lower than the value for the bulk fluid. The lengthscales for the inner, slip and outer regions are \( 7.2 \times 10^{-10} \) m, \( 1.55 \times 10^{-7} \) m and \( 3.21 \times 10^{-5} \) m respectively.

6 Conclusions

In this paper, we have shown that the theory developed by Shikhmurzaev, [18], for the motion of a contact line along a solid surface is incomplete. Although the theory has many attractive features, a careful analysis of its application to steady Stokes flow with strong surface tension reveals that there is a one-parameter family of asymptotic solutions, and that Shikhmurzaev’s original analysis implicitly uses the requirement that there should be just two, rather than three, asymptotic regions. By considering the thermodynamics of the contact line, Bedeaux, [4], has shown that there is an additional condition that relates the flux through the contact line to the chemical potentials at the interfaces, and hence to the deviation of the surface densities from equilibrium, [4]. This leads to a linear relationship between the cosine of the contact angle and the contact line velocity when the surface layers are assumed to be almost incompressible. We find that, in order to fit the corrected theory to the experimental data of Blake and Shikmurzaev, [9], we need to assume that the surface layers are not almost incompressible, and take into account the effect of both viscous bending and the viscosity of the surrounding air. A reasonable fit is then possible.

Our results show that fitting the theoretical predictions to experimental data for Stokes flow at low capillary number is now rather less convincing than fits based on the original, flawed analysis presented by Shikhmurzaev, [18], [21]. After all, we now have seven parameters with which to fit to the data, two of which (\( \lambda \) and \( \text{Ca}_0 \)) appear to take unexpectedly small and large values, respectively. In particular, the low value of \( \lambda \), and hence the unexpectedly high compressibility of the surface layers, suggests that the assumption of a linear relationship between surface layer density and surface tension, (2.2), is
Figure 13. The best fit curves to the experimental data sets (solid lines).
probably incorrect, and that, although this cannot help but introduce extra parameters, a nonlinear relationship should be used. This also suggests that the linear relationships (2.23) and (2.24) that relate the flux of fluid through the contact line to the difference in chemical potential should also be nonlinear.

My assertion is that the claims of Shikhmurzaev are significantly weakened by this corrected analysis, but that it is hard to draw firm conclusions. One of the claims made for the theory is that it has the potential to explain some fascinating experimental results from curtain coating, which suggest that the microscopic contact angle is a function, not just of the contact line velocity, but of the whole flow field, [7], [8]. Shikhmurzaev’s theory clearly has the potential to explain this type of behaviour. However, until a simulation of curtain coating using Shikhmurzaev’s theory can be shown to be in even qualitative agreement with these observations, and can rule out inertial effects, a convincing case either for or against this new theory remains to be made.

Acknowledgements

I would like to thank Yulii Shikhmurzaev for many lively discussions, and note that he objects to all of my methods, both numerical and asymptotic, disagrees with all of my interpretations of the facts, both theoretical and experimental, and therefore discounts all of my conclusions. I am also grateful to Dick Bedeaux for providing the missing boundary condition and Terry Blake for many helpful discussions and for providing me with the experimental data discussed in section 5.

Appendix A The eigenvalue problem

Consider the eigenvalue problem given by (3.39) to (3.42). The only parameter is $\theta_c$, the angle of the wedge. We will solve this problem using Mellin integral transforms. We define the Mellin transform of $\Psi$ to be

$$\bar{\Psi}(s, \theta) = \int_0^{\infty} r^{s-1} \Psi(r, \theta) dr,$$

(A 1)
dropping the hats on $r$ for notational convenience. A coordinate expansion shows that $\Psi = O(r)$ for $r \ll 1$. Since we also have $\Psi \rightarrow 0$ as $r \rightarrow \infty$, we know that

$$\bar{\Psi}(s, \theta)$$

is analytic for $-1 \leq \text{Re}(s) < 0$, except for a simple pole at $s = -1$. (A 2)

It is straightforward to show that the Mellin transform of a solution of the biharmonic equation, (3.39), is

$$\bar{\Psi}(s, \theta) = A(s) \sin s\theta + B(s) \cos s\theta + C(s) \sin(s+2)\theta + D(s) \cos(s+2)\theta,$$

for some functions $A(s)$, $B(s)$, $C(s)$ and $D(s)$. On applying the simpler of the three boundary conditions, we find that we can write

$$\bar{\Psi}(s, \theta) = K(s)G(s, \theta),$$

(A 3)

where

$$G(s, \theta) = \left\{ \frac{(s+2) \sin s\theta - s \sin s\theta_c}{(s+2) \sin \theta_c - s \sin \theta_c} \right\} - \left\{ \frac{\cos s\theta - \cos(s+2)\theta_c}{\cos \theta_c - \cos(s+2)\theta_c} \right\}. (A 4)$$
Applying the final boundary condition shows that \( K(s) \) satisfies the functional difference equation

\[
K(s) = F(s)K(s-1),
\]
(A 5)

where,

\[
F(s) = s(s+1) \left\{ (s^2-1) \frac{\cos(s-1)\theta_c - \cos(s+1)\theta_c}{(s+1)\sin(s-1)\theta_c - (s-1)\sin(s+1)\theta_c} \right. \\
+ \left. \frac{(s-1)\sin(s-1)\theta_c - (s+1)\sin(s+1)\theta_c}{\cos(s-1)\theta_c - \cos(s+1)\theta_c} \right\}
\]
(A 6)

Before we solve (A 5), note that \( G(s, \theta) \) is bounded for \(-1 \leq \text{Re}(s) \leq 0\), and nonzero at \( s = -1 \), so that, using (A 2),

\[
K(s) \text{ is analytic for } -1 \leq \text{Re}(s) < 0, \text{ except for a simple pole at } s = -1.
\]
(A 7)

Let’s begin by considering what happens in a slender wedge, for which \( \theta_c \ll 1 \). In this case, we find that

\[
G(s, \theta) \sim \theta_c^2 \theta_c^4 \left( 1 - \frac{\theta}{\theta_c} \right), \quad F(s) \sim \frac{1}{4} s(s+1)\theta_c.
\]

For \( \theta_c \ll 1 \), the solution of (A 5) that satisfies (A 7) and decays rapidly enough as \( s \to \pm\infty \) that the inverse Mellin transform exists is therefore

\[
\Psi(s, \theta) = k_0 \left( \frac{1}{\theta_c} \right)^s \Gamma(s+1)\Gamma(s+2)\theta_c^2 (\theta_c - \theta),
\]

for some arbitrary constant \( k_0 \). Note that this function has a simple pole at \( s = -1 \), double poles at \( s = -2, -3, \ldots \), and is analytic for \( \text{Re}(s) > -1 \). This is consistent with the coordinate expansion (3.43), and also shows that \( \Psi \) decays to zero exponentially fast as \( r \to \infty \). Moreover, this is the Mellin transform of a known function, with the correct behaviour for large and small \( r \), namely

\[
\Psi = \Psi_0 \theta_c^2 (\theta_c - \theta) r^{3/2} K_1 \left( 4 \sqrt{\frac{r}{\theta_c}} \right),
\]
(A 8)

for some arbitrary constant \( \Psi_0 \). We can verify that this is the correct solution by noting that, for \( \theta_c \ll 1 \), the biharmonic equation becomes, at leading order, \( \partial^4 \Psi / \partial \theta^4 = 0 \). Therefore,

\[
\Psi(r, \theta) \sim \theta_c^2 (\theta_c - \theta) f(r),
\]

and the second of the boundary conditions (3.41) gives

\[
\frac{d^2}{dr^2} \left( \frac{1}{r^2} f \right) - \frac{4}{r^2} f = 0.
\]

This equation does, as expected, have as its bounded solution (A 8).

In order to solve (A 5) for general \( \theta_c \), we use a method described in the appendix to
A reappraisal of a model for the motion of a contact line [1], based on treating (A 5) as a Riemann-Hilbert problem. Firstly, we need to note that

\[ F(s) = \pm \frac{1}{2} i(s + 1) \left\{ 1 + O(|s|^{-2}) \right\} \quad \text{as} \quad s \to \pm i\infty. \]

We now seek to solve the two separate functional difference equations,

\[ \hat{K}(s) = \frac{1}{2} (s + 1) \tan \pi s \hat{K}(s - 1), \quad (A 9) \]

and

\[ \bar{K}(s) = \bar{F}(s) \bar{K}(s - 1), \quad (A 10) \]

where

\[ \bar{F}(s) = \frac{2}{(s + 1) \tan \pi s} F(s). \]

The point of this is that \( \hat{K}(s) \bar{K}(s) \) is a solution of (A 5), and that \( \bar{F}(s) \) has been defined so that

\[ \bar{F}(s) = 1 + O(|s|^{-2}) \quad \text{as} \quad s \to \pm i\infty, \]

which will be crucial later.

By inspection, a solution of (A 9) is

\[ \hat{K}(s) = 2^{-4} \Gamma(s + 2) \frac{G\left(\frac{3}{2} - s, 1\right) G\left(\frac{3}{2} + s, 1\right)}{G\left(2 - s, 1\right) G\left(1 + s, 1\right)}, \quad (A 11) \]

where \( G(z, \delta) \) is the Barnes double gamma function, [2], which gives a convenient representation of the solution of functional difference equations that involve products of trigonometric functions, [13]. The Barnes double gamma function is defined to be the solution of the functional difference equation

\[ G(z + 1, \delta) = \Gamma(z/\delta) G(z, \delta), \]

subject to the normalization condition, \( G(1, \delta) = 1 \). An integral representation for the Barnes double gamma function that allows it to be computed in a straightforward manner is given in [13], and asymptotic expansions in various limits are derived in [6]. Now, since \( G(z, 1) \) has zeros at \( z = 0, -1, -2, \ldots \) and no poles, \( \hat{K}(s) \) is analytic for \( -1 \leq \text{Re}(s) < 0 \), except for a simple pole at \( s = -1 \).

Using the method described in [1], the unique solution of (A 10) that has \( \hat{K}(s) \to 1 \) as \( |s| \to \infty \) is

\[ \hat{K}(s) = \exp \left\{ \frac{1}{2i} \int_{-\infty}^{\infty} \cot \pi (t - s) \log \bar{F}(t) \, dt \right\}, \quad (A 12) \]

for \(-1 \leq \text{Re}(s) < 0\). After analysing the behaviour of the gamma functions and Barnes double gamma functions for \( s \) large and imaginary, we find that the solution of the original functional difference equation, (A 5), that is analytic for \(-1 \leq \text{Re}(s) < 0\), except for a simple pole at \( s = -1 \), and decays rapidly enough as \( s \to \pm i\infty \) that the Mellin inversion integral converges, is

\[ K(s) = k_0 2^{-4} \Gamma(s + 2) \frac{G\left(\frac{3}{2} - s, 1\right) G\left(\frac{3}{2} + s, 1\right)}{G\left(2 - s, 1\right) G\left(1 + s, 1\right)}. \]
We now need to determine the pole structure of the solution to which this corresponds outside the strip $-1 \leq \text{Re}(s) < 0$ in order to find out how $\Psi$ behaves for large and small $r$. Now that we know $K(s)$ in this strip, we can simply use the original functional difference equation, (A 5), to determine $K(s)$ elsewhere. It is clear that the location of the poles and zeros of $F(s)$ will be crucial.

A zero of $F(s)$ at $s = s_0$ with $\text{Re}(s_0) < 0$ corresponds to poles of $K(s)$ at $s = s_0 - n$, $n = 1, 2, \ldots$. It is clear from the definition, (A 6), of $F(s)$ that it has zeros at $s = 0$ and $s = -1$. The zero at $s = 0$ has already been taken into account (in effect it generates the simple pole at $s = -1$), but the zero at $s = -1$ leads to double poles at $s = -2, -3, \ldots$, ignoring the effect of any other possible zeros for the moment. This will generate a coordinate expansion of the form (3.43), as required. If $F(s)$ has a zero with $-1 < \text{Re}(s) < 0$, the coordinate expansion (3.43) will not be valid, and the asymptotic structure that we have constructed will not work. Although we have not been able to prove this, a numerical investigation of $F(s)$ indicates that no such zero exists.

A pole of $F(s)$ at $s = s_1$ with $\text{Re}(s_1) > 0$ corresponds to poles of $K(s)$ at $s = s_1 + m$, $m = 0, 1, 2, \ldots$. Therefore, we can investigate how $\Psi$ behaves as $r \to \infty$ by determining the pole of $F(s)$ with smallest real part in $\text{Re}(s) > 0$. Starting with the real axis, figures A 1 and A 2 show that $F(s)$ has poles (zeros of $1/F(s)$ in the figures) that approach the origin as $\theta_c$ increases. This shows that, although at leading order the decay of $\Psi$ as $r \to \infty$ is exponential when $\theta_c \ll 1$, in general this decay is algebraic with the rate of decay decreasing as $\theta_c$ increases, at least for $0 \leq \theta_c \leq \pi/2$. Further numerical
investigation of $|F(s)|$ suggests that, although there may be off-axis poles, they do not greatly affect the rate of decay as $r \to \infty$.

In conclusion, although we have not investigated what the eigensolutions look like (this would involve evaluating numerically a double integral, one in (A 13), and one in the Mellin inversion formula, for each value of $r$ and $\theta$, which is a very tough proposition), we have shown that they exist by constructing an explicit formula for them. The key point is that (A 13) gives the correct pole structure and decays rapidly enough as $s \to \pm \infty$ that the Mellin inversion integral exists.

Appendix B The two fluid problem

The analysis of a fluid/fluid contact line presented in [21] is based on the assumption that the interface between two fluids can be modelled using two surface layers, with densities $\rho_{sk}$ and velocities $v_{sk}^i$, where $k = 1,2$ for the two fluids. After eliminating these surface layer velocities, as we did in the main part of the paper, we arrive at the steady surface layer equations

$$\alpha_k \gamma_k \frac{d}{ds_i} \left( \rho_{sk}^i \frac{d\rho_{sk}^i}{ds_i} \right) - \frac{1}{2} \frac{d}{ds_i} \left( \rho_{sk}^i \left( u_{sk}^i + U^i \right) \right) - \frac{\rho_{sk}^i - \rho_{esk}^i}{\tau_k} = 0, \quad (B 1)$$

$$\beta_k \left( u_{sk}^i - U^i \right) = f_{1k}^i \cdot t^i - \frac{1}{2} \gamma_k \frac{d\rho_{sk}^i}{ds_i}, \quad (B 2)$$

in each layer, coupled by the stress continuity conditions

$$f_{1i}^i \cdot t^i + f_{2i}^i \cdot t^i = \gamma_1 \frac{d\rho_{1k}^i}{ds_i} + \gamma_2 \frac{d\rho_{2k}^i}{ds_i}, \quad (B 3)$$
\[ f_i^1 \cdot n_1 + f_i^2 \cdot n_2 = \left\{ \gamma_1 (\rho_{s1}^i - \rho_{01}^i) + \gamma_2 (\rho_{s2}^i - \rho_{02}^i) \right\} \kappa, \]

where \( U^i \) is the velocity at the interface between the two layers and \( t^i \) is the tangent to the interface. We can use (B 2) to eliminate \( U^i \) from (B 1), which gives two nonlinear diffusion equations for \( \rho_{sk}^i \). Boundary conditions at infinity and at the contact line analogous to (2.21), (2.22) and (2.24), along with surface layer equations on the solid surface in each fluid then close the system.

Note that in [21] it is postulated without justification that conservation of angular momentum at the interface between the fluids leads to

\[ \gamma_1 d\rho_{s1}^i ds_i = \gamma_2 d\rho_{s2}^i ds_i. \]

This equation is incorrect, and not needed. Conservation of angular momentum is expressed through the symmetry of the stress tensor in the fluid layers (although this does not appear explicitly), and not through (B 5). Moreover, it is clear that, if (B 5) holds, the surface layer densities are linearly related through \( \gamma_1 (\rho_{s1}^i - \rho_{es1}^i) = \gamma_2 (\rho_{s2}^i - \rho_{es2}^i) \). There is then no way to satisfy the two independent nonlinear diffusion equations that govern \( \rho_{sk}^i \). This is not immediately obvious in [21] since the equilibrium solution \( \rho_{sk}^i = \rho_{esk}^i \) is used throughout the analysis.

We can recover the equations for a liquid/air system by neglecting all of the surface layer densities in fluid 2 relative to those in fluid 1, and the interfacial stresses in fluid 2 relative to those in fluid 1 \( (\mu_2 \ll \mu_1) \). However, when the air forms a sufficiently thin layer, the interfacial shear stress due to the flow in the air will not be negligible, and we retain this. As we might expect, (2.14) becomes, retaining the subscripts on fluid 2 quantities only,

\[ f^i \cdot t^i + f_2^i \cdot t^i = \gamma d\rho_{s}^i, \]

whilst the diffusion equation (2.13) becomes

\[ \frac{\gamma \alpha}{4A} \frac{d}{ds_i} \left( \rho_{s}^i d\rho_{s}^i ds_i \right) - \frac{d}{ds_i} \left\{ \rho_{s}^i \left( u_{s}^i + \frac{1}{2\beta} f_2^i \cdot t^i \right) \right\} - \frac{\rho_{s}^i - \rho_{es}^i}{\tau} = 0, \]

which now contains the shear stress due to the air, \( f_2^i \cdot t^i \).

At the interface, the tangential velocity of the air is coupled to that in the fluid through the slip relation

\[ u_{s2}^i = u_{s}^i + \frac{1}{\beta_2} f_2^i \cdot t^i - \frac{1}{\beta} f^i \cdot t^i + \frac{\gamma}{2\beta} \frac{d\rho_{s}^i}{ds_i}, \]

On the solid surface in contact with the air, we have the Navier slip condition

\[ u_{s2} = U - \frac{1}{\beta_2} f_2 \cdot t. \]

We modified our numerical solution method to include the boundary integral solution for Stokes flow in the air, coupled to the flow in the fluid through (B 6), (B 8) and (B 9), taking \( \beta_2 = \mu_2 \beta / \mu h_2 \). Here, \( h_2 \) is the ratio of the mean free path in air, which we took to be \( 3 \times 10^{-7} \) m, and the inner lengthscale, \( K^{1/2}L \). For the best fit discussed in the text, \( h_2 \approx 400 \).
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References


