Mathematical Modelling of Electrochemical Machining Processes

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To Fiona and Duncan.
Abstract

The solution to free boundary problems arising from electrochemical machining processes is considered. A mathematical description of the machining process is presented with particular consideration given to its electrochemical properties and to the appropriateness of its treatment as a potential problem with Dirichlet boundary conditions. A number of different machining configurations are considered, for which the evolution of the workpiece is determined. In all but the simplest of cases the use of numerical techniques is necessary to include geometric and electrochemical effects upon machining rates. The adoption of these techniques allows realistic problems to be considered when the surface geometries are irregular and the associated boundary conditions are nonlinear.

In the one-dimensional case, the smoothing of surface irregularities is examined by a perturbation procedure and previous work is extended to include higher order terms and a more general description of metal dissolution. The numerical solution of Laplace's Equation in two-dimensional regions is considered by using a boundary integral technique. This formulation determines electric potentials and fields throughout the machining domain solely through the use of the boundary conditions and a description of the surface geometry. Irregular boundary geometries are considered and nonlinear boundary conditions are applied through the adoption of a suitable iterative procedure. The evolution of the workpiece with time is readily calculated, rather than merely a final steady state configuration. The presence of overpotential effects upon workpiece evolution is also considered, together with the effects of insulated portions of the electrode.

Electrochemical effects immediately adjacent to a metallic surface have been analysed in some detail. A singular perturbation analysis of the Nernst-Planck equations is performed with the inclusion of curvature effects. An analysis is made of the case of a simple, symmetric electrolyte and is extended to include the more general case of an electrolyte containing several species of differing valencies. A complete description of the current and species distributions throughout the computational domain is derived. Within the boundary layer analysis it is demonstrated that surface curvature effects have the greatest influence on the solution.
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Declaration

I declare that this thesis was composed by myself and that the work contained therein is my own, except where explicitly stated otherwise in the text.

(Gordon Darling)
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Chapter 1
Introduction

1.1 A Description of the Machining Problem

The process of electrochemical machining (ECM) is a highly efficient method of shaping hard metals by means of electrolysis - first put in to industrial use in the early sixties [1, 2]. A metal workpiece - the anode - is shaped through electrochemical dissolution occurring during the application of an electrostatic potential between the workpiece and a tool - the cathode. As an electric current flows across the gap through an electrolyte solution, metal is removed at the surface of the anode at a rate proportional to the current density. A small gap is maintained between the electrodes in order that the anode be dissolved electrochemically to a shape complementary to the cathode. The electrolyte is pumped through the gap to remove gas, debris and heat. An illustration of the electrode configuration is provided by Figure 1.1.

The rate at which metal is removed depends on the current density at the anode which in turn depends upon the conductivity of the electrolyte, the applied voltage across the electrodes, the curvature of the electrode surfaces and the gap width [3, 4]. To maintain the rate of erosion and the shaping of the anode, the tool is fed towards the workpiece. In time, the machining process attains an equilibrium state where the electrode surfaces no longer change in relation to each other and continued machining will merely result in a uniform metal removal rate across the entire anode surface. The workpiece shape attained at this equilibrium state is therefore dependent upon the cathode shape but also upon the machining conditions such as the applied voltage, the feed-rate and the conductivity of the electrolyte [5]. Since, however, the electrode gap cannot be made arbitrarily small the workpiece surface cannot exactly complement the tool surface and the appropriate design of tools has proven to be a problem. Two

1Problems with short-circuiting can occur and with excessively high pressures being generated.
approaches to tackling the tool design problem are commonly adopted:

- **the cathode problem** to determine the tool shape and the machining conditions that are necessary to produce a desired workpiece shape [6, 7, 8];

- **the anode problem** to predict the workpiece shape that will be produced by a tool shape under prescribed machining conditions (e.g. [9, 10]).

It is the purpose of this thesis to develop mathematical models that encapsulate features of the machining process that affect the shaping of the workpiece and our focus therefore will be primarily on the anode problem. Tool design issues will be examined, however, particularly with regard to the use of insulation on the cathode and its effects upon anodic shaping. Further, our models provide a description of the evolution of the anode profile rather than merely determining the equilibrium electrode configurations (e.g. [3, 9, 11]). As a consequence, important practical matters can be examined such as the volume of stock metal that is lost prior to an equilibrium electrode configuration being attained.
1.2 ECM, EDM and ECAM

Electrochemical arc machining (ECAM) is a process that relies on the occurrence of sparks of long time-duration (arcs) in electrolytes to effect metal removal [5, 12]. It combines features of ECM and of electro-discharge machining (EDM), a well-established process under which metal is removed by the effects of sparks discharged across a dielectric [1, 13].

Commonly EDM is employed for small-hole drilling and for the manufacture of dies and moulds. Drilling by ECM is also common but it has additional applications such as the smoothing and finishing of surfaces, in die-sinking and in wire-cutting. EDM is a far more accurate process than ECM but it is much slower and the surface layers of both the tool and workpiece often are metal-lurgically damaged during machining. Under ECM sparking is not desired and its unwanted occurrence is controlled by detection apparatus. Damage to electrodes is less common but the unwanted loss of stock metal is much greater than in the case of EDM. ECAM has been developed as a method that attempts to utilise the attractive features of ECM and EDM and without the inclusion of their disadvantages.

Studies of ECAM [5, 14] indicate that the advantages of ECAM over ECM and EDM are:

1. Higher machining rates will occur if both ECM and EDM take place in the same machining period. Rates of metal removal can be as much as four or forty times greater than ECM and EDM respectively [12].

2. The configuration of ECAM is the same as that of ECM. This should be cheaper to operate that ECM and/or EDM systems.

3. The ECM phase that follows the ECAM sparking phase can be utilised to provide a surface smoothing and finishing. Specifically, heat-damaged zones can be removed.

In our work, we consider the inclusion of ECAM in our mathematical models and compare directly its performance with ECM.

1.3 Previous Work

The general equations describing the ECM process are described by the work of Fitzgerald & McGeough [15], McGeough [2] and McGeough & Rasmussen [16] and are described in some detail in Chapter 3. In this approach, the electric field
is assumed to be quasi-static and hence the gradient of a potential and a quasi-
steady model is formulated in terms of Laplace's equation [16] together with an
equation relating the rate of change of the anode surface to the electric field at the
anode surface. In a series of papers Fitzgerald & McGeough applied the model
using a perturbation analysis to the shaping and smoothing of small deviations
to planar electrodes [2, 15, 17, 18]. The assumption, however, that the height
of the irregularities be small in comparison to the gap width\(^2\) severely limits the
application of their method to a small group of practical problems.

In practice the surface of the tool can be extremely complex for which the
determination of a solution using a perturbation approach is inapplicable. For
these cases, more sophisticated analyses are required. In the two-dimensional
case, progress can be made by reformulating the problem in terms of the complex
potential and employing the theory of harmonic functions and complex analytic
functions and obtaining an explicit expression for the geometries of the physical
boundaries of interest [9, 7, 11, 19]. This formulation of the problem is useful
for a variety of simple tool shapes and is useful in cases where the tool surface
can be split into a set of local problems treated independently [3]. Note, however,
that the complex formulation is applicable only in two-dimensions and cannot
therefore be extended to the three-dimensional case. Further, to examine the
evolution of the workpiece necessitates an inverse mapping from the complex to
the spatial variables to be undertaken at each point of interest.

By approaching the problem directly in terms of the spatial variables a numeri-
cal technique must be employed for all but the simplest cases. This is necessitated
by the irregular nature of the computational domain but also because part of the
boundary is unknown and its position must be determined as part of the solution
[8, 20, 21]. The problem thus formulated is classed as a time-dependent moving
boundary problem [22, 23].

A number of different approaches can be employed in examining the "direct"
moving boundary problem for a number of fixed electrode configurations. Finite
difference approaches were employed by Tipton [24] to examine two-dimensional
planar problems with rectangular cathodes and by Prentice & Tobias [25] in the
determination of current distributions on electrodes undergoing electro-deposition.
Alkire & Bergh [10] employed finite element techniques in the prediction of the
electro-deposition of material on an initially planar cathode within a fixed rectangu-
lar cell and Christiansen & Rasmussen [26] exploited integral equation methods
to obtain solutions to two dimensional annular machining problems. Forsyth &
Rasmussen [27] derived a numerical procedure for calculating the solution to two-
\(^2\)and indeed in comparison to the characteristic wavelength of the irregularities

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dimensional time-dependent problems by transforming the variational integral to a domain where the boundaries become straight lines and discretising the resultant integral. An implicit finite difference technique is used to integrate the free surface equation.

One clear advantage of a direct approach to the problem is that, in addition to the complex form of the boundaries, the boundary conditions applied there are generally non-trivial. For example, even with simple electrode configurations, the modelling of overpotential effects implies the application of complex nonlinear boundary conditions that require to be treated numerically [25, 28, 29, 30]. Methods employing coordinate or variable transformations can have difficulties coping with the nonlinear form of these boundary condition, restricting their general applicability.

1.4 An Outline of the Present Work

The present work was motivated initially by the studies of McGeough et al [2, 5, 12, 13, 14, 15, 16, 17, 18, 31] and of Parker [32] regarding the problems of Electrochemical Machining (ECM), Electro-discharge Machining (EDM) and Electrochemical Arc Machining (ECAM). The assumptions underlying this work either limited the applicability of the models to simple tool and workpiece surfaces or important aspects of the physical problem were neglected. A procedure to predict workpiece shaping by arbitrary tool shapes reflecting some of the important aspects of the process (e.g. overpotential effects, conductivity, controlled tool movement, the application of insulation, variation in the applied voltage etc.) was required. Further, comparatively few studies of the ECAM problem had been undertaken and comparisons between the ECM, EDM and ECAM machining regimes have not been performed in any detail. The development of models and tools that would enable these comparisons was highly desirable.

Chapter 2 summarises some basic electrochemical effects that influence the machining process and places these in a mathematical context. The underlying physical principles, assumptions and definitions are introduced and the important concept of the electrical double layer discussed. The influence on boundary conditions of the modelling of boundary layer phenomena is presented. Chapter 3 incorporates the mathematical developments of Chapter 2 in the formulation of a general mathematical description of the machining process. The concept of a wear function is introduced and incorporated in the model together with general boundary conditions. Finally, it is illustrated how anodic dissolution under ECAM process can be modelled by considering the form of an evolution equation.
Chapter 4 employs a perturbation approach to solving the ECM and ECAM problems presented in the previous chapter. The approach is applicable to those cases where either or both of the electrodes are almost plane. This work extends that of McGeough et al [15, 16, 17, 18, 31] through the inclusion of secondary machining effects for both smoothing and shaping of the anode and comparing directly some different dissolution regimes. The inapplicability of the perturbation approach to modelling the shaping of general electrode configurations is made apparent and the need for an alternative approach is indicated.

Chapter 5 introduces the Boundary Integral Method (BIM) [33, 34, 35] approach to model the shaping of general, two-dimensional, electrode configurations. Rather than covering the entire computational domain by a regular mesh, the BIM provides a numerical solution to the Laplace equation based upon the calculation of data at nodes distributed solely along the computational boundaries. An integral formulation is derived by using the free space Green’s function in two-dimensional space and a theoretical justification for the technique provided. Following the example of Otta et al [34] and Alarcon et al [36], the development of a numerical implementation of the BIM is described and issues concerning the updating of the free surface position are discussed. Issues relating to the application of the BIM to machining problems are discussed and mechanisms to incorporate these in the model are presented. A validation of the approach and some applications of the BIM that display the versatility of the method are demonstrated.

In the final chapter an examination of boundary layer phenomena is undertaken. Previous work concerning the electrical double layer is reviewed [37, 38, 39, 40] and the importance of developing accurate models of double layer discussed. A consideration of the electrochemical phenomena within an electrolytic cell leads to models based upon the Nernst-Planck equations that predict the concentration, potential and current distributions governed by the diffusion, convection and migration of ions. A separation of the problem into “inner” and “outer” regions is presented and a singular-perturbation expansion performed. The development of models that deal with “non-symmetric” species\(^3\) is presented and an extension of the numerical approach of Barcilon et al to include multiple\(^4\) species is demonstrated. The matching of inner and outer solutions is discussed with regard to the incorporation of a boundary layer analysis within the BIM.

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\(^3\)That is, for which the ions have valencies of different magnitudes.

\(^4\)Greater than two.
Chapter 2
Some Basic Electrochemistry

2.1 Introduction

Electrochemical Machining (ECM) and Electro-Discharge Machining (EDM) involve the removal of metal from a polarised workpiece by anodic dissolution and by discharges in an aqueous electrolyte respectively. Both these processes are crucially dependent upon the behaviour of the workpiece, tool and electrolyte under the application of an externally applied potential and the distribution of charge within an electrochemical system. It is, therefore, necessary to develop an appreciation of the fundamental electrochemical effects that will influence machining processes. In this chapter, these basic electrochemical principles will be presented and placed in a mathematical context for use in later work.

2.2 Physical Principles, Assumptions and Definitions

A system consisting of electrodes and electrolyte is known as an electrolytic cell. An electric current may pass between the two electrodes and must therefore be carried by the electrolyte filling the gap between the two electrodes. The difference between the current flow in the metal electrodes and that within the electrolyte is that on the electrodes the current is carried by electrons but within the electrolyte it is carried by ions - atoms that have either lost or gained electrons and have acquired a positive or negative charge [2].

Figure 2.1 schematically represents the movement of ions and electrons in the case of the dissolution of a metal anode under the application of an external voltage. The negatively charged anions in the electrolyte are attracted to the positively charged anode while the positively charged cations travel, by definition, in the direction of positive current towards the cathode. The positive metal ions that are released from the anode during dissolution similarly are attracted to the
cathode. The movement of ions is balanced by the flow of electrons outside the cell. These electrons are obtained from the metal atoms at the anode and flow to the cathode. The reactions that occur at the cathode surface depend largely on the metal/electrolyte combination that has been selected. In some cases the electrons will neutralise the positive metal ions that arrive at the cathode. This process is how the electroplating of one metal onto another takes place, involving the movement of the anodic metal ions to the surface of the cathode where they are neutralised and deposited. When, however, the concern is with shaping the anode to complement the shape of the cathode, the deposition of machined metal on the cathode surface is undesirable as it effectively alters the tool shape. Often, therefore, the electrolyte is chosen such that the cathodic reaction will be the release of hydrogen gas accompanied by the formation of hydroxyl ions that will combine with the positive metal ions. These precipitates are then washed away by the flow of the electrolyte. In this latter case the shape of the cathode will remain unaltered as hydrogen is released and hence will remain unaffected by the dissolution process.

To assist in developing a model of the behaviour of species within an electrolytic cell and to predict phenomena such as current distribution, electric field
strengths and electrode reactions, some definitions and assumptions are now introduced and discussed.

2.2.1 The Electrostatic Potential

In electrochemical and electro-discharge machining, electric fields are quasi-static so that magnetic effects may be neglected and Maxwell’s equations imply that \( \nabla \times \mathbf{E} = 0 \), where \( \mathbf{E} = \mathbf{E}(r) \) is the electric field vector. Consequently, at any point \( r = (x, y, z) \), the field may be expressed as

\[
\mathbf{E} = -\nabla \phi
\]

where \( \phi(r) \) is the electrostatic potential which may be interpreted as the work required to bring a unit charge from a reference position to the point \( r \). Thus,

\[
\phi(r) - \phi(r') = -\int_{r}^{r'} \mathbf{E} \cdot dl.
\]

where \( dl \) is a line element along any path from \( r \) to \( r' \).

Gauss’ Law [37] relates the total charge \( Q \) within any region \( \mathcal{R} \) having boundary surface \( \partial \mathcal{R} \) to the flux of electric displacement \( \mathbf{D} \) through \( \partial \mathcal{R} \). Thus

\[
\int_{\partial \mathcal{R}} \mathbf{D} \cdot \mathbf{n} \, dS = Q
\]

where \( \mathbf{n} \) is the unit outward normal to \( \partial \mathcal{R} \) with the associated area element \( dS \) and where

\[
\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}
\]

with \( \varepsilon_0 \) the permittivity of free space and \( \mathbf{P} \) the electric polarisation of the material at \( r \). Restricting attention to electrolytes which are linear and isotropic so that \( \mathbf{P} = \varepsilon_0 \chi \mathbf{E} \) gives

\[
\mathbf{D} = \varepsilon \mathbf{E},
\]

where \( \varepsilon = \varepsilon_0 (1 + \chi) \) is the material permittivity. In this case, Gauss’ Law reduces to

\[
\int_{\partial \mathcal{R}} \varepsilon \mathbf{E} \cdot \mathbf{n} \, dS = Q.
\] (2.3)

Treating charge distributions as continuous, with charge density \( \rho = \rho(r) \), and applying the divergence theorem to (2.3) gives the standard result

\[
\int_{\mathcal{R}} \int_{\mathcal{R}} \{ \nabla \cdot (\varepsilon \mathbf{E}) - \rho \} \, dV = 0,
\]

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where $dV$ is a volume element within $\mathcal{R}$. Thus we obtain from Gauss' Law in differential form,

$$\nabla \cdot (\varepsilon E) = \rho$$  \hspace{0.5cm} (2.4)

which may be combined with (2.1) to give

$$\nabla \cdot (\varepsilon \nabla \phi) = -\nabla \cdot (\varepsilon E) = -\rho.$$  \hspace{0.5cm} (2.5)

In regions of uniform permittivity equation (2.5) is just Poisson's equation. One immediately obvious consequence is that in regions of non-zero charge density, the field and potential must be nonuniform.

2.2.2 Conductivity

The earlier example of an electrolytic cell indicated how important is the choice of electrolyte in determining the reactions at the electrodes. The conductivity, $\kappa$, of an electrolyte is an indication of its ability to carry charge and is determined by the types and numbers of ions present. The discussion regarding Figure 2.1 and the movement of ions hints at the fact that ion concentrations need not be uniform throughout the electrolyte as the ions will prefer to move toward the anode or cathode depending upon their own polarity. As a result, the conductivity of an electrolyte need not be constant throughout an electrolytic cell. We will merely comment that the conductivity is related to the charge carried by the ionic species, their concentrations, their mobilities $^1$ and the electrolyte temperature but often an assumption of uniform conductivity throughout a cell is made for reasons of simplification.

2.2.3 Ohm's Law

In metallic conductors, under most circumstances the current density $J$ is usually taken to be directly proportional to the gradient of electric potential, so obeying Ohm's Law which is commonly written as

$$J = -\kappa \nabla \phi$$  \hspace{0.5cm} (2.6)

where $\kappa$ is the conductivity of the metal. In an electrolyte, this is also a good approximation to the law of current flow wherever the flux of ions is essentially directly proportional to field strength. (We shall see later that this requires

$^1$The ionic mobility of a species is the limiting velocity in a field of unit strength. It is derived by considering the balance of the frictional drag imposed on an ion of the species under the application of an electric field. [37]
modification in regions of high gradients of ion density, where diffusive effects become significant.)

In using (2.6), we observe that the conductivity \( \kappa \) need not be uniform throughout an electrolytic cell. Observe also that, at an insulating surface, with outward normal \( \mathbf{n} \), the current flux vanishes giving \( \mathbf{J} \cdot \mathbf{n} = 0 \) so that from (2.1) and (2.6)

\[
\frac{\partial \phi}{\partial n} = \mathbf{n} \cdot \nabla \phi = 0. \tag{2.7}
\]

### 2.2.4 Faraday’s Law

Experimental studies of the machining process have indicated that the rate of metal ion removal from the anode - the *machining rate* - is characterised by the current flow at the anode surface. The simplest relationship between the machining rate, \( \dot{m} \), and the current density at the conducting boundary, \( \mathbf{J} = \mathbf{J} \cdot \mathbf{n} \), is given by Faraday’s Law\(^2\),

\[
\dot{m} = \frac{A J}{z F}, \tag{2.8}
\]

\( A \) being the atomic weight of the metal, \( z \) the valency of the metal ions and \( F \) is Faraday’s constant. Faraday’s Law rests on the assumption that all charge arriving at the anode is utilised in dissolving metal atom with no other reactions taking place.

### 2.2.5 Electroneutrality

When the local charge density in an electrolyte is zero the solution is said to be *electrically neutral*. This state of electroneutrality is an extremely good approximation in all electrolytic cells except in thin layers adjacent to the interface between the electrolyte and the electrode (or other boundaries).\(^3\) This arises because the conductivity of an electrolyte is sufficiently large that in electrostatics the charge resides at the boundary of the electrolyte in the same manner as it resides at metal surfaces.

We note that for an electrolyte in which the concentration and valency of the \( i \)th species are \( c_i \) and \( z_i \) respectively, the charge density is

\[
\rho = \sum_i z_i c_i. \tag{2.9}
\]

\(^2\)Strictly, Faraday’s Law relates the magnitude of the current density, \( |\mathbf{J}| \), to the machining rate. If, however, the electrode surfaces are regarded as equipotential, the tangential components of the electric field at the anode surface are zero and \( \mathbf{J} = \mathbf{J} \cdot \mathbf{n} = |\mathbf{J}| \).

\(^3\)In reality, it is a state of *quasi-electroneutrality* that exists as some charge separation must exist in order for current to flow through the bulk electrolyte. The assumption of electroneutrality has, however, been found to be a sufficiently accurate approximation for behaviour in the bulk region of an electrolyte, i.e. away from the electrodes.
In regions of electroneutrality

\[ \rho = \sum_i z_i c_i = 0. \]  \hspace{1cm} (2.10)

### 2.2.6 Current Efficiency

*Current efficiency* is defined as the ratio (percent) of the observed amount of metal dissolved during anodic dissolution to the theoretical amount predicted by Faraday's law, under the same specified conditions [2].

One would expect that different metal/electrolyte combinations would display different current efficiencies which is indeed the case but other physical and chemical phenomena will also affect the dissolution process and, accordingly, the current efficiency. At higher current densities, various anodic processes will occur, some of which will influence the machining performance. For example, the evolution of gas may occur in preference to metal dissolution, so resulting in a decrease in current efficiency. An increased fluid flow-rate at higher current densities may, however, increase the current efficiency, as the increased flushing removes products formed by the dissolution process, reduces species concentration gradients in the diffuse layer and thus lowers the anodic potential. In turn, this lowers the current density, creating conditions that are less favourable to the evolution of gas. Consequently, the current efficiency will be increased.

Often a simple modification to Faraday's Law is made by including, \( \theta \), a term representing current efficiency, such that,

\[ \dot{m} = \frac{A \theta J}{zF}. \]  \hspace{1cm} (2.11)

The value of \( \theta \) can be obtained experimentally with a dependence upon the choice of the electrolyte, the current density, the electrolyte flow and other machining factors [2].

### 2.3 The Electrical Double Layer

In section 2.2.5 it was indicated that, although the bulk of an electrolyte may be regarded as electrically neutral, a non-zero charge density arises in thin layers at the boundaries of the system. Modelling of these layers requires a different approach from that of the bulk of the electrolyte.

Following the discussion by Bard and Faulkner [37], consider, for the moment, the interface at a single metal electrode. At a given potential, electrons in the metal and the electrolyte are free to flow and there will be a resulting charge on the electrode and a charge in the solution. The electrons will move either toward
or away from the electrode depending upon the polarity of the system. Within the metal, charge is located in a very thin layer (< 1Å) at the metal surface, whereas within the electrolyte, charge resides in a region close to the electrode surface but of greater thickness.

It is the distribution of species at this metal/electrolyte interface that is known as the electrical double layer. On the electrolyte side, the thickness of the charged region is affected by physical and chemical effects, such as, for example, the total ionic concentration and it may, in fact, require to be significantly thick to amass the excess charge to effectively balance the charge on the electrode side of the interface.

To illustrate the importance of the double layer in modelling electrochemical processes, a typical potential difference across the layer is \( \sim 1 \) V but as the layer is only \( \sim 10-100 \) Å thick the electrical field strength (the gradient of potential) at the electrode is large. In ECM the field strength is related to machining rates and therefore an accurate model of double layer effects is highly desirable.

As described above, a separation of charge occurs across the interface but the interphase as a whole remains virtually electrically neutral. Commonly, the double layer is regarded as behaving like a capacitor. A capacitor consists of two metal sheets separated by a dielectric, such that, when a potential is applied across the capacitor, the charge accumulation on the plates is given by

\[
C = \frac{q}{\Phi}
\]

where \( q \) is the charge on the capacitor (in coulombs), \( \Phi \) is the potential across the capacitor (in volts) and \( C \) is the capacitance (in farads). This is a useful starting point in the modelling of the electrical double layer [37].

Figure 2.2 is a schematic representation of the nature of the electrical double layer. The layer closest to the electrode consists of oriented solvent molecules and specifically adsorbed species that are in contact with the electrode. Note that it is possible for ions of the same charge sign as the electrode to be in contact, indicating that it may be chemical aspects rather than the charge of the ion that is of importance.\(^4\) In general, however, the charge of the ion will be highly influential in determining the entire double layer structure. The layer closest to the electrode is known as the Inner Helmholtz Layer (IHL) with the locus of the average distance of the centres of the specifically adsorbed ions forming the Inner Helmholtz Plane (IHP). It is sufficient for our purposes to indicate that there can be special features that will result in the formation of an IHL whose specific feature is that solvated ions as well as solvent molecules may be in contact with the electrode.

\(^4\)Cations are generally not specifically adsorbed [39].
surface. Beyond the IHP the solvated ions are unable to approach closer to the electrode than a distance known as the *Outer Helmholtz Plane* (OHP). The interaction of these *nonspecifically adsorbed* ions with the charged electrode is through electrostatic rather than chemical forces, the charge of the metal electrode attracting solvated ions of the opposing charge sign towards the metal. These ions position themselves beyond the OHP, their concentration progressively decaying throughout the *diffuse layer* - a region stretching from the plane of closest approach (the OHP), where the greatest concentration of species will occur, to a distance from the electrode where electrostatic forces are sufficiently weakened that ion movements are more readily influenced by, for example, the flow of the electrolyte.

The electrolyte side of the electrode/electrolyte interface thus can be considered to comprise of three layers: the IHL with surface charge density $q_1$; the diffuse layer with distributed charge density $\rho = \sum_i z_i c_i$ and a bulk region that is electrically neutral.

The Gouy-Chapman Model of the Double Layer Structure provides an accu-
rate description of the qualitative behaviour of species and potential distributions but it regards ions as point charges able to approach arbitrarily close to the electrode surface. This leads to unphysically large potential gradients. Stern's Modification of the Gouy-Chapman Model [37] introduces the concept of a plane of closest approach but neglects the effect of specific adsorption. We comment here that specific adsorption can have a positive or negative effect on electrode kinetics and can substantially alter the potential profile in the interfacial zone. In principle, these effects can be accounted for by using the Frumkin correction factor [37]. An examination of the effects of specific adsorption and of the existence of a charge density within the Inner Helmholtz Layer is not attempted at this stage.

The analogy between double layer behaviour and that of a capacitor is simplest when the presence of the IHL is considered while specific adsorption effects are neglected. Charge will accumulate at the electrode surface and at the OHP a short distance away, with a potential difference proportional to the total charge occurring across the separating gap.

In the above discussion the concentration of ionic species has hardly been considered. Since, however, ions are charged particles, a potential difference will affect and be affected by their concentrations within the electrolyte. Where departures from electroneutrality occur we should expect variations in ion concentrations, as the ions respond to the perturbed electrical state within the electrolyte. This indicates that the changes in electric potential are largest at the electrode/electrolyte interfaces, associated also with a significant departure in ion species concentrations from their bulk values. The opposing and/or complementary effects of polarity, electric fields, concentration gradients and convective transport upon species distributions are considered in the formulation of the Nernst-Plank equations. These equations and the Poisson-Boltzmann equation relating electric potential to charge density are considered in Section 6.4.

Under practical ECM conditions, the boundary layer thickness is sufficiently small - approximately three orders of magnitude smaller than the gap width - that the phenomena occurring at the electrodes can, under certain assumptions, be accommodated by a suitable choice of boundary conditions for Laplace's equation taken to hold everywhere in the electrolyte:[15],[41],[39]. Otherwise, the full Nernst-Plank equations and the Poisson-Boltzmann equation must be solved.
2.4 Applied Voltage and Overpotentials

The presence of the electrical double layer adjacent to electrode surfaces has consequences upon the determination of potential and current distributions. For this reason, overpotentials are included in the model to account for the effects of the boundary layers upon the potential distribution. The total potential difference across a cell, \( V \), is therefore regarded as consisting of three parts

\[
V = V_{\text{ohm}} + V_o^a + V_o^c
\]

(2.13)

where \( V_{\text{ohm}} \) is the voltage drop across the electrolyte and \( V_o^a \) and \( V_o^c \) are the overpotentials at the anode and cathode respectively.

In the simplest of models, the interface voltages are taken equal to the bulk values so that \( V_o^a = V_o^c = 0 \), and \( V = V_{\text{ohm}} \). Electrode kinetics and ionic behaviour, however, can cause variations from this equipotential case to occur, giving rise to the existence of the overpotentials. A model of overpotentials must, therefore, explain the extent of and the causes of a departure from the uniform potential case.

2.4.1 Concentration Overpotentials

Passage of current to an electrode surface causes a change in ionic concentrations. The resulting change in the potential difference is the concentration overpotential, denoted by \( \eta_a \) at the anode and \( \eta_c \) at the cathode. It represents the difference between the potential drop that would exist in the absence of a concentration gradient and that which occurs in its presence. One may think of the concentration overpotential as characteristic of the passage of current owing to the diffusive properties of ions when experiencing concentration gradients.\(^5\)

2.4.2 Surface Overpotentials

The surface overpotential, \( \eta_s \), is a consequence of the rate of reactions that occur within an electrochemical system. Consider a metal atom and an ion in solution. At a metal electrode surface, each metal ion will require an amount of energy, \( W_1 \), to pass through the metal/solution interface into the solution, similarly, electrolyte ions will require an amount of energy, \( W_2 \), to pass in the opposite direction.

\(^5\)Newman [39] defines concentration overpotential as "the potential difference of a concentration cell plus an ohmic contribution due to the variation of conductivity within the diffusion layer, which can logically be associated with concentration variations near electrodes"
The rates of crossing can be deduced using Maxwell’s energy distribution law as

\[ R_1 = K_1 \exp(-W_1/kT) \]  \hspace{1cm} (2.14)
\[ R_2 = CK_2 \exp(-W_2/kT) \]  \hspace{1cm} (2.15)

where \( K_1 \) and \( K_2 \) are characteristic rate constants for the metal and electrolyte, \( C \) is the free metal ion concentration in the electrolyte, \( T \) is absolute temperature and \( k \) is Boltzmann’s constant [2]. In descriptive terms, if \( R_1 \) exceeds \( R_2 \) ions will dissolve faster than they are deposited whereas if \( R_1 \) is less than \( R_2 \) they will deposit faster than they are dissolved. A change in the potential will also occur owing to the change in the conditions at the interface. It will now be easier or more difficult (i.e. will require less or more energy) for an ion to pass through the metal/solution interface depending upon its polarity and the relative values of \( R_1 \) and \( R_2 \). The change in electric potential is known as the surface overpotential and \( \eta_a \) and \( \eta_c \) are the surface overpotentials at the anode and cathode respectively.

Notice that the surface overpotential denotes a potential difference occurring across the metal/electrolyte interface and is, therefore, characteristic of the current density at the electrode surface. For analysing the behaviour of electrochemical systems it is usually necessary to determine the relationship between current density and the surface overpotential.

The definitions introduced in this section allow the potential difference, \( V \), between electrodes to be written, by convention\(^6\), as

\[ V = \eta_a + \eta_c + V_{ohm} - \eta_a - \eta_c. \]  \hspace{1cm} (2.16)

### 2.5 Current Distribution

It has been outlined above that the passage of current at the anode surface characterises the rate of metal removal. An accurate description of the current distribution is, therefore, a pre-requisite to any model of the machining process and ought to reflect a wide range of effects, for example, the geometry, the anodic reaction kinetics, the electrolyte conductivity and species concentration.

Levich [42] describes the passage of current in an electrolytic cell as consisting of three steps:

1. the transfer of ions from the bulk of the electrolyte to the vicinity of the surface of the electrode;

2. the electrode reaction itself, involving ions or molecules;

\(^6\)Generally, \( \eta_a \) and \( \eta_c \) are negative, thus making a positive contribution to the cell potential.
3. the formation of the final products of the reaction and their deposition on the surface of the electrode or their removal from that surface, and it is the slowest of these steps that determines the overall rate of current flow. This description is a useful indication of the influence of overpotentials upon current distributions, but also suggests that there are limitations imposed on the current by the speed at which each step proceeds.

### 2.5.1 Limiting Currents

A schematic representation of the relationship between electrode potential and current density is given in Figure 2.3. The form of this *polarisation curve* relates in particular to the electrode phenomena described above. When the electrode potential is sufficiently low (region A) no current runs through the cell as no electron transfer can take place through the double layer. An increase in the potential difference (region B) allows the transfer of electrons to take place and current to flow. In anodic dissolution cations are removed from the metal anode. There comes a stage (region C), however, where the current density no longer increases with an increase in potential and it reaches a limiting value, $J_{\text{lim}}$. This occurs because the current will be limited by the availability of ions at one or other of the electrode surfaces. A further increase in potential (region D) now results in a second electrode reaction, for example, the production of hydrogen at the cathode, and the current may increase once more. In practical situations, increasing the fluid flow within the bulk electrolyte can raise the limiting value of the current as flushing can increase the concentration of ions near an electrode.
surface.

The current distribution in an electrochemical cell can, therefore, be seen to possess a number of regimes with resulting effects on machining performance. For example, although current flow may increase in region D, current efficiency will decrease. The effects of the magnitude of current density upon the modelling of the machining problem are now considered.

2.5.2 Primary Current Distribution

Under conditions well below the limiting current, primary current distributions apply when the surface overpotential and concentration overpotential can be neglected and the electrode potential treated as equal to the electrolyte potential. All of the passing current can be assumed to be contributing to the removal of metal ions. This is the simplified case of the potential problem where the current density and electric field are obtained by solving Laplace’s equation,

\[ \nabla^2 \phi = 0 \quad \text{within the electrolyte,} \tag{2.17} \]

with the boundary conditions

\[ \phi = V \quad \text{at the anode,} \tag{2.18} \]
\[ \phi = 0 \quad \text{at the cathode,} \tag{2.19} \]
\[ \frac{\partial \phi}{\partial n} = 0 \quad \text{at any insulating surface,} \tag{2.20} \]

where \( V \) is the applied voltage. It is solely the geometry of the electrolytic cell and the applied voltage that will determine the current distribution. The erosion rate is then taken as directly proportional to surface current.

2.5.3 Secondary Current Distribution

Secondary current distributions include the effects of electrode kinetics in the determination of the current density at a point on the electrode surface. As described above, the electrode kinetics are characterised by surface overpotentials and models of the secondary current distribution must, therefore, include the influences of surface overpotentials. In general, the problem of Section 2.5.2 is modified at metallic surfaces and the effective potential at the electrode surface is adjusted by the surface overpotential. In practice, for example, the current density is often assumed to be exponentially dependent upon the surface overpotential:

\[ J = J_0 \left[ \exp \left( \frac{\alpha_a F}{RT} \eta_s \right) - \exp \left( -\frac{\alpha_c F}{RT} \eta_s \right) \right], \tag{2.21} \]
where \( \alpha_a \) and \( \alpha_c \) are the anodic and cathodic transfer coefficients, \( R \) is the universal gas constant, \( F \) is Faraday’s constant and \( T \) is the absolute temperature. This is the Butler-Volmer equation which represents the rates of anodic and cathodic process proceeding independently and has been found to be appropriate to a large class of electrode reactions [38]. Modifications of (2.21) are often employed when the overpotential is small so that the relationship may be linearised, or where one of the exponential terms is negligible so that a *Tafel behaviour* arises, such that,

\[
\eta_s = A + B \ln(J) \tag{2.22}
\]

where \( A \) and \( B \) are constants.

The boundary value problem under secondary current distribution can be solved using Laplace’s equation but with more general, nonlinear, conducting boundary conditions. Since the surface overpotential occurs at the electrode surface, the appropriate boundary conditions for the potential \( \phi \) taken to satisfy (2.17) may be written (Fitzgerald and McGeough ([15])) as

\[
\phi = V - \eta^a(J) \quad \text{at the anode}, \tag{2.23}
\]

\[
\phi = \eta^c(J) \quad \text{at the cathode}, \tag{2.24}
\]

where the functions \( \eta^a \) and \( \eta^c \) are the overpotentials at the anode and cathode respectively. Their form is determined by the structure of the equations relating the current density and overpotential at an electrode, such as, for example, (2.21). In general, the nonlinear nature of the boundary conditions will require that the boundary value problem for \( \phi \) be solved *iteratively* even for simple geometries. This is discussed further in later chapters.
3.1 Laplace’s Equation and Boundary Conditions

Away from the electrodes the conservation of charge, together with electroneutrality and the occurrence of negligible concentration gradients, reduces the relevant mass transport equations - see Chapter 6 - to

\[ \nabla \cdot \mathbf{J} = 0 \]  

(3.1)

where in the inter-electrode gap it is assumed that electric current \( \mathbf{J} \) flows in the electrolyte according to Ohm’s Law

\[ \mathbf{J} = -\kappa \nabla \phi, \]  

(3.2)

\( \kappa \) is the electric conductivity of the electrolyte and \( \phi \) is the electric potential. When the conductivity is uniform we can conclude that, in the region outside the boundary layer, the potential satisfies Laplace’s equation

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

(3.3)

Solving (3.3) with appropriate boundary conditions gives the potential \( \phi \) at any point in the electrolyte and, in particular, can yield the potential at the anode surface. Also, it can be used to determine the electric field or normal derivative of the potential at the anode surface\(^1\), which through (3.2) permits the current density \( J = \mathbf{J} \cdot \mathbf{n} \) to be calculated, \( \mathbf{n} \) being the normal to the anode surface. Faraday’s Law [15]

\[ \dot{m} = \frac{a}{zF} J, \]  

(3.4)

\(^1\)Some techniques - e.g. Boundary Integral Methods - will explicitly calculate the electric field or the normal potential derivative at the anode surface rather than calculating the potential at and close to the surface and then using approximation methods to estimate the electric field.
is commonly used to relate $\dot{m}$ which is the anode dissolution rate per unit area to the current, $a$ being the atomic weight and $z$ the valency of the metal ions. $F$ is Faraday’s constant. Fitzgerald & McGeough [15] discuss the applicability of both of these laws within an ECM model. They conclude that the assumption of a constant conductivity $\kappa$ is reasonable under the assumption that the electrolyte is sufficiently agitated to offset effects such as Joule heating or hydrogen formation which can influence the electrolyte conductivity. Further, Faraday’s Law is applicable under the assumption that all charge arriving at the anode is used in the dissolution process, i.e. to dissolve the metal ions.

We mention at this stage that this assumption can be violated and that current density characteristics can affect the machining rate. For example, there sometimes exist threshold currents below which no machining will occur [20], [12]. In these circumstances, Faraday’s Law is no longer an accurate description of the machining rate of the anode [12].

It is more appropriate to consider (3.4) as a particular example of an evolution equation which may depend also upon effects such as current efficiency, current density and the electric field.

The approach described above indicates that the formulation is quasi-steady with time-dependence arising only through an equation giving the law of evolution of the anode surface.

### 3.2 A General Mathematical Model

Let $\mathbf{r}(t)$ be a position vector characterising a point $(x, y, z)$ at an instant $t$. Referring to Figure 3.1, let $A$ denote the anode surface, $C$ denote the cathode surface and $D$ denote the inter-electrode gap. Mathematically, the surface $A$ is a free boundary as its position changes with time. To determine its position with time, a law for the speed at which the surface advances into the material must be spec-
ified. Letting \( \rho_m \) be the density of the electrode, the volume erosion rate per unit area is defined by the wear function \( W(r, t, J, \nabla \phi, n) = \rho_m m \). The precise form of the components of the erosion law will depend on the machining process and operating conditions. For example, the velocity of the electrolyte can play an important role in affecting limiting currents at the electrodes and might be included as a variable in an appropriate wear function. In this work, whilst the wear function will have different forms to describe Faradaic and ECAM machining the arguments listed above for \( W \) are sufficient for our purposes. In general, however, one would expect current flux and/or the electric field at the anode surface and the surface geometry to be of prime importance whilst machining parameters such as current efficiency and threshold current levels will also be relevant. Faraday's Law (3.4) is, as outlined earlier, an example of a possible choice of the erosion function. Finally, let \( V \) be the external potential difference applied between the electrodes.

Let \( h(x, y, z, t) = 0 \) describe the location of the anode surface at successive times \( t \), so that the vector \( \nabla h / |\nabla h| \) is the unit normal \( n \) to that surface. Utilising subscripts to denote partial differentiation, then along any path \( r = r(t) \) lying within the moving surface differentiation gives

\[
h_t + \nabla h \cdot \frac{dr}{dt} = 0. \tag{3.5}
\]

Since \( dr/dt \) is the velocity of the point moving along the path, we deduce from the relation

\[
- \frac{h_t}{|\nabla h|} = \frac{\nabla h}{|\nabla h|} \cdot \frac{dr}{dt} = n \cdot \frac{dr}{dt}
\]

that the speed \( v \) at which the surface moves normal to itself is

\[
v = - \frac{h_t}{|\nabla h|}. \tag{3.7}
\]

If the material of the anode is stationary, then \( v = \dot{m} \), the anodic dissolution rate.

Writing the normal derivative of the electric potential as \( a_o \)

\[
\phi_n = \frac{\partial \phi}{\partial n} = n \cdot \nabla \phi, \tag{3.8}
\]

the following mathematical model is now obtained:

\[
\nabla^2 \phi(r, t) = 0, \quad r \in \mathcal{D}, \tag{3.9}
\]

\[
\phi(r, t) = V - \eta^a(J), \quad r \in A, \tag{3.10}
\]

\[
\phi(r, t) = \eta^e(J), \quad r \in C, \tag{3.11}
\]

\[
- \frac{h_t}{|\nabla h|} = n \cdot \frac{dr}{dt} = W(r, t, J, \phi_n), \quad r \in A. \tag{3.12}
\]

\(^2\text{Ohm's Law, (3.2), indicates that knowing either the current density or the electric field is normally sufficient.}\)
The functions $\eta^a$ and $\eta^c$ are general functions specifying the overpotentials near the anode and cathode surfaces respectively, in terms of the current density at the electrode surface. They may take a variety of forms and are, in general, nonlinear. Appropriate forms can be motivated by analysing transport effects which are significant within a boundary layer but which may be treated as "local", so allowing description purely as modified boundary conditions. This is discussed further in Chapter 6. However, if the overpotential effects are ignored, conditions (3.10) and (3.11) are simplified to

$$\phi(r, t) = V \quad r \in A,$$

$$\phi(r, t) = 0 \quad r \in C. \quad (3.13)$$

$$q_5(r, t) = 0 \quad r \in C. \quad (3.14)$$

The problem then reduces to determining the solution at each instant $t$ of the linear quasi-static problem (3.9), (3.13) and (3.14) coupled with the use of equation (3.12) to determine the evolution of the electrode surface. More generally, the quasi-static problem is replaced by the nonlinear problem (3.9)-(3.11), but the incremental changes in surface shape are still governed by (3.12).

### 3.3 Boundary Conditions and The Evolution Equation

We now discuss the specific forms for the boundary conditions (3.10) and (3.11) and the evolution equation (3.12). As outlined earlier, a number of phenomena can occur at the electrode surfaces and within a thin layer close to the electrode surface. It is the influence of these processes upon the passage of current and upon the electric field that requires closer examination.

#### 3.3.1 Boundary Conditions

Previously it has been highlighted that reactions at the electrodes cause significant departure from electroneutrality to occur, so altering the boundary conditions for (3.9) by causing an appreciable jump in the potential across a thin layer at the electrodes. In fact, this boundary layer is sufficiently thin that it is often treated as of negligible thickness so that the boundary conditions for (3.9) are altered to account for its presence, but are still applied at $A$ and $C$ as in (3.10) and (3.11). The need to solve the full mass transport equations is then avoided [30]. Relevant alternative forms of the boundary conditions are now presented.

A current $J$ at the electrode surface is driven by potential gradients within the electrolyte, but since ions must exchange electrons at the metal/electrolyte
interface the current is proportional to the rate at which the reactions occur. Since both the potential at a point on the boundary and the electrode kinetic behaviour are related to the electric current density at that point, a simple proportionality relationship for $\eta^a$ and $\eta^c$ leads to relationship is

$$\phi = V - a \phi_n \quad \text{at the anode} \quad (3.15)$$

$$\phi = b \phi_n \quad \text{at the cathode} \quad (3.16)$$

where $a$ and $b$ are constants, $n$ is the outward unit normal and we have made use of Ohm’s Law relating the current density to the normal derivative of the potential [8]. More generally, if the surface properties depend upon position along the electrodes equations (3.10) and (3.11) take the form

$$\phi = V - a(r_a) \phi_n \quad \text{at the anode} \quad (3.17)$$

$$\phi = b(r_c) \phi_n \quad \text{at the cathode} \quad (3.18)$$

where $r_a$ and $r_c$ are positions on the anode and cathode respectively. This description may be needed, for example, if flow entry or exit effects are considered, as in the case of the electrolyte being pumped along the electrode gap and machining behaviour at the extremities of the electrodes is being examined.

A clear description of the relationship between current and potential is given by Bard and Allen [37]. In particular, the effects of overpotentials upon current distributions in the one-dimensional case are discussed. Crucial to modelling these effects is the exchange current density $J_0$. This is the equilibrium level at which the net current is zero and the cathodic and anodic currents densities, $J_a$ and $J_c$ respectively, are equal in magnitude. Thus,

$$J_0 = -J_a = J_c. \quad (3.19)$$

The role of $J_0$ is apparent when considering the relation between current and overpotential $\eta$. A standard case is

$$J = J_0 \left[ \frac{C_O}{C_O^*} \exp \left( \frac{\alpha_a F \eta}{RT} \right) - \frac{C_R}{C_R^*} \exp \left( \frac{-\alpha_c F \eta}{RT} \right) \right] \quad (3.20)$$

where $C_O^*$ and $C_R^*$ are the bulk concentrations of the reactants and $C_O$ and $C_R$ are their concentrations at the electrode/electrolyte interface [37]. If the exchange current is large then the system can supply large currents at small overpotentials. The lower the exchange current, the more sluggish are the kinetics. The transfer coefficients $\alpha_a$ and $\alpha_c$ indicate the symmetry of the energy barrier to reactions and they consequently influence the net rates of reactions and directions of current flow. The exchange current density and the transfer coefficients can be obtained
Figure 3.2: Relationship between the overpotential $\eta$ and the ratio $J/J_i$ of current density to the exchange current density [37]: $\alpha_a = \alpha_c = 0.5$, $n = 1$, $T = 298$ K, $J_{i,c} = -J_{i,a} = J_i$. Curves are labelled by the value of $J_0/J_i$.

from experimental data. In most systems $\alpha_a$ and $\alpha_c$ lie between 0.3 and 0.7 but they are often approximated by 0.5 in the absence of experimental data.

At the limiting current, the electrode erosion process is occurring at the maximum rate possible, as reduction or oxidation takes place as fast as ions can be brought to the electrode surface. By defining the anodic and cathodic limiting currents as $J_{i,a}$ and $J_{i,c}$ respectively, the ratios of surface to bulk value concentrations in equation (3.20) may be written in terms of the current density,

$$\frac{C_O}{C^*_O} = 1 - \frac{J}{J_{i,a}}, \quad \frac{C_R}{C^*_R} = 1 - \frac{J}{J_{i,c}}. \quad (3.21)$$

In turn, equation (3.20) may be rewritten [37] as

$$J = J_0 \left[ \left(1 - \frac{J}{J_{i,a}}\right) \exp \left(\frac{\alpha_a F}{RT} \eta\right) - \left(1 - \frac{J}{J_{i,c}}\right) \exp \left(\frac{-\alpha_c F}{RT} \eta\right) \right]. \quad (3.22)$$

---

---

When electricity starts to flow, chemical changes begin to take place. At the positive electrode, oxidation occurs as electrons are pulled from negatively charged ions. The DC source pumps these electrons through the external electrical circuit to the negative electrode, the cathode. At the cathode, reduction takes place as the electrons are picked up by positively charged ions.
This formulation is extremely useful when mass transfer effects cannot be ignored and is rearranged easily to give $J$ as an explicit function of $\eta$. See Figure 3.2.

A widely used example is the Butler-Volmer equation, describing the system kinetics for an electrode where the exchange current density $J_0$ is insensitive to the reactant concentration and the surface concentrations do not differ appreciably from the bulk values. Thus,

$$J = J_0 \left[ \exp \left( \frac{\alpha_a F}{RT} \eta \right) - \exp \left( \frac{-\alpha_c F}{RT} \eta \right) \right].$$  (3.23)

A dimensionless number that is useful in characterising the current distribution is the Wagner number,

$$Wa = \frac{\kappa}{L} \left( \frac{\partial \eta}{\partial J} \right)_{m}$$  (3.24)

where $L$ is a characteristic length and $J_m$ is the average current density. The Wagner number is a measure of the sensitivity of the overpotential to the current distribution. At higher levels of the Wagner number the overpotential is more sensitive to changes in the current density, so that the current distribution over the electrode surface becomes more uniform. In general, an explicit expression for the partial derivative in equation (3.24) cannot be obtained from the expressions (3.20) - (3.23) except in the limiting cases of high and low overpotentials - corresponding to Tafel and linear kinetics respectively - and in the special case when $\alpha_a = \alpha_c$. For the Butler-Volmer equation, in the limiting cases, the Wagner numbers are defined as

$$Wa_T = \frac{\kappa RT}{LJ_m F \alpha_i} \quad \text{and} \quad Wa_L = \frac{\kappa RT}{LJ_0 F (\alpha_a + \alpha_c)}$$  (3.25)

respectively, where $\alpha_i = \alpha_a$ at high positive overpotentials and $\alpha_i = \alpha_c$ at high negative overpotentials.

3.3.2 The Evolution Equation

A Steady State Description: The Cosine Law

Let a point $r_c$ lie on the cathode surface as shown in Figure 3.3. In most practical machining conditions the inter-electrode gap $h$ is very small and in the case where the electrodes may be regarded as equipotential surfaces - $\phi = 0$ on the cathode and $\phi = V$ on the anode - it may be reasonable to expect the potential to vary linearly across the electrode gap. A first-order approximation to the steady-state anode position is then given by the Cosine Law.

Let the feed rate of the cathode be $u$. Let $\gamma$ be the angle between the direction of feed and the unit normal $\mathbf{n}$ at $r_C$. In the stationary state each point on the
anode surface can be related to a point on the cathode surface through the normal vector to the cathode and must move the distance $u$ per unit time in the feed direction. The dissolution rate, therefore, must be

$$\dot{m} = \rho_m u \cos[\gamma(r_C)]. \quad (3.26)$$

where $\rho_m$ is the density of the anode metal. Using Ohm's Law (3.2) and Faraday's Law (3.4) it is readily shown that

$$h = \frac{1}{c \cos[\gamma(r_C)]]} \quad (3.27)$$

where we define the constant

$$c = \frac{\rho_m u z F}{\alpha \kappa V}. \quad (3.28)$$

The anode surface may therefore be constructed as

$$r_A = r_C + \frac{n(r_C)}{c \cos[\gamma(r_C)]}. \quad (3.29)$$

This approach locally approximates the curved surface problem by the planar problem that arises by considering the machining of the tangent plane at $r_C$. It has, however, a number of drawbacks. No transient effects are considered as it relies on a steady-state assumption and it approximates only final relative configurations. Further, the linearisation is inappropriate where the radius of curvature of the cathode is comparable to the gapwidth. In addition, the assumption of the electrodes being equipotential surfaces is restrictive.
Transient Descriptions

Let \( r(t) = (x, y, z) \) be a point on the moving anode surface \( h(x, y, z, t) = 0 \). When conditions are such that Faraday’s Law is applicable the rate of erosion of metal is directly proportional to the normal derivative of the electric potential at the anode surface,

\[
\mathbf{n} \cdot \frac{d\mathbf{r}}{dt} = M \phi_n
\]  

(3.30)

where \( M \) is a positive constant. To cover cases when the machining rate is non-Faradaic we generalise (3.30) to

\[
\mathbf{n} \cdot \frac{d\mathbf{r}}{dt} = F(\phi_n)\phi_n \text{ on } h(x, y, z, t) = 0
\]  

(3.31)

where \( F(\phi_n) \) is a function dependent upon the local electric field strength. Note that, this generalisation is equivalent to setting \( W = F(\phi_n)\phi_n \) in equation (3.12), relating the rate of local metal removal to the local electric field strength. It is now readily shown that the evolution equation may be written as

\[
\frac{\partial h}{\partial t} = W(\phi_n)|\nabla h|.
\]  

(3.32)

If the coordinate system is fixed in the cathode surface and it is assumed that the cathode is moved towards the anode workpiece at a uniform velocity \( v \), then the evolution equation becomes

\[
\frac{\partial H}{\partial t} - v \cdot \nabla H = -W(\phi_n)|\nabla H| \text{ on } H(x, y, z, t) = 0,
\]  

(3.33)

where \( H(x, y, z, t) \) describes the evolution of the workpiece relative to the position of the cathode surface at time \( t \).

It remains to discuss the form taken by the function \( F(\phi_n) \). When the machining is Faradaic, then \( F(\phi_n) = M \) a constant, but, as discussed by McGeough and Rasmussen [12], the appropriate form of \( F(\cdot) \) is more generally dependent upon a number of variables such as current efficiency, the local current density and the local field strength. In the case of electrochemical arc machining, the rate of gas production and the breakdown of the electrolyte-gas mixture at critical values of the applied voltage and the electric field are also extremely important.

For some electrolytes the current efficiency is relatively constant over a wide range of current densities whereas for others the current efficiency changes with current density. In ECM, McGeough and Rasmussen [12] suggest a function \( \mathcal{H}(J) \) of the form

\[
\mathcal{H}(J) = \mu \left\{ 1 - \exp \left[ -\beta_e J^2 \right] \right\},
\]  

(3.34)
where \( J = -\kappa \phi_n \), as suitable for describing the change in the current efficiency with current density for electrolytes such as sodium nitrate - see Figure 3.4. \( M_e \) is a proportionality constant, \( \mu \) is the maximum value of current efficiency for that electrolyte and \( \beta_e \) is a parameter embodying the process variables. In this case,

\[
F = M_e \mu \left( 1 - \exp \left[ -\beta_e J^2 \right] \right).
\] (3.35)

In arc erosion, the breakdown of an electrolyte-gas mixture is the basis for the formation of arc discharges across the electrode gap. These discharges are only to be expected when both the applied voltage and the local electric field exceed critical values \( V_c \) and \( E_c \) respectively and experimental evidence indicates that the rate of metal removal is proportional to the energy of the arcs [43]. Thus, McGeough and Rasmussen [12] suggest

\[
\mathbf{n} \cdot \frac{dr}{dt} \propto E^2
\] (3.36)

and a form of \( F(\phi_n) \) consistent with the observed behaviour and experimental evidence is

\[
F(\phi_n) = \frac{1}{2} M_a E \left( 1 + \tanh \left[ \beta_a \left( E - E_c \right) \right] \right)
\] (3.37)
Figure 3.5: Schematic representation of the variation of the electric field function with field [12].

where \( E = |\nabla \phi|, \beta_a \) is a parameter that controls the steepness of \( F \) near \( E = E_c \) and \( M_a \) is a constant of proportionality. A representation of this relation is given in Figure 3.5.\(^5\)

A complete description of the ECAM process is provided by a combination of the ECM and arc erosion models. In practice, the applied voltage varies with time, typically as a fully-rectified d.c. voltage of frequency 100 Hz and maximum amplitude of 30 V. Whilst ECM takes place throughout the process, arcing will only occur when the threshold voltages and fields are reached. Consequently, the evolution equation may be written as equation (3.33) where

\[
W(\phi_n) = [\varphi F_a + (1 - \varphi) F_e] \phi_n, \tag{3.38}
\]

\( F_a \) and \( F_e \) describe respectively the erosion process in the arcing and ECM sections of the process and \( 0 \leq \varphi \leq 1 \)[12]. The parameter \( \varphi \) indicates the extent to which ECM takes place relative to arc machining. Whilst the examples of ECAM

\(^4\)When the anode is treated as an equipotential surface, \( E = |\phi_n| \) at the anode. When overpotential effects are included and the electric field is gradually varying over the anode surface then \( |\phi_n| \) is an approximation to \( E \).

\(^5\)The values of parameters \( M_a, M_e, \beta_a, \beta_e, E_c \) and \( \mu \) and have been estimated by the use of experimental data and the adjustment of process conditions. They are presented by McGeough and Rasmussen [12].
machen presented in later sections stress the arcing element of the machining process and assume $\varphi = 1$, a contribution due to ECM can be readily incorporated through varying the value of $\varphi$.

With the choice of models described above one would set

$$F_a = \frac{1}{2} M_a E \{1 + \tanh [\beta_a (E - E_c)]\}$$

(3.39)

and

$$F_e = M_e \mu \{1 - \exp \left[-\beta_e J^2\right] \}$$

(3.40)

respectively.

The transient descriptions of the anode surface evolution are utilised in the following chapter whilst examining anode dissolution under Faradaic and ECAM machining conditions.
Chapter 4

A Perturbation Approach

4.1 General Functions

This chapter describes the erosion of an anode having surface \( y = g(x,t) \) as a cathode \( y = f(x) \) advances vertically towards it at constant speed, \( v \). At each time \( t \) the electric field is taken as quasi-static, so that the erosion process is assumed to be governed by a sequence of electrostatic fields \( E = -\nabla \phi \), where the potential \( \phi(x,y) \) is harmonic and given by

\[
\nabla^2 \phi = 0, \quad -\infty < x < \infty, \quad f(x) < y < g(x,t) \\
\phi(x,f(x)) = 0 \\
\phi(x,g(x,t)) = V. 
\]

In this, we have neglected any overpotential effects and have taken the coordinate system to be fixed in the cathode so that \( g(x,t) \) specifies the anode position at time \( t \) relative to the cathode position. The problem is to determine the anode shape \( g(x,t) \) for \( t > 0 \) when the initial shape \( g(x,0) \) is specified and when, in this two-dimensional case, the evolution equation (3.33) is written as an equation for \( g(x,t) \):

\[
\frac{\partial g}{\partial t} = W(\phi_n) \sqrt{1 + g_x^2} - v. 
\]

Let the irregularities on the electrode surfaces be small in comparison to the "average" gap width, \( p(t) \), and define \( \epsilon = \epsilon_0/p(0) \ll 1 \) where \( \epsilon_0 \) is the maximum deviation of the initial irregularities from a plane case.

Nondimensionalising this problem using

\[
\bar{x} = \frac{x}{\lambda}, \quad \bar{y} = \frac{y}{\lambda}, \quad \bar{t} = \frac{t}{\tau}, \quad \bar{\phi} = \frac{\phi}{V}, \quad \bar{v} = \frac{\tau v}{\lambda}, 
\]

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where \( \tau \) is a characteristic time scale suggested by the wear function and \( \lambda \) is an appropriate characteristic length in the problem\(^1\) and describing the electrode surfaces as expansions in the small parameter \( \epsilon \)

\[
g(x,t) = p(0) \tilde{g}(\tilde{x}, \tilde{t}) = p(0)\{\tilde{p}(\tilde{t}) + \epsilon \tilde{g}_1(\tilde{x}, \tilde{t}) + \epsilon^2 \tilde{g}_2(\tilde{x}, \tilde{t}) + O(\epsilon^3)\} \quad (4.8)
\]

\[
f(x) = p(0) \tilde{f}(\tilde{x}) = p(0)\{\epsilon \tilde{f}_1(\tilde{x}) + \epsilon^2 \tilde{f}_2(\tilde{x}) + O(\epsilon^3)\} \quad (4.9)
\]

suggests that we seek solutions as perturbations to the planar case. Thus we define

\[
\tilde{\phi}(\tilde{x}, \tilde{y}, \tilde{t}) = \tilde{\phi}_0(\tilde{y}, \tilde{t}) + \epsilon \tilde{\phi}_1(\tilde{x}, \tilde{y}, \tilde{t}) + \epsilon^2 \tilde{\phi}_2(\tilde{x}, \tilde{y}, \tilde{t}) + O(\epsilon^3). \quad (4.10)
\]

Dropping bars for simplicity, we seek perturbation solutions to the nondimen-

\(^1\)If \( \lambda \neq p(0) \) it may be more natural to scale the \( y \)-variables by the gapwidth rather than by the fundamental half-wavelength. In this case, writing \( \Lambda = \lambda/p(0) \),

\[
\frac{\partial g}{\partial x} = \frac{1}{\Lambda} \frac{\partial \tilde{g}}{\partial \tilde{x}} \quad (4.6)
\]

and the Laplacian operator becomes

\[
\nabla^2 = \lambda^{-2} \left[ \frac{\partial^2}{\partial \tilde{x}^2} + \Lambda^2 \frac{\partial^2}{\partial \tilde{y}^2} \right]. \quad (4.7)
\]

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sional problem

\[ \nabla^2 \phi = 0 \quad -\infty < x < \infty, \quad (4.11) \]

\[ f(x) < y < g(x, t) \]

\[ \phi(x, f(x)) = 0 \quad (4.12) \]

\[ \phi(x, g(x, t)) = 1, \quad (4.13) \]

together with the evolution equation on \( y = g(x, t) \),

\[ \frac{\partial g}{\partial t} = W(\phi_n) \sqrt{1 + g_x^2} - \nu, \quad (4.14) \]

where

\[ \phi(x, y, t) = \phi_0(y, t) + \epsilon \phi_1(x, y, t) + \epsilon^2 \phi_2(x, y, t) + O(\epsilon^3), \quad (4.15) \]

\[ g(x, t) = p(t) + \epsilon g_1(x, t) + \epsilon^2 g_2(x, t) + O(\epsilon^3), \quad (4.16) \]

\[ f(x) = \epsilon f_1(x) + \epsilon^2 f_2(x) + O(\epsilon^3). \quad (4.17) \]

Substitution of (4.15) - (4.17) into (4.11) - (4.14) and expansion of the boundary values as functions using Taylor Series, produces a set of BVPs and evolution equations at each order in \( \epsilon \):

**O(1) Problem**

\[ \frac{\partial^2 \phi_0}{\partial y^2} = 0 \quad -\infty < x < \infty \]

\[ 0 < y < p(t) \]

\[ \phi_0(0, t) = 0 \quad (4.19) \]

\[ \phi_0(p, t) = 1 \quad (4.20) \]

\[ \frac{dp}{dt} = W(\phi_{0,y}(p)) - \nu \quad (4.21) \]

where \( \phi_{0,y} \) denotes the partial derivative of \( \phi_0(y, t) \) with respect to \( y \).

**O(\epsilon) Problem**

\[ \nabla^2 \phi_1 = 0 \quad -\infty < x < \infty \]

\[ 0 < y < p(t) \]

\[ \phi_1(x, 0, t) = -f_1(x) \phi_{0,y}(0, t) \quad (4.23) \]

\[ \phi_1(x, p, t) = -g_1(x, t) \phi_{0,y}(p, t) \quad (4.24) \]

\[ \frac{\partial g_1}{\partial t} = W'(\phi_{0,y}(p, t)) \phi_{1,y}(x, p) \quad (4.25) \]
\( O(\epsilon^2) \) Problem

\[
\nabla^2 \phi_2 = 0 \quad -\infty < x < \infty \\
0 < y < p(t)
\]

\[
\phi_2(x,0,t) = -f_2(x)\phi_{0,y}(0,t) - f_1(x)\phi_{1,y}(x,0,t)
\]

\[
\phi_2(x,p,t) = -g_2(x,t)\phi_{0,y}(p,t) - g_1(x,t)\phi_{1,y}(x,p,t)
\]

\[
\frac{\partial g_2}{\partial t} = \left[ \frac{g_{1,x}^2}{2} \right] W(\phi_{0,y})
\]
\[
+ \left[ g_1\phi_{1,y} + \phi_{2,y} - g_1 x \phi_{1,x} - \frac{g_{1,x}^2}{2} \phi_{0,y} \right] W'(\phi_{0,y})
\]
\[
+ \left[ \frac{\phi_{1,y}^2}{2} \right] W''(\phi_{0,y})
\]

In (4.29) all values of \( \phi_i \) \( (i = 0, 1, 2) \) and their derivatives are evaluated at \((x, p(t))\).

A comparison of the \( O(\epsilon^2) \) and \( O(\epsilon) \) BVPs shows that the \( O(\epsilon^2) \) problem is an “inhomogeneous version” of the \( O(\epsilon) \), the “inhomogeneous part” incorporating the solutions of \( \phi_0(y) \) and \( p(t) \) to the \( O(1) \) problem and \( \phi_1(x, y) \) and \( g_1(x, t) \) to the \( O(\epsilon) \) problem.

Note that the nonlinearity in the problem first occurs in the \( O(\epsilon^2) \) evolution equation, the right side of (4.29) being quadratic in the \( O(1) \) and \( O(\epsilon) \) solutions which are of course time-dependent.

### 4.2 The Periodic Case - Using Fourier Series

In this section we consider cases where the form of the electrode surfaces may be described by Fourier Series with time-dependent coefficients. The approach is demonstrated using the even, periodic case leading to the use of Fourier cosine series but is readily extended to cover arbitrary, periodic cases.

At time \( t \), in nondimensional terms, let the anode surface be given by

\[
g(x, t) = p(t) + \epsilon \left[ p_1(t) + \sum_{n=1}^{\infty} a_{1,n}(t) \cos(n\pi x) \right] + \epsilon^2 g_2(x, t) + O(\epsilon^3)
\]

and the cathode surface be given by

\[
f(x) = \epsilon \left[ \sum_{n=1}^{\infty} b_{1,n} \cos(n\pi x) \right]
\]
where $2\lambda$ is the fundamental wavelength of the irregularities. In terms of the model outlined in Section 4.1,

$$g_1(x, t) = p_1(t) + \sum_{n=1}^{\infty} a_{1,n}(t) \cos(n\pi x), \quad (4.32)$$

$$f_1(x) = \sum_{n=1}^{\infty} b_{1,n} \cos(n\pi x), \quad (4.33)$$

$$f_2(x) = 0 \quad (4.34)$$

and it will be necessary to determine a suitable form for $g_2(x, t)$. Substitution of (4.32) - (4.34) and the form of $g_2(x, t)$ into the BVPs given by expressions (4.18) - (4.29), solving for the potential at each order in terms of the Fourier coefficients and equating coefficients of $\cos(n\pi x)$ in each order of the evolution equation produces for the Fourier coefficients a set of ordinary differential equations with $t$ as the independent variable. Solving these ODEs determines the evolution of the electrode surface. The initial values of the Fourier coefficients are determined from the initial configuration of the electrodes. Notice that, although it is generally the case that the cathode is treated as being unaltered by the machining process, in principle, it is quite straightforward to extend this approach to model the evolution of the cathode profile and to incorporate an appropriate machining law for the cathode to produce a set of ODEs describing its evolution.\(^2\)

Unsurprisingly, the $O(1)$ problem of course predicts a uniform electric field with potential

$$\phi_0(y) = \frac{y}{p(t)} \quad (4.35)$$

and the evolution of the “$O(1)$ gap width” is given by

$$\frac{dp(t)}{dt} = W \left( \frac{1}{p(t)} \right) - v, \quad (4.36)$$

an ordinary differential equation governing the evolution of the gap width towards an equilibrium value of $p^*$ such that

$$W \left( \frac{1}{p^*} \right) - v = 0. \quad (4.37)$$

For the $O(\epsilon)$ problem, separation of variables gives

$$\phi_1(x, y, t) = -\frac{p_1(t)}{[p(t)]^2} y$$

$$+ \sum_{n=1}^{\infty} \left( \frac{b_{1,n} \sinh[n\pi(y - p)] - a_{1,n} \sinh[n\pi y]}{p \sinh[n\pi p]} \right) \cos(n\pi x) \quad (4.38)$$

\(^2\)Difficulties primarily lie in the determination of an appropriate “wear function” for the cathode.
and substitution of (4.38) into (4.25) and the equating of coefficients produces
the differential equations

\[ \frac{dp_i(t)}{dt} = -\frac{p_i(t)}{[p(t)]^2} W' \left( \frac{1}{p(t)} \right), \quad (4.39) \]

\[ \frac{da_{1,n}(t)}{dt} = -W' \left( \frac{1}{p(t)} \right) (n\pi) \left( \frac{a_{1,n} \cosh[n\pi p] - b_{1,n}}{p \sinh[n\pi p]} \right). \quad (4.40) \]

Note that (4.39) merely describes perturbations $\epsilon p_1(t)$ to solutions to (4.36) - indeed

\[ \frac{d(p + \epsilon p_1)}{dt} = W \left( \frac{1}{p(t)} \right) - \epsilon \frac{p_1(t)}{[p(t)]^2} W' \left( \frac{1}{p(t)} \right) - \nu \]

\[ = W \left( \frac{1}{p(t) + \epsilon p_1(t)} \right) - \nu + O(\epsilon^2). \]

Hence it is simplest to set $p_1(0) = 0$ giving $p_1(t) = 0$ for all time $t$. Consequently (4.39) becomes redundant.

At this stage, we highlight the fact that the derivation of the $O(\epsilon)$ solutions, relies upon the assumption that the evaluation of hyperbolic functions at the electrode surfaces $y = g(x,t)$ and $y = f(x)$ may be adequately approximated by their values at the leading order approximations, $y = p$ and $y = 0$ respectively. Consequently, a further restriction $n\pi \varepsilon_0/\lambda \ll 1, \forall n \in \mathcal{N}$ must be imposed. An analysis of the error has been carried out by Fitzgerald [15] concluding that the potential approximation is in fact a good one even for $n\pi \varepsilon_0/\lambda \gg 1$ and the field approximation is good for values of $n\pi \varepsilon_0/\lambda$ up to order unity. For values of $n\pi \varepsilon_0/\lambda \gg 1$ it is concluded that in practice these contributions are rapidly smoothed or are of negligible influence in shaping. This is demonstrated by an inspection of the form of equation (4.40). The coefficients of the higher harmonics will be most rapidly reduced during a smoothing ($b_{1,n} = 0$) process and, as discussed by Fitzgerald and McGeough [15], while the results presented here will not be appropriate to the initial smoothing of profiles with wavelengths that are small in comparison to the height of the irregularities, it will be the lower order harmonics that will dominate the smoothing process and the overall smoothing times will be largely unaffected.

For the special case of shaping for constant gapwidth $p = p^*$ of an initially flat anode $a_{1,n}(0) = 0$ by a surface with $b_{1,n} \neq 0$, equation (4.40) has solution

\[ a_{1,n}(t) = b_{1,n} \text{sech}[n\pi p] \left\{ 1 - \exp \left( -W' \left( \frac{1}{p} \right) \frac{n\pi t}{p} \coth[n\pi p] \right) \right\}. \quad (4.41) \]

Notice that for $a_{1,n}(t) \to b_{1,n} \text{sech}[n\pi p]$ for suitably large $t$ a restriction on the form of $W$ is that $W'(1/p) \geq 0$. This is consistent with the greater rates of
dissolution that occur as the electrode gap is narrowed and Fourier components with small wavelength \((n \text{ large})\) will have only a small effect on the shaping process. Whilst this behaviour agrees with the physical machining process of smoothing, it also highlights the unsuitability of our perturbation approach to cases where the final, desired workpiece surface is to possess sharp corners in its profile and it is a stimulus for the adoption of the \textit{Boundary Integral Method} approach detailed in Chapter 5.

An examination of the \(O(1), O(\epsilon)\) and \(O(\epsilon^2)\) problems indicates that since \(g_1(x,0)\) is even in \(x\) both \(\phi_1(x,y)\) and \(g_1(x,t)\) will be even functions of \(x\). Further, it will only be necessary to seek \textit{even} solutions to the higher order problems.

Proceeding with the \(O(\epsilon^2)\) problem, we seek, therefore, even solutions

\[
g_2(x,t) = p_2(t) + \sum_{n=1}^{\infty} a_{2,n}(t) \cos(n\pi x) \tag{4.42}
\]

and

\[
\phi_2(x,y,t) = \alpha_{2,0}(t) y + \Lambda_2(t) + \sum_{n=1}^{\infty} \left( \gamma_{2,n}(t) e^{n\pi y} + \delta_{2,n}(t) e^{-n\pi y} \right) \cos(n\pi x) \tag{4.43}
\]

where \(\alpha_{2,0}, \gamma_{2,n}\) and \(\delta_{2,n}\) are time-dependent, Fourier cosine coefficients to be determined by the boundary conditions (4.27) and (4.28). Notice that the form of these boundary conditions also indicate that a time-dependent term \(\Lambda_2(t)\) be included in (4.43) to account for the alteration to the contribution at the zeroth harmonic that can arise with the multiplication of Fourier series.

For notational clarity, we define

\[
R_{1,n}(t) = n\pi \frac{b_{1,n} - a_{1,n} \cosh[n\pi p]}{p \sinh[n\pi p]}, \tag{4.44}
\]

\[
Q_{1,n}(t) = n\pi \frac{b_{1,n} \cosh[n\pi p] - a_{1,n}}{p \sinh[n\pi p]}, \tag{4.45}
\]

such that

\[
\phi_{1,y}(x,p,t) = \sum_{n=1}^{\infty} R_{1,n}(t) \cos(n\pi x) \tag{4.46}
\]

and

\[
\phi_{1,y}(x,0,t) = \sum_{n=1}^{\infty} Q_{1,n}(t) \cos(n\pi x). \tag{4.47}
\]

In equations (4.27) and (4.28) the final term is now written as

\[
\sum_{n=1}^{\infty} b_{1,n} \cos(n\pi x) \sum_{n=1}^{\infty} Q_{1,n} \cos(n\pi x) = D_{2,0}(t) + \sum_{n=1}^{\infty} D_{2,n}(t) \cos(n\pi x) \tag{4.48}
\]
and
\[ \sum_{n=1}^{\infty} a_{1,n} \cos(n\pi x) \sum_{n=1}^{\infty} R_{1,n} \cos(n\pi x) = C_{2,0}(t) + \sum_{n=1}^{\infty} C_{2,n}(t) \cos(n\pi x) \quad (4.49) \]
respectively, where the coefficients \( C_{2,0}, C_{2,n}, D_{2,0} \) and \( D_{2,n} \) are determined by evaluating the product of the series on the left side and equating term-by-term the coefficients of \( \cos(n\pi x) \).

Applying the boundary conditions (4.27) and (4.28) to (4.43) and solving for \( \alpha_{2,0}, \gamma_{2,n} \) and \( \delta_{2,n} \) yields \( \Lambda_2 = -D_{2,0} \) and
\[ \alpha_{2,0} = -\frac{p_2(t)}{|p(t)|^2} + \left( \frac{D_{2,0} - C_{2,0}}{p(t)} \right), \]
and
\[ \begin{pmatrix} \gamma_{2,n} \\ \delta_{2,n} \end{pmatrix} = \frac{1}{2 \sinh[n\pi p]} \begin{pmatrix} 1 & -e^{-n\pi p} \\ -1 & e^{n\pi p} \end{pmatrix} \begin{pmatrix} -a_{2,n}/p - C_{2,n} \\ -D_{2,n} \end{pmatrix}. \quad (4.51) \]

Finally, this yields the \( O(\epsilon^2) \) contribution to the potential
\[ \phi_2(x, y, t) = -\frac{1}{p(t)} \left( \frac{p_2 - D_{2,0} + C_{2,0}}{p} \right) y - D_{2,0} \]
\[ + \sum_{n=1}^{\infty} (\gamma_{2,n}(t) e^{n\pi y} + \delta_{2,n}(t) e^{-n\pi y}) \cos(n\pi x). \quad (4.52) \]

It is now possible to determine the form of the \( O(\epsilon^2) \) evolution equations. Consider equation (4.29),
\[ \frac{\partial g_2}{\partial t} = \begin{bmatrix} \frac{g_{1,x}}{2} \\ g_{1,y} \end{bmatrix} W(\phi_0, y) \]
\[ + \frac{g_{1,y} + \phi_{2,y} - g_{1,x} \phi_{1,x} - \frac{g_{1,x}^2}{2} \phi_{0,y}}{\phi_{0,y}} \]
\[ + \frac{\phi_{1,y}^2}{2} W''(\phi_0, y). \]

Only the term \( \phi_{2,y}(x, p, t) W''(\phi_0, y) \) involves \( p_2(t) \) or \( a_{2,n}(t) \) - all other terms being known from the \( O(1) \) and \( O(\epsilon) \) problems. Consequently, it is convenient to write (4.29) in the form
\[ \frac{\partial g_2}{\partial t} = \phi_{2,y} W''(\phi_0, y) + B_{2,0} + \sum_{n=1}^{\infty} B_{2,n} \cos(n\pi x) \quad (4.53) \]
where \( B_{2,0} + \sum_{n=1}^{\infty} B_{2,n} \cos(n\pi x) \) is the series produced by the evaluation of the lower order terms and the grouping together of the coefficients of \( \cos(n\pi x) \). The
differential equations determining the evolution of the $O(\varepsilon^2)$ correction to the planar anode case can now be derived as

$$\frac{dp_2(t)}{dt} = -p_2 + D_{2,0} - C_{2,0} W'(\phi_{0,y}) + B_{2,0}, \quad (4.54)$$

$$\frac{da_{2,n}(t)}{dt} = (\gamma_{2,n}(t)e^{\varepsilon y} - \delta_{2,n}(t)e^{-\varepsilon y}) (n\pi) W'(\phi_{0,y}) + B_{2,n}. \quad (4.55)$$

In conclusion, to order $\varepsilon^2$, the full solution to the potential problem is

$$\phi(x, y, t) = \frac{y}{p(t)} + \eps \left[ \frac{-p_1(t)}{[p(t)]^2} y + \sum_{n=1}^{\infty} \left( \frac{b_{1,n} \sinh[n\pi(y-p)] - a_{1,n} \sinh[n\pi y]}{p \sinh[n\pi p]} \right) \cos(n\pi x) \right]$$

$$+ \eps^2 \left[ -\frac{1}{p(t)} \left( \frac{p_2 - D_{2,0} + C_{2,0}}{p} \right) y - D_{2,0} \right.$$  
$$\left. + \sum_{n=1}^{\infty} \left( \gamma_{2,n}(t)e^{\varepsilon y} + \delta_{2,n}(t)e^{-\varepsilon y} \right) \cos(n\pi x) \right], \quad (4.56)$$

with $\gamma_{2,n}$ and $\delta_{2,n}$ given by (4.50) and the anode profile, to order $\varepsilon^2$, is described by

$$g(x, t) = p(t) + \eps \left[ \sum_{n=1}^{\infty} a_{1,n}(t) \cos(n\pi x) \right]$$

$$+ \eps^2 \left[ p_2(t) + \sum_{n=1}^{\infty} a_{2,n}(t) \cos(n\pi x) \right] + O(\varepsilon^3) \quad (4.57)$$

together with the solutions to the ODEs (4.36), (4.39), (4.40), (4.54) and (4.55).

### 4.2.1 Machining Regimes

It is profitable at this point to review the different methods of machining presented in this work, namely Faradaic, ECAM and ECM with current efficiency.

Recall from Chapter 2 that under Faradaic machining, it is assumed that all charge arriving at the surface is utilised in dissolving the metal atoms with no other reactions taking place. The machining process is described by Faraday's Law relating the machining rate $\dot{m}$ to the current density $J$ at the anode surface,

$$\dot{m} = \frac{AJ}{zF}$$

where $A$ is the atomic weight of the metal, $z$ the valency of the metal ions and $F$ is Faraday's constant. In this case, wear function $W(\phi_n) = F(\phi_n)\phi_n$ of equation (4.14)

$$\frac{\partial g}{\partial t} = W(\phi_n)\sqrt{1 + g_x^2} - v,$$
takes the form

\[ W(\phi_n) = M\phi_n, \]  

(4.58)

- i.e. \( F(\phi_n) = M \) where \( M \) is a constant machining parameter.

The Faradaic description of the machining process is an idealised one and in practice other physical and chemical phenomena occur that affect the dissolution process. For example, the evolution of gas can occur in preference to the dissolution of metal. A more appropriate description of the machining process is then given by models that include the effects of current efficiency. The discussion of Section 2.2.6 and of equation (3.34) indicate the importance of current efficiency effects upon the machining rate. The significant effect upon our work is that the rate of metal dissolution is no longer linearly related to the current density. Indeed, it is possible that the rate of metal dissolution is reduced rather than increased as the current density increases. In the present work, this variable relationship between the metal dissolution and the current density is not examined other than through the inclusion of some representative behaviour of current efficiency effects in the evolution equation. Thus, our form of the wear function incorporating the effects of current efficiency is

\[ W(\phi_n) = M \frac{e^{J_n}}{\mu} \exp \left\{ -\beta_e J_n^2 \right\} \phi_n \]  

(4.59)

where \( J = \kappa \nabla \phi \cdot \mathbf{n} \). In practice, the model can be easily amended to include a description of the current efficiency appropriate to the particular choice of electrolyte\(^4\).

In contrast to these ECM-based machining techniques, ECAM is a method of metal removal that also incorporates the effects of electrical discharges or arcs within an electrolyte. Metal is removed from the anodic workpiece by both electrochemical dissolution and the arcs formed between the electrodes. Electrochemical machining occurs throughout the machining cycle while arc discharges occur only when the electrolyte is broken down. The ECAM machining process is described by equation (3.37)

\[ F_a(\phi_n) = \frac{1}{2} M_a E \left\{ 1 + \tanh \left[ \beta_a (E - E_c) \right] \right\} \phi_n \]

and the form of the wear function that incorporates both the ECAM and ECM regimes is (3.38)

\[ W(\phi_n) = [\varphi F_a + (1 - \varphi) F_e] \phi_n. \]

\(^3\)See the discussion of equation (3.35) for further details.

\(^4\)We assume a description consistent with the current efficiency of sodium nitrate. See Figure 3.5
Table 4.1: Machining Parameter Values

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Faradaic</th>
<th>ECAM</th>
<th>ECM + curr.eff</th>
</tr>
</thead>
<tbody>
<tr>
<td>V (V)</td>
<td>20</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>$M_e$ ($cm^2 sec^{-1} V^{-1}$)</td>
<td>$1.7 \times 10^{-5}$</td>
<td>-</td>
<td>$1.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>$M_a$ ($cm^2 sec^{-1} V^{-2}$)</td>
<td>-</td>
<td>$7.0 \times 10^{-7}$</td>
<td>-</td>
</tr>
<tr>
<td>$\beta_a$ ($cmV^{-1}$)</td>
<td>-</td>
<td>0.005</td>
<td>-</td>
</tr>
<tr>
<td>$\beta_e$ ($cm^2 V^{-2}$)</td>
<td>-</td>
<td>-</td>
<td>$1.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\mu$ (dimensionless)</td>
<td>-</td>
<td>-</td>
<td>0.8</td>
</tr>
<tr>
<td>$\lambda$ ($cm$)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>$E_c$ ($V cm^{-1}$)</td>
<td>-</td>
<td>450</td>
<td>-</td>
</tr>
<tr>
<td>$p$ ($cm$)</td>
<td>0.05</td>
<td>0.005</td>
<td>0.05</td>
</tr>
<tr>
<td>$\epsilon$ ($cm$)</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
</tbody>
</table>

The function $F_e$ describes the ECM machining process and in our model can be chosen appropriately to represent ECM machining under the Faradaic or current efficiency regimes.

Some examples are now presented of the model applied under each of the machining regimes.

### 4.2.2 Results

In this section we present some examples of both the smoothing and the shaping of the anode surface whilst ignoring the effects of overpotentials.\(^5\) In particular, we consider the evolution of the anode surface, firstly, when it is initially either sinusoidal or nearly sawtooth\(^6\) in profile and the cathode is planar (smoothing) and, secondly, when the anode is planar and the cathode profile is either sinusoidal or nearly sawtooth (shaping). Further, the effects of the machining regime - Faradaic, ECAM or ECM with Current Efficiency - are also presented. In each case, the cathode is moved at a constant velocity, so maintaining a constant mean gap width. Parameter values used in these calculations are given in Table 4.1.

Important factors in a practical machining process are, besides the accuracy of smoothing or shaping of the anode surface, the time taken to machine to some prescribed level of tolerance and the related amount of stock metal removed. We present details of these in the following examples.

---

\(^5\)These effects are considered in the next section.

\(^6\)In this case the anode surface is regarded as a rounded wedge where the discontinuity in the normal at the top and base of sawtooth has been eliminated. For example, for a wedge described by $f(x) = \epsilon \left(1 - \frac{|x|}{\delta}\right)$, for a small value $\delta$, $f(x)$ is replaced by $w(x) = ax^2 + c$ whenever $x \in (-\delta, \delta)$ with $a$ and $c$ chosen to preserve continuity in the function and its derivatives.
Faradaic Smoothing

Figures 4.2 (a) and (b) show the evolution of the electrode gap and the time required to smooth the initial maximum irregularity of a sinusoidal anode profile by a planar cathode, under Faradaic machining conditions. As expected, the anode becomes smooth with time, the electrode gap settling uniformly at the constant non-dimensional mean value \((p/\lambda)\). The accompanying table displays the loss of stock metal in terms of equivalent gap widths and the time taken to smooth the initial maximum irregularity to the specified percentage tolerance of its initial value. Thus, to reduce the irregularity to 20\% of its initial value takes 9.8 seconds with the depth of metal removed along the anode surface being equivalent to 1.33 gap widths. The earlier stages of machining are detailed in Figure 4.3(a), the initial machining being greatest at the peaks whilst favouring points closer to the plane cathode. Further, the effects of including the \(O(\epsilon^2)\) terms can be seen in a small reduction in the machining times displayed in Figure 4.3(b). Similarly, Figures 4.4 and 4.5 illustrate the smoothing of a sawtooth anode.
### Table 4.2: Tolerance Stock Metal Loss (gap widths) and Machining Times (secs)

<table>
<thead>
<tr>
<th>Tolerance</th>
<th>Stock Metal Loss (gap widths)</th>
<th>Machining Times (secs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%</td>
<td>1.33</td>
<td>9.8</td>
</tr>
<tr>
<td>10%</td>
<td>1.92</td>
<td>14.1</td>
</tr>
<tr>
<td>5%</td>
<td>2.47</td>
<td>18.2</td>
</tr>
</tbody>
</table>

(a) Time evolution of the gap width.

(b) Smoothing times to $O(\varepsilon^2)$ of the maximum initial irregularity.

Figure 4.2: Faradaic smoothing of a sinusoidal anode whilst maintaining a constant average gap. Intermediate profiles are at 3 second time intervals.
(a) Time evolution of the gap width.

(b) Smoothing times to $O(\epsilon)$ and $O(\epsilon^2)$ of the maximum initial irregularity.

Figure 4.3: Faradaic smoothing of a sinusoidal anode whilst maintaining a constant average gap. Intermediate profiles are at 1 second time intervals.
<table>
<thead>
<tr>
<th>Tolerance</th>
<th>Stock Metal Loss (gap widths)</th>
<th>Machining Times (secs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%</td>
<td>1.14</td>
<td>8.4</td>
</tr>
<tr>
<td>10%</td>
<td>1.77</td>
<td>13.0</td>
</tr>
<tr>
<td>5%</td>
<td>2.34</td>
<td>17.2</td>
</tr>
</tbody>
</table>

(a) Time evolution of the gap width.

(b) Smoothing times to $O(c^2)$ of the maximum initial irregularity.

Figure 4.4: Faradaic smoothing of a sawtooth anode profile whilst maintaining a constant average gap. Intermediate profiles are at 3 second time intervals.
(a) Time evolution of the gap width.

(b) Smoothing times to $O(\varepsilon)$ and $O(\varepsilon^2)$ of the maximum initial irregularity.

Figure 4.5: Faradaic smoothing of a sawtooth anode profile whilst maintaining a constant average gap. Intermediate profiles are at 1 second time intervals.
A comparison of these two cases is presented in Figure 4.6. As expected, the initial removal of metal is greater for the sawtooth anode - the greater curvature of the surface towards the points of the sawtooth enhancing the current flow to the anode. After some time, as we would expect, the erosion rates in the two cases become similar as the effects of higher harmonics diminish and machining is dominated by the leading order coefficient. Notice, also, that the machining times and the corresponding stock metal losses are lower when the anode is a sawtooth rather than sinusoidal. This is consistent with the greater initial smoothing rates that occur in the sawtooth case.

As explained in sections 4.1 and 4.2 it is necessary that \( E_0 \ll p(0) \) and \( n\pi\epsilon_0/\lambda \ll 1 \). These conditions restrict the applicability of the perturbation analysis to a small class of problems, providing the main justification for the more general modelling approach described in the following chapter. The restrictiveness of the first of these conditions is now discussed with reference to Figures 4.7, 4.8 and 4.9 where the effect of the magnitude of the mean gap width upon the anode potential and the electric field are displayed.

Figure 4.9 shows the calculated non-dimensionalised potential \( (\phi/V) \) along the anode surface for the cases when \( p = 0.05\text{cm} \) and \( p = 0.005\text{cm} \) with a fixed value of \( \epsilon = 0.001\text{cm} \). When \( p = 0.05\text{cm} \) the variation in potential from the expected unit value is extremely small - a maximum of 0.001 % - whereas when \( p = 0.005\text{cm} \) the variation is much larger - a maximum of 0.8 %. Although, this second variation from the true potential is not large, it has a significant effect upon the calculation of the electric field. This is shown in Figures 4.7 and 4.8. In Figure 4.7, when \( p = 0.05\text{cm} \), the variation in the electric field is at most 3.75% of the leading order value whereas in Figure 4.8 the electric field can vary from the leading order value by as much as 25%. The large contribution of higher order corrections that this necessitates indicates the inapplicability of the method to describe accurately machining under the second electrode configuration. The use, therefore, of this method to describe ECAM machining under the conditions described by McGeough and Rasmussen [12] is inappropriate.

The results of the calculation of the electric field require further consideration. An examination of Figure 4.7 indicates that there is indeed a higher electrical field - and, therefore, current density - at the points closest to the cathode. Further, the higher values of the electric field around \( x = 0 \) in Figure 4.7(b) in comparison to those of Figure 4.7(a) confirm the effect that the local geometry of the anode

\[ \text{To cover the general case of a shaped anode, upon calculating the potential and its derivatives at } y = p \text{ for each order of } \epsilon, \text{ a Taylor series about } y = p \text{ produces the potential along the anode surface.} \]
Figure 4.6: Comparison of the gap evolution and smoothing times during the Faradaic smoothing of sinusoidal and sawtooth anode profiles whilst maintaining a constant average gap. Intermediate profiles are at 3 second time intervals.
Figure 4.7: The nondimensional electric field to $O(1)$, $O(\epsilon)$ and $O(\epsilon^2)$ calculated on the anode surface, prior to smoothing: $V = 25V$, $p = 0.05cm$, $\epsilon = 0.001cm$, $\lambda = 0.2cm$
Figure 4.8: The nondimensional electric field to $O(1)$, $O(\epsilon)$ and $O(\epsilon^2)$ calculated on the anode surface, prior to smoothing: $V = 25V$, $p = 0.005cm$, $\epsilon = 0.001cm$, $\lambda = 0.2cm$
Figure 4.9: The nondimensional potential calculated on the anode surface, prior to smoothing: $V = 25V$, $\epsilon = 0.001cm$, $\lambda = 0.2cm$

Figure 4.10: The smoothing times of a sinusoidal anode at applied voltages of 10, 20 and 25 volts. In this case, $M_e = 10^{-5}cm^2sec^{-1}V^{-1}$.
will play in the machining process - a "lightning conductor effect" taking place. Under Faradaic machining, since current density is directly proportional to the electric field, the anode dissolution will be greatest around \( x = 0 \) and smallest where \( |x| = 1 \). The local geometry is also responsible for the higher values of the electric field at \( |x| = 1 \) in the sinusoidal case than in the sawtooth case. This is consistent with the more rapid smoothing times of sawtooth profiles as more metal is removed at the peaks but less at the troughs of the wedge than in the sinusoidal case. Consequently, the electrode gap width becomes uniform more rapidly. The greater stock metal loss at each level of tolerance during the smoothing of the sinusoidal profile is explained, therefore, by the larger initial removal of metal from "troughs" than in the sawtooth case, compounded by the comparatively smaller removal of metal from the "peaks".

Finally, Figure 4.10 displays the effect of the applied voltage upon smoothing times. As one would expect, smoothing is faster with higher applied voltages. The accompanying loss of stock metal in machining to a fixed level of tolerance, however, is the same in each case. This is because under Faradaic machining, the rate of dissolution of metal is directly proportional to the applied voltage. When overpotential effects are included or when ECAM machining occurs, it is to be expected that these stock metal losses will vary as the applied voltage is altered.

**ECAM Smoothing**

In this section the ECAM smoothing of the anode is considered. As discussed in the previous section, the model is inapplicable under the typical ECAM machining configurations described by McGeough and Rasmussen [12]. It is, however, worthwhile applying the model with favourable electrode configurations and evolution equation (3.37)

\[
F(\phi_n) = \frac{1}{2} M_a E \{1 + \tanh[\alpha (E - E_c)]\}
\]

in order to examine possible effects and influences on ECAM smoothing.

Figures 4.11 and 4.12 detail the ECAM smoothing of a sinusoidal and sawtooth anode, respectively, when the mean electrode gap is 0.05cm. Figure 4.13 displays a comparison of the evolution and smoothing times. Once again, to smooth to a specified tolerance is quicker in the sawtooth case than in the sinusoidal case.

---

8 The small-scale oscillations in the profile are due to a frequency cut-off with higher order frequencies being ignored. Here we consider the first 100 modes.

9 For example, at each applied voltage, the equivalent to 1.33 gap widths of stock metal are eroded when smoothing to a tolerance of 20%.

10 For example, replacing \( p = 0.005\text{cm} \) by \( p = 0.05\text{cm} \).
case with less stock metal being lost. In both cases, however, by comparing
the entries in the accompanying Tables, appreciably less stock metal is lost under
ECAM machining regimes than in the Faradaic case, despite the longer smoothing
times. This is explained by the presence of threshold field strengths and current
densities below which no metal is eroded. It is possible, therefore, that only some
parts of the anode (where the field strength is above the threshold level) are
shaped while other parts (where the field strength is below the threshold level)
are left unaltered. This differs from the Faradaic model where anode dissolution
occurs whenever a current passes. For the case of a sinusoidal anode profile under
both machining regimes, Figures 4.14 and 4.15 display the difference in the gap
evolution and the smoothing times.

The influence of the electric field threshold parameter $E_c$ upon smoothing
times is shown in Figure 4.16. It is interesting to note that, as $E_c$ is increased,
smoothing times do not necessarily also increase. For example, as it is increased
from 200 to 450 V/cm, smoothing times actually decrease. This is because for
lower potential differences the threshold level restricts metal dissolution to only
those areas where the electric field is sufficiently high and there is little or no stock
metal loss outwith these areas. This is reflected in the entries in the accompany-
ing Table. The irregularities on the anode surface will thus be eliminated more
rapidly. As the threshold level is increased further still, a point is reached where
dissolution is reduced everywhere sufficiently to increase the overall smoothing
time.
<table>
<thead>
<tr>
<th>Tolerance</th>
<th>Stock Metal Loss (gap widths)</th>
<th>Machining Times (secs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%</td>
<td>0.40</td>
<td>18.6</td>
</tr>
<tr>
<td>10%</td>
<td>0.59</td>
<td>27.3</td>
</tr>
<tr>
<td>5%</td>
<td>0.72</td>
<td>33.2</td>
</tr>
</tbody>
</table>

Figure 4.11: ECAM smoothing of a sinusoidal anode. Intermediate profiles are at 3 second time intervals.
<table>
<thead>
<tr>
<th>Tolerance</th>
<th>Stock Metal Loss</th>
<th>Machining Times</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%</td>
<td>0.37</td>
<td>16.9</td>
</tr>
<tr>
<td>10%</td>
<td>0.54</td>
<td>24.7</td>
</tr>
<tr>
<td>5%</td>
<td>0.61</td>
<td>27.9</td>
</tr>
</tbody>
</table>

(a) Time evolution of the gap width.

(b) Smoothing times to \(O(\varepsilon)\) and of the maximum initial irregularity.

Figure 4.12: ECAM smoothing of a sawtooth anode. Intermediate profiles are at 3 second time intervals.
Figure 4.13: Comparison of the gap evolution and smoothing times during the ECAM smoothing of sinusoidal and sawtooth anode profiles whilst maintaining a constant average gap. Intermediate profiles are at 3 second time intervals.
Figure 4.14: Comparison of the smoothing of a sinusoidal profile under Faradaic and ECAM machining. Intermediate profiles are at 3 second time intervals.

Figure 4.15: Smoothing times of a sinusoidal profile under Faradaic and ECAM machining
<table>
<thead>
<tr>
<th>Tolerance</th>
<th>Stock Metal Loss (gap widths)</th>
<th>Machining Times (secs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%</td>
<td>0.54</td>
<td>15.9</td>
</tr>
<tr>
<td>10%</td>
<td>0.78</td>
<td>23.6</td>
</tr>
<tr>
<td>5%</td>
<td>1.04</td>
<td>31.2</td>
</tr>
</tbody>
</table>

Ec = 450

<table>
<thead>
<tr>
<th>Tolerance</th>
<th>Stock Metal Loss (gap widths)</th>
<th>Machining Times (secs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%</td>
<td>0.30</td>
<td>13.9</td>
</tr>
<tr>
<td>10%</td>
<td>0.45</td>
<td>20.7</td>
</tr>
<tr>
<td>5%</td>
<td>0.60</td>
<td>27.4</td>
</tr>
</tbody>
</table>

Figure 4.16: Comparison of the ECAM smoothing of a sawtooth profile with varying threshold values, $E_c$. 
Table 4.2: Smoothing times and Stock metal losses for a sinusoidal irregularity

<table>
<thead>
<tr>
<th>Process</th>
<th>Tolerance</th>
<th>Stock Metal Loss (gap widths)</th>
<th>Stock Metal Loss (mm)</th>
<th>Machining Times (secs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Faradaic</td>
<td>20%</td>
<td>1.33</td>
<td>0.67</td>
<td>9.8</td>
</tr>
<tr>
<td>ECAM</td>
<td>20%</td>
<td>0.40</td>
<td>0.20</td>
<td>18.6</td>
</tr>
<tr>
<td>ECM + c.e</td>
<td>20%</td>
<td>0.75</td>
<td>0.37</td>
<td>8.6</td>
</tr>
<tr>
<td>Faradaic</td>
<td>10%</td>
<td>1.92</td>
<td>0.95</td>
<td>14.1</td>
</tr>
<tr>
<td>ECM</td>
<td>10%</td>
<td>0.59</td>
<td>0.30</td>
<td>27.3</td>
</tr>
<tr>
<td>ECM + c.e</td>
<td>10%</td>
<td>1.07</td>
<td>0.53</td>
<td>12.3</td>
</tr>
<tr>
<td>Faradaic</td>
<td>5%</td>
<td>2.47</td>
<td>1.20</td>
<td>18.2</td>
</tr>
<tr>
<td>ECAM</td>
<td>5%</td>
<td>0.72</td>
<td>0.36</td>
<td>33.2</td>
</tr>
<tr>
<td>ECM + c.e</td>
<td>5%</td>
<td>1.40</td>
<td>0.69</td>
<td>16.1</td>
</tr>
</tbody>
</table>

Comparing Smoothing Regimes

The entries in Table 4.2 indicate the machining times required to smooth a sinusoidal irregularity by a planar tool under three varying machining regimes. The parameters employed in the calculation of these entries are given in Table 4.1. The stock metal loss and the smoothing times are presented when the irregularity is smoothed to a proportion - the tolerance - of its initial value. For completeness, Table 4.2 includes the effect of current efficiency upon the smoothing process as described by equation (3.35). Note that when compared to Faradaic machining, the inclusion of the effects of current efficiency serve to reduce the smoothing times and the stock metal loss. This improvement is explained by the form of equation (3.35) which increases further the variation in the machining rate at extremes of current density. Thus, regions of high current density will operate at levels of higher current efficiency than those of low current density. As current efficiency is a measure of the difference between the observed and theoretical machining rate, its inclusion causes a localisation of the metal dissolution with regions of high curvature being smoothed more rapidly and regions of low curvature being smoothed more slowly than in the Faradaic case. Indeed, the smoothing times under the inclusion of current efficiency are also considerably lower than in the case of ECAM machining, although there is a greater accompanying loss of stock metal. In practice, however, the inter-electrode gap is considerably smaller in ECAM machining than in ECM techniques. This leads to faster rates of metal removal. As mentioned in Section 4.2.2 the application of this perturbation method is inappropriate under typical ECAM machining conditions.
Faradaic Shaping

Some brief results for the shaping of the anode under Faradaic machining conditions are now presented. Results for ECAM shaping are not presented, since the model is unsuitable under realistic ECAM electrode configurations\textsuperscript{11}.

Figures 4.17 and 4.18 display the final profiles and gap evolution of the shaping of a planar anode by a sinusoidal and sawtooth cathode, respectively. In the upper figure in each case the fixed cathode profile has been plotted next to the final anode profile. It is clear that in Figure 4.17, there is a close similarity between the two profiles but there is a "rounding" of the anode in Figure 4.18. This is consistent with the true machining behaviour and is explained by the dominance of the leading order harmonics in the machining process. The lower figures indicate the gap width. In the case where the anode is perfectly machined to match the cathode profile, a horizontal line at the equilibrium gap width \((p - e)/\lambda\) would be observed. Figure 4.19 is a measure of the "rounding" effect with the lower lying curves indicating a closer resemblance to the cathode profile.

\textsuperscript{11}That is, small electrode gap widths relative to the surface variations.
Figure 4.17: Faradaic etching of a sinusoidal cathode whilst maintaining a constant average gap: $V = 20$ volts, $p = 0.5$ mm, $\epsilon = 0.01$ mm, $\lambda = 2.0$ mm, $\Delta t = 0.01$. Intermediate profiles are at 3 second time intervals.
Figure 4.18: Faradaic etching of a sawtooth cathode whilst maintaining a constant average gap: $V = 20$ volts, $p = 0.5$ mm, $\epsilon = 0.01$ mm, $\lambda = 2.0$ mm, $\Delta t = 0.01$. Intermediate profiles are at 3 second time intervals.
Figure 4.19: Comparison of the Faradaic primary etching times of a sinusoidal and sawtooth cathode at an applied voltage of 20V. The y-axis indicates the difference between the anode peak-to-trough height \((A_p - A_t)\) and that of the cathode \((C_p - C_t)\) as a proportion of \(C_r = 1 - (A_p - A_t) / (C_p - C_t)\).

### 4.3 Modelling the Effect of Overpotentials

When overpotential effects are present, the boundary condition applied to Laplace’s equation at the true anode surface must be modified. Traditionally, the overpotential \(\eta = V - \phi\), the difference between the anode potential \(V\) and the value of \(\phi\) predicted by Laplace’s equation in the electrolyte, is given by the Tafel equation,

\[
\eta = A + B \ln J
\]

with \(a\) and \(b\) constant and \(J\) the current density. This equation is, however, derived from the more complex boundary condition represented by the Butler-Volmer equation (3.23)

\[
\kappa \frac{\partial \phi}{\partial n} = J_0 \left[ \exp \left( \frac{\alpha a F \eta}{RT} \right) - \exp \left( -\frac{\alpha c F \eta}{RT} \right) \right].
\]

It is necessary in the derivation of the Tafel equation to assume that the chemical reaction opposed by the overpotential is negligible [44]. This section gives a closer examination of how this boundary condition affects the machining model.

Using the non-dimensionalisation employed earlier, the boundary condition (4.61) is re-written in the form

\[
\frac{\kappa V \partial \tilde{\phi}}{\lambda J_0 \partial \tilde{n}} = \left[ \exp \left( \frac{\alpha a F V \tilde{\eta}}{RT} \right) - \exp \left( -\frac{\alpha c F V \tilde{\eta}}{RT} \right) \right],
\]

68
where $V\bar{\eta} = \eta$. Dropping the bars for simplicity, if the heights of the initial irregularities in the anode surface are $O(\epsilon)$ then [44]

$$\frac{\kappa V}{\lambda J_0} \sim O\left(\frac{1}{\epsilon^q}\right) \quad \text{and} \quad \frac{\alpha_a F V}{RT} \sim O\left(\frac{1}{\epsilon}\right),$$

where $q \sim 2$ and, introducing the parameter $\beta = \alpha_c/\alpha_a \sim O(1)$, we now consider a boundary condition of the form

$$\frac{K}{\epsilon^q} \frac{\partial \phi}{\partial n} = \left[ \exp\left(\frac{1}{\epsilon \eta}\right) - \exp\left(-\frac{\beta}{\epsilon \eta}\right)\right], \quad (4.63)$$

where $K$ is a constant reflecting the conductivity of system. An examination of equation (4.63) reveals that if $\eta \sim O(\epsilon^m)$ where $0 \leq m < 1$ such that $\eta/\epsilon$ is large, the second term is exponentially small. Fitzgerald & McGeough [15] suggest that $\eta \sim O(\sqrt{\epsilon})$ and the Tafel formulation will be valid in these cases.

With reference to the approach adopted earlier in this chapter, when the Tafel formulation is valid, the non-dimensional boundary value problem is

$$\nabla^2 \phi = 0 \quad -\infty < x < \infty$$

$$f(x, t) < y < g(x, t)$$

$$\phi(x, f(x, t)) = 0$$

$$\phi(x, g(x, t)) = 1 + \epsilon q \ln(\epsilon) - \epsilon \ln\left(K \frac{\partial \phi(x, g(x, t))}{\partial n}\right)$$

prompting a search for solutions in the form

$$\phi(x, y, t) = \phi_0(y) + \epsilon \ln \epsilon \psi_1(x, y) + \epsilon \phi_1(x, y) + \epsilon^2 \ln^2 \epsilon \psi_2(x, y) + \epsilon^2 \ln \epsilon \psi_3(x, y) + \epsilon^2 \phi_2(x, y) + O(\epsilon^3 \ln^3 \epsilon), \quad (4.67)$$

$$g(x, t) = g_0(t) + \epsilon \ln \epsilon G_1(x, t) + \epsilon g_1(x, t) + \epsilon^2 \ln^2 \epsilon G_2(x, t) + \epsilon^2 \ln \epsilon G_3(x, t) + O(\epsilon^3 \ln^3 \epsilon). \quad (4.68)$$

Note, the first correction to the leading order solution is now expected at $O(\epsilon \ln \epsilon)$ rather than at $O(\epsilon)$. This contrasts with the approach of Fitzgerald and McGeough [15] where the correction term in the presence of overpotentials remains at order $\epsilon$. Rather than the above Tafel formulation, however, we will use the forms of solution (4.67) and (4.68) to examine the boundary value problem when the boundary condition (4.66) is replaced by the more general condition (4.63).

Equation (4.63) may be re-written in the form

$$\frac{\partial \phi}{\partial n} = \epsilon^q F\left(\frac{1 - \phi}{\epsilon}\right). \quad (4.69)$$
where \( F(u) = \frac{\exp(u) - \exp(-\beta u)}{K} \). With the chosen scaling, \( \phi_n(x, g(x, t)) \sim O(1) \) and hence \( F(u) \sim O(\epsilon^{-q}) \) when \( u = \epsilon^{-1}(1 - \phi) \sim O(1) \). Thus,

\[
e^u \sim O(\epsilon^{-q})
\]

and since on \( y = g(x, t) \)

\[
u = \frac{1 - \phi_0}{\epsilon} - \ln \epsilon \psi_1 - \phi_1 + O(\epsilon \ln^2 \epsilon)
\]

it can be shown that by expanding \( \exp(u) \) as a Taylor series about \( y = g_0(t) \),

\[
1 - \phi_0 = 0,
\psi_1 + G_1 \phi_{0,y} = q.
\]

Hence

\[
\exp(u) = \epsilon^{-q} \exp(-\phi_1 + g_1 \phi_{0,y}) \{ 1 + O(\epsilon \ln^2 \epsilon) \}
\]

and expanding the right side of (4.69) as a Taylor series about \( y = g_0(t) \) it is easily shown that

\[
F(u) = \frac{1}{K} \exp \left( \frac{1 - \phi_0}{\epsilon} \right) \epsilon^{-(\psi_1 + G_1 \phi_{0,y})} \exp \left( -\phi_1 + g_1 \phi_{0,y} \right) \left\{ 1 - \exp \left( \frac{-(\beta + 1)(1 - \phi_0)}{\epsilon} \right) \epsilon^{(\beta + 1)(\psi_1 + G_1 \phi_{0,y})} \exp \left( ((\beta + 1)(\phi_1 + g_1 \phi_{0,y})) + O(\epsilon \ln^2 \epsilon) \right) \right\}.
\]

Further, \( \phi_1 + g_1 \phi_{0,y} \sim O(1) \) and consequently, using (4.72) and (4.73)

\[
F(u) = \epsilon^{-q} \frac{1}{K} \exp \left( -\phi_1 + g_1 \phi_{0,y} \right) \{ 1 + O(\epsilon \ln^2 \epsilon) \}.
\]

An examination of the \( \exp(-\beta u) \) term indicates that its contribution will be \( O(\epsilon^{q(\beta + 1)}) \), verifying the appropriateness of the Tafel form of the boundary condition.

Expanding the boundary conditions as Taylor series and equating appropriate coefficients produces the following BVPs and evolution equations.\(^\text{12}\)

\[O(1)\] Problem

\[
\frac{\partial^2 \phi_0}{\partial y^2} = 0 \quad -\infty < x < \infty
\]

\[
0 < y < g_0(t)
\]

\[
\phi_0(0, t) = 0
\]

\[
\phi_0(g_0, t) = 1
\]

\[
\frac{dg_0}{dt} = W(\phi_0, g_0) - \nu
\]

\(^\text{12}\)Recall, the cathode profile is \( f(x) = \epsilon f_1(x) + \epsilon^2 f_2(x) + O(\epsilon^3) \).
where $\phi_{0,y}$ denotes the partial derivative of $\phi_0$ with respect to $y$.

\textbf{$O(\epsilon \ln \epsilon)$ Problem}

\begin{equation}
\nabla^2 \psi_1 = 0 \quad -\infty < x < \infty \quad (4.81)
\end{equation}

\begin{equation}
0 < y < g_0(t)
\end{equation}

\begin{equation}
\psi_1(x, 0) = 0 \quad (4.82)
\end{equation}

\begin{equation}
\psi_1(x, g_0) = q - G_1(x, t)\phi_{0,y}(g_0) \quad (4.83)
\end{equation}

\begin{equation}
\frac{\partial G_1}{\partial t} = W'(\phi_{0,y}(g_0))\psi_{1,y}(x, g_0) \quad (4.84)
\end{equation}

\textbf{$O(\epsilon)$ Problem}

\begin{equation}
\nabla^2 \phi_1 = 0 \quad -\infty < x < \infty \quad (4.85)
\end{equation}

\begin{equation}
0 < y < g_0(t)
\end{equation}

\begin{equation}
\phi_1(x, 0) = -f_1(x)\phi_{0,y}(0) \quad (4.86)
\end{equation}

\begin{equation}
\phi_1(x, g_0) = -\ln(K) - \ln(\phi_{0,y}(g_0)) - g_1(x, t)\phi_{0,y}(g_0) \quad (4.87)
\end{equation}

\begin{equation}
\frac{\partial g_1}{\partial t} = W'(\phi_{0,y}(g_0))\phi_{1,y}(x, g_0) \quad (4.88)
\end{equation}

\textbf{$O(\epsilon^2 \ln^2 \epsilon)$ Problem}

\begin{equation}
\nabla^2 \psi_2 = 0 \quad -\infty < x < \infty \quad (4.89)
\end{equation}

\begin{equation}
0 < y < g_0(t)
\end{equation}

\begin{equation}
\psi_2(x, 0) = 0 \quad (4.90)
\end{equation}

\begin{equation}
\psi_2(x, g_0) = -G_2(x, t)\phi_{0,y}(g_0) - G_1(x, t)\psi_{1,y} \quad (4.91)
\end{equation}

\begin{equation}
\frac{\partial G_2}{\partial t} = \left[ \frac{G_{1,x}^2}{2} \right] W(\phi_{0,y})
\end{equation}

\begin{equation}
+ \left[ G_1\psi_{1,yy} + \psi_{2,y} - G_1\psi_{1,x} - \frac{G_{1,x}^2}{2}\phi_{0,y} \right] W'(\phi_{0,y})
\end{equation}

\begin{equation}
+ \left[ \frac{\psi_{1,y}^2}{2} \right] W''(\phi_{0,y}) \quad (4.92)
\end{equation}
\( O(\epsilon^2 \ln \epsilon) \) Problem

\[ \nabla^2 \psi_3 = 0 \quad -\infty < x < \infty \]
\[ 0 < y < g_0(t) \]

\[ \psi_3(x, 0) = -f_1(x) \psi_{1,y}(x, 0) \quad (4.94) \]

\[ \psi_3(x, g_0) = -G_3(x, t) \phi_{0,y}(g_0) - g_1(x, t) \psi_{1,y} \]
\[ -G_1(x, t) \phi_{1,y} - \frac{\psi_{1,y}}{\phi_{0,y}} \quad (4.95) \]

\[ \frac{\partial G_3}{\partial t} = \left[ G_{1,x} g_{1,x} \right] W(\phi_{0,y}) \]
\[ + \left[ g_1 \phi_{1,y} + G_1 \phi_{1,y} + \phi_{3,y} - g_1 x \psi_{1,x} - G_{1,x} g_{1,y} - G_{1,x} \phi_{1,x} \right] W'(\phi_{0,y}) \]
\[ + \left[ \psi_{1,y} \phi_{1,y} \right] W''(\phi_{0,y}) \quad (4.96) \]

\( O(\epsilon^2) \) Problem

\[ \nabla^2 \phi_2 = 0 \quad -\infty < x < \infty \]
\[ 0 < y < g_0(t) \]

\[ \phi_2(x, 0) = -f_2(x) \phi_{0,y}(0) - f_1(x) \phi_{1,y}(x, 0) \quad (4.98) \]

\[ \phi_2(x, g_0) = -\phi_{0,y}(g_0) g_2 - g_1(x, t) \phi_{1,y}(g_0) - \frac{\phi_{1,y}}{\phi_{0,y}} \quad (4.99) \]

\[ \frac{\partial g_2}{\partial t} = \left[ \frac{g_{1,x}^2}{2} \right] W(\phi_{0,y}) \]
\[ + \left[ g_1 \phi_{1,y} + \phi_{2,y} - G_{1,x} \phi_{1,x} - \frac{g_{1,x}^2}{2} \phi_{0,y} \right] W'(\phi_{0,y}) \]
\[ + \left[ \frac{\phi_{1,y}^2}{2} \right] W''(\phi_{0,y}) \quad (4.100) \]

Notice that, in comparison to the primary machining model described by equations (4.18) - (4.29), the nonlinearity in the problem now occurs at \( O(\epsilon^2 \ln \epsilon) \) rather than at \( O(\epsilon^2) \). Further, the first correction to the leading order solution occurs at \( O(\epsilon \ln \epsilon) \) rather than \( O(\epsilon) \). These corrections are due solely to the presence of overpotentials but the \( O(\epsilon^2 \ln \epsilon) \) terms provide a measure of the interaction of the electrochemical and geometrical effects.

Numerical solutions to the boundary value problems represented by equations (4.77) - (4.100) are now presented.

4.3.1 Results

Results for the smoothing and shaping of the anode in the presence of overpotentials are now presented. Only Faradaic machining conditions are considered where a direct comparison with the primary machining cases (overpotential effects not modelled) can be made.
Faradaic Smoothing

Figure 4.20 compares the gap evolution during the primary and secondary smoothing of a sinusoidal and a sawtooth anode. The profiles describing the evolution under secondary machining include the modelling of overpotentials as described in the previous section. Most strikingly, the equilibrium gap width is altered from the primary machining case owing to the presence of higher order constant gap-width contributions. Figure 4.21 shows that there is a slight increase in smoothing times. The nondimensional overpotential along the anode surface is displayed in Figure 4.22(a). These values are in good agreement with Fitzgerald and McGough [15]. Figure 4.22(b) indicates how the current density varies with the overpotential. The gradient of this curve is inversely proportional to the Wagner number which is a measure of the sensitivity of the overpotential to the current distribution.
(a) Gap evolution of a sinusoidal anode.

(b) Gap evolution of a sawtooth anode.

Figure 4.20: Gap evolution under Faradaic smoothing conditions whilst maintaining a constant leading order gap: (a) Primary machining, ignoring the effect of overpotentials; (b) Secondary machining where overpotentials are included ($q = 2$). Intermediate profiles are at 3 second time intervals.
Figure 4.21: Faradaic smoothing times of sinusoidal and sawtooth anodes under primary and secondary machining conditions ($q = 2$) whilst maintaining a constant average gap.

Faradaic Etching

The etching of a sinusoidal and sawtooth cathode on a plane anode are represented in Figures 4.23 and 4.24. A comparison with the primary cases - Figures 4.17 and 4.18 - indicates that the “rounding” is more pronounced when overpotentials are present. This is to be expected as they serve the purpose of bringing greater uniformity in the current density across the anode surface. Consequently, the effects of extreme values are diminished. It is also interesting to note that the equilibrium electrode gap is also greater in the secondary case than in the primary case. Figure 4.26 shows a comparison of the degree of shaping in the primary and secondary cases.

4.4 A Final Comment

In this Chapter a variety of machining configurations have been examined. It has been highlighted, however, that a model based upon a perturbation approach is only applicable in a limited number of cases and is not suitable for the modelling of ECAM machining under “real-world” configurations. Further examination of this is, therefore, left to the following chapter.
(a) Comparison of etched anode workpiece profile to the cathode.

(b) Time evolution of the gap width.

Figure 4.23: Faradaic secondary etching of a sinusoidal cathode whilst maintaining a constant leading order gap: $V = 20$ volts, $p = 0.5$ mm, $\epsilon = 0.01$ mm, $\lambda = 2.0$ mm, $\Delta t = 0.01$. Intermediate profiles are at 3 second time intervals.
(a) Overpotential along the anode surface.

(b) Overpotential ($\eta$) v Current Density ($J_a = -J$).

Figure 4.22: A comparison of the overpotential and current density on sinusoidal and wedge shaped anodes at the outset of smoothing ($K=1$).
Figure 4.24: Faradaic secondary etching of a sawtooth cathode whilst maintaining a constant leading order gap: $V = 20$ volts, $p = 0.5$ mm, $\varepsilon = 0.01$ mm, $\lambda = 2.0$ mm, $\Delta t = 0.01$. Intermediate profiles are at 3 second time intervals.
Figure 4.25: Comparison of Faradaic primary and secondary etching of plane anode whilst maintaining a constant leading order gap: $V = 20$ volts, $p = 0.5$ mm, $\epsilon = 0.01$ mm, $\lambda = 2.0$ mm, $\Delta t = 0.01$. 
Figure 4.26: Comparison of the Faradaic primary and secondary etching times of a sinusoidal and wedge-shaped cathode at an applied voltage of 20V. The y-axis indicates the difference between the anode peak-to-trough height ($A_p - A_t$) and that of the cathode ($C_p - C_t$) as a proportion of $C_p - C_t : 1 - (A_p - A_t) / (C_p - C_t)$.
Chapter 5

The Boundary Integral Method

As outlined in previous chapters, the rate of dissolution (machining) of the work-
piece (the anode) at each point of its surface depends upon the current normal to
the workpiece surface and any reasonable model of the dissolution process must
accurately determine the distribution of this current. A full and rigorous analysis
of the ECM process would require formulating and solving a set of mass trans-
port equations along with equations for the distribution of the electric potential
while also considering the flow of electrolyte in the inter-electrode gap. Clearly,
this is an extremely large undertaking leading to extensive calculations. In some
situations, however, the model may be considerably simplified by neglecting those
processes which are known to have little influence.

It is known physically that, during anodic dissolution, the inter-electrode gap
can be treated as two regions: one, the boundary layer, at the electrode surface
where effects of ionic species transport must be considered and where the elec-
tric potential gradient and species concentration gradients can be significant; the
other, away from the electrode surfaces, in the bulk solution, where the electrolyte
concentration can be assumed to be governed by convective transport processes
and where derivatives of concentration are small. The presence of these two dif-
fering regions requires separate mathematical treatment and leads to a boundary
layer analysis of the problem. This is examined more closely in the chapter 6 .
It is mentioned here, however, that the transport mechanisms and the thickness
of the diffusion layer are extremely important in determining the rate of anodic
dissolution.

In this chapter, we will examine the situations where it is possible to incor-
porate the boundary layer behaviour within the potential problem by choosing a
suitable boundary condition. A Boundary Integral Method for solving the prob-
lem is described that yields the current distribution for electrodes of irregular
shape. The machining rate at points on the workpiece boundary is subsequently
determined. A theoretical justification of the technique and a description of its
numerical implementation are presented.

We summarise our solution procedure as follows.

1. From a given electrode configuration, determine the electric field by solving Laplace's equation with suitably imposed boundary conditions at the electrode surfaces.

2. Use an evolution equation to determine the rate of metal removal from the anode surface and to describe the change in the anode surface position over a small time increment.

3. Reformulate the boundary value problem in terms of the new electrode configuration.

4. Re-solve for the updated electric field.

It should be noted that solving the potential problem in a region of general shape is not a straightforward undertaking and involves numerical techniques. In the next section we will formulate a more rigorous mathematical model of the above problem, describe the method utilised to solve the potential problem and will discuss forms of the evolution equation.

5.1 An Integral Representation of Laplace's Equation

Referring to Figure 5.1, suppose that Laplace's equation

\[ \nabla^2 \phi = 0 \quad (5.1) \]

is valid within an irregularly-shaped domain \( \Omega \) described by a finite boundary \( \Gamma = \Gamma_1 \cup \Gamma_2 \cup \ldots \cup \Gamma_N \). On each subinterval \( \Gamma_j \) the potential \( \phi \), its normal derivative \( \phi_n \) or, more generally, a relation between them is prescribed. Only in a small number of simple cases is it possible to determine \( \phi \) analytically and, in general, it is necessary to solve (5.1) using numerical techniques. One standard approach is to rewrite Laplace's equation and the accompanying boundary conditions in the form of an integral equation. Under suitable assumptions, it is then possible to use information derived from the boundary data to determine the form of the potential or its derivatives throughout the computational domain, \( \Omega \cup \Gamma \).
5.1.1 Integral Equation based on Green's Theorem

The foundations for the construction of an integral representation of the solution to (5.1) lie in Green's identities [45]. The Second Identity states that for twice differentiable, scalar functions $\phi$ and $G$ in a bounded, closed domain $\Omega$ with boundary $\Gamma$,

$$\int_{\Omega} (G \nabla^2 \phi - \phi \nabla^2 G) \, d\Omega = \int_{\Gamma} (G \phi_n - G_n \phi) \, d\Gamma \tag{5.2}$$

where the subscript "n" denotes differentiation in the direction of the outward normal to $\Gamma$.

By choosing $G$ as a fundamental solution of Laplace's equation $\nabla^2 G = 0$ in $\Omega$, which is singular only at a point $q \in \Gamma$, Green's second identity may be reduced to an integral equation relating $\phi$ to $\phi_n$ on $\Gamma$. With reference to Figure 5.2 illustrating the manner in which the domain and its boundary may be formed in a practical machining example, we comment that it is sufficient that $\Gamma$ be piecewise smooth\(^1\) and that discontinuities in the normal derivative may occur. It is permissible, therefore, for the boundary $\Gamma$ to contain sharp edges and corners.

---

\(^1\)We define a surface $S$ to be parametrically represented in the form $r(u, v) = x(u, v)i + y(u, v)j + z(u, v)k$ for $(u, v) \in \mathcal{R}$ where $\mathcal{R}$ is some region in the $uv$-plane. A normal vector, $n$ of $S$ at a point $P$ given by $(x(u, v), y(u, v), z(u, v))$ is $n = r_u \wedge r_v$, where the subscript denotes partial differentiation. $S$ is described as a smooth surface if at every point $P$ on $S$, there is a unique definition for $n$. $S$ is piecewise smooth if it consists of finitely many smooth portions. [45]
Furthermore, the portions $\Gamma_1, \ldots, \Gamma_4$ of $\Gamma$ may consist of several smaller segments possessing distinct boundary conditions. For example, some sections of the tool or workpiece may be insulated, other parts conducting and the boundary conditions on these sections will correspondingly differ.

The standard choice of $G$ for two-dimensional potential problems is

$$G(p, q) = \ln |p - q|$$

(5.3)

where $p \in (\Omega \cup \Gamma)$ and $q \in \Gamma$.

With this choice, the identity (5.2) reduces to Green's Boundary Formula [46], [47]

$$\alpha(p)\phi(p) = \int_{\Gamma} \ln |p - q| \frac{\partial \phi}{\partial n}(q) dq - \int_{\Gamma} \frac{\partial \ln |p - q|}{\partial n} \phi(q) dq$$

(5.4)

where $\alpha(p) = 2\pi$ if $p \in \Omega$ and $\alpha(p) = \theta(p)$ if $p \in \Gamma$, where $\theta(p)$ is the internal angle at the point $p$ between the tangents to $\Gamma$ on either side of $p$. The normal derivative $\partial/\partial n$ denotes differentiation at the point $q$ along the outward normal and $dq$ is the differential increment of $\Gamma$ at $q$.

Inspection of (5.4) reveals that if $\phi$ is known at all points of $\Gamma$, then by choosing $p \in \Gamma$ an integral equation for $\phi_n$ is obtained, so allowing $\phi_n$ to be determined at all points $p \in \Gamma$. Equation (5.4) then yields a construction for $\phi$ at all points $p \in \Omega$. Moreover, choosing $p$ as a point on $\Gamma$ gives

$$\theta(p)\phi(p) = \int_{\Gamma} \ln |p - q| \frac{\partial \phi}{\partial n}(q) dq - \int_{\Gamma} \frac{\partial \ln |p - q|}{\partial n} \phi(q) dq, \quad p \in \Gamma,$$

(5.5)

a linear relationship between the values of $\phi$ and $\phi_n$ on the boundary. Insertion of boundary conditions (3.10) and (3.11) ( or (3.13) and (3.14)) then yields an integral equation for $\phi$ or $\phi_n$. After discretization, equation (5.5) can be solved.
numerically as a set of simultaneous equations, producing the values of \( \phi \) and \( \phi_n \) on the boundary. In general, however, the boundary condition relates \( \phi \) to \( \phi_n \) nonlinearly so that an iterative approach must be adopted. Once a complete description of \( \phi \) and \( \phi_n \) on \( \Gamma \) is obtained, \( \phi \) may subsequently be calculated at any point in the computational domain through the use of the discretized form of equation (5.5).

This numerical approach is now considered in more detail.

5.2 The Numerical Implementation of the BIM

At instant \( t \), the two basic steps in the numerical procedure are

1. to solve Laplace’s equation within a region of known geometry subject to an accompanying set of boundary conditions, and

2. to evaluate the new free surface geometry a short time, \( \Delta t \), later.

The Boundary Integral Method is utilized to solve for the distribution of current along the free surface and the use of this solution with an evolution equation and a knowledge of the tool motion allows the geometry of the domain at time \( t + \Delta t \) to be determined. This implementation computes the electric fields via the boundary integral method as if they were static fields, so ignoring unsteady electromagnetic effects and so focuses on the numerical solution of equation (5.5) describing static fields.

It is necessary to discretize equation (5.5). Let \( \Gamma \) be divided into \( N \) intervals, \( \Gamma_j \), such that no corner lies within any interval \( \Gamma_j \). Thus,

\[
\Gamma = \bigcup_{j=1}^{N} \Gamma_j.
\]

The integral on the right hand side of (5.2) is now expressed as the sum of integrals

\[
\int_{\Gamma} (G\phi_n - G_n\phi) d\Gamma = \sum_{j=1}^{N} \int_{\Gamma_j} (G\phi_n - G_n\phi) d\Gamma.
\] (5.6)

A similar restatement of (5.5) is

\[
\theta(p)\phi(p) = \sum_{j=1}^{N} \left( \int_{\Gamma_j} \ln |p - q| \frac{\partial \phi}{\partial n}(q) dq - \int_{\Gamma_j} \frac{\partial \ln |p - q|}{\partial n}(q) dq \right) \] (5.7)

and the next step is to estimate the integrals within the large brackets. This requires approximations for \( \phi \) and \( \phi_n \) and for the geometry over each segment \( \Gamma_j \).
Figure 5.3: Approximation of the boundary of the computational domain by straight line segments.

In the two dimensional case, the simplest description of the boundary $\Gamma$ is an approximation by a set of straight line segments - see Figure 5.3 - with $\phi$ and $\phi_n$ treated as constant along each interval $\Gamma_j$. In such a formulation, let $q^j$ be the midpoint of the interval $\Gamma_j$ and define $\phi^j = \phi(q^j)$ and $\phi^j_n = \frac{\partial \phi}{\partial n}(q^j)$.

Then, choosing $p = q^j$ we obtain the approximation

$$\int_{\Gamma_j} \ln |q^j - q| \frac{\partial \phi}{\partial n}(q) dq \simeq \phi(q^j) \int_{\Gamma_j} \ln |q^j - q| dq \equiv \phi^j K^j_i \quad (5.8)$$

and

$$\int_{\Gamma_j} \frac{\partial \ln |q^j - q| \phi(q)}{\partial n} dq \simeq \phi(q^j) \int_{\Gamma_j} \frac{\partial \ln |q^j - q|}{\partial n} dq \equiv \phi^j L^j_i \quad (5.9)$$

where $K^j_i$ and $L^j_i$ are defined by the geometry of $\Gamma_j$ and $q^j$. Writing $\theta(q^j) = \theta_i$, allows equation (5.7) to be approximated by

$$\theta_i \phi^i = \sum_{j=1}^{N} \left( \phi^j K^j_i - \phi^j L^j_i \right), \quad (5.10)$$

so reducing (5.7) to a linear algebraic system in terms of discrete nodal values $\phi^j$ and $\phi^j_n$. When a set of boundary conditions is specified on $\Gamma$ it is possible through equation (5.7) to relate the values of $\phi^j$ and $\phi^j_n$ or to use an iterative procedure to determine an estimate of one of these quantities to a preset level of accuracy.

The next stage is to evaluate the integrals represented by $K^j_i$ and $L^j_i$.

---

2In our case, as no interval $\Gamma_i$ contains a corner and $q^i$ is the midpoint of $\Gamma_i$, $\theta(q^i) = \theta_i = \pi$. 

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5.2.1 The Evaluation of the Integrals

Let \( p \) and \( q \) be the position vectors of the points \((x_0, y_0)\) and \((x, y)\) respectively. Taking \( G(p, q) = \ln |p - q| \), it is readily shown that

\[
G_n(p, q) = \frac{\partial \ln |p - q|}{\partial n} = -\frac{1}{r^2} n \cdot (p - q)
\] (5.11)

where \( n \) is the normal to \( \Gamma \) at \((x, y)\), and \( r = |p - q| \). Therefore, since the integrands in \( K_i^j \) and \( L_i^j \) are known, it is possible, in principle, to evaluate them exactly.\(^3\) In general, the contribution from segment \( \Gamma_i \) containing \( q^i \) gives trouble since the integrand of \( K_i^j \) has a logarithmic singularity and both the numerator and denominator of \( L_i^j \) tend to zero as \( q \to q^i \). However, when straight line segments are used as an approximation to the geometry of \( \Gamma \), it is possible to perform analytically the integrations of both \( G(p, q) \) and \( G_n(p, q) \) over \( \Gamma_i \) even when \( q^i \in \Gamma_i \). Hence, the singular behaviour of the integrands is readily resolved.

Let \( \Gamma_j \) be a straight line segment of length \( 2h \) in the direction of \( t \), with normal \( n \), endpoints \( a_j \) and \( b_j \) and midpoint \( r_j \). Let \( r_0 \) be the position vector of some reference point. Then, for \( r \) representing a point in \( \Gamma_j \),

\[
r = r_j + s t
\] (5.12)

where \( s \in [-h, h] \),

\[
\int_{\Gamma_j} \ln |r - r_0| ds = \frac{1}{2} \int_{-h}^{h} \ln (|r_j + s t - r_0|^2) ds
\] (5.13)

and

\[
\int_{\Gamma_j} \frac{\partial \ln |r - r_0|}{\partial n} ds = \int_{-h}^{h} n \cdot \frac{(r_j + s t - r_0)}{|r_j + s t - r_0|^2} ds.
\] (5.14)

\(^3\)If a more sophisticated method of approximating the boundary geometry is employed, for example the use of shape functions, in general an analytic evaluation of the integrals is not possible and a numerical technique must be adopted.
Some manipulation yields, for \( r_0 \notin \Gamma_j \),
\[
\int_{\Gamma_j} \ln |r - r_0| \, ds = (b_j - a_j) \cdot t + \frac{1}{2} (b_j - r_0) \cdot t \ln (|b_j - r_0|^2) + (b_j - r_0) \cdot n \tan^{-1} \left( \frac{(b_j - r_0) \cdot t}{(b_j - r_0) \cdot n} \right) - \frac{1}{2} (a_j - r_0) \cdot t \ln (|a_j - r_0|^2) - (a_j - r_0) \cdot n \tan^{-1} \left( \frac{(a_j - r_0) \cdot t}{(a_j - r_0) \cdot n} \right)
\] (5.15)

and
\[
\int_{\Gamma_j} \frac{\partial \ln |r - r_0|}{\partial n} \, ds = \tan^{-1} \left( \frac{(b_j - r_0) \cdot t}{(b_j - r_0) \cdot n} \right) - \tan^{-1} \left( \frac{(a_j - r_0) \cdot t}{(a_j - r_0) \cdot n} \right).
\] (5.16)

In the case where \( r_0 = r_j \in \Gamma_j \),
\[
\int_{\Gamma_j} \ln |r - r_0| \, ds = \frac{1}{2} \int_{-h}^{h} \ln (s^2) \, ds
= (b_j - a_j) \cdot t \left[ \ln \left( \frac{1}{2} (b_j - a_j) \cdot t \right) - 1 \right]
\] (5.17)

and
\[
\int_{\Gamma_j} \frac{\partial \ln |r - r_0|}{\partial n} \, ds = \int_{-h}^{h} \left( n \cdot \frac{t}{s} \right) \, ds = 0.
\] (5.18)

The result (5.16) has a geometric interpretation. The right-hand side is the negative of the angle subtended by the straight lines from the endpoints of \( \Gamma_j \) to \( r_0 \). Result (5.18) agrees with this geometric interpretation since, for \( r_0 \in \Gamma_j \), any line from \( r_0 \) to the endpoints of \( \Gamma_j \) coincides exactly with \( \Gamma_j \).

### 5.2.2 Derivation and Solution of a Linear Algebraic System

Equation (5.7) relates the value of \( \phi \) at any point \( p \in \Omega \cup \Gamma \) to the values of \( \phi \) and its normal derivative on \( \Gamma \). At any instant \( t \), the boundary \( \Gamma \) has been subdivided into \( N \) subintervals on each of which either an estimated, or the exact, value of either \( \phi \) or \( \phi_n \) is specified. By choosing to evaluate (5.10) at the midpoint of each of these subintervals - i.e. where \( p = q^i, \, i = 1, \ldots, N \) - a system of \( N \) linear equations in \( N \) unknowns is produced. In matrix form, the system may be written as,
\[
Ax = b
\] (5.19)
where

$$A_{i,j} = \begin{cases} \quad L_i^j + \delta_i^j \theta_j & \text{if } \phi^j_n \text{ is specified} \\ \quad K_i^j & \text{if } \phi^j \text{ is specified} \end{cases} \quad (5.20)$$

with $\delta_i^j$ the Kronecker-delta symbol, and

$$x_i = \begin{cases} \quad \phi^j_i & \text{if } \phi^j_i \text{ is specified} \\ \quad \phi^j_n & \text{if } \phi^j \text{ is specified} \end{cases} \quad (5.21)$$

The entries forming the $(N \times 1)$ vector $b$ consist of those terms within (5.10) that are already known. Thus, the contributing terms $b^j_i$ to $b_i = \sum_{j=1}^{N} b^j_i$ are

$$b^j_i = \begin{cases} \quad K_i^j \phi_n^j & \text{if } \phi^j_n \text{ is specified} \\ \quad (L_i^j + \delta_i^j \theta_j) \phi^j_i & \text{if } \phi^j_i \text{ is specified} \end{cases} \quad (5.22)$$

In solving for the unknown boundary values $x$, LU-decomposition of the $(N \times N)$ coefficient matrix $A$ is employed. This approach has one large advantage over the Gaussian elimination or Gauss-Jordan methods of solving the linear system (5.19), namely, that, for a fixed computational domain, the LU-decomposition of $A$ need only be computed once and thereafter the system may be solved with multiple right-hand vectors $b$ [48]. This is of particular importance, for example, when secondary machining is included in the machining model and at each timestep, an iterative method must be adopted to obtain the electric field strength on the boundary of a fixed computational domain, parameterised by $t$.

To determine an approximation to the electric potential throughout the computational domain, the solutions $x$ of (5.19) are inserted into equation (5.7), the discrete version of the integral formulation.

### 5.2.3 Updating the position of the free surface

The solution vector $x$ will include the numerical approximation to $\phi_n$ at midpoints $r(x, y, z, t) = q^i$ on exposed sections of the anode surface $h(x, y, z, t) = 0$. These approximations can be used in an appropriate form of the evolution equation,

$$\frac{dr}{dt} = F(\phi_n) \nabla \phi,$$  \quad (5.23)

to update the position of a point on the anode surface over a time increment $\Delta t$. In two-dimensions, the change in position of each exposed point $(x(t), y(t))$ on the anode surface is thus determined by the expressions

$$\frac{dx}{dt} = F(\phi_n) \phi_n \cos \theta \quad \text{and} \quad \frac{dy}{dt} = F(\phi_n) \phi_n \sin \theta,$$  \quad (5.24)

$^4$Recall that for Faradaic machining, $F(\phi_n) = M$. 

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where $\theta$ is the angle formed by the normal to the surface and the $x$-axis\(^5\). For an anode surface $y - g(x, t) = 0$ it is readily shown that
\[\cos \theta = \frac{-g_x}{\sqrt{1 + g_x^2}} \quad \text{and} \quad \sin \theta = \frac{1}{\sqrt{1 + g_x^2}} \quad (5.25)\]

and hence the updated position of an anode midpoint is approximated by the expressions
\[x(t + \Delta t) = x(t) + \Delta t F(\phi_n)\phi_n \left( \frac{-g_x}{\sqrt{1 + g_x^2}} \right) \quad (5.26)\]
\[y(t + \Delta t) = y(t) + \Delta t F(\phi_n)\phi_n \left( \frac{1}{\sqrt{1 + g_x^2}} \right) \quad (5.27)\]

### 5.2.4 Describing the free surface

At time $t$, the position of the surface is recorded as a set of points $x_j$ at ends of segments with associated midpoints $q^j$. After each midpoint has been updated to a new position at time $t + \Delta t$, cubic splines parameterized by arc length are fitted through these midpoints and a new set of endpoints of segments of equal arc length is calculated. This ensures that the computational boundary points are evenly spaced and that clustering is avoided.

The procedure is summarised below and in Figure 5.5.

1. The distance between consecutive pairs of midpoints $q^j$ is calculated,
\[l_j = \sqrt{(x_j - x_{j-1})^2 + (y_j - y_{j-1})^2} , \quad j \geq 2 , \quad (5.28)\]
where we set $l_1 = 0$ and the distance along $\Gamma$ from $q^0$ to the midpoint $q^j$ is approximated by
\[s_j = \sum_{i=2}^{j} l_i . \quad (5.29)\]

2. Cubic splines parameterized by the $s_j$ are now fitted through each of the locations of $q_j$ [48].

3. A new discretization takes place by calculating the positions of new endpoints spaced at equal arc lengths along the cubic spline representation of the boundary.

4. The position of endpoints lying before or after the first or last of the updated midpoints are calculated by extrapolation.

\[\phi_x = \phi_n \cos \theta, \phi_y = \phi_n \sin \theta.\]
5. A new set of straight line segments of equal arc length is calculated for the next timestep.

A great advantage in using arc length as a parameter for fitting the cubic splines and for determining the spacing between nodes is that around corners the distance between points can be chosen to remain small. It also avoids the problems that occur when parameterizing points by either the $x$ or $y$ coordinate. In that case it must be decided upon which of the $x$ or $y$ coordinate to choose as the parameter as gradient of the curve varies.

5.2.5 Using an adaptive timestep

When considering the movement of points as described above there can be a problem in regions of high curvature and at corners when the ordering of midpoints may "cross over" during updating from one time to the next. This physically unrealistic situation is demonstrated in Figure 5.6 but can be avoided by ensuring that the timestep is taken sufficiently small that a new discretization takes place prior to the time at which the crossing would occur.

With reference to Figure 5.6, it is clear that if the sum of the angles $\alpha$ and $\beta$ exceeds $\pi$ radians then no crossing of nodes can occur. Letting $L_j$ and $L_{j+1}$ be the distances along the normal to the anode surface from each midpoint position $q^j$ and $q^{j+1}$ to the crossover point, it is readily shown that

$$L_j = \frac{d \sin \alpha}{\sin(\pi - \alpha - \beta)} = \frac{d \sin \alpha}{\sin(\alpha + \beta)}$$
A suitable timestep $\Delta t$ is now selected by considering in turn each midpoint $q^j$ and comparing it to its neighbouring midpoints. If the predicted movement of any pair of midpoints is such that a node $q^j$ is predicted to move a distance $D_j$ that is greater than a quarter of its associated maximum $L_j$, the timestep is halved until this is no longer the case and this value $\delta t_j$ is stored. Hence we choose $\delta t_j$ such that

$$D_j(\delta t_j) \leq \frac{1}{4} L_j \quad \text{and} \quad D_{j+1}(\delta t_j) \leq \frac{1}{4} L_{j+1}.$$  \hspace{1cm} (5.30)

Once all $N$ midpoints have been compared the maximum permissible timestep $\Delta t$ is selected as the minimum value of the stored timesteps

$$\Delta t = \min \{\delta t_1, \delta t_2, \ldots, \delta t_{N-1}\}.$$  \hspace{1cm} (5.31)

At the next timestep this selected value of $\Delta t$ is used as the initial timestep and a test is made to determine whether it can be increased or requires to be
further decreased. To avoid possible problems caused by too large an increase in the timestep, the growth per timestep cannot exceed two and the timestep is bounded by a preset maximum permissible value.

An example of the use of this approach is given in Figure 5.7 which displays the smoothing of a cusp-shaped irregularity by a planar cathode with an initial timestep of 0.01 seconds. Figure 5.7(b) displays the smoothing time of the maximum irregularity with each highlighted point on the curve indicating the output time of each of the anode profiles in Figure 5.7(a). The use of an adaptive timestep is clear by examining the differences between the output times.

5.3 The BIM Related to ECM/EDM

ECM, EDM and ECAM are all machining processes that cause the surface of the anode to change shape with time. The rate of erosion of the anode surface is, as previously indicated, characterised by the current density and described by an evolution equation. When the electric potential is described by Laplace’s equation, the current density is given by Ohm’s Law and therefore, in principle, only \( \phi_n \) on the boundary need be calculated, rather than \( \phi(x, y) \) throughout the whole domain.

This section outlines how a Boundary Integral Method may be used to model an ECM/EDM process.

5.3.1 A Specification of the Computational Domain

The first practical problem in using the integral formulation (5.2) as the basis for a model of the machining problem is the requirement that the boundary \( \Gamma \) of the computational domain be closed. In some cases, the electrode configuration will be such that this is immediately satisfied. For example, annular electrode configurations such as those that occur in cross-sections of a drilling process - see Figure 5.8 - naturally give rise to closed computational domains. Other cases, however, require more careful consideration.

For example, when considering an open-ended electrode configuration such as that in Figure 5.9, this criterion requires that an artificial boundary be introduced to “close” the electrode gap. It is not immediately apparent, however, how or where the “closure” ought to be taken\(^6\). In addition, it is necessary that suit-

\(^6\)Other methods of tackling the machining problem do not necessarily have this problem. A conformal mapping approach, for example, permits the entire open-ended computational domain to be considered. Problems arise, however, both with the determination of a suitable mapping and with the requirement of its recalculation at each time-step as the anode profile evolves.
The numerical values indicate the time in milliseconds at which the profile is output. For example, 51 => 51x10^-3 secs.

(a) Anode profile evolution during Faradaic smoothing.

(b) Smoothing time of the maximum irregularity. Nodes indicate the time at which each profile in (a) is output.

Figure 5.7: An example of using an adaptive timestep in the smoothing of a cusp-shaped anode by a planar cathode situated at y = 0. Δt = 0.01 seconds if no adaptation is required. 128 segments have been used to approximate the anode.
Figure 5.8: An annular configuration of electrodes. The inter-electrode gap $\Omega$ is closed.

\[ \phi = 1 \]

\[ \Gamma_2 \]

Figure 5.9: An electrode configuration where the inter-electrode gap $\Omega$ can not naturally be treated as closed.

\[ \phi = 0 \]

\[ S_1 \]

\[ S_2 \]

\[ \Gamma_1 \]

able boundary conditions be specified on the artificial boundary. An appropriate choice of these boundary conditions is clearly essential to the solution procedure.

The machining of the anode depends, however, on local values of $\phi$ and $\nabla \phi$. Since $\phi$ is governed by Laplace’s equation for which the influence of small changes at one point decay rapidly with distance from that point, it is reasonable to close the computational domain by an approximation to $\phi$ in regions where the field is almost uniform or known to be small. With a suitable set of boundary conditions imposed upon this artificial boundary, a Boundary Integral Method of solving for the unknown gradients or potentials may then be applied.

When the anode and cathode are treated as *equipotential surfaces*, at each point $P$ in $\Omega$ the gradient of the electric potential $\phi$ is perpendicular to the surface at $P$. Also, if $\Gamma_j$ is tangential to a field line, then $\phi_n = 0$ on $\Gamma_j$. This
suggested that we try to place any required artificial boundaries on field lines by imposing the condition $\phi_n = 0$ along that boundary, solving for $\phi$ along that boundary and then recalculating $\phi_n$. If the field direction $\nabla \phi$ differs significantly from the tangent to the assumed artificial boundary, then the artificial boundary must be adjusted.

There are particular cases in which the decision as to where to close the computational domain is relatively straightforward. For example, if at some distance from the point of machining interest the electrodes are initially planar it is sensible to close the domain, using straight field lines at a suitable position, where the error in assuming uniform electric field is readily checked. One such case is depicted in Figure 5.9 where it is possible to define a closed domain by introducing a surface $S$ such that the closed boundary $\Gamma$ comprises $S_1 \cup \Gamma_1 \cup S_2 \cup \Gamma_2$.

### 5.3.2 Problems Arising from Corners and Moving Boundaries

It is recognised that the Boundary Integral Method has large errors and poor convergence near a corner [34]. Whilst errors at corners in large computational domains may not significantly affect results in other parts of the domain, in a time-marching scheme for the evolution of the domain shape the error may not remain confined to the vicinity of the corner. This can have a serious effect on the accuracy and stability of the scheme throughout the computational domain. Otta et al [34] discuss the nature of the difficulties near corners and recommend the use of a double node technique and adaptive integration to overcome some of
5.3.2.1 Double Nodes

A critical feature of the computational domain is that its boundary \( \Gamma \) is not smooth, the normal vector being discontinuous at certain nodes. The numerical procedure must allow for this multiplicity even if \( \nabla \phi \) is smooth. One method of doing this to define "double nodes" at corners. Here two nodes have the same coordinates (that of the corner point) but each belongs to a different segment with distinct normals. - see Figure 5.11.

![Figure 5.11: Double node placement at a corner. Each corner node belongs to a different side.](image)

With the use of double nodes, however, one has to be careful in forming the coefficient matrix \( A \) so as to prevent it becoming ill-conditioned or degenerating to less than full-rank [34]. Otta et al [34] discuss the manner in which the discrete form of the integral equation must be modified.

The use of double nodes is particularly relevant in our study when modelling the junction of segments of boundary which are insulated (where \( \phi_n \) is specified) with exposed segments (\( \phi \) specified).

**Neumann-Dirichlet or Neumann-Neumann Junctions**

In this case, the unknown to be computed on at least one of the segments is the potential \( \phi \). Otta et al suggest that if the Neumann boundary condition occurs on at least one of the relevant segments - say \( I_B \) - then the continuity of potential at the corner is used to improve the conditioning of the coefficient matrix. Thus

\[
\phi_{I_A} - \phi_{I_B} = 0
\]

replaces the \( I_B \)th row of \( A \), where \( \phi_{I_A} \) and \( \phi_{I_B} \) represent the potential at the corner nodes belonging to sides \( I_A \) and \( I_B \) respectively.
Dirichlet-Dirichlet Junctions

In this case the unknown to be computed on each segment is the normal flux. By requiring that the x and y components of $\nabla \phi$ at each corner node are the same on each segment, one can derive the relations

$$\phi_{s,A} \cos \beta_A - \phi_{n,A} \sin \beta_A = \phi_{s,B} \cos \beta_B - \phi_{n,B} \sin \beta_B, \quad (5.33)$$

$$\phi_{s,A} \sin \beta_A + \phi_{n,A} \cos \beta_A = \phi_{s,B} \sin \beta_B + \phi_{n,B} \cos \beta_B. \quad (5.34)$$

where $\tan \beta_A$ and $\tan \beta_B$ are the slopes at the corner of sides $I_A$ and $I_B$, respectively, (see Figure 5.12). We define $\phi_{s,A}$ and $\phi_{n,A}$ as the tangential and normal flux respectively for the node at the corner belonging to side $I_A$, with a corresponding definition for $\phi_{s,B}$ and $\phi_{n,B}$ relating to the node belonging to side $I_B$.

![Figure 5.12: Example of definition of $\beta_A$ and $\beta_B$ at corner nodes.](image)

The tangential flux terms can be approximated using the known values of $\phi$ on the boundary, so that rearranging (5.33) and (5.34) with the unknown normal fluxes on the left-hand sides gives\(^7\)

$$\phi_{n,A} \sin \beta_A - \phi_{n,B} \sin \beta_B = \phi_{s,A} \cos \beta_A - \phi_{s,B} \cos \beta_B, \quad (5.35)$$

$$\phi_{n,A} \cos \beta_A - \phi_{n,B} \cos \beta_B = -\phi_{s,A} \sin \beta_A + \phi_{s,B} \cos \beta_B. \quad (5.36)$$

Otta et al suggest that either of (5.35) or (5.36) may be used to replace row $I_A$ or $I_B$ of the coefficient matrix $A$. The choice is determined by the coefficient of diagonal terms. For example, if row $I_A$ is to be replaced and if $|\sin \beta_A| \geq |\cos \beta_A|$ choose (5.35) as the replacement, otherwise replace row $I_A$ by (5.36). Similarly, if

\(^7\)During primary machining the electric potential on the anode surface is fixed at $\phi = V$. As a consequence, no tangential fluxes exist and the right hand sides of (5.35) and (5.36) are zero, if O lies on the anode surface.
row $I_B$ is to be replaced and if $|\sin \beta_I B| \geq |\cos \beta_I B|$ then choose (5.35), otherwise choose (5.36).

5.3.2.2 Evaluation of the Integrals Near a Corner

An analysis of the accurate numerical evaluation of the integrals near a corner was performed by Otta et al [34]. They recommended the use of an adaptive integration technique where, for the purposes of integration, the original integration interval is suitably subdivided. In Figure 5.13, let a corner exist at $O$ where segments $I_A$ and $I_B$ meet. Choose $A$ as a collocation point while $I_B = OB$ is the interval of integration. If the angle $\theta$ subtended at $A$ by the integration interval exceeds $45^\circ$, then divide that interval into two subintervals. If necessary repeat for each subinterval. The integration over the original integral is obtained by summing the integrations over the subintervals.

![Figure 5.13: Subdivision of an interval $I_B$ based upon the subtended angle at $A$. (In the diagram $BC$ is taken parallel to $OA$.)](image)

In our approach, however, since the discretisation uses straight line segments to model the geometry, the integrals are evaluated analytically and their numerical accuracy is not, therefore, an issue. It was found, however, that stability and convergence was improved by ensuring that nodes were placed on the computational domain such that the above condition was satisfied during the evaluation of the integrals over the intervals intersecting the eroding boundary. More sophisticated approaches to modelling the geometry such as the use of shape functions and the quasi-spline method to approximate geometrical variation [34] would, however, need to utilize a scheme such as the one described above.
5.3.3 Secondary Machining: Incorporating the Effect of Overpotentials

Thus far in this chapter, no explicit reference to the boundary conditions has been made. In previous chapters, the need to modify the boundary condition when the effects of overpotentials are incorporated has been discussed. In subsection 3.3.1 conditions allowing the electric overpotential \( \eta \) to be related to the electric field \( \phi_n \) as governed by Laplace’s equation through the Butler-Volmer equation (3.23)

\[
\kappa \frac{\partial \phi}{\partial n} = J_0 \left[ \exp \left( \frac{\alpha_a F}{RT} \eta \right) - \exp \left( -\frac{-\alpha_e F}{RT} \eta \right) \right]
\]

were outlined. This is now used together with \( \eta = V - \phi \) as the boundary condition on the anode surface. The nonlinear nature of this equation means, however, that the boundary integral procedure problem must now be solved iteratively. This process is described schematically in Figure 5.14.

At each stage, once the anode configuration is determined and suitably discretized, the potential at each point along the anode surface is set initially to the external applied voltage \( V \) and the potential gradients are then computed at the anode using the BIM. A new approximation to the anode potential distribution is obtained by solving the Butler-Volmer equation for the effective potential \( \phi = V - \eta \) at each point along the anode surface. The potential gradients are then recomputed and the process repeated iteratively until the changes in consecutive values of potential at each point along the anode surface are below a prescribed tolerance level. The calculated values of the potential gradient are then used in the surface evolution equation (5.23) to determine how the anode surface is modified before the next time instant.

The use of an LU-decomposition approach to solving the linear system

\[
Ax = b
\]

is of great value as the approximated values to the potential distribution will affect only the vector \( b \) whilst the iteration converges during a timestep. Hence, only one LU-decomposition of \( A \) need be performed at each timestep. Its values are stored to be re-used with each new form of \( b \) that occurs whilst the overpotential is being calculated iteratively.

In our calculation of each new approximation to \( \eta \) we employed a bisection method. Whilst slow, this method has the advantage of ensuring that, provided a suitable search interval is initially given, the root will be found. To improve convergence rates, smaller search intervals can be chosen as the iteration continues. One advantage of some alternative root finding methods\(^8\) is that the solution for

\(^8\)For example, Newton-Raphson.
READ DATA

DISCRETISE SPACE

SET BOUNDARY CONDITIONS

DETERMINE MATRIX OF COEFFICIENTS IN BIM

SOLVE LINEAR SYSTEM

CALCULATE GRADIENTS

SOLVE BUTLER-VOLMER EQUATION TO CALCULATE NEW BOUNDARY POTENTIAL

CHANGE IN POTENTIAL LESS THAN TOLERANCE LEVEL

YES

MODIFY SURFACE PROFILE

NO

Figure 5.14: Flowchart describing the calculation of electric field including over-potential effects.

\( \eta \) at one timestep can be employed as the first approximation to the solution at the next timestep resulting in improved convergence rates.
5.3.4 Movement of the Cathode

In practice it is usually the case that the position of the cathode - the tool - is altered during machining to affect the machining rates and nature of the anode - the workpiece - evolution. In Chapter 4 the cathode was treated as moving vertically at a rate that would maintain the average gap-width between the tool and workpiece (or the total current). In general, however, this need not be the case. For example, when smoothing the irregularities on a workpiece, horizontal movement of the cathode may be more practical.

The BIM is well suited to the inclusion of both vertical and horizontal cathodic movement as this involves merely a new definition of the computational domain. This has been included in the model as follows:

1. The anode profile is updated.
2. The cathode position is determined at the start of the new timestep.
3. The endpoints of the cathode profile determine the new endpoints of the computational domain.
4. The positions of the anode at these new endpoints are calculated.
5. The new computational domain is discretised.
6. The BIM is applied with appropriate boundary conditions.
7. The process is repeated, starting from 1.

Thus, in principle, it is possible to include within the model a description of cathode movement in which the velocity varies with time. An illustration of this generalisation of the cathode movement is given in Figure 5.15.

5.4 Some Applications of the BIM

5.4.1 Verification of the numerical implementation of the BIM

In this section, to verify the suitability of the BIM for dealing with more general electrode configurations, results of the numerical calculation of the electric potential and electric field are presented in some simple cases.
Figure 5.15: An illustration of the inclusion within the model of both horizontal and vertical cathode movement. In the example, the vertical velocity of the cathode is such that a constant average gapwidth is maintained during Faradaic machining. The horizontal velocity is 0.5mm/sec. Here $V = 25V$ and $\Delta t = 0.01$sec.

Figure 5.16: Circular annulus with uniform boundary conditions
Primary machining

Consider a circular annulus with inner radius $\rho_1$ and outer radius $\rho_2$ as in Figure 5.16. Converting to polar co-ordinates\(^9\) allows the boundary value problem to be expressed as

\[
\nabla^2 \phi = 0, \quad \rho_1 < r < \rho_2, \quad 0 < \theta < 2\pi \tag{5.39}
\]

\[
\phi(\rho_1, \theta) = 0 \tag{5.40}
\]

\[
\phi(\rho_2, \theta) = V \tag{5.41}
\]

The solution to this BVP is independent of $\theta$ and is

\[
\phi(r) = V \frac{\ln(r) - \ln(\rho_1)}{\ln(\rho_2) - \ln(\rho_1)} \tag{5.42}
\]

so that the normal derivative of the electric potential is

\[
\frac{d\phi(r)}{dr} = \frac{V}{r} \left( \ln(\rho_2) - \ln(\rho_1) \right)^{-1}. \tag{5.43}
\]

This analytic solution is compared to the numerical BIM solutions in Table 5.1 and in Figure 5.17.

It is clear from these results that the Boundary Integral Method gives good accuracy.

A further example is now presented where the boundary condition on the outer circle is replaced by $\phi(\rho_2, \theta) = V \cos \theta$. This introduces an angular dependence into the solution but the analytic solution is readily found as

\[
\phi(r, \theta) = V \frac{\rho_2}{(\rho_2)^2 - (\rho_1)^2} \left( \frac{r^2 - \rho_1^2}{r} \right) \cos \theta. \tag{5.44}
\]

The corresponding normal derivative of the electric potential is

\[
\frac{\partial \phi(r, \theta)}{\partial r} = V \frac{\rho_2}{\rho_2^2 - \rho_1^2} \frac{\rho_1^2 + r^2}{r^2} \cos \theta. \tag{5.45}
\]

Reference to Table 5.2 and Figure 5.18 once more indicates that the method has good accuracy.

Secondary Machining

An example of the effect of incorporating overpotentials in the model is shown in Figures 5.19 and 5.20. The boundary condition (5.41) has been replaced by

\[x = r \cos \theta, \quad y = r \sin \theta.\]
Table 5.1: A comparison of the analytic and numerical solutions to equations (5.42) and (5.43) for the potential and electric field at differing values of $r$. $\phi(r_1, \theta) = 0, \phi(r_2, \theta) = V, r_1 = 0.2, r_2 = 0.3, V = 10$. The numerical grid consisted of 400 evenly-spaced nodes on the outer circle, 280 on the inner circle.

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<th>numerical potential</th>
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Table 5.2: A comparison of the analytic and numerical approximation to equations (5.44) and (5.45) for the potential and electric field. $\phi(r_1, \theta) = 0, \phi(r_2, \theta) = V \cos \theta, r_1 = 0.2, r_2 = 0.3, V = 10$. The numerical grid consisted of 400 evenly-spaced nodes on the outer circle, 280 on the inner circle.

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<th>numerical potential</th>
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<td>$\pi/4$</td>
<td>0.41909</td>
<td>0.41930</td>
</tr>
<tr>
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<td>$\pi/4$</td>
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<td>4.16373</td>
</tr>
<tr>
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<td>$\pi/4$</td>
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<td>6.76312</td>
</tr>
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<td>-5.88840</td>
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<tr>
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<td>$\pi$</td>
<td>-9.56441</td>
<td>-9.56449</td>
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</tbody>
</table>

<table>
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<th>$\theta$</th>
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<th>numerical field</th>
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<td>$\pi$</td>
<td>-86.6667</td>
<td>-86.6682</td>
</tr>
</tbody>
</table>

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Figure 5.17: A comparison of the analytical and numerical values of the electric potential $\phi$ within a circular annulus: $\phi(\rho_1, \theta) = 0, \phi(\rho_2, \theta) = V, \rho_1 = 0.2\text{mm}, \rho_2 = 0.3\text{mm}, V = 10V$. The numerical grid consisted of 400 evenly-spaced nodes on the outer circle, 280 on the inner circle.
Calculated potential in a circular annulus \( \phi(0.2, \theta) = 0, \phi(0.3, \theta) = 10 \cos(\theta) \).

Figure 5.18: A comparison of the analytical and numerical values of the electric potential \( \phi \) within a circular annulus: \( \phi(\rho_1, \theta) = 0, \phi(\rho_2, \theta) = V \cos(\theta), \rho_1 = 0.2\text{mm}, \rho_2 = 0.3\text{mm}, V = 10\text{V} \). The numerical grid consisted of 400 evenly-spaced nodes on the outer circle, 280 on the inner circle.
Figure 5.19: A comparison of the calculated numerical values of the electric potential $\phi$ and boundary values of the normal derivative $\phi_n$ within a circular annulus under both primary and secondary machining. The applied potential difference is $V = 10$, $P_1 = 0.2$ and $P_2 = 0.3$. 
overpotential

0.7
0.698
0.696
0.694
0.692
0.69

-0.3
-0.2
-0.1
0
0.1
0.2
0.3

x
y

-0.3 0.3

Figure 5.20: The calculated values of overpotential \( \eta \) on the outer boundary of a circular annulus. The applied potential difference is \( V = 10, \rho_1 = 0.2 \) and \( \rho_2 = 0.3 \).

equation (5.37) and it is assumed that a constant potential \( V \) is applied to the outer boundary. The iterative approach, described in section 5.3.3, of calculating the overpotential distribution is applied. The reduction in the normal component of the electric field is apparent in Figure 5.19, while Figure 5.20 displays the calculated uniform value of the overpotential on the outer circle.

5.4.2 Some Simple Applications

The BIM is now applied to model the workpiece evolution in some simple cases. Some more sophisticated applications of the BIM are presented in subsequent sections.

Anodic Smoothing

For smoothing of both a sinusoidal and sawtooth anode by a planar cathode, Figure 5.21 compares the smoothing times predicted by the BIM method to those of the perturbation method described in Chapter 4. Parameters listed in Table 4.1 were employed. Clearly, in both cases the BIM smoothing time closely matches those predicted by the perturbation method with \( \epsilon = 0.01 \), providing further evidence of the accuracy of the Boundary Integral model.
Figure 5.21: Comparing the BIM and Perturbation approaches. The smoothing times of a sinusoidal and a sawtooth anode by a planar cathode whilst maintaining a constant gap width under primary, Faradaic machining conditions: $V = 20V$, $p = 0.5mm$, $\varepsilon = 0.01mm$, $\lambda = 2mm$. 

(a) A sinusoidal anode.

(b) A sawtooth anode.
Figure 5.22: The effect of varying the wavelength $\lambda$ for primary, Faradaic smoothing of a sinusoidal anode by a plane cathode. The anode surface is initially given as $y = p - \epsilon \cos(\pi x / \lambda) : V = 25V, \epsilon = 0.01, p = 0.5\text{mm}$. 400 evenly-spaced nodes were used in the discretization of the anode and cathode surfaces.

Figure 5.23: The effect of varying the average gapwidth $p$ for primary, Faradaic smoothing of a sawtooth anode by a plane cathode. The anode surface is periodic, with wavelength $\lambda$ and amplitude $\epsilon : V = 25V, \epsilon = 0.01, \lambda = 2.0\text{mm}$. 400 evenly-spaced nodes were used in the discretization of the anode and cathode surfaces.
The clear advantage of the BIM over the perturbation method of Chapter 4 is that the restrictions upon the height of the electrode irregularities are no longer applicable and more general electrode configurations can be examined. For example, Figure 5.22 demonstrates the effect of varying the wavelength on the smoothing of a sinusoidal irregularity by a planar cathode. Similarly, Figure 5.23 displays the influence of the initial gapwidth $p$ upon the smoothing times of a sawtooth anode.

To model the evolution of the workpiece profile under ECAM rather than Faradaic machining the equation (3.37)

$$F(\phi_n) = \frac{1}{2} M_a E \{1 + \tanh [\beta (E - E_c)]\},$$

replaces the Faradaic form of the evolution equation. Under ECAM machining regimes, the erosion rate diminishes greatly for $E$ significantly below a threshold value $E_c$ with a consequent "localisation" of the anode dissolution and a reduction in the overall stock metal loss. Figure 5.24 provides an illustration of the secondary machining effects upon the ECAM smoothing process. In the upper figure the reduced stock metal loss is clearly seen by the difference in the uppermost primary and secondary profiles. The smoothing times shown in the lower figure, however, remain similar.

Anodic Shaping

Figure 5.25 demonstrates the influence of the critical field strength parameter $E_c$ upon anodic ECAM shaping. As one would expect, the anodic shaping is most pronounced when $E_c$ is close to the "average gapwidth" electric field strength $\sim 500 \text{ V/mm}$ in this case. In cases where the value of $E_c$ is greater than $V/p$, dissolution occurs only in those anodic regions of greatest field strength and hence of current density. Once, the gapwidth becomes more uniform, however, dissolution reduces as field strengths on the anode surface drop below the critical level. This is indicated by the flattening of the etching time curves in Figure 5.25(b). For $E_c \leq V/p$, shaping is less pronounced as dissolution is able to occur on all areas of the anode dampening the effects of regions of high curvature and lesser gapwidth. This is demonstrated in the lower lying etching time curves in Figure 5.25(b).

A further example of the shaping of the anode is given in Figure 5.26. Here, the anode profile is eroded to reflect qualitatively that of the cathode. Rounding effects, however, cause a reduction in the sharpness of the anode profile in

---

10 The departures from a planar electrode must be small in comparison to both the gapwidth and the wavelength, see Section 4.2
Figure 5.24: A comparison of the primary and secondary smoothing of the anode under ECAM machining: $V = 25\text{V}$, $E_c = 45\text{ V/mm}$, $\Delta t = 0.01\text{secs}$. 
Figure 5.25: The effect of the critical field strength $E_c$ upon Secondary ECAM shaping of an initially plane anode by a shaped cathode: $V = 25V$, $\Delta t = 0.01$secs. 64 evenly-spaced nodes were used in the discretization of the anode and cathode surfaces.
Figure 5.26: Shaping the anode by a stepped cathode moving both horizontally and vertically with a variable timestep: $V = 25V$, $\Delta t = 0.01$secs. 128 evenly-spaced nodes were used in the discretization of the anode and cathode surfaces.

comparison to that of the cathode.

The rounding of the anode profile can be reduced through the application of insulation, cathode control and ECAM machining. The ability of the BIM to incorporate these approaches is illustrated in the following sections.

5.4.3 The Effects of Tool Insulation

An advantage of adopting a Boundary Integral Method to describe the machining process is that, in principle, it is straightforward to include within the model the effects of insulated portions of the boundary. The general model (2.17) - (2.20) implies that at an insulated section of the electrode the current flux vanishes and the Neumann boundary condition $\phi_n = 0$ is applicable. Consequently, the effects of insulated electrode sections can be modelled by implementing the BIM with the Neumann rather than the Dirichlet boundary condition appropriately incorporated. Care must be taken, however, at the junction between insulated and exposed sides and here the approaches discussed in section 5.3.2.1 are adopted.

The accurate shaping of an anode is a more difficult process to accomplish than its smoothing. Edges and sharp transitions in curvature tend to be smoothed out by “rounding”. Insulation of sections of the electrodes is one means by which more
angular features can be retained or imposed. The modelling of insulated sections is incorporated by modifying the linear system of equations (5.19) through the appropriate choice of entries given by equations (5.20), (5.21) and (5.22). An example of the effects of insulation is given in Figure 5.27. The rounding effect or overcut is clearly reduced by the inclusion of insulation on the cathode surface, as demonstrated by the sharper change in the anode profile. As one would expect, when only the uppermost horizontal portion of the cathode is not insulated, the overcut is less pronounced than in the case when only the vertical section of the cathode is insulated. In the absence of any insulated regions on the cathode, the overcut is most pronounced.

Figures 5.28 and 5.29 illustrate both the primary and secondary machining of a planar anode by a stationary, stepped cathode with insulated vertical sides. Figure 5.28(b) illustrates the calculated overpotentials for secondary machining and Figure 5.29 also indicates an increase in the rounding and a decrease in metal removal rate of secondary machining.

It is clear, too, that the use of insulation on sections of a plane cathode can allow shaping to take place on the anode, where the electric field will be affected by the presence of the insulation. This is demonstrated in Figure 5.30 in which the thick horizontal lines are used to illustrate the insulated regions on the
Figure 5.28: Secondary Faradaic shaping of an initially plane anode by a stationary, stepped cathode with insulated, vertical sides: $V = 25V$, $\Delta t = 0.01$secs. 400 evenly-spaced nodes were used in the discretization of the anode and cathode surfaces.
Figure 5.29: A Comparison of Primary and Secondary Faradaic shaping of an initially plane anode by a stationary, stepped cathode with insulated, vertical sides: $V = 25V$, $\Delta t = 0.01$ secs. 400 evenly-spaced nodes were used in the discretization of the anode and cathode surfaces.
Figure 5.30: The electric field strength along the initial anode surface for the shaping of a plane anode by a plane cathode with insulated sections: $V = 25V$, $\Delta t = 0.001\text{secs}$. Here, $a/p = 1$ - i.e. 5% of the cathode is exposed, centred around $x = 0$. 200 evenly-spaced nodes were used in the discretization of the anode and cathode surfaces. The thicker lines are used to indicate the insulated regions of the cathode.

Figure 5.31: The anode profile after 1 time increment during the shaping of a plane anode by a plane cathode with insulated sections: $V = 25V$, $\Delta t = 0.001\text{secs}$, $a/p = 1$. 200 evenly-spaced nodes were used in the discretization of the anode and cathode surfaces. The thicker lines are used to indicate the insulated regions of the cathode.
Figure 5.32: The initial potential calculated throughout the electrode gap during the shaping of a plane anode by a plane cathode with insulated sections: $V = 25\text{V}$, $\Delta t = 0.001\text{secs}$, $a/p = 1$. Two hundred evenly-spaced nodes were used in the discretization of the anode and cathode surfaces. The contours display lines of equipotential.

cathode surface, ie. where $|x| > 0.005$. Figure 5.31 illustrates the erosion of the anode where only a small section of the anode surface is eroded but as one would expect, the anode shaping occurs in a region of greater extent than $a$, where $a$ is defined as the length of the exposed region in the cathode. In Figure 5.30, the ratio $a/p$ represents the extent of the exposed cathodic section as a proportion of the gapwidth $p$. Finally, the calculated potential throughout the electrode gap is shown in Figure 5.32. From the contour lines illustrating the lines of equipotential one can clearly see the variation of the electric field is closely centred around the exposed part of the cathode.

Figure 5.33 illustrates the manner in which varying the cathode insulation can affect the machining of the anode. In this case, the exposed cathodic section of length $a$ is centred around $x = 0$ and varies from 5% to 33% of the total length of the cathode. Interestingly, not only does the horizontal range of the “eroded” section of the anode surface increase with $a/p$, as less of the cathode surface is insulated, but the depth of the erosion also increases.

The ability of the algorithm to calculate secondary effects in the presence of insulated regions is shown in Figure 5.34 which illustrates the difference between the primary and secondary machining case after 3 timesteps: $\Delta t = 0.001\text{secs}$, $p = 0.05\text{mm}$. The calculated overpotentials are displayed in Figure 5.35.
Figure 5.33: The anode profile calculated after $t = 0.001$ secs with varying proportions of the central section of the cathode exposed. Two hundred evenly-spaced nodes were used in the discretization of the anode and cathode surfaces.

Figure 5.34: The anode profile calculated for primary and secondary machining with $\Delta t = 0.001$ secs and $a/p = 3.33$. Two hundred evenly-spaced nodes were used in the discretization of the anode and cathode surfaces.
5.5 Some More Detailed Examples

Figures 5.36 and 5.37 provide illustrations of the shaping of the workpiece by a semi-circular tool of radius $R$ with insulated vertical sections. In this case, the leading gapwidth $h_l$ can be determined exactly - see Figure 5.38. Converting to polar coordinates with $r = \sqrt{x^2 + y^2}$ and assuming a potential difference of $V$ between the electrodes, the function

$$\phi = V \frac{\ln(r/R)}{\ln((R + h_l)/R)}$$

is readily shown to be a solution to Laplace’s equation. This potential approximates the potential in the gap between the semicircular part of the cathode and an approximately semicircular part of the anode once equilibrium has been established. The evolution equation (3.33) can be written as

$$\frac{dr}{dt} = M_e \frac{d\phi}{dr} - v$$

(5.48)

where $M_e$ is the constant machining parameter and $v$ is the velocity of the tool normal to the workpiece surface. In equilibrium, some manipulation of equation (5.48) indicates that at the anode (i.e. where $r = R + h_l$) yields

$$\frac{R + h_l}{R} = \exp \left( \frac{VM_e}{v(R + h_l)} \right)$$

(5.49)

from which the leading gapwidth $h_l$ can be determined numerically. Figure 5.39 provides a comparison of the computed and theoretical equilibrium gapwidth for various values of the tool radius $R$ in the case when $V = M_e = v = 1.0$. Clearly
Figure 5.36: The machining of a planar anode by an insulated cathode with a semi-circular exposed section and moved vertically at 2.5 mm/sec. The thicker lines indicate the insulated sections of the cathode in its initial and final configurations: $V = 25$, $\Delta t = 0.002$, 10 timesteps. The intermediate steps are illustrated in Figure 5.37.

Figure 5.37: The evolution of a planar anode under machining by an insulated cathode with a semi-circular exposed section and moved vertically at 2.5 mm/sec. The configuration of the cathode is illustrated in Figure 5.36.
Figure 5.38: An illustration of the leading gap $h_l$, and the overcut $h_w$ for the machining of the anode by a semi-circular tool with insulated vertical sections.

Figure 5.39: The computed and theoretical equilibrium gapwidth for semi-circular tools of radius $R$ with insulated vertical sections: $V = 1, M_e = 1.0, v = 1.0.$
Figure 5.40: The convergence of the computed equilibrium gapwidth for semi-circular tools of radius $R$ with insulated vertical sections: $V = 1, M_e = 1.0, v = 1.0$.

Table 5.3: The overcut $h_w$ for semi-circular tools of varying radii, $R$.

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<tr>
<td>1</td>
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<td>2</td>
<td>1.625</td>
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<tr>
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<td>1.826</td>
</tr>
<tr>
<td>4</td>
<td>2.012</td>
</tr>
<tr>
<td>5</td>
<td>2.171</td>
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the equilibrium values of the leading gap $h_l$ as computed by the BIM closely approximate the theoretical values. This is a further validation of the BIM. The convergence of $h_l$ is displayed in Figure 5.40. Figure 5.41 illustrates the steady state workshape profiles determined by monitoring the value of the overcut $h_w$ and terminating the procedure when successive calculations of $h_w$ differ by less than a tolerance level $tol$. Clearly, the larger the radius of the tool, the greater the machining depth attained before $h_w$ converges and the greater the overcut (Table 5.3).

For the example of an insulated rectangular tool, introduced in Section 5.4.3, Figure 5.42 illustrates the evolution of the workpiece under Faradaic machining by a rectangular tool with insulated vertical sections being advanced with speed $v = 1$. This problem has an exact equilibrium solution [11] against which physical lengths such as the leading gap $h_l$, the overcut $h_o$, the leading edge gap $h_c$ and the interelectrode gap at infinite distance $h_{\infty}$ can be determined (see Figure 5.43). Table 5.4 contains the values of these lengths computed using the BIM and the
Figure 5.41: Workshape profiles determined by the convergence of the overcut $h_w$ for machining by semi-circular tools of radius $R$: $V = 1$, $M_e = 1.0$, $v = 1.0$, $tol = 10^{-3}$.

Figure 5.42: The evolution of the workshape profile for machining by a rectangular tool with insulated sections: $V = 1$, $M_e = 1.0$, $v = 1.0$. 

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Table 5.4: A comparison of the theoretical [11] and computed values of machining lengths.

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<td>0.731</td>
</tr>
<tr>
<td>$h_o/h_t$</td>
<td>0.7162</td>
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</tr>
<tr>
<td>$h_\infty/h_t$</td>
<td>0.9658</td>
<td>1.0</td>
</tr>
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Theoretical values of [11]. The computed values are a fair approximation to the theoretical values. The implementation of a more sophisticated discretisation scheme - e.g. shape functions - should improve these approximations further.

5.5.1 Cathode control and Pulsed-ECM

In practical situations, the movement of the tool can be controlled to influence the shaping of the workpiece. Thus, whilst we have so far considered the movement of the tool solely in the vertical or horizontal directions, in practice, both movements may be simultaneously combined. Within this section we present some results displaying the movement of the tool and its effect on the machining of the anode.

Figure 5.44 shows how the shaping resulting from the steady horizontal motion of a stepped cathode which is insulated on both horizontal portions. Calculations were performed using the BIM, with the time interval divided into 20
Figure 5.44: Shaping of a plane anode by a cathode moved horizontally with insulated horizontal sections: $V = 20V$, $\Delta t = 0.002$secs. The insulated sections are indicated by the thicker lines in the initial cathode profile. The thick broken lines indicate the position of the insulated sections after $t = 0.04$ seconds. 128 evenly-spaced nodes were used in the discretization of the anode and cathode surfaces.

Figure 5.45: Shaping of a plane anode by a shaped cathode moved sinusoidally with insulated horizontal sections: $V = 20V$, $\Delta t = 0.002$secs. The insulated sections are indicated by the thicker lines in the initial cathode profile. 150 evenly-spaced nodes were used in the discretization of the anode and cathode surfaces.
Figure 5.46: The initial electrode configurations prior to the application of pulsed-ECM. Figure 5.47 indicates the evolution of the anode as the insulated cathode is moved horizontally with velocity $u$ and with a pulsed applied voltage $V(t)$.

equal timesteps. Figure 5.45 shows the result of a similar BIM calculation over 40 timesteps for a rectangular spiked tool, insulated everywhere except at its tip, and advancing along a sinusoidal path. In each case, it has been assumed that the unmachined anode is plane for $x > 0$. The development of a near sinusoidal profile is seen.

A final parameter that can be controlled to affect the machining process is the applied voltage itself. Rather than remaining constant throughout, the voltage may be varied slowly or pulsed intermittently. When combined with a controlled movement of the cathode, the ability to control the applied voltage can be of great use in the shaping of the workpiece. An example of this is given in Figures 5.46 and 5.47. An insulated planar tool is moved horizontally at speed $u$ and a voltage $V$ is applied for time $\delta_{on}$ then switched off for time $\delta_{off}$ before being reapplied. As displayed by Figure 5.46, the initial tool was assumed to be 20 units in length, of which only the central 2 units ($|x| < 1$) are exposed. In Figure 5.47 the upper graph illustrates the machining of the anode to an oscillatory profile whilst the lower graph indicates both the position of the central section of the cathode and the corresponding time-dependent applied voltage $V(t)$ ($V = 1$ or $V = 0$) as the cathode is moved horizontally. The anode is clearly machined in a manner that is affected by the applied voltage pulse heights and durations. The lower lying curves of the upper graph indicate the anode profile at intermediate points in the
machining process whilst the final anode profile is given by the uppermost curve. An immediate application of this work would be to examine the effects of the pulse durations, insulation and tool velocity on the machining.

5.6 Summary

In this chapter an implementation of the Boundary Integral Method (BIM) has been presented and examples of its application to the electrochemical machining problem have been illustrated. The implemented method has a number of significant features:

- The BIM enables an examination of general electrode configurations and profiles, beyond the greatly restrictive cases of considering small perturbations about linear electrodes.

- A variety of boundary conditions can be incorporated within the model, allowing it to be extended to include the effects upon machining of insulated regions, of overpotentials and of variations in the applied potential.

- The form of the model allows various machining rules to be easily incorporated - eg. Faradaic or ECAM.
• The dynamic updating of the computational domain facilitates the modelling of the movement of the tool and the machining of the anode. In particular, the implementation includes the facility to model general tool movements.
Chapter 6

Modelling of the Diffuse Double Layer

A consideration of the electrochemical phenomena within an electrolytic cell leads to models predicting the concentration, potential and current distributions that are governed by the diffusion, convection and migration of ions. When, as in the study of electrochemical machining, one is interested in processes that occur at, or close to, an interface there is locally a considerable departure from electro-neutrality. This suggests that mathematically the problem is treated as consisting of two regions: an inner region at the interface where there is a large departure from electro-neutrality and an outer region where the charge density is small and there is no significant departure from electro-neutrality. Matched asymptotic expansions provide a procedure for using solutions to the inner and outer problems to generate a smooth solution describing conditions over the entire region. Thus, the final solution will be a combination of the inner and outer solutions.

The ion concentration, potential and current within an electrochemical cell are governed by the diffusion, convection and migration of ions. The influence of the electric field upon the ion movements yields a system of nonlinear partial differential equations describing the transport processes.

For a dilute solution of $N$ species, at a constant temperature and pressure, the flux, $\hat{N}_i$, of the $i$th species is given [38] by

$$\hat{N}_i = -z_i \mu_i F \hat{c}_i \nabla \hat{\phi} - D_i \nabla \hat{c}_i + \hat{c}_i \hat{v}, \quad (6.1)$$

where $\hat{c}_i$ is the concentration of species $i$ (mole/cm$^3$), $\hat{v}$ is the velocity of the electrolyte (cm/sec), $z_i$ is the ionic valency, $\mu_i$ is the ionic mobility (cm$^2$ mol/J-sec), $F$ is Faraday’s Number (C mol$^{-1}$), $\hat{\phi}$ is the electric potential (Volts) and $D_i$ is the diffusion coefficient of species $i$ (cm$^2$/sec).
For each species, conservation of mass, requires that

\[
\frac{\partial \hat{c}_i}{\partial t} = -\nabla \cdot \hat{\mathbf{N}}_i + R_i \quad i = 1, \ldots, N
\]  

(6.2)

where \( \nabla \cdot \hat{\mathbf{N}}_i \) is the divergence of the flux vector and \( R_i \) is the production rate of the \( i \)th species due to reactions within the solution.

At the anode surface, the normal flux \( \hat{n} \cdot \hat{\mathbf{N}}_i = \hat{Q}_i \) of each species is related to the erosion rate of the anode, while within the metal there is a surface charge distribution \( \sigma_m \) per unit area. In the fluid interior, each species has a concentration \( \hat{c}^b_i \) which may depend on \( \hat{x} \) and \( \hat{t} \).

Introduce nondimensional variables by writing,

\[
\begin{align*}
\hat{x} = \frac{x}{L}, \\
\hat{t} = \frac{t}{\tau}, \\
\hat{c}_i = \frac{c_i}{c^*}, \\
\hat{\phi} = \frac{\phi}{\phi_0}, \\
\hat{E} = \frac{\hat{E}L}{\phi_0}, \\
\hat{v} = \frac{\hat{v}T}{L},
\end{align*}
\]

where \( L \) is a typical length scale of the problem (eg. gap width) and \( \tau = L^2 / D \). \( D \) is a value typifying the diffusion coefficients, \( D_i \), of all species, \( c^* \) is a typical bulk concentration of a species and \( \phi_0 \) is an appropriate choice of potential.

In terms of the non-dimensional variables this yields

\[
\hat{\mathbf{N}}_i = -\frac{D_i c^*}{L} \left( \frac{F \phi_0}{RT} z_i c_i \nabla \phi + \nabla c_i \right) + \frac{c^* L}{\tau} c_i \hat{v},
\]

(6.3)

where \( \hat{\nabla} = \frac{1}{L} \nabla \) and the Einstein relation, \( D_i / \mu_i = RT \), relating ion mobility to diffusivity, has been used. \( R \) is the Universal Gas Constant (J/mol-K) and \( T \) is the electrolyte temperature (°K).

In the absence of ionic interactions within the electrolyte \( (R_i = 0) \), species conservation gives

\[
\frac{c^*}{\tau} \frac{\partial \hat{c}_i}{\partial t} + \frac{1}{L} \nabla \cdot \hat{\mathbf{N}}_i = 0.
\]

(6.4)

Substituting for \( \hat{\mathbf{N}}_i \) and introducing the electric field, \( \mathbf{E} = -\nabla \phi \) gives

\[
\frac{L^2}{\tau D_i} \left[ \frac{\partial \hat{c}_i}{\partial t} + \nabla \cdot (\hat{c}_i \mathbf{v}) \right] = \nabla \cdot \left[ \nabla c_i - z_i \frac{F \phi_0}{RT} c_i \mathbf{E} \right].
\]

(6.5)

The model is completed by using Gauss' Law to relate the electric field to charge density by

\[
\hat{\nabla} \cdot (\varepsilon \hat{\mathbf{E}}) = F \sum_{i=1}^{N} z_i \hat{c}_i,
\]

(6.6)

where \( \varepsilon \) is the permittivity of the electrolyte. In terms of the nondimensional variables, (6.6) becomes
\[ \nabla \cdot E = \frac{L^2 F c^*}{\epsilon \phi_0} \sum_{i=1}^{N} z_i c_i. \]  

(6.7)

Introducing the parameters

\[ \alpha = \frac{RT}{F \phi_0}, \quad \beta = \frac{\epsilon \phi_0}{c^* F L^2}, \quad \eta_i = \frac{D}{D_i}, \]

we obtain

\[ \alpha \eta_i \left[ \frac{\partial c_i}{\partial t} + \nabla \cdot (c_i v) \right] = \nabla \cdot \left[ \alpha \nabla c_i - z_i c_i E \right] \]  

(6.8)

and

\[ \beta \nabla \cdot E = \sum_{i=1}^{N} z_i c_i, \]  

(6.9)

where physical considerations give \( \alpha \ll 1, \beta \ll 1 \) and \( \beta \ll \alpha \) for relevant values of \( \phi_0 \) and \( L \). Noting that \( v \cdot n = 0 \) at the anode surface, the flux conditions at the boundary become

\[ (\alpha \nabla c_i - z_i c_i E) \cdot n = -Q_i \]  

(6.10)

where

\[ Q_i = \frac{\alpha L \hat{Q}_i}{D_i c^*} \]

while the dimensionless bulk concentrations are

\[ c_i^b = \frac{c_i}{c^*}. \]  

(6.11)

Notice that choosing \( \phi_0 = \frac{RT}{F} \) sets \( \alpha = 1 \) while a choice of length scale as

\[ L = \sqrt{\frac{\phi_0 \epsilon}{F c^*}}, \]

proportional to the Debye length [38], would give \( \beta = 1 \) appropriate to a balance of the divergence of the electric field with the charge in the electrolyte.

In the special case of the steady-state with zero fluid flow, the system (6.8) and (6.9) simplifies to

\[ \nabla \cdot \left[ \alpha \nabla c_i - z_i c_i E \right] = 0 \quad i = 1..N \]  

(6.12)

\[ \beta \nabla \cdot E = \sum_{i=1}^{N} z_i c_i. \]  

(6.13)
These possess solutions in which each concentration, $c_i$, is uniform so that, for each $i$, $\nabla c_i = 0$. In this case, the field $E$ is divergence-free, so giving

$$\nabla \cdot E = 0 \quad \text{i.e.} \quad \nabla^2 \phi = 0$$

(6.14)

together with the condition of electroneutrality

$$\sum_{i=1}^{N} z_i c_i = 0.$$  

(6.15)

This behaviour underlies the Laplace equation model for electric fields used previously and is valid away from the electrode surfaces. We may treat it as the leading order description for the outer region for $\alpha \ll 1$.

Taking $\beta \neq 0$ but $\beta \ll 1$ indicates that for concentrations $c_i$ giving a negligible deviation from electro-neutrality, a considerable deviation from $\nabla \cdot E = 0$ can arise so that derivatives of $E$ become large. Alternatively, $\beta \ll 1$ indicates that, in an unsteady situation, any initial charge density, $F \left( \sum_{i=1}^{N} z_i c_i \right) \neq 0$, would rapidly cause charge to flow to the conducting boundaries. Consequently, for $\alpha \ll 1$, $\beta \ll 1$ we anticipate that departure from electro-neutrality is confined essentially to layers near the electrode.

Finally, in order to analyse the diffuse double layer the value of the surface charge $\sigma_m$ is taken as a convenient parameter [38, 39]. Analyses that deal with the electric potential rather than the electric field [40, 49] do not have this requirement and the behaviour of the electric field at the electrode/electrolyte interface is determined by considering descriptions of the electrical potential.

### 6.1 The Boundary Layer, Electrode Shape and Transverse Effects

Near a metal/electrolyte interface we expect variations of field $E$ and concentrations $c_i$ to occur on a scale that is short in comparison to the electrode gap width. This suggests the presence of a boundary layer in which a rescaled coordinate normal to the boundary is appropriate.

Introduce *curvilinear* coordinates $\chi^1$ and $\chi^2$ on the boundary such that the boundary surface is given parametrically as

$$r = R(\chi^1, \chi^2)$$

(6.16)

and a coordinate system near the boundary is

$$r = R(\chi^1, \chi^2) + \chi^3 n,$$

(6.17)
where \( \mathbf{n} \) is the unit normal to the surface at the point given by \( \mathbf{R}(\chi^1, \chi^2) \) and with \( \chi^3 > 0 \) in the electrolyte. \( \chi^3 \) is, therefore, the distance from the boundary to a point \( P \) in the electrolyte having position vector \( \mathbf{r} \). Note that, at this stage, no specific choice of the surface coordinates has been made and the system considered is a curvilinear set of coordinates in which surfaces \( \chi^3 = \text{constant} \) are parallel to the material surface \( \chi^3 = 0 \).

To describe effects varying rapidly with \( \chi^3 \) we introduce the scaled coordinate \( s \) such that

\[
\delta s = (\mathbf{r} - \mathbf{R}) \cdot \mathbf{n} = \chi^3
\]  

(6.18)

where \( \delta \to 0 \) as \( (\alpha, \beta) \to (0, 0) \).

The operator \( \nabla \) is rewritten as

\[
\nabla = \delta^{-1} \mathbf{n} \frac{\partial}{\partial s} + \nabla_{\parallel},
\]  

(6.19)

where \( \nabla_{\parallel} \) is the tangential vector derivative\(^2\), which may be written in terms of the chosen surface coordinates \( \chi^1 \) and \( \chi^2 \).

By redefining \( \mathbf{E} \) in terms of its component \( E_\perp \) normal to the surface and its transverse components, such that

\[
\mathbf{E} = E_\perp \mathbf{n} + \mathbf{E}_{\parallel},
\]  

(6.20)

---

\(^1\text{Strictly, } \nabla = g^1 \frac{\partial}{\partial \chi^1} + g^2 \frac{\partial}{\partial \chi^2} + g^3 \frac{\partial}{\partial \chi^3} \text{ where } g^i \text{ are the contravariant base vectors of a curvilinear coordinate system with } g^3 = \mathbf{n} \text{ [50]. Further details are given in Section 6.2.}

\(^2\nabla_{\parallel} = g^1 \frac{\partial}{\partial \chi^1} + g^2 \frac{\partial}{\partial \chi^2}. \)
and by incorporating the rescaling above, the differential equations (6.12) and (6.13) are replaced by,

\[
\frac{\alpha}{\delta^2} \frac{\partial^2 c_i}{\partial s^2} - \frac{1}{\delta} \frac{\partial (z_i c_i E_\perp)}{\partial s} + \alpha \nabla_\parallel^2 c_i - \nabla_\parallel \cdot (z_i c_i E_\parallel) = 0 \tag{6.21}
\]

\[
\frac{\beta}{\delta} \frac{\partial E_\perp}{\partial s} + \beta \nabla_\parallel \cdot E_\parallel = \sum_{i=1}^{N} z_i c_i. \tag{6.22}
\]

A principal balance from (6.21) and (6.22), in which \(E_\perp\) interacts predominantly with the normal variations of \(c_i\), suggests the rescaling

\[
E_\perp = \frac{\alpha}{\delta} \mathcal{E}, \quad c_i = \frac{\beta \alpha}{\delta^2} u_i. \tag{6.23}
\]

This, in turn, determines the relevant choice of \(\delta(\alpha, \beta)\).

Matching requires that \(c_i\), the concentration of species \(i\), is \(O(1)\) in the outer region. The choice of \(\delta\) must reflect this condition. Hence,

\[
\alpha \beta = \delta^2 \quad \text{or, equivalently,} \quad \delta = \sqrt{\alpha \beta} \tag{6.24}
\]

so that the scalings are

\[
c_i = u_i, \quad E_\perp = \sqrt{\frac{\alpha}{\beta}} \mathcal{E} \tag{6.25}
\]

and the differential equations become

\[
\frac{\partial^2 u_i}{\partial s^2} - \frac{\partial (z_i u_i \mathcal{E})}{\partial s} - \beta \nabla_\parallel \cdot (z_i u_i E_\parallel) + \alpha \beta \nabla_\parallel^2 u_i = 0 \tag{6.26}
\]

\[
\frac{\partial \mathcal{E}}{\partial s} - \sum_{i=1}^{N} z_i u_i + \beta \nabla_\parallel \cdot E_\parallel = 0. \tag{6.27}
\]

Some manipulation shows that the boundary conditions become

\[
\frac{\partial u_i}{\partial s} - z_i u_i \mathcal{E} = -\frac{\delta}{\alpha} Q_i \quad \text{at} \quad s = 0, \tag{6.28}
\]

\[
\lim_{s \to \infty} u_i = c_i^b \tag{6.29}
\]

The form of the system described by equations (6.26) to (6.29) suggests a further appropriate scaling, namely of the transverse electric field \(E_\parallel\). The scaling

\[
E_\parallel = \alpha e_\parallel \tag{6.30}
\]

makes all the perturbation terms in (6.26) and (6.27) of \(O(\alpha \beta) = O(\delta^2)\).

In the more general unsteady case which includes fluid flow effects the mass transport equation (6.8) becomes, in terms of the rescaled variables,

\[
\frac{\partial^2 u_i}{\partial s^2} - \frac{\partial (z_i u_i \mathcal{E})}{\partial s} + \delta^2 \left(- \nabla_\parallel \cdot (z_i u_i e_\parallel) + \nabla_\parallel^2 u_i \right)
\]

\[
= \delta \eta_i v_\perp \frac{\partial u_i}{\partial s} + \delta^2 \eta_i \left( \frac{\partial u_i}{\partial t} + \mathbf{v}_\parallel \cdot \nabla_\parallel u_i \right), \tag{6.31}
\]

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under the assumption that the electrolyte is an incompressible fluid satisfying the continuity equation, $\nabla \cdot \mathbf{v} = 0$.

Here the electrolyte velocity has been written in terms of its normal and transverse components as

$$\mathbf{v} = v_n \mathbf{n} + v_\parallel \mathbf{v}_\parallel. \quad (6.32)$$

Notice that equation (6.31) suggests that the effect of the electrolyte flow normal to the anode surface will influence the transport process more significantly than the transverse and unsteady effects. However, this is inconsistent with the vanishing of the normal velocity at the electrode, so that the continuity equation suggests a further rescaling

$$v_n = \sqrt{\alpha \beta} v_n. \quad (6.33)$$

The final rescaled form of equation (6.31) and the incompressibility equation is

$$\frac{\partial^2 u_i}{\partial s^2} + \frac{\partial (z_i u_i \mathcal{E})}{\partial s} + \delta^2 \left( \nabla_\parallel \cdot (z_i u_i \mathbf{e}_\parallel) + \nabla_\parallel^2 u_i \right)$$

$$= \delta^2 \eta_i v_n \frac{\partial u_i}{\partial s} + \delta^2 \eta_i \left( \frac{\partial u_i}{\partial t} + \mathbf{v}_\parallel \cdot \nabla_\parallel u_i \right) \quad (6.34)$$

and

$$\frac{\partial v_n}{\partial s} + \nabla_\parallel \cdot \mathbf{v}_\parallel = 0 \quad , \quad (6.35)$$

where all perturbation terms occur at $O(\delta^2)$.

### 6.2 A Closer Examination of Transverse Effects

It is appropriate at this stage to consider further the transverse terms in the above model and their corresponding effects. In general, it is necessary to employ curvilinear coordinates to describe a surface and this necessitates a closer examination of the model. In particular, it is important to determine at what order in any perturbation procedure the transverse terms first contribute. In this instance, we are interested in a surface coordinate system where one coordinate orientation is normal to the surface at the local origin of the system [50].

Let points $\mathbf{r} = R(\chi^1, \chi^2)$ of the electrode surface have cartesian coordinates $(x_1, x_2, x_3)$ related to the curvilinear coordinates $(\chi^1, \chi^2)$ by

$$x_1 = x_1(\chi^1, \chi^2), \quad x_2 = x_2(\chi^1, \chi^2), \quad x_3 = x_3(\chi^1, \chi^2). \quad (6.36)$$

Coordinates near the surface are defined by

$$\mathbf{x} = R(\chi^1, \chi^2) + \chi^3 \mathbf{v} \quad (6.37)$$

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Figure 6.2: Surface curvilinear coordinates $(\chi^1, \chi^2)$

where

\[ v = \frac{R_1 \wedge R_2}{|R_1 \wedge R_2|} \]  
(6.38)

and we define

\[ R_1 = \frac{\partial R}{\partial \chi^1} \quad \text{and} \quad R_2 = \frac{\partial R}{\partial \chi^2} \]  
(6.39)

so that $v$ is the unit vector normal to the surface at $R(\chi^1, \chi^2)$. Then, at points near the surface

\[ g_1 = R_1 + \chi^3 v_1, \]  
(6.40)

\[ g_2 = R_2 + \chi^3 v_2. \]  
(6.41)

Hence

\[ v \cdot g_1 = v \cdot R_1 + \chi^3 v \cdot v_1 = 0 \]  
(6.42)

since $v \perp R_1$ and $v \cdot v = 1$. Similarly $v \perp R_2$, hence $v$ is parallel to $g_1 \wedge g_2$. But $v$ is a unit vector, so by continuity when $\chi^3 = 0$, we have

\[ v = \frac{g_1 \wedge g_2}{|g_1 \wedge g_2|} \]  
(6.43)

\[ = n. \]  
(6.44)
Consequently, the tangent vectors \( g_1 \) and \( g_2 \) to the coordinate curves on the surfaces \( \chi^3 = \text{constant} \) are

\[
\begin{align*}
g_1 &= \frac{\partial \mathbf{r}}{\partial \chi^1} = \frac{\partial \mathbf{R}}{\partial \chi^1} + \chi^3 \frac{\partial \mathbf{n}}{\partial \chi^1} \\
g_2 &= \frac{\partial \mathbf{r}}{\partial \chi^2} = \frac{\partial \mathbf{R}}{\partial \chi^2} + \chi^3 \frac{\partial \mathbf{n}}{\partial \chi^2}.
\end{align*}
\] (6.45) (6.46)

and the unit tangent vector to the straight line \((\chi^1, \chi^2) = \text{constant}\) is

\[
g_3 = \mathbf{n} = \frac{g_1 \wedge g_2}{\sqrt{g}}
\] (6.47)

where, by convention \([50][51]\), \( g = |g_1 \wedge g_2|^2 \).

We define

\[
\begin{align*}
g^1 &= \frac{g_2 \wedge g_3}{\sqrt{g}}, & g^2 &= \frac{g_3 \wedge g_1}{\sqrt{g}}, & g^3 &= \frac{g_1 \wedge g_2}{\sqrt{g}}
\end{align*}
\] (6.48)

and note that \( g^3 = g_3 = \mathbf{n} \). Further, we define, the covariant and contravariant components of the metric tensor as

\[
g_{ij} = g_i \cdot g_j \quad \text{and} \quad g^{ij} = g^i \cdot g^j
\] (6.49)

respectively \([50]\).

An examination of the properties of the chosen coordinate system, as described above, indicates that

\[
\begin{align*}
g^{11} &= g_{22}, & g^{22} &= \frac{g_{11}}{g}, & g^{33} &= 1, \\
g^{12} &= g^{21} = -\frac{g_{12}}{g}, \\
g^{3j} &= g^{33} = 0, & j \neq 3,
\end{align*}
\]

and employing (6.45), (6.46) and (6.47) gives

\[
\begin{align*}
g_{\mu\nu} &= R_{\mu} \cdot R_{\nu} + \chi^3 (R_{\mu} \cdot n_{\nu} + R_{\nu} \cdot n_{\mu}) + (\chi^3)^2 n_{\mu} \cdot n_{\nu}, \\
g_{\mu3} &= 0 \\
g_{33} &= 1,
\end{align*}
\] (6.50) (6.51) (6.52)

where \( \mu, \nu = 1, 2 \) and we define

\[
R_{\mu} = \frac{\partial \mathbf{R}}{\partial \chi^\mu}, \quad R_{\nu} = \frac{\partial \mathbf{R}}{\partial \chi^\nu}, \quad n_{\mu} = \frac{\partial \mathbf{R}}{\partial \chi^\mu}, \quad n_{\nu} = \frac{\partial \mathbf{R}}{\partial \chi^\nu}.
\] (6.53)

By rescaling \( e_\parallel \) in equation (6.30) as

\[
E_\parallel = \alpha e_\parallel = \alpha (e^1 g_1 + e^2 g_2)
\] (6.54)
and by employing (6.23) we transform equations (6.26) and (6.27) into surface curvilinear coordinates as (6.27)

\[
\frac{1}{\sqrt{g}} \left( \frac{\partial}{\partial s} \left( \sqrt{g} \frac{\partial u_i}{\partial s} \right) \right) + z_i \mathcal{E} \frac{\partial u_i}{\partial s} + z_i u_i \frac{1}{\sqrt{g}} \frac{\partial (\sqrt{g} \mathcal{E})}{\partial s} + \delta^2 z_i \left[ e^1 \frac{\partial u_i}{\partial \chi^1} + e^2 \frac{\partial u_i}{\partial \chi^2} + u_i \frac{1}{\sqrt{g}} \left( \frac{\partial}{\partial \chi^1} (\sqrt{g} e^1) + \frac{\partial}{\partial \chi^2} (\sqrt{g} e^2) \right) \right] \\
+ \delta^2 \frac{1}{\sqrt{g}} \left[ \frac{\partial}{\partial \chi^1} \left( \sqrt{g} \left( g^{11} \frac{\partial u_i}{\partial \chi^1} + g^{12} \frac{\partial u_i}{\partial \chi^2} \right) \right) + \frac{\partial}{\partial \chi^2} \left( \sqrt{g} \left( g^{21} \frac{\partial u_i}{\partial \chi^1} + g^{22} \frac{\partial u_i}{\partial \chi^2} \right) \right) \right] = 0
\]

and

\[
\frac{1}{\sqrt{g}} \frac{\partial}{\partial s} (\sqrt{g} \mathcal{E}) - \sum_{i=1}^{N} z_i u_i + \delta^2 \frac{1}{\sqrt{g}} \left( \frac{\partial}{\partial \chi^1} (\sqrt{g} e^1) + \frac{\partial}{\partial \chi^2} (\sqrt{g} e^2) \right) = 0.
\]

The boundary conditions (6.28) and (6.29) are unchanged.

In the more general case in which mass transport is included, equation (6.31) now becomes

\[
\frac{1}{\sqrt{g}} \left( \frac{\partial}{\partial s} \left( \sqrt{g} \frac{\partial u_i}{\partial s} \right) \right) + z_i \mathcal{E} \frac{\partial u_i}{\partial s} + z_i u_i \frac{1}{\sqrt{g}} \frac{\partial (\sqrt{g} \mathcal{E})}{\partial s} + \delta^2 z_i \left[ e^1 \frac{\partial u_i}{\partial \chi^1} + e^2 \frac{\partial u_i}{\partial \chi^2} + u_i \frac{1}{\sqrt{g}} \left( \frac{\partial}{\partial \chi^1} (\sqrt{g} e^1) + \frac{\partial}{\partial \chi^2} (\sqrt{g} e^2) \right) \right] \\
+ \delta^2 \frac{1}{\sqrt{g}} \left[ \frac{\partial}{\partial \chi^1} \left( \sqrt{g} \left( g^{11} \frac{\partial u_i}{\partial \chi^1} + g^{12} \frac{\partial u_i}{\partial \chi^2} \right) \right) + \frac{\partial}{\partial \chi^2} \left( \sqrt{g} \left( g^{21} \frac{\partial u_i}{\partial \chi^1} + g^{22} \frac{\partial u_i}{\partial \chi^2} \right) \right) \right] = 0
\]

In (6.57), the electrolyte velocity has been written in terms of its components in the normal and transverse directions as

\[
v = \delta v_n \mathbf{n} + v^1 g_1 + v^2 g_2.
\]

Introducing $K_m$ as the mean curvature of the surface at $(\chi^1, \chi^2, 0)$ as in Appendix A, allows equations (6.57) and (6.56) to be written to $O(\delta)$ as

\[
\frac{\partial}{\partial s} \left( \frac{\partial u_i}{\partial s} - z_i \mathcal{E} u_i \right) + 2\delta K_m \left( \frac{\partial u_i}{\partial s} - z_i \mathcal{E} u_i \right) + O(\delta^2) = 0,
\]

\[
\frac{\partial \mathcal{E}}{\partial s} - 2\delta K_m \mathcal{E} - \sum_{i=1}^{N} z_i u_i + O(\delta^2) = 0,
\]

respectively. The boundary conditions (6.10) and (6.11) are

\[
\frac{\partial u_i}{\partial s} - z_i u_i \mathcal{E} = -\frac{\delta}{\alpha} Q_i \quad \text{at} \quad s = 0,
\]

\[
u_i \rightarrow c_i^b \quad \text{as} \quad s \rightarrow \infty.
\]
and, assuming the total electric charge in the double layer is $\sigma_m$,

$$\int_0^\infty \mathcal{E}' ds = \sqrt{\frac{\beta L \sigma_m}{\alpha \varepsilon \phi_0}} = \sigma.$$  \hspace{1cm} (6.63)

where evaluation of the appropriate parameters indicates $\sigma \sim O(1)$. Inspection of (6.59)-(6.63) indicates that the effect of the curvature of the electrode surface upon the normal electric field and species concentration will influence the system behaviour at lower order than transverse effects. That is, the geometry of the surface will be more important than the tangential variations in electric field and species concentrations. It is only at $O(\delta^2)$ that the transverse and temporal effects will appear. As a consequence, to $O(\delta)$, the system of partial differential equations defining the boundary value problem (6.8) - (6.11) may be treated as a set of simultaneous ordinary differential equations (6.59) and (6.60) with boundary conditions (6.61), (6.62) and (6.63). It is this latter problem that is now considered, for the case of a two species electrolyte\(^3\).

In the case of a 2-species electrolyte, introducing the perturbation expansions,

$$u_i = u_i^{(0)} + \frac{\delta}{\alpha} u_i^{(1)} + \delta u_i^{(2)} + \cdots,$$  \hspace{1cm} (6.64)

$$\mathcal{E} = \mathcal{E}^{(0)} + \frac{\delta}{\alpha} \mathcal{E}^{(1)} + \delta \mathcal{E}^{(2)} + \cdots$$  \hspace{1cm} (6.65)

and substituting these expansions into equations (6.59) to (6.63) produces the following leading order problem:

$$-\frac{du_1^{(0)}}{ds} + z_1 u_1^{(0)} \mathcal{E}^{(0)} = 0,$$  \hspace{1cm} (6.66)

$$-\frac{du_2^{(0)}}{ds} + z_2 u_2^{(0)} \mathcal{E}^{(0)} = 0,$$  \hspace{1cm} (6.67)

$$\frac{d \mathcal{E}^{(0)}}{ds} - z_1 u_1^{(0)} - z_2 u_2^{(0)} = 0$$  \hspace{1cm} (6.68)

with

$$u_1^{(0)} \rightarrow c_1^b, \quad u_2^{(0)} \rightarrow c_2^b \text{ as } s \rightarrow \infty.$$  \hspace{1cm} (6.69)

In deriving equations (6.66) and (6.67) the $O(1)$ form of equation (6.59) has been integrated with respect to $s$ and the $O(1)$ form of boundary conditions (6.61), namely

$$\frac{\partial u_i^{(0)}}{\partial s} - z_i u_i^{(0)} \mathcal{E}^{(0)} = 0 \text{ at } s = 0,$$  \hspace{1cm} (6.70)

$$\frac{\partial \mathcal{E}^{(0)}}{\partial s} = 0 \text{ at } s = 0.$$  \hspace{1cm} (6.71)

\(^3\)A symmetric electrolyte contains species such that $|z_i| = z$. It is therefore a special case of the two species problem.
has been applied. Outside the double layer

$$E = -\delta^{-1} \frac{\partial \phi}{\partial s} \mathbf{n} - \nabla_{\|} \phi. \quad (6.72)$$

Hence, sufficiently far from the electrode surface,

$$\mathcal{E} \sim -\frac{\delta}{\alpha} \frac{\partial \phi}{\partial \chi^3}, \quad (6.73)$$

where $\phi$ is the electric potential and by expanding this expression as a MacLaurin series about $\chi^3 = \delta s = 0$, we can conclude that

$$\mathcal{E}(\infty) \sim -\alpha^{-1} \delta \frac{\partial \phi}{\partial \chi^3}(\chi^1, \chi^2, 0) + O(\delta^2/\alpha). \quad (6.74)$$

Applying the third boundary condition (6.63) gives,

$$\mathcal{E}(\infty) - \mathcal{E}(0) = \sigma \quad (6.75)$$

and having chosen

$$\mathcal{E} = \mathcal{E}^{(0)} + \frac{\delta}{\alpha} \mathcal{E}^{(1)} + \delta \mathcal{E}^{(2)} + \cdots, \quad (6.76)$$

equations (6.74) and (6.75) imply that at leading order

$$\mathcal{E}^{(0)} \rightarrow 0 \quad \text{as} \quad s \rightarrow \infty \quad (6.77)$$

and

$$\mathcal{E}^{(0)}(0) = -\sigma. \quad (6.78)$$

Notice also that

$$\mathcal{E}^{(1)}(0) = 0; \quad \mathcal{E}^{(1)} \rightarrow -\frac{\partial \phi}{\partial \chi^3} = \mathcal{E}_{\text{bulk}} \quad \text{as} \quad s \rightarrow \infty, \quad (6.79)$$

$$\mathcal{E}^{(i)}(0) = 0; \quad \mathcal{E}^{(i)} \rightarrow 0 \quad \text{as} \quad s \rightarrow \infty, \quad i > 1. \quad (6.80)$$

From equations (6.66) and (6.67) it can be shown that

$$\frac{u_2^{(0)}}{u_1^{(0)}} = K \quad (K \text{ constant, } \gamma = z_2/z_1 < 0). \quad (6.81)$$

Consideration of (6.81) and the bulk conditions indicates that $K = c_2^b/[c_1^b]^{\gamma}$. By rescaling $r = z_1 s$ and using the identity (6.81), equations (6.66)-(6.68) can be reduced to a pair of ordinary differential equations

$$\frac{du_1^{(0)}}{dr} - u_1^{(0)} \mathcal{E}^{(0)} = 0, \quad (6.82)$$

$$\frac{d\mathcal{E}^{(0)}}{dr} - u_1^{(0)} - \gamma K \left[ u_1^{(0)} \right]^{\gamma} = 0 \quad (6.83)$$
from which a differential equation describing the relation between \( \mathcal{E}^{(0)} \) and \( u_i^{(0)} \)
can be determined:

\[
\frac{d \mathcal{E}^{(0)}}{du_i^{(0)}} = \frac{u_i^{(0)} + \gamma K \frac{u_i^{(0)}}{\mathcal{E}^{(0)}}}{u_i^{(0)}}. \tag{6.84}
\]

This equation has critical points at \( u_i^{(0)} = 0 \) and at \( \gamma K \frac{u_i^{(0)}}{\mathcal{E}^{(0)}}(\gamma - 1) = -1 \) (\( \gamma < 0 \)).

Introducing \( \tau = 1/(1 - \gamma) \), rescaling \( \mathcal{E}^{(0)} \) and \( u_i^{(0)} \) as

\[
K^\tau U = u_i^{(0)}, \tag{6.85}
\]

\[
e = \frac{\mathcal{E}^{(0)}}{\sqrt{2K^\tau}}, \tag{6.86}
\]

and integrating equation (6.84), gives the following relation between the rescaled electric field and the species concentrations,

\[
e^2 = U + U^\tau + L \quad (L \text{ constant}). \tag{6.87}
\]

Let \( U_\infty = c_i^2/K^\tau \) be the bulk value of concentration such that \( U \rightarrow U_\infty \) as \( r \rightarrow \infty \).

Then, defining \( f(U) = U + U^\tau \) we require \( f(U_\infty) = -L \) and for large \( r \) where \( U \approx U_\infty \),

\[
f(U) \approx -L + (U - U_\infty) f'(U_\infty) \tag{6.88}
\]

\[
\Rightarrow e \approx \sqrt{(U - U_\infty)} f'(U_\infty). \tag{6.89}
\]

Hence, in terms of the rescaled variables, equation (6.82) can be approximated for large \( r \) by

\[
\frac{dU}{dr} = -U_\infty \sqrt{(U - U_\infty)} f'(U_\infty), \tag{6.90}
\]

from which it is readily deduced that, as \( U \rightarrow U_\infty \),

\[
(U - U_\infty)^{1/2} \propto -U_\infty \sqrt{f'(U_\infty)}(\tau - r_0), \quad r_0 \text{ constant}. \tag{6.91}
\]

Thus, in order that the solution at large distances from the electrode surface has
the correct behaviour, we require that the algebraic equation \( e^2 = 0 \) has a double
root at \( U_\infty \). A plot of \( e^2 \) against \( U \) is given in Figure 6.3. Qualitatively, the relation
between \( e^2 \) and \( U \) is largely independent of \( \gamma \) for the range of parameters in which
we are interested and therefore, since physically \( e^2 \) decreases as \( U \) decreases, only
the right side of the curve is relevant to our calculations. It remains to determine
the bulk values and the values at the surface where \( r = 0 \).

Hence, writing

\[
e^2 = f(U) + L \tag{6.92}
\]

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Figure 6.3: $U$ plotted against $e^2$ when $\gamma = -1/3$.

we require roots of

$$\frac{df}{dU} = 0 \Rightarrow 1 + \gamma U^{-1} = 0.$$  \hspace{1cm} (6.93)

It is readily deduced that

$$U_\infty = \left(-\frac{1}{\gamma}\right)^{1/(\gamma-1)} \quad \text{and} \quad L = -\left(1 - \frac{1}{\gamma}\right) \left(-\frac{1}{\gamma}\right)^{1/(\gamma-1)}.$$  \hspace{1cm} (6.94)

A further rescaling, $\xi = \sqrt{2K^{1/(1-\gamma)}}t = z_1 \sqrt{2K^{1/(1-\gamma)}}s$ and (6.82) gives

$$\frac{dU}{d\xi} = -U \sqrt{U + U^\gamma + L},$$  \hspace{1cm} (6.95)

using (6.87), and integration provides the value of $U(\xi)$ throughout the double layer. The constant of integration is determined by applying boundary condition (6.78).

The solution to (6.95), in general, must be calculated numerically. In the case of a symmetric electrolyte where $\gamma = z_2/z_1 = -1$, however, analytic solutions can be determined for $U$ and $e$ namely,

$$U(\xi) = \left(\frac{1 + A \exp(-\xi)}{1 - A \exp(-\xi)}\right)^2 = \coth^2 \left(\frac{\xi + B}{2}\right)$$  \hspace{1cm} (6.96)
where $A = \exp(-B)$ and
\[
\begin{align*}
e(\xi) &= \frac{\mathcal{E}^{(0)}}{\sqrt{2K_\tau}} \\
&= \left[ \left( \frac{1 + A \exp(-\xi)}{1 - A \exp(-\xi)} \right)^2 - 1 \right] \left( \frac{1 + A \exp(-\xi)}{1 - A \exp(-\xi)} \right) \\
&= 2 \cosech(\xi + B).
\end{align*}
\]

The application of the boundary condition (6.78) and some consideration of the form of the solutions indicate that the constant $A$ is the solution to the quadratic equation $\sigma A^2 + 4\sqrt{2K_\tau} A - \sigma = 0$ such that $0 < A < 1$ - i.e. $\sigma [\exp(-B) - \exp(B)] + 4 = 0 \iff \sinh B = 2\sqrt{2K_\tau}/\sigma \Rightarrow B = \sinh^{-1}(2\sqrt{2K_\tau}/\sigma)$.

In the general case where $|z_2/z_1| \neq 1$, the solution to (6.95) was determined numerically using a Runge-Kutta-Merson method and Newton iteration in a shooting technique [52]. The value of $U$ at $\xi = 0$ was determined by calculating the appropriate root of
\[
U(0) + U(0)^\gamma + L - \frac{\sigma^2}{2K_\tau} = 0.
\]

The procedure is checked for the case $\gamma = -1$, in which the analytical solution (6.96) is available, by a comparison with the numerical solution as displayed in Figure 6.4. The effects on $U$ and $\mathcal{E}^{(0)}$ of varying $\gamma$ are indicated in Figures 6.5 and 6.6 respectively. Notice in Figure 6.5 that the bulk values of concentration, $U_\infty$ given in Table 6.1, are approached.

Extracting the $O(\delta/\alpha)$ terms from equations (6.59)-(6.63) produces the following boundary value problem
\[
\begin{align*}
-\frac{du_1^{(1)}}{ds} + z_1 \left( u_1^{(1)} \mathcal{E}^{(0)} + u_1^{(0)} \mathcal{E}^{(1)} \right) &= Q_1, \\
-\frac{du_2^{(2)}}{ds} + z_2 \left( u_2^{(1)} \mathcal{E}^{(0)} + u_2^{(0)} \mathcal{E}^{(1)} \right) &= Q_2, \\
\frac{d\mathcal{E}^{(1)}}{ds} - z_1 u_1^{(1)} - z_2 u_2^{(1)} &= 0,
\end{align*}
\]
with boundary conditions,
\[
u_1^{(1)} \to 0; \quad u_2^{(1)} \to 0; \quad \mathcal{E}^{(1)} \to \mathcal{E}_{\text{bulk}} \quad \text{as} \quad s \to \infty
\]
and with $\mathcal{E}^{(0)}(\xi)$, $u_1^{(0)}(\xi)$ and $u_2^{(0)}(\xi)$ determined from (6.81)-(6.83), with $\xi = \sqrt{2K^{1/(1-\gamma)}_\tau} = z_1 \sqrt{2K^{1/(1-\gamma)}_\tau} s$.

The value of the electric field predicted outside of the double layer is represented by $\mathcal{E}_{\text{bulk}}$. An analysis such as that performed by Newman [38, 39] indicates that the solution to the problem within the double layer requires to be matched
Comparison of numerical and analytic calculations of $U$:  gamma = -1; sigma = 1

Figure 6.4: A comparison of the numerical and analytical solutions to equation (6.95) in the case when $\gamma = -1$ and $\sigma = 1$.

Concentration profile of $U$ for various values of gamma - sigma = 1 in each case

Figure 6.5: The profile $U(\xi)$ for $\gamma = -1/3, -1/2, -1, -2, -3$ with $\sigma = 1$.

Table 6.1: The bulk values of $U$ for values of $\gamma$.

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>$U_\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1/3</td>
<td>0.43865</td>
</tr>
<tr>
<td>-1/2</td>
<td>0.62996</td>
</tr>
<tr>
<td>-1</td>
<td>1.00000</td>
</tr>
<tr>
<td>-2</td>
<td>1.25992</td>
</tr>
<tr>
<td>-3</td>
<td>1.31607</td>
</tr>
</tbody>
</table>
to an “outer” solution. In particular, the solution to the electric field \( \varepsilon \) in the double layer should match the field solution of an “outer” region. Whilst a full, formal matching procedure has not been performed in this work, matching the inner solution to the electric field calculated using the Boundary Integral Method provides a numerical solution to the problem throughout the computational domain. Note that, in terms of our scaling, \( \varepsilon_{\text{bulk}} \) is an \( O(1) \) quantity. By considering the behaviour of the BVP (6.99)-(6.102) for large \( s \) the values of the fluxes can be determined, namely,

\[
Q_1 = z_1 c_1^0 \varepsilon_{\text{bulk}}, \\
Q_2 = z_2 c_2^0 \varepsilon_{\text{bulk}}.
\]

(6.103)  
(6.104)

Figures 6.7-6.9 illustrate the effect of the bulk electric field upon the field and species concentrations within the double layer and display the profiles of \( \varepsilon^{(1)} \), \( u_1^{(1)} \) and \( u_2^{(1)} \). Recall, that in terms of the outer variables

\[
E_\perp = \frac{\alpha}{\delta} \varepsilon^{(0)} + \varepsilon^{(1)} + \alpha \varepsilon^{(2)} \ldots \\
c_i = u_i = u_i^{(0)} + \delta u_i^{(1)} + \delta u_i^{(2)} \ldots
\]

and hence \( \varepsilon^{(1)} \) is the first correction to the electric field whereas \( \delta \alpha^{-1} u_i^{(1)} \) constitutes the first correction to the species concentrations.

Illustrations of the solutions including the correction terms to the electric field and the species concentrations are given in Figures 6.10 - 6.12. Notice that
Figure 6.7: The correction $E^{(1)}$ to the electric field for the bulk electric field $E_{bulk} = 1, 10, 100$ with $\sigma = 0.6, \gamma = -1$.

Figure 6.8: The correction $u_1^{(1)}$ to the anion concentration for the bulk electric field $E_{bulk} = 1, 10, 100$ with $\sigma = 0.6, \gamma = -1$. 
Figure 6.9: The correction $u^{(1)}_2$ to the cation concentration for the bulk electric field $E_{bulk} = 1, 10, 100$ with $\sigma = 0.6, \gamma = -1$.

Figure 6.10: The electric field $E$ for the bulk electric field $E_{bulk} = 1, 10, 100$ with $\sigma = 0.6, \gamma = -1$.

the effect including the first perturbation to the electric field is that a uniform non-zero contribution remains throughout the double layer.

In this case, a symmetric electrolyte is assumed with $\sigma = 0.6$ and $K_m = 100$. The greater the value of the field $E_{bulk}$, the greater is the flux of species across
Figure 6.11: The anion concentration $u_1$ for the bulk electric field $E_{bulk} = 1, 10, 100$ with $\sigma = 0.6, \gamma = -1$.

Figure 6.12: The anion concentration $u_1$ for the bulk electric field $E_{bulk} = 1, 10, 100$ with $\sigma = 0.6, \gamma = -1$. 

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Figure 6.13: The correction $u_1^{(1)}$ to the anion concentration for $\gamma = -1/3, -1/2, -1, -2, -3$ with the bulk electric field $E_{bulk} = 1, \sigma = 0.6$.

the double layer and the correction to the leading order solution. This greater flux causes the anion concentrations to be reduced below those values predicted at leading order and causes a small increase in the cation concentrations above those predicted at leading order. More generally, the effect of the ratio of the ionic valencies $\gamma = z_2/z_1$ upon the $O(\delta/\alpha)$ correction to the solution is indicated in Figures 6.13, 6.14 and 6.15. Interestingly, whilst in Figure 6.15 the profiles of the electric fields are ordered consistently with the correction to the field - reducing as $|\gamma|$ is reduced - in Figures 6.13 and 6.14 the magnitude of the correction to the species concentrations does not follow this pattern. More precisely, the correction to the cation concentration increases as $|\gamma|$ decreases but the correction to the anion concentration appears to be affected in a less predictable manner. Figure 6.13 indicates that the greatest correction to the anion concentration at the electrode surface occurs when $\gamma = -1$. When $-1 < \gamma < 0$, however, the correction to the leading order solution increases as $\gamma \to 0$. In contrast, for $\gamma < -1$, the correction increases as $|\gamma|$ increases. Notice, also that the ordering of these corrections is not preserved the whole way across the double layer.
Figure 6.14: The correction $u_2^{(1)}$ to the cation concentration for $\gamma = -1/3, -1/2, -1, -2, -3$ with the bulk electric field $E_{bulk} = 1, \sigma = 0.6$.

Figure 6.15: The correction $E^{(1)}$ to the electric field for $\gamma = -1/3, -1/2, -1, -2, -3$ with the bulk electric field $E_{bulk} = 1, \sigma = 0.6$. 
An examination of equations (6.59)-(6.63) indicates that the effects of the mean curvature of the anode surface are of $O(\delta)$. Hence, extracting the $O(\delta)$ terms from equations (6.59)-(6.63) produces the following boundary value problem

\[
\begin{align*}
-\frac{d u_1^{(2)}}{d s} + z_1 \left( u_1^{(2)} E^{(0)} + u_1^{(0)} \varepsilon^{(2)} \right) &= 0, \\
-\frac{d u_2^{(2)}}{d s} + z_1 \left( u_2^{(2)} E^{(0)} + u_2^{(0)} \varepsilon^{(2)} \right) &= 0, \\
\frac{d \varepsilon^{(2)}}{d s} - z_1 u_1^{(2)} - z_2 u_2^{(2)} &= 2K_m \varepsilon^{(0)},
\end{align*}
\]

with boundary conditions,

\[
\begin{align*}
 u_1^{(2)} &\to 0; \quad u_2^{(2)} \to 0; \quad \text{as} \quad s \to \infty, \\
\varepsilon^{(2)}(0) &= 0. 
\end{align*}
\]

Here $u_1^{(2)}$, $u_2^{(2)}$, and $\varepsilon^{(2)}$ are the perturbations proportional to the local mean curvature $K_m$. Figures 6.16-6.18 illustrate the effects of the mean curvature upon the electric field within the double layer. As expected, the electric field strength and the concentration of the anions at the electrode surface depend linearly upon the mean curvature. Figure 6.18 indicates the further reduction in the cation concentrations. Finally, the effect of the ratio of the species valencies $\gamma$ is illustrated in Figures 6.19 and 6.20.

Figure 6.16: The correction $\varepsilon^{(2)}$ to the electric field for various values $K_m = 1, 10, 20, 100$ of the mean curvature of the electrode surface: $\sigma = 0.6, \gamma = -1$. 

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Figure 6.17: The correction $u_1^{(2)}$ to the anion concentration for various values $K_m = 1, 10, 20, 100$ of the mean curvature of the electrode surface: $\sigma = 0.6, \gamma = -1$.

Figure 6.18: The correction $u_2^{(2)}$ to the cation concentration for various values $K_m = 1, 10, 20, 100$ of the mean curvature of the electrode surface: $\sigma = 0.6, \gamma = -1$. 
6.3 Potentials and Overpotentials

From the model described in the previous section the value of the electric field $E$ was predicted throughout the double layer. In order to determine the value of the overpotential - the change in potential due to the double layer - a further integration is required. For this reason an alternative approach to the problem would have been to express the model in terms of the electric potential rather than its derivative, the electric field. Indeed, this is the approach taken by other authors [37, 40]. These approaches, however, assume a potential difference across the electrochemical cell in the order of millivolts rather than volts and a corresponding scaling will result in a potential boundary condition of order $1/\alpha$. The work of Chazalviel [49] is perhaps most relevant to our studies and that model is also expressed in term of electric potential. His matching procedure, however, is not at all rigorous and the overpotential is expressed in terms of the boundary conditions rather than being calculated by the application of the Nernst-Planck equations throughout the double layer.

In Table 6.2 the values of the overpotential $\eta$ are presented. These are calculated by integrating the electric field $\alpha E = -\frac{\partial \phi}{\partial z}$ throughout the double layer and rescaling,

$$\eta = -\frac{\alpha \phi_0}{z h \sqrt{2K^{1/(1-\gamma)}}} \int_0^\infty E(\xi) d\xi. \quad (6.110)$$

The values are comparable to those indicated as typical by Fitzgerald and McGeough [15]. As one would expect, the main influence on the overpotential is the ratio $\gamma$ of the valencies, with the greatest overpotentials corresponding to the lowest values of $|\gamma|$. This situation arises because each anion carries a larger negative charge and these anions are concentrated close to the anode surface. As the relative charge per ion alters (ie. $|\gamma|$ increases) the overpotential diminishes. Similarly, as the value of the bulk field $E_{\text{bulk}}$ decreases and the flux of species - and consequently the electric current - is reduced, so does the overpotential. Finally, an increase in the charge in the double layer $\sigma$ results in an increase in the calculated overpotential.

6.4 PNP Systems

In the previous section it was indicated that previous work on the Poisson-Nernst-Planck (PNP) systems has expressed the system in terms of the electric potential $\phi$. Such an approach is more naturally related to the boundary integral formulation of Chapter 5 in which the boundary conditions on the electrodes reflected
Table 6.2: The effect of various parameters upon calculated overpotential $\eta$.

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>$\sigma$</th>
<th>$E_{\text{bulk}}$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1</td>
<td>0.095</td>
</tr>
<tr>
<td>-3</td>
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<td>10</td>
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</tr>
<tr>
<td>-3</td>
<td>6</td>
<td>100</td>
<td>0.104</td>
</tr>
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<td>-3</td>
<td>10</td>
<td>1</td>
<td>0.125</td>
</tr>
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<td>10</td>
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<tr>
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<td>6</td>
<td>10</td>
<td>0.129</td>
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<td>-1/3</td>
<td>6</td>
<td>100</td>
<td>0.133</td>
</tr>
<tr>
<td>-1/3</td>
<td>10</td>
<td>1</td>
<td>0.158</td>
</tr>
</tbody>
</table>
the applied potential difference across the cell. Further, the model described in
Section 6.2 required surface charge $\sigma_m$ to be taken as a convenient parameter and
a value provided. It was assumed that the charge resides solely at the surface
of the electrode, whereas in practice the charge resides throughout the double
layer. In this section, we examine PNP systems in terms of the electric potential
in order to extend previous work to cover more general cases and to provide a
justification for the approach adopted in the previous section.

Here, the approach of Barcilon et al [40] is summarised and in Section 6.4.2
an implementation of a numerical method is discussed. This numerical method
enables their approach to be extended to cover the case of multiple species rather
than being restricted to the 2-species case. A fundamental difference between the
model presented within this section and those previously discussed is that it is
assumed that the concentration of species at the electrode surfaces is known.

The one-dimensional, 2-species system presented by Barcilon et al [40] con-
cerns the distributions $p$ and $n$ of ions with, repsectively, unit positive and unit
negative charges and is governed by the Poisson equation,

$$\epsilon^2 \phi'' - n + p = 0,$$  \hspace{1cm} (6.111)

with the Nernst-Planck equations governing the the distribution of ions. The ions
are assumed to have identical mobilities,

$$n' - n\phi' = J_n,$$  \hspace{1cm} (6.112)
$$p' + p\phi' = -J_p,$$  \hspace{1cm} (6.113)

in $\Omega = \{x : 0 < x < 1\}$ with general boundary conditions

$$p(0) = p_L > 0, \quad n(0) = n_L > 0,$$  \hspace{1cm} (6.114)
$$p(1) = p_R > 0, \quad n(1) = n_R > 0,$$  \hspace{1cm} (6.115)
$$\phi(0) = V, \quad \phi(1) = 0.$$  \hspace{1cm} (6.116)

Equations (6.111)-(6.116) constitute a 4th order system for $n$, $p$ and $\phi$ with six
boundary conditions and two free parameters $J_n$ and $J_p$. Here, $\epsilon$ is treated as a
small parameter such that $\epsilon^2 \ll 1$ and a matched asymptotic expansion is used
to derive the solutions. We comment that the scaling adopted here differs from
that previously adopted in this chapter and, in particular, it is assumed here
that the flux of species and the diffusive and drift terms are all significant at the
zeroth-order.
6.4.1 A Perturbation Approach

In the interior of the domain $\Omega$ a solution is sought of the form

$$\phi = \phi^{(0)} + \epsilon\phi^{(1)} + \cdots,$$  \hspace{1cm} (6.117)
$$n = N^{(0)} + \epsilon N^{(1)} + \cdots,$$  \hspace{1cm} (6.118)
$$p = P^{(0)} + \epsilon P^{(1)} + \cdots.$$  \hspace{1cm} (6.119)

Defining $C^{(0)} = N^{(0)} = P^{(0)}$ the leading order "outer" solutions within the interior of $\Omega$ are shown to be

$$C^{(0)} = \frac{J^{(0)}}{2}(x + a^{(0)}),$$  \hspace{1cm} (6.121)
$$\Phi^{(0)} = -\frac{I^{(0)}}{J^{(0)}} \ln(x + a^{(0)}) + b^{(0)},$$  \hspace{1cm} (6.122)

containing four unknown constants $J^{(0)}$, $I^{(0)}$, $a^{(0)}$ and $b^{(0)}$.

In the boundary layer near $x = 0$, the stretched coordinate $x = \epsilon \zeta$ is introduced and in terms of this coordinate the fields are redefined as

$$p(\epsilon\zeta; \epsilon) = \varpi(\zeta; \epsilon),$$  \hspace{1cm} (6.123)
$$n(\epsilon\zeta; \epsilon) = \mu(\zeta; \epsilon),$$  \hspace{1cm} (6.124)
$$\phi(\epsilon\zeta; \epsilon) = \psi(\zeta; \epsilon).$$  \hspace{1cm} (6.125)

Each field is written as an asymptotic series

$$\varpi(\zeta; \epsilon) = \varpi^{(0)}(\zeta) + \epsilon\varpi^{(1)}(\zeta) + \cdots,$$  \hspace{1cm} (6.126)
$$\mu(\zeta; \epsilon) = \mu^{(0)}(\zeta) + \epsilon\mu^{(1)}(\zeta) + \cdots,$$  \hspace{1cm} (6.127)
$$\psi(\zeta; \epsilon) = \psi^{(0)}(\zeta) + \epsilon\psi^{(1)}(\zeta) + \cdots.$$  \hspace{1cm} (6.128)

Integrating the leading order problem of the Nernst-Planck equations and applying the boundary conditions at $\zeta = 0$ gives

$$\varpi^{(0)} = p_L e^{-\psi^{(0)} + V}, \quad \mu^{(0)} = n_L e^{\psi^{(0)} - V},$$  \hspace{1cm} (6.129)

and some manipulation yields the ordinary differential equation

$$-\psi^{(0)}_{\zeta\zeta} = p_L e^{-\psi^{(0)} - V} - n_L e^{\psi^{(0)} - V}.$$  \hspace{1cm} (6.130)

Integrating this equation once after multiplying by $\psi^{(0)}_{\zeta}$ gives

$$-\frac{1}{2} (\psi^{(0)}_{\zeta})^2 + (c^{(0)})^2 = -p_L \left( e^{-\psi^{(0)} - V} - 1 \right) - n_L \left( e^{\psi^{(0)} - V} - 1 \right).$$  \hspace{1cm} (6.131)
Matching the boundary layer and interior representations of the problem suggests

\[ C^{(0)}(0) = \varphi^{(0)}(\infty), \quad (6.132) \]
\[ C^{(0)}(0) = \mu^{(0)}(\infty), \quad (6.133) \]
\[ \Phi^{(0)}(0) = \psi^{(0)}(\infty), \quad (6.134) \]

with

\[ \psi^{(0)}(\infty) = 0. \quad (6.135) \]

By employing these matching conditions and the forms of the solution in each region it can be deduced that

\[ (C^{(0)}(0))^2 = \frac{1}{4} \left( J^{(0)}(1) \right)^2 (a^{(0)})^2 = p_L n_L \quad (6.136) \]

and

\[ \Phi^{(0)}(0) = -\frac{I^{(0)}}{J^{(0)}} \ln a^{(0)} + b^{(0)} = \frac{1}{2} \ln \frac{p_L}{n_L} + V. \quad (6.137) \]

Two additional relations between the constants \( J^{(0)} \), \( I^{(0)} \), \( a^{(0)} \) and \( b^{(0)} \) can be derived by considering the boundary layer near \( x = 1 \) and thus a complete solution can be determined. By considering the stretched variable

\[ \eta = \frac{-1 + x}{\epsilon} \quad (6.138) \]

and a similar procedure to the earlier one the additional relations can be shown to be

\[ (C^{(0)}(1))^2 = \frac{1}{4} \left( J^{(0)}(1) \right)^2 (1 + a^{(0)})^2 = p_R n_R, \quad (6.139) \]
\[ \Phi^{(0)}(1) = -\frac{I^{(0)}}{J^{(0)}} \ln (1 + a^{(0)}) + b^{(0)} = \frac{1}{2} \ln \frac{p_R}{n_R} + V. \quad (6.140) \]

Now the interior solution can be completely determined,

\[ C^{(0)} = \sqrt{p_L n_L} (1 - x) + \sqrt{p_R n_R} x \quad (6.141) \]
\[ \Phi^{(0)}(x) = \Phi^{(0)}(0) (1 - F(x)) + \Phi^{(0)}(1) F(x), \quad (6.142) \]

where

\[ F(x) = \frac{\ln \left\{ 1 - x + \left( \frac{p_R n_R}{p_L n_L} \right)^{1/2} x \right\}}{\ln \left( \frac{p_R n_R}{p_L n_L} \right)^{1/2}} \quad (6.143) \]
The boundary layer equation at the left end (6.131) and the matching condition (6.135) imply that

\[ (c^{(0)})^2 = 2(\sqrt{p_L} - \sqrt{n_L})^2. \]  

Barcilon et al [40] introduce a new variable

\[ s = e^{(\psi^{(0)}(\zeta) - V)/2} \]  

and define

\[ a = \left( \frac{p_L}{n_L} \right)^{1/4} \]  

Equation (6.131) is then rewritten as

\[ s' = \pm \frac{1}{\sqrt{2}} \left( n_L^{1/2} s^2 - p_L^{1/2} \right). \]  

For consistency it is the minus sign that must be chosen and equation (6.147) is integrated with respect to \( \zeta \) to yield

\[ s = \frac{a(1 + t)}{1 - t} \]  

where

\[ t = \left( \frac{1 - a}{1 + a} \right) e^{-\sqrt{2n_L}a\zeta}. \]  

The form of the solution is dependent upon the boundary conditions for \( n \) and \( p \) with three possible cases arising:

1. If \( n_L = p_L \), then \( \psi^{(0)} = V \).

2. If \( n_L < p_L \), then

\[ \psi^{(0)}(\zeta) = V + 2 \ln \left( \frac{a \left( 1 + \frac{1-a}{1+a} e^{-a\sqrt{2n_L}\zeta} \right)}{\left( 1 - \frac{1-a}{1+a} e^{-a\sqrt{2n_L}\zeta} \right)} \right), \]  

an increasing function of \( \zeta \) on \([0, \infty)\).

3. If \( n_L > p_L \), the solution (6.150) is a decreasing function of \( \zeta \) with \( V + 2 \ln a \geq \psi^{(0)}(\zeta) \geq V \).

Using the form of the species solution through the boundary layer

\[ \varphi^{(0)} = p_L e^{-\psi^{(0)} + V}, \quad \mu^{(0)} = n_L e^{\psi^{(0)} - V}, \]  

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on \([0, \infty)\) the species concentrations are determined,

\[
\nu(\zeta)^{(0)} = \sqrt{\frac{p_Ln_L}{n_L}} \left( \frac{1 - \frac{1-a}{1+a}e^{-a\sqrt{2n_L\zeta}}}{1 + \frac{1-a}{1+a}e^{-a\sqrt{2n_L\zeta}}} \right)^2 ,
\]

(6.152)

\[
\mu(\zeta)^{(0)} = \sqrt{\frac{p_Ln_L}{n_L}} \left( \frac{1 + \frac{1-a}{1+a}e^{-a\sqrt{2n_L\zeta}}}{1 - \frac{1-a}{1+a}e^{-a\sqrt{2n_L\zeta}}} \right)^2 .
\]

(6.153)

A similar analysis can be performed at the right end of \(\Omega = (0, 1)\) to produce formulas in the interval \((-\infty, 0]\), namely,

1. If \(n_R = p_R\), then \(\tilde{\psi}^{(0)} = 0\).

2. If \(n_R < p_R\), then

\[
\tilde{\tilde{\psi}}^{(0)}(\zeta) = 2 \ln \left( \frac{a \left( 1 + \frac{1-a}{1+a}e^{-a\sqrt{2n_R\eta}} \right)}{1 - \frac{1-a}{1+a}e^{-a\sqrt{2n_R\eta}}} \right) ,
\]

(6.154)

a decreasing function of \(\eta\) on \((-\infty, 0]\).

3. If \(n_R > p_R\), the solution (6.154) is a increasing function of \(\eta\) on \((-\infty, 0]\).

Finally, the species concentrations at the right-end boundary layer are determined as

\[
\tilde{\nu}^{(0)}(\zeta) = \sqrt{\frac{p_Rn_R}{n_R}} \left( \frac{1 - \frac{1-a}{1+a}e^{a\sqrt{2n_R\eta}}}{1 + \frac{1-a}{1+a}e^{a\sqrt{2n_R\eta}}} \right)^2 ,
\]

(6.155)

\[
\tilde{\mu}^{(0)}(\zeta) = \sqrt{\frac{p_Rn_R}{n_R}} \left( \frac{1 + \frac{1-a}{1+a}e^{a\sqrt{2n_R\eta}}}{1 - \frac{1-a}{1+a}e^{a\sqrt{2n_R\eta}}} \right)^2 .
\]

(6.156)

To form a uniformly valid approximation throughout \(\Omega\), the boundary layer and the interior solutions are added and the common parts subtracted. To \(O(\epsilon)\) these are

\[
\phi(x) = \psi^{(0)}(\epsilon^{-1}x) + \Psi^{(0)}(x) + \tilde{\psi}^{(0)}(\epsilon^{-1}(1 - x)) - \frac{1}{2} \ln \frac{p_Rp_L}{n_Rn_L} - V + O(\epsilon) ,
\]

(6.157)

\[
n(x) = n_Le^{[\psi^{(0)}(\epsilon^{-1}x) - V]} + C^{(0)}(x) + n_Re^{[\tilde{\psi}^{(0)}(\epsilon^{-1}(x-1))] - (p_Ln_L)^{1/2}} - (p_Rn_R)^{1/2} + O(\epsilon) ,
\]

(6.158)

\[
p(x) = p_Le^{[-\psi^{(0)}(\epsilon^{-1}x) + V]} + C^{(0)}(x) + p_Re^{[\tilde{\psi}^{(0)}(\epsilon^{-1}(x-1))] - (p_Ln_L)^{1/2}} - (p_Rn_R)^{1/2} + O(\epsilon) .
\]

(6.159)

Equations (6.157)-(6.159) describe profiles of the species of the PNP system that exhibit sharp boundary layers near \(x = 0\) and \(x = 1\) but are smooth throughout \(\Omega\).
Away from the boundary regions the profiles are dominated by the outer solution indicating that the solution in the boundary layer near \(x = 0\) is independent of that near \(x = 1\) and \textit{vice-versa}. This validates the approach of Section 6.2 that adopted solutions to the outer problem (e.g. \(E_{\text{bulk}}\)) as boundary conditions for the inner solution.

6.4.2 A Numerical Implementation

The PNP system of equations (6.111)-(6.113) with boundary conditions (6.114)-(6.116) form a \textit{stiff} two-point boundary value problem containing a perturbation parameter \(\epsilon \ll 1\). Such a stiff system requires to be solved numerically, in this case by employing Automatic Continuation with Collocation [53] and Broyden’s Method [48] - a globally convergent method for nonlinear systems of equations.

The idea of the continuation is to solve a chain of problems in which the perturbation parameter decreases monotonically towards some desired value. Thus, a sequence of solutions are determined to the PNP system (6.111)-(6.116) for

\[
\epsilon_{\text{start}} > \epsilon_1 > \epsilon_2 > \cdots > \epsilon_{\text{min}} > 0
\]  

(6.160)

where \(\epsilon_{\text{start}}\) is a user-defined starting value and \(\epsilon_{\text{min}}\) is the desired final value of the parameter. The code automatically selects intermediate values of \(\epsilon\) and passes on meshes and solutions at each step.

Rather than applying boundary conditions for all species and the potential, a final desired value for each of the species concentrations is specified at the left or right of the computational domain. The system is solved using the continuation approach described above with an estimated initial value of the flux imposed. This estimate is refined using Broyden’s Method until the predicted species concentrations match the specified species concentrations (to within a level of tolerance). The continuation code outputs the data for the minimum value of \(\epsilon\) at which a solution can be determined and at that point, by integrating (6.112) and (6.113) from left to right, the flux of the \(i\)-th species \(J_i\) is calculated as

\[
J_i = \frac{c_{i,R}e^{\epsilon_0 \phi_R} - c_{i,L}e^{\epsilon_0 \phi_L}}{\int_0^1 e^{\epsilon_0 \phi(x)} dx},
\]

(6.161)

where \(\phi_L, \phi_R, c_{i,L}, c_{i,R}\) represent the calculated values of the potential and the concentration of the \(i\)-th species at \(x = 0\) and \(x = 1\), respectively. Updated values of the flux of each species are determined via Broyden’s method and the problem solved with the updated flux. The procedure continues until all the desired boundary conditions are satisfied and the system is solved for \(\epsilon_{\text{min}}\).
Table 6.3: A comparison of the numerical solution of the PNP system (6.111)-(6.116) to those of Barcilon [40]. The superscripts \( b \) and \( SPFS \) indicate respectively the numerical and the singular perturbation full solution of [40].

<table>
<thead>
<tr>
<th>( p_L )</th>
<th>( n_L )</th>
<th>( p_R )</th>
<th>( n_R )</th>
<th>( V )</th>
<th>( J_{SPFS}^p )</th>
<th>( J_{SPFS}^n )</th>
<th>( J_{SPFS}^b )</th>
<th>( I_{SPFS}^b )</th>
<th>( \epsilon )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>4</td>
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<td>1.29</td>
<td>7.45</td>
<td>6.16</td>
<td>8.74</td>
<td>8.72 ( \times 10^{-2} )</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.32</td>
<td>7.33</td>
<td>6.00</td>
<td>8.66</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.31</td>
<td>7.36</td>
<td>6.05</td>
<td>8.67</td>
<td></td>
</tr>
<tr>
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<td>1</td>
<td>4</td>
<td>4</td>
<td>8</td>
<td>12.2</td>
<td>20.5</td>
<td>8.27</td>
<td>32.7</td>
<td>8.72 ( \times 10^{-2} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>14.3</td>
<td>20.3</td>
<td>6.00</td>
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<td></td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>13.3</td>
<td>20.1</td>
<td>6.80</td>
<td>33.4</td>
<td></td>
</tr>
<tr>
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<td>4</td>
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<td>1</td>
<td>-0.821</td>
<td>1.36</td>
<td>2.19</td>
<td>0.543</td>
<td>8.72 ( \times 10^{-2} )</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>-0.831</td>
<td>1.35</td>
<td>2.18</td>
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</tr>
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<td>1.35</td>
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</tr>
<tr>
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<td>6</td>
<td>6</td>
<td>9</td>
<td>1</td>
<td>-3.10</td>
<td>6.82</td>
<td>9.93</td>
<td>3.73</td>
<td>5.81 ( \times 10^{-2} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-3.18</td>
<td>6.66</td>
<td>9.84</td>
<td>3.49</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-3.35</td>
<td>6.47</td>
<td>9.82</td>
<td>3.12</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.3 compares values calculated in our numerical studies\(^4\) with some of the numerical results\(^5\) and the solution to the singular perturbation full solution\(^6\) presented by Barcilon et al [40]. In general, our numerically calculated values of flux and current more closely match the singular perturbation solutions than those of Barcilon.

Our implementation generalises the numerical simulations of Barcilon et al [40] by allowing more than two species of varying valencies \( z_i \) to be considered. This is illustrated in Figure 6.21 where the concentration profiles are shown and in Figure 6.22 which compares the electric potential of this case to that of a symmetric electrolyte.

Finally, Table 6.4 is a comparison of the species fluxes \( J_i \) under various conditions. In particular, note that for the case of a three species symmetric electrolyte\(^7\) the sum of the cation fluxes are equal to the anion flux, as one would expect.

### 6.4.3 Relating the previous sections

In the previous section a numerical approach to solving the Poisson-Nernst-Planck equations was presented. Here, we use this work to validate the boundary layer analysis presented in the first section of this chapter.

---

\(^4\)Appearing without superscripts - e.g. \( J_p \).

\(^5\)e.g. \( J_{SPFS}^p \).

\(^6\)e.g. \( J_{SPFS}^p \).

\(^7\)That is, the fourth entry in Table 6.4.
Figure 6.19: The corrections $u_1^{(2)}$ and $u_2^{(2)}$ to the anion and cation concentrations respectively for values of $\gamma = -1/2, -1, -2$ with $\sigma = 0.6$, $K_m = 1$, $E_{bulk} = 1$.

Table 6.4: A comparison of species fluxes.

<table>
<thead>
<tr>
<th>$z_i$</th>
<th>$c_i(0)$</th>
<th>$c_i(1)$</th>
<th>$V$</th>
<th>$J_i$</th>
<th>$\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>4.916</td>
<td>$8.72 \times 10^{-2}$</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>5</td>
<td></td>
<td>1.918</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>5</td>
<td></td>
<td>0.350</td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>4.22</td>
<td>$8.72 \times 10^{-2}$</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>10</td>
<td></td>
<td>4.22</td>
<td></td>
</tr>
<tr>
<td>-2</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>0.65</td>
<td>$8.72 \times 10^{-2}$</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>10</td>
<td></td>
<td>5.23</td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>3.72</td>
<td>$1.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>5</td>
<td></td>
<td>1.86</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>5</td>
<td></td>
<td>1.86</td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>5.33</td>
<td>$1.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>10</td>
<td></td>
<td>0.60</td>
<td></td>
</tr>
</tbody>
</table>
The one-dimensional form of equations (6.12) and (6.13) within the interval \( \Omega = (0, 1) \) is

\[
\frac{d}{dx} \left[ \alpha \frac{d}{dx} c_i + z_i c_i \frac{d\phi}{dx} \right] = 0 \quad i = 1..N \tag{6.162}
\]

\[-\beta \frac{d^2\phi}{dx^2} = \sum_{i=1}^{N} z_i c_i, \tag{6.163}
\]

with the boundary conditions

\[
\alpha \frac{d}{dx} c_i + z_i c_i \frac{d\phi}{dx} = -Q_i \quad \text{at} \quad x = 0, \tag{6.164}
\]

and

\[
c_i(0) = c_{i,L} > 0, \quad c_i(1) = c_{i,R} \tag{6.165}
\]

\[
\phi(0) = 1, \quad \phi(1) = 0. \tag{6.166}
\]

Recall, the parameters

\[
\alpha = \frac{RT}{F\phi_0}, \quad \beta = \frac{\varepsilon \phi_0}{c^2 FL^2}, \quad \eta_i = \frac{D}{D_i},
\]

where \( \beta \ll \alpha \ll 1 \) and \( \phi_0 \) is the applied voltage and \( L \) is the average gapwidth. Expressing \( \beta \) as \( \alpha^k \), it is readily shown that \( k = \ln(\beta)/\ln(\alpha) \) and the problem can be expressed solely in terms of the small parameter \( \alpha \). By applying the numerical approach of the Section 6.4.2 to the boundary value problem (6.162)-(6.166),
Figure 6.21: The profiles of 3 species concentrations $c_i(x)$ with varying valencies: $z_1 = -1; z_2 = 1; z_3 = 2; V = 1$ and $\epsilon = 8.72 \times 10^{-2}$. The boundary conditions are $c_1(0) = 10, c_1(1) = 1, c_2(0) = 0.5, c_2(1) = 5, c_3(0) = 0.5, c_3(1) = 5$.

Figure 6.22: The profiles of the electric potential for electrolytes comprising species with valencies: (a) $z_1 = -1; z_2 = 1; z_3 = 2$; and (b) $z_1 = -1; z_2 = z_3 = 2$. Here, $V = 1$ and $\epsilon = 8.72 \times 10^{-2}$. The boundary conditions are $c_1(0) = 10, c_1(1) = 1, c_2(0) = 0.5, c_2(1) = 5, c_3(0) = 0.5, c_3(1) = 5$. 
the potential, potential gradient and concentration profiles can be determined throughout \( \Omega = (0, 1) \). Figures 6.23 - 6.25 show these profiles for the case where 
\[ c_1(0) = 2, \ c_1(1) = 1, \ c_2(0) = 1, \ c_2(1) = 2, \ \phi(0) = 1, \ \text{and} \ \phi(1) = 0. \]
A boundary layer of width \( O(\delta) \) units is apparent. Note that Figure 6.23 indicates an nondimensional overpotential of approximately \( 3.5 \times 10^{-4} \) units.

The scalings used within the first section of this chapter indicated that the electric field within the boundary layer can be written as

\[
E = \frac{\delta}{\alpha} E_\perp = -\frac{\delta}{\alpha} \frac{d\phi}{dx}
\]

where \( E_\perp, \phi \) and \( x = \delta s \) are variables of the outer region of the computational domain. Thus, the value of the potential gradient at \( x = 0 \) - calculated in the solution to equations (6.162)-(6.166) - can be used to provide an initial value of the electric field \( E(0) \) in the boundary layer analysis of Section 6.2. Similarly, the bulk value of the electric field \( E_{bulk} \) can also be determined.

Thus, for the example of Figures 6.23-6.25,

\[
\frac{d\phi}{dx}(0) = -261.277 \Rightarrow E(0) = 0.588,
\]

and

\[
-\frac{d\phi}{dx}(0.5) = E_{bulk} = 0.999.
\]

Notice, that the values of \( E(0) \) and \( E_{bulk} \) agree with the orders of magnitude of these in our earlier analyses.

Utilising this approach, Table 6.5 displays the overpotentials calculated by the boundary layer methods of Section 6.2 and Section 6.4, \( \eta^{darling} \) and \( \eta^{ppm} \) respectively. In these cases, the applied potential difference is fixed at \( \phi = 1 \) and the concentration of the species at \( x = 0 \) and \( x = 1 \) are altered. The values of \( \eta^{darling} \) and \( \eta^{ppm} \) are similar and, as one would expect, the overpotential increases as the concentrations of species increase at the electrode surface (\( x = 0 \)).
Figure 6.23: The profile of the electric potential in the boundary layer: $z_1 = -1$; $z_2 = 1$, $\phi_0 = 25\text{V}$, $L = 0.05\text{cm}$, $\alpha = 1.0398\times10^{-3}$, $\beta = 5.2674\times10^{-9}$, $\delta = 2.3403\times10^{-6}$. The boundary conditions are $c_1(0) = 2$, $c_1(1) = 1$, $c_2(0) = 1$, $c_2(1) = 2$, $\phi(0) = 1$, $\phi(1) = 0$.

Figure 6.24: The profile of the gradient of the electric potential in the boundary layer: $z_1 = -1$; $z_2 = 1$, $\phi_0 = 25\text{V}$, $L = 0.05\text{cm}$, $\alpha = 1.0398\times10^{-3}$, $\beta = 5.2674\times10^{-9}$, $\delta = 2.3403\times10^{-6}$. The boundary conditions are $c_1(0) = 2$, $c_1(1) = 1$, $c_2(0) = 1$, $c_2(1) = 2$, $\phi(0) = 1$, $\phi(0) = 0$. 

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Figure 6.25: The profile of $c_1$ and $c_2$ in the boundary layer: $z_1 = -1; z_2 = 1$, $\phi_0 = 25\text{V}, L = 0.05 \text{ cm}, \alpha = 1.0398 \times 10^{-3}, \beta = 5.2674 \times 10^{-9}, \delta = 2.3403 \times 10^{-6}$. The boundary conditions are $c_1(0) = 2, c_1(1) = 1, c_2(0) = 1, c_2(1) = 2, \phi(0) = 1, \phi(0) = 0$.

Table 6.5: The a comparison of the overpotentials $\eta^{\text{darling}}$ and $\eta^{\text{ppm}}$ calculated by the methods of Sections 6.2 and 6.4 respectively: $\phi(0) = 1, \phi(1) = 0, z_1 = -z_2 = 1, 0 < x < 1$.

<table>
<thead>
<tr>
<th>$c_1(0)$</th>
<th>$c_1(1)$</th>
<th>$c_2(0)$</th>
<th>$c_2(1)$</th>
<th>$\eta^{\text{darling}}$</th>
<th>$\eta^{\text{ppm}}$</th>
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Chapter 7

Conclusions

7.1 Resume

In this study we have focused on the development of models to describe electrochemical machining processes and upon the numerical treatment of these methods. Techniques are described that determine the evolution of workpiece surfaces produced under electrochemical machining regimes.

Chapter 1 gives a description of the machining problem and of the ECM, EDM and ECAM machining processes. A review of work relating to the machining problem is presented and the relevance of this study is provided.

In Chapter 2 some basic electrochemistry is presented and the effect of important electrochemical phenomena (e.g. overpotentials and the electrical double layer) is discussed. A mathematical description of the electrochemistry is provided from which, in Chapter 3, a general mathematical model describing the machining process is derived. It is demonstrated how the electrochemical phenomena presented in Chapter 2 can be incorporated in the model through the application of a variety of boundary conditions. In particular, the inclusion of overpotential effects is demonstrated and an equation is constructed to describe the evolution of the anode surface under Faradaic and ECAM machining regimes.

In Chapter 4 a solution to the machining problem is presented that employs a perturbation method, assuming that the electrode surfaces vary only slightly from the plane case. This work provides an extension to earlier studies by the incorporation of ECAM machining effects and through the inclusion of overpotential effects. Some specific examples are considered and a comparison of machining regimes is provided. It is clear, however, that this perturbation approach applied only to a small class of machining problems and is not applicable to most practical cases.

To extend the model to apply to a wider class of problems the development of a two-dimensional model based upon a boundary integral method (BIM) was
undertaken. This work is described in Chapter 5. A theoretical justification of the BIM and its applicability to the machining problem is given and a description of its numerical implementation provided. Techniques of resolving numerical issues - e.g. the updating of the free surface and the evaluation of integrals near corner regions - are presented and the inclusion of nonlinear boundary conditions reviewed. In the final sections of the chapter the accuracy of the method is validated through a comparison with analytical solutions of some simple cases and its application to a wider class of problems is demonstrated by a number of examples. In particular, the BIM approach is demonstrated to cope with the presence of regions of insulation, variations in the applied potential difference, general tool movements and the incorporation of a variety of machining rules.

In Chapter 6 an analysis of the electrical double layer is conducted. The diffusion, convection and migration of ions within an electrolytic cell together with the distribution of the electric field are described by the Poisson-Nernst-Planck equations. This system of partial differential equations is written in terms of curvilinear coordinates consisting of two surface coordinates and a third coordinate normal to the electrode surface. An analysis of the system is conducted with regard to effects in the normal and transverse direction and a singular perturbation method is applied that permits the system to be treated as a set of simultaneous ordinary differential equations. Electrode curvature effects are included in the model and a method of determining the boundary layer solutions described. Previous work is extended to determine the profile of species in "non-symmetric" electrolytes and to examine the influence of electrode curvature. In addition, an extension is undertaken to work that formulates the problem in terms of the electric potential. This numerical procedure permits the profile of multiple species to be calculated.

7.2 Future Work

Whilst this study has examined a wide variety machining configurations the practical problems exists in a three-dimensional world. Further, our two-dimensional boundary integral method largely uncouples the electrostatic problem from the ion concentrations for which a fuller set of equations are required. This does not invalidate the work undertaken here but the fuller problem requires examination for special cases to compare and validate our models. The numerical procedures adopted within the boundary integral method can also be made more sophisticated - e.g. through the use of shape functions - and the author is now aware of other advanced numerical techniques that could be employed in alter-
native approaches. In particular, parallel numerical techniques and libraries are now available that could be employed in solving the computationally demanding problem in both two and three dimensions. Finally, it was intended that the solutions of the boundary layer problem be coupled to those of the BIM method to provide a complete description of the distribution of the electric potential, the electric field and of species concentrations throughout the computational domain. This problem was partly addressed in Chapter 6.
Appendix A

Terms in the Mass Transport Equations in Terms of a Curvilinear Coordinate System

Using the definitions in Chapter 6, for $\alpha, \beta = 1, 2,$

$$g_\alpha = \frac{\partial r}{\partial \chi^\alpha} = \frac{\partial R}{\partial \chi^\alpha} + \chi^3 \frac{\partial n}{\partial \chi^\alpha}, \quad (A.1)$$

and

$$g_3 = n = \frac{g_1 \wedge g_2}{\sqrt{g}}, \quad (A.2)$$

where

$$g_{\alpha\beta} = g_\alpha \cdot g_\beta \quad (A.3)$$

and

$$g = g_{11}g_{22} - (g_{12})^2. \quad (A.4)$$

Assuming $\delta \ll 1,$ writing $\delta s = \chi^3$ and defining, at $\chi^3 = s = 0,$

$$G_{\alpha\beta} = \frac{\partial R}{\partial \chi^\alpha} \cdot \frac{\partial R}{\partial \chi^\beta}, \quad (A.5)$$

$$H_{\alpha\beta} = \frac{\partial R}{\partial \chi^\alpha} \cdot \frac{\partial n}{\partial \chi^\beta} + \frac{\partial R}{\partial \chi^\beta} \cdot \frac{\partial n}{\partial \chi^\alpha}, \quad (A.6)$$

$$L_{\alpha\beta} = \frac{\partial n}{\partial \chi^\alpha} \cdot \frac{\partial n}{\partial \chi^\beta}, \quad (A.7)$$

it follows that

$$g_{\alpha\beta} = G_{\alpha\beta} + \delta sH_{\alpha\beta} + \delta^2 s^2 L_{\alpha\beta} \quad (A.8)$$

\footnote{By convention $\alpha$ and $\beta$ are used to denote indices running from 1 to 2. In this Appendix we follow that convention and stress that $\alpha$ and $\beta$ no longer denote the small parameters introduced in Chapter 6. It is still assumed, however, that $\delta \ll 1.$}
and
\[
g = G_{11}G_{22} - G_{12}^2 + \delta s [G_{11}H_{22} + G_{22}H_{11} - 2G_{12}H_{12}] + \delta^2 s^2 [G_{11}L_{22} + H_{11}H_{22} + L_{11}G_{22} - 2G_{12}L_{12} - (H_{12})^2] + \delta^3 s^3 [H_{11}L_{22} + L_{11}H_{22} - 2H_{12}L_{12}] + \delta^4 s^4 [L_{11}L_{22} - (L_{12})^2]. \tag{A.9}
\]

For a surface vector \( w(\chi^1, \chi^2, 0) \), let \( w_\alpha \) denote \( \partial w / \partial \chi^\alpha \) and define
\[
E = R_1 \cdot R_1, \quad F = R_1 \cdot R_2, \quad G = R_2 \cdot R_2, \\
L = -R_1 \cdot n_1, \quad M = -\frac{1}{2} (R_1 \cdot n_2 + R_2 \cdot n_1), \quad N = -R_2 \cdot n_2,
\]
The Mean and Gaussian curvatures of the surface are [51]
\[
K_m = \frac{EN + GL - 2FM}{2(EG - F^2)}, \tag{A.10}
\]
\[
K_g = \frac{LN - M^2}{EG - F^2}, \tag{A.11}
\]
respectively and equation (A.9) can now be re-expressed as
\[
g = EG - F^2 - 2\delta s [EN + GL - 2FM] + 2\delta^2 s^2 [(EN + GL - 2FM)K_m - (EG - F^2)K_g + 2(LN - M^2)] + 2\delta^3 s^3 [(EN + GL - 2FM)K_g - 4(LN - M^2)K_m] + \delta^4 s^4 [(EG - F^2)K_g^2 - 2(EN + GL - 2FM)K_mK_g + 4K_m^2(LN - M^2)].
\]
Writing, \( \Delta = EG - F^2 \) and using definitions (A.10) and (A.11) it is readily shown that
\[
g = \Delta \{1 - \delta s [4K_m] + \delta^2 s^2 [4K_m^2 + 2K_g] - \delta^3 s^3 [4K_mK_g] + \delta^4 s^4 [K_g^2] \}
\]
and, for \( \delta s K_m \) small,
\[
\ln(g) \simeq \ln \Delta - 4\delta s K_m + O(\delta^2). \tag{A.12}
\]
Thus,
\[
\frac{1}{\sqrt{g}} \frac{\partial(\sqrt{g})}{\partial s} = \frac{1}{2} \frac{\partial \ln(g)}{\partial s} \simeq -2\delta K_m + O(\delta^2), \tag{A.13}
\]
\[
\frac{1}{\sqrt{g}} \frac{\partial(\sqrt{g})}{\partial \chi^\alpha} = \frac{1}{2} \frac{\partial \ln(g)}{\partial \chi^\alpha} \simeq \frac{1}{2} \frac{\partial \ln \Delta}{\partial \chi^\alpha} - 2\delta s \frac{\partial K_m}{\partial \chi^\alpha} + O(\delta^2). \tag{A.14}
\]

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and for a scalar \( \theta = \theta(\chi^1, \chi^1, s) \)

\[
\frac{1}{\sqrt{g}} \frac{\partial (\sqrt{g} \theta)}{\partial s} \approx \frac{\partial \theta}{\partial s} - 2\delta K_m \theta + O(\delta^2), \quad (A.15)
\]

\[
\frac{1}{\sqrt{g}} \frac{\partial (\sqrt{g} \theta)}{\partial \chi^\alpha} \approx \frac{\partial \theta}{\partial \chi^\alpha} + \frac{1}{2} \theta \frac{\partial \ln \Delta}{\partial \chi^\alpha} - 2\delta s \theta \frac{\partial K_m}{\partial \chi^\alpha} + O(\delta^2). \quad (A.16)
\]

The covariant and contravariant components of the surface metric tensor, \( g_{\alpha\beta} \)
and \( g^{\alpha\beta} \) respectively, are related such that

\[
g^{\alpha\beta} = \frac{1}{g_{\alpha\beta}} \quad (A.17)
\]

and hence, for small \( \delta \)

\[
g^{\alpha\beta} \approx \frac{1}{G_{\alpha\beta}} \left( 1 - \delta s \frac{H_{\alpha\beta}}{G_{\alpha\beta}} + O(\delta^2) \right) \quad (A.18)
\]

and

\[
\frac{\partial}{\partial \chi^\alpha} \left( g^{\alpha\beta} \frac{\partial \theta}{\partial \chi^\beta} \right) \approx \frac{1}{G_{\alpha\beta}} \frac{\partial^2 \theta}{\partial \chi^\alpha \partial \chi^\beta} - \frac{1}{(G_{\alpha\beta})^2} \frac{\partial G_{\alpha\beta}}{\partial \chi^\alpha} \frac{\partial \theta}{\partial \chi^\beta} \\
+ \delta s \left\{ \left( \frac{2H_{\alpha\beta}}{(G_{\alpha\beta})^3} \frac{\partial G_{\alpha\beta}}{\partial \chi^\alpha} - \frac{1}{G_{\alpha\beta}} \frac{\partial H_{\alpha\beta}}{\partial \chi^\alpha} \right) \frac{\partial \theta}{\partial \chi^\beta} - \frac{H_{\alpha\beta}}{(G_{\alpha\beta})^2} \frac{\partial^2 \theta}{\partial \chi^\alpha \partial \chi^\beta} \right\} + O(\delta^2). \quad (A.19)
\]

Finally, we can conclude that

\[
\frac{1}{\sqrt{g}} \frac{\partial}{\partial \chi^\alpha} \left( \sqrt{g} g^{\alpha\beta} \frac{\partial \theta}{\partial \chi^\beta} \right) \approx \frac{1}{2G_{\alpha\beta}} \frac{\partial \ln \Delta}{\partial \chi^\alpha} \frac{\partial \theta}{\partial \chi^\beta} + \frac{1}{G_{\alpha\beta}} \frac{\partial^2 \theta}{\partial \chi^\alpha \partial \chi^\beta} - \frac{1}{(G_{\alpha\beta})^2} \frac{\partial G_{\alpha\beta}}{\partial \chi^\alpha} \frac{\partial \theta}{\partial \chi^\beta} \\
+ O(\delta s). \quad (A.20)
\]
Bibliography


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   http://www.ma.ic.ac.uk/~jcash/BVP_software/readme.html.