Shear Flow Over A Chemically Patterned Surface

James E. Sprittles (321948)

April 2005
I warrant that the content of this dissertation is the direct result of my own work and that any use in it of published or unpublished material is fully and correctly referenced.

Signed..........................................

Date...........................................
CONTENTS

1. Introduction ................................................................. 1
   1.1 The contact line and contact angle ................................. 1
   1.2 Wettability ........................................................... 2
   1.3 Flow over patterned surfaces ....................................... 4
      1.3.1 Patterning of surfaces ........................................ 4
      1.3.2 Observations ................................................... 5
      1.3.3 Applications .................................................. 6
   1.4 Investigation summary ............................................... 6

2. Theory .............................................................................. 8
   2.1 Modelling approaches ................................................ 8
   2.2 The interface formation/disappearance model .................... 8

3. Problem formulation ........................................................ 11
   3.1 Bulk equations ....................................................... 11
   3.2 Boundary conditions ................................................ 12
      3.2.1 Interpretation of equations ................................... 13
   3.3 Contact line conditions ............................................... 15
      3.3.1 Continuity of flux ............................................... 15
      3.3.2 Force balance ................................................... 15
   3.4 Problem outline ....................................................... 16
   3.5 Non-dimensionalisation and simplification ....................... 16
      3.5.1 Bulk equations .................................................. 17
      3.5.2 Boundary conditions .......................................... 18
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5.3</td>
<td>Contact line conditions</td>
<td>18</td>
</tr>
<tr>
<td>3.6</td>
<td>Problem specification</td>
<td>19</td>
</tr>
<tr>
<td>4.</td>
<td>Near-field asymptotics</td>
<td>20</td>
</tr>
<tr>
<td>4.1</td>
<td>The stream function</td>
<td>20</td>
</tr>
<tr>
<td>4.2</td>
<td>Boundary conditions</td>
<td>21</td>
</tr>
<tr>
<td>4.3</td>
<td>Expansion of variables</td>
<td>22</td>
</tr>
<tr>
<td>4.4</td>
<td>Form of the stream function</td>
<td>22</td>
</tr>
<tr>
<td>4.5</td>
<td>First order analysis</td>
<td>23</td>
</tr>
<tr>
<td>4.6</td>
<td>Second order analysis</td>
<td>24</td>
</tr>
<tr>
<td>4.7</td>
<td>Qualitative analysis</td>
<td>27</td>
</tr>
<tr>
<td>4.8</td>
<td>Pressure</td>
<td>31</td>
</tr>
<tr>
<td>5.</td>
<td>Parametric asymptotics</td>
<td>33</td>
</tr>
<tr>
<td>5.1</td>
<td>Estimating parameter size</td>
<td>33</td>
</tr>
<tr>
<td>5.1.1</td>
<td>Use of Couette-Poiseuille analogy</td>
<td>34</td>
</tr>
<tr>
<td>5.2</td>
<td>Asymptotics</td>
<td>35</td>
</tr>
<tr>
<td>5.3</td>
<td>Zeroth order</td>
<td>36</td>
</tr>
<tr>
<td>5.4</td>
<td>First order</td>
<td>37</td>
</tr>
<tr>
<td>5.5</td>
<td>Inner region</td>
<td>38</td>
</tr>
<tr>
<td>5.6</td>
<td>Summary</td>
<td>39</td>
</tr>
<tr>
<td>6.</td>
<td>Numerics</td>
<td>40</td>
</tr>
<tr>
<td>6.1</td>
<td>Finite difference schemes</td>
<td>40</td>
</tr>
<tr>
<td>6.2</td>
<td>Evaluation at boundaries</td>
<td>42</td>
</tr>
<tr>
<td>6.3</td>
<td>The checkerboard effect</td>
<td>42</td>
</tr>
<tr>
<td>6.4</td>
<td>Matrix inversion</td>
<td>43</td>
</tr>
<tr>
<td>6.5</td>
<td>The programming procedure</td>
<td>44</td>
</tr>
<tr>
<td>6.6</td>
<td>Further work</td>
<td>47</td>
</tr>
<tr>
<td>6.6.1</td>
<td>Use of staggered grids</td>
<td>47</td>
</tr>
<tr>
<td>Contents</td>
<td>iii</td>
<td></td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>6.6.2 Mesh generation</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>7. Future work</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>Appendix</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>A. Couette-Poiseuille analogy</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td>B. The programme</td>
<td>55</td>
<td></td>
</tr>
</tbody>
</table>
1. INTRODUCTION

The flow of thin films over chemically patterned surfaces is an exciting new fluid mechanical area with applications in the fabrication of microreactor arrays, thin-film electronic technology and microfluidic devices (Darhuber & Troian 2005; Xia, Qin & Yin, 2001; Whitesides et al. 1996; Topics in Current Chemistry Vol. 194). In all these processes a certain flow of liquid is promoted due to the deliberate patterning of the surface. To describe such regimes both qualitatively and quantitatively is the target of much research at present, with contributions from all areas of science and engineering.

1.1 The contact line and contact angle

The type of processes mentioned above are often associated with the phenomena of dynamic wetting; the spreading of a liquid over a solid substrate. Often a region occurs where three substances intersect at a point, creating a region where molecules are subject to forces from three bulk phases. Macroscopically this region is known as the contact line, the dynamics of which are important to describing the flow. In dynamic wetting this line exists between two immiscible fluids and a solid (e.g. the spreading of a liquid drop) but it could equally well occur between two solids and one liquid (as we consider in our investigation). In the former case, the angle formed between the spreading fluid and solid is known as the contact angle and has been measured in numerous experimental studies (e.g. Gutoff & Kendrick 1982, Blake et al. 1999; Lam et al. 2002). There has been widespread interest in the area of dynamical wetting due to the failure of classical fluid mechanics to satisfactorily describe the flow in a fluid/fluid/solid system, which is the so called ‘moving contact-line problem’ (Dussan & Davis 1974).

The classical model for viscous fluids assumes that the Navier-Stokes equations describe the dynamics of the bulk, while at solid boundaries a no-slip condition is assumed. The no-slip
boundary condition has become favoured by scientists due to its ability to describe flows accurately when coupled with the Navier-Stokes equations (Batchelor 1967, p. 149). Its ease to implement during mathematical analysis is an added advantage.

The ‘moving contact-line problem’ results from imposing a no-slip condition on the solid surface combined with the capillarity equation, zero tangential stress and normal kinematic condition on the free surface (see Dussan & Davis 1974). One finds that in the general case there is no solution in the neighbourhood of the contact line; the curvature of the free surface in the vicinity of the contact line is such, that the liquid does not actually meet the solid. This suggests that prescribing the free surface shape (so that the interface is forced to meet the solid boundary) is a sensible simplification but this leads to un-physical singularities in the shear stress at the contact line (see Dussan 1979). Various models have been proposed to overcome these flaws, often a combination of (a) prescribing the contact angle as a function of the contact line speed and (b) using a boundary condition that allows slip (for a review see Dussan 1979; Shikhmurzaev 1997, §10).

1.2 Wettability

When modelling the flow of a liquid over a patterned surface we search for a concept that defines the properties of different liquid/solid systems and enables us to determine how a change in solid will effect the solution. We consider ‘wettability’ which we define for a certain liquid/gas/solid or liquid/liquid/solid combination by measurement of the equilibrium contact angle when partial wetting occurs (otherwise the liquid spreads completely, known as perfect wetting).

A surface is said to be more wettable the smaller the contact angle as this represents more of the surface being covered in liquid (see Fig. 1.1). The question of why the equilibrium contact angle is a good choice of how to define a certain liquid/solid system still remains and to address this we must consider the mechanism that causes flows for various liquid/solid systems to behave in different ways. The dominant mechanism appears to be the surface tension, the phenomena caused in this case by bulk mass in the fluid being attracted to the dense solid phase leading to a compressed mass near the interface. This is the same phenomena that determines the equilibrium contact angle, which can be calculated via the use of Young’s momentum balance.
equation and hence this angle seems to be a fair measure of a liquid/solid systems properties (i.e. its wettability). Young’s equation gives that at the contact line

\[ \sigma_{lg} \cos \theta_e = \sigma_{sg} - \sigma_{ls}, \]  

(1.1)

where \( \sigma_{lg}, \sigma_{sg} \) and \( \sigma_{ls} \) represent the surface tensions in the liquid/gas, solid/gas and liquid/solid interfaces and \( \theta_e \) is the equilibrium contact angle.

**Fig. 1.1:** The contact angle is determined by balancing the liquid/gas (lg), liquid/solid (ls) and solid/gas (sg) surface tensions at the contact line using Young’s equation (1.1). Solid A has comparatively high wettability (small contact angle) while solid B is a surface of comparatively low wettability (large contact angle).

Typical values of the static equilibrium contact angle are shown in Table 1.2 for various liquid/gas/solid and liquid/liquid/solid combinations (Gutoff & Kendrick 1982). This experiment was conducted with a gelatin coated polyester tape immersed in the liquid/liquid or liquid/gas of choice using what is known as the ‘tilting plate technique’. The whole experiment was conducted at room temperature.

<table>
<thead>
<tr>
<th>Upper fluid/gas</th>
<th>Lower fluid</th>
<th>Solid</th>
<th>Equilibrium contact angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>Water</td>
<td>Gelatin coated polyester</td>
<td>32</td>
</tr>
<tr>
<td>Air</td>
<td>Mineral oil</td>
<td>Gelatin coated polyester</td>
<td>53</td>
</tr>
<tr>
<td>Air</td>
<td>Castor oil</td>
<td>Gelatin coated polyester</td>
<td>65</td>
</tr>
<tr>
<td>Mineral oil</td>
<td>Water</td>
<td>Gelatin coated polyester</td>
<td>68</td>
</tr>
<tr>
<td>Castor oil</td>
<td>Water</td>
<td>Gelatin coated polyester</td>
<td>74</td>
</tr>
</tbody>
</table>


1. Introduction

1.3 Flow over patterned surfaces

Chemically patterned surfaces have areas of comparatively high (hydrophillic) and low (hydrophobic) wettability and experiments (Meyer & Braun 2000; Chaudhury & Whitesides 1992) observe that the flow of a liquid over such a surface has, in general, a different behaviour to that of a flow over a homogenous substrate. Understanding the behaviour of these flows is of great interest from a theoretical point of view (Lenz, 1999; Thiele, 2003), which is motivated by the fact they hold the key to many new technologies (Xia, Qin & Yin, 2001).

1.3.1 Patterning of surfaces

One of the reasons why the study of flows on patterned surfaces has become an area of widespread interest recently is due to new techniques that enable the patterning of surfaces, to a high degree of accuracy from the milimetre to nanometre scale, at a reasonable cost (Xia, Rogers et al. 1999; Whitesides et al. 1996). In particular the incorporation of self-assembled monolayers (SAMs) into various patterning techniques has enabled the creation of surfaces with regions of controlled wettability. Below a brief description of some of the main patterning techniques is given.

Dip pen nanolithography (DPN) In this technique an atomic force microscope (AFM) acts as a nib and is applied to a solid substrate (often gold). Molecules with an affinity for the solid act as ink and are transported to the substrate via capillary transport (see Fig. 1.2) forming SAMs. Using this method patterns can be ‘written’ in submicrometre length scales as small as 5nm. This technique is often used to pattern master copies for microcontact printing.

Microcontact Printing An elastomeric stamp is ‘wetted’ with a molecular ink and brought into contact with a surface for a few seconds leading to the formation of SAMs on the surface. These SAMs help protect the surface against erosion so that an etching process can remove other parts of the surface. This method allows an entire pattern to be deposited in one step, an advantage over DPN when selective placing of sites is not important. At present the smallest features to be patterned using this technique are parallel lines of width $\sim 35\text{nm}$.
Photolithography In this method the surface of a solid is first coated with a thin layer of photosensitive polymer. When the surface is then exposed to ultraviolet light through a photomask a pattern is formed on the polymer. This image can then be developed into relief structures using a wet etching process. The pattern can then be further transferred to the underlying solid using another etching process. The depth of the relief structures can be precisely controlled by varying the etching time. This introduces another parameter, the depth, which can also be used to control the flow of liquids over a patterned surface. Features as small as 250nm have been created using this technique but are extremely expensive to routinely produce.

1.3.2 Observations

In both wetting and dewetting experiments (Cubaud & Fermigier 2003) it is observed that parts of a patterned surface are able to ‘pin’ the leading/receding edge (see Fig. 1.3), a behaviour not associated with wetting of homogenous substrates. It is also observed that for dewetting of a thin film over a patterned surface, the heterogeneity of the substrate may cause the film to rupture and break into smaller droplets (Troian et al. 2000), advantageous to some processes (for example in the creation of a liquid array) while disadvantageous when the aim is to maintain a uniform film (for example in coating processes). Understanding the dynamics of such flows.
would allow for optimisation of the process involved and is of great interest to industry.

![Large sessile drop on model heterogenous substrate. Courtesy of T.Cubaud and M.Fermigier (2003)](image)

1.3.3 Applications

Products that are manufactured using the phenomena of flow over a patterned surface often use dewetting techniques to create the desired structure. This is when a surface is wetted, often by dip-coating (Braun & Meyer 1999) and the wettable regions of the substrate act as a template, for the liquid to be retained during dewetting. Alternatively microdroplets may be dispersed onto the more wettable regions via condensation, with these droplets then acting as a template for a film, deposited using a dip-coating process (see Fig. 1.4). These techniques have been used in the manufacture of two-dimensional arrays of microlenses (Whitesides et al. 1995) and for optical waveguides (Whitesides et al. 1996).

An alternative way to deposit the liquid onto the substrate is by droplet release (Basaran 2002), in a process similar to inkjet printing. This process has been used to directly print transistors (Sirringhaus et al. 2000) and offers an alternative approach where the original location of wetting can be more controlled. In both processes it is observed that the final wetted area can be manipulated to varying degrees by changing the surface properties.

1.4 Investigation summary

We would like to investigate how a change in surface properties affects the flow of a liquid above and leads to the various phenomena described. To do so we consider the behaviour of a shear
1. Introduction

Fig. 1.4: An array of water microdroplets in polystyrene film, formed on hydrophillic surface areas via a process of preferential condensation. These drops acted as a template during film formation of polymers which occurred as the result of dip-coating. In this instance some droplets have coalesced due to the small distance between hydrophillic regions, which has lead to the film structure shown. Courtesy of Braun & Meyer (1999)

...
2. THEORY

As discussed, experiments show that a change in wettability of a surface does indeed alter the flow of a liquid above. We will investigate whether the model we are going to use reflects this fact in a realistic manner. Our approach will be to consider the dynamics of the fluid so that the properties of the solid manifest themselves through the choice of boundary conditions for the solid/liquid interface. Clearly a no-slip condition will not be sufficient as it contains no information about the nature of the solid involved, only that the velocity of the fluid adjacent to it will be zero. We will investigate how the dynamics of this interface can be described in order to provide boundary conditions for our flow.

2.1 Modelling approaches

The two main methods for modelling fluid mechanical flows can be broadly split into the macroscopic or molecular approach. This applies to research into the flow of a liquid over a heterogeneous solid, where given the small length scales involved, a lot of work is done using the latter approach. Molecular modelling involves considering the dynamics of discrete particles connected via an interaction potential (Barrat & Bocquet 1999; Voué & De Connick 2001) whereas in the macroscopic (or continuum) approach we consider the fluid as a continuous medium which satisfies certain conservation laws (e.g. mass, momentum and energy).

2.2 The interface formation/disappearance model

The model we shall use for our investigation was proposed by Shikhmurzaev (1993) to provide a mathematical tool to address the process of interface formation/disappearance and use this to describe a number of flows where the classical formulation leads to unsatisfactory conclusions. Its first achievement was to find a self-consistent model that could be applied to moving
contact lines in liquid/gas/solid systems (Shikhmurzaev 1993). Since then it has been applied to liquid/liquid/solid systems (Shikhmurzaev 1997), the spreading of drops on solid surfaces (Shikhmurzaev 1997) and the coalescence and breakup of drops (Shikhmurzaev 2000). Until now this model has not been applied to the solid/solid/liquid system we consider and so the results of this investigation will be new.

The notion of an interface is used in continuum mechanics to describe a mathematical surface that separates two bulk phases. In the problem we are considering it occurs between the fluid and solids involved. This interface may have certain properties, most notably a surface tension, that are caused by the asymmetry of forces acting on it from the two bulks. In actual fact the interface is a three dimensional object and its properties correspond to the action of microscopic processes in the layer, however in the continuum approximation this layer becomes negligibly thin as molecular length scales $\ell$ are neglected in comparison with macroscopic length scales $L$ (we take the limit $\ell/L \to 0$). The surface properties survive as they are much stronger than the hydrodynamic forces considered in the bulk and hence have an effect even when the interface’s thickness becomes negligible. This means that the dynamics of the interface must be taken into account when attempting to model the flow of fluids, as often they can significantly affect the bulk dynamics via capillary effects. Having said this clearly there are cases where no such analysis is necessary and a no-slip condition will suffice. As we shall see the interface formation/disappearance model can reflect this fact.

The interface formation/disappearance model is based on the theory of non-equilibrium thermodynamics (see de Groot & Mazur 1984) whereby equations relating the flux of mass, momentum and energy between the bulk and interface are considered. The interface has certain macroscopic properties that are defined per unit area and represent the microscopic processes taking place across the interface. As they are confined to a surface they have normal derivative zero. The result of this consideration is boundary conditions for the bulk flow.

Attempts to model the dynamics of interfaces is by no means a new concept, much previous research in this field has been carried out, including work by famous scientists such as Gibbs (1928) who attempted to model what he describes as “a surface of discontinuity\(^1\)” between

\(^1\) On p. 219.
two phases in equilibrium. More recently Bedeaux, Albano and Mazur (BAM) (1976) used the non-equilibrium thermodynamics approach to derive boundary conditions for a fluid/fluid interface. The approach used by Shikhmurzaev (1993) is similar to that of BAM (1976) except Shikhmurzaev’s formulation leads to a set of equations that are closed and are fully applicable to fluid mechanical problems and hence to experimental verification.
3. PROBLEM FORMULATION

We consider the flow of a liquid over two solids, without loss of generality in the direction from solid 1 towards solid 2, see Fig. 3.1. We investigate how the change in wettability of the surface affects the dynamics of the bulk flow.

\[ \nabla \cdot \mathbf{u} = 0, \quad (3.1) \]

\[ \rho (\mathbf{u} \cdot \nabla \mathbf{u}) = \rho \mathbf{F} + \nabla \cdot \mathbf{P}, \quad (3.2) \]

where...

Fig. 3.1: Sketch of the problem

3.1 Bulk equations

We now study the equations that will allow us to model the problem of a shear flow passing over two different solids, joined at a contact line, that we wish to investigate. We consider the solid to be stationary and assume that the bulk of the flow can be adequately described by the Navier-Stokes equations, so that if we have a steady flow and incompressible fluid then the conservation of mass and the Navier-Stokes equations are...
\( P = -pI + \mu [\nabla u + (\nabla u)^*] \)  

and \( u, F, P, p, \rho, \mu \) are the (dimensional) bulk velocity, body force, stress tensor, pressure, density, coefficient of viscosity and \( I \) is the metric tensor.

Equations (3.1)–(3.3) require boundary conditions to specify the particular solution we are looking for.

### 3.2 Boundary conditions

As our problem is elliptic we specify velocities on all boundaries. In the far field we assume that the presence of the contact line has no affect and hence we retain our shear flow

\[
    u \to Ky \quad \text{and} \quad v \to 0 \quad \text{as} \quad x^2 + y^2 \to \infty
\]

where \( K \) is the shear and we have considered Cartesian components of velocity \( (u,v) \).

As discussed above the classical boundary conditions at a liquid/solid interface for a viscous flow is the no-slip condition. However the no-slip condition is unable to explain how a change of solid may affect the flow, so we turn to the interface formation/disappearance model to provide our boundary equations. The derivation of these equations is not included but can be found in Shikhmurzaev (1993). They are listed as follows

\[
    v_i \cdot n_i = 0, \quad (3.5)
\]

\[
    \mu n_i \cdot [\nabla u + (\nabla u)^*] \cdot (I - n_i n_i) + \frac{1}{2} \nabla \sigma_i = \beta u_{\parallel}, \quad (3.6)
\]

\[
    \rho u \cdot n_i = \frac{\rho^s_i - \rho^e_i}{\tau}, \quad (3.7)
\]

\[
    \nabla \cdot (\rho^i v^s_i) = -\frac{\rho^s_i - \rho^e_i}{\tau}, \quad (3.8)
\]

\[
    (v^s_i)_{\parallel} = \frac{1}{2} u_{\parallel} + \alpha \nabla \sigma_i, \quad (3.9)
\]

\[
    \sigma_i = \gamma (\rho^s_i(0) - \rho^s_i), \quad (3.10)
\]

Where \( \rho^s \) is the surface density, \( \sigma \) is the surface tension, \( v^s \) is the interface velocity, a double line subscript indicates we are considering the tangential component of the vector and the subscript
3. Problem formulation

$i = 1, 2$ represents which solid/liquid interface we are considering. The normal to the surface is given by the vector $\mathbf{n}$ and the tensor $(\mathbf{I} - \mathbf{nn})$ extracts tangential components of vectors.

### 3.2.1 Interpretation of equations

All constants involved in equations (3.5)-(3.10) refer to properties of the liquid (and hence have the same value throughout the interface) apart from $\rho_{se}^e$, which is related to the equilibrium surface tension ($\sigma_e \equiv \sigma (\rho_{se}^e)$) via the equation of state (3.10). By considering Young’s equation (1.1) again we can see that higher values of surface tension on the liquid/solid interface $\sigma_{ls}$ lead to higher values of equilibrium contact angle $\theta_e$ and hence lower wettability (as less surface will be ‘wet’). So we find that the equilibrium surface density is indeed the key when considering the wettability of a surface and we expect the two surfaces to have differing values of $\rho_{se}^e$, dependent on the properties of the surface. So we define

$$
\rho_{se}^e = \begin{cases} 
\rho_{1e}, & \text{on solid 1;} \\
\rho_{2e}, & \text{on solid 2.}
\end{cases}
$$

(3.11)

We expect the surface tension to be negative for most liquid/solid systems as the surface density at the interface will be increased due to the presence of the solid ($\rho_{1e}^s > \rho_{se}^s (0)$, $\rho_{2e}^s > \rho_{se}^s (0)$). This situation corresponds to the contact angle formed by a liquid/gas interface with a solid surface being less than $90^\circ$, however without loss of generality the analysis below applies to the positive equilibrium surface tensions as well.

The other constants present have the following relevance; $\alpha$ is the coefficient of proportionality between the surface tension gradient and interface velocity, $\rho_{e}^s (0)$ is the surface density corresponding to zero surface tension, $\tau$ is a relaxation time, $\gamma$ describes the compressibility of the interface and the coefficient of sliding friction is $\beta$.

The Navier slip condition has often been used in contact line problems to overcome paradoxes associated with the classical formulation (Dussan 1976; Hocking 1977), the basic assumption being that the velocity on the surface is proportional to the tangential stress

$$
\beta u = \mu \frac{\partial u}{\partial n}
$$

(3.12)
where \( n \) is normal to the surface, \( \beta \) is a constant and \( \mu / \beta \) forms a length scale which is zero for no-slip.

Equation (3.6) is the generalised Navier condition, derived in a self consistent manner. We find that \emph{apparent} slip on the surface can be caused by shear stress from the bulk as well as surface tension gradients in the interfacial layer. This allows for the so called Marangoni effect where surface tension gradients, caused by surface inhomogeneity, thermal gradients or other mechanisms can lead to motion. Chaudhury & Whitesides (1992) observed that by creating a surface tension gradient with a drop of liquid, the drop was capable of spontaneously moving uphill.

It is important to note that there is no \emph{actual} slip on the solid surface but that there is a (surface) velocity gradient across the layer, see Fig. 3.2. It must be emphasised that under the continuum approximation the layer that is shown as having finite thickness will become a mathematical surface of zero thickness.

![Fig. 3.2: Sketch of the flow for a Couette type regime with the velocity distribution across the layer manifesting itself in a slip boundary condition. The layer is shown as being finite in thickness but will become infinitesimally thin in the continuum approximation](image)

Equation (3.8) has the form of a conservation law and we shall refer to it as the surface continuity equation. The classical no-slip condition gives that the normal velocity at an interface is zero however in the interface formation/disappearance model the interface is considered a thermodynamic system in its own right so that there is a possibility of mass exchange between the interface and bulk, caused by fluctuations in the surface density. This consideration is reflected in (3.7) which allows for a non-zero normal velocity. It is important to note that although the
interface is permeable, the solid substrate itself is still impermeable which is described by (3.5).
Equation (3.9) can be illustrated by considering a Couette-Poiseuille flow between parallel walls
with upper plate moving and with the role of the pressure gradient being played by the surface
tension with opposite sign. The mean average velocity across the layer is represented by $v^s$. Finally (3.10) is the equation of state that closes the system, relating surface tension to surface
density via a linear relation.
This set of boundary conditions (3.5)–(3.10) to the bulk are a set of partial differential equations
themselves, which require their own boundary conditions, to be specified at the contact line.

3.3 Contact line conditions

At the contact line we apply a continuity of flux condition and a force balance equation

$$
(r^s v^s)|_1 \cdot e_1 = (r^s v^s)|_2 \cdot e_2,
$$

(3.13)

$$
F = \sigma_2 - \sigma_1.
$$

(3.14)

Subscripts $i = 1, 2$ will always refer to the surface involved and $e_i$ is a unit vector in the tangent
plane of surface $i$ at the contact line.

3.3.1 Continuity of flux

It has been initially assumed that at the actual contact line the flux between the surface phase
and bulk can be neglected. So the continuity of flux condition simply states that the product of
surface density $\rho^s_i$ and surface velocity $v^s_i$ will be continuous across the contact line (3.13).

3.3.2 Force balance

At the contact line there will be a discontinuity in surface tension/density caused by the change
in solid. We expect that one of the solids will attract the fluid more than the other, leading to
a higher surface density on that solid. This would lead to mass near the contact line naturally
moving towards the area of lower density, associated with the other solid, unless somehow
balanced by the action of a force. This balance is provided by an asymmetry at the contact line
where the presence of the more attractive solid leads to a tangential force on the fluid, opposing the natural flow of mass from the more dense region. This reaction force $F$ at the contact line makes equilibrium possible by balancing the difference in surface tensions. This defines the force $F$ as

$$F = \sigma_{2e} - \sigma_{1e}. \quad (3.15)$$

We assume this force must also act when the system is perturbed in some manner except that the surface tensions may now deviate from their equilibrium values (3.14). We take this opportunity to eliminate $F$ from our calculations with the use of (3.14) and (3.15), so forming a different contact line condition

$$\sigma_2 - \sigma_1 = \sigma_{2e} - \sigma_{1e}. \quad (3.16)$$

The validity of both (3.13) and (3.16) must be judged on the results of our investigation.

### 3.4 Problem outline

Thus to solve our problem we must consider equations (3.1)–(3.3) subject to the boundary conditions (3.4)–(3.10), which also require their own contact line conditions (3.13) and (3.16) to relate the two solids. Unfortunately attempting to analytically solve these equations in their current form is unrealistic and we must look at ways to simplify the problem to allow analytic progress.

### 3.5 Non-dimensionalisation and simplification

We consider a steady, two dimensional, incompressible flow with the solid boundary stationary and all body forces negligible (i.e. we consider flows at low Bond number $Bo = \frac{gL^2}{\sigma_{1e}} \ll 1$ where gravitational forces are negligible compared to capillary ones). It is convenient to non-dimensionalise both the bulk equations and the boundary conditions using the following quantities
where $\sigma_{1e}$ is the equilibrium surface tension on the first interface ($\sigma_{1e} = \sigma(\rho_{1e}^s)$) and $\rho_{(0)}^s$ is the surface density corresponding to zero surface tension. By considering a shear flow in the far field we will not have information about the characteristic velocity $U$ and length scale $L$ separately but will instead know their ratio $K = \frac{U}{L}$, the shear. So that we arrive at the familiar non-dimensional groups they will be included in the non-dimensionalisation and then eliminated after. Assuming viscous and capillarity forces are of the same order we set the capillary number $Ca = \frac{\mu U}{\sigma_{1e}} = 1$ and hence specify a characteristic velocity and length scale in terms of the far field shear $K$

$$U \equiv \frac{\sigma_{1e}}{\mu} \quad \text{and} \quad L \equiv \frac{\sigma_{1e}}{\mu K}.$$ (3.17)

3.5.1 Bulk equations

The conservation of mass (3.1) and Navier-Stokes (3.2) equations become

$$\nabla \cdot \mathbf{u} = 0.$$ (3.18)

$$We (\mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p + Ca \nabla^2 \mathbf{u}.$$ (3.19)

where $We = \frac{\mu U^2 L}{\sigma_{1e}}$ is the Weber number and all variables are now non-dimensional (e.g. $\frac{\rho}{\rho_{(0)}} \rightarrow u$).

To simplify the problem further consider a low Weber number flow $We \ll 1$ where inertial effects are considered negligible compared to capillarity effects, characterised by a creeping type flow. Then the bulk flow will be modelled by the non-dimensional incompressible Stokes equations

$$\nabla \cdot \mathbf{u} = 0,$$ (3.20)

$$\nabla^2 \mathbf{u} = \nabla p.$$ (3.21)

where we have used $Ca = 1$. 
3.5.2 Boundary conditions

We find that our boundary conditions (3.4) and (3.5)-(3.10) after non-dimensionalisation are given by

\[ u \to y \text{ and } v \to 0 \text{ as } x^2 + y^2 \to \infty \] (3.22)

and

\[ \mathbf{v}^s_i \cdot \mathbf{n}_i = 0, \] (3.23)
\[ \mathbf{n}_i \cdot [\nabla \mathbf{u} + (\nabla \mathbf{u})^*] \cdot (\mathbf{I} - \mathbf{n}_i \mathbf{n}_i) + \frac{1}{2} \nabla \sigma_i = \tilde{\beta} u_\parallel, \] (3.24)
\[ \mathbf{u} \cdot \mathbf{n}_i = Q(\rho_i^s - \rho_e^s), \] (3.25)
\[ \epsilon \nabla \cdot (\rho_i^s \mathbf{v}_i^s) = -(\rho_i^s - \rho_e^s), \] (3.26)
\[ (\mathbf{v}_i^s)_\parallel = \frac{1}{2} u_\parallel + \tilde{\alpha} \nabla \sigma_i, \] (3.27)
\[ \sigma_i = \lambda (1 - \rho_i^s). \] (3.28)

Where all variables and parameters are now non-dimensional quantities (e.g. \( \frac{\rho_i^s}{\rho(0)} \to \rho_e^s \)) and the following parameters have been used

\[ \lambda = \frac{\alpha \rho_i^s}{\sigma_{1e}}, \quad \epsilon = K\tau, \quad Q = \frac{\rho_i^s \mu}{\rho \sigma_{1e} \tau}, \quad \tilde{\beta} = \frac{\beta \sigma_{1e}}{\mu^2 K} \text{ and } \tilde{\alpha} = \frac{\alpha \mu^2 K}{\sigma_{1e}}. \] (3.29)

3.5.3 Contact line conditions

We finish the process of non-dimensionalisation with the contact line conditions (3.13) and (3.16) which become

\[ (\rho^s \mathbf{v}^s)|_1 \cdot \mathbf{e}_1 + (\rho^s \mathbf{v}^s)|_2 \cdot \mathbf{e}_2 = 0, \] (3.30)
\[ \sigma_2 - \sigma_1 = \sigma_{2e} - \sigma_{1e}. \] (3.31)

where again we now consider non-dimensional variables (e.g. \( \frac{\sigma_i}{\sigma_{1e}} \to \sigma_1 \)).
3.6 Problem specification

Equations (3.20) and (3.21) subject to (3.22)–(3.31) now fully specify our problem. In the next chapters we consider simplifications that will allow analytic progress, notably we consider the behaviour of the equations in various limits, both coordinate and parameter based.
4. NEAR-FIELD ASYMPTOTICS

To understand how the flow in the immediate vicinity of the contact line behaves consider coordinate asymptotics in the limit \( r \to 0 \), where \( r \) is the distance from the contact line.

4.1 The stream function

We use plane polar coordinates in the frame of the flow with angle \( \theta \) measured (in the anticlockwise direction) from the line formed by the interface between solid 2 and the liquid. Then we utilise the following expressions for radial \( u_r \) and tangential \( u_\theta \) velocities in terms of the stream function \( \psi(r, \theta) \), which is defined so that the equation of continuity \( 3.20 \) is automatically satisfied

\[
  u_r = \frac{1}{r} \frac{\partial \psi}{\partial \theta} \quad \text{and} \quad u_\theta = -\frac{\partial \psi}{\partial r}.
\]

For two dimensional motion the vorticity only has one component, into the third dimension \( k \) (which can be thought of as the \( z \) component of a cylindrical polar coordinate system in this case), not used in our equations as we consider a plane flow. We find that in our formulation the vorticity \( \omega \) in term of the stream function satisfies

\[
  \omega = \nabla \wedge \mathbf{u} = -\nabla^2 (\psi k).
\]

Taking the curl of \( 3.21 \), noting that \( \nabla \wedge \nabla p = 0 \) and that the vorticity \( \omega \) is defined by \( \omega = \nabla \wedge \mathbf{u} \) we find that the vorticity also satisfies

\[
  \nabla^2 \omega = 0.
\]

So from \( 4.2 \) and \( 4.3 \) we find that \( \psi \) satisfies the bi-harmonic equation
\[ \nabla^4 \psi = 0. \]  \hfill (4.4)

The pressure can then be calculated up to a constant by substituting the velocities back into (3.21). If we know the form of the stream function we can then immediately determine the form of the streamlines as in plane polar coordinates they satisfy

\[ \frac{dr}{u_r} = \frac{d\theta}{u_\theta}, \]  \hfill (4.5)

or more conveniently

\[ \frac{d\theta}{u_\theta} - \frac{dr}{u_r} = 0, \]  \hfill (4.6)

which expresses the fact that the direction of the tangent to a streamline is the direction of the velocity. Substituting our expressions for velocity (4.1) we find

\[ d\psi = \frac{\partial \psi}{\partial r} dr + \frac{1}{r} \frac{\partial \psi}{\partial \theta} d\theta = 0, \]  \hfill (4.7)

and hence \( \psi = \text{constant on streamlines}, \) giving a family of curves that define the flow. As we consider steady equations our particle paths will be identical to the streamlines.

4.2 Boundary conditions

Equations (3.23)-(3.28) are now re-written in plane polar coordinates. As surface variables are confined to the surface we find that partial derivatives of them become full derivatives with respect to \( r \) as they cannot be functions of \( \theta \), which is normal to the surface.

On solid 1, at \( \theta = \pi \)

\[ - \left[ \frac{1}{r} \frac{\partial u_r}{\partial \theta} + r \frac{\partial}{\partial r} \left( \frac{u_\theta}{r} \right) \right] + \frac{1}{2} \frac{d\sigma_1}{dr} = \beta u_r, \]  \hfill (4.8)

\[ -u_\theta = Q(\rho_1^s - \rho_{1e}^s), \]  \hfill (4.9)

\[ \epsilon \frac{d\rho_1^s v_1^s}{dr} = -(\rho_1^s - \rho_{1e}^s), \]  \hfill (4.10)

\[ v_1^s = \frac{1}{2} u_r + \alpha \frac{d\sigma_1}{dr}, \]  \hfill (4.11)

\[ \sigma_1 = \lambda (1 - \rho_1^s). \]  \hfill (4.12)
On solid 2, at $\theta = 0$

$$\left[ \frac{1}{r} \frac{\partial u_r}{\partial \theta} + r \frac{\partial}{\partial r} \left( \frac{u_\theta}{r} \right) \right] + \frac{1}{2} \frac{d \sigma_2}{dr} = \bar{\beta} u_r, \quad (4.13)$$

$$u_\theta = Q (\rho^s_2 - \rho^s_{2e}), \quad (4.14)$$

$$\epsilon \frac{d \rho^s_2 v^s_2}{dr} = - (\rho^s_2 - \rho^s_{2e}), \quad (4.15)$$

$$v^s_2 = \frac{1}{2} u_r + \alpha \frac{d \sigma_2}{dr}, \quad (4.16)$$

$$\sigma_2 = \lambda (1 - \rho^s_2). \quad (4.17)$$

Where (3.23) has been used to eliminate normal components of $v^s$ so that now $v^s = (v^s, 0)$.

The contact line conditions (3.30) and (3.31) become

$$\rho^s_1 v^s_1 + \rho^s_2 v^s_2 = 0, \quad (4.18)$$

$$\sigma_2 - \sigma_1 = \sigma_{2e} - \sigma_{1e}. \quad (4.19)$$

and the far field conditions (3.22) become un-applicable due to the nature of the limit taken.

4.3 Expansion of variables

Variables are then expanded as infinite sums in powers of $r$ as shown below

$$\psi = \sum_{n=1}^{\infty} r^n F_n(\theta), \quad \rho^s_1 = \sum_{n=0}^{\infty} r^n \rho^s_{1n}, \quad \sigma_1 = \sum_{n=0}^{\infty} r^n \sigma_{1n}, \quad v^s_1 = \sum_{n=0}^{\infty} r^n v^s_{1n},$$

$$\rho^s_2 = \sum_{n=0}^{\infty} r^n \rho^s_{2n}, \quad \sigma_2 = \sum_{n=0}^{\infty} r^n \sigma_{2n}, \quad v^s_2 = \sum_{n=0}^{\infty} r^n v^s_{2n}. \quad (4.18)$$

4.4 Form of the stream function

To obtain a general expression for $F_n$ we must substitute $\psi$ into the biharmonic equation (4.4) describing our bulk flow. Then

$$F_1 = a_1 \cos \theta + a_2 \sin \theta + a_3 \theta \cos \theta + a_4 \theta \sin \theta, \quad (4.20)$$

$$F_2 = b_1 \cos 2\theta + b_2 \sin 2\theta + b_3 \theta + b_4, \quad (4.21)$$
and for \( \lambda \neq 1, 2 \) we find a general solution for \( \psi = r^\lambda F_\lambda(\theta) \)

\[
F_\lambda = k_1 \cos \lambda \theta + k_2 \sin \lambda \theta + k_3 \cos [(\lambda - 2)\theta] + k_4 \sin [(\lambda - 2)\theta].
\] (4.22)

Where \( a_j, b_j \) and \( k_j \) (for \( j = 1, 2, 3, 4 \)) are the constants of integration.

### 4.5 First order analysis

The simple procedure used to obtain our near-field approximation is to substitute the expanded variables into equations (4.8)-(4.17) and equate powers of \( r \). We find that at first order

\[
-F''_1(\pi) - F_1(\pi) = 0,
\] (4.23)

\[
F''_1(0) + F_1(0) = 0,
\] (4.24)

\[
F_1(\pi) = Q(\rho_{10}^s - \rho_{1e}^s),
\] (4.25)

\[
-F_1(0) = Q(\rho_{20}^s - \rho_{2e}^s),
\] (4.26)

\[
\epsilon(\rho_{10}^s v_{11}^s + \rho_{11}^s v_{10}^s) = -(\rho_{10}^s - \rho_{1e}^s),
\] (4.27)

\[
\epsilon(\rho_{20}^s v_{21}^s + \rho_{21}^s v_{20}^s) = -(\rho_{20}^s - \rho_{2e}^s),
\] (4.28)

\[
v_{10}^s = \frac{1}{2} F'_1(\pi) + \bar{\alpha} \sigma_{11},
\] (4.29)

\[
v_{20}^s = \frac{1}{2} F'_1(0) + \bar{\alpha} \sigma_{21},
\] (4.30)

\[
\sigma_{10} = \lambda(1 - \rho_{10}^s),
\] (4.31)

\[
\sigma_{20} = \lambda(1 - \rho_{20}^s).
\] (4.32)

And expanding our variables at the contact line (ie at \( r = 0 \)) we obtain from (4.18) and (4.19) that

\[
\rho_{10}^s v_{10}^s + \rho_{20}^s v_{20}^s = 0,
\] (4.33)

\[
\sigma_{20} - \sigma_{10} = \sigma_{2e} - \sigma_{1e}.
\] (4.34)

It follows from (4.31) and (4.32) that (4.34) is equivalent to

\[
\rho_{20}^s - \rho_{2e}^s = \rho_{10}^s - \rho_{1e}^s.
\] (4.35)
From equations (4.23), (4.25), (4.26), (4.29) and (4.35) we find that

\begin{align*}
a_1 &= -Q(\rho_{10}^s - \rho_{1e}^s), \\
a_2 &= -2v_{10}^s + 2\bar{\alpha}\sigma_{11}, \\
a_3 &= a_4 = 0,
\end{align*}

Eliminating constants of integration in (4.29) and (4.30) we also find an extra relation

\begin{equation}
\rho_{20}^s - \bar{\alpha}\sigma_{21} = -v_{10}^s + \bar{\alpha}\sigma_{11}.
\end{equation}

Our first order solution is in fact of the form \( \psi = a_1x + a_2y \), so we find that our leading order streamlines are straight with gradient defined by the undetermined constants. These constants are dependent on the outer flow and in this analysis they will stay unknown, as the far field conditions and the near-field asymptotics cannot be analytically matched due to the nature of the limit taken. However some useful conclusions can be drawn by studying different cases, i.e. what happens for different values of these constants.

If we take \( \rho_{10}^s > \rho_{1e}^s \) then \( a_1 < 0 \) and we find that our normal velocity \( v \) will be positive as \( v = \frac{\partial \psi}{\partial x} = -a_1 > 0 \). For reasons that will become obvious after the second order analysis we will not be concerned with the sign of \( v_{10}^s \) but will assume that \( \sigma_{11} > 0 \) implies that \( a_2 > 0 \), so that our flow goes from left to right \( (u = \frac{\partial \psi}{\partial y} = a_2) \) at the contact line, as we expect given our shear flow in the outer field is going in that direction. Then the gradient of our straight lines will be positive and our solution will look like Fig. 4.1.

If instead we assumed that \( \rho_{10}^s < \rho_{1e}^s \) then we would find that our normal velocity was negative and the flow goes towards the surface near the contact line. This is what we expect in this case as the surface density is lower than its equilibrium value and hence bulk mass is attracted to the mass starved surface. This case looks like Fig. 4.2:

### 4.6 Second order analysis

Now that our first order equations have been satisfied we continue our procedure to consider the second order equations. This result will act as a correction to our first order solution which is
From equations (4.40), (4.42), (4.43) and (4.46) we find

\[ b_1 = \frac{1}{4} \left( \frac{\sigma_{11}}{2} + \bar{\beta} a_2 \right), \]
Fig. 4.2: A graph of the first order solution obtained in the near field asymptotics where we have assumed $a_1 > 0$ and $a_2 > 0$.

\[ b_2 = v_{11}^s - 2\bar{\alpha}\sigma_{12}, \quad (4.51) \]

\[ b_3 = 0, \quad (4.52) \]

\[ b_4 = \frac{Q\rho_{11}^s}{2} + \frac{1}{4} \left( \frac{\sigma_{11}^s}{2} + \bar{\beta}a_2 \right). \quad (4.53) \]

Given $a_4 = 0$ and $b_3 = 0$ we have that $F''_2(\pi) = F''_2(0)$ and $F'_1(\pi) = -F'_1(0)$. So adding together (4.40) and (4.41) we find that

\[ \sigma_{11} = -\sigma_{21} \quad (4.54) \]

and hence from (4.48) and (4.49) we see that

\[ \rho_{11}^s = -\rho_{21}^s. \quad (4.55) \]

Continuing our analysis we substitute (4.54) into (4.39) and find immediately that

\[ v_{20}^s = -v_{10}^s. \quad (4.56) \]

Now using this relation in our continuity of flux condition (4.33) we find that

\[ v_{10}^s(\rho_{10}^s - \rho_{20}^s) = 0 \quad (4.57) \]

and so using (4.35)

\[ \rho_{10}^s - \rho_{20}^s = \rho_{1e}^s - \rho_{2e}^s \neq 0, \quad (4.58) \]
and noting that the surface equilibrium densities of the two surfaces will differ, we have that

\[ v_{s20}^s = v_{s10}^s = 0. \]  

(4.59)

Hence there is no flux through the contact line and condition (4.33) is automatically satisfied. This result was not expected and is highly counter-intuitive as we imagine that the bulk flow would force the surface velocity through the contact line. However our asymptotics show this is not the case. The presence of the contact line affects the bulk flow by acting as an obstacle to motion, irrelevant of the wettabilities of the two sides and the direction of the shear flow in the far field. We go on to consider what consequences this discovery may have on the dynamics of the flow.

4.7 Qualitative analysis

It is instructive to study how the two surface densities \( \rho_{s1}^i \) and \( \rho_{s2}^i \) vary near the contact line (where \( \rho_{s1}^i \simeq \rho_{s10}^i + r\rho_{s11}^i, \quad i = 1, 2 \)) in the hope of being able to qualitatively describe what our flow field may look like.

To do so we use the force balance equation (4.35), the relation (4.55) and the information that in the far field the surface densities tend to their equilibrium values. The balance equation gives what the difference is between surface densities at the contact line and by considering a Taylor expansion (about \( r = 0 \)) we see that the terms \( \rho_{s11}^i \) in (4.55) show how the gradients of the two densities compare at the line (i.e. that \( \frac{\partial \rho_{s1}^i}{\partial r} = -\frac{\partial \rho_{s2}^i}{\partial r} \)).

If we assume that our streamlines go from left to right at the contact line then we have, as with our first order analysis, that \( a_2 > 0 \) and hence from (4.37), (4.48) and (4.55) we have that in this case \( \rho_{11} < 0 \) and \( \rho_{21} > 0 \). When considering the gradient of the surface density near the contact line it is more intuitive to consider Cartesian coordinates (with \( x \) tangential to the surface, increasing in the direction of solid 2). We then see that in this case the surface density increases on both sides of the contact line with increasing \( x \).

We are left with three possible cases for how the surface density varies at the contact line. They correspond to the surface density \( \rho_{1s}^i \) being greater than, less than or equal to its equilibrium value \( \rho_{1e}^i \) at the contact line. From (4.35) we see that the same relation between surface density
and its equilibrium value will occur on the other side of the discontinuity. For each of these cases the actual quantitative behaviour of the surface density and flow field are unknown and we rely on our intuition to make progress.

For our first case we consider the surface density to be higher than its equilibrium value at the contact line. Given that there will be flux out of the region near the contact line (3.25) and that the surface velocity is zero at the contact line we may expect that this region will become so starved of mass that there may be a flux of mass from the right hand side of the contact line as well as the left (the latter of which is natural given the outer flow). So then the surface velocity on the second interface may oppose the far field flow in some region, behaviour that could not be predicted before our analysis. Then we expect the surface density and flow field to look like Fig. 4.3.

**Fig. 4.3:** On the left a graph of surface density in the vicinity of the contact line for $\rho_{10}^s > \rho_{1e}^s$ and $\rho_{11} < 0$. Dotted lines show surface equilibrium densities to which the solution asymptotes. On the right a diagram showing how the velocity field may behave.

So given that in the far field the surface velocity is in the direction of increasing $x$ and near the contact line the surface velocity has opposite sign we require there to be another position (as well as the contact line) where $v_2^s = 0$. There will also occur a point where we have a change of flux in the surface from out to in, characterised by the surface density passing its equilibrium value. These effects could manifest themselves in the bulk flow, downstream from the contact line, in the form of a vortex which may look like Fig. 4.4. Again this conclusion is drawn from intuition but the possibility of such a flow is quite astounding, especially given that the main effect could take place not at the contact line but downstream.
4. Near-field asymptotics

Fig. 4.4: A drawing of streamlines near the contact line for $\rho_{10}^s > \rho_{1e}^s$ and $\rho_{11} < 0$, where a vortex is presumed to be present.

We then consider the case where the surface density is below its equilibrium value at the contact line. The graph for this case may look like Fig. 4.5.

Fig. 4.5: A graph of surface density and flow field in the vicinity of the contact line for $\rho_{10}^s < \rho_{1e}^s$ and $\rho_{11} < 0$.

In this case our normal velocity will be negative at the contact line and hence the contact line will act as a sink to motion. This is to be expected as the contact line is starved of density and hence promotes flow from the bulk towards the surface. We expect that this build up of mass near the contact line and a lack of flux through the contact line may lead to the surface velocity again changing sign, but this time on the first solid where the far field flow naturally causes a flux into the contact line. There would also be a position where the flux changes from out of, to into the surface. These effects may cause a vortex as shown in Fig. 4.6, this time upstream of the contact line.

Finally we consider the case where the surface density has its equilibrium value at the contact
Fig. 4.6: A drawing of streamlines near the contact line for $\rho_{10}^s < \rho_{1e}^s$ and $\rho_{11} < 0$, where a vortex is presumed to be present.

line and hence may behave like Fig. 4.7.

Fig. 4.7: A graph of surface density and flow field in the vicinity of the contact line for $\rho_{10}^s = \rho_{1e}^s$ and $\rho_{11} < 0$.

For this case we find $a_1 = 0$ and so our normal velocity is zero and hence our flow is parallel to the x-axis at the contact line. As can be seen from the surface density graph this case combines features of the two previous cases. There is now the possibility of vortices on either side of the contact line and the surface velocity may be zero in three separate positions, once at the contact line and once on either side. The reasoning and visualisation of the flow can be considered by looking at the two previous cases.

If $\rho_{1e}^s < \rho_{2e}^s$ then our qualitative analysis would lead to similar effects. For streamlines to go from left to right at the contact line we would still require that $\rho_{11} < 0$ and the results will be similar to those obtained above.

The effects described are extremely interesting and to gain some kind of experimental verifica-
tion of them would be of real scientific interest. At this stage however we remember that our conclusions after the near field asymptotics are heavily based on assumption and so we search for further proof of such phenomena.

Although we have only considered Stokes’ equations for our near-field asymptotics (i.e. zero Weber number) the results are also valid for all finite Weber numbers as in the limit \( r \to 0 \) we will regain Stokes’ equations from the Navier-Stokes equations (3.19).

4.8 Pressure

We have found that the stream function has the following form

\[
\psi = r \left( a_1 \cos \theta + a_2 \sin \theta \right) + r^2 \left( b_1 \cos 2\theta + b_2 \sin 2\theta + b_4 \right),
\]

(4.60)

where the constants below now take into account (4.59) and equations (4.25) and (4.48) have been used to eliminate \( \nu_{11} \) and \( \rho_{11} \) respectively leaving us with only \( \sigma_{11} \) and \( \rho_{10} \) to characterise the flow

\[
a_1 = -Q (\rho_{10}^s - \rho_{1e}^s),
\]

(4.61)

\[
a_2 = 2\bar{\alpha}\sigma_{11},
\]

(4.62)

\[
b_1 = -\frac{\sigma_{11}}{8} \left( 1 + 4\bar{\alpha}\bar{\beta} \right),
\]

(4.63)

\[
b_2 = -\frac{\rho_{10}^s - \rho_{1e}^s}{\epsilon \rho_{10}^s} - 2\bar{\alpha}\sigma_{11},
\]

(4.64)

\[
b_4 = \frac{\sigma_{11}}{8} \left( 1 - \frac{4Q}{\lambda} + 4\bar{\alpha}\bar{\beta} \right).
\]

(4.65)

We may now substitute our velocities, found from the stream function (4.1), back into Stokes’ equations (3.21) to obtain an expression for pressure up to a constant of integration. Using Stokes’ equations in polar coordinates

\[
\frac{\partial p}{\partial r} = \left[ \frac{1}{r^3} \frac{\partial^3}{\partial r^3} + \frac{1}{r^2} \frac{\partial^2}{\partial r \partial \theta} + \frac{1}{r^3} \frac{\partial^3}{\partial \theta^3} \right] \psi,
\]

(4.66)

\[-1 \frac{\partial p}{r \partial \theta} = \left[ \frac{\partial^3}{\partial r^3} + \frac{1}{r} \frac{\partial^2}{\partial r^2} + \frac{1}{r^2} \frac{\partial^3}{\partial r \partial \theta^2} - \frac{1}{r^2} \frac{\partial}{\partial r} - \frac{2}{r^3} \frac{\partial^2}{\partial \theta^2} \right] \psi.
\]

(4.67)
Upon substitution of (4.60) we find that pressure is constant at first two orders. So the pressure is regular in the limit we consider, which is not a trivial result as in moving contact line problems we often find that the pressure is divergent as \( r \to 0 \) (Dussan 1979).
5. PARAMETRIC ASYMPTOTICS

We again consider our problem to be specified by the non-dimensional bulk equations (3.20)–(3.21), boundary conditions (provided by the interface formation/disapperance model on the surface) (3.22)–(3.28) and contact line conditions (3.30) and (3.31). In order to simplify these equations we now consider a parametric asymptotics approach (see Van Dyke 1977) in the hope of obtaining the whole flow field based on a sensible use of small parameters found in the problem.

5.1 Estimating parameter size

To understand the limiting process it is intuitive to consider a new length scale $\ell$. This length can be thought of as characterising the width of our layer which we may associate with the continuum approximation $\ell/L \to 0$, where $L$ is the length scale from the macroscopic flow previously described. In this limit the width of the layer becomes negligible compared to the bulk length scales.

It is interesting and relevant to quote a passage from Goldstein’s ‘Notes On The Conditions At The Surface Of Contact Of A Fluid With A Solid Body’ where the author claims that if slip is to take place according to Navier’s equation (3.12)

Then another length $\ell$, enters in addition to the length $L$ specifying the dimensions of the systems, namely, the thickness of the layer, or $\mu/\beta$; and when the other dimensions of the system are changed, force coefficients and other non-dimensional quantities would depend on $\ell/L$ as well as on the Reynolds number. Hence unless in some curious way $\ell$ varies in proportion to $L$, the experiments mentioned above indicate that $\ell$ is zero (or so small that its effects are negligible).

\footnote{On p. 680}
The experiments he refers to are those that support no-slip behaviour at the boundaries such as the agreement between Taylor's (1923) calculations and observations on the stability of flow between rotating cylinders.

In the interface formation/disappearance model there appear forces that are singularly strong when compared to the hydrodynamic forces associated with the bulk phase, so that in the limit $\ell/L \to 0$ they are comparable to those in the bulk. At the zeroth order ($\ell/L = 0$) all surface variables in the interface formation/disappearance model reduce to their equilibrium values and the whole set of equations (3.5)–(3.10) collapse to the classical no-slip condition (this will be illustrated in the zeroth order expansion). However with the interface formation/disappearance model it is then possible to consider an expansion in $\ell/L$, where slip will occur at higher orders. The interface formation/disappearance model is a generalisation of the classical boundary conditions and we no longer have to specify slip or no-slip as with Goldstein, where he dismisses a slip condition due to its incompatibility with no-slip models.

### 5.1.1 Use of Couette-Poiseuille analogy

As mentioned earlier one can obtain considerable insight by considering an analogy of the surface equations with a two dimensional, steady Couette-Poiseuille flow between parallel walls a distance $\ell$ apart, with the bulk flow forcing the upper wall to move with constant speed $u$, a pressure gradient imposed and no-slip on the surface. This analogy gives that $\alpha \sim 1/\beta \sim \ell/\mu$ and we use this information to understand how the non-dimensional groups can be expected to behave in various limits. The derivation of this can be found in Appendix A.

There is currently much research being done on the layer of slip for various liquid/solid systems (Barrat & Bocquet 1999; Thompson & Troian 1997) and it appears that this layer is approximately 1-3nm for most fluids. So if we take $L \sim 1mm$ then we see that the number $\ell/L \leq 3.10^{-6}$ and as the non-dimensional parameter $\tilde{\alpha} \sim \ell/L$, using $\tilde{\alpha}$ as a small parameter for our asymptotics seems a sensible consideration.
5.2 Asymptotics

So if we take our small parameter $\delta$ to have order $\delta \sim \bar{\alpha}$ and initially assume\(^2\) that $\epsilon \sim \bar{\alpha}$ then our non-dimensional parameters will behave as follows

$$\epsilon \sim \bar{\alpha} \sim \frac{1}{\beta} \sim \delta , \quad Q \sim \lambda \sim 1 \quad \text{as} \quad \delta \to 0 \quad (5.1)$$

So there exists a constant $E$ such that $E\epsilon = \delta$ and a constant $A$ such that $A = \bar{\alpha}\bar{\beta} \sim 1$. It now becomes sensible to use Cartesian coordinates and more transparent to keep the primitive variables rather than eliminate them using the stream function. We find that our bulk equations (3.20)–(3.21) are

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0, \quad (5.2)$$

$$\frac{\partial p}{\partial x} = \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}, \quad (5.3)$$

$$\frac{\partial p}{\partial y} = \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2}, \quad (5.4)$$

and after eliminating (3.23) so that $v^s = (v^s, 0)$, our surface equations (3.24)–(3.28) become

$$\delta \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} + \frac{1}{2} \frac{d\sigma_i}{dx} \right) = Au, \quad (5.5)$$

$$v^s = Q(\rho_i^s - \rho_{ie}^s), \quad (5.6)$$

$$\delta \frac{d(\rho_i^s v_i^s)}{dx} = -E(\rho_i^s - \rho_{ie}^s), \quad (5.7)$$

$$v_i^s = \frac{1}{2}u + \delta \frac{d\sigma_i}{dx}, \quad (5.8)$$

$$\sigma_i = \lambda(1 - \rho_i^s). \quad (5.9)$$

and our far field conditions (3.22) are unchanged

\(^2\) There is an element of freedom in the choice of $\epsilon$ as it is not proportional to the other terms considered. In this case our choice provides a compatible set of equations for the limit considered. In doing so we are effectively setting $\ell \sim U\tau$, which is a reasonable estimate.
\[ u \to y \quad \& \quad v \to 0 \quad \text{as} \quad x^2 + y^2 \to \infty \quad (5.10) \]

Where \( i = 1, 2 \) represents the surface involved and the bulk velocity is split into tangential and normal components \( u = (u, v) \). Contact line conditions (3.13) and (3.16) must again be used as boundary conditions for the set of partial differential equations (5.5)–(5.9) and now take the form

\[
\rho_i^s v_i^s = \rho_2^s v_2^s, \quad (5.11)
\]

\[
\sigma_2 - \sigma_1 = \sigma_{2e} - \sigma_{1e}. \quad (5.12)
\]

The set of equations (5.2)–(5.12) fully specifies our parametric asymptotic problem and we now consider each order of \( \delta \) by expanding all variables as follows

\[
u = \sum_{n=0}^{\infty} \delta^n u_n, \quad v = \sum_{n=0}^{\infty} \delta^n v_n, \quad p = \sum_{n=0}^{\infty} \delta^n p_n, \quad \rho_i^s = \sum_{n=0}^{\infty} \delta^n \rho_i^s, \quad v_i^s = \sum_{n=0}^{\infty} \delta^n v_i^s, \quad \sigma_i = \sum_{n=0}^{\infty} \delta^n \sigma_i.
\]

Where again \( i = 1, 2 \) gives two separate expansions for each surface (i.e. for \( x < 0 \) and \( x > 0 \)).

### 5.3 Zeroth order

Upon substitution of the expansions into our bulk equations (5.2)–(5.4), our boundary conditions (5.5)–(5.10) and our contact line conditions (5.11)–(5.12) at zeroth order (\( \delta = 0 \)) we find, in the bulk

\[
\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} = 0, \quad (5.13)
\]

\[
\frac{\partial p_0}{\partial x} = \frac{\partial^2 u_0}{\partial x^2} + \frac{\partial^2 u_0}{\partial y^2}, \quad (5.14)
\]

\[
\frac{\partial p_0}{\partial y} = \frac{\partial^2 v_0}{\partial x^2} + \frac{\partial^2 v_0}{\partial y^2}, \quad (5.15)
\]

and on the surface

\[
u_0 = v_0 = v_{10}^s = v_{20}^s = 0, \quad (5.16)
\]
\[ \rho_{10}^s = \rho_{1e}^s, \quad \rho_{20}^s = \rho_{2e}^s. \]  
(5.17) \\
\[ \sigma_{10} = \sigma_{1e}, \quad \sigma_{20} = \sigma_{2e}. \]  
(5.18) 

We find that the contact line conditions are automatically satisfied as (5.18) tells us that the surface tensions are at their equilibrium value and (5.16) tells us there is no surface velocity. 

To asymptotically match our zeroth order solution with the shear flow in the far field (5.10) we require 

\[ u_0 \to y \quad \& \quad v_0 \to 0 \quad \text{as} \quad x^2 + y^2 \to \infty \]

So we have a shear flow \( u_0 = y \), \( v_0 = 0 \) and \( p_0 = \text{constant} \) for all \( x, y \) in the bulk that satisfies the bulk equations (5.13)–(5.15) trivially and satisfies a no-slip boundary condition on the surface. 

This result should not be a surprise because, as discussed the interface formation/disappearance model is in fact a generalisation of the classical boundary conditions (i.e. the no-slip condition), reducing to them in the asymptotic limit that we are considering (at zeroth order). 

### 5.4 First order

The real interest comes when we attempt look at the first order correction to our zeroth order shear flow solution with no-slip at the boundary. At this order we find on the surface that 

\[ \frac{\partial u_0}{\partial y} = Au_1, \]  
(5.19) \\
\[ v_1 = 0, \]  
(5.20) \\
\[ v_{11}^s = \frac{1}{2} u_1, \quad v_{21}^s = \frac{1}{2} u_1, \]  
(5.21) \\
\[ \sigma_{11} = \sigma_{21} = \rho_{11} = \rho_{21} = 0 \]  
(5.22) 

The force balance condition (5.12) is again satisfied due to (5.22) but the continuity of flux condition (5.11) must now be considered. Using (5.17) we find that at \( x = y = 0 \): 

\[ \rho_{1e}^s v_{11}^s = \rho_{2e}^s v_{21}^s \]  
(5.23)
But as we have assumed surfaces of different wettabilities we have that $\rho_{s1} \neq \rho_{s2}$ and hence $v_{11}^s \neq v_{21}^s$. Using our zeroth order solution $u_0 = y$ in equation (5.19) we find $u_1 = \frac{1}{X}$ for all $x$ (note this is non zero). Equation (5.21) tells us that if the tangential velocity is to be continuous across the line $x = 0$, which we require, at the contact line we must have $v_{11}^s = v_{21}^s$ which we have previously shown to be impossible.

### 5.5 Inner region

Looking at equations (5.5)–(5.9) we see that in the limit we are considering we lose all our derivatives at zeroth order and this leads to us being unable to satisfy our contact line conditions (5.11)–(5.12) first order. This suggests we have a singular perturbation problem which can be solved by considering an inner region that will satisfy the contact line conditions and tend to the shear flow solution in the outer region associated with $y \sim 1$. To obtain a solution valid in this inner region we must look to rescale our variables and coordinates in a suitable manner. We introduce inner coordinates $X$ and $Y$ by defining $X = x/\bar{\alpha}$ and $Y = y/\bar{\alpha}$. By doing so we are effectively ‘zooming in’ on the contact line so that we can consider the dynamics there and match them with our outer solution.

As we have a first order solution that is valid throughout the flow field we expand the inner variables (denoted with a tilde) as follows:

\[
\begin{align*}
    u &= \sum_{n=0}^{\infty} \delta^{n+1} \tilde{u}_n, \quad v = \sum_{n=0}^{\infty} \delta^{n+1} \tilde{v}_n, \quad p = \sum_{n=0}^{\infty} \delta^n \tilde{p}_n, \quad v_{x_i}^s = \sum_{n=1}^{\infty} \delta^{n+1} \tilde{v}_{x_i}^s, \\
    \rho_{s_i}^s &= \rho_{s_i}^{ie} + \sum_{n=0}^{\infty} \delta^{n+1} \rho_{s_i}^{in}, \quad \sigma_i = \sigma_{ie} + \sum_{n=0}^{\infty} \delta^{n+1} \sigma_{in}.
\end{align*}
\]

Where we have used the fact that at zeroth order our surface density and tension must take their constant equilibrium values in order to match the far field conditions. Now we find that the bulk equations (5.2), (5.3) and (5.4) become

\[
\frac{\partial \tilde{u}_0}{\partial X} + \frac{\partial \tilde{v}_0}{\partial Y} = 0, \quad (5.24)
\]
\[
\frac{\partial \tilde{p}_0}{\partial X} = \frac{\partial^2 \tilde{u}_0}{\partial X^2} + \frac{\partial^2 \tilde{u}_0}{\partial Y^2}, \tag{5.25}
\]
\[
\frac{\partial \tilde{p}_0}{\partial Y} = \frac{\partial^2 \tilde{v}_0}{\partial X^2} + \frac{\partial^2 \tilde{v}_0}{\partial Y^2}, \tag{5.26}
\]
while the surface equations (5.5)–(5.9) are given by

\[
\frac{\partial \tilde{u}_0}{\partial Y} + \frac{\partial \tilde{v}_0}{\partial X} + \frac{1}{2} \frac{d \tilde{\sigma}_{10}}{dX} = A \tilde{u}_0, \tag{5.27}
\]
\[
\tilde{v}_0 = Q \tilde{\rho}_{00}, \tag{5.28}
\]
\[
\frac{d(\rho^s \tilde{v}^s_{10})}{dX} = -E \tilde{\rho}_{11}, \tag{5.29}
\]
\[
\tilde{v}^s_{10} = \frac{1}{2} \tilde{u}_0 + \frac{d \tilde{\sigma}_{10}}{dX}, \tag{5.30}
\]
\[
\tilde{\sigma}_{10} = -\lambda \tilde{\rho}_{10}^s. \tag{5.31}
\]

With conditions at the contact line \(X = Y = 0\)

\[
\rho^s_{1e} \tilde{v}^s_{20} = \rho^s_{2e} \tilde{v}^s_{20}, \tag{5.32}
\]
\[
\tilde{\sigma}_{10} = \tilde{\sigma}_{20}, \tag{5.33}
\]
And finally conditions in the far field as \(X^2 + Y^2 \to \infty\)

\[
\tilde{u}_0 = Y \tag{5.34}
\]
\[
\tilde{v}_0 = 0 \tag{5.35}
\]

5.6 Summary

To complete the asymptotics we must now solve (5.24)–(5.26) subject to (5.27)–(5.35). The equations themselves are still complex, however we have simplified our original problem by eliminating all small and large parameters in the problem so that remaining constants are of \(O(1)\). This will ensure that if using computational methods, no effect will be neglected due to the computers inability to accurately handle small numbers.
In order to solve (5.24)–(5.26) subject to (5.27)–(5.35) we choose to implement a finite difference scheme, which will then be solved computationally. Other options exist\(^1\) but as the equations are elliptic (so stability is not an issue) and linear the computational approach is probably the simplest.

### 6.1 Finite difference schemes

To use the finite difference method we must first discretise our domain, which, in the simplest case involves laying a mesh with steps of constant size \(\Delta x\) in the \(x\)-direction and \(\Delta y\) in the \(y\)-direction. This is what we will work with for a start but later we will consider how coordinate transforms can improve the accuracy of our solution. When using finite differences we approximate derivatives of a function in terms of the function evaluated at local points. Firstly we note for a function \(f(x)\), Taylor’s theorem tells us that

\[
f(x + h) = f(x) + hf(x) + \frac{h^2}{2}f''(x) + \frac{h^3}{6}f'''(x) + O(h^4) \quad (6.1)
\]

and

\[
f(x - h) = f(x) - hf(x) + \frac{h^2}{2}f''(x) - \frac{h^3}{6}f'''(x) + O(h^4). \quad (6.2)
\]

By simple manipulation of (6.1) and (6.2) we arrive at the central difference formulas for the first and second derivative

\[
f'(x) = \frac{f(x + h) - f(x - h)}{2h} + O(h^2) \quad (6.3)
\]

\(^1\) For example the use of the Mellin transform applied to the equations in polar coordinate form should give the required result.
and
\[ f''(x) = \frac{f(x + h) + f(x - h) - 2f(x)}{h^2} + O(h^2). \] (6.4)

The important thing to note is the error of the approximation we have for the central difference formulas is \( O(h^2) \). At boundary points it is clear that the central difference formulas cannot always be applied in their current form as if we wish to take a derivative normal to this boundary they will require information from outside our domain. There are many solutions to this problem including the use of imaginary points outside the domain that are then eliminated by considering the bulk equations applied at the boundary, by use of symmetry in the problem or most simply the use of forward and backward difference formulas the boundary. This last approach is what we shall use for first derivatives at the boundary while for second derivatives we must use the slightly more subtle approach of imaginary points. By considering (6.1) and (6.2) we see that the first derivative can be given by

\[ f'(x) = \frac{f(x + h) - f(x)}{h} + O(h), \] (6.5)

which is the forward difference expression for the first derivative and by considering \( h \to -h \) we derive the backward difference

\[ f'(x) = \frac{f(x) - f(x - h)}{h} + O(h). \] (6.6)

Note that the forward/backward difference schemes have an error of order \( O(h) \) and hence are less accurate than the central difference schemes. This would suggest using the central difference wherever possible and the forward/backward difference when needed at boundaries, however as we shall see this is not always possible.

Higher order expressions can be found by considering more points but for a start we search for the most simple representation of our equations, further accuracy can be added when our programme is working for the lower accuracy case.
6.2 Evaluation at boundaries

When we have a second derivative at a boundary and normal to it, the use of forward/backward difference will not work as we need at least three points to calculate the second derivative. The solution is to introduce a point that is not in the domain and then eliminate it using one of the other equations. For example to be able to calculate the pressure on the surface we must apply one of Stokes equations (5.25) or (5.26), both of which contain a second derivative normal to the boundary. If we consider the Stokes equation for $\tilde{v}$ then we must consider the derivative \( \frac{\partial^2 \tilde{v}}{\partial Y^2} \), which if applied on the surface at a point \((i, 1)\), (where \(j=1\) is associated with \(Y = 0\)) with a central difference will include a variable $\tilde{v}_{i,0}$ which is outside our domain. Equation (5.25) is discretised at a point \((i, 1)\) as follows

\[
p_{i,2} - p_{i,1} \frac{\Delta Y}{2} = \frac{\tilde{v}_{i+1,1} + \tilde{v}_{i-1,1} - 2\tilde{v}_{i,1}}{(\Delta X)^2} + \frac{\tilde{v}_{i,2} + \tilde{v}_{i,0} - 2\tilde{v}_{i,1}}{(\Delta Y)^2}
\]

(6.7)

In this case a simple solution (there are more than one) is to consider applying the continuity equation (5.24) at the same point so that we obtain

\[
\frac{\tilde{v}_{i,2} - \tilde{v}_{i,0}}{2\Delta Y} + \frac{\tilde{u}_{i+1,1} - \tilde{u}_{i-1,1}}{2\Delta X} = 0
\]

(6.8)

and hence we have another equation from which we can eliminate $v_{i,0}$ in terms of other variables and substitute this result into (6.7).

6.3 The checkerboard effect

Although we would like to use the central difference formulas (6.3) and (6.4) wherever possible, the procedure is complicated by the so called ‘checkerboard’ distribution of velocities and pressures (Anderson 1995, p. 251; Ferziger & Perić, p. 198). If we consider the continuity equation represented using the central difference scheme

\[
\frac{\tilde{v}_{i,j+1} - \tilde{v}_{i,j-1}}{2\Delta Y} + \frac{\tilde{u}_{i+1,j} - \tilde{u}_{i-1,j}}{2\Delta X} = 0
\]

(6.9)

then we see that the type of zigzag behaviour of velocities shown in Fig. 6.1 satisfies continuity (6.9) even though the distribution of velocities makes no sense. This is caused by the fact that
adjacent points are not used in the approximation of the derivative involved. This effect is only present for the first derivative as higher derivatives take into account adjacent points (e.g. (6.4)).

Fig. 6.1: Checkerboard distribution of velocities satisfying continuity discretised using the central difference scheme. Anderson 1995, p. 251.

There are two solutions to such a problem, the use of forward/backward differences for all first derivatives or the use of a staggered grid. The second solution has the advantage that the central difference scheme may still implemented and hence second order accuracy obtained. At first we will attempt to use the first, more simple approach before moving onto the staggered grids, which are discussed in more detail in the further work section. So for a start we use the simple forward and backward differences wherever we envisage there may be a problem with the central difference scheme, i.e. for all first derivatives.

6.4 Matrix inversion

Once we have re-written our equations in terms of finite difference we should be left with a set of $t$ equation in $t$ unknowns, including bulk and surface variables. As our equations are linear we can write this set of equations in matrix form

$$Ax = b$$  \hspace{1cm} (6.10)
where $A$ is our matrix of coefficients to $x$, which contains our unknowns and $b$ is a vector containing known values resulting from boundary conditions. To find the unknowns in $x$ we must invert the matrix $A$ and multiply by $b$. We do so by implementing the available Numerical Algorithm Group (NAG) routines f07ADF and f07AEF. The former factorises the matrix $A$ while the latter inverts the factorised matrix using forward and backward substitution (see Golub & Loan (1932) for further information) and multiplies by $b$.

### 6.5 The programming procedure

Due to the availability of compatible NAG routines and its robust nature we choose to write the programme in FORTRAN. To attempt to write the final programme immediately would be foolish so we break down the programming into stages which make finding errors in our programme far easier. We proceed as follows

1. Write a programme to model the dynamics of the bulk flow and prescribe velocities on all boundaries.

2. Include the surface equations in the programme, at first without the presence of a contact line.

3. Add the contact line and associated conditions. Check that the programme still works for equilibrium surface densities the same, $\rho_{1e}^s = \rho_{2e}^s$.

4. Run the final programme to find the solution to our problem.

Each of these stages can be split but these are the basic steps. To test the bulk equations we use two different flows to which an analytic solution is available. Firstly the extensional flow where the velocity on the boundary is given by

$$
\tilde{u} = AX + B, \quad \tilde{v} = -AY + C
$$

(6.11)

where $A$, $B$ and $C$ are constants. We expect this flow to continue through the bulk as the distribution of velocities (6.11) satisfy our bulk equations (5.24)–(5.26). Fig. 6.2 shows that this
was indeed the case. Each arrow represents a vector of magnitude proportional to the arrow’s length and we can see that as expected there is a stagnation point at \((X, Y) = (-B/A, C/A)\).

![Bulk Test 1 - Extensional Flow, Centre (0.3,0.7)](image)

**Fig. 6.2:** The flow field for extensional flow which was used to check the bulk equations.

Having tested the bulk’s ability to handle velocity distributions we now need to make sure it can handle variations in pressure as well. This is done by considering a Poiseuille flow where again velocities are prescribed on all boundaries. Pressure need only be defined at one point, as to calculate its distribution in Stokes’ equations it need only be defined up to a constant. Fig. 6.3 shows how the bulk can indeed handle such a flow.

Being sure that our bulk equations are indeed correct we move on to consider our specific problem. As the problem is elliptic we must specify velocities on all four boundaries in some manner. Three of the boundaries can be considered ‘far field’ boundaries where we require that all effects caused by the presence of the contact line have died out while the fourth boundary is the surface itself which will be modelled by equations (5.27)–(5.33). For the far field conditions we realise that if the distance from the contact line is far enough then the dynamics there should not be important. However incorrect far field conditions will effect our solution in a negative manner. The solution is to allow the most free flow adjustment that still gives the correct answer (Roache 1972, p. 154). This is done by specifying the values of derivatives at the far field boundaries instead of explicitly prescribing velocities. For example at the far fields in the
X direction our boundary conditions for the bulk are

\[
\frac{\partial u}{\partial X} = \frac{\partial v}{\partial X} = 0 \quad \text{as} \quad |X| \to \infty,
\]

which defines the far field as the place where variation in \(u, v\) in this direction has died out. The exception to this treatment of the far field is on the top boundary where we create the shear flow that will propagate through the flow field, although again we do this using the less restrictive derivative form

\[
\frac{\partial \tilde{u}}{\partial Y} = k \quad \text{as} \quad |Y| \to \infty,
\]

where \(k\) is the shear, a constant. When choosing the step size and number of steps it is important that the far field is a sensible distance from the contact line. In this problem, as all constants are of order one (after rescaling for the inner region) a minimum distance of about ten from the contact line in all directions is a reasonable estimate.

Equations (5.27)–(5.31) provide the boundary conditions we require for our problem on the surface. The discretisation of our equations at the contact line requires a little more thought as it represents a discontinuity in some variables. At the contact line we have two sets of variables, one set representing the left and one set the right. Some of these variables are connected via
the contact line conditions (5.32) and (5.33) while some of the surface equations must also be implemented, with care not to take differentials of discontinuous variables.

We firstly test our new programme with surface equations (5.27)–(5.31) included and with the presence of a contact line for the case $\rho_{1e} = \rho_{2e}$. The result of this should be a simple shear flow with some slip on the surface which will be dependent on the constant $A$. This is indeed the case, when $A = 1/2$ we observe the following flow field shown in Fig. 6.4.

![Inner region with equilibrium surface densities equal.](image)

**Fig. 6.4:** The flow field for our problem when $\rho_{1e} = \rho_{2e}$ and $A = 1/2$.

At present the programme is being modified to solve the full problem (5.24)–(5.26) subject to (5.27)–(5.35). Unfortunately this was not complete in time to be included here but it is hoped that it will be producing results in the near future. The programme in its current form is shown in Appendix B.

### 6.6 Further work

#### 6.6.1 Use of staggered grids

As described above, the use of central differences everywhere when evaluating all variables at the same nodes can lead to non-sensical results. The simplest way to solve this problem is to use some forward and backward differences however in doing so we lose accuracy. An alternative approach is to *stagger* the grid which has the advantage that we may still use the central
difference schemes. In this method velocities and pressure are calculated at different points, examples of such setups are shown in Fig. 6.5, where A is the non-staggered grid. This setup has the advantage that we may use the central difference scheme without worrying about the ‘checkerboard’ effect described earlier. Implementing such a scheme in the future is essential to gain the kind of accuracy that we would like to obtain.

Fig. 6.5: Grids showing where each variable is to be evaluated. Velocity components are represented with arrows while pressure is represented by a disk.

6.6.2 Mesh generation

Due to the nature of the problem we would like to use a mesh transform so that we gain a high resolution near the contact line where we expect the flow gradients to change rapidly. In the far field we know that the solution is a simple shear flow with all surface variables at their equilibrium values and hence this region is of little interest to us. From our previous work, notably the near-field asymptotics we know that the contact line will act as an obstacle to the shear flow and what we wish to investigate is the flow in the vicinity of this point. Ideally we would use an incredibly larger number of grid points so that our resolution is high everywhere, however we are limited by the power of the computer. For each grid point on the surface we have five equations/variables and for each in the bulk we have three, so for an \( n \times m \) grid we require \( 5(n + 1) + 3(n - 1)m \) equations/variables (noting there are extra equations at the contact line). As discussed we are also limited by the fact we must have our far field a certain distance away from the contact line. At best we may be able to have our far field a distance
10 away from the contact line in all directions. For simplicity if we consider using the same step size in both directions so that $\Delta x = \Delta y$ then our far field constraints give $n\Delta x = 20$ and $m\Delta x = 10$. If we assume as a rough estimate that the computer cannot handle (in a reasonable time) inverting any matrix greater than $15000 \times 15000$ then we find that the minimum step size we can use is approximately $\Delta x = 0.2$, which is not that small when considering the rapid changes near the contact line.

![Diagram](image)

**Fig. 6.6:** A diagram showing the effect of our mesh transform $(x, y) \rightarrow (X, Y)$. Above the actual domain and below the computational domain.

The result is that with the simple mesh scheme we have used we have no hope of gaining the kind of accuracy we would like to obtain near the contact line, however it should be realised that the
transform we will implement is simply an extension to the programme already written, so that we have not been deluding ourselves. As the standard finite difference scheme is implemented using a uniform grid, our approach will be to transform from non-uniform coordinates \((x,y)\) (that will have high resolution near the contact line) into uniform coordinates \((X,Y)\) where we can use our finite difference scheme as usual, see Fig. 6.6. The coordinate transform we wish to use is known as the ‘exponential stretch’ (Roache 1972, p. 292; Anderson 1995, p. 186) and for our case is defined by the relations

\[
x = \begin{cases} 
  b_1(1 - e^{-a_1 X}), & x \leq 0; \\
  b_1(e^{a_1 X} - 1), & x > 0.
\end{cases}
\]  

\(\text{(6.14)}\)

\[
y = b_2(e^{a_2 Y} - 1).
\]  

\(\text{(6.15)}\)

where \(a_1,a_2,b_1\) and \(b_2\) are arbitrary constants that may be adjusted to ‘stretch’ the regions. Then we transform equations (5.24)–(5.35) using the normal rules of partial differentiation, for example

\[
\frac{\partial}{\partial y} = \frac{\partial}{\partial Y} \frac{\partial Y}{\partial y} + \frac{\partial}{\partial X} \frac{\partial X}{\partial x} = e^{-a_2 Y} \frac{\partial}{a_2 b_2 \partial Y}.
\]

This procedure will result in us having the required information near the contact line without having to worry about the limitations described above.
7. FUTURE WORK

Once the work on shear flow over a chemically patterned surface is complete there are many areas for further work. We may wish to adapt our work to include a free surface as an upper boundary and consider what effect the contact line has on its shape. This may lead to a physical effect which could be compared to experiments by simple observation. Another similar extension would be to consider the dynamics of thin films over patterned surfaces which, as discussed, are observed to break up in some cases. This investigation may reveal the cause of such an effect and the parameters involved which would be of considerable interest.

As opposed to the above examples where the liquid is already in contact with the surface an alternative would be to consider the dynamics of a droplet impacting and then spreading on a patterned surface. In this case the method of delivery to the surface would be similar to that of an inkjet printer where a droplet is released on demand to a certain area. This problem would combine issues of dynamic wetting (notably the ‘moving contact line problem’) with the effects caused by the heterogeneity of the surface.
A. COUETTE-POISEUILLE ANALOGY

If we consider a unidirectional flow \( u = u(y) \) between the walls, then if our fluid is incompressible we have that \( \frac{\partial u}{\partial x} = 0 \) and hence the Navier-Stokes equations (3.2) give us that

\[
\frac{\partial p}{\partial y} = 0, \tag{A.1}
\]

\[
0 = -\frac{1}{\mu} \frac{\partial p}{\partial x} + \nabla^2 u. \tag{A.2}
\]

From the second equation we can see that by separation of variables we must have that \( \frac{\partial p}{\partial x} = \text{constant} \) and hence our equations (A.1) and (A.2) reduce to

\[
\frac{\partial^2 u}{\partial y^2} = \frac{1}{\mu} \frac{\partial p}{\partial x}. \tag{A.3}
\]

As \( \frac{\partial p}{\partial x} = \text{constant} \) we may simply integrate (A.3) twice and apply our conditions at the top, \( u = U \) at \( y = \ell \) and bottom of the channel, \( u = 0 \) at \( y = 0 \) to obtain

\[
u = \frac{1}{\mu} \frac{\partial p}{\partial x} \frac{y^2}{2} + \left( \frac{U}{\ell} - \frac{\ell}{2\mu} \frac{\partial p}{\partial x} \right) y. \tag{A.4}
\]

To compare this expression to our surface equations we must note that the surface velocity \( v^s \) is defined as the average velocity over the layer, which we remember becomes infinitesimal in the continuum approximation. So for our analogy

\[
v^s = \int_0^\ell u dy, \tag{A.5}
\]

which using (A.4) gives us that

\[
v^s = \frac{U}{2} - \frac{\ell^2}{12\mu} \frac{\partial p}{\partial x}. \tag{A.6}
\]
If we compare this to our fifth dimensional equation in the interface formation model that we are using

\[ \mathbf{v}_\parallel = \frac{1}{2} \mathbf{u}_\parallel + \alpha \nabla \sigma, \quad (A.7) \]

and use an estimate that \( \sigma \sim p\ell \) then we see by comparison of (A.7) and (A.6) that \( \alpha \sim \ell/\mu \).

By similar arguments, this time considering the analogy between (3.24) and Couette flow in a channel of width \( \ell \) and viscosity \( \mu \) we have that \( \beta \sim \mu/\ell \), as noted by Goldstein.
program Main
implicit none
integer M, N, T, mc, nc, lda, ldb,tots,tot
double precision dx, dy
parameter (M=20, N=25, dy=1, dx=1,tots=5*N+5,tot=3*N)
parameter (T=tots+(M-1)*tot))
parameter (mc=t, nc=t, lda=t, ldb=t)

integer u1n, u1e, u1s, u1w, u1c, p1e, p1w,p1c,row1 !Bulk
integer u1se,u1sw,v1e,v1c,v1w
integer v2n, v2e, v2s, v2w, v2c, p2n, p2s,row2
integer u2s,u2c,u2e,u2w,p2e,p2w,p2c
integer u3e, u3w, v3n, v3s, row3, pts,v3c,v3e,v3w,u3c
integer u1sn,u1sc,v1se,v1sc,v1sw,r1se,r1sc,r1sw,rows1 !surface
integer v2sc,r2sc,v2se,rows2,r2se,v2sw
integer s3se,s3sc,s3sw,r3sc,r3se,rows3
integer s4sc,u4sc,r4sc,r4se,s4se,rows4
integer p5sc,p5sn,v5se,v5sc,v5sn,v5sw
integer p5se,rows5,u5se,u5sw,u5sc
integer nor,puw
integer k, i, j, info, ipiv(t) !nag routine
integer poss,no,norcl,totp,pt !variables

double precision u1le, u1re, u1lw, u1rw, u1an, uias !Bulk
double precision u1lc, u1rc, p1lc, p1lw, p1re, p1rc
double precision v2le, v2re, v2lw, v2rw, v2an, v2as
double precision v2lc, v2rc, p2an, p2ac, p0, p2as
double precision v2us, v2uss, p2us, p2uc
double precision u3lc, u3lw, u3re, u3rc, v3an, v3ac, v3as
double precision uuas, uuac  !boundary conditions
double precision v2lc, vrrc
double precision u1sle, u1sre, u1sac, u1san  !surface
double precision v1sre, v1src, v1sle, v1slc, v1slw, v1srw
double precision r1sre, r1src, r1sle, r1slw, r1srw
double precision v2sac, r2sac
double precision s3src, s3slc, s3sre, s3sle, s3srw, s3slw, r3sac
double precision s4sac, u4sac, r4sre, r4sle, r4src, r4slc, r4srw, r4slw
double precision r4sce, r4scc
double precision p5san, p5sac, v5san, v5slc, v5srw, v5sle, u5slw
double precision v5src, v5sle, v5srw, v5sre, u5srw, u5sre, u5sle
double precision x, y
double precision el, ea, q, cel, cer, eq, ks, one

Double Precision u(N,M), v(N,M), p(N,M), xx(N,1), xs(N+1,1)
Double Precision r(N+1,1), A(t,t), b(t,1), s(N+1,1), yy(M,1)
Double Precision rg(N+1,1), sg(N+1,1)

************************************************************************
* Define constants *
************************************************************************
ks=10  !Shear
p0=10  !Pressure
eA=2   !A
eQ=1   !Q
cel=1  !\rho_{s\{1e}}
cer=1  !\rho_{s\{2e}}
el=1   !\Lambda

************************************************************************
* Define value of variables for the *
* finite difference scheme *
************************************************************************

************************************************************************
* Bulk coefficients *
************************************************************************
!Tangential Stokes
u1lw=1/(dx**2)
u1rw=1/(dx**2)
u1le=1/(dx**2)
u1re=1/(dx**2)
u1an=1/(dy**2)
u1as=1/(dy**2)
u1lc=-2*(1/(dx**2)+1/(dy**2))
u1rc=-2*(1/(dx**2)+1/(dy**2))
p1lw=1/(dx)
p1lc=-1/(dx)
p1re=-1/(dx)
p1rc=1/(dx)

!Normal Stokes
v2lw=1/(dx**2)
v2rw=1/(dx**2)
v2le=1/(dx**2)
v2re=1/(dx**2)
v2an=1/(dy**2)
v2as=1/(dy**2)
v2lc=-2*(1/(dx**2)+1/(dy**2))
v2rc=-2*(1/(dx**2)+1/(dy**2))
p2an=-1/(dy)
p2ac=1/(dy)

!Continuity
vllc=-2/(dy**2)
vrrc=-2/(dy**2)
u3lc=1/(dx)
u3rc=-1/(dx)
u3re=1/(dx)
u3lw=-1/(dx)
v3ac=1/(dy)
v3as=-1/(dy)

* Surface coefficients *
! General Navier
u1sac=-(1/(dy)+eA)
u1san=1/(dy)
v1slc=1/(dx)
v1sre=1/(dx)
v1slw=-1/(dx)
v1src=-1/(dx)
r1slc=-el/(2*dx)
r1sre=-el/(2*dx)
r1src=el/(2*dx)
r1slw=el/(2*dx)

! Normal Velocity
v2sac=1
r2sac=-eq

! Mass conservation
s3slc=cel/(dx)
s3slw=-cel/(dx)
s3src=-cer/(dx)
s3sre=cer/(dx)
r3sac=1

! Darcy
s4sac=1
u4sac=-0.5
r4slc=el/(dx)
r4slw=-el/(dx)
r4sre=el/(dx)
r4src=-el/(dx)

! Surface Pressure
p5sac=1/dy
p5san=-1/dy
v5san=2/(dy**2)
v5src=-2*(1/(dy**2)+1/(dx**2))
v5slc=-2*(1/(dy**2)+1/(dx**2))
v5sle=1/(dx**2)
v5slw=1/(dx**2)
v5sre=1/(dx**2)
v5srw=1/(dx**2)
\begin{align*}
\text{u5sre} &= 1/(dy*dx) \\
\text{u5srw} &= -1/(dy*dx) \\
\text{u5sle} &= 1/(dy*dx) \\
\text{u5slw} &= -1/(dy*dx)
\end{align*}

************************************************************************
* Begin loop that will fill matrix A of unknowns and         *
* matrix b with knowns s.t. Ax=b                          *
************************************************************************

\begin{align*}
do 1001, j=1,M \\
do 1002, i=1,N
\end{align*}

************************************************************************
* Define variables that relate positions in the mesh to     *
* matrix entries                                          *
************************************************************************

\begin{align*}
!Bulk Points \\
\text{pt} &= 3*(i+(j-2)*(N))+(tots)
\end{align*}

\begin{align*}
!Surface Points (taking into account contact line) \\
\text{if}(i.\le.((N+1)/2)) \text{then} \\
\text{poss} &= 5*(i) \\
\text{else} \\
\text{poss} &= 5*(i)+5 \\
\text{end if}
\end{align*}

\begin{align*}
!Bulk Upper Coordinate \\
\text{no} &= \text{tot}
\end{align*}

\begin{align*}
!Surface Upper Coordinate (taking into account contact line) \\
\text{if}(i.\le.(N+1)/2) \text{then} \\
\text{nor} &= \text{tots}-(5*(i-1))+(3*(i-1)) \\
\text{else} \\
\text{nor} &= \text{tots}-(5*(i-1))+(3*(i-1))-5 \\
\text{end if}
\end{align*}

************************************************************************
* Fill the matrix A with unknowns with coefficients         *
* from finite difference discretisation                     *
************************************************************************
if (j.ne.1) then

!Tangential Stokes
  u1e=pt+1
  u1w=pt-5
  u1c=pt-2
  u1n=pt-2+no
  p1e=pt+3
  p1w=pt-3
  p1c=pt
  row1=pt-2
  if (j.eq.2) then
  u1s=pt-2-nor
  else
  u1s=pt-2-no
  end if

if (i.lt.((N+1)/2)) then
  if(j.ne.M) then
    if (i.ne.1) then
      A(row1,p1w)=p1lw
      A(row1,p1c)=p1lc
      A(row1,u1c)=u1lc
      A(row1,u1w)=u1lw
      A(row1,u1e)=u1le
      A(row1,u1n)=u1an
      A(row1,u1s)=u1as
    else
      A(row1,u1c)=1 !zero derivative
      A(row1,u1e)=-1
    end if
  else
    A(row1,u1c)=1
    A(row1,u1s)=-1
    b(row1,1)=b(row1,1)+(ks*dy)
  end if
end if
if(i.ge.((N+1)/2)) then
  if(j.ne.M) then
    if (i.ne.N) then
      A(row1,p1e)=pire
      A(row1,p1c)=pirc
      A(row1,u1c)=uirc
      A(row1,u1w)=u1rw
      A(row1,u1e)=uire
      A(row1,u1n)=uian
      A(row1,u1s)=ulas
    else
      A(row1,u1c)=1
      A(row1,u1w)=-1 !zero derivative
    end if
  else
    A(row1,u1c)=1 !prescribe shear-simple derivative
    A(row1,u1s)=-1
    b(row1,1)=b(row1,1)+(ks*dy)
  end if
end if

!Normal Stokes
  v2e=pt+2
  v2w=pt-4
  v2c=pt-1
  v2n=pt-1+no
  row2=pt-1
  p2n=pt+no
  p2c=pt
  p2e=pt+3
  p2w=pt-3
  if (j.eq.2) then
    v2s=pt-1-nor
    p2s=pt-nor
  else
    p2s=pt-no
    v2s=pt-1-no
  end if
  u2e=pt+1
  u2w=pt-5
if (i.lt.((N+1)/2)) then
  if (j.ne.M) then
    if (i.ne.1) then
      A(row2,v2w)=v2lw  
      A(row2,v2e)=v2le    
      A(row2,v2s)=v2as    
      A(row2,v2c)=v2lc    
      A(row2,p2c)=p2ac    
      A(row2,p2n)=p2an    
      A(row2,v2n)=v2an    
    else
      A(row2,v2e)=2/(dx**2)  
      A(row2,v2s)=v2as     
      A(row2,v2c)=v2lc     
      A(row2,p2c)=p2ac     
      A(row2,p2n)=p2an     
      A(row2,v2n)=v2an     
    end if
  else
    if(i.eq.1) then
      b(row2,1)=b(row2,1)-((1/dx)*p0)  
      A(row2,u2e)=2/(dx**2)      
      A(row2,u2c)=-2/(dx**2)     
      A(row2,p2e)=-1/(dx)        
    else
      A(row2,p2c)=1/(dx)   
      A(row2,u2e)=1/(dx**2)  
      A(row2,u2w)=1/(dx**2)  
      A(row2,u2c)=-2/(dx**2) 
      A(row2,p2e)=-1/(dx)    
    end if
  end if
else
  if(i.eq.1) then
    b(row2,1)=b(row2,1)-((1/dx)*p0)  
    A(row2,u2e)=2/(dx**2)      
    A(row2,u2c)=-2/(dx**2)     
    A(row2,p2e)=-1/(dx)        
  else
    A(row2,p2c)=1/(dx)   
    A(row2,u2e)=1/(dx**2)  
    A(row2,u2w)=1/(dx**2)  
    A(row2,u2c)=-2/(dx**2) 
    A(row2,p2e)=-1/(dx)    
  end if
end if

if(i.ge.((N+1)/2)) then
  if(j.ne.M) then
    if (i.ne.N) then
      A(row2,v2e)=v2re    
      A(row2,p2n)=p2an    
      A(row2,v2n)=v2an    
      A(row2,v2w)=v2rw    
    end if
  end if
end if
A(row2,v2s)=v2as
A(row2,v2c)=v2rc
A(row2,p2c)=p2ac
else
A(row2,v2c)=vrrc
A(row2,v2n)=v2an
A(row2,v2s)=v2as
A(row2,p2c)=p2ac
A(row2,p2n)=p2an
end if
else
if(i.eq.N) then
A(row2,u2w)=2/(dx**2)
A(row2,u2c)=-2/(dx**2)
A(row2,p2c)=-1/(dx)
A(row2,p2w)=1/(dx)
else
A(row2,u2e)=1/(dx**2)
A(row2,u2w)=1/(dx**2)
A(row2,u2c)=-2/(dx**2)
A(row2,p2c)=-1/(dx)
A(row2,p2w)=1/(dx)
end if
end if
end if

!Continuity
u3e=pt+1
u3w=pt-5
v3n=pt-1+no
u3c=pt-2
row3=pt
v3w=pt-4
v3c=pt-1
v3e=pt+2 !bc's
if (j.eq.2) then
v3s=pt-1-nor
else
v3s=pt-1-no
end if

if (i.lt.((N+1)/2)) then
if (j.ne.M) then
  if (i.ne.1) then
    A(row3,u3c)=u3lc
    A(row3,u3w)=u3lw
    A(row3,v3c)=v3ac
    A(row3,v3s)=v3as
  else
    A(row3,v3c)=1 !zero derivative on boundary
    A(row3,v3e)=-1
  end if
else
  A(row3,u3e)=u3re
  A(row3,u3c)=u3rc
  A(row3,v3s)=v3as
end if
end if

if(i.ge.((N+1)/2)) then
  if (j.ne.M) then
    if (i.ne.N) then
      A(row3,u3e)=u3re
      A(row3,u3c)=u3rc
      A(row3,v3c)=v3ac
      A(row3,v3s)=v3as
    else
      A(row3,u3c)=u3lc
      A(row3,u3w)=u3lw
      A(row3,v3s)=v3as
    end if
  else
    A(row3,v3c)=1 !zero derivative on boundary
    A(row3,v3w)=-1
  end if
end if
end if !end bulk loop

************************************************************************
* Surface Equations *
************************************************************************
if(j.eq.1) then
  if(j.eq.1) then
!Generalised Navier
  
u1sc=poss-4
  
u1se=poss+1
  
u1sn=poss-4+nor
  
u1sw=poss-9
  
v1se=poss+2
  
v1sw=poss-8
  
v1sc=poss-3
  
r1se=poss+5
  
r1sw=poss-5
  
r1sc=poss
  
rows1=poss-4

if (i.lt.((N+1)/2)) then
  if(i.ne.1) then
    A(rows1,u1sc)=u1sac
    A(rows1,u1sn)=u1san
    A(rows1,v1se)=1/(2*dx)
    A(rows1,v1sw)=-1/(2*dx)
    A(rows1,r1se)=-el/(4*dx)
    A(rows1,r1sw)=el/(4*dx)
  else
    A(rows1,u1sc)=-1 !at boundary, zero x derivs
    A(rows1,u1se)=1
  end if
end if

if (i.eq.(N+1)/2) then
  A(rows1,u1sc)=u1sac !backward diff on left
  A(rows1,u1sn)=u1san
  A(rows1,v1se+5)=1/(2*dx)
  A(rows1,v1sw)=-1/(2*dx)
  A(rows1,r1sc)=-el/(4*dx)
  A(rows1,r1sw)=el/(4*dx)
  A(rows1,r1sc+5)=el/(4*dx)
  A(rows1,r1sw+5)=-el/(4*dx)
  A(rows1+5,u1sc)=1 !poss-2 at N
  A(rows1+5,u1sc+5)=-1
end if
if (i.gt.(N+1)/2) then
  if (i.ne.N) then
    A(rows1,u1sc)=u1sac
    A(rows1,u1sn)=u1san
    A(rows1,v1se)=1/(2*dx)
    A(rows1,r1se)=-el/(4*dx)
    A(rows1,v1sw)=-1/(2*dx)
    A(rows1,r1sw)=el/(4*dx)
  else
    A(rows1,u1sc)=-1         ! at boundary, zero x derivs
    A(rows1,u1sw)=1
  end if
end if

! Normal Velocity
v2sw=poss-8
v2sc=poss-3
v2se=poss+2
r2sc=poss
r2se=poss+5
rows2=poss-3

if(i.ne.(N+1)/2) then
  if((i.ne.1).and.(i.ne.N)) then
    A(rows2,v2sc)=v2sac       ! no change
    A(rows2,r2sc)=r2sac
  end if

  if(i.eq.1) then
    A(rows2,v2sc)=-1
    A(rows2,v2se)=1
  end if

  if(i.eq.N) then
    A(rows2,v2sc)=-1
    A(rows2,v2sw)=1
  end if
else
  A(rows2,v2sc)=v2sac       ! no change
  A(rows2,r2sc)=r2sac
  A(rows2+5,r2sc+5)=v2sac
A(rows2+5,v2sc+5)=r2sac
end if

!Mass Conservation
s3se=poss+4
s3sc=poss-1
s3sw=poss-6
r3sc=poss
r3se=poss+5
rows3=poss-2

if (i.lt.(N+1)/2) then
  if(i.ne.1) then
    A(rows3,s3se)=cel/(2*dx)
    A(rows3,r3sc)=r3sac
    A(rows3,s3sw)=-cel/(2*dx)
  else
    A(rows3,s3sc)=-1
    A(rows3,s3se)=1
  end if
end if

if (i.eq.(N+1)/2) then
  A(rows3,s3sc)=-cel !bc for cl-flux
  A(rows3,s3sc+5)=cer
  A(rows3+5,r3sc+5)=-1
  A(rows3+5,r3sc)=1 !bc’s for cl-force
end if

if (i.gt.((N+1)/2)) then
  if(i.ne.N) then
    A(rows3,r3sc)=r3sac
    A(rows3,s3se)=cer/(2*dx)
    A(rows3,s3sw)=-cer/(2*dx)
  else
    A(rows3,s3sc)=-1 !rho=0
    A(rows3,s3sw)=1
  end if
end if

!Darcy
B. The programme

\begin{verbatim}
s4sc=poss-1
s4se=poss+4
u4sc=poss-4
u4sc=poss-4
r4se=poss+5
r4sc=poss
r4sw=poss-5
rows4=poss-1

if (i.lt.((N+1)/2)) then
  if(i.ne.1) then
    A(rows4,s4sc)=s4sac
    A(rows4,u4sc)=u4sac
    A(rows4,r4se)=el/(2*dx)
    A(rows4,r4sw)=-el/(2*dx)
  else
    A(rows4,r4sc)=1
  end if
end if

if(i.eq.((N+1)/2)) then
  A(rows4,s4sc)=s4sac !apply either side
  A(rows4,u4sc)=u4sac
  A(rows4,r4sw)=-el/(dx)
  A(rows4,r4sc)=el/(dx)

  A(rows4+5,s4sc+5)=s4sac !for shear
  A(rows4+5,u4sc+5)=u4sac
  A(rows4+5,r4se+5)=el/(dx)
  A(rows4+5,r4sc+5)=-el/(dx)
end if

if (i.gt.((N+1)/2)) then
  if(i.ne.N) then
    A(rows4,s4sc)=s4sac
    A(rows4,u4sc)=u4sac
    A(rows4,r4se)=el/(2*dx)
    A(rows4,r4sw)=-el/(2*dx)
  else
    A(rows4,r4sc)=1
  end if
end if
\end{verbatim}
! Surface Pressure
v5se=poss+2
v5sw=poss-8
v5sn=poss-3+nor
v5sc=poss-3
p5sn=poss-2+nor
p5sc=poss-2
p5se=poss+3
u5sc=poss-4
u5se=poss+1
u5sw=poss-9
rows5=poss

if (i.lt.(N+1)/2) then
  if(i.ne.1) then
    A(rows5,v5sc)=v5slc
    A(rows5,v5se)=v5sle
    A(rows5,v5sw)=v5slw
    A(rows5,v5sn)=v5san
    A(rows5,p5sc)=p5sac
    A(rows5,p5sn)=p5san
    A(rows5,u5se)=u5sle
    A(rows5,u5sw)=u5slw
  else
    A(rows5,v5sc)=-1/(dy**2)
    A(rows5,v5sn)=1/(dy**2)
    A(rows5,u5se)=1/(dy*dx)
    A(rows5,u5sc)=-1/(dy*dx)
    A(rows5,p5sc)=p5sac
    A(rows5,p5sn)=p5san
  end if
end if

if (i.eq.(N+1)/2) then
  A(rows5,v5sc)=v5slc ! ok to apply over cl?
  A(rows5,v5se+5)=v5sle
  A(rows5,v5sw)=v5slw
  A(rows5,v5sn)=v5san
  A(rows5,p5sc)=p5sac
  A(rows5,p5sn)=p5san
  A(rows5,u5se+5)=u5sle
A(rows5,u5sw)=u5slw

A(rows5+5,p5sc)=1 !cl conditions for pressure
A(rows5+5,p5sc+5)=-1

if (i.gt.(N+1)/2) then
  if(i.ne.N) then
    A(rows5,v5sc)=v5src
    A(rows5,v5se)=v5sre
    A(rows5,v5sw)=v5srw
    A(rows5,v5sn)=v5san
    A(rows5,p5sc)=p5sac
    A(rows5,p5sn)=p5san
    A(rows5,u5se)=u5sre !only central difference left
    A(rows5,u5sw)=u5srw
  else
    A(rows5,v5sc)=-1/(dy**2)
    A(rows5,v5sn)=1/(dy**2)
    A(rows5,u5sw)=-1/(dy*dx)
    A(rows5,u5sc)=1/(dy*dx)
    A(rows5,p5sc)=p5sac
    A(rows5,p5sn)=p5san
  end if
end if

end if !end surface loop

1002  continue 1001  continue

************************************************************************
* Solve Ax=b for x using NAG routines *
************************************************************************

call f07adf(mc, nc, A, lda, ipiv, info)
call f07aef('N', nc, 1, A, nc, ipiv, b, ldb, info)

************************************************************************
* Assign values of x to problem variables *
************************************************************************
k=1
   do 1003, j=1,M
      do 1004, i=1,N

      if (j.eq.1) then
         if(i.lt.(N+1)/2) then
            u(i,j)=b(k,1)
            v(i,j)=b(k+1,1)
            p(i,j)=b(k+2,1)
            s(i,j)=b(k+3,1)
            r(i,j)=b(k+4,1)
            k=k+5
         end if

         if(i.eq.(N+1)/2) then
            u(i,j)=b(k,1)
            v(i,j)=b(k+1,1)
            p(i,j)=b(k+2,1)
            s(i,j)=b(k+3,1)
            r(i,j)=b(k+4,1)
            s(i+1,j)=b(k+8,1)
            r(i+1,j)=b(k+9,1)
            k=k+10
         end if

         if(i.gt.(N+1)/2) then
            u(i,j)=b(k,1)
            v(i,j)=b(k+1,1)
            p(i,j)=b(k+2,1)
            s(i+1,j)=b(k+3,1)
            r(i+1,j)=b(k+4,1)
            k=k+5
         end if
      else
         u(i,j)=b(k,1)
         v(i,j)=b(k+1,1)
         p(i,j)=b(k+2,1)
         k=k+3
      end if

   1004 continue 1003 continue
B. The programme

************************************************************************
* Write data to file for analysis                               *
************************************************************************

open(1,file="datax.txt",form='formatted')

do j=1,m
    do i=1,n
        xx(i,1)=(i-(N+1)/2)*dx
        write(1,*), xx(i,1)
    end do
end do

end program
BIBLIOGRAPHY


