Modelling the Static and Dynamic Behaviour of Electrolytes: A Modified Poisson-Nernst-Planck Approach

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Abstract

In this thesis a method is presented for the modelling the effects of the excluded volume (ion-ion) and ion excess polarisability (ion-solvent) interactions in an electrolyte at a smooth planar electrode. The impact of these interactions is studied in terms of the equilibrium state of single and mixed electrolytes, the dynamic response of single electrolytes to a time-dependent applied potential, and their effect on the reaction rate, for both steady and time-dependent applied potentials. For reacting systems, the reaction rate is modelled using a modified form of the Frumkin-Butler-Volmer equation, in which the interactions are explicitly accounted for.

At equilibrium, the model offers improvement over models which only account for the excluded volume interaction, in terms of both the predicted electrolyte structure and the electrical properties of the electrode. For example accounting for the polarisability interaction is shown to limit and then reverse the growth in the differential capacitance at the point of zero charge as the bulk concentration increases, an effect is not seen when only the excluded volume interaction is accounted for. Another example is for mixed electrolytes, in which accounting for the polarisability interaction leads to better agreement with experimental data regarding the composition of the double layer.

For the response of an electrolyte to a potential step, the two interactions both lead to peaks in the time taken to reach equilibrium as a function of the potential. The effect of the domain length on the equilibration time is qualitatively discussed, together with the differences between the two interaction models. The response to a time-dependent potential is analysed through simulated electrochemical impedance spectroscopy and consideration of the capacitance dispersion effect. Between this and the potential step response data it is shown that the interactions themselves have little direct effect on the dynamic processes beyond the way in which they limit the ion concentrations in the double layer and alter the differential capacitance of the system.

The investigation of the effect of the ion interactions on the reaction rate shows that both terms can either increase or decrease the rate, relative to a system with no interactions, depending on the details of the reaction and the applied potential. This is linked to the changes in the electric field within the double layer, which are caused by the interactions, and how this affects the reactant flux in that region. In terms of simulated EIS, deviations are observed relative to the equivalent circuit for the system, the reasons for which are discussed.

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Declaration

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Geraint Minton
September 2013
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Nomenclature

\( \alpha_j \)       excess ion polarisability of species \( j \), m\(^3\)
\( \beta \)         the inverse thermal energy, equal to \( \frac{1}{k_B T} \)
\( \Delta G_{\text{RXN}} \)   Gibbs free energy of reaction, J
\( \Delta G_{\text{RXN}}^\ominus \)   Gibbs free energy of reaction in the standard state, J
\( \Delta \phi^\Theta \)   reaction equilibrium potential in the standard state, V
\( \Delta \phi^f \)      formal electrode potential, V
\( \Delta \phi_s \)      potential drop across the Stern layer, V
\( \Delta \phi_{\text{RXN}} \) reaction equilibrium potential, V
\( \epsilon(z) \)  local relative permittivity of the solvent
\( \epsilon^0 \) permittivity of free space = \( 8.85 \times 10^{-12} \) F m\(^{-1}\)
\( \epsilon_r \) relative permittivity of electrolyte
\( \epsilon_w \) relative permittivity of bulk water (taken to be 78)
\( \eta \) occupied volume fraction
\( \gamma \) transfer coefficient
\( \kappa^2 \) the Debye screening parameter, equal to \( 4\pi \beta \sum_j \epsilon_0^j z_j^2 e_0^2 / \epsilon_r \),
\( \kappa_c \) electrolyte conductivity, S m\(^{-1}\)
\( \Lambda_j \) thermal wavelength of species \( j \), equal to \( \frac{h}{\sqrt{2\pi m_j k_B T}} \), m
\( \mu_j \) (electro)chemical potential of species \( j \), J
\( \mu_j^{\text{ex}} \) excess chemical potential of species \( j \), J
\( \mu_j^{\text{res}} \) residual chemical potential, J
\( \nu \) viscosity, Pa s
\( \nu_j \)  
stoichiometric coefficient of reactant \( j \)

\( \Omega \)  
grand potential

\( \omega \)  
angular frequency, \( \text{rad} \, \text{s}^{-1} \)

\( \phi^0 \)  
applied electrode potential, \( \text{V} \)

\( \phi_\eta \)  
reaction overpotential, \( \text{V} \)

\( \phi_d \)  
diffuse layer potential drop, \( \text{V} \)

\( \rho \)  
charge density, \( \text{C} \, \text{m}^{-3} \)

\( \sigma \)  
surface charge density, \( \text{C} \, \text{m}^{-2} \)

\( \theta \)  
phase angle

\( \xi \)  
extent of reaction

\( \zeta \)  
unoccupied volume fraction

\( A \)  
surface area, \( \text{m}^2 \)

\( A_f \)  
reaction affinity

\( a_j \)  
diameter of species \( l \), \( \text{m} \)

\( a_{\text{c},j} \)  
activity of species \( j \)

\( b_j \)  
mobility of ion \( j \), \( \text{m}^2 \, \text{V}^{-1} \, \text{s} \)

\( C_d \)  
specific differential capacitance, \( \mu \text{F} \, \text{m}^{-2} \)

\( C_i \)  
specific instantaneous capacitance, \( \mu \text{F} \, \text{m}^{-2} \)

\( c_j \)  
number concentration of species \( j \), \( \text{m}^{-3} \)

\( c^0_j \)  
bulk number concentration of species \( j \), \( \text{m}^{-3} \)

\( c_{j,\text{max}} \)  
maximum number concentration of species \( j \), \( \text{m}^{-3} \)

\( D_j \)  
diffusion coefficient of species \( j \), \( \text{m}^2 \, \text{s}^{-1} \)

\( D_j^* \)  
dimensionless diffusion coefficient, equal to \( D_j/D_c \)

\( E \)  
électric field, \( \text{V} \, \text{m}^{-1} \)

\( e_0 \)  
elementary charge, \( 1.6 \times 10^{-19} \, \text{C} \)

\( F \)  
Helmholtz free energy, \( \text{J} \)

\( f^\circ \)  
free energy per unit volume, \( \text{J} \, \text{m}^{-3} \)
$i$ (as subscript) grid point label

$I_0$ exchange current density, $\text{A m}^{-2}$

$j$ (as subscript) ion label

$J_j$ flux of species species $j$, $\text{m}^{-2} \text{s}^{-1}$

$k^\oplus$ standard rate constant

$k_B$ Boltzmann constant, $1.38 \times 10^{-23} \text{JK}^{-1}\text{mol}^{-1}$

$k_f$ forward rate constant

$k_r$ reverse rate constant

$l_B$ the Bjerrum length, equal to $\frac{\beta e^2}{4\pi\epsilon_0\epsilon_r}$

$m^D$ dipole moment, $\text{A m}^2$

$m_j$ mass of species $j$

$N$ number of grid points

$N_A$ Avagadro’s number, $6.022 \times 10^{23} \text{M}^{-1}$

$n_e$ number of electrons transferred per reaction

$n_j$ number of particles of type $j$

$n_{RI}$ optical refractive index

$p$ pressure, $\text{Pa}$

$R$ resistance, $\Omega$

$r$ reaction rate, $\text{m}^{-2} \text{s}^{-1}$

$r_d$ hydrated ion radius, $\text{m}$

$S$ entropy, $\text{JK}^{-1}$

$s$ Stern layer width, $\text{m}$

$T$ absolute temperature, $\text{K}$

$t$ time, $\text{s}$

$u(r)$ convective velocity, $\text{m s}^{-1}$

$V$ system volume, $\text{m}^3$

$v_j$ ion volume, $\text{m}^3$
\( v_{pl} \) excluded volume between two particles, \( \text{m}^3 \)

\( Z \) impedance, \( \Omega \)

\( z \) position, \( \text{m} \)

\( Z^P \) partition function

\( z_j \) valency of species \( j \)

\( n \) normal vector to the boundary (equal to +1 at \( z = 0 \) and −1 at \( z = L \))

\( u \) convective velocity, \( \text{m} \text{s}^{-1} \)

\( \text{Ox} \) oxidised species

\( \text{Re} \) reduced species

\( \tilde{v}_{pl} \) mvdW excluded volume term
Chapter 1

Introduction

This thesis presents the development of a dynamic model for the behaviour of an electrolyte in the vicinity of an electrode in response to changes in the potential of the electrode. The model goes beyond the standard Gouy-Chapman model by accounting for the excluded volume interaction between the ions and the effect of the interaction between the ions and the solvent particles on the permittivity of the solvent. Furthermore, surface reactions are accounted for using a method which accounts for these ion interactions. This chapter presents a summary of the background and motivation for the research, together with a summary of the structure of the remainder of the thesis.

1.1 Background and motivation

A bulk aqueous ionic solution contains an equal amount of mobile positive and negative ionic charge, meaning that the solution is electrically charge neutral throughout. The introduction of a charged surface into the solution causes a rearrangement of the ions in the vicinity of the surface, with one set (the counter-ions) being attracted to the surface and the other set (the co-ions) being repelled. The result is for the properties of the electrolyte near the surface to differ from the bulk, with significantly different ion concentrations and, as a result, a net local charge density. This region is referred to as the electric double layer (EDL) and its effect is to shield the bulk electrolyte from the surface charge or, equivalently, it is the region which forms because of the potential difference between the surface and the bulk electrolyte.

Any interactions between the electrolyte and the surface must take place within the EDL, meaning that its structure and behaviour are more than a curiosity on the microscopic scale and can instead determine properties at a macroscopic scale. Furthermore the general surface/solution interface described is ubiquitous, being found in a number of different types of system and so making the its study relevant to several fields of science.

In biology, cell membranes are formed from two parallel layers of amphiphilic lipid molecules. In each layer, the molecules align such that the polar heads point in one direction and the hydrophobic tails in the other. The bilayer structure of the cell membrane is formed from two lipid layers arranged such that the hydrophobic side of each layer points in to the centre of the
membrane, leaving the two polar surfaces exposed as the surfaces of the membrane (Yeagle 2011). Within an organism, dissolved ions are found both inside outside cells, so there is an EDL on both sides of the membrane (Bohinc et al. 2008). Many biological processes involve the transfer of ions across the membrane, so the double layer structure will affect the surface concentrations and thus may affect the rate of transport. Furthermore, this ion transport occurs through ion channels, which are selective to specific ions. For modelling purposes, these are often considered to be cylindrical openings with a charge along the surface (Chen et al. 1997; Gillespie et al. 2002). By assuming that an EDL forms within the channel and accounting for the differences in ion sizes in the model, it is possible to explain the ion selectivity of some ions (Gillespie 2008).

The type of ion selectivity seen in biological systems can also be reproduced in man-made membranes. These can be used in devices for filtration and separation, such as dialysis or purification, and understanding how selectivity takes place may lead to the development of more efficient devices. Technologically, the development of micro- and nano-fluidic devices (Laser and Santiago 2004), wherein ion transport is controlled using an applied oscillating electric field, represents an additional system in which understanding the EDL is important. The scale of these devices is such that most or all of the transport occurs within an EDL, which can lead to unexpected behaviour, such as changes in the direction of flow as a function of the frequency of the applied field (Bazant et al. 2009).

The transport systems described above require a minimum of two dimensions for a full description (e.g. across and along the ion channel). Thus, although they demonstrate the importance of the EDL, they can only be partially described by the model developed in this work, which details a single-dimensional model of an electrode/electrolyte interface, for example the equilibrium structure of the EDL near the cell membrane, as opposed to the transport through an ion channel, where the transport occurs perpendicularly to the double layer. However, it may be possible to infer reasons for some types of behaviour seen in real-world systems, as discussed in the final chapter.

The EDL also plays an important role in the stability and electrokinetic properties of colloidal suspensions (Attard 2001; Quesada-Pérez et al. 2003) and in the formation and behaviour of clays and cements (Tripathy et al. 2013; Friedmann et al. 2012) although, as with transport in ion channels, these are not discussed in any depth in this work.

The model more directly relates to understanding the results of certain electrochemical measurements and experiments used in materials characterisation, such as the differential capacitance, cyclic voltammetry and electrochemical impedance spectroscopy, when performed on flat electrode surfaces. It also relates to understanding electrochemical electricity generation and energy storage devices such as batteries, fuel cells and supercapacitors. All three of these contain mobile ions between two electrodes and, with the exception of the latter, they also have electrochemical reactions at the surface, so their behaviour is partly defined by the structure of the EDL. Furthermore, the ion motion in these systems occurs perpendicularly to the electrode surfaces, in a similar fashion to that in the model which is developed. However, the model
represents an idealised electrode/electrolyte system aimed at understanding the influence of the excluded volume and the polarisability on the system and it is only in the final chapter that the means for modelling a specific real-world system are discussed.

The model presented in this work describes the surface/solution interface as a simple planar, ideally polarisable electrode adjacent to a region of electrolyte, of which a finite-length region is modelled, bound by the electrode at one side and the bulk electrolyte at the other. The electrolyte is described using a mean-field, local density approximation, similar to the Gouy-Chapman model. However, in contrast to that model, it moves away from the assumption that the ions are point-like charges which do not interact with the solvent by accounting for the excluded volume interactions and the ion excess polarisability, which alters the permittivity of the solvent. These have both previously been considered for single-electrolyte systems at equilibrium and, in the case of the excluded volume interaction, for some dynamic systems. In this work, however, a modified van der Waals excluded volume model is used, which permits mixtures of differently sized ions, marking it as different to the most commonly used excluded volume model which only permits one ion size to be used for all ions in a system. This is combined with a polarisability model to look at mixed electrolyte systems at equilibrium, the dynamic response of the electrolyte to a time-dependent electrode potential, and how the two ion properties affect reaction rates, both at steady state and under the condition of a time-dependent (oscillating) potential.

The predictions of the model are largely considered in terms of commonly measured experimental properties, such as the differential capacitance, the electric current at the electrode or electrochemical impedance spectra. For systems at equilibrium, comparison is made to experimental data, with the result that the model offers a significant improvement over models based on the assumption of point charges and some improvement over other mean-field models which only account for the excluded volume interaction. When considering dynamic and reacting systems, the effects of accounting for the ion volume and polarisability are considered relative to the predictions of models which do not account for these properties.

1.2 Structure of the thesis

This thesis is divided into eight chapters, the contents of which are as follows:

**Chapter 1: introduction.** In this chapter, a brief outline of the background and motivation for the research is presented.

**Chapter 2: background.** This chapter describes the methods by which the EDL is commonly modelled in the literature. The first part of the chapter covers models for the equilibrium state, the middle part describes the means by which the dynamic behaviour is accounted for, and in the final part the means by which electrochemical reactions are accounted for are discussed.
Chapter 3: theory. The derivation of the model from the starting point of the free energy functional for the system is described, leading to a mean-field, local-density approximation expression for the electrochemical potential. This is combined with the Nernst-Planck equation for the dynamics and the Poisson equation for the electrostatic potential, resulting in a set of simultaneous equations describing the system.

Chapter 4: method. The means for numerically solving the equations are discussed, whereby the equations are discretised in the spatial domain and the method of lines is used to solve the differential-algebraic expressions which result. A discussion of the errors inherent in the numerical solution of the equations is presented, as well as details of how the model was run to generate the data.

Chapter 5: equilibrium systems. The first of the results chapters, this presents a discussion of the effects of the inclusion of the ion interaction terms (the excluded volume and excess polarisability). The general changes to the structure which arise from ion interactions are described and the numerical output is compared to experimental differential capacitance data. An analytical model is presented for the differential capacitance of an electrolyte at zero potential and is used to discuss the changes the polarisability causes on the differential capacitance at the point of zero charge (when the applied potential is zero). Finally, electrolyte mixtures are discussed.

Chapter 6: dynamics at blocking electrodes. The behaviour of non-equilibrium systems is described in terms of (i) a step change in the potential, (ii) a small amplitude sinusoidal input of the type used in electrochemical impedance spectroscopy (EIS) and (iii) a larger amplitude linear potential sweep of the type used in cyclic voltammetry. Discussion of these is made in terms of an equivalent circuit analogue, which is commonly used to describe a blocking electrode system.

Chapter 7: reacting systems. A model is derived for the rate of an electrochemical reaction from the starting point of the reaction affinity, leading to a Frumkin-Butler-Volmer-like expression which also accounts for the ion interaction terms. The effects of the interactions are considered in terms of the current generated under steady state conditions and also in terms of simulated EIS.

Chapter 8: conclusions and further work. A summary of the findings of the work is presented together with suggestions of possible directions for future study.
Chapter 2

Background

Understanding and modelling the behaviour of electrolytes is not generally a simple matter as they exist in a liquid state. This means that they lack the regularity and rigidity of solids and also that the particles undergo interactions much more frequently than they would in a gas, so many of the simplifications which can be made when describing such systems do not apply. Additionally, while the ions in an electrolyte undergo the same non-electrostatic interactions as found in uncharged liquid materials, the ionic charge introduces long range electrostatic interactions between the particles, complicating the system even further.

The charge and mobility of the ions do, however, provide additional means to probe the structure of a system. Various voltammetric techniques can be applied to improve our understanding of electrolyte (and thereby liquid) behaviour at a microscopic level. As is common with much experimental data though, a good theoretical understanding is required in order to interpret the data — for example the differential capacitance of an electrode/electrolyte interface cannot be well explained by treating the electrolyte as an ideal solution (see the Gouy-Chapman (GC) model in Section 2.1). A good theoretical understanding of a system also means that there is potential for predicting the behaviour of a system without conducting an experiment, using modelling to avoid (or at least guide) what may be costly or more time-consuming experiments. Clearly a good model is required for this to be useful and, as discussed in Section 2.3, detailed models can be derived. Unfortunately, moving much beyond the ideal approximation invariably leads to very complex equations to solve, meaning that the GC or Gouy-Chapman-Stern (GCS) models remain the de facto means for describing a wide range of systems (Sprague and Dutta 2011).

In terms of modelling electrolyte behaviour, the basic physics underpinning the behaviour of the constituent particles and their interactions is, in principle, known down to the quantum level, but for practical purposes it is mostly unnecessary to describe the system using this level of detail. The de Broglie wavelength of the particles is usually smaller than the average inter-particle distance and so they can be treated in a classical manner, essentially as a many-body system of interacting physical objects as opposed to a superposition of wavefunctions. Although this represents a significant simplification, the sheer number of particles in the system means that developing a detailed description remains a challenge and further simplifications are common.
The most detailed results which can be obtained from modelling come from one of two direct simulation methods — molecular dynamics (MD) and the Monte Carlo (MC) technique.

In MD simulations, initial positions and momenta are assigned to a system of model particles and then Newton’s equations of motion are solved for each particle, using a discrete difference method, to calculate their new positions and momenta. The macroscopic thermodynamic properties of the system can be found by time-averaging each corresponding microscopic property through the simulation. This method can give very detailed information about the model system but the complexity, combined with difficulties in implementing the algorithm, means that only limited time spans can be simulated. This means that it is only really possible to obtain equilibrium values for properties with a short relaxation time. The method is inherently dynamic so dynamic system properties can be calculated, but the limitation on the length of the simulated time span means that this only applies for quicker processes. Finally, the number of equations that have to be solved increases with the number of particles, meaning that the size of a system is limited by the hardware on which it is simulated. Thanks to the continual increase in computing power over the past few decades, ever larger systems can be simulated, but the numbers of particles still remain relatively small compared to those in a real system (Wu and Li 2007).

In contrast to MD simulations, the MC method uses random sampling to generate different microscopic configurations of a system which share the same macroscopic state. Each configuration is weighted according to how realistic it is using a Boltzmann factor and the state of the system is calculated by the weighted average. Further techniques are available to make the process more efficient, such as preferentially sampling systems in which the Boltzmann factor is significant, but the process remains computationally intensive.

Despite the time and scale limitations, direct simulation methods can be successfully used to calculate such properties as the distribution factor of a liquid and to investigate phase change behaviour. Of relevance to understanding how electrolytes respond to charged surfaces, they have been used to calculate equilibrium double layer structures and potential profiles for different systems (Zarzycki and Rosso 2010; Zarzycki et al. 2010; Nagy et al. 2011; Bhuiyan et al. 2011; Wang et al. 2012; Fawcett and Ryan 2010).

The data which the two direct simulation methods generate is generally considered to be of equal value to experimental data in terms of understanding the liquid state and they therefore provide a second means to verify more approximate models. Such approximate models further simplify the system with the intent of capturing some of its essential features and behaviour while being much simpler to solve. They also provide a means for modelling longer time-scales which are inaccessible to direct simulation because of the growth of numerical errors and hardware limitations.

The general route to deriving an approximate model is to use statistical mechanics, which is valid because of the high temperature and large number of particles (Schwabl 2006), to develop equations which describe the system. While they represent a significant simplification to the system, and they do not require as much computational power to solve, these models are not necessarily simple in and of themselves. The complexity of the model chosen in a particular
case will depend on what microscopic system properties are to be included and the manner in which they are modelled. The greater the simplification, the easier the resulting equations are to solve but the less well they represent the reality of a system as determined from experiment or simulation. However, even the simplest of models can help to interpret experimentally observed behaviour or give an idea of the relevance of certain properties.

Aside from the level of detail used in a model, the other determining factor in how complex it is to solve is the number of species in the system. At the minimum, an electrolyte must contain three species in the form of the positive ions, the negative ions and the solvent. However, in many systems of interest there may well be others: supporting electrolytes are used experimentally to minimise capacitive charging currents, electrode reactions may take place, changing some of one species in to another species, or there may be other charged or neutral species present for some other reason. A very common simplification to reduce the number of species is to treat the solvent in the so-called “primitive” manner, which is to say that it is assumed to provide a continuum background dielectric in which the ions move, but its particles are not specifically accounted for.

In terms of the ions themselves, the complexity introduced by having differently sized ions can be reduced by using a restricted model in which all ions are the same size. On top of this, further simplification is possible by assuming the ions form a continuum (MacDonald 1987). These are popular approaches because at this level of modelling the equations are easier to handle and less computationally intensive (Levin 2002). Much of the focus of the following sections will be on primitive or restricted primitive models.

The remainder of this chapter aims to cover some of the background to the types of modelling which takes place for electrolytes with regards to the double layer which forms at a charged surface, with particular reference to the simpler and more commonly used models, into which category the model developed later in this work fits. In keeping with the general structure of the thesis as a whole, equilibrium models for the structure of an electrolyte at a charged electrode are discussed first, starting with some of the simplest and most commonly applied models, as these are almost exclusively the ones which are adapted to dynamic modelling. Some consideration will be given to the more detailed statistical mechanics methods, although their inherent complexity precludes discussion of many of their finer points. Some of the simpler models which include ion-specific properties will then be described and finally dynamic modelling techniques and models for electrode reactions will be discussed.

2.1 Early models for the electric double layer

The earliest quantitative attempt to describe the structure of the space charge present in the region of an electrolyte near an electrode was developed by Helmholtz (1879), based on earlier work of Quincke who had postulated the existence of such a region (Wall 2010). The model assumes that when an excess charge is present in an electrode which is immersed in an electrolyte, a monolayer of hydrated counter-ions forms at the interface where the electrode and electrolyte...
meet as shown in Fig. 2.1. The electrode is assumed to be a perfect conductor, meaning that it cannot support an electric field inside it and so the excess charge must all be located at its surface. The charge in the ions is assumed to be located exactly at the centre of the water-ion cluster and is thus restricted from approaching the electrode surface more closely than the radius of the cluster (length \( r \) in Fig. 2.1(b)).

![Diagram of the Helmholtz double layer and analogy to a capacitor](image)

**Figure 2.1: The Helmholtz double layer structure**

The total charge on the electrode surface equals that in the monolayer and the two sets of charges are separated by the distance \( s \), which in this case is equal to the radius of the hydrated ion, \( r \). The total potential drop between the electrode and the electrolyte bulk must be entirely contained in the double layer otherwise the potential gradient would drive charge movement in the bulk and the system would not be in equilibrium. With the ionic charge being located at the centre of the water-ion clusters, there is no charge in the double layer and it is possible to solve for the surface charge density on the electrode, \( \sigma \), in terms of the applied electrostatic potential \( \phi^0 \) using the Poisson equation to find (Koryta et al. 1993):

\[
\sigma = \frac{\epsilon_r}{4\pi r_d} \phi^0
\]  

(2.1)

where \( \epsilon_r \) is the relative permittivity of the electrolyte and \( r_d \) is the hydrated ion radius.

The structure proposed is directly analogous to a dielectric capacitor, leading to the concepts of the double layer total capacitance, \( C_i \), and differential capacitance \( C_d \), calculated respectively for the Helmholtz model as

\[
C_i^H = \frac{\sigma}{\phi^0} = \frac{\epsilon_r}{4\pi r_d}
\]  

(2.2a)

\[
C_d^H = \frac{\partial \sigma}{\partial \phi^0} = \frac{\epsilon_r}{4\pi r_d}
\]  

(2.2b)

The total capacitance represents the total amount of energy stored at a given potential, while the differential capacitance represents how this changes as the potential is changed. The latter is useful as it is possible to measure its value directly. For the Helmholtz model the two are identical and both are predicted to have a constant value dependent only on the radius of the hydrated ion. This is in direct contrast to experimental data which shows that \( C_d \) should show
a dependence on the ion radius, applied potential and the bulk ion concentration, in addition
to other parameters (Grahame 1947; Valette 1981), although the numerical value the model
predicts for the differential capacitance is within an order of magnitude. For example, for an
ion diameter of \( a = 0.6 \text{ nm} \), \( C_d^H \) has a value of 230.1 \( \mu \text{F cm}^{-1} \). Compared to the experimental
data of Valette (1981), presented later in Fig. 2.3, this is only between four and ten times larger
than reality.

A significant improvement in the theory of the double layer was made early in the 20th century
by Gouy (1910) and Chapman (1913). They made the same assumption as to the position of the
charge in the electrode, but rather than the ionic charge being found in a compact layer at the
electrode surface they proposed that it is smeared out near to the electrode surface, as shown in
Fig. 2.2.

![Figure 2.2: The Gouy-Chapman double layer structure](image)

The electric potential at the surface pulls a counter charge towards the electrode while thermal
motion/entropy effects resist the increase in ion concentration that this entails. In relation to the
methods being used later in this work, it is possible to describe the structure using the electro-
chemical potentials, \( \mu_j \), of the species in the system, which are functions of the environment
of the ions. The GC model assumes the ions behave in an ideal manner but with an additional
contribution from the interaction of the ions with the local electrostatic potential, \( \phi(r) \) (Bazant
et al. 2009):

\[
\mu_j(r) = k_B T \ln [c_j(r) \Lambda_j^3] + z_j e_0 \phi(r)
\]

(2.3)

where \( r \) is the general position vector and, for species \( j \), \( c_j \) is its number density, \( \Lambda_j \) is
its thermal wavelength and \( z_j \) is its valence. \( e_0 \) is the elementary charge, \( T \) is the absolute
temperature and \( k_B \) is the Boltzmann constant. To determine the concentration profile it is
noted that \( \mu_j \) must be constant in space at equilibrium, although the individual terms may vary.

In the bulk, the electrolyte has a constant concentration, \( c_j^0 \), and since \( \mu_j \) must be constant
overall, this means there can be no variation in the electrostatic potential. This allows the
\( \phi \) in the bulk to be defined as zero and \( \mu_j \) in the bulk to be defined as a reference value, with

\[
\mu_j^0 = k_B T \ln c_j^0 \Lambda_j^3
\]

(Koryta et al. 1993). By subtracting the reference value from \( \mu_j \), it is possible
to show that the concentration profile near to the electrode follows a Boltzmann distribution,
with

\[
c_j(r) = c_j^0 \exp(-z_j \phi(r))
\]

which is one of the assumptions of the GC model (Girault 2004).
The model assumes quasi-thermal equilibrium and that any local charge fluctuations average out over time so that the electric field at a point is a function only of the overall charge density – the widely used mean field (MF) approximation. This allows the use of the Poisson equation to link the local electric field to the charge density, in this case giving the Poisson-Boltzmann (PB) equation. For a binary, symmetric electrolyte, i.e. one in which \( z_+ = -z_- = z_n \) and \( c_+^0 = c_-^0 = c^0 \), where the subscripts “+” and “-” refer to the cation and anion respectively, the PB equation takes the form:

\[
\frac{1}{4\pi} \frac{d}{dz} \left( \epsilon_r \frac{d\phi(z)}{dz} \right) = c_+^0(z) \exp[-z_+\beta e_0\phi(z)] + c_-^0(z) \exp[-z_-\beta e_0\phi(z)] = 2z_n e_0 c^0(z) \sinh(z_n\beta e_0\phi(z)) \tag{2.4}
\]

where \( \beta \) is the inverse thermal energy, \( 1/k_B T \), and \( z \) (no subscript) is the perpendicular distance from the electrode. This can be solved analytically for the potential, the result of which is (Girault 2004):

\[
\phi(z) = \frac{4}{z_n \beta e_0} \text{arctanh} \left[ \tanh \left( \frac{z_n \beta e_0 \phi^0}{4} \right) \exp(-\kappa z) \right] \tag{2.5}
\]

in which \( \kappa \) is the Debye screening parameter, whose definition is

\[
\kappa^2 = \frac{4\pi \beta e_0^2}{\epsilon_r} \sum_j z_j^2 c_j^0 = 4\pi l_B \sum_j c_j^0 z_j^2 \tag{2.6}
\]

The screening parameter is related to the Debye length of the electrolyte, \( \lambda_D \), through the relationship \( \lambda_D = 1/\kappa \). The Debye length is a characteristic length for a double layer, relating to the distance over which the surface charge is screened (Bard and Faulkner 1980). The equation above states two definitions of the screening parameter, the first of which as it is commonly written and the second in terms of the Bjerrum length, \( l_B \), itself defined as \( l_B = \beta e_0^2/4\pi e_0^0 \epsilon_r \). This length is the separation at which the electrostatic interaction and thermal energies are equal for two charged particles. The second definition above is included as the Bjerrum length is used as the base length scale for defining the dimensionless forms of the equations used later in this work (see Section 3.8).

Once the potential is known, an expression for the surface charge density as a function of the potential can be derived through the application of Gauss’ law, which then leads to an expression for the Gouy-Chapman (GC) differential capacitance, defined in the same manner as Eq. (2.2b) (Bard and Faulkner 1980):

\[
C_{d}^{GC} = \frac{\epsilon_r}{4\pi} \kappa \cosh \left( \frac{z\beta e_0 \phi^0}{2} \right) \tag{2.7}
\]

In contrast to the Helmholtz model, the GC differential capacitance is dependent on both the bulk ion concentration and the potential, but shows no dependence on the ion size. A plot of the experimental data for a silver electrode in KPF\(_6\) solution of varying bulk concentrations is
shown in Fig. 2.3, using the data of Valette (1981), along with the predictions of the Helmholtz and GC models calculated using Eqs. (2.2b) and (2.7) respectively. In common with the model data presented in later chapters, the left and lower axes show the dimensionless form of the parameters, defined in terms of the units in which the model is solved, and the right and upper axes show the dimensional equivalents. Details of the conversion to dimensionless units will be discussed in Section 3.8 and a summary of conversion factors can be found in Table 3.1.

Neither model shown agrees with the data over the whole potential range, although near the point of zero charge (PZC) at \( \phi^0 = 0 \) the GC model gives a reasonable fit at low concentrations. In addition to the poor fitting to differential capacitance data, there are a number of other problems with the model. Firstly, the counter-ion concentration predicted at the electrode surface (which can be inferred from line one of Eq. (2.4)) rapidly becomes larger than is physically possible. This results from the fact that the model neglects the finite volume of the ions and contains no mechanism to limit the concentration. This is also reflected in the values the model predicts for the width of the double layer, which can be inferred from the differential capacitance. Writing Eq. (2.7) in the following form

\[
C_d^{GC} = \frac{\epsilon_r}{4\pi \lambda(\kappa, \phi^0)}
\]

where

\[
\lambda(\kappa, \phi^0) = \frac{1}{\kappa \cosh \left( \frac{1}{2} z \beta e_0 \phi^0 \right)},
\]

the differential capacitance is now in a similar form to Eq. (2.2b) where \( \lambda(\kappa, \phi^0) \) corresponds to the effective width of the double layer, and is a function of the screening parameter and the surface potential. \( \kappa \) increases with the bulk concentration, while the \( \cosh \) term always increases with the magnitude of the potential, so the value of \( \lambda \) decreases as either \( c^0 \) or \( |\phi^0| \) increase. This shrinking of the width of the double layer as the concentration increases is counter-intuitive to how a system of finite-sized particles should behave, as it would be expected that once the maximum possible number of ions occupy the surface, any additional ions must result in a

![Figure 2.3: Experimentally measured differential capacitance curves for a silver electrode in KPF_6 solution (crosses) (Valette 1981) and the predicted curves from the Helmholtz (dashed line) and GC (solid lines) models at a selection of bulk ion concentrations.](image)
thickening of the double layer.

In an attempt to improve on the GC model, Stern (1924) combined the Helmholtz and Gouy-Chapman models to describe the double layer. Taking from the Helmholtz model the idea of a point of closest approach for the hydrated ions, outside which they behaved in a GC-like manner, the structure of his model was as depicted in Fig. 2.4

![Figure 2.4: The Gouy-Chapman-Stern double layer structure](image)

The double layer is now composed of an inner (Stern) layer and an outer (diffuse) layer. Individually these layers are described mathematically as they are in the Helmholtz and GC models respectively, but they combine to curb the divergences of the GC model while retaining the improvements that model made over the Helmholtz model.

The inner (Stern) layer is the width of the hydrated ion and contains no charge. Solving the Poisson equation for this region then shows that the potential varies linearly over its width. In the outer (diffuse) layer the ions are treated in exactly the same manner as the GC model. The difference is that the potential effectively causing the formation of the diffuse layer is the potential at the Stern layer boundary $\phi_s$. The derivation can be found elsewhere (for example Bard and Faulkner (1980)), but the result for the total differential capacitance is of the form

$$\frac{1}{C_{dGCS}} = \frac{1}{C_{dH}} + \frac{1}{C_{dGC}}$$

(2.9)

where $C_{dH}$ is constant, calculated as in Eq.(2.2b), and $C_{dGC}$ is calculated as in Eq. (2.7). The exponential growth of $C_{dGC}$ with the potential means that $1/C_{dGC}$ dominates the above equation at low potentials but that $1/C_{dH}$ dominates at high potentials. The Gouy-Chapman-Stern (GCS) differential capacitance therefore follows $C_{dGC}$ at low potentials and converges on $C_{dH}$ at higher potentials, as shown in Fig. 2.5 (a) and, with an expanded $\phi^0$ scale, Fig. 2.5 (b) below.

From the two graphs it is clear that in addition to curbing the exponential growth seen in the GC model, the GCS structure also gives a much better fit near the PZC over a wider range of bulk concentrations, although this does not quite extend as far as the 0.1 M case. While this model curbs some of the excessive behaviour of the GC model, it still permits ion concentrations which are much larger than physically possible at the Stern layer boundary, although they are much smaller than those in the GC model.
Figure 2.5: (a) The Gouy-Chapman-Stern differential capacitance (solid lines) compared to the experimental data of Valette (1981) (crosses) and (b) the same data with an expanded $\phi^0$ scale

Although the GCS model curbs the growth in the differential capacitance at higher potentials, experimental data shows that there should be a decrease in the differential capacitance with the potential above a certain threshold. Additionally, both experiment and simulation suggest that under certain conditions (for example high bulk concentrations, low permittivities or large ions) the PZC should be a peak rather than a trough. This is a fundamental effect which neither of these two models are able to predict, but which can be explained by accounting for ion interactions (Oldham 2008; Lamperski et al. 2009; Jiang et al. 2011; Hatlo et al. 2012), as will be discussed shortly.

In addition to the problems with the shape of the differential capacitance curves, there are a number of other problems relating to the electrolyte structures which they predict. The concentration profiles in general do not agree with those of simulated data (Antypov et al. 2005; Henderson and Boda 2009; Guerrero-Garcia et al. 2010; Bhuiyan et al. 2011) and in electrolytes containing multi-valent ions, the disagreement with simulation data becomes significantly worse (Torrie and Valleau 1982; Henderson and Boda 2009). The models are also unable to describe certain properties of mixed electrolytes, such as the exclusion of a larger counter-ion from the electrode surface in favour of a smaller one of the same charge (Biesheuvel and Soestbergen 2007).

Despite these drawbacks, the simplicity of the GC/GCS models means they are the most common starting point when fitting models to experimental data at low concentration or potential. In part this is because they offer analytical solutions (or ones which only require simple numerical techniques), but also it is because they are reasonably successful, provided the conditions are correct. They can also qualitatively shed some light on effects occurring in the double layer — for example the GCS model has been used to look at the equilibrium properties of electrolytes with unequally sized ions by including separate Stern layer widths for each ion (Valleau and Torrie 1982), showing a shift in the potential of the PZC with the difference in ion sizes.

They have also been further adapted to include such effects as specific adsorption, in which partially de-solvated co-ions may be bound to the electrode surface (Grahame 1947; Devanathan 1954) and to include the effects of the solvent in the double layer (Bockris et al. 1963). Fur-
thermore, they were until recently almost exclusively used for modelling dynamic behaviour in electrolyte systems over long time-scales. Ultimately, however, the underlying limitations of the GC and GCS models mean that they may not be applicable to modelling many situations of interest. From experiments such as voltammetry through to devices such as batteries or fuel cells, operational ion concentrations and applied potentials place them firmly out of reach of a basic PB-based model. For this reason there has been an interest in improving on the model for almost as long as it has existed.

2.2 Moving beyond the Poisson-Boltzmann approximation

The fundamental problem with models based on the PB equation is that there is no limit to the concentration of the ions, as a result of their being treated as point-like particles which experience no short-range repulsive forces to prevent crowding. The attraction of counter-ions to the electrode increases the local concentration at the surface/Stern layer, but as long as this concentration remains small, such that the average inter-ion distance remains large, the GC or GCS models are adequate to describe the system because these short range effects do not significantly alter the ion interactions. Unfortunately this is only the case for very low potentials.

If a particular repulsive force between the ions is one which is zero until the ion separation becomes smaller than the length \( b \), at which point it becomes infinite (as for the interaction between hard spheres), the maximum possible density, \( c_j^{\text{max}} \), for species \( j \) is a face-centred cubic lattice, with \( c_j^{\text{max}} = 0.74 \frac{6}{\pi b^3} \), assuming a cubic lattice structure is formed. According to the Boltzmann distribution, the potential at which this concentration is reached is (Bazant et al. 2009)

\[
\phi_c = \frac{1}{z_j \beta e_0} \ln \left[ \frac{c_j^0}{c_j^{\text{max}}} \right] \tag{2.10}
\]

where \( \phi_c \) is the critical potential at which the maximum concentration is reached, i.e. the potential at which the PB model cannot describe the system. If the interaction length of the repulsive force is \( b = 3 \) Å (as for hydrated bulk K\(^+\)-Cl\(^-\) interactions (Bazant et al. 2009; Mancinelli et al. 2007)) the cut-off voltage is \( \phi_c \approx 0.42 \) V when \( e^0 = 1 \times 10^{-5} \) M and \( z = 1 \), and this value decreases with increasing \( c_0 \). Although this calculation is simplistic, it highlights the limitations of the model. In reality the forces preventing ion crowding are not only active when the threshold is reached, but grow continuously as the concentration increases and particle interactions become more frequent.

The finite size of the ions is the most obvious factor in limiting the ion concentrations, but other properties also play a role. The total charge in the double layer must equal the total charge on the electrode at equilibrium, to ensure electroneutrality. The charge on the electrode depends on the electric field and the permittivity, smaller values of each leading to a smaller surface charge. The permittivity decreases as either the electric field or the ion concentration increase (Hasted et al. 1948; Booth 1951), meaning that a given increment in the potential (which increases both of these properties in the double layer) has a smaller effect at higher
potentials. The permittivity also affects the energy of the ions in the double layer, leading to a finite limit to the concentration even in the absence of volume effects (Paunov et al. 1996; Hatlo et al. 2012; Ben-Yaakov et al. 2011), as will be discussed further in Section 2.4.2.

In addition to discounting the interactions between the ions, the GC and GCS models also ignore the impact of the electrode on the behaviour of the system. In practice, electrodes are rarely ideally polarisable, meaning there will be a difference in the permittivities of the electrode and the electrolyte. This leads to the presence of image charges in the electrode surface with which the ions are able to interact, further altering the behaviour of the system (Torrie et al. 1982; Torrie et al. 1984). It is also noticeable from experimental data that different crystal faces of the electrode can have a significant effect on the structure of the double layer, with electrodes constructed such that only a particular crystal face is exposed to the electrolyte having different differential capacitance profiles depending on the face when in the presence of the same electrolyte (Vitanov et al. 1982; Hamelin et al. 1983; Jovi and Jovi 2003).

As well as presenting a highly simplified electrode structure, at a fundamental level the basis of the GC(S) models in the mean-field (MF) approximation can be questioned. In reality the local electric field which an ion experiences varies over very short spatial scales due to the motion of the surrounding ions and their electrons. These effects give rise to charge correlations which can be difficult to model in the MF approximation.

There are two possibilities for making improvements to the models so far described: one is to modify the PB model to include ion-specific effects while retaining the continuum form; the other is to derive a new set of equations based more closely on exactly what is happening in the system. The former option leads to a set of “modified Poisson-Boltzmann” (mPB) models, which necessarily retain the underlying assumptions of the PB equation, while the latter encompasses a raft of statistical models derived from the Hamiltonian for the system which is used in the MD and MC direct simulation techniques. With a couple of exceptions for mPB models, moving beyond the PB approach results in models which are analytically intractable, so numerical techniques of varying levels of complexity are required.

For reasons which will be discussed shortly, much of the dynamic modelling for electrolyte systems takes place using mPB models which retain the MF approximation and are also local density approximation (LDA) theories. These can be shown to be simplified forms of the statistical mechanics models which describe many essential features of the double layer. Since the starting point for the mPB model used in this work is described from the basis of statistical mechanics, a brief discussion of this approach is given below, together with some of the main results for features of the double layer which they predict.

### 2.3 The statistical physics approach

The high temperature and vast number of particles in a typical fluid system means that statistical methods may be used to describe the system. Such methods use techniques developed for the theory of thermodynamics and kinetics and the mechanical theory of heat (Henderson 1992) and
Microscopically the particles in a system are defined only by their positions and momenta. The state of a system of $N$ particles is a function of the $N$ position and $N$ momentum values in three dimensions, making it a function of $6N$ parameters, and it is possible to write the macroscopic mechanical properties of the system, such as the internal energy, pressure or heat capacity, in terms of averages of functions of the state. Although the system is always in continual motion at a microscopic level, for systems in thermal equilibrium the macroscopic averages of the microscopic properties must be independent of the time, a property which can be used to derive two routes to linking the microscopic state to the macroscopic system properties (Hansen and McDonald 2006; Wu and Li 2007; Helrich 2009). The first method is to take the time average of microscopic properties, an approach which leads to a form of the virial equation of state, a generalised form of the ideal gas law which includes particle interactions. The second method is to use ensemble averaging, an approach which is generally more useful and more commonly used. It involves using the effective Hamiltonian of a model system to derive an expression for its classical partition function, a state function from which the other mechanical properties may be calculated (Hansen and McDonald 2006; Schwabl 2006).

While the partition function can be used directly, for inhomogeneous systems it is usually simpler to use it to calculate one of the thermodynamic potentials of the system, which are also state functions and can also be used to calculate its macroscopic mechanical properties. Two are of particular use in electrolyte interface modelling: the grand potential $\Omega$ and the Helmholtz free energy $F$. The grand potential of a species in a system can be shown to be a unique functional of the one body particle density and whose minimum value corresponds to the equilibrium state (Hansen and McDonald 2006). This can be used in conjunction with the Helmholtz free energy, also a unique functional of the one-body density, to calculate the state of an inhomogeneous system using the variational principle, which will be discussed further in Chapter 3. The Helmholtz free energy is particularly useful because its form does not depend on the source of an external potential. When an external potential is applied and causes an inhomogeneity, the known form of the free energy in the absence of the external potential can be used to calculate the resulting structure, whether the inhomogeneity is caused by an electric field, a confining wall or some other external source (Evans 1992).

In principle the method for deriving expressions for the thermodynamic potentials is straightforward, but in practice there are several complications. The partition function is derived from the many-body interacting Hamiltonian for the system, which necessarily includes the interaction potential between two particles. The precise form of this potential is complex even for neutral atoms, which experience a long-range attraction due to van der Waals forces and a strong short range repulsive force due to Pauli exclusion (Schwabl 2006). In order to simplify the models, approximations are made for the interaction potential (Wu and Li 2007). Examples of these approximate interaction potentials include the square well and hard-core Yukawa potentials as well as the well known Lennard-Jones potential, but even these can be difficult to
solve analytically, so one of the most commonly used interaction potentials is the simple hard sphere potential, for which the interaction is zero above a certain particle separation and infinite for smaller separations, essentially modelling the particles as solid balls. For electrolytes, the situation is more complex still because the ions also interact through the Coulomb potential, so this must also be accounted for.

Following the selection of an interaction potential, a further complication arises because it describes only the pair-wise interaction of two particles. The density of the liquid state means that interactions may be mediated by other particles. The total interaction between two particles is therefore the sum of the direct and indirect interactions, where the indirect interaction is the sum over all possible mediated interactions. The resulting calculation can be written exactly in terms of ion correlations (for example the Ornstein-Zernike equation (Hansen and McDonald 2006)), but such a statement contains two unknown properties and so a closure relationship is needed to make use of it. Such a relationship is necessarily an approximation, since an exact expression would require the solution of every possible combination of interactions, which is precisely what the models are trying to avoid. Several closure relations have been described, including the Percus-Yevick (Percus and Yevick 1958; Wertheim 1963) and Hypernetted Chain equations (Rowlinson 1965), as well as the Mean Spherical Approximation (Lebowitz and Percus 1966; Blum 1975). The use of an approximate interaction potential and closure relation means that, while the framework is exact, the resulting models are necessarily approximate.

There are other approaches to deriving the state of the system including Density Functional Theory (DFT), which was born out of the quantum theory of the same name (Evans 1992; Wu and Li 2007), Fundamental Measure Theory (FMT) (Rosenfeld 1989; Roth 2010), itself a very successful form of DFT, field theoretical approaches (Netz 2001; Caprio et al. 2003b; Caprio et al. 2003a) and scaled particle theory (Reiss et al. 1959; Mandell and Reiss 1975; Latifi and Modarress 2010). All of these models inherently include the ion volume because of the form of the interaction potential and, to varying degrees, they show very good agreement with data from both simulation and experiment. In particular many of them are capable of predicting ion crowding and overscreening, two double layer properties which are not observed in the GC or GCS models but which do show up in simulated data and explain experimental observations.

Overscreening, or charge inversion, occurs when more counter-charge is attracted to a charged surface than is needed to balance the surface charge, resulting in the charge facing the electrolyte being slightly of the same charge as the counter-ions. As a result, co-ions are attracted in to the double layer. The counter ion layer may then itself be overscreened by the co-ion layer, resulting in alternating layers of positive and negative charge and non-monotonic electric potential profiles near the electrode surface (Lozada-Cassou et al. 1982; Yu et al. 2004; Gillespie et al. 2011; Guerrero-Garcia et al. 2010). This double layer feature has been used to describe attraction between large particles of the same charge such as DNA (Allahyarov et al. 2005) or colloids (Patey 1980; Guldbrand et al. 1984), ion selectivity in biological channels (Gillespie 2008), a reduction and reversal of the electrophoretic mobility of charged colloids (Martin-Molina et al. 2003) and its effects have been observed in experimental measurements of streaming currents (Heyden et
al. 2006). The effect is the result of electrostatic correlations between the various components of the system (Levin 2002), although MC simulations of asymmetrically sized ions at a charged surface show that the relative ion size does have an impact, with the extent of overcharging being increased near the PZC because the smaller ion is preferentially adsorbed (Guerrero-Garcia et al. 2010) regardless of whether it is a co- or counter-ion. It has also been suggested that the counter-ion is not always dominant in the double layer, depending on the relative charges and sizes of the ions (Messina et al. 2002; Guerrero-Garcia et al. 2005).

Ion crowding is a result of there being a maximum density which the ions are able to attain. The mPB models discussed below set a limit to the concentration at a point, but since they are local density approximations (LDA) they cannot account for non-local contributions to the chemical potential which result from short range particle correlations (Evans 1992). Furthermore, LDA models for the density at a sharp boundary are technically not thermodynamically self-consistent, because they do not satisfy the relevant thermodynamic sum rules (Evans 1992; Gillespie et al. 2011). In common with the charge oscillations induced by the inclusion of electrostatic correlations, the result of properly accounting for non-locality is density oscillations in the double layer (Yu and Wu 2002).

While statistical mechanics theories are generally applied in the context of describing the structure of the system, they have also been applied to modelling more macroscopic properties of charged interfaces. This includes the differential capacitance, although in recent years there has been much more interest in room temperature ionic liquids (RTIL) than electrolytes (Kornyshev 2007; Fedorov and Kornyshev 2008b; Fedorov and Kornyshev 2008a; Forsman et al. 2011; Henderson and Wu 2012). Ionic liquids are largely incompatible with models which do not account for charge or density correlations because the low dielectric constant and high bulk concentration amplifies these effects. Even so, there are similarities between electrolyte and RTIL systems in terms of the shape of the differential capacitance curves and the way that they change shape with the concentration, although these changes occur at much lower concentrations in RTIL systems compared to electrolyte systems (Lamperski et al. 2009; Jiang et al. 2011).

Despite the fact that the types of statistical mechanics models described above can provide a great deal of accuracy in modelling, they are complex and require advanced knowledge of statistical mechanics to use correctly. As a result, they are not particularly well suited to facilitate simple understanding of experimental data (Vlachy 1999). Furthermore, when moving on to describing non-equilibrium situations the complexities become significantly greater, leading not only to difficulties in setting up models but also in running them, due to the additional computing power required. For this reason, many equilibrium state studies and almost all dynamic studies are still carried out using some form of mPB model.
2.4 Equilibrium modified Poisson-Boltzmann models

As a result of the complexity of statistical mechanics models, mPB models remain the simplest and most commonly used improvement over the GC and GCS models, most commonly being used to account for the excluded volume interactions of ions in the system. As the name suggests, they are based on the PB formalism but include some additional terms in order to account for non-ideal properties of the system. As such they remain in the mean-field approximation of the PB theory and are rooted in the local density approximation, in which the properties of a species at a point in the system are dependent only on the state of the system at that point, as opposed to the non-local theories which arise from a pure statistical mechanics approach.

As a result of using the mean-field local-density approximation (MF-LDA), charge and density correlations are unaccounted for, meaning that the gains in terms of simplicity come at a loss of the fine structural detail of the electrolyte. The use of the LDA also means that interactions between the ions in an inhomogeneous system are assumed to remain the same as they are in the bulk (Biesheuvel and Soestbergen 2007; Bazant et al. 2009), as will be discussed further in Chapter 3.

In terms of solving the equations which the models propose, the MF approximation implies that the Poisson equation can be used to self-consistently solve for the ion concentrations and the potential using modified Boltzmann distributions, which define the concentrations in terms of the potential. Although the forms of the equations in some mPB models may look relatively simple, this does not necessarily translate into analytical solutions, so numerical approaches are still often required. The methods required are usually simpler to handle than the statistical models of the previous section, however. The relative simplicity feeds through to simpler dynamic models as well, meaning that they are still the starting point for the relatively recent trend to include ion-specific effects when considering time-dependent behaviour (Kilic et al. 2007a).

As will be discussed in Chapter 3, the derivation of mPB models can be shown to start from the Helmholtz free energy in the same way as many statistical mechanics models. By making a number of assumptions, it is possible to derive an expression for the electrochemical potential of each species which includes a residual chemical potential term, \( \mu_{\text{res}} \). This term accounts for the non-ideal components of the chemical potential, and the resulting electrochemical potential takes the general form (Bazant et al. 2009)

\[
\mu_j(r) = k_B T \ln c_j(r) \Lambda_j^3 + \mu_{\text{res}}^j(r) + z_j e_0 \phi(r) \tag{2.11}
\]

The exact form of \( \mu_{\text{res}}^j(r) \) depends on the additional effects being described. In the absence of the residual term, the system follows GC-like behaviour, whereby the reduction in the local energy caused by a local potential difference causes an increase in the ion concentration, which effects an increase in the entropy. This increases the ion’s energy until eventually an equilibrium is reached once the electrostatic and entropic components of the electrochemical potential are equal. Including the residual term adds an additional energy, meaning that the local potential difference does not have to be balanced entirely by the entropy term. Depending on the form of


\( \mu_{\text{res}} \), the structure of the electrolyte can differ significantly from that predicted by the GC model. For example, if it is defined to diverge as the concentration approaches a particular value, this effectively limits the concentration of the ions.

While the form of the electrochemical potential is changed in mPB theories, the mean-field approximation implies that the Poisson equation is still used to determine the local electric potential. Despite the inherent loss of detail that these assumptions entail, they accurately capture observed trends in behaviour and can in some cases, and for some properties, provide reasonably accurate predictions (see Bazant et al. (2009) and Hatlo et al. (2012), for example).

Although there are differences in the expressions which result from mPB theories compared to the GC and GCS models, the general method of solution remains the same: the chemical potential is used to derive an expression for the concentration of a species in terms of the local potential by defining the bulk chemical potential as a reference. The concentration is then used to define the local charge density which is used to self-consistently solve the Poisson equation, Eq. (2.4). The main effects to which mPB theories lend themselves to modelling in a simple manner are in accounting for the ion excluded volume interactions and the dielectric decrement of the solvent. Both of these have a significant impact on the double layer structure and electrical properties, which the models are able to describe, at least in a qualitative manner, although the neglect of ion correlations means that exact agreement is rare. The following two sections deal with each of these two modifications in turn.

### 2.4.1 Excluded volume effects

The omission of the excluded volume interactions of ions — the short range interactions which prevent ions from occupying the same volume of space, also known as steric repulsion — from models of the double layer structure has long been recognised as a significant flaw in the GC model. Attempts to account for it have been around for almost as long as Gouy and Chapman’s theory of the diffuse double layer. The first systematic derivation of a model which included these effects was made by Bikerman (1942), in a paper which dealt with both excluded volume and the effects of the ions on the solvent permittivity. The form of his model has subsequently been rediscovered by many groups over the following 60 years, a detailed history of which can be found in Biesheuvel and Soestbergen (2007). Using a “free volume” approach, Bikerman defined the occupied volume fraction of the ions as \( \eta = \sum_j v_j c_j \), the sum over the product of the concentration of each ion type and its volume, \( v \). For aqueous electrolytes this volume is commonly assumed to be the hydrated radius of the ion, which is of the order of 0.5 Å (Nightingale 1959)

In terms of the electrochemical potential, the component of \( \mu_{\text{res}} \) which is due to the excluded volume interaction is denoted \( \mu_{\text{ex}} \), the excess chemical potential. The Bikerman model is equivalent to this taking the form

\[
\mu_{\text{ex}}^j = -k_B T \ln(1 - \eta),
\]

which can be derived from the continuum limit of the bulk statistical mechanics of ions on a
cubic lattice of spacing $a$, the ion diameter (Borukhov et al. 1997; Ben-Yaakov et al. 2009).

The free volume fraction — the value of the bracket — is always between zero and one, so $\mu_j^{ex}$ always makes a positive contribution to the chemical potential. As will be discussed in Section 3.2, and as shown in Fig. 3.3 therein, the excess term in this model is small until the occupied volume fraction, $\eta$, is large, at which point it rapidly diverges. If a region of a non-homogeneous system has a lower free volume fraction than the bulk, the local ion concentration must be larger than in the bulk and so both the excess and entropy terms are larger. As the free volume fraction approaches zero, the excess term grows much faster than the ideal gas term, dominating the ion interaction energy and preventing further increases to the concentration.

This model is unusual in mPB theories in that analytical solutions can be derived, provided the systems considered are the same as those for which the GC model can be solved analytically, namely they must be binary, symmetric, monovalent electrolytes with bulk concentrations $c_0^+ = c_0^- = c_0$. The volume fraction in the bulk is $\eta_0 = \frac{2v}{c_0}$ such that the concentrations of the ions in terms of the potential is (Bard and Faulkner 1980)

$$c_\pm = \frac{c_0 \exp(\pm z_n \beta e_0 \phi)}{1 + 2\eta_0 \sinh^2(z_n \beta e_0 \phi/2)} \quad (2.13)$$

In the limit of point particles ($v \to 0$) the GC model is recovered, while in the limit $\phi_0 \to \infty$ the ion concentrations at the surface can be seen to approach the value $c_\pm^{max} = 2c_0/\eta_0 = 1/a^3$, which is the maximum permitted if all of the available volume is filled at the maximum concentration.

After coupling the concentrations to the PB equation it is possible to derive an analytical expression for the surface charge density. This was first rigorously presented by Grimley (1950) (Stern had suggested a very similar equation some 25 years earlier, but it is reported that the derivation was not clear and some of the constants were incorrect (Bazant et al. 2009)) and from this expression Freise derived the expression for the differential capacitance as a function of the potential, allowing him to discuss the qualitative effects of the excluded volume on the system (Freise 1952) (as cited in Bazant et al. (2009)).

The surface charge density and differential capacitance predictions of this model are presented in Figs. 2.6(a) and (b) respectively below. Since the model only permits a single ion diameter as an input, for the purposes of the plots the value of 6 Å was used so as to match the K$^+$ ion in the data of Valette, which is again presented in the second figure (the same legend applies to both figures).

While the surface charge density curves are initially identical to the GC model, the effect of the excluded volume is to prevent $\sigma$ from growing as rapidly at higher potentials. Furthermore, while the curves are initially concave upwards, they become concave downwards at higher potentials, implying the inflection point which is seen most clearly in the differential capacitance curves on the right, in the form of the peaks. Compared to the GCS curves, $\sigma$ at lower potentials is slightly larger, but the rate of increase in the values at higher potentials is much lower.

The Bikerman differential capacitance curves qualitatively agree with the experimental data.
Figure 2.6: Dependence of (a) the surface charge density, and (b) the differential capacitance, on the applied potential in the GC (dashed lines), GCS (dotted lines) and Bikerman (solid lines) models. Legend applied to both figures

in terms of the shape, with the potentials at which the peaks occur also being approximately correct, including their shift towards the PZC at higher concentrations. Although it is not shown here, at sufficiently large concentrations the transition from a twin-peaked curve to a single peaked curve also takes place, again qualitatively matching what is observed experimentally.

The shape of the differential capacitance curve can be explained in terms of the double layer width. At low concentrations and potentials the excluded volume interactions are negligible and the model behaves like the GC model, complete with a shrinking of the double layer width and increased differential capacitance. At higher potentials the concentration approaches the maximum, so additional ions in the double layer have to be located further from the electrode surface. This widens the double layer, making the effective width of the “capacitor” formed by the double layer larger. This increase in the width causes the differential capacitance to grow much more slowly. In the high potential region, the differential capacitance decreases at a rate proportional to $1/\sqrt{\phi^0}$, regardless of the bulk concentration, in agreement with experiment and simulation (Fedorov and Kornyshev 2008a; Kornyshev 2007; Jiang et al. 2011) and a property which has been described as a universal consequence of ion crowding near to a charged surface (Bazant et al. 2009).

The fact that the Bikerman model is identical to the GC model at the PZC means that it suffers the same limitations in that potential region. A Stern layer can be added to it in the same manner used in the GCS model, improving the accuracy and resulting in better agreement at low concentrations. This can be seen in the solid curves of Fig. 2.7, in which the Stern layer width is $s = a/2$ (i.e. the ion radius). While this improves upon the agreement near the PZC, significant disagreement remains away from this region. This can be improved by increasing the size of the ion (and with it the corresponding width of the Stern layer), but good agreement can only really be achieved following an unrealistic increase of up to 50%, also shown by the dashed curves in the figure.

The fact that increased ion sizes improve agreement with experimental data suggests that steric effects are underestimated in the Bikerman model, although at higher potentials it fares
Figure 2.7: Differential capacitance in the Stern layer modified Bikerman model with ion diameters of 0.6 nm (solid lines) and 1 nm (dashed lines) compared with the experimental data of Valette

better than some other models, such as the BMCSL model which will be discussed shortly. It has been suggested that the reason for this is that the LDA itself breaks down under these conditions so the error in the model is cancelled out elsewhere (Bazant et al. 2011). Comparisons of the model with MC simulations have shown that the model is appreciably successful in predicting the electronic properties of the double layer (such as the potential drop in the double layer and the differential capacitance) (Lou and Yong Lee 2010), although it struggles significantly for charge asymmetric electrolytes (Ibarra-Armenta et al. 2009).

The qualitative successes of the model definitively demonstrate that short range interaction are indeed responsible for the observed deviations between the GC model and experimental/simulation data for the differential capacitance and other electrical properties of electrode/electrolyte systems. Structurally, since correlation effects are not accounted for, the concentration profiles are not correctly predicted by the model, with the model always predicting monotonic concentration curves and never showing any density oscillations. However they do provide a reasonable general approximation (Ibarra-Armenta et al. 2009).

The problems with the model also extend to the fact that it is only able to account for a single ion diameter, explaining why the curves in the previous two figures are symmetrical. This means that the curves can only hope to be valid when the ion of the defined diameter is the counterion (in this case the K$^+$ ion and negative potentials). Additionally, since both ions are present in appreciable quantities near the PZC, differences between from the Bikerman predictions and reality are likely (although it will be shown in Section 5.2 that the actual value of the differential capacitance at the PZC itself is independent of the ion volumes).

Even though there are drawbacks to the model, and despite some attempts to improve on it, specifically in regards to the value of the excluded volume around an ion (Sparnaay 1958), this type of model remains a common tool for describing double layer structures and their effects on electrochemical systems. This includes descriptions of polyelectrolytes (Israels et al. 1994; Biesheuvel 2004; Gonzalez-Amezcua and Hernandez-Contreras 2004), polymeric elec-
trolytes (Soestbergen et al. 2008), electrolytes with biological molecules (Wiegel et al. 1993), the effects of large ion sizes and charge asymmetry on adsorption (leading to a modified Gra-
hame equation) (Borukhov et al. 1997; Borukhov et al. 2000; Borukhov 2004), solvent-free
electrolytes/ionic liquids (Kornyshev 2007; Fedorov and Kornyshev 2008b; Fedorov and Ko-
rnyshev 2008a; Oldham 2008), electrolytes under the influence of high voltages (Kilic et al.
2007a; Kilic et al. 2007b; Bazant et al. 2009) and electrowetting phenomena (Hua et al. 2010).

Although the model provides a good starting point for modelling, there are a couple of funda-
mental physical problems with it. First is that the model predicts the pressure to tend to infinity
as the volume fraction tends to unity. That the model permits volume fractions so high is itself a
problem, since the closest packing for spherical particles is either body-centred or face-centred
cubic packing, which both have maximum packing (volume) fractions of 0.74. This arises
because of the basis of the model in a lattice gas approximation, which is a questionable as-
sumption for modelling the liquid state, arguably being only realistic for crystalline solids and
solid electrolytes (Bazant et al. 2009).

The other commonly used excess chemical potential term has its origins in the virial equation
for hard spheres, so from the outset is more closely linked to statistical mechanics. Based on
the observation that the virial equation of state for hard spheres can be approximated by an
infinite geometric sum, which can subsequently be reduced to a single expression, Carnahan
and Starling proposed the following form of $\mu^\text{ex}$ (Carnahan and Starling 1969; Carnahan and
Starling 1972):

$$\beta \mu_j^\text{ex} = \eta(8 - 9\eta + 3\eta^2) \frac{1}{(1 - \eta)^3}$$

(2.14)

where $\eta$ is again the occupied volume fraction. This equation, known as the Carnahan-Starling
(CS) equation of state, has in common with the Bikerman model that it can only treat one-
component systems, although it was later extended to treat multi-component systems, leading
to the Boublik-Mansoori-Carnahan-Starling-Leland (BMCSL) equation of state (Boublik 1970;
Mansoori et al. 1971; Biesheuvel and Lyklema 2005; Lue and Woodcock 1999). The corre-
sponding excess chemical potential for this form of the model is stated in Section 3.2.2, and
it can be shown to reduce to the CS model in the limit of equally sized ions or the Bikerman
model in the limit that the volume of the $j^{th}$ ion (namely the particular ion in the mixture which
is being solved for) is zero.

Although derived from a more physically justifiable starting point, the most apparent practical
problem with the CS/BMCSL equations of state is that they cannot lead to analytical solutions.
However, numerically solving these equations in the context of an mPB model is not signif-
ically more challenging than numerically solving the original PB equations. The BMCSL
model predicts much stronger steric repulsion than the Bikerman model, with $\mu^\text{ex}$ rising much
more quickly as a function of the occupied volume fraction at lower potentials (see Fig.3.3 in
Section 3.2.

Since the excess chemical potential is much larger at a given concentration in the BMCSL
model than the Bikerman model, the counter-ion concentrations in the double layer are lower.
However, the fact that it takes much more energy to increase the charge density near the elec-
trode surface (where it is already largest) also means that the counter charge extends further from the electrode surface as the potential increases and that the potential decays more slowly with distance from the electrode surface. This increase in the double layer width means that the differential capacitance is smaller in the BMCSL model and also that it decays at a slower rate outside the peaks (Bazant et al. 2009).

The BMCSL model itself can be shown to be very accurate for predicting certain properties of liquid behaviour, for example the pressure and chemical potential, correctly predicting values which agree with simulations over the whole fluid range (Hansen and McDonald 2006; Mulero et al. 1999; Song et al. 1989). However, as with the Bikerman model, the volume fraction is able to approach unity (although a lot of energy would be required to make this happen). Furthermore, as mentioned above, it has been suggested that the strength of the steric repulsion, while more accurate than the Bikerman model at low concentrations (Biesheuvel and Soestbergen 2007), is less accurate at high concentrations. Rather than being because the Bikerman model is more accurate, the LDA itself is thought to break down and in this regime the weaker repulsion represented by the Bikerman model is a better approximation (Antypov et al. 2005; Bazant et al. 2011). This breakdown can be seen in the weaker decay of the differential capacitance for the CS model at high potentials relative to experimental data, as shown in Bazant et al. (2009) and can be seen in Fig. 5.25.

The significant benefit of the BMCSL model is that it is able to account for differences between the sizes of the ions in an electrolyte. The main result is that smaller ions are able to out-compete larger ions in the double layer, even when the larger ions have a higher bulk concentration or a higher valency (Biesheuvel and Soestbergen 2007), in general agreement with experimental observations (Shapovalov and Brezesinski 2006; Shapovalov et al. 2007), although quantitative agreement in Biesheuvel and Soestbergen (2007) could only be achieved by increasing the size of the larger, higher valence ion by 20%. The reason for this exclusion of the larger ion is that, above a certain concentration, it is energetically more favourable to move a smaller ion in to the double layer than it is to move a larger ion in, even when the larger ion has a higher charge.

Beyond the Bikerman or BMCSL models, there are a number of other mPB expressions which can be derived, for example the MPB1 to MPB5 hierarchy developed by Outhwaite et al (Outhwaite et al. 1980; Outhwaite and Bhuiyan 1983). In general, these are much more involved in their formalism and therefore much less commonly used. This is particularly true for models which include steric effects into dynamic models, for which it is rare to move beyond a Bikerman-like expression.

Overall, continuum mPB models provide a simple means to account for the ion size in a manner that is solvable using straightforward methods. The results which they predict qualitatively, and in some cases quantitatively, agree with experimental data, but they are unable to describe the fine structure of the double layer due to the lack of correlation effects. Furthermore, the width of the double layer is generally of the same order as the size of the ion (or lattice spacing), meaning that it is questionable as to whether they will ever be able to model these fine
structural details (Bazant et al. 2009). Nevertheless, they are usually the starting point for moving beyond the GCS approach because they can be used without necessarily having a thorough background in statistical mechanics and they do show many of the correct trends.

2.4.2 Solvent effects on the system

In much of the modelling which takes place regarding electrolytes, be it through the statistical or mPB approaches, the solvent is usually assumed to take no active part in the system beyond defining its permittivity, which relates to how well the solvent is able to resist an electric field. Through Eq. (2.6), the permittivity determines the screening parameter, $\kappa$, and hence the width of the double layer, so if its value is able to change locally then the overall system will be affected. Such changes can be driven both by the electric fields found in the double layer and also by those generated by individual ions, leading to changes in the local permittivity relative to that of the bulk solvent (Booth 1951; Gavryushov and Linse 2003; Joshi et al. 2004; Gongadze et al. 2011a; Gongadze et al. 2011b).

For aqueous electrolytes, the shape of a water molecule combined with the differing electronegativities of the hydrogen and oxygen from which it is composed leads to the withdrawal of electrons by the oxygen atom. This gives it a slight negative charge and leaves the hydrogen atoms slightly positive, as depicted in Fig 2.8. This separation of charge, which remains bound together in the molecule, forms a permanent charge dipole which generates an internal electric field $E_{\text{int}}$. In bulk water at high (e.g. room) temperatures, random thermal motion of the molecules means that the dipoles are on average unaligned, so that all $E_{\text{int}}$ cancel and there is no net field. Each dipole will, however, respond to an externally applied field as the charges attempt to move in opposite directions, causing $E_{\text{int}}$ to rotate and point anti-parallel to the applied field. Thermal motion means that the degree of alignment depends on the strength of the applied field, but a net alignment over all molecules remains, leaving the total local field smaller than the global applied field. Effectively, the material resists the imposition of an external electric field.

![Figure 2.8: Representation of a water dipole’s structure and the bulk arrangement of dipoles in the absence (left) and presence (right) of an external electric field, $E_{\text{ext}}$.](image)

The extent to which a material resists an electric field is embodied in its relative permittivity,
which for bulk water at room temperature has a value of about $\epsilon_w = 78$. Since the relative permittivity depends on the alignment of water molecules, it can be inferred that both the number of water molecules and the extent to which they are able to align with the field affect its value. If there are fewer molecules there will be a smaller net induced field generated by their alignment, while if the dipoles present are already aligned, increasing the field strength cannot lead to further alignment. Both of these limits may play a role in an electrode/electrolyte system.

The importance of accounting for changes in the relative permittivity in the electrode/electrolyte system comes from the fact that it defines the relationship between the electric field at the electrode surface and the surface charge density on it. Both an increased global electric field and an increased ion concentration can lower the local permittivity, as will be discussed shortly, and such a reduction in the permittivity reduces the amount of surface charge on the electrode at a given electric field. Increasing the surface potential tends to increase both the electric field and the counter-ion concentration, further reducing the permittivity and causing the surface charge density to increase at a different rate with an increasing potential potential compared to how it would if the permittivity were constant. Modelling the effect of the reduced permittivity on the double layer structure has long been of interest (Bikerman 1942; Grahame 1947; Macdonald and Carl A. Barlow 1962; Outhwaite 1976; Wang and Anderko 2001; Ben-Yaakov et al. 2011), although often only the field dependence or the concentration dependence is accounted for, not both.

As indicated in the above figure, the external field causes an alignment of the dipoles, thus restricting their ability to further align with the field and causing a decrease in the permittivity. The stronger the field, the more aligned the dipoles are and the less they are able to respond to further increases in the field (Joshi et al. 2004). In the double layer region next to a charged surface, the electric field can be large enough that significant ordering of the water molecules occurs, resulting in the dipoles pointing perpendicularly to the surface and causing significant changes to the local permittivity (Yeh and Berkowitz 1999). As a result, even in the absence of ion-related effects on the permittivity there can be a significant field-dependent reduction in the value.

Attempts to model the dielectric response of a bulk dielectric material at high field strengths date back to Debye, but the most common means to describe the field-dependent permittivity is by use of the Booth equation (Gur et al. 1978; Paunov et al. 1996; Wang et al. 2011), which takes the form (Booth 1951)

$$\epsilon_r = n_{RI}^2 + \frac{7\epsilon^*(n_{RI}^2 + 2)m^D}{3\sqrt{73}e^0E} \left( \frac{\sqrt{73}m^D(n_{RI}^2 + 2)E}{6k_B T} \right)$$

(2.15)

where $n_{RI}$ is the optical refractive index, $\epsilon^*$ the number density of solvent molecules, $m^D$ is the dipole moment of the water molecule, $E$ is the electric field strength and $L$ is the Langevin function, $L(x) = \coth(x) - 1/x$. The model predicts that the permittivity changes little until the applied field is large — for example in water a field of $2.5 \times 10^7$ V m$^{-1}$ reduces the permittivity by just 1% (Booth 1951). Further increases to the field strength however cause a rapid change.
in the permittivity of up to an order of magnitude (Bockris and Reddy 1970); the Booth equation predicts this to occur for applied electric fields of $\sim 2.5 \times 10^9 \text{ V m}^{-1}$ or larger. The size of the field in the double layer inevitably depends on the applied potential or charge, but for sufficiently large fields the field dependence of the permittivity should really be accounted for.

Beyond the Booth equation, the alignment of the solvent molecules which results from an applied field has been investigated more recently, with several other models proposed (Sandberg and Edholm 2002; Jha and Freed 2008), as well as the use of MD simulations to understand the microscopic processes underlying the change in the permittivity (Yeh and Berkowitz 1999; Aguilella-Arzo et al. 2009). Ultimately, the specific value of the dielectric constant is defined by correlations between the solvent molecules, which can be difficult to reduce to simple expressions in the same way that difficulties arise with the correlations in statistical theories of double layer structures. A detailed review of several approaches and comparisons to simulation data can be found in Fulton (2009)

On top of the field-dependence of the relative permittivity, there is an experimentally observed ion concentration dependence for bulk electrolytes (Hasted et al. 1948; Harris and O’Konski 1957; Buchner et al. 1999; Asaki et al. 2002). This arises partly because the ions displace water molecules, reducing their concentration, but also because the strong local electric field causes an alignment of the solvent molecules (Ben-Yaakov et al. 2011). This second factor is the source of the formation of the hydration shell depicted in Fig. 2.1(b), although in this updated picture of the system the water dipoles should be marked and aligned anti-parallel with the ionic field. In a similar manner to the aforementioned external field dependence of the relative permittivity, this alignment means the hydrated ion has a different dielectric response than the water molecules forming the hydration layer have in the absence of the ion, so the permittivity in the region of the ion is changed. Since increasing the concentration of ions changes the number of these altered permittivity regions, the overall dielectric constant of the electrolyte will be different to that in the bulk.

The actual dependence of the relative permittivity on the concentration is both ion and solvent specific, but is seen to be linear for concentrations of up to between 2 M and 4 M for numerous aqueous electrolytes (Hasted et al. 1948; Buchner et al. 1999; Wei and Sridhar 1990; Harris and O’Konski 1957), so this provides a simple means to estimate the variation in the permittivity. Accurately modelling the effects of the ion concentration requires models both for the hydration shell structure of a single ion and also for how the hydration shells interact, neither of which are simple.

For a single ion, the hydration shell is akin to that of an electrode double layer, with a counter charge being attracted to the ionic charge. The obvious difference is in both the scale and the fact that the counter-charge brings with it a region of co-charge on the other side of the dipole, but in terms of modelling this structure on its own there are similar difficulties. In particular is the fact that the sizes of the particles play a significant role, introducing all of the complexities which accounting for volume effects entails and generally leading back either to statistical mechanics models (Outhwaite 1976; Outhwaite and Bhuiyan 1983) or to lattice gas-type approximations in
the form of the Langevin-Bikerman model (Iglič et al. 2010; Gongadze et al. 2011b; Gongadze and Iglič 2012).

Once a model for the hydration shell is formed, a further difficulty is found in describing what happens in a solution as the concentration of ions increases, because the structure of the single hydrated ion will change. Initially, more frequent interactions between pairs of ions and their hydration shells will occur, altering the behaviour of the shells. More significant is when the ion concentration increases to the point at which hydration shells overlap or there are not enough water molecules present for each ion to have a full hydration shell (Levy et al. 2012). Finally, at high concentrations there may also be ion-ion interactions such as dipole or quadrupole formation (Copestake et al. 1985; Wei and Sridhar 1990).

There have been some successful attempts to build models which describe the concentration dependence of the permittivity of bulk electrolytes (Abrashkin et al. 2007; Levy et al. 2012; Gavish and Promislow 2012), but these usually either entail solving a secondary set of equations to derive the permittivity at a particular concentration or require a set of fitted parameters which are specific to individual systems. For this reason they are more difficult to incorporate into structural models for inhomogeneous electrolytes, leading to the use of simpler approximations in these situations. These simpler models are based on the aforementioned experimental observation that the bulk permittivity varies linearly with the ion concentration within a certain concentration range, with the bulk permittivity having the following dependence on the concentration of the ions in the solution

\[ \epsilon_r = \epsilon_w + 4\pi \sum_j \alpha_j c_j \]  

(2.16)

where \( \alpha_j \) is the excess polarisability of ion \( j \) and the sum, in common with all summation terms in this work, represents the sum over all of the ions in the system. The value of \( \alpha_j \) is negative for most ions in water, as can be deduced from the Clausius-Mossotti relation, which links the excess polarisability to the permittivity inside the hydrated ion structure, \( \epsilon_j \), and the permittivity of the bulk water, \( \epsilon_w \):

\[ \alpha_j = r_d^{3}\epsilon_w \frac{\epsilon_j - \epsilon_w}{\epsilon_j + 2\epsilon_w} \]  

(2.17)

The hydrated ions are usually less polarisable than pure water molecules, so \( \epsilon_i < \epsilon_w \) and so \( \alpha_i \) is negative. Values for the excess ion polarisability can be determined from experimental data, a range of which are presented in Table 2.1

Despite the limitation of the linear approximation at higher concentrations, its use in modelling the double layer has yielded a number of results. For negative excess polarisabilities, there is an energy cost to increasing the concentration of the ions which is related to the electric field strength. This unfavourable polarisability interaction grows with the magnitude of the field, preventing the counter-ion concentration from growing larger than \( c_{\text{max}} = -\frac{\epsilon_w}{8\pi \alpha} \) (Hatlo et al. 2012). At this limit the permittivity, rather than approaching the permittivity of free space, \( \epsilon^0 \), converges on half the value of the bulk solvent (Ben-Yaakov et al. 2009; Ben-Yaakov et al. 2011). As a result of these limits on the double layer structure, it has also been shown that
Table 2.1: List of experimentally measured ion excess polarisabilities (Hasted et al. 1948)

<table>
<thead>
<tr>
<th>Cation</th>
<th>$4\pi\alpha$ (M$^{-1}$)</th>
<th>Anion</th>
<th>$4\pi\alpha$ (M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>-17</td>
<td>F$^-$</td>
<td>-5</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>-11</td>
<td>Cl$^-$</td>
<td>-3</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>-8</td>
<td>I$^-$</td>
<td>-7</td>
</tr>
<tr>
<td>K$^+$</td>
<td>-8</td>
<td>OH$^-$</td>
<td>-13</td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>-7</td>
<td>SO$_4^-$</td>
<td>-7</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>-24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>-35</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The ion polarisability, in the absence of excluded volume effects, can explain the twin peaked differential capacitance curves (Hatlo et al. 2012).

2.5 Modelling electrolyte dynamics

Understanding the equilibrium structures of the double layer is useful in its own right, allowing the properties of systems in which equilibrium is actually reached to be studied. However, in many cases, of equal or greater importance are the dynamics of the system. A good example of this is the electric double layer capacitor: the equilibrium double layer structure gives information as to the amount of energy the capacitor can store, but understanding the charge/discharge behaviour of the capacitor in response to changes in the applied potential is necessary to see how that energy can be used.

In general, dynamic modelling encompasses systems in which movement occurs in both the perpendicular and parallel directions to the electrode surface. The ion motion may be driven directly, for example by a change in the applied potential, or by some less direct means, for example it might be a result of a concentration gradient (which could of course be the direct result of a reaction taking place at the electrode surface), or by some other factor which makes it more or less energetically favourable for ions to be at a particular point in space.

Many examples exist for situations in which the double layer affects the dynamic behaviour of a system. It is relevant for explaining the selectivity of ion channels through membranes of biological cells (Eisenberg 1998; Eisenberg and Liu 2007; Kurnikova et al. 1999; Radak et al. 2008; Valent et al. 2012), and helps to define the behaviour of novel micro-fluidic technologies such as electro-osmotic pumps (Wang 2009), ion filters (Nishizawa et al. 1995; Vlassiouk et al. 2008) and drug delivery systems (Chung et al. 2008; Chen et al. 2007). In addition to electrochemical capacitors, other devices such as batteries and fuel cells involve dynamic processes occurring in electrolyte solutions (Verbrugge and Hill 1990; Dunn and Newman 2000; Kötz and Carlen 2000; Weber and Newman 2004; Sakaguchi and Baba 2007), making an understanding of them relevant to new forms of electrical power generation and storage. In many of these cases there may also be charge transfer reactions taking place which, since they must take place at the electrode surface, will be affected by the double layer environment in which they occur.

In contrast to modelling equilibrium systems, direct simulation is rarely a possibility. While
MD is inherently dynamic in nature, for reasons stated previously it is generally not possible to simulate large enough numbers of particles for long enough time spans to be able to determine macroscopically measurable dynamic properties, such as (for example) the current along an ion channel (Chung and Kuyucak 2002; Zheng et al. 2011).

As with equilibrium systems, there exist statistical methods for describing the dynamic behaviour of particulate systems. Such non-equilibrium statistical mechanics models provide a means for modelling systems of arbitrarily large numbers of particles, using the Langevin equation for stochastic motion or otherwise the Boltzmann equation for the time-evolution of the single particle distribution function (Schwabl 2006).

Building on these non-equilibrium approaches, dynamic density functional theory (DDFT) has been developed to account for the additional position correlations which arise when accounting for the interactions between particles in a fluid (Wu and Li 2007). The term encompasses a range of different approaches to extending DFT to describe time dependent systems, using different equations of motion depending on the type of system being described (e.g. suspended colloids, atomic gases) (Marconi and Tarazona 1999; Archer 2006; Archer 2009; Goddard et al. 2012). Although some of the specifics differ between approaches, they share a use of the Helmholtz free energy as the driving force for the particle movement, making the assumption that the free energy of a non-equilibrium system with a particular one-body density is the same as the free energy of a system at equilibrium with the same one body density. A significant development with regards to this is the proof that, as with the equilibrium state at a constant applied potential, the one body density is also a unique functional of a general time-dependent external field (Chan and Finken 2005).

The extension to dynamic systems is not particularly simple, however; in addition to the position correlations which arise in DFT models, non-equilibrium statistical models also have velocity correlations. Handling these is a significant problem, meaning that they are often ignored (Marconi and Tarazona 1999; Archer 2006; Archer 2009; Goddard et al. 2012). Even with this simplification, the resulting equations are usually integro-differential in form, making them complex to handle and computationally intensive to solve.

An example of a slight simplification to the full DFT approach can be found in Gillespie et al. (2011). Here, equilibrium DFT was used to consider flow in nano-pores, whereby the double layer structure perpendicular to the wall was calculated using DFT and then a pressure or potential difference was applied along the pore, parallel to the wall, to drive a flow. The current and mass flow directions in the pore were seen to be dependent on whether charge inversion of the double layer had taken place, i.e. how much charge was present on the walls of the pore. Although this approach permits some additional features to be added to the system being modelled, it does not readily permit flow in the perpendicular direction to the wall, as this would require a full DDFT solution.

A much simpler approach is to assume that the dynamics can be described using continuum modelling. As with the equilibrium models for the electrolyte structure, the non-equilibrium statistical models can be simplified, the result being a continuity equation based on mass con-
observation, which links the change in the concentration at a point in space to the flux, $J(r)$, at that point.

$$\frac{\partial c_j(r)}{\partial t} = -\nabla \cdot J_j(r) \quad (2.18)$$

Derivation of this equation is possible from a microscopic perspective by using the overdamped limit of the Langevin dynamics in the absence of ion velocity correlations, giving the model a sound theoretical basis (Lu et al. 2010). These simplifications imply that it is technically limited to descriptions of dilute gases, but the extent to which it eases some of the difficulties of dynamic modelling means that it is widely used for more concentrated solutions and even ionic liquids (Zhao 2011). The equation holds true for any continuum model of electrolyte structure, neatly providing a means to describe the dynamics in an MF-LDA model.

The continuity equation can also be derived from the Helmholtz free energy functional (Archer 2006; Archer 2009), which provides a means to include effects such as the finite ion size and correlations in to continuum dynamics modelling, as will be discussed below. This route also yields the general connection between the electrochemical potential and the flux of a species in motion (Olesen et al. 2010)

$$J_j(r) = \sum_l L_{jl} c_l \nabla \mu_l(r) + c_j(r) u(r), \quad (2.19)$$

where the sum term describes diffusion and electro-migration transport and the second term describes convective flow at the mean field velocity, $u(r)$. $L_{jl}$ is the Onsager mobility tensor, related to the diffusivity tensor through the relationship $\beta D_{jl} = L_{jl}$, and is usually assumed to be diagonal, with $D_{jj}$ written as $D_j$, although this is strictly only true for dilute solutions and at higher concentrations there may be off diagonal components (Taylor and Krishna 1993).

In the simplest case of the Poisson-Boltzmann (GC) model for an electrolyte, substituting the ideal electrochemical potential from Eq. (2.3) into Eq. (2.19) yields the well known Nernst-Plank equation, a modified form of Fick’s law which includes the electromigration which results from the response of the ions to the electric field (Koryta et al. 1993; Girault 2004):

$$\frac{\partial c_j(r)}{\partial t} = D_j \nabla^2 c_j(r) + z_j \beta D_j \nabla \cdot (c_j(r) \nabla \phi(r)) - \beta D_j \nabla \cdot (c_j(r) u(r)). \quad (2.20)$$

This equation applies to each of the species in an electrolyte system. If there are $M$ species in the system, there are two more unknown parameters than there are equations, however, and two more equations are required to solve for all of the unknown parameters. Although the system contains moving charges and possibly an oscillating electric field, for mathematical convenience the electric field is treated as quasi-static and the Poisson equation is used to solve for the potential. The second equation, used if the convective velocity is non-zero, is the Navier-Stokes equation, which relates $u(r)$ to both the electric field and a pressure gradient under the
assumption of incompressible, Newtonian flow (Storey and Bazant 2012):

\[
c_m \left( \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \nu \nabla^2 \mathbf{u} - \rho \nabla \phi
\]

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

where \( c_m \) is the mass density, \( \rho \) is the charge density, \( p \) is the pressure and \( \nu \) is the viscosity.

The full complement of Nernst-Planck, Poisson and Navier-Stokes equations provide the means for calculating flow in continuum models, although they are non-linear and require numerical solution, so it can be seen that even under the assumption of ideal behaviour, electrolyte modelling can be computationally challenging. Models based on these equation have been applied to a wide variety of electrokinetic situations though, including descriptions of AC electroosmosis for micro-fluidic pumps (Bazant et al. 2009; Hrdlička et al. 2010), studying flow and ion selectivity through nano-channels (Vlassiouk et al. 2008; Choi and Kim 2009; Movahed and Li 2011) and modelling transport in fuel cells (Sprague and Dutta 2011).

For systems in which there is no convective flow, \( \mathbf{u} = 0 \) and the Navier-Stokes equation is not required. In this case, the dynamics of the system can be described using only the Poisson and Nernst-Planck equations alone, which are collectively known as the Poisson-Nernst-Planck (PNP) equations. Even without a convective term though, solution to these equations remains challenging due to the non-linearity introduced by the Poisson equation which precludes a general analytical solution. That said, in certain limiting cases it is possible to solve the equations analytically, examples of which include linearising the equations at low potentials and solving for the steady state (Golovnev and Trimper 2009; Golovnev and Trimper 2010), using the drift approximation (diffusion-limited flow) (Syganow and Kitzing 1999) or the use of asymptotic analysis (Bazant et al. 2004; Abaid et al. 2008; Olesen et al. 2010; Zhao 2011). This last approach has been used to identify four regimes for charge transport in response to a step potential applied to an electrode, being the combinations of high and low ion concentration with high and low applied potentials (Beunis et al. 2008). Within these four limits, analytical approximations can be derived for the behaviour of the system which agree well with experiment and numerical simulation, althought between the limits significant deviations arise. While the aforementioned paper dealt with the transient behaviour of a system in response to a constant applied potential, similar methods have also been used to develop analytical solutions to systems in which there is a time-dependent potential (Olesen et al. 2010). This was applied in the limit of thin double layers, showing that a significant depletion of the salt can arise in the electrolyte near to the electrode in response to the time-varying potential.

In order to calculate general solutions to the model equations, it is necessary to solve them numerically, for which a number of different approximation schemes have been proposed over the last 50 years (Cohen and Cooley 1965; Brumleve and Buck 1978; Mathur and Murthy 2009; Jasielec et al. 2012). Success has been had with respect to modelling flow in to porous electrodes (Sakaguchi and Baba 2007; Biesheuvel and Bazant 2010) and polymeric electrolytes (Soestbergen et al. 2008), as well as many of the systems outlined at the start of this section.
An alternative means for understanding the dynamic response of electrode/electrolyte systems is found in the use of equivalent circuits (EC), most commonly used to interpret electrochemical impedance spectroscopy (EIS) data (Macdonald 1992; Macdonald 2006; Chang and Park 2010). These use basic electronic circuit building blocks, including a voltage source, resistors, capacitors and certain special elements (such as the Warburg impedance element or constant phase elements), to represent parts of the physical system, creating an analogue of it. Once the circuit is built its complex impedance can be calculated mathematically using Kirchoff’s laws and from this the predicted response (typically the current) of the system to a given input signal (commonly a sinusoidal potential) analysed. This analysis is typically carried out by plotting the magnitude and phase of the impedance as a function of the frequency in a Bode plot or by making a parametric plot of the real and imaginary components of the impedance in a Nyquist plot. By comparing the output of a particular EC analogue to experimental data, it is possible to extract the properties of the real system by considering the properties of the components in the EC. The relationships between the input and output signals and the impedance are discussed further in Section 6.3.

ECs were introduced at the end of the nineteenth century to describe the ac electrochemical response of an electrode in terms of a bulk resistance due to transport of the electroactive species and a frequency dependent capacitance term (Bazant et al. 2004). This idea was combined with the Helmholtz model for the double layer to give what is now known as the Randles-Erschler circuit (Girault 2004), one of the simplest analogues for the electrode/electrolyte interface. The components of the EC should correspond to processes in the real system, for example the resistance of the bulk to charge transport is represented by a resistor and the double layer is represented by a capacitor. In this way, proper use of ECs can help interpret a set of experimental results, with particular features in the Bode and Nyquist plots being typical of certain processes. However, a particular set of EIS data, for example, may not have a unique EC which fits the data, which has led to the suggestion that, given enough of the basic building blocks in some combination, any response can be generated (Macdonald 2006). As a result, interpretation of results using ECs may be ambiguous and also the link between the physical processes occurring and the elements of the EC may be lost, removing one of the benefits of the technique.

The method also requires that the response of the system to the input is linear. In an electrochemical system this can at best only be approximated by ensuring that the variation in the input signal is small. If the potential changes by a large amount, for example, depletion of ions from the bulk may occur, causing the resistance to change and therefore invalidating its treatment as a fixed value resistor. It is possible to derive these models from the (unmodified) PNP equations using asymptotic analysis in the joint limit of thin double layers and small voltages (Bazant et al. 2004; Olesen et al. 2010), which confirms the relationship to the physical processes but further shows the limitations in that the double layer must be small in comparison to the whole system such that the equilibration time of the double layer is small in comparison to that of the entire system.
2.5.1 Ion interactions in dynamic models

The PNP equations as historically and still commonly applied retain the limitations of the underlying equations on which they are built, specifically that the electrolyte is assumed to behave as an ideal solution. The lack of particle interactions in these models means that as well as unrealistic concentrations in the double layer, the simple fact that more ions are required in the double layer can be expected to mean longer equilibration times and greater ion depletion from the bulk of an electrolyte, further altering the dynamics, since this will affect the diffusive component of the flow.

There has been a relatively large amount of interest in the inclusion of steric effects in modelling dynamic behaviour, largely commencing with two papers published in 2007 by Kilic et al. (Kilic et al. 2007a; Kilic et al. 2007b). Prior to this, various authors had accounted for steric effects to some extent, for example in the investigation of the current efficiency of permselective membranes (Cervera et al. 2001), in considering electrophoretic mobility of colloidal particles (Lopez-Garca et al. 2007), the sedimentation of colloids due to gravity (Dufriche et al. 1999) and also in the context of a time-dependent applied potential at an electrode-electrolyte interface (Baker-Jarvis et al. 1999). These works tend to be characterised by low potentials/surface charges, however, and it seems that it is only since the work of Kilic et al, coinciding with an increased interest in fluid flow in micro- and nano-fluidic devices, for which steric effects may have a significant impact, that there has been an increase in the study of such systems.

As indicated in the previous section, being able to derive the continuity equation from the Helmholtz free energy functional provides a route to moving beyond the assumption that the ions behave ideally. By deriving forms of the electrochemical potential which account for the excluded volume around an ion, for example, modified forms of the Poisson and Nernst-Planck equations may be developed. Given this relatively straightforward route to modifying the PNP equations, it is perhaps surprising that it is only relatively recently that the approach has been taken for modelling electrolyte dynamic solutions outside the limits of low concentration, low potential and long domains (Kilic et al. 2007a).

Within the two papers of Kilic et al, the authors develop two dynamic models which include steric effects, one based on an mPB theory using Bikerman’s model and the other for a system in which the concentration is calculated according to the Boltzmann distribution but for which the growth in the concentration with the potential is cut off at a maximum value of $c_{\text{max}} = 1/a^3$. These modified Poisson-Nernst-Planck (mPNP) models were used to calculate the relaxation/charging time of an electrode in response to a step change in the applied potential and are compared to an equivalent circuit model and also to the basic PB description of the electrolyte. They were able to demonstrate that the inclusion of steric effects alters the relaxation/charging time depending on the applied potential. For potentials below that corresponding to the peak in the differential capacitance, the relaxation time is seen to increase in the same way as it does in the PNP model, but for larger potentials it was predicted to decrease, following the shape of the differential capacitance curves. In comparison to the equivalent circuit model, their mPNP model was able to describe the depletion of the salt from the bulk as the ions were
used to form the double layer which, as stated previously, is a known limitation to equivalent circuit models.

In the time since these two papers, steric effects have been built in to many of the models for the types of systems mentioned at the outset of the previous section. This includes improved models of flow reversal in ac electro-osmosis (Storey et al. 2008; Bazant et al. 2009), transport in ion channels, demonstrating how the ion volume leads to ion selectivity (Horng et al. 2012), together with some studies of the formation of the double layer (Zhao 2010).

With the obvious exception of ac driven flow, much of this work only considers steady flow through constant potential (or constant surface charge) systems or the response of systems to a step change in the potential. Furthermore, the models almost invariably account for the excluded volume interactions using the Bikerman model, which means that all ions in the system have the same excluded volume. As discussed previously, this precludes effects such as large ion exclusion from the double layer in favour of smaller ions. This latter effect could be important in understanding systems in which there is a supporting electrolyte, since the relative sizes of the two counter-ions in the mixture may have significant effects on the overall system behaviour.

For fully time-dependent models of the type considered in part of this work, most relevant to experimental techniques such as cyclic voltammetry or electrochemical impedance spectroscopy (EIS), there are a limited number of papers which consider steric effects. Wang and Pilon (Wang and Pilon 2012a; Wang and Pilon 2012b) have considered their influence, first on EIS and second on cyclic voltammetry, using an mPNP model. They identify a characteristic diffusion time \( \tau_m = \frac{\lambda_m^2}{D} \), where \( \lambda_m \) is the value that the Debye length takes if the concentration was equal to the maximum allowed by excluded volume interaction and \( D \) is the diffusion coefficient of the ions. They show that peaks in cyclic voltammetry curves may arise as a consequence of the finite ion size, in addition to other processes with which they are commonly associated, such as reactions or adsorption. Olesen and co-workers (Olesen et al. 2010) have used asymptotic analysis to consider the double layer structure and response to a large ac voltage at a frequency comparable to the inverse of the relaxation time of the cell, defined as \( \tau = \frac{\lambda_D L}{D} \), where \( L \) is the length of the modelling domain. They demonstrate the relative contributions the Stern and diffuse layers make to shielding the bulk from the applied potential and demonstrate that under certain conditions it is possible for there to be regions near to the electrode which contain very little of either ion species at certain points in the potential cycle.

Beyond the excluded volume interaction, little work has been carried out which accounts for other effects in dynamic modelling. As regards the model described later, there has been the aforementioned recent work relating to the effect of the ion excess polarisability on the equilibrium state but, in terms of dynamics, the permittivity is often treated as being constant or as having fixed values in certain regions of the domain, although there has been some work which incorporates the field-dependent effects into dynamic models using the Booth equation (Wang et al. 2012). The effect of the ion polarisability on the dynamics does not seem to have been considered, so it is of interest to see whether and what changes arise when they are accounted for. For example, the electric field, which drives the electro-migration flux of the ions, increases
as the permittivity decreases, so there may be changes in properties such as the relaxation time of an electrode relative to both the GC and excluded-volume-only models of the double layer.

### 2.5.2 Surface reactions in electrochemical systems

In many electrochemical systems, the electrode surface does not represent an inert blocking surface against which the counter-ions in the electrolyte pile up when a potential is applied, but plays an active role in the behaviour of the system as a source or sink of electrons, facilitating electrochemical reactions. This transfer of electrons can be measured as a current, providing a means to probe the properties of the reaction. The general form of an electrochemical reaction is commonly written as

\[ \text{Ox} + n_e e^- \rightleftharpoons \text{Re} \tag{2.22} \]

where Ox is the oxidised form of the reacting species and Re is the reduced form and where \( n_e \) is the number of electrons transferred (i.e. it is the magnitude of the electron stoichiometric coefficient). Associated with the reaction is a change in the Gibbs free energy, \( \Delta G_{\text{RXN}} \), a thermodynamic quantity which determines the direction of spontaneity of the reaction. Its value is equal to the difference between the Gibbs free energy of formation, \( G_f^j \), of the reactants and products, which can be written as (Prigogine and Defay 1954)

\[ \Delta G_{\text{RXN}} = \sum_j \nu_j G_f^j \tag{2.23} \]

where \( \nu_j \) is the stoichiometric coefficient of species \( j \) in the reaction. Negative values of \( \Delta G_{\text{RXN}} \) mean that the energy of formation of the reduced form is lower than that of the oxidised form and so the reaction will spontaneously run from left to right in the above reaction, while positive values \( \Delta G_{\text{RXN}} \) mean the reverse is true.

In addition to defining the direction the reaction spontaneously moves, \( \Delta G_{\text{RXN}} \) also defines the equilibrium condition and the equilibrium ion concentrations. In the process of reacting, electrons are transferred between the ions and the electrode in such a manner as to change the charge on the electrode: forward (reduction) reactions remove electrons and reverse (oxidation) reactions add them. The overall charge depends on the dominant direction of the reaction. Whichever this is, the resultant electrode charge is such that the reactant in the dominant direction is repelled from the surface and the product attracted to it. This slows the dominant reaction and accelerates the reverse reaction while also causing the formation of a double layer. Eventually an equilibrium will be reached in which two conditions are met. First, the forward and reverse rates of the reaction will be equal, so the net rate is zero, and second, the potential drop across the double layer is sufficient to shield the bulk electrolyte from the accumulated charge on the electrode. For this to happen, the potential drop across the double layer at equilibrium, \( \Delta \phi \), must be equal to \( \Delta G_{\text{RXN}} \), allowing an additional equality to be added to the previous
equation (Bard and Faulkner 1980):

\[
\Delta G_{\text{RXN}} = \sum_j \nu_j G_j^f = -n_e e_0 \Delta \phi_{\text{RXN}}
\]  

(2.24)

In principle, this provides a means to directly measure \( \Delta G_{\text{RXN}} \), but in practice this is not possible because the potential of the bulk electrolyte cannot be measured. Instead, a second electrode is required to measure the potential against. However, this will have its own surface reaction and equilibrium double layer potential drop, meaning that the measured difference between the two electrodes is equal to the total drop across both double layers, providing no information about each individually.

In order to bypass this problem, a standard electrode is selected for which the reaction potential is defined as zero. This electrode is the standard hydrogen electrode (SHE), which consists of a platinum electrode at which the redox reaction of hydrogen takes place (Bard and Faulkner 1980). Taking this as one electrode in a system with a test electrode in a particular electrolyte, the measured potential difference is taken as being entirely due to the reaction occurring at the test electrode.

Given that changes to the bulk concentration, temperature and pressure alter the double layer structure, these will also have an impact on the reaction rate and therefore also the equilibrium potential. For this reason, in addition to requiring a standard electrode to define the point of zero potential, a standard electrolyte state is used when reporting data. This standard state consists of a temperature of 298 K, a pressure of 1 atm and an electrolyte concentration of 1 M (IUPAC 1997). Furthermore, despite the high concentration, the state also requires there to be no influence from ion interactions, making it a purely hypothetical condition. Since the standard state does not exist in practice, the equilibrium potential in the standard state cannot be directly measured and is instead extrapolated from measured values at low concentration, for which the requirement of no ion interactions is approximately valid. The equilibrium potential in the standard state is denoted \( \Delta \phi^\circ \) and, using Eq. (2.24), can be used to calculate the Gibbs free energy of reaction in the standard state, \( \Delta G_{\text{RXN}}^\circ \). Values of \( \Delta \phi^\circ \) for different electrochemical reactions can be found in many publications, a selection of which is shown in Table 2.2.

If the reactants in a system are not in the standard state, the actual reaction potential can be calculated using the Nernst equation, a fundamental thermodynamic relationship which any reaction model must obey at equilibrium. This can be expressed either in terms of the bulk ion activities, \( a_{c,j}^0 \), or their bulk concentrations, \( c_{0,j}^0 \) (Lefrou et al. 2012):

\[
\Delta \phi = \Delta \phi^\circ + \frac{1}{n_e \beta e_0} \ln \frac{a_{c,\text{Ox}}^0}{a_{c,\text{Re}}^0} = \Delta \phi^f + \frac{1}{n_e \beta e_0} \ln \frac{c_{\text{Ox}}^0}{c_{\text{Re}}^0}
\]  

(2.25)

where \( \Delta \phi^f \) is the formal potential of the electrode, the value the equilibrium double layer potential difference takes once the activities of the ions have been accounted for. The form of this equation is similar to that of the trans-membrane potential (resting potential) in biology, which relates the concentrations of ions either side of a cell membrane to the potential difference.
Table 2.2: List of some standard electrode potentials (Haynes 2012)

<table>
<thead>
<tr>
<th>reaction</th>
<th>potential</th>
<th>reaction</th>
<th>potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺ + e⁻ ⇌ Ag</td>
<td>0.779</td>
<td>Ba²⁺ + 2e⁻ ⇌ Ba</td>
<td>−2.912</td>
</tr>
<tr>
<td>Ag⁺⁺ + e⁻ ⇌ Ag⁺</td>
<td>1.980</td>
<td>Cr⁺⁺ + 2e⁻ ⇌ Cr</td>
<td>−0.913</td>
</tr>
<tr>
<td>AgF + e⁻ ⇌ Ag + F⁻</td>
<td>0.779</td>
<td>Cr³⁺ + e⁻ ⇌ Cr²⁺</td>
<td>−0.407</td>
</tr>
<tr>
<td>Cu⁺ + e⁻ ⇌ Cu</td>
<td>0.521</td>
<td>Cr⁺⁺ + 3e⁻ ⇌ Cr</td>
<td>−0.744</td>
</tr>
<tr>
<td>Cu²⁺ + e⁻ ⇌ Cu⁺</td>
<td>0.153</td>
<td>Mg²⁺ + e⁻ ⇌ Mg</td>
<td>−2.70</td>
</tr>
<tr>
<td>Cu²⁺⁺ + 2e⁻ ⇌ Cu⁺⁺</td>
<td>0.3419</td>
<td>Mg²⁺⁺ + 2e⁻ ⇌ Mg²⁺⁺</td>
<td>−2.372</td>
</tr>
<tr>
<td>Cl₂ + 2e⁻ ⇌ 2Cl⁻</td>
<td>1.35827</td>
<td>Na⁺ + e⁻ ⇌ Na</td>
<td>−2.71</td>
</tr>
<tr>
<td>F₂ + 2e⁻ ⇌ 2F⁻</td>
<td>2.866</td>
<td>K⁺ + e⁻ ⇌ K</td>
<td>−2.931</td>
</tr>
<tr>
<td>I₂ + 2e⁻ ⇌ 2I⁻</td>
<td>0.5355</td>
<td>Li⁺ + e⁻ ⇌ Li</td>
<td>−3.0401</td>
</tr>
<tr>
<td>I³⁻ + 2e⁻ ⇌ 3I⁻</td>
<td>0.536</td>
<td>Rb⁺⁺ + e⁻ ⇌ Rb</td>
<td>−2.98</td>
</tr>
<tr>
<td>OH + e⁻ ⇌ OH⁻</td>
<td>2.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂ + 2H⁺ ⇌ H₂O₂</td>
<td>0.695</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

across it. The potential difference in that case arises due to ions being pumped across the membrane, causing their concentrations to differ on either side of the membrane. At equilibrium, the electrochemical potentials of the ions must be the same on both sides of the membrane so, by assuming GC theory, the two electrochemical potentials can be defined (i.e. \( \mu_1 = \ln c_1 + z \phi_1 \) and \( \mu_2 = \ln c_2 + z \phi_2 \)) where \( \phi_1 \) and \( \phi_2 \) are the potentials on either side of the membrane. By equating \( \mu_1 \) and \( \mu_2 \) and then rearranging the result to \( \ln(c_2/c_1)/z = \phi_1 - \phi_2 \), the trans-membrane potential, \( \Delta \phi_m = \phi_1 - \phi_2 \), can be calculated.

The Nernst equation for reacting systems also includes a concentration difference, but this time between the concentrations of reactant and product at the electrode surface. Rather than a physical separation as in the trans-membrane potential, they are separated by an energy barrier (the activation energy), the crossing of which depends on the concentration, giving rise to a similar logarithm term. However, the reactant and product are different species, with different energies in the solution, meaning that in a reacting system there is also an additional fixed potential contribution to the equilibrium potential in the form of the \( \Delta \phi^\ominus \) term.

The thermodynamic relationships described above define the equilibrium state, but say nothing about non-equilibrium systems. Electrochemical oxidation is a first order process with respect to the surface concentration of the reduced species, while reduction can be considered pseudo first order with respect to the surface concentration of the oxidised species, provided there is an excess of electrons in the electrode compared to the surface concentration of ions (Girault 2004). On the basis of these assumptions, the net reaction rate can be written as the difference between the forward and reverse rates:

\[
r = k_f c_{Ox} - k_{b} c_{Re}
\]

where \( k_f \) and \( k_b \) are the forward and backward rate constants. Since electrons are transferred between the electrode and the electrolyte, this rate is directly proportional to the current generated when the reaction occurs. By convention, the reduction reaction (removal of electrons
from the electrode) generates a negative current and the oxidation reaction a positive current so, for Eq. (2.22), the current density \( I \) is

\[
I = -n_e e_0 r = z e_0 (k_b c_{Re} - k_f c_{Ox})
\]

(2.27)

Despite their name, \( k_f \) and \( k_b \) are not true constants, in that they depend on the electrostatic potential. By far the most common means for determining their values is through the use of the Butler-Volmer equation, in which they are related to the rate constant in the standard state through the following relationships (Zanello 2003)

\[
k_f = k_f^{BV} = k^\oplus \exp[-(1 - \gamma) n_e \beta e_0 (\Delta \phi - \Delta \phi^f)]
\]

(2.28)

\[
k_b = k_b^{BV} = k^\oplus \exp[\gamma n_e \beta e_0 (\Delta \phi - \Delta \phi^f)]
\]

where \( k^\oplus \) is the standard rate constant and \( \gamma \) is the transfer coefficient or symmetry factor, a measure of the different extents to which each rate constant responds to the potential difference. By combining Eqs. (2.25), (2.27) and (2.28), a form of the Butler-Volmer (BV) equation can be derived:

\[
I = I_0 \left[ \frac{c_{Re}(z = 0)}{c_{Re}^0} \exp[\gamma n_e \beta e_0 \phi_\eta] - \frac{c_{Ox}(z = 0)}{c_{Ox}^0} \exp[-(1 - \gamma) n_e \beta e_0 \phi_\eta] \right]
\]

(2.29)

in which the exchange current density, \( I_0 = n_e e_0 k^\oplus (c_{Re}^0)^{1-\gamma} (c_{Ox}^0)^\gamma \), and the overpotential, \( \Delta \phi_\eta = \Delta \phi - \Delta \phi^f \), have been introduced. A further simplification to this expression can be made by assuming that the charge transfer limits the reaction rate, in which case the two concentration ratios in Eq. (2.29) reduce to unity and the equation becomes equal to the basic Butler-Volmer (BV) equation (Bard and Faulkner 1980; Girault 2004).

The simple analytical nature of the BV equation explains its widespread use, for example in models for fuel cells, electrochemical supercapacitors and fundamental descriptions of the electrode/electrolyte interface (Rowe and Li 2001; Rubio et al. 2010; Chu and Bazant 2005; Sokirko and Bark 1995). It is also possible to build it into equivalent circuit models, being represented as the series combination of a resistor and the Warburg element, together placed in parallel to the capacitor which represents the double layer (Girault 2004; Chang and Park 2010). Through this, it is possible to understand the steps involved in reaction processes using ECs although, as can be seen from the form of the equation, \( I \) is non-linear with respect to the potential, so this reinforces the limitation on small amplitude variations of the input signal to ensure the response is approximately linear.

Despite its ease of use, the BV equation requires a reference value and condition against which the potential difference is measured, which physically does not make that much sense, as it defines the rate in terms of a property which is not local to the site of the reaction. Furthermore, the concentration in the BV equation is the value at the interface between the diffuse layer and the bulk, which is ill defined in a number of situations, for example when the current is larger than the diffusion limited value or when there are overlapping double layers (Soestbergen 2012).
It is common in macroscopic models to apply the BV equation as a boundary condition on an electrolyte solution in which electroneutrality is enforced throughout (Newman 1973). This ignores the microscopic structure but is reasonably valid provided mass transport is the rate-limiting step in the reaction process.

While its use can be justified in macroscopic models, at a microscopic level the BV equation begins to make less physical sense. The rate is dependent on the potential difference across the double layer but there is no physical reason why this entire value should determine the activation barrier to a process which occurs within the Stern layer (Bazant et al. 2005). For microscopic modelling, in which the double layer structure is explicitly accounted for, it is therefore more common to use Frumkin’s correction to the BV equation (Frumkin 1933; Bazant et al. 2005; Newman 1973). In this, the concentrations are defined specifically as the concentrations at the reaction plane (assumed to coincide with the Stern layer boundary) and the rate is only modified by the potential difference across the Stern layer, $\Delta \phi_s$. Referred to as the generalised Frumkin-Butler-Volmer (gFBV) model, this effectively separates the model into the compact part, where the reaction actually occurs, and the diffuse part, which can be modelled using a suitable structural model (Newman 1973). The form of the gFBV reaction rate is

$$r = k_0^f c_{\text{Re}}(0) \exp[\gamma n_e \beta e_0 \Delta \phi_s] - k_0^b c_{\text{Ox}}(0) \exp[-(1 - \gamma) n_e \beta e_0 \Delta \phi_s] \quad (2.30)$$

Physically, this makes more sense than the BV model as the rate of the reaction is only dependent on the properties of the system which the ion undergoing the reaction actually experiences, namely the potential drop across the Stern layer and the local concentration. These depend on the potential difference between the electrode and the bulk electrolyte, but the potential difference does not directly define the reaction rate.

From the form of the gFBV equation it may not be obvious that it reduces to the Nernst equation at equilibrium, but this can be shown by noting that the concentrations of the ions are related to the potential drop across the double layer, $\Delta \phi_d$. In the GCS model the surface concentration of the reacting species are $c_j(z = 0) = c_j^0 \exp(-z_j \Delta \phi_d)$ and by substituting this into the Eq. (2.30) with $r = 0$ it can be shown that the ratio of the rate constants becomes

$$\frac{k_b^0}{k_f^0} = \frac{c_{\text{Re}}^0}{c_{\text{Ox}}^0} \exp[n_e \beta e_0 (\phi_d + \phi_s)] \quad (2.31)$$

The ratio of the rate constants is equal to the equilibrium rate constant, which is in turn defined by the Gibbs free energy of the reaction in the standard state, which relates to the standard state equilibrium potential of the reaction. These relationships are summarised in the following sequence of equations:

$$\frac{k_f^0}{k_b^0} = K^0 = \exp(-\beta \Delta G^0_{\text{RXN}}) = \exp(n_e \beta e_0 \Delta \phi^0) \quad (2.32)$$

Combining these with the Eq. (2.31) and noting that $\phi_s + \phi_d = \Delta \phi^{eq}$ at equilibrium, it is possible to demonstrate agreement with Eq. (2.25) under the assumption of ideally behaving
particles (i.e. the activities are equal to unity).

While it is less commonly applied than the BV model, the gFBV model has been used in a wide variety of models in which the microscopic properties of the electrolyte are accounted for. These include in modelling porous electrodes (Biesheuvel et al. 2011), fuel cell membranes (Biesheuvel et al. 2009), fuel cell electrodes (Franco et al. 2006; Sprague and Dutta 2011), electrochemical thin films (Bazant et al. 2005) and analyses of the effects of reactions on the dynamic response of electrolytes (Bonnefont et al. 2001; Soestbergen 2012).

Although commonly used, both the BV and gFBV equations show an exponential growth dependence of the rate on the potential difference so, in principle the rate is able to grow indefinitely, which is unphysical. However, there exists an alternative model for the potential dependence of the rate constant in the form of Marcus-Hush (MH) theory, developed independently by each of the people for which it is named (Marcus 1956; Marcus 1957; Hush 1958; Hush 1968). The theory considers in detail the processes occurring during the reaction to determine how the potential modifies the rate constants, leading to expressions for them of the form (Henstridge et al. 2011):

\[
\begin{align*}
    k_f^{MH} &= k_0 \frac{I(\lambda, \phi - \phi_f)}{I(\lambda, 0)} \exp \left[ n_e e_0 \beta (\phi - \phi_f) \right] \\
    k_b^{MH} &= k_0 \frac{I(\lambda, \phi - \phi_f)}{I(\lambda, 0)} \exp \left[ -n_e e_0 \beta (\phi - \phi_f) \right]
\end{align*}
\]

(2.33)

where the functions \( I \) are defined by the integral

\[
I(\lambda, \phi - \phi_f) = \int_{-\infty}^{\infty} d\varepsilon \frac{\exp \left[ (\varepsilon - \beta e_0 (\phi - \phi_f))^2 \right] \cosh \left( \frac{\varepsilon}{2} \right)}{2 \cosh \left( \frac{\varepsilon_0}{2} \right)}
\]

(2.34)

in which \( \varepsilon \) is an integration variable and \( \lambda \) is the reorganisation energy in moving from the reactants to the products. The most apparent difference between this and the BV model is the complexity: rather than giving an analytical expression, this requires the solution of a complex integral. Furthermore, it requires knowledge of the reorganisation energy. Although based on possibly sounder foundations than the BV model or its variants, the two models do not differ significantly in most situations (Stevenson et al. 2013), since if the reorganisation energy is large the MH model reduces to the BV model.

While there is a growing body of work relating to redox reactions in which MH theory is applied and the differences between it and the BV model explored (Henstridge et al. 2011; Laborda et al. 2011; Henstridge et al. 2012a; Henstridge et al. 2012b), for the purposes of this work the differences between the two models are assumed sufficiently small that MH theory is not considered.

The high concentration of ions in the double layer means that ion interactions will likely affect the reaction rate. However, these are generally not accounted for when describing surface reactions, in neither the BV nor MH formalisms. There is, however, much less work in the literature regarding this for dynamic systems and, for what there is, it limited to the excluded
volume interaction. In terms of electrochemical cells, Biesheuvel et al. (2009), accounting for
the ion volume using the Bikerman model, have shown that there is a drop in the voltage of
an electrochemical cell operating at a fixed current as the size of the reactants increased. Lu
and Zhou (2011) used a similar excluded volume model which was adapted to allow ions of
different sizes to be accounted for in describing diffusion reaction processes in biomolecular
systems, suggesting that reaction rates are increased when the reactant sizes are accounted for.
In terms of the ion polarisability, there is no prior work concerning its effect on reaction rates.

2.6 Summary of modified Poisson-Boltzmann models and their
applications

The table below provides a brief comparison of the three common modified Poisson-Boltzmann
models, together with the polarisability model of Hatlo et al. (2012). In all four cases the final
two columns give an indication of prior use in the stated situations.

<table>
<thead>
<tr>
<th>Model</th>
<th>Ion volumes</th>
<th>Analytical equilibrium solution</th>
<th>Fits differential capacitance</th>
<th>Dynamic modelling</th>
<th>Reaction modelling</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>zero</td>
<td>yes</td>
<td>at small c and φ</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Bikerman</td>
<td>set by lattice</td>
<td>yes</td>
<td>correct trend</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>BMCSL</td>
<td>yes</td>
<td>no</td>
<td>correct trend</td>
<td>rarely</td>
<td>rarely</td>
</tr>
<tr>
<td>Polarisability</td>
<td>no</td>
<td>no</td>
<td>correct trend</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>

Each of the models can be improved through the use of a Stern layer, although in this case
none of the models may be solved analytically.
Chapter 3

Theory

The aim of this work is to investigate what effect ion-specific properties have on the equilibrium properties and dynamic response of electrolyte systems in response to either constant or time-dependent potentials. This chapter will cover the derivation of the model used to describe the electrolyte and its dynamic behaviour.

In general, the description of the electrolyte is derived from a mean-field-local-density approximation (MF-LDA) free energy functional. Excluded volume effects are described using a slightly modified van der Waals term and the dielectric decrement resulting from the ion polarisability is accounted for, yielding a modified Poisson-Boltzmann model. The dynamics are derived from the free energy functional of the system, reducing to a modified Nernst-Planck equation. The solution is attained by coupling the electrolyte structural equations to the dynamic equation, giving a modified Poisson-Nernst-Planck (mPNP) model.

The system to which the model is applied is that of an electrolyte at a single smooth, planar electrode. As a result, the number of spatial dimensions is reduced to one, the perpendicular distance from the electrode, simplifying the method of solution as described in chapter 4.

3.1 The model system

The model system consists of a semi-infinite planar electrode adjacent to a region of electrolyte, representing either an electrode that is assumed to be large enough that its curvature should not have a significant effect on the structure of the double layer or one half of a slit pore structure. The modelling domain, the region over which the equations derived in the following section apply, extends from the Stern layer boundary to a point in the bulk electrolyte a distance $z = L$ from the Stern layer. The existence of the Stern layer itself is accounted for in the boundary conditions for the domain while the position of $L$ depends on the particular system being examined. The domain is summarised in Fig. 3.1 below.

The ion concentrations and the potential are all defined at the bulk boundary, equal to the bulk concentrations and zero respectively. The boundary conditions for the Stern layer will be discussed in more detail in the following sections, but are derived from the electrode species flux and electric potential at the electrode surface.
3.2 The Helmholtz free energy and uniform systems

For the systems of interest in this work, the relevant thermodynamic potential is the Helmholtz free energy, $F$, a function of the state of the system defined by the system temperature, $T$, entropy, $S$, pressure, $p$ and volume, $V$, and the number of each ion type in the system, $n_l$, together with their (electro-)chemical potentials, $\mu_l$:

$$dF = -SdT - pdV + \sum_l \mu_l dn_l$$  \hspace{1cm} (3.1)

Once an expression for $F$ is known, all the thermodynamic properties of the system can be calculated. Of particular interest to this work are the chemical potential of a specific species $j$, $\mu_j$, and the pressure, $p$, which are defined as (Prigogine and Defay 1954)

$$\mu_j = \left( \frac{\partial F}{\partial n_j} \right)_{V,T,n_{l\neq j}} = \frac{1}{V} \left( \frac{\partial F}{\partial c_j} \right)_{V,T,n_{l\neq j}}$$ \hspace{1cm} (3.2a)

$$p = - \left( \frac{\partial F}{\partial V} \right)_{n_j,T}$$ \hspace{1cm} (3.2b)

where $c_j = n_j / V$ is the concentration of species $j$ and the subscripts on the brackets indicate that those properties are held constant when the derivative is taken.

The benefit of using the Helmholtz free energy is that it allows for a straightforward decomposition of the structural model into two terms, one relating to the internal interactions between the particles in a homogeneous system (the particle interaction term), $\mathcal{F}$, and the other relating to the interactions of the particles with any external potentials which cause inhomogeneities (the field interaction term), $\mathcal{F}^{\text{el}}$. In an inhomogeneous system the particle interaction term can be related to the form it would have in a homogeneous system, in this case by using the local density approximation (see section 3.3). The expression for the homogeneous system can be derived from the theoretical starting point of an infinite uniform fluid. The field interaction term, in this case the interaction of the ions with an electric field, can simply be added to the
particle interaction term such that the total free energy is (Hansen and McDonald 2006):

$$ F = F + F^\text{id} $$ \hfill (3.3)

The remainder of this section is devoted to a discussion of the excluded volume interaction terms which are applied in the context of homogeneous electrolyte models. The LDA itself and how it connects the free energy of a uniform system to that of an inhomogeneous one can be found in the next section and finally the field interaction term (and the effect of the ion excess polarisability) will be discussed in section 3.4. Three particle interaction terms are discussed here: the Bikerman model, the BMCSL model and the modified van der Vaals ($\text{mvdW}$) model. The first two provide a reference of comparison (predominantly in terms of the equilibrium properties discussed in chapter 5) for the third, which has not previously been applied in electrolyte modelling.

The particle interaction component of the free energy can be further decomposed into ideal and residual components, $F^\text{id}$ and $F^\text{res}$, respectively:

$$ F(T, \{c_l\}) = F^\text{id}(T, \{c_l\}) + F^\text{res}(T, \{c_l\}) $$ \hfill (3.4)

The ideal part is the free energy the system would have if the particles within it behaved in an ideal manner, while the residual term describes the effects of all the non-electrostatic interactions between the particles. Note that this separation also means that the thermodynamic properties of the system can also be separated into ideal and excess components in the same manner, each related to the corresponding component of the overall free energy through Eqs. (3.2a) and (3.2b). For example the chemical potential can be written as

$$ \mu_j = \mu_j^\text{id} + \mu_j^\text{res} = \left( \frac{\partial F^\text{id}}{\partial n_j} \right)_{V,T,n_{\neq j}} + \left( \frac{\partial F^\text{res}}{\partial n_j} \right)_{V,T,n_{\neq j}} $$ \hfill (3.5)

where the residual free energy is the deviation from the ideal free energy at the same temperature, concentration and number of moles.

The ideal free energy can be derived from the single particle translational partition function, the result for a single species being (Hansen and McDonald 2006)

$$ \beta F^\text{id}(T, c_j) = n_j (\ln[c_j \Lambda^3_j] - 1) $$ \hfill (3.6)

where $\beta = 1/k_B T$ is the inverse thermal energy of the system. From this, and using Eq. (3.2a), the ideal component of the chemical potential is

$$ \beta \mu_j^\text{id} = \ln[c_j \Lambda^3_j] $$ \hfill (3.7)

and the pressure, calculated from Eq. (3.2b) under the assumption of ideal behaviour and the presence of only one species, is

$$ \beta p = c $$ \hfill (3.8)
which can be rearranged to give the familiar ideal gas equation of state: $pV = nk_B T$.

The excluded volume interaction between the ions in the electrolyte accounts for part of $\mu^{\text{res}}$, that part being the excess chemical potential, $\mu^{\text{ex}}$. As discussed in the previous chapter, there are several different models for this interaction, and it is in the specific form of the excess free energy term that they differ. The particular form of $\mu^{\text{ex}}$ used in most of this work is based on a slightly modified van der Waals (vdW) equation of state, which will be discussed shortly. This is a relatively simple model, similar to the Bikerman model, but which allows for different ion sizes. Furthermore, in terms of being able to adapt it to dynamic modelling, it poses a similar level of difficulty to the Bikerman or BMCSL models.

### 3.2.1 The Bikerman model

This is one of the most commonly used means for accounting for excluded volume effects in electrolyte modelling, owing to the fact that it leads to analytical solutions, as discussed in the previous chapter. By treating the ions as a lattice gas, the excess free energy can be derived (Borukhov et al. 1997), the result being

$$
\beta F^{\text{ex,B}} = \frac{1}{a^3} \left( 1 - a^3 \sum_l c_l \right) \ln \left( 1 - a^3 \sum_l c_l \right) \tag{3.9}
$$

where $a$ is the spacing of the lattice, set to a nominal diameter of the ions in the system. The model essentially accounts for the entropy of the solvent through the $1 - a^3 \sum_l c_l$ term, altering the overall free energy. Using Eq. (3.2a), the excess chemical potential in the Bikerman model is

$$
\beta \mu_j^{\text{ex,B}} = \ln \frac{1}{1 - a^3 \sum_l c_l} \tag{3.10}
$$

and the compressibility factor, calculated from Eq. (3.2b), is

$$
\frac{\beta p}{\sum_l c_l} = -\frac{1}{V} \left[ \ln \left( 1 - a^3 \sum_l c_l \right) + 1 \right] \tag{3.11}
$$

While this model leads to analytical solutions, the particle sizes are fixed by the lattice spacing, meaning that only one particle size can be used. Since different ions have different sizes, this restricts the relevance of the model to many electrolyte systems.

The pressure in this model diverges as the occupied volume fraction tends to unity, although this represents all lattice sites being occupied, rather than all of the actual volume being taken up by ions. The lattice gas structure on which the Bikerman model is based means that when the occupied volume fraction is unity the number of particles is $V/a^3$ and that the ions effectively have a simple cubic lattice structure. As a result the packing fraction at the maximum concentration is approximately 0.52.
3.2.2 The BMCSL model

The BMCSL model, or the simpler Carnahan-Starling (CS) model, as discussed previously, is the other commonly used free energy expression. Derived from an observed pattern in the series of virial coefficients, and developed as a multi-component model (in the case of the BMCSL model), the free energy takes the form (Boublík 1970; Mansoori et al. 1971)

\[
\beta F_{\text{ex,BMCSL}}(T, \{c_l\}) = -\sum_l n_l \ln(1-\eta_3) + \frac{18V}{\pi} \frac{\eta_2 \eta_1}{(1-\eta_3)} + \frac{6V \eta_2^2}{\pi} \left[ \ln(1-\eta_3) + \frac{1}{\eta_3 (1-\eta_3)^2} \right]
\]

(3.12)

where \( \eta_n = \frac{\pi}{6} \sum_l c_l a_l^n \) and \( a_l \) is the diameter of species \( l \). As before, Eq. (3.2a) gives the chemical potential for each individual species, resulting in the expression

\[
\beta \mu_{j,\text{BMCSL}} = -\ln(1-\eta_3) + \frac{3\eta_2}{(1-\eta_3)} a_j + \frac{3\eta_1}{(1-\eta_3)} a_j^2
\]

(3.13)

and the compressibility factor takes the form (Mansoori et al. 1971)

\[
\frac{\beta p}{c} = Z = 1 + \frac{\eta_3 + 3\eta_2 \eta_1}{(1-\eta_3)} + \frac{3(\eta_3 \eta_2 \eta_1 + \eta_2^2)}{(1-\eta_3)^2} + \frac{2\eta_2^3 \eta_3}{(1-\eta_3)^3}
\]

(3.14)

In the case of a single component system this reduces significantly to the CS equation of state (Carnahan and Starling 1969; Carnahan and Starling 1972):

\[
\frac{\beta p}{c} = 1 + \eta_3 + \frac{\eta_3^2 + \eta_3^3}{(1-\eta_3)^3}
\]

(3.15)

3.2.3 Modified van der Waals model

The Bikerman and BMCSL models described above are common when accounting for steric effects in electrolyte systems, in particular the simpler Bikerman model, although there are limitations to each of them. The Bikerman model suffers from the fact that it is limited to a single particle size, which is a problem considering that electrolytes inherently contain two components and that it is unlikely they will be identically sized. This problem becomes more pronounced when considering electrochemical experiments and processes, many of which use a supporting electrolyte, so there may be at least four ions of different sizes in the system. Additionally, the Bikerman model, as seen in the previous chapter, requires the diameters of the ions to be defined as larger than their measured values in order to achieve agreement with experimental data.

The BMCSL model, which inherently allows for different ion sizes, is a significant improvement over the Bikerman model at low concentrations (Song et al. 1989; Bazant et al. 2009), but
as the concentration increases, such as happens in a double layer, it overestimates steric repulsion (Levin 2002) and its predictions can become incorrect (Antypov et al. 2005). Rather than being a fault with the model itself, the deviations result from a breakdown in the local density approximation in which each of these models is applied (Levin 2002). The Bikerman model, with its weaker steric repulsion, provides a better description at higher concentrations (Bazant et al. 2011).

In an attempt to bridge the benefits of each of these models, a modified van der Waals equation of state is used in this work. This equation does not yield analytical solutions, but this advantage of the Bikerman model is largely negated by the fact that, in general, modelling dynamic systems requires a numerical solution anyway. It does however allow for different ion sizes while yielding a similarly sized excess chemical potential as the Bikerman model, with the aim of maintaining that model’s effectiveness at higher concentrations.

The van der Waals (vdW) equation of state is not commonly used as it has a low maximum packing fraction of $0.25$. This is accounted for in the modified van der Waals (mvdW) equation by reducing the excluded volume around the ions, allowing an increase in the packing fraction at the maximum concentration.

The van der Waals partition function, $Z^P$ for a mixture of $M$ differently sized hard spheres in the absence of an attraction term can be shown to have the following form (Gorenstein et al. 1999)

$$Z^P = \prod_{l=1}^{M} \frac{1}{n_l! \Lambda^{3n_l}} \left[ V - \left( \sum_{p=1}^{M} n_p \tilde{v}_{pl} \right) \right]^{n_l}$$  \hspace{1cm} (3.16)

where $\tilde{v}_{pl}$ is related to the excluded volume around an ion. For mixtures of differently sized ions the excluded volume depends on which pair of ions is being considered, with the definition being shown in Fig. 3.2.

![Figure 3.2: Excluded volume around particles of different sizes.](image)

The excluded volume per particle, $v_{pl}$, between two particles is defined as (Gorenstein et al. 1999)

$$v_{pl} = \frac{2\pi}{3} (r_p + r_l)^3$$  \hspace{1cm} (3.17)
and this is related to $\tilde{v}_{pl}$ in the partition function by the equation (Gorenstein et al. 1999)

$$
\tilde{v}_{pl} = 2 \frac{\nu_{pp}\nu_{pl}}{\nu_{pp} + \nu_{ll}}
$$

(3.18)

While the $v$ is indifferent to a change in the order of the subscripts, $\tilde{v}$ is not. From the partition function, the free energy of this mvdW system is (Gorenstein et al. 1999)

$$
\beta F_{\text{mvdW}} = - \ln Z \\
\approx - \sum_{l=1}^{M} \left( -n_l \ln n_l + n_l + n_l \ln \left[ \frac{V - \sum_{p=1}^{M} n_p \tilde{v}_{pl}}{\Lambda^3} \right] \right) \\
= \sum_{l=1}^{M} n_l \left( \ln \left[ \frac{c_l \Lambda^3}{1 - \sum_{p=1}^{M} c_p \tilde{v}_{pl}} \right] - 1 \right) \\
= \sum_{l=1}^{M} n_l \left( \ln \left[ \frac{c_l \Lambda^3}{\varsigma_l} \right] - 1 \right)
$$

(3.19)

where $\varsigma$ is the unoccupied volume fraction in the system

$$
\varsigma_l = 1 - \sum_{p=1}^{M} c_p \tilde{v}_{pl}
$$

(3.20)

In this last equation, the summation term is also the total occupied volume fraction, $\eta$. Note that $\eta$ and $\varsigma$ are not the same for each particle type, since the value of $\tilde{v}_{pl}$ differs between them.

For a system containing a single species, the free energy reduces to the same form as the standard vdW model, so has the same maximum packing fraction of 0.25. In order to increase this value to that permitted by the Bikerman model, the radii of the ions used to calculate the excluded volumes are reduced by a factor of $\sqrt{\frac{2}{3\pi}} \approx 0.78$. This modifies the excluded volume calculation in Eq.(3.17) to the following expression

$$
v_{pl} = v_{lp} = (r_p + r_l)^3
$$

(3.21)

The result of this change is to increase the maximum packing fraction to a value of 0.52 (assuming equally sized ions), slightly above the fluid-solid phase transition and equal to the value for simple cubic packing. Physically, this reduction in the excluded volume corresponds to some degree of overlap of the ions. The actual ion sizes used in the model are the hydrated ion sizes (the radius used is the Stokes radius), so this overlap can be seen as the actual ions moving closer together with some of the water molecules being squeezed out of the space between them. Technically this picture would alter the electrostatic interactions between the ions and also alter the polarisability effects discussed in section 2.4.2, but these changes are neglected in order to simplify the polarisability model introduced in section 3.4.1. In essence, the aim is to describe enough of the fundamental physics of the system to capture behavioural trends which result from ion interactions without necessarily developing an exact picture of the structure of
the system.

The mvdW free energy, Eq. (3.19), separates into ideal and excess components, the excess component being

\[
\beta F_{\text{ex,mvdW}} = \sum_{l=1}^{M} n_l \ln \frac{1}{\zeta_l} \tag{3.22}
\]

From Eq. (3.2a) the excess chemical potential for this model is

\[
\beta \mu_{\text{ex,mvdW}}^j = \ln \left( \frac{1}{\zeta_j} \right) + \sum_l c_l \tilde{v}_{jl} \tag{3.23}
\]

and from (3.2b) the pressure is

\[
\beta p = \sum_l \frac{c_l}{\zeta_l} \tag{3.24}
\]

### 3.2.4 Comparison of the excess chemical potential terms

The excess chemical potentials of the three models mentioned above make different contributions to the overall system energy as a function of the potential, having differing effects on the structure in the process. Plotted in Fig. 3.3 below is the way each excess chemical potential term grows as a function of the occupied volume fraction, \( \eta \), for a system containing equally sized ions.

![Figure 3.3: Comparison of the excess chemical potentials for the Bikerman, BMCSL and mvdW models.](image)

In all cases \( \mu_{\text{ex}} \) diverges as the occupied volume fraction, \( \eta \) tends to unity, although in each case the rate at which this occurs differs. The BMCSL model shows the fastest growth, with the energy increasing significantly even at low concentrations. Of the other two terms, the rate of increase in the excess energy is much smaller at lower occupied volume fractions, with a rapid increase in the energy as \( \eta \to 1 \).
The larger the increase in $\mu^{ex}$ with the occupied volume fraction, the more energy is required to increase the concentration beyond that point. Hence the surface concentrations in the BMCSL model at a particular electrode potential will be lower than those in the mvdW model, which will in turn be lower than those in the Bikerman model. A lower surface concentration means that the electrode potential is shielded less well, as there is less ionic charge to shield it, so the electric field will be smaller in the mvdW model than the Bikerman model and smaller than both in the BMCSL model. This should translate to a smaller surface charge density and a wider double layer. The wider double layer arises because, regardless of the model used, the same electrostatic potential drop over the double layer must occur. If the potential is shielded less well then the electric field is smaller and, since this is proportional to the gradient of the potential, the physical distance over which the potential reduces to the value in the bulk must be longer. The smaller electric field at a given potential also means that the surface charge density is smaller, meaning that the electrical properties of the electrode change, meaning that the differential capacitance is largest in the Bikerman model and smallest in the BMCSL model (as can be seen in Bazant et al. (2009)) and that the mvdW model should sit between them, as will be shown in section 5.1.1.

3.3 Non-uniform systems and the density functional

The free energy expressions outlined in the previous section are for uniform systems, but the presence of an external field causes an asymmetry to develop in the fluid. In the case of the system represented by this model, the electric field created by charge on the electrode results in one set of ions being attracted to the surface and the other set being repelled from it, removing the uniformity. The field interaction itself will be dealt with in the following section, but this section outlines the way in which the uniform system particle interaction free energy relates to the free energy of a non-uniform system. Specifically, the local density approximation (LDA) of density functional theory is used.

Shifting the picture away from uniform systems means that consideration must be given to what the equilibrium state of a non-uniform system is and what it means to be away from that equilibrium. The model system is open, meaning that mass can be transferred into or out of the system, so the corresponding thermodynamic potential is the grand potential, $\Omega$. It is defined by the volume, temperature and chemical potential of the species in the system and has two properties which enable non-uniform systems to be considered. The first is that it can be shown to be a unique functional of the one-body densities of all of the species in the system, i.e. $\Omega = \Omega[\{c_l(r)\}]$ (Hansen and McDonald 2006). Note that because the concentration is no longer constant throughout the system, $\Omega$ is a functional of the concentration, which is itself a function of the position. The second property is that when the densities have their equilibrium values the grand potential has its minimum value, so if $c^0_l$ is the equilibrium concentration of species $l$, $\Omega[\{c^0_l\}] = \Omega$ and the inequality $\Omega[\{c_l \neq c^0_l\}] > \Omega$ holds for non-equilibrium states (Hansen and McDonald 2006). These properties allow the following variational principle to be derived.
which defines the equilibrium state:

\[
\frac{\delta \Omega[\{c_l\}]}{\delta c_j} \bigg|_{c_j=c_j^0} = 0 \tag{3.25}
\]

where the \(\delta /\delta c_j\) represents the functional differential with respect to the concentration of the specific species \(j\) in the system. As already stated, the Helmholtz free energy is the easiest of the thermodynamic potentials to work with for non-uniform systems, and it related to the grand potential through the equation (Hansen and McDonald 2006)

\[
\Omega = F - \sum_l \mu_l \int dr \, n_l(r) \tag{3.26}
\]

Combining the previous two equations yields

\[
\frac{\delta \Omega[\{c_l\}]}{\delta c_j} \bigg|_{c_j=c_j^0} = \frac{\delta F[\{c_l\}]}{\delta c_j} \bigg|_{c_j=c_j^0} - V \mu_j = 0 \tag{3.27}
\]

from which it can be shown that the equilibrium chemical potential is

\[
\mu_j = \frac{1}{V} \left( \frac{\delta F[\{c_l\}]}{\delta c_j} \right)_{V,T,\{c_l \neq j\}} \tag{3.28}
\]

which mirrors the definition of the chemical potential of a uniform system as given by Eq. (3.2a).

At equilibrium, the chemical potential must be constant in space, since a gradient in the chemical potential would drive a flux, meaning the system would not be in equilibrium. Once an expression for \(\mu_j\) has been derived, methods similar to those described in section 2.1 for the GC model can be applied to derive the state of a non-uniform system. In order to do this, however, there needs to be a link between the \(F[\{c_l\}]\) of a non-uniform system and the \(F\) of the uniform system.

The approach to deriving an expression for \(F[\{c_l\}]\) taken here is to use the local density approximation (LDA). The modelling domain is divided up into a series of non-interacting boxes of volume \(V_b\). The contents of each box may differ, but within each box the contents are assumed to be uniform. The free energy per unit volume of each box \(f_v^b(\{c_l\})\) can be calculated using \(F\), the free energy of a uniform system which is in the same state as that box

\[
f_v^b(\{c_l\}) = \frac{F_b}{V_b} \tag{3.29}
\]

The total free energy of the system is the sum of the free energies of all the boxes. In the limit that the size of the box tends to zero while holding the state of the box constant, \(f_v\) becomes the local free energy density and the sum over the boxes becomes an integral over the volume of the system:

\[
\beta F[\{c_l\}] = \int dr \, \beta f^v(\{c_l\}) \tag{3.30}
\]
where \( f^v \) is a continuous function of all local ion concentrations \( c_l \). The value of \( f^v \) at a particular point is the same as that which a uniform system would have if it had the same composition as the point in question.

Since the uniform free energy can be separated into ideal and excess components, so can \( f^v \):

\[
\beta F[c_l] = \int d\mathbf{r} \beta f^{v,\text{id}}(\{c_l(\mathbf{r})\}) + \int d\mathbf{r} \beta f^{v,\text{ex}}(\{c_l(\mathbf{r})\})
\] (3.31)

Eq. (3.6) defines the ideal component of the free energy per unit volume for each species, and \( f^{v,\text{id}} \) is the sum over each of these ideal contributions, so \( F \) is

\[
\beta F[c_l] = \int d\mathbf{r} \sum_l n_l (\ln[c_l(\mathbf{r})]^{3l} - 1) + \int d\mathbf{r} \beta f^{v,\text{ex}}(\{c_l(\mathbf{r})\})
\] (3.32)

The ideal term is exact whether the LDA is used or not, as it already assumes no particle interactions. The deviation of the LDA from reality is therefore a limitation in the excess term. The expression for \( f^{v,\text{ex}} \) is defined by the particular method for used to account for the particle interactions. For the excluded volume models outlined in the previous section, \( f^{v,\text{ex}} \) is equal to \( 1/V \) multiplied by Eqs. (3.9) (Bikerman model), (3.12) (BMSCL model) or (3.19) (mvdW model).

Use of the LDA results in models which only depend on the local state of the system. In reality, the initial assumption that the boxes the domain was split into do not interact is false, since the environment around a box will affect its free energy. However, accounting for this leads to non-local theories for \( F \) in which the free energy at a point depends on the state of the system at that point as well as points nearby. For the purposes of this work, these non-local effects were neglected in order to simplify as much as possible the later dynamic equations.

While the details of the equation for the free energy differ between uniform and non-uniform systems, the general connection between the free energy and the thermodynamic properties remains the same as stated in Eqs. (3.2a) and (3.2b). The only difference is a change to a functional differential in each case, so the equations now take the form

\[
\mu_j = \frac{1}{V} \left( \frac{\delta F[\{c_l\}]}{\delta c_j} \right)_{V,T,(c_{l\neq j})}
\] (3.33a)

\[
p = - \left( \frac{\delta F[\{c_l\}]}{\delta V} \right)_{\{c_l\},T}
\] (3.33b)

### 3.4 The effect of the electric field

The system consists of a large number of charged particles, be they the positive or negative ions in the electrolyte or the electrons at the electrode surface. Each of these particles generates its own electric field through which it interacts with every other particle, resulting in an exceedingly large number of interactions should they be modelled individually. Rather than attempt to do this, this model uses the common mean field approximation for the electric field, in which each
charged particle interacts with the mean field generated by all the other particles, reducing a complex many body problem to a much simpler one-body problem in which the field interaction free energy is (Kilic et al. 2007a; Borukhov et al. 1997)

\[ F^\text{cel} = \int dr \rho(r)\phi(r) - \frac{1}{8\pi} \int dr \epsilon(r)\nabla\phi(r) \cdot \nabla\phi(r) \]  

(3.34)

where \(\epsilon(r)\) is the local dielectric constant of the solution, the form of which will be discussed in section 3.4.1, and \(\rho(r)\) is the charge density, related to the ion concentrations and electrode surface charge density \(\sigma\) by the relationship

\[ \rho(r) = \sum_l z_l e_0 c_l(r) + \sigma(r) \]  

(3.35)

Through the use of Eq. (3.3), the total free energy of the mvdW system once the electric field is included is

\[ F[c_l],\phi = \frac{1}{\beta} \int dr \sum_l \left( \ln[c_l(r)\Lambda_l^3] - 1 \right) + \int dr f^{v,ex}(\{c_l\}) + \int dr \left[ \sum_l z_l e_0 c_l(r) + \sigma(r) \right] \phi(r) - \frac{1}{8\pi} \int dr \epsilon(r)\nabla\phi(r) \cdot \nabla\phi(r) \]  

(3.36)

The total free energy is now a functional of the potential and the set of concentrations, all of which are functions of the position. The electric potential dependent terms are not independent of the concentration, so the functional derivative in Eq. (3.33a) will yield additional terms dependent on the potential. The addition of the electrostatic potential-dependence of the free energy means that \(\mu\), which if only the ideal and excess components of the free energy are accounted for is the chemical potential, now becomes the more general electrochemical potential.

In addition to the variational principle which leads to Eqs. (3.33a) and (3.33b), another variational principle applies to the free energy with respect to the electric potential. Under the assumption that the electric field is always arranged such that it minimises its contribution to the free energy, the following functional differential equation holds (Jackson 1962; Allen et al. 2001)

\[ \left( \frac{\delta F}{\delta \phi} \right)_{c_l,T,V} = 0 \]  

(3.37)

Using this expression it is possible to derive a modified form of the Poisson equation which self-consistently fits a given free energy functional.

### 3.4.1 Accounting for the ion polarisability

The hydrated ions in the electrolyte have a different polarisability to the water molecules, so when an electric field is applied to the solution, a different induced charge density results. It can be shown that this effect can be accounted for by allowing the permittivity to vary depending on the concentration of the ions. The method described below assumes that the electric potential
is described by the Poisson equation, which will subsequently be shown to be the case when the expressions for the system potentials are derived (see section 3.5.1).

The hydrated ions have a different dipole moment to the water molecules, which is why the induced charge differs from the pure water value at the same electric field strength. For electric field strengths smaller than $\sim 0.25 \text{ V nm}^{-1}$, the hydrated ion dipole moment density, $m^D_i$, varies linearly with the electric field (Gavryushov and Linse 2003), so we may write

$$m^D_i = -\chi_i \nabla \phi,$$  \hspace{1cm} (3.38)

where $\chi_i$ is the susceptibility of the ion, which is a function of the dipole (hydrated ion) concentration. Assuming that the susceptibility is directly proportional to the concentration, a valid assumption for low to moderate concentrations (Hasted et al. 1948), the function can be written

$$\chi_i = \alpha_i c_i,$$  \hspace{1cm} (3.39)

where $\alpha_i$ is the excess polarisability of ion $l$, which can be measured experimentally and for which a selection of values is shown in Table 2.1. Finally, the relationship between the dipole moment density and the induced charge density which results from a distribution of ions of type $l$, $\rho^{\text{ind}}_l$, is

$$\rho^{\text{ind}}_l(r) = -\nabla \cdot m^D_i$$  \hspace{1cm} (3.40)

In an electrolyte, the different hydrated ions may have different dipole moments, so their response will differ. However, the total induced charge density is the sum of the individual charge densities. Using this in combination with the previous three equations, the total induced charge density in an ionic mixture is

$$\rho^{\text{ind}}(r) = -\sum_l \nabla \cdot m^D_i = \sum_l \nabla \cdot (\alpha_i c_i \nabla \phi)$$  \hspace{1cm} (3.41)

where the sum is over all species of ion.

The Poisson equation relates the gradient in the electric field to the charge density at a point:

$$-\frac{1}{4\pi} \nabla \cdot [\epsilon_w \nabla \phi] = \rho$$  \hspace{1cm} (3.42)

where $\epsilon_w$ is the permittivity of the bulk solvent. The charge density is comprised of the “bare” charge density (which is that due simply to the presence of the ions calculated as the sum over the product of the ion charges and their densities) and the induced charge which is that stated in
Eq. (3.41), so by explicitly separating the term we can write

\[-\frac{1}{4\pi} \nabla \cdot [\varepsilon \nabla \phi] = \rho^{\text{bare}} + \rho^{\text{ind}} = \sum_l z_l e_0 c_l + \sum_l \nabla \cdot (\alpha_l c_l \nabla \phi) \]

(3.43)

This can be rearranged to the following equation

\[-\frac{1}{4\pi} \nabla \cdot [(\varepsilon_w + 4\pi \sum_l \alpha_l c_l) \nabla \phi] = \sum_l z_l e_0 c_l \]

(3.44)

and comparison of this with the original Poisson equation shows that modelling the excess ion polarisability can be treated as an effect which modifies the permittivity of the solvent. The effective local, concentration-dependent, permittivity is

\[\varepsilon(r) = \varepsilon_w + 4\pi \sum_l \alpha_l c_l(r) \]

(3.45)

This equation can now be substituted into Eq. (3.36) for the free energy of the system

### 3.5 The system potentials

The Helmholtz free energy functional stated in eq (3.36) accounts for the ion volume while the concentration-dependent permittivity given by Eq. (3.45) accounts for the ion excess polarisability. In this section, the variational principle is applied according to Eqs. (3.33a) and (3.37) to derive equations for the electrochemical and electrostatic potentials of the system.

In general, an infinitesimal change in the free energy is:

\[\delta F[{\{c_l(r)\}, \phi(r)}}] = \frac{1}{\beta} \int d\mathbf{r} \left[ \sum_l \delta c_l(r)(\ln[c_l(r)\Lambda_3^3] - 1) \right] + \int d\mathbf{r} \delta f^{v,ex}(\{c_l(r)\}) \]

\[+ \int d\mathbf{r} \delta \left[ \left( \sum_l z_l e_0 c_l(r) + \sigma(r) \right) \phi(r) \right] \]

\[- \frac{1}{8\pi} \int d\mathbf{r} \delta [\varepsilon(r) \nabla \phi(r) \cdot \nabla \phi(r)] \]

\[= \frac{1}{\beta} \int d\mathbf{r} \sum_l \delta c_l(r) \ln[c_l(r)\Lambda_3^3] + \int d\mathbf{r} \delta f^{v,ex}(\{c_l(r)\}) \]

\[+ \int d\mathbf{r} \sum_l z_l e_0 \phi(r) \delta c_l(r) + \int d\mathbf{r} \left[ \sum_l z_l e c_l(r) + \sigma(r) \right] \delta \phi(r) \]

\[- \frac{1}{8\pi} \int d\mathbf{r} |\nabla \phi(r)|^2 \delta \varepsilon(r) - \frac{1}{4\pi} \int d\mathbf{r} \varepsilon(r) \nabla \phi(r) \nabla \phi(r) \]

(3.46)

To resolve the \(\delta \nabla \phi\) term in the final integral, Gauss’ Theorem is applied. For a general
quantity \( B(\mathbf{r}) \), this can be summarised as
\[
\int d\mathbf{r} \nabla \cdot B(\mathbf{r}) = \oint dA B(\mathbf{r}) \cdot \mathbf{n}
\] (3.47)

where \( \mathbf{n} \) is the normal vector to the surface and \( A \) is the surface area. If \( B(\mathbf{r}) \) is defined as \( B(\mathbf{r}) = \epsilon(\mathbf{r}) \nabla \phi(\mathbf{r}) \delta \phi(\mathbf{r}) \) such that the divergence of \( B(\mathbf{r}) \) is
\[
\nabla \cdot B(\mathbf{r}) = \nabla \cdot [\epsilon(\mathbf{r}) \nabla \phi(\mathbf{r})] \delta \phi(\mathbf{r}) + \epsilon(\mathbf{r}) \nabla \phi(\mathbf{r}) \delta \nabla \phi(\mathbf{r})
\] (3.48)

then the application of Gauss’ theorem means the following statement is true:
\[
\int d\mathbf{r} \nabla \phi(\mathbf{r}) \epsilon(\mathbf{r}) \delta \nabla \phi(\mathbf{r}) = - \int d\mathbf{r} \nabla \cdot [\epsilon(\mathbf{r}) \nabla \phi(\mathbf{r})] \delta \phi(\mathbf{r}) + \oint dA \epsilon(\mathbf{r}) \nabla \phi(\mathbf{r}) \delta \phi \cdot \mathbf{n}
\] (3.49)

Inserting this back into equation (3.46) gives the final form of the change in the free energy functional:
\[
\delta F[\{c_i(\mathbf{r})\}, \phi(\mathbf{r})] = \frac{1}{\beta} \int d\mathbf{r} \sum_l \delta c_l(\mathbf{r}) \ln [c_l(\mathbf{r}) \Lambda_i^3] + \int d\mathbf{r} \delta f^{v,ex}(\{c_i(\mathbf{r})\})
\]
\[
+ \int d\mathbf{r} \sum_l z_l \epsilon(\mathbf{r}) \delta c_l(\mathbf{r}) + \int d\mathbf{r} \left[ \sum_l z_l \epsilon_0 c_l(\mathbf{r}) + \sigma(\mathbf{r}) \right] \delta \phi(\mathbf{r})
\]
\[
- \frac{1}{8\pi} \int d\mathbf{r} |\nabla \phi(\mathbf{r})|^2 \delta \epsilon(\mathbf{r}) + \frac{1}{4\pi} \int d\mathbf{r} \nabla \cdot [\epsilon(\mathbf{r}) \nabla \phi(\mathbf{r})] \delta \phi(\mathbf{r})
\]
\[
- \frac{1}{4\pi} \oint dA \epsilon(\mathbf{r}) \nabla \phi(\mathbf{r}) \delta \phi \cdot \mathbf{n}
\] (3.50)

The \( \delta \epsilon(\mathbf{r}) \) term is simply a function of the species concentrations which can be shown from Eq. (3.45) to be
\[
\delta \epsilon(\mathbf{r}) = 4\pi \sum_l \alpha_l \delta c_l(\mathbf{r})
\] (3.51)

and so the change in the free energy functional is
\[
\delta F[\{c_i(\mathbf{r})\}, \phi(\mathbf{r})] = \frac{1}{\beta} \int d\mathbf{r} \sum_l \delta c_l(\mathbf{r}) \ln [c_l(\mathbf{r}) \Lambda_i^3] + \int d\mathbf{r} \delta f^{v,ex}(\{c_i(\mathbf{r})\})
\]
\[
+ \int d\mathbf{r} \sum_l z_l \epsilon(\mathbf{r}) \delta c_l(\mathbf{r}) + \int d\mathbf{r} \left[ \sum_l z_l \epsilon_0 c_l(\mathbf{r}) + \sigma(\mathbf{r}) \right] \delta \phi(\mathbf{r})
\]
\[
- \frac{1}{2} \int d\mathbf{r} |\nabla \phi(\mathbf{r})|^2 \sum_l \alpha_l \delta c_l(\mathbf{r}) + \frac{1}{4\pi} \int d\mathbf{r} \nabla \cdot [\epsilon(\mathbf{r}) \nabla \phi(\mathbf{r})] \delta \phi(\mathbf{r})
\]
\[
- \frac{1}{2} \int d\mathbf{r} \nabla \cdot [\epsilon(\mathbf{r}) \nabla \phi(\mathbf{r})] \delta \phi \cdot \mathbf{n}
\] (3.52)

Up to this point the equations are valid for any geometry, but the system being modelled is assumed to be an electrolyte adjacent to a smooth, flat, planar electrode. The dimensions of the
electrode are assumed to be sufficiently large that edge effects may be ignored, in which case
the electric field is perpendicular to the surface. As a result, deviations from a uniform structure
in the electrolyte can only occur in the perpendicular direction and the concentrations must be
constant in any plane parallel to the surface. Likewise, the free energy can only vary along
the perpendicular direction, in which case the r-dependence of the concentration and potential
are reduced to a z-dependence, where z is the perpendicular distance from the electrode. The
change in the free energy reduces to the following expression
\[
\delta F[\{c_l(z)\}, \phi(z)] = \frac{1}{\beta} \int_0^L dz \left[ \sum_l z_l e_0 c_l(z) \ln[c_l(z) \Lambda_l^3] + \int_0^L dz \delta f^{v,ex}(\{c_l(z)\}) \right] + \int_0^L dz \sum_l z_l e_0 c_l(z) \delta \phi(z) + \frac{1}{2} \int_0^L dz |\phi'(z)|^2 \sum_l \alpha_l \delta c_l(z) \\
+ \int_0^L dz \left[ \sum_l z_l e_0 c_l(z) + \sigma(z) \right] \delta \phi(z) + \frac{1}{4\pi} \int_0^L dz (\epsilon(z) \phi'(z))' \delta \phi(z) \\
- \frac{1}{4\pi} [\epsilon(z) \phi'(z) \cdot \mathbf{n}]_0^L \delta \phi(z)
\] (3.53)
where 0 and L are the boundaries of the domain.

From this expression, equations for the two system potentials (electrostatic and electrochemical) can be calculated.

### 3.5.1 Electrostatic potential

The expression for the electrostatic potential is found using Eqs. (3.37) and (3.53). As the functional derivative of the free energy with respect to the electric potential is taken while holding the densities constant, all \( \delta c \)-dependent terms in Eq. (3.53) are zero, leaving the following terms relating to the electrostatic component of the free energy:

\[
\delta F[\{c_l\}, \phi] = \int dz \left[ \sum_l z_l e_0 c_l(z) + \sigma(z) \right] \delta \phi(z) + \frac{1}{4\pi} \int dz [\epsilon(z) \phi'(z)]' \delta \phi(z) \\
- \frac{1}{4\pi} [\epsilon(z) \phi'(z) \cdot \mathbf{n}]_0^L \delta \phi(z)
\] (3.54)

The functional derivative can now be taken in a straightforward manner, and equating it to zero yields the following equation:

\[
\sum_l z_l e_0 c_l(z) + \frac{1}{4\pi} [\epsilon(z) \phi'(z)]' + \sigma - \frac{1}{4\pi} [\epsilon(z) \phi'(z) \cdot \mathbf{n}]_0^L = 0
\] (3.55)

Since the system only varies in one dimension, and the surface charge is all found at the
boundaries, which are infinitesimally narrow, the total surface charge density can be written
as \( \sigma = \sigma_0 \delta(z - 0) + \sigma_L \delta(z - L) \), where the boundaries of the domain are located at \( z = 0 \) and \( z = L \). By definition, the third and fourth terms in Eq. (3.55) are zero for \( z \neq 0 \) and \( z \neq L \), so the first and second relationship describe the relationship between the charge density and electric
potential in the electrolyte:

\[-\frac{1}{4\pi} [\epsilon(z)\phi'(z)]' = \sum_l z_l e_0 c_l(z)\] (3.56)

i.e. the Poisson equation is recovered, albeit with a position-dependent permittivity, \(\epsilon(z)\), owing to its dependence on the ion concentrations.

Now, since the first and second terms in Eq. (3.55) sum to zero, the same must be true of the third and fourth terms for the overall equation to be true. Furthermore, the third and fourth terms each contain a component which relates to one or other of the boundaries. Since the surface charge at one boundary can only be a function of the electric field at that boundary, a further separation of the terms is possible to give equations relating the surface charge density to the electric field at each boundary:

\[
\sigma_0 = -\frac{1}{4\pi} \epsilon(0)\phi'(0) \quad (3.57a)
\]

\[
\sigma_L = \frac{1}{4\pi} \epsilon(L)\phi'(L) \quad (3.57b)
\]

where the normal vector has been defined to point from the surface in towards the domain and is positive as \(z\) increases.

### 3.5.2 Electrochemical potential

The electrochemical potential, \(\mu_j\), of a specific species \(j\) in the electrolyte is calculated from the functional derivative of \(F\) with respect to that species’ density, as stated in equation (3.33a), although an additional constraint of holding the electric potential constant is now required. From equation (3.53) it can be seen that the \(\delta\phi\)-dependent terms are zero and the change in the free energy in response to a change in the concentration is

\[
\delta F[c_l,\phi] = \frac{1}{\beta} \int dz \sum_l \delta c_l(z) \ln[c_l(z)\Lambda_3^j] + \int dr \delta f^{v,ex}(\{c_l(z)\})
\]

\[+ \int dz \sum_l z_l e_0 \phi(z) \delta c_l(z) - \frac{1}{2} \int dz |\phi'(z)|^2 \sum_l \alpha_l \delta c_l(z) \] (3.58)

From this, the electrochemical potential of \(j\) is calculated as the functional derivative of \(F\) with respect to the density of species \(j\) while holding the densities of all other species constant as per equation (3.33a). Since \(\delta c_{l\neq j} = 0\) and the functional differential of the term dependent on \(f^{v,ex}\) is equal to the excess chemical potential of species \(j\), the result is

\[
\beta \mu_j(z) = \ln[c_j(z)\Lambda_3^j] + \beta \mu_j^{ex}(z) + z_j e_0 \beta \phi(z) - \frac{\beta}{2} \alpha_j |\phi'(z)|^2 \] (3.59)

In keeping with the way in which the free energy, and therefore the chemical potential, can be written as contributions from the ideal and excess components according to Eq. (3.4) or (3.5),
the above can be written as contributions from ideal, excess and an additional electrostatic term:

\[ \mu_j = \mu_{ij}^d + \mu_{ij}^e + \mu_{ij}^e \] (3.60)

where \( \mu_{ij}^d \) is defined in Eq. (3.7), \( \mu_{ij}^e \) is defined by Eqs. (3.10), (3.13) or (3.23), depending on the excluded volume model used, and \( \mu_{ij}^e \) is

\[ \beta \mu_{ij}^e = z_j e_0 \beta \phi(z) - \frac{\beta}{2} \alpha_j |\phi'(z)|^2 \] (3.61)

### 3.6 Summary of equations for a non-uniform system

Prior to describing the means for modelling the dynamics of the system, the relevant equations for describing a non-uniform system are collected below for ease of reference.

**Electrochemical potential:**

\[ \beta \mu_j(z) = \ln[c_j(z) \Lambda_j^3] + \beta \mu_{ij}^e(z) + z_j e_0 \beta \phi(z) - \frac{\beta}{2} \alpha_j |\phi'(z)|^2 \] (3.62)

**Modified Poisson equation:**

\[ -\frac{1}{4\pi} \left[ \epsilon(z) \phi(z)' \right]' = \sum_l z_l e_0 c_l(z) \] (3.63)

**Permittivity:**

\[ \epsilon(z) = \epsilon_w + 4\pi \sum_l \alpha_l c_l(z) \] (3.64)

**Electrostatic potential boundary equations:**

\[ \sigma_0 = -\frac{1}{4\pi} \epsilon(0) \phi'(0) \] (3.65a)

\[ \sigma_L = \frac{1}{4\pi} \epsilon(L) \phi'(L) \] (3.65b)

These equations represent a mean-field, local density approximation (MF-LDA) model from which the equilibrium structure of an electrolyte near to an electrode can be calculated. The volume of the ions is accounted for using a van der Waals type model which allows for ions of different sizes but which does not include an attraction term. The MF-LDA means that ion correlations are not accounted for, so it is not expected that such effects as charge layering will be observed but, to a simple approximation, the results should be comparable with reality.

The way in which the polarisability is handled assumes that the hydrated ions behave as point dipoles and that the induced charge density varies linearly with both the ion concentration and the electric field. Again, these simplifications are chosen partly because they reflect the true behaviour over a certain range of situations and partly because moving beyond this can lead to significant complications to the structural model of the electrolyte, which is undesirable.
because these would also significantly complicate the dynamic model. As regards the dynamics, the dipoles are assumed to respond instantly to changes in the electric field, meaning that the permittivity is independent of the frequency of any time-dependent electric field.

At this point, the equations could be solved simultaneously for the concentrations of each of the ionic species in the electrolyte as well as the electrostatic potential. This is the same principle which is followed when solving for the system dynamics except that the concentration and potential functions are also allowed to evolve in time. The result is that the above equations are solved simultaneously at each time step and any variation in the resulting electrochemical potential drives a flux of the ions.

3.7 The system dynamics

Expressions for the electrochemical and electrostatic potentials have so far been derived for non-uniform systems. These systems may or may not be in equilibrium and if they are not then the system will rearrange itself until it reaches equilibrium. This rearrangement is observed as ionic fluxes. As discussed earlier in this chapter, the system is in equilibrium when the grand potential is minimised with respect to the density. The extension of this is that if it is not minimised then there is a gradient in the grand potential, and hence in the Helmholtz free energy of the system, and that this provides the impetus for the fluxes.

Within the framework of DFT it has been proved that the one-body density (and hence the free energy) is a unique function of a time-dependent external field (Chan and Finken 2005) and that the dynamics of species $j$ in a system can be approximated by the following relationship (Archer 2006)

$$\frac{\partial^2 c_j(r, t)}{\partial t^2} + \nu_j \frac{\partial c_j(r, t)}{\partial t} = \frac{1}{m_j} \nabla \cdot \left[ c_j(r, t) \nabla \frac{\delta F[\{c_l(r, t)\}, \phi(r, t)]}{\delta c_j(r, t)} \right]$$

(3.66)

where $\nu^c_j = k_B T / m_j D_j$ is the collision frequency, $m_j$ is the mass of the particle in question and $D_j$ is its self-diffusion coefficient. The equation assumes that the two particle correlations in the non-equilibrium case are identical to those in the equilibrium fluid (Archer 2006). Furthermore, if the collision frequency is large, as is the case in a liquid, then the second term on the left dominates and the equation may be rewritten as

$$\frac{\partial c_j(r, t)}{\partial t} = \beta D_j \nabla \cdot \left[ c_j(r, t) \nabla \frac{\delta F[\{c_l(r, t)\}, \phi(r, t)]}{\delta c_j(r, t)} \right]$$

(3.67)

The functional differential term on the right is equal to the electrochemical potential $\mu_j$ of species $j$, so if the pre-factor on the right is moved inside the bracket and a comparison made with the convection-independent continuity equation, which is

$$\frac{\partial c_j(r, t)}{\partial t} = -\nabla \cdot J_j(r, t),$$

(3.68)
it is possible to see that the flux, $J_j$, of the species can be approximated by the function

$$J_j(r, t) = -\beta D_j c_j(r, t) \nabla \mu(r, t)$$

(3.69)

As before, all non-uniformity in the system occurs in the perpendicular direction to the surface, so fluxes may only occur in that direction. Furthermore, it is assumed that the moving ions do not induce magnetic fields, which would alter the dynamics of the system. The resulting equations for continuity and flux are thus:

$$\frac{\partial c_j(z, t)}{\partial t} = -J'_j(z, t)$$

(3.70a)

$$J_j(z, t) = -\beta D_j c_j(z, t) \mu'(z, t)$$

(3.70b)

### 3.7.1 The modified Nernst-Planck equation

The continuity equation above states that the rate at which the concentration at position $z$ changes with time is equal to the negative of the flux gradient at the same point. For the following three chapters, no reactions are allowed at the electrode surface, which is assumed to be perfectly blocking in nature. The additional theory concerning the reaction kinetics will be discussed in section 7.1.

Inserting the expression for the electrochemical potential into Eq. (3.70b) and substituting the result into Eq. (3.70a) yields the following result:

$$\frac{\partial c_j}{\partial t} = D_j \frac{\partial}{\partial z} \left[ c_j \alpha_j' \right] + \beta D_j \frac{\partial}{\partial z} c_j \frac{\partial \mu^\text{ex}}{\partial z}$$

$$+ D_j \frac{\partial}{\partial z} c_j \frac{\partial}{\partial z} z_j e_0 \beta \phi - \beta D_j \frac{\partial}{\partial z} c_j \frac{\partial}{\partial z} \alpha_j' |\phi'|^2$$

$$= D_j \alpha_j' + \beta D_j [c_j \mu^\text{ex}']$$

$$+ z_j e D_j \beta (c_j \phi') - \frac{\beta D_j \alpha_j}{2} \left[ c_j (|\phi'|^2) ' \right] '$$

(3.71)

In the absence of steric and polarisability effects, i.e. $\alpha = 0$, and $\mu^\text{ex} = 0$, the above-stated continuity equation reduces to

$$\frac{\partial c_j}{\partial t} = D_j c_j'' + z_j e_0 \beta D_j [c_j \phi']',$$

(3.72)

which is simply a statement of the Nernst-Planck equation for systems with no convective flow and in which the diffusion coefficient is a constant throughout the domain. Equation (3.71) therefore represents a modified Nernst-Planck (mNP) equation in which steric and polarisability effects are accounted for. With the chemical potentials of each of the species being dependent on the concentrations of each of the other species, the dynamics of a particular species therefore also depends on what is happening with each of the other species.

The mNP equations cannot in general be solved analytically. As with solving for the equilibrium state, there are $M + 1$ unknown properties (the $M$ species concentrations and the electro-
static potential) which can be solved for using the coupled mNP and Poisson equations, which are all dependent on the same variables. The modified Nernst-Planck equation represented by Eq. (3.71) combined with the modified Poisson equation is a type of modified PNP (mPNP) model. Note that the manner in which these equations have been derived implies that any time-variance of the electric field has no effect on the system. Instead, it is assumed that it is instantaneously defined by the boundary conditions and the arrangement of the charge in the system according to the Poisson equation.

3.8 Re-scaling the equations and deriving the dimensionless forms

So far all of the equations describing the system have been stated in dimensional form. Standard SI units have been used in most cases, except for the potential-dependent terms, for which Gaussian units have been used to define \( 4\pi\varepsilon_0 = 1 \), and the concentration, which is the number concentration rather than the molar concentration. In principle there is no problem with this, but there is an extremely wide range in the scale of typical numbers using these units. For example a typical concentration might be 0.01 M (=6.022 \times 10^{18} \text{ m}^{-3}) while the size of the double layer (the screening length) is of the order of 10^{-8} m. For this reason it is convenient to re-scale everything such that the values are more manageable. This will also be relevant when it comes to solving the equations because the finite differencing scheme used becomes increasingly inaccurate as the gradients of the functions become steeper and in SI units the gradients can be numerically very large.

The first scaling factor used it the Bjerrum length, which is the length at which the interaction energy between two charged particles is equal to their thermal energy and is defined as

\[
l_B = \frac{\beta e^2}{4\pi\varepsilon_0\varepsilon_w}
\]  

(3.73)

Unless otherwise stated, the temperature used in this work is 298 K and the relative permittivity of water is taken to be 78 (Malmberg and Maryott 1956). The Bjerrum length therefore has a value of about 7 Å. Using this, the length is re-scaled as

\[
z \rightarrow \frac{z}{l_B} = \tilde{z}
\]  

(3.74)

where \( \tilde{z} \) is the dimensionless length. From this, the dimensionless number density, excluded volume and polarisability volume are related to the dimensional equivalents as

\[
c(\text{m}^{-3}) \rightarrow \tilde{c} = \tilde{c} \\
\tilde{v}(\text{m}^3) \rightarrow \tilde{v} = \tilde{v} \\
\tilde{\alpha}(\text{m}^3) \rightarrow \tilde{\alpha} = \tilde{\alpha}
\]  

(3.75)

Note that polarisability volume in Table 2.1 is listed as the volume per unit mole, so a further factor of \( 1/N_A \), where \( N_A \) is the Avagadro number, is required to convert those values to the
The unit of energy is defined by the Boltzmann constant and the system temperature as \( k_B T \), i.e. \( \frac{1}{\beta} \). As a result, the conversion of the potentials to dimensionless units is achieved using the following relationships:

\[ \mu \rightarrow \beta \mu = \bar{\mu} \quad \phi \rightarrow e_0 \beta \phi = \bar{\phi} \] (3.76)

The substitution of the dimensionless forms of the variables into the expression for the chemical potential, Eq. (3.59), shows that these are sufficient to render the whole equation dimensionless:

\[ \frac{\beta}{\bar{\beta}} \bar{\mu}_j = \ln \left[ \frac{\bar{c}_j \bar{l}_B^3 \Lambda_j^3}{l_B^3} \right] + \frac{\beta}{\bar{\beta}} \bar{\mu}_j^{\text{ex}} + \frac{z_j e_0 \beta}{e_0 \beta} \bar{\phi} - \frac{\beta}{2} \frac{\bar{l}_B^3}{l_B^3} \bar{\alpha}_j \left[ \frac{1}{e_0 l_B} \frac{d\bar{\phi}}{d\bar{z}} \right]^2 \]

\[ \bar{\mu}_j = \ln \left[ \bar{c}_j \Lambda_j^3 \right] + \bar{\mu}_j^{\text{ex}} + z_j \bar{\phi} - \frac{1}{2e_w} \bar{\alpha}_j |\bar{\phi}'|^2 \] (3.77)

where the dimensionless thermal wavelength, \( \bar{\Lambda}_j = \Lambda_j / l_B \), has been used and in the final term the Bjerrum length has been used again to remove as many parameters as possible.

Similarly for the Poisson equation, these dimensionless substitutions are sufficient to remove the dimensions from the equation:

\[ \sum_l z_l e_0 \frac{\bar{c}_l}{l_B^3} = -\frac{1}{4\pi} \int \frac{d}{dz} \left[ \frac{1}{e_0 \beta l_B} \epsilon \frac{d\bar{\phi}}{d\bar{z}} \right] \]

\[ \sum_l z_l \bar{c}_l = -\frac{1}{4\pi \epsilon_w} \left[ \epsilon \bar{\phi}' \right]' \] (3.78)

and the relationship between the charge and the potential at the boundaries becomes

\[ \bar{\sigma}_0 = -\frac{1}{4\pi \epsilon_w} \epsilon(0) \bar{\phi}'(0) \] (3.79a)

\[ \bar{\sigma}_L = \frac{1}{4\pi \epsilon_w} \epsilon(L) \bar{\phi}'(L) \] (3.79b)

where the conversion to the dimensionless surface charge density is

\[ \sigma \rightarrow \frac{l_B^2}{e_0} \sigma = \bar{\sigma} \] (3.80)

Equations (3.77), (3.78) define the dimensionless potentials in the domain. The final step here is to substitute the dimensionless variables into the mNP equation for the dynamics in the domain. Starting from Eq. (3.71), the following expression is derived:

\[ l_B^2 \frac{\partial \bar{c}_j}{\partial t} = D_j e'' + D_j [c_j \bar{\mu}_j^{\text{ex}}]' + z_j D_j \left( \bar{c}_j \bar{\phi}' \right)' - D_j \frac{\bar{\alpha}_j}{\epsilon_w} \left[ \bar{c}_j \left( |\bar{\phi}'|^2 \right)' \right]' \] (3.81)

At this point there remain three dimensional parameters: the Bjerrum length, the diffusion coefficient and the time. In order to remove these, a reference diffusion rate \( D^c \) is set and the mNP equation is divided through by it on both sides. The result is then a fully dimensionless
equation:
\[
\frac{\partial \bar{c}_j}{\partial \bar{t}} = D^r_j \bar{c}_j'' + D^r_j [c_j \bar{\mu}_j']' + z_j D^r_j \left( \bar{c}_j \bar{\varphi}' \right)' - D^r_j \frac{\bar{\alpha}_j}{\epsilon_\infty} \left[ \bar{c}_j \left( |\bar{\varphi}'|^2 \right) \right]' \tag{3.82}
\]

where the \( D^r_j = D_j/D^c \) is the ratio of the diffusion coefficient to the reference value and the dimensionless time has the value
\[
\bar{t} = \frac{D^c}{l_B^2} t \tag{3.83}
\]

By changing the value of \( D^c \), the amount of real time represented by each time-step can be altered. This was used throughout the work to help reduce simulation times and, for particularly slow systems, to enable them to be run at all. The specific values used were between \( 10^{-7} \) and \( 10^{-14} \). Despite the range being so large, little difference was observed in the output of the model, beyond the loss of precision which comes with redefining the amount of time that a single time step represents. Although a range of values were used to run the simulations, all data has been converted and presented as if a standard value of \( 10^{-9} \) was used to maintain consistency when presenting data using the dimensionless values of the various parameters. This value was chosen as the standard as it represents an order of magnitude approximation to typical diffusion coefficients, meaning that \( D^r \) in the previous equations is approximately equal to unity.

Finally, while the equations take the number density as their input, the concentration data is discussed and presented in dimensionless or molar form, the conversion between the two values being:
\[
c[M] = \frac{\bar{c}}{10^3 N_A l_B^3} \tag{3.84}
\]

Through the remainder of this chapter and also for the methods chapter which follows, the dimensionless forms of the equations are used. For notational convenience through these sections, the overbar is not displayed and it is to be assumed that all parameters are in dimensionless form. Commencing from chapter 5, the results are presented in both dimensionless and dimensional units, where possible. Dimensional parameters will be represented as the symbol with the units, while the dimensionless equivalent will be represented by the symbol with the overbar. In most cases, data is presented with the dimensionless parameters on the left and bottom axes of figures while the dimensional equivalents are on the right and upper axes. Throughout the text, most input parameters are described using their dimensional values and it should be noted that the molar concentration is used. The exceptions are the domain length, which is quoted as multiples of the Bjerrum length, and the potential, which is quoted as the dimensionless value for numerical simplicity. Compound and calculated values are all discussed using their dimensionless form. In all cases, distinction is made through the use of the overbar to indicate the dimensionless form and stating the units for the dimensional form. A list of the conversions used for these parameters is shown in Table 3.1. Note that the impedance is always considered as the grouping \( ZA \), where \( Z \) is the impedance and \( A \) is the area, and that the admittance is
likewise discussed as the grouping Y/A

Table 3.1: List of dimensionless parameter conversions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol (units)</th>
<th>Dimensionless form</th>
<th>Numerical conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>c (M)</td>
<td>( \tilde{c} = 10^3 N_A l_B c )</td>
<td>( \tilde{c} = 4.49 \text{ M} )</td>
</tr>
<tr>
<td>Potential</td>
<td>( \phi ) (V)</td>
<td>( \tilde{\phi} = \beta \epsilon_0 \phi )</td>
<td>( \tilde{\phi} = 0.026 \text{ V} )</td>
</tr>
<tr>
<td>Electric field</td>
<td>E (V nm(^{-1}))</td>
<td>( \tilde{E} = \beta \epsilon_0 l_B E )</td>
<td>( \tilde{E} = 27.9 \text{ V nm}^{-1} )</td>
</tr>
<tr>
<td>Length</td>
<td>z (m)</td>
<td>( \tilde{z} = \frac{z}{l_B} )</td>
<td>( \tilde{z} = 7.18 \text{ nm} )</td>
</tr>
<tr>
<td>Surface charge density</td>
<td>( \sigma ) (C m(^{-2}))</td>
<td>( \tilde{\sigma} = \frac{l_B}{\epsilon_0} \sigma )</td>
<td>( \tilde{\sigma} = 0.31 \text{ C m}^{-2} )</td>
</tr>
<tr>
<td>Differential capacitance</td>
<td>( C_d ) (m)</td>
<td>( \tilde{C_d} = \frac{\epsilon_0 l_B}{l_B} C_d )</td>
<td>( \tilde{C_d} = 1208.8 \mu \text{F m}^{-2} )</td>
</tr>
<tr>
<td>Time</td>
<td>t (s)</td>
<td>( \tilde{t} = \frac{l_B}{l_B} t )</td>
<td>( \tilde{t} = 5.14 \times 10^{-10} \text{ s} )</td>
</tr>
<tr>
<td>Frequency</td>
<td>f (Hz)</td>
<td>( \tilde{f} = \frac{l_B}{l_B} f )</td>
<td>( \tilde{f} = 1.94 \times 10^9 \text{ Hz} )</td>
</tr>
<tr>
<td>Impedance</td>
<td>Z (Ω)</td>
<td>( \tilde{Z} = \frac{\epsilon_0 l_B}{l_B} Z )</td>
<td>( \tilde{Z} = 1.2 \times 10^{-8} \text{ Ω} )</td>
</tr>
<tr>
<td>Admittance</td>
<td>Y (Ω(^{-1}))</td>
<td>( \tilde{Y} = \frac{\epsilon_0 l_B}{l_B} Y )</td>
<td>( \tilde{Y} = 8.3 \times 10^7 \text{ Ω}^{-1} )</td>
</tr>
<tr>
<td>Current density</td>
<td>I (A m(^{-2}))</td>
<td>( \tilde{I} = \frac{l_B}{l_B} I )</td>
<td>( \tilde{I} = 6.03 \times 10^8 \text{ A} )</td>
</tr>
<tr>
<td>Flux</td>
<td>J (mol m(^{-2}) s(^{-1}))</td>
<td>( \tilde{J} = \frac{l_B}{l_B} J )</td>
<td>( \tilde{J} = 6261 \text{ mol m}^{-2} \text{ s}^{-1} )</td>
</tr>
</tbody>
</table>

### 3.9 Boundary and initial conditions

Equations (3.78) and (3.82) together describe how the system behaves in the modelling domain. Both are second order ordinary differential equations in z and the mNP equation is also a first order ordinary differential equation in t, so two boundary conditions and an initial condition are required in order to solve them.

The boundary conditions for both sets of equations are simplest to define at \( z = L \), far from the electrode surface and where the conditions are defined as being those found in the bulk (see fig. 3.1). Here, both the electrostatic and electrochemical potentials are assumed to take a reference value, relative to which the values in the domain are measured.

The electrostatic potential in the bulk is defined to be zero, such that when the potential at the electrode is also zero the electrolyte is uniform up to the surface of the electrode. This assumption also fixes the Fermi level of the electrode as the zero, otherwise there would be a potential difference between the electrons and the electrolyte to which the ions would respond. Furthermore, if the electric potential in all of the bulk (outside the modelling domain) is zero, there can be no potential gradients and so the ion densities are always equal to their bulk values. The following expressions will therefore always be true at \( z = L \).

\[
c_j(z = L, t) = c_j^0 \quad \text{(3.85a)}
\]
\[
\phi(z = L, t) = 0 \quad \text{(3.85b)}
\]

At the \( z = 0 \) boundary at the edge of the Stern layer, the conditions are simple to state but
involve some calculation in their use. These calculations will be discussed in section 4.2, but the physical arguments to justify their use are made here. The boundary condition for the mNP equation is defined by the flux of ions at the boundary. If a reaction can occur at the surface, this flux is defined by the reaction rate:

$$J_j(z = 0, t) = r$$  \hspace{1cm} (3.86)

For the next three chapters, however, the reaction rate is set to zero and so the electrode represents a flat impenetrable barrier at which the surface flux is zero. The derivation of an expression for the flux which allows the use of this condition is made in section 4.2.1. Discussion of the form of $r$ for reacting systems will be made in section 7.1.

The boundary condition for the potential at $z = 0$, at the edge of the Stern layer, is derived from the way in which the Stern layer is defined. As with the GCS model the boundary represents a point of closest approach for the ionic charge, so on the assumption that there is no specific adsorption the Stern layer contains no charge itself. Using the Poisson equation, the potential can be shown to vary linearly within the layer, a fact that can be used to define the Stern layer potential (i.e. $\phi(0)$ in Fig. 3.1) in terms of the applied potential, $\phi^0$, which lies outside the modelling domain:

$$\phi(0) = \phi^0 + s\phi'(0)$$  \hspace{1cm} (3.87)

where $s$ is the Stern layer width. This equation can be further developed by using the boundary condition derived from the free energy functional, Eq. (3.57a). In the general case, the Stern layer permittivity may differ from that in the electrolyte at the Stern layer boundary, so rather than $\epsilon(0)$, the Stern layer permittivity $\epsilon_s$ is used instead

$$\phi(0) = \phi^0 + \frac{4\pi\epsilon ws_0\sigma_0}{\epsilon_s}$$  \hspace{1cm} (3.88)

Although the surface charge density calculated in Eq. (3.57a) refers only to the edge of the modelling domain, i.e. at the Stern layer boundary, there is no charge in the Stern layer itself so the surface charge density on the electrode must be identical otherwise the system would not be electroneutral. This, of course, assumes that the permittivity across the Stern layer is equal to that at $z = 0$, which means that the field-dependent dielectric decrement is ignored, consistent with the rest of the model. It can further be noted that since the permittivity is assumed to be the same either side of the Stern layer boundary, both the potential and its gradient are continuous across it.

From Eq. (3.88), the potential at the Stern layer is a function of the electrode surface potential, the Stern layer width, the surface charge density and the permittivity at $z = 0$. If the ion concentrations at the surface are known, the only unknown quantity is the surface charge density, which can be calculated self-consistently within the model, as discussed in section 4.2.2. In the event that the Stern layer width is zero, the boundary condition simply reduces to $\phi(0) = \phi^0$, the applied potential.

Finally, the initial condition is defined by assuming that the potential is applied as a step
change at $t = 0$, and that for all times $t < 0$ the potential is zero. As a result, the ion densities are equal to their bulk values right up to the Stern layer boundary for all $t < 0$. At $t = 0$, when the potential is applied, the domain remains electroneutral because the ions have not yet had time to respond and still take their bulk values. It is therefore also possible to solve the Poisson equation in the domain, defining the potential for all $z$. Taking into account the width of the Stern layer, the initial conditions can be summarised as

$$c_j(z, t = 0) = c_j^0 \quad (3.89a)$$
$$\phi(z, t = 0) = \phi_0 \frac{L - z}{L + s} \quad (3.89b)$$

### 3.10 Summary

The work in this chapter presents the development of a model for the behaviour of an electrolyte at an electrode surface based on the Helmholtz free energy of the system. This was used to derive expressions for the electrochemical and electrostatic potentials, which are used in conjunction with the continuity equation to develop equations describing how the ions in the system respond to an applied potential.

Two ion interactions are accounted for in the model. The first is the ion-ion excluded volume interaction, which is described using a form of the van der Waals equation of state which permits different ion sizes, empirically modified such that the interaction energy is similar to that of the Bikerman model. While the model is not intrinsically new, it has not previously been applied in the context of electrolyte modelling and is of interest as a means to retain the simplicity of the Bikerman model while also permitting different ion sizes, as in the BMCSL model. The second interaction accounted for is that of the ion and the solvent, in terms of how the ions alter the polarisability of the solvent molecules, and thereby the permittivity of the bulk solvent (through this work, this is commonly referred to simply as the polarisability interaction). The form of the model for this interaction is also not new in and of itself, having been developed and applied elsewhere for single electrolyte systems (Netz 2001; Ben-Yaakov et al. 2009; Hatlo et al. 2012).

While the components of the model are largely not new for single electrolyte systems, there is limited prior work regarding either ion interactions in mixed electrolytes, the dynamics of electrolytes when ion interactions are accounted for, and the effects of ion interactions in reacting systems. These last two are particularly true for systems which contain ions of different sizes and for systems which account for the polarisability. In particular, for the polarisability interaction there appears to be no prior work regarding its effects on the system dynamics or reaction kinetics.
Chapter 4

Method

The previous chapter outlined a model for describing an electrode/electrolyte system having $M$ types of ion in which ion interactions are accounted for in terms of the excluded volume and the excess polarisability (see Fig. 3.1). The model is comprised of a set of $M+1$ coupled differential mPNP equations (Eqs. (3.71) and (3.56)), which can in principle be solved simultaneously to calculate the ion concentration and electrostatic potential profiles, subject to the boundary conditions laid out in Eqs. (3.85a), (3.85b), (3.86) and (3.88) and to the initial conditions stated in Eqs. (3.89a) and (3.89b). While it is possible in certain limiting cases to derive analytical solutions (Beunis et al. 2008; Golovnev and Trimper 2011), in general a numerical solution is required due to the highly non-linear nature of the structure and coupling of the equations.

In order to solve the equations, the Method of Lines (MOL) is employed, in which the $z$ axis is discretised into $N$ regions and a finite differencing scheme is used to develop algebraic approximations for the spatial dependence of the Poisson and Nernst-Planck equations. This creates a system of coupled differential algebraic equations (DAEs) for each of the equations in the mPNP set, i.e. for each of the Poisson and NP equations in the set there are $N+1$ DAEs and the full mPNP set contains $(M+1)(N+1)$ equations in total. The time evolution of the system of equations is then solved as a set of coupled initial value problems using numerical integration. The grid points are given the general label $i$ and run from $i = 0$ at $z = 0$ to $i = N$ at $z = L$ to give $N+1$ grid points.

The numerical integration was handled using the IDA routine from the SUNDIALS DAE solver package (Hindmarsh et al. 2005). The routine is designed to solve initial value problems of the form

$$F(t, y, y') = 0, \quad y(t_0) = y_0, \quad y'(t_0) = y'_0.$$  \hspace{1cm} (4.1)

To compute the integration it uses a variable order, variable coefficient backward differentiation formula in leading coefficient form (Hindmarsh et al. 2006). Specifically, at time step $d$ it calculates the gradient with respect to the time of each of the concentrations and the potential at a grid point using a polynomial expression of order $q$, which takes the following form

$$h_d y'_d = \sum_{l=0}^{q} b_{d,l} y_{d-l}.$$ \hspace{1cm} (4.2)
where \( h_d \) is the size of the step at \( t = t_d \), \( y_{d-l} \) is the value of the function at time step \( d - l \) and \( b_{d,l} \) is the coefficient relating to that time step. The values of the coefficients are calculated uniquely for each time step and are dependent on both the order and the history of the step sizes, which are variable. This gradient is used in an implicit backward differentiation formula of order \( q \) to estimate the value of the function at \( t_d \), using Newton’s method to solve the equation (Hindmarsh et al. 2006). Since the equations of the mPNP system are inter-dependent, the integration step has to be calculated simultaneously for the whole system.

While the solver handled the integration of the equations, a C++ code was written to interface with and control it. This code consisted of a means to define the parameters for the solver code (the output step length, tolerances, the sizes and initial values of the arrays on which the solver runs and so forth), to define the equations to solve and also to set up the domain and all the system variables for the particular run. It was also used to handle the global output for the model. The main code requested data from the solver at regular time steps which could be orders of magnitude smaller than the times taken for the overall processes occurring in the system being modelled, resulting in a significant amount of data for such runs. To reduce this, the main code could be set either to store the output regularly but less frequently or to store the data based on how quickly the calculated surface charge density or concentration was changing with respect to the time.

The values of the concentration, potential and other domain properties of interest were output at each output time step to a single file which was then sorted automatically into a more user-friendly form using a bash script. Surface properties such as the concentrations, reaction fluxes and current were also output from the main code. The script was also used to automate running the code as it allowed different runs to be made easily without having to enter the data manually for every run.

Returning to the specifics of the model, the DAE expressions used to approximate the mPNP equations are derived in the following section. As with the continuous forms of the mPNP expressions, boundary conditions are required to define the ion concentrations and the potential at grid points \( i = 0 \) and \( i = N \) in terms of known values. These will be discussed in section 4.2. Section 4.3 details the means for varying the grid spacing in across the modelling domain and 4.4 summarises the equations to be solved. Finally section 4.5 will discuss the numerical error which arises from solving the equations in this manner.

### 4.1 Approximating the spatial dependence of the equations

The approximate forms of the mPNP equations at a grid point \( i \), with \( i \neq 0 \) and \( i \neq N \), were derived using a centred difference finite differencing scheme. The general form of all the spatial derivative terms in the mPNP equations is

\[
f(z) = A \frac{d}{dz} \left( B(z) \frac{dC(z)}{dz} \right). \tag{4.3}
\]
Approximating the outer differential term using the values of the function half way between the grid points yields

\[
A \frac{d}{dz} \left( B(z) \frac{dC(z)}{dz} \right) \approx A \frac{B_{i+1/2}C'_{i+1/2} - B_{i-1/2}C'_{i-1/2}}{\Delta z} \quad (4.4)
\]

The derivatives on the half interval were then approximated using the grid points either side, while the value of the non-derivative term was approximated by linearly interpolating between the points to give

\[
A \frac{d}{dz} \left( B(z) \frac{dC(z)}{dz} \right) = A \frac{(B_{i+1} + B_i)(C_{i+1} - C_i) - (B_i + B_{i-1})(C_i - C_{i-1})}{2\Delta z^2} \quad (4.5)
\]

This general scheme was used to derive the approximate forms of the mNP and Poisson equations, as described below.

### 4.1.1 The Nernst-Planck equation

Directly substituting the terms of the NP equation, as stated in Eq. (3.82), into the previous relationship yields the following result

\[
\frac{\partial c_{j,i}}{\partial t} = \frac{D_r}{\Delta z^2} (c_{j,i+1} - 2c_{j,i} + c_{j,i-1}) + \frac{D_r}{2\Delta z^2} \left[ (c_{j,i+1} + c_{j,i})(\mu^{\text{ex}}_{j,i+1} - \mu^{\text{ex}}_{j,i}) - (c_{j,i} + c_{j,i-1})(\mu^{\text{ex}}_{j,i} - \mu^{\text{ex}}_{j,i-1}) \right] + \frac{D_r}{2\Delta z^2} \left[ (c_{j,i+1} + c_{j,i})(\mu^{\text{el}}_{j,i+1} - \mu^{\text{el}}_{j,i}) - (c_{j,i} + c_{j,i-1})(\mu^{\text{el}}_{j,i} - \mu^{\text{el}}_{j,i-1}) \right] \quad (4.6)
\]

where \( \mu^{\text{el}} \) is defined by Eq. (3.61).

While this equation is valid, in practice the logarithm terms on which the various forms of \( \mu^{\text{ex}} \) depend were calculated analytically prior to discretising the equations in order to reduce the stiffness of the problem. By way of example, taking the mvdW form of \( \mu^{\text{ex}} \) from Eq. (3.23), the derivative with respect to \( z \) is

\[
[c_j(\mu_j^{\text{ex}})]' = \left[ c_j \left( \ln \frac{1}{\zeta_j} + \sum_l \tilde{v}_{jl} \frac{c_l}{\zeta_l} \right) \right]' = \left[ c_j \zeta_j \left( \frac{1}{\zeta_j} \right) \right]' + \left[ c_j \left( \sum_l \tilde{v}_{jl} \frac{c_l}{\zeta_l} \right) \right]' \quad (4.7)
\]

Both of these terms can be discretised according to the expression stated in the previous section. A term similar to the first term on the right in the above equation results from all of the excess chemical potentials mentioned in section 3.2, but the second term differs between them. After combining the ideal and excess logarithm terms and then applying the above transforma-
tion, the NP equation for the mvdW equation takes the different form
\[
\frac{\partial c_{j,i}}{\partial t} = \frac{D_r}{2\Delta z^2} \left[ (c_{j,i+1} + c_{j,i})(\ell_{j,i+1} - \ell_{j,i}) - (\ell_{j,i} - \ell_{j,i-1}) \right] \\
+ \frac{D_r}{2\Delta z^2} \left[ (c_{j,i+1} + c_{j,i})(\mu_{\text{rem},j,i+1} - \mu_{\text{rem},j,i}) - (\mu_{\text{rem},j,i} - \mu_{\text{rem},j,i-1}) \right] \\
+ \frac{D_r}{2\Delta z^2} \left[ (c_{j,i+1} + c_{j,i})(\mu_{\text{el},j,i+1} - \mu_{\text{el},j,i}) - (\mu_{\text{el},j,i} - \mu_{\text{el},j,i-1}) \right] 
\]
(4.8)

where \( \ell_j = c_j / \zeta_j \) and \( \mu_{\text{rem},j} = \left[ c_j \left( \sum_l \bar{v}_{jl} \tilde{G}_l \right) \right]^\prime \).

The above expression was the form in which the equation was used in the solver code, but it hides one last problem in that the \( \mu_{\text{el}} \) term still contains a term dependent on the differential of the electric potential (see Eq. (3.61)). This term was not directly discretised at this stage, since doing so would mean that grid points outside the domain would be needed in order to calculate the value of \( \mu_{\text{el}} \) at the boundary. Instead, the value was approximated self-consistently in the same manner as the potential gradient at the boundaries, as will be discussed in section 4.2.2.

### 4.1.2 The Poisson equation

The approximate form of the Poisson equation is found in the same manner as above, by applying the generalised approximation defined in equation (4.5), resulting in the following expression
\[
\sum_l z_l c_{l,i} = \frac{1}{8\pi \epsilon \Delta z^2} \left[ (\epsilon_{i+1} + \epsilon_i)(\phi_{i+1} - \phi_i) - (\epsilon_i + \epsilon_{i-1})(\phi_i - \phi_{i-1}) \right] 
\]
(4.9)

This equation and Eq. (4.8) together represent the discretised forms of the continuum equations on the grid which represents the modelling domain. The equation for a particular grid point is always dependent on the adjacent grid points, defining the coupling between all of the points on the grid. Since the grid is finite, the boundaries do not have grid points on both sides, which means that these equations cannot apply at those points and different equations are required.

### 4.2 Boundary conditions

The boundary conditions have already been defined in terms of the continuum form of the equations (see eqs. (3.85a), (3.85b), (3.86) and (3.88)). At the \( i = N \) (\( z = L \)) boundary, representing the bulk electrolyte on the right of Fig. 3.1, there are a set of Dirichlet boundary conditions which completely define the values of the functions at that point (i.e. \( \phi_N = 0 \) and \( c_{j,N} = c_0 \)). At the electrode boundary on the left of the figure (\( i = 0 \) or \( z = 0 \)), the equations are either Neumann or mixed boundary conditions, dependent on the gradient of the functions as well as their values. While it is technically possible to write down expressions for the gradient at the boundary using a forward difference scheme of the same order as the centred difference used in the rest of the domain, the result would not be exactly compatible with the equations
used in the domain — for example integrating the discretised form of the NP equation across the domain would not be equal to the total flux if the approach were used. Instead, the approximate domain equations were integrated over the domain to derive boundary conditions which are consistent with the finite differencing scheme used.

4.2.1 The Nernst-Planck equation

The known quantity at the electrode surface is the flux and, from the way in which the model is defined, the flux conditions at the Stern layer boundary \((z = 0)\) are identical to those at the surface \((z = -s)\). Integrating the continuous form of the continuity equation, Eq. (3.70a), with respect to \(z\) yields an expression for the total change in flux across the domain for each species:

\[
\int_0^L dz \frac{dc_j}{dt} = - \int_0^L dz \frac{dJ_j}{dz} = - [J_j(L) - J_j(0)] \tag{4.10}
\]

At the same time, the discretised mNP equations, Eq. (4.6), are integrated using the trapezium method, defined as

\[
\int dz f_j(z) = \frac{\Delta z}{2} [f_{j,0} + f_{j,N}] + \Delta z \sum_{i=1}^{N-1} f_{j,i}, \tag{4.11}
\]

where the sum is over the labelled grid points, to give the following expression

\[
\int_0^L dz \frac{dc_j}{dt} = \frac{\Delta z}{2} \left\{ \frac{dc_j}{dt} \bigg|_0 + \frac{dc_j}{dt} \bigg|_N \right\} + \frac{D_j}{2\Delta z} \left[ (\zeta_j,N + \xi_j,N-1)(\mu_{j,N}^{\text{rem}} - \mu_{j,N-1}^{\text{rem}}) - (\zeta_j,1 + \xi_j,0)(\mu_{j,1}^{\text{rem}} - \mu_{j,0}^{\text{rem}}) \right]
\]

\[
+ \frac{D_j}{2\Delta z} \left[ (\epsilon_j,N + \epsilon_j,N-1)(\mu_{j,N}^{\epsilon} - \mu_{j,N-1}^{\epsilon}) - (\epsilon_j,1 + \epsilon_j,0)(\mu_{j,1}^{\epsilon} - \mu_{j,0}^{\epsilon}) \right] \tag{4.12}
\]

The approximate function for grid points 0 and \(N\) both contain references to non-existent grid points outside the domain. Since these do not exist, the approximate functions for the boundary points are replaced with the time differential of the densities at those points, according to Eq. (4.6). In the interior of the domain all of the finite difference terms cancel out, so the only terms which remain relate to the two boundary points and their neighbours inside the domain.

The two expressions (4.10) and (4.12) are equal to each other, since they both represent the integral over the domain of \(dc_j/dt\). By equating them, it is possible to write the difference between the boundary fluxes in terms of the following grid points:

\[
J_j(0) - J_j(L) = J_{j,0} - J_{j,N}
\]

\[
= \frac{\Delta z}{2} \left\{ \frac{dc_{j,0}}{dt} + \frac{dc_{j,N}}{dt} \right\}
\]

\[
+ \frac{D_j}{2\Delta z} \left[ (\zeta_j,N + \xi_j,N-1)(\mu_{j,N}^{\text{rem}} - \mu_{j,N-1}^{\text{rem}}) - (\zeta_j,1 + \xi_j,0)(\mu_{j,1}^{\text{rem}} - \mu_{j,0}^{\text{rem}}) \right]
\]

\[
+ \frac{D_j}{2\Delta z} \left[ (\epsilon_j,N + \epsilon_j,N-1)(\mu_{j,N}^{\epsilon} - \mu_{j,N-1}^{\epsilon}) - (\epsilon_j,1 + \epsilon_j,0)(\mu_{j,1}^{\epsilon} - \mu_{j,0}^{\epsilon}) \right]
\]

\[
+ \frac{D_j}{2\Delta z} \left[ (\zeta_j,N + \xi_j,N-1)(\mu_{j,N}^{\epsilon} - \mu_{j,N-1}^{\epsilon}) - (\zeta_j,1 + \xi_j,0)(\mu_{j,1}^{\epsilon} - \mu_{j,0}^{\epsilon}) \right]
\]
The fluxes at each of the two boundaries should only depend on the density and electric potential values at those boundaries, which means that the equation can be separated into two expressions, one for each boundary:

\[
J_{j,0} = \frac{\Delta z}{2} \frac{dc_{j,0}}{dt} - \frac{D_r}{2\Delta z^2} (\zeta_{j,1} + \zeta_{j,0})(\iota_{j,1} - \iota_{j,0}) \\
- \frac{D_r}{2\Delta z^2} (c_{j,1} + c_{j,0})(\mu_{j,1}^{\text{rem}} - \mu_{j,0}^{\text{rem}}) - \frac{D_r}{2\Delta z^2} (c_{j,1} + c_{j,0})(\mu_{j,1}^{\text{el}} - \mu_{j,0}^{\text{el}})
\]

(4.14a)

\[
J_{j,N} = \frac{\Delta z}{2} \frac{dc_{j,N}}{dt} - \frac{D_r}{2\Delta z^2} (\zeta_{j,N} + \zeta_{j,N-1})(\iota_{j,N} - \iota_{j,N-1}) \\
- \frac{D_r}{2\Delta z^2} (c_{j,N} + c_{j,N-1})(\mu_{j,N}^{\text{rem}} - \mu_{j,N-1}^{\text{rem}}) - \frac{D_r}{2\Delta z^2} (c_{j,N} + c_{j,N-1})(\mu_{j,N}^{\text{el}} - \mu_{j,N-1}^{\text{el}})
\]

(4.14b)

As with the approximation to the equations in the interior of the domain, \(\mu_{j,i}^{\text{el}}\) is dependent on the gradient of the potential, which is as yet undefined. Also, the flux expressions are dependent on the differential of the concentration with respect to time. This latter term is not known explicitly, but is equal to the value of \(y'\) used in the backward differentiation formula, which the solver routine calculates in equation (4.2) and can be used to solve the boundary conditions self-consistently. Now, with a suitable value for the surface flux, which in the absence of reactions is zero, the boundary condition equations are defined in a fashion that is consistent with equations which describe the system in the interior of the domain.

4.2.2 Poisson equation

The process for deriving the boundary condition at the left hand side of the domain, at the Stern layer boundary, is essentially the same as that for deriving the boundary equations for the NP equation. However in this case the known property at the electrode surface is the electric potential, which has a different value at the Stern layer boundary, at the edge of the modelling domain, compared to the electrode surface. The relationship between the two values is defined by equation (3.87).

First, the continuum Poisson equation is integrated, but this time the integration extends from the electrode surface at \(z = -s\) out to the bulk at \(z = L\):

\[
\int_{-s}^{L} dz \frac{1}{4\pi} \frac{d}{dz} \left[ \epsilon \frac{d\phi}{dz} \right] = \int_{-s}^{L} dz \sum_{l} z_{l} c_{l} = Q
\]

(4.15)

where \(Q\) is the total charge per unit area along the \(z\)-axis. Since the system has to be electroneutral over the whole domain, \(Q\) must be of equal magnitude, but opposite sign, to the sum
of the charge densities at the boundaries, \( \sigma(0) \) and \( \sigma(L) \). Furthermore, the Stern layer makes no contribution to the charge density, so the integration limits can be changed such that the Poisson equation is integrated from the Stern layer boundary out to the bulk and the result will be the same.

\[
\int_{0}^{L} dz \frac{1}{4\pi d z} \left[ \epsilon \frac{d \phi}{d z} \right] = Q = -(\sigma(0) + \sigma(L))
\]  

(4.16)

As before, the discrete form of the Poisson equation is integrated using the trapezium rule, the result being

\[
\int_{0}^{L} dz \frac{1}{4\pi d z} \left[ \epsilon \frac{d \phi}{d z} \right] = \Delta z \left( \sum_{l} z_{l} c_{l,0} + \sum_{l} z_{l} c_{l,N} \right) - \frac{1}{8\pi \epsilon_{w} \Delta z} ((\epsilon_{N} + \epsilon_{N-1})(\phi_{N} - \phi_{N-1}) - (\epsilon_{1} + \epsilon_{0})(\phi_{1} - \phi_{0}))
\]  

(4.17)

where, again, the approximate equations for the boundary grid points involve grid points outside the domain, so have been replaced with the charge densities at those points by using Eq. (4.9).

The integrals of the continuous and discrete forms of the equations are equal and, as before, the terms of the resulting equation can be separated by virtue of the fact that the surface charge density at each boundary can only depend on the grid points at that boundary. The result is two separate equations for the surface charge density at each boundary:

\[
\sigma_{0} = -\frac{\Delta z}{2} \sum_{l} z_{l} c_{l,0} - \frac{1}{8\pi \epsilon_{w} \Delta z} (\epsilon_{1} + \epsilon_{0})(\phi_{1} - \phi_{0})
\]  

(4.18a)

\[
\sigma_{L} = -\frac{\Delta z}{2} \sum_{l} z_{l} c_{l,N} + \frac{1}{8\pi \epsilon_{w} \Delta z} (\epsilon_{N} + \epsilon_{N-1})(\phi_{N} - \phi_{N-1})
\]  

(4.18b)

The surface charge density calculated by this equation is also equal to the surface charge density of the electrode. This means that it can be substituted into Eq. (3.79a), together with the permittivity at the domain boundary, and used to calculate the potential gradient at the surface. In turn, this can be substituted into Eq. (3.87) to derive the discretised form of Eq. (3.88) (the Stern layer boundary condition). The result is an expression which depends on the values of the electrode surface potential and the potentials and concentrations at grid points \( i = 0 \) and \( 1 \):

\[
\phi_{0} = \phi^{0} - \frac{4\pi \epsilon_{w} s}{\epsilon_{0}} \left( \frac{\Delta z}{2} \sum_{l} z_{l} c_{l,0} + \frac{1}{8\pi \epsilon_{w} \Delta z} (\epsilon_{1} + \epsilon_{0})(\phi_{1} - \phi_{0}) \right),
\]  

(4.19)

The surface potential is known, while the other properties are all values of the functions being solved for, so the boundary condition can be calculated self-consistently with the domain equations.

An extension of the equations in this section is that by placing an imaginary boundary at any point in the domain and then integrating the Poisson equation from the electrode surface to that boundary, the effective surface charge at that boundary can be calculated. This can in turn be
used to calculate the potential gradient at that grid point using the set of equations outlined above, the result being of the same form as equation (4.18b), generalised to the grid point at which the boundary is located. Combined with equation (3.79b), with $L$ replaced by the position of the imaginary boundary in the domain, the potential gradient at the general grid point $i$ can be written in the following form:

$$
\phi_i' = \frac{2\pi \epsilon_0 \Delta z}{\epsilon_i} \sum_l z_i c_{l,i} - \frac{1}{2\epsilon_i \Delta z} (\epsilon_i + \epsilon_{i-1})(\phi_i - \phi_{i-1})
$$

(4.20)

This is the expression which is used to calculate the gradient of the electric potential in the domain when calculating $\mu_{\text{el}}^l$ in the NP equations and their boundary conditions. It represents the final equation required to be able to express the mPNP equations in discretised form, yielding a set of approximations to the equations which define the model system that was set up in Fig. 3.1.

### 4.3 Varying the grid spacing

The derived numerical equations describing the system are approximations, so there is an error inherent in using them in place of the continuous equations. A more detailed discussion of these errors will be presented in the following section, but there is a final development to the model which was made in order to help minimise the error while maintaining a reasonably short simulation time, and this is most easily discussed here.

For the centred difference approximation to the spatial derivatives used, the error $E$ should be proportional to $\Delta z^2$, the square of the grid spacing. It was found from early runs of the model that reducing the error to an acceptable level required a small grid spacing, of the order of 0.05 $l_B$. However, the use of such a small spacing generates two problems, one related to the amount of memory required to run a simulation and the other related to how long the simulation takes to run.

The IDA solver routine stores the values of the concentration and potential functions in arrays which have a length equal to the number of grid points multiplied by the number of equations to solve at each point. For a system of $M$ ions there are $M + 1$ mPNP equations and therefore $(M + 1)(N + 1)$ values to store. As the arrays become larger, more memory is required to store them, so there is a physical limit on their size, which for the computers used to run the models was about 30,000 equations. More than this results in the solver returning a memory error. Practically, for a two species system there are three equations per grid point and therefore a limit of 10,000 grid points. At a required grid spacing of 0.05 $l_B$, this translates to a maximum domain length of 500 $l_B$, or about 0.36 $\mu$m. Increasing the number of species, either because there is a supporting electrolyte or because there are reaction products, increases the number of equations per grid point, meaning that the domain has to be even smaller.

The other problem is that the amount of time taken to run the simulation increases quadratically with the number of equations. Because of this, even if a domain length of 500 $l_B$ were sufficiently large to model a system of interest, the amount of time taken to run a single simula-
tion would render the model impractical.

These problems were addressed by utilising the fact that the grid spacing only needs to be small when there are steep spatial gradients in the concentrations or the potential. These steep gradients only occur near to the electrode surfaces; further out the values of the parameters of interest differ little from their bulk values so the gradients are correspondingly small. Using this, the modelling domain was split into a number of sub-domains, each with its own grid spacing.

At all points in the sub-domains the mPNP equations previously derived apply, albeit using that sub-domain’s grid spacing $\Delta z_{sd}$. The exception is at the boundary between two sub-domains, at which point there is a single grid point which has a different grid spacing on either side and the discretised equations do not apply. To connect the model equations at these internal boundaries, the fact that the concentrations and the potential on the boundary grid point can only have a single value together with the knowledge that particle fluxes and the electric field must be constant across the boundary is used.

Using the same integration procedure as was used to derive the overall domain boundary conditions, the flux and the electric field of a particular sub-domain can be written in terms of the boundary grid point and the point adjacent to it. The value calculated from one direction in a given sub-domain must equal to the value calculated in the opposite direction from the adjacent sub-domain. Equating the flux and electric field boundary conditions at the boundary is therefore sufficient to connect the two sub-domains. If the shared grid point is point $i = m$ between sub-domains 1 and 2, the expressions linking the functions in the sub-domains either side are given in equations (4.21) and (4.22), respectively, below.

\[
\begin{align*}
\Delta z_1 \frac{dc_{j,i}}{dt} + \frac{D_r}{\Delta z_1} \left\{ (\zeta_{j,m} + \zeta_{j,m-1})(t_{j,m} - t_{j,m-1}) + (c_{j,m} + c_{j,m-1})(\mu_{j,m}^{\text{rem}} - \mu_{j,m-1}^{\text{rem}}) \\
+ (c_{j,m} + c_{j,m-1})(\mu_{j,m}^{\text{el}} - \mu_{j,m-1}^{\text{el}}) \right\} \\
= -\Delta z_2 \frac{dc_{j,m}}{dt} + \frac{D_r}{\Delta z_2} \left\{ (\zeta_{j,m+1} + \zeta_{j,m})(t_{j,m+1} - t_{j,m}) + (c_{j,m+1} + c_{j,m})(\mu_{j,m+1}^{\text{rem}} - \mu_{j,m}^{\text{rem}}) \\
+ (c_{j,m+1} + c_{j,m})(\mu_{j,m+1}^{\text{el}} - \mu_{j,m}^{\text{el}}) \right\} \\
\end{align*}
\]

(4.21)

\[
\begin{align*}
&- \Delta z_1 \sum_l z_l c_{l,m} + \frac{1}{4\pi \varepsilon_w \Delta z_1} (\epsilon_m + \epsilon_{m-1})(\phi_m - \phi_{m-1}) \\
&= \Delta z_2 \sum_l z_l c_{l,m} + \frac{1}{4\pi \varepsilon_w \Delta z_2} (\epsilon_{m+1} + \epsilon_m)(\phi_{m+1} - \phi_m) \\
\end{align*}
\]

(4.22)

Each sub-domain is now fully described by approximate forms of the equations, which are consistent despite changes in the grid spacing. The effect which this has on the numerical error will be discussed in section 4.5 below, but in general only the grid spacing in the domain adjacent to the electrode significantly affects the output. The result of setting up the model like this is that domain lengths up to twenty or more times larger can be simulated in a small fraction of the time it would have taken to simulate a short domain with a constant grid spacing.
4.4 Summary of equations

This section summarises all of the important equations relevant to describing the system. A diagram of the final discretised system is shown in Fig. 4.1, where the codes in the diagram refer to the list below.

**NP**

NP_{j,x} Nernst-Planck equation for species \( j \) in region \( x \)

\[
\frac{\partial c_{j,i}}{\partial t} = \frac{D^r_j}{2\Delta z^2_x} \left[ (\zeta_{j,i+1} + \zeta_{j,i})(\iota_{j,i+1} - \iota_{j,i}) - (\zeta_{j,i} + \zeta_{j,i-1})(\iota_{j,i} - \iota_{j,i-1}) \right]
+ \frac{D^r_j}{2\Delta z^2_x} \left[ (c_{j,i+1} + c_{j,i})(\mu_{j,i+1}^{\text{rem}} - \mu_{j,i}^{\text{rem}}) - (c_{j,i} + c_{j,i-1})(\mu_{j,i}^{\text{rem}} - \mu_{j,i-1}^{\text{rem}}) \right]
+ \frac{D^r_j}{2\Delta z^2_x} \left[ (c_{j,i+1} + c_{j,i})(\mu_{j,i+1}^{\text{el}} - \mu_{j,i}^{\text{el}}) - (c_{j,i} + c_{j,i-1})(\mu_{j,i}^{\text{el}} - \mu_{j,i-1}^{\text{el}}) \right] \tag{4.23}
\]

**P**

P \_x Poisson equation in region \( x \)

\[
\sum_l z_l c_{l,i} = \frac{1}{8\pi \epsilon_w \Delta z^2_x} \left[ (\epsilon_{i+1} + \epsilon_i)(\phi_{i+1} - \phi_i) - (\epsilon_i + \epsilon_{i-1})(\phi_i - \phi_{i-1}) \right] \tag{4.24}
\]

**NPBC**

NPBC_{j,\text{s}} Nernst-Planck equation Stern layer boundary condition for species \( j \)

\[
J_0 = \frac{\Delta z}{2} \frac{dc_{j,0}}{dt} - \frac{D^r_j}{2\Delta z^2_x} (\zeta_{j,1} + \zeta_{j,0})(\iota_{j,1} - \iota_{j,0}) - \frac{D^r_j}{2\Delta z} (c_{j,1} + c_{j,0})(\mu_{j,1}^{\text{rem}} - \mu_{j,0}^{\text{rem}})
- \frac{D^r_j}{2\Delta z} (c_{j,1} + c_{j,0})(\mu_{j,1}^{\text{el}} - \mu_{j,0}^{\text{el}}) \tag{4.25}
\]

**NPBC**

NPBC_{j,\text{b}} Nernst-Planck equation bulk boundary condition for species \( j \)

\[
c_{j,N}(t) = c_j^0 \tag{4.26}
\]

Figure 4.1: Diagram of the variable grid discretised domain and where the equations listed in the text apply
**PBC** _a_ Poisson equation Stern layer boundary condition

\[
\phi_0 = \phi^0 - \frac{4\pi \varepsilon_w s}{\varepsilon_0} \left( \frac{\Delta z}{2} \sum_l z_l c_{l,0} + \frac{1}{8\pi \varepsilon_w \Delta z} (\varepsilon_1 + \varepsilon_0)(\phi_1 - \phi_0) \right) 
\]  

(4.27)

**PBC** _b_ Poisson equation bulk boundary condition

\[
\phi_N = 0 
\]  

(4.28)

**iNPBC** _j_ internal boundary Nernst-Planck equation for species _j_

\[
\Delta z_1 \frac{dc_{j,m}}{dt} + \frac{D_r^j}{\Delta z_1} \left\{ (\zeta_{j,m} + \zeta_{j,m-1})(t_{j,m} - t_{j,m-1}) + (c_{j,m} + c_{j,m-1})(\mu^r_{j,m} - \mu^r_{j,m-1}) \right. \\
+ (c_{j,m} + c_{j,m-1})(\mu^i_{j,m} - \mu^i_{j,m-1}) \left\} 
\]  

\[= -\Delta z_2 \frac{dc_{j,m}}{dt} + \frac{D_r^j}{\Delta z_2} \left\{ (\zeta_{j,m+1} + \zeta_{j,m})(t_{j,m+1} - t_{j,m}) + (c_{j,m+1} + c_{j,m})(t_{l,m+1} - t_{l,m}) \right. \\
+ (c_{j,m+1} + c_{j,m})(\mu^i_{j,m+1} - \mu^i_{j,m}) \left\} 
\]  

(4.29)

**iPBC** internal boundary Poisson equation

\[
-\Delta z_1 \sum_l z_l c_{l,m} + \frac{1}{4\pi \varepsilon_w \Delta z_1} (\varepsilon_m + \varepsilon_{m-1})(\phi_m - \phi_{m-1}) \\
= \Delta z_2 \sum_l z_l c_{l,m} + \frac{1}{4\pi \varepsilon_w \Delta z_2} (\varepsilon_{m+1} + \varepsilon_m)(\phi_{m+1} - \phi_m) 
\]  

(4.30)

### 4.5 Numerical method errors

The equations used to solve the mPNP equations are discretised analytical expressions which approximate the continuous functions of the concentration and potential which were derived in Chapter 3. As a result, the calculated solutions will differ from the actual values to a certain extent. This error in the calculated values extends to both the spatial and temporal dimensions, meaning both that the equilibrium calculated concentration and potential distributions will differ from the actual equilibrium values and also that the calculated amount of time taken to reach that equilibrium may differ from the actual time.

With both the position and time variables (_z_ and _t_) being discretised, each contributes to the overall error. The extent of the error depends on the grid separation for _z_ or the step length over which the solution is integrated for _t_, with larger values increasing the error in both cases. Minimising the values was therefore important for maintaining reasonably accurate results. As discussed below, the length of the time step was handled adaptively by the solver code, meaning that this error was minimised automatically. The error in the grid spacing has to be fixed prior to the start of a run, so a reasonable grid spacing had to be defined, the discussion of which is
made in the following sections.

In terms of stepping the system forwards in time to calculate the dynamics, the initial state is input to the solver together with the allowed relative and absolute errors and the value of the time at which the output is to be given. While the output is reported at the requested output time value, internally the solver uses a number of intermediate steps. The length of the intermediate steps, and therefore the number of them taken to reach the requested output time, is variable, with their length being determined iteratively until the relative and absolute tolerances are satisfied. Once the solver has worked through all the necessary intermediate steps and reached the requested output time value, the result of the calculation is sent to the main part of the code and the solver repeats the process for the next requested output time value. A limit can be placed on the number of intermediate steps to prevent the solver infinitely reducing the step size, but in essence these errors are handled automatically.

Both the absolute and relative tolerances were set to a maximum value of $1 \times 10^{-7}$. In general, the error is dominated by the grid spacing and changes to the tolerance did not have a significant effect on the model output. The exception to this was found to be for time-dependent applied potentials, for which too large a tolerance led to oscillations of some of the calculated properties about the true value which could be reduced by reducing the tolerance. However, the cost of doing this was an increased frequency of simulations which would not complete their run, a problem which is discussed further at the end of this chapter.

While the adaptive step length used by the solver handles the error which results from the time variable, the errors which result from the grid spacing are handled manually by defining a grid spacing on which the errors are deemed reasonable. There are two possible types of error in the model, one being the error in the actual values of the concentrations and the potential and the other being the error in the amount of time taken to reach a particular state. The first of these can be looked at by calculating the equilibrium state of a system with a fixed potential and comparing that to the analytical solution (if it exists) or looking at how the solution converges as the grid spacing is decreased. The error in the time taken to reach a particular state can be considered by looking at the convergence of the equilibration time for a step potential change at $t = 0$ or at how the output changes with the grid spacing for a time-dependent potential. Each of these will be examined at in the remainder of this chapter.

### 4.5.1 Error in the output at equilibrium

All systems in which the electrode potential is constant with respect to the time will reach an equilibrium state. The error in the concentrations and the potential are greatest when their gradients are steepest, i.e. adjacent to the electrode surface. Furthermore, since the gradients increase with the applied potential and the bulk concentration, these changes also cause the error to increase. The way in which the numerical approximation deviates from the actual solution can be seen in Figs. 4.2(a) and (b), which respectively show the surface charge density and differential capacitance as functions of the potential for a range of bulk concentrations.

For the purposes of the figures, the grid spacing used in the numerical solution was relatively
Figure 4.2: (a) The surface charge density and (b) the double layer differential capacitance as a function of the surface potential for the Gouy-Chapman model. Solid lines represent analytical solutions and crosses show the numerical calculation.

low, so this can and will be improved upon, but the trends are clear and it is apparent that the errors can be significant if they are not managed. For the centred finite difference scheme used in the model, the error $E_{rr}$ should be proportional to the square of the grid spacing, i.e. $E_{rr} \propto \Delta z^2$. This can be confirmed by plotting the logarithm of $E$ against the logarithm of $\Delta z$ and ensuring that the resulting line has a gradient equal to two. The error in the system can be calculated relative to an analytical solution, if there is one, or by defining a run with a very small grid spacing as being the actual solution and comparing other runs to it, or by using non-linear curve fitting to estimate the convergence point from a data set. The relative error is defined as

$$E_{rr} (%) = 100 \times \frac{f_{\text{numerical}} - f_{\text{analytical}}}{f_{\text{analytical}}}$$

(4.31)

where $f$ is one of the calculated values in the system. The values used to measure the error were the surface concentration and the surface charge density, the latter being used because it is a function of the potential gradient and so is a good measure of its error (the actual surface potential is fixed, so cannot be used to look at the errors).

The errors are largest when the gradients of the concentrations and potential are largest. The concentration gradients will always be largest in the GC model, so this was used for the first test of the error. The GC model also has the benefit of an analytical solution, so it is easy to calculate an accurate relative error. In the test, the domain was set to $500l_B$, divided into three sub-domains, or regions, of lengths $10l_B$ (“left sub-domain” or “region 1,” adjacent to the electrode), $90l_B$ (“middle sub-domain” or “region 2”) and $400l_B$ (“right sub-domain” or “region 3,” adjacent to the bulk). To look at how the grid spacing of each affects the error in the equilibrium values, a base-line low number of grid points was set of 100 on the left, 180 in the middle and 40 on the right, giving grid spacings of $0.1l_B$, $0.5l_B$, $1l_B$, respectively. Sets of simulations were then run in which one of the grid numbers was increased up to a maximum of 2500, from which the effect of the grid spacing could be analysed. For the test, the electrolyte concentration used was 0.01 M and the applied potential was $\beta e_0 \phi^0 = 7$. Plots of the relative
error as a function of the number of grid points and $\log(Err)$ vs. $\log(\Delta z)$ are shown for the left sub-domain in Figs. 4.3(a) and (b) below.

![Figure 4.3](image1)

Figure 4.3: (a) The relative error in the analytical surface charge density and concentration as a function of the number of grid points in region 1 and (b) log-log plot of the relative error as a function of the grid spacing in region 1.

Even at this fairly low potential the relative error is very large when the number of grid points is small. However, the gradient of the lower region of the log-log plot is two, confirming that the error does vary with the square of the grid spacing. The top parts of the curves deviate slightly from the linearity of the lower parts. This is a typical feature of convergence where in the errors become significantly worse at very large grid spacings. As a result these points were disregarded when considering the rate of convergence.

In contrast to the above variation in $Err$ with grid spacing in the inner domain, the spacing in the other two domains has no effect on the error, as can be seen in Figs. 4.4(a) and (b). In Fig. 4.4(a), the grid spacing is taken to be $0.1 l_B$, at which the relative error can be seen from Fig. 4.3(a) to be about $85\%$ (surface charge density) and $95\%$ (concentration), values which are not changed at all by changes in the grid spacing of the middle or right hand sub-domains.

![Figure 4.4](image2)

Figure 4.4: Relative error between the numerical and analytical surface charge density and concentration as a function of the number of grid points in the middle and outer regions when the grid separation in the inner region is (a) $\Delta z = 0.1 l_B$ and (b) $\Delta z = 0.02 l_B$ (only the middle region data is shown).

To confirm that any impact on the error is not masked by the excessively large error caused
by the low grid spacing in the inner region, the simulations were run again after reducing the grid spacing in the there to 0.02\(l_B\). The results are shown in part (b) of Fig. 4.4, confirming that it is only the region adjacent to the electrode surface which has an effect on the error. This also confirms that only the regions in which the gradients of the concentrations and the potential are large contribute significantly to the error and justifies the division of the modelling domain into sub-domains with different grid spacings.

The target relative accuracy for all the data presented in this work is < 1%. For the GC model, using the particular sub-domain parameters described above, this means that the inner sub-domain has to have a minimum grid spacing of about 700. However, these calculations do not take account of the ion interactions, the inclusion of which inherently increases the accuracy of the approximation. A further improvement in the accuracy can be achieved by refinement of the sub-domain structure. These two factors are considered in turn below.

The limit to the concentration which the excluded volume interaction or polarisability effects cause means that the surface concentrations are prevented from becoming excessively large and, as a result, the magnitudes of their gradients are restricted. Shown in Fig. 4.5 is the relative error in the numerical solution for the Bikerman model using a nominal ion diameter of 0.2 nm.

![Relative error between numerical and analytical surface charge density and concentration](image)

Figure 4.5: The relative error between the numerical and analytical surface charge density and concentration as a function of the number of grid points in regions one and two

Although the rate of convergence is the same (\(Err \propto \Delta z^2\)) the relative error is much lower, becoming smaller than 1% for a grid spacing of \(\Delta z \approx 0.02l_B\). All of the diameters considered throughout this work are larger than 0.2 nm, placing a smaller limit on the concentration. Furthermore all values of the ion polarisability which are considered lead to smaller maximum concentrations. As a result, the errors are correspondingly smaller and so a grid spacing of 0.02\(l_B\) in the sub-domain adjacent to the electrode is sufficient to achieve the desired relative error if the ion interaction terms are accounted for.

As well as the aforementioned memory issue, keeping the number of grid points as low as possible was desirable in order to maintain a reasonable simulation time. An idea of the amount of time taken to complete a single run as a function of the total number of grid points is shown in Fig. 4.6. Each datum point corresponds to the single run which generated the output at that number of grid points, so while it is not an accurate representation under controlled conditions,
the trend is common to all such runs.

Figure 4.6: Simulation time as a function of the number of grid points in region one

The growth in the run time with the number of grid points is approximately quadratic, rather than a linear growth which may be expected. This results from the increased stiffness of the DAE system which occurs as the number of grid points is increased. In order to maintain the same level of accuracy, this increased stiffness leads to the requirement for shorter time-steps when integrating the solution forwards in time, and so to an increased overall number of integration steps and longer total simulation time (Hamdi et al. 2001).

The generation of a differential capacitance curve from equilibrium data, for example, may require upwards of 60 individual runs, so small changes in the number of grid points can be significant to the total run time, meaning that larger numbers of grid points were impractical. Furthermore, adding species to the system, as either reaction products or supporting electrolyte, increases the number of equations to solve at each grid point, leading to significantly longer simulation times. In such cases, having more than about 2000 grid points overall was found to lead to simulation times on the order of days.

In practice, to reduce the number of grid points further, more than three sub-domains were used, although the specific number was varied depending on the total domain length. While the number of regions was variable, the grid spacing in each region was fixed, so for a domain of a particular length, there were typically a certain number of whole regions and one fractional region. Since the number of grid points in the fractional region has to be an integer, the domain length could only grow in discrete intervals, although the size of the jumps was small in comparison to the overall length of the domain. Table 4.1 sets out the details of the first seven regions, where region one (or zero) starts at \( z = 0 \).

The first sub-domain, denoted as region one, had a length of \( 4l_B \), covering the region with the steepest function gradients, and a grid separation of \( \Delta z = 0.02l_B \). However, when the electrolyte was described by the GC model, the first region was split, allowing a tighter grid spacing to be used in the first \( 1l_B \) (denoted as region zero) to cover the much steeper gradients which arise in this region for that model, leaving region one with a reduced length of \( 3l_B \). For domains longer than the \( 500l_B \) which the above Table 4.1 covers, further sub-domains were added with increasingly sparse grid spacings. These are not listed as the exact values depended
Table 4.1: Detail of the grid spacing close to the left boundary at $z = 0$

<table>
<thead>
<tr>
<th>Region</th>
<th>Length ($l_B$)</th>
<th>Number of grid points</th>
<th>$\Delta z$ ($l_B$)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(1)</td>
<td>200</td>
<td>0.005</td>
<td>GC model only</td>
</tr>
<tr>
<td>1</td>
<td>4 (3)</td>
<td>200(150)</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>50</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>60</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>16</td>
<td>64</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>100</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>130</td>
<td>65</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>240</td>
<td>60</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

on the total domain length. The total number of grid points as a function of the total domain length is shown in Fig. 4.7. The line shows discrete regions of linear growth between a set of discontinuities. The numbers at each discontinuity refer to the total number of sub-domains used as the domain length increases beyond that point. In brackets, the grid spacing of the right-most sub-domain (the one which grows to increase the total domain length, measured in $l_B$) is shown. The discontinuities in the line indicate that either the number of sub-domains has been increased or that the grid spacing in the right-most domain has been increased while maintaining the same number of sub-domains.

![Graph](image)

**Figure 4.7:** Number of grid points as a function of the domain length. Inset shows the same data in the short length region

This particular set of values was used on the grounds that it resulted in a sufficiently small error (since only the sub-domain at the boundary affects the errors at equilibrium) yet short run times could be maintained.

### 4.5.2 Error in the equilibration time

The particle fluxes are dependent on the gradients of the concentration and potential and, since the accuracy of these depends on the grid spacings, the dynamics of the system also depend on the grid spacing. The easiest way to look at the extent of the deviations is to look at how
long the model predicts the system will take to reach equilibrium when a constant potential is applied to the electrode.

As seen in the previous section, the grid spacing affects the actual values of the functions at equilibrium, so the equilibrium point changes depending on the grid spacing. Because of this, the equilibration time cannot be measured by running the system until an analytical (or iteratively solved) solution is found, because the numerical approximation may never reach that value due to the errors in the equilibrium result. To calculate the equilibration time for each grid spacing, a suitable electrode/electrolyte system was defined and two runs were made. In the first, the model was run for a sufficiently long time that equilibrium was reached, while in the second the system was re-run but stopped once it reached 99.999\% of the equilibrium value (later, the equilibrium point is defined as 99.9\% of the equilibrium value, but the higher fraction is used here to demonstrate the error more clearly).

Using the system of sub-domains and grid spacings outlined in Table 4.1, a series of domain lengths and bulk concentrations was tested. The mvdW model was used to include an ion diameter of 0.2 nm in all cases. Shown in Fig. 4.8 (a) is a plot of the predicted equilibration time as a function of the number of grid points in each of the first three regions for the 300\,\text{B}, 0.01\,\text{M} case, while part (b) of the same figure shows a log-log plot of the relative error as a function of the grid spacing in the region adjacent to the left boundary.

![Figure 4.8](image_url)

Figure 4.8: (a) equilibration time as a function of the number of grid points in the first, second and third sub-domains, (b) log-log plot of the relative error as a function of the grid spacing in the first sub-domain. $c_{\text{bulk}} = 0.01\,\text{M}$ and $L = 300\,\text{B}$.

The equilibration time clearly converges as a function of the grid spacing in the first region but is largely unaffected by the spacings in the second or third regions. Increasing the number of grid points in the second region has a small effect, but the relative difference between the lowest and highest grid spacings is less than $10^{-3}\%$. Regression analysis on the log-log plot shows that the rate of convergence is proportional to $\Delta z^{2.16}$, approximating to the value of $\Delta z^2$ which would be expected. The differences arise in part because of the rounding error in the output, which leads to there being no distinction between the equilibration times of the systems with 1000 and 1200 grid points. Despite this, the relative difference between the lowest and highest grid spacings in region one is only 0.03\%, so it is apparent that, in this case, the errors in the dynamics are sufficiently small provided the grid spacing is set such that the error in the
equilibrium value is small. This order of error was typical throughout all the systems tested, with changes to the domain length and bulk concentration being found to have little effect on the error in the equilibration time, which remained of the order of 0.03% or smaller.

### 4.5.3 Error when using a time-dependent potential

As with the equilibration time, the number of grid points affects the output when a time-dependent potential is applied. For such a system, the application of a sine waveform at the electrode surface results in a series of peaks and troughs in the surface charge density as a function of time of the type shown in Fig. 4.9. The test system had a potential amplitude of $\beta e_0 \Delta \phi = 10$ and frequency of $f l_B^2 / D_e = 10^{-9}$, with a domain length of 5000Å and bulk concentration of 1 M and, as with the previous tests, the number of grid points in each of the first three sub-domains was independently increased.

The figure shows the surface charge data for all sets overlaid on each other, and the inset shows a magnification of the second peak. The legend refers to the number of grid points in the first sub-domain.

![Figure 4.9: Effect of the number of grid points on the surface charge density for a time dependent applied potential. Inset magnifies the second peak of the main curve. See text for details.](image)

No differences can be observed in the main figure and from the inset there are only four distinct lines, one corresponding to each of the grid spacings in the first sub-domain — all other curves are indistinguishable from these four. The actual change in the output as a function of the grid spacing is very small.

In general, a reduction in the number of grid points causes the amplitude of the output to increase, so in the inset the highest peak corresponds to the lowest grid spacing. From this plot it is clear that the system converges, with the point of convergence being very close to the lowest curve. Assuming that the 800 grid point curve corresponds to the converged value, the use of 200 grid points in the left-hand sub-domain introduces a relative error of 0.3%, an acceptably small value for the large reduction in simulation time which results. As with the error in the equilibration time, the errors for fully dynamic systems as a function of factors such as the bulk
concentration, domain length or amplitude and frequency of the applied potential had some effect on the error, but this was small. In all cases, the error was below 1% and, for most cases, equal to or smaller than the 0.3% seen for this system.

There were two other problems which arose with setting the grid spacing which played a significant role in determining the actual grid values used, beyond the need for sufficiently high accuracy and low simulation time. First was that increasing the number of grid points too much in any one domain led to the simulation slowing significantly, beyond the quadratic growth in the time which might be expected to result, or else stopping entirely, without returning an error code. The frequency with which this occurred increased as the number of grid points increased or the relative and absolute tolerances for the solver code was reduced. This is thought to be linked to a known feature of the MOL, whereby a smaller spatial grid separation leads to the need for a shorter temporal step length and thus more simulation steps between each output time step.

Second, as described previously the IDA solver routine returns solutions at user-defined time values, but internally it uses a shorter step length to minimise the error. The maximum number of internal steps between two output times is user-defined, and if the limit is reached an error is usually returned. However, in the instances described above, no error message was returned and yet neither was a solution. It was found that reducing the number of grid points, increasing the tolerance values or increasing the size of $D^c$ (effectively reducing the size of the time step in the simulation) resolved the problem.

4.6 Summary

In this chapter the means for solving the equations developed in Chapter 3 were described and the errors inherent in that method discussed. The method of lines was applied to the system, whereby the spatial dependence of the model equations was discretised, using a second-order centred differencing scheme, resulting in a series of coupled differential-algebraic equations. These were solved by numerical integration, using the IDA routine in the SUNDIALS software library, which was incorporated in to a C++ code developed by the author of this work.

The errors in numerical solution were shown to vary as the square of the grid spacing, as expected given the discretisation scheme used. However, the total length of the system which it is possible to simulate was shown to be limited by the requirement of a small grid spacing near the electrode. To resolve this, a means for dividing the domain in to several sub-domains, each with different grid spacings, was described. The total error in the numerical solution was shown to strongly depend on the grid spacing at the domain boundary representing the electrode surface, but to show little dependence on the spacing in the other sub-domains. On the basis of this, the structure of the domain in terms of the lengths and grid spacings in each of the sub-domains was described.
Chapter 5

Equilibrium systems

In this chapter, the effects of the excluded volume interaction and the excess ion polarisability on the equilibrium properties of an electrode/electrolyte system are discussed. Where appropriate, comparison is made to the GC and GCS models as well as between the three excluded volume models presented in Chapter 3, although the main focus is on the mvdW model which, along with the polarisability interaction, is also compared to experimental data. In general it will be shown that the mvdW model is capable of providing improved predictions for the physical and electrical properties of these systems relative to the GC or GCS models, while the inclusion of the ion excess polarisability results in further improvements over other models which only account for excluded volume interactions.

The bulk of the chapter focuses on single electrolyte systems, looking at the effects of the excluded volume and polarisability terms individually. The double layer structures in both cases are shown to consist of monotonically varying concentrations of the co- and counter-ions, in common with other mean-field models, and the electrostatic potential is likewise shown to vary monotonically with distance from the electrode. Given the simplifications introduced through the use of the MF-LDA, the predictions in terms of the double layer structure are limited to some extent (for example charge layering and overcharging do not feature) but the externally measurable electrical properties can be modelled reasonably accurately for single electrolytes, using only the Stern layer as a fitting parameter, as will be demonstrated using experimental data.

The latter part of the chapter looks at mixed electrolytes and how relative difference in the sizes and polarisabilities of the ions in such systems alters the overall structure of the double layer. This has not previously been considered for the polarisability interaction and it is shown that this, combined with the alternative model for the excluded volume, leads to some improved agreement between the model and experimental data, compared to models which do not account for the polarisability.

The first section of the chapter considers the effect of the ion volume and polarisability, both in isolation and for systems in which both terms are accounted for. In Section 5.2, the behaviour of the system as the bulk concentration changes is looked at and then in Section 5.3 the effect of Stern layer is considered. In these sections, a new analytical expression is developed for the
differential capacitance at the PZC which qualitatively explains observed experimental trends. Following this, in Section 5.4, comparison is made to experimental data. In Section 5.5 the trends in the behaviour of the model system at high potentials are considered and in Section 5.6 the model is used to look at mixed electrolytes. The final part of the chapter summarises the main points.

5.1 The impact of ionic interactions

The full model as defined in Chapter 3 adds three parameters to those which define the GC model, namely the ion diameter, the ion polarisability and the Stern layer width. The impact of the Stern layer is well known in the absence of the other two properties, causing the differential capacitance to converge at high potentials while significantly reducing the number density of ions in the double layer compared to the GC model. Within the context of this work, the Stern layer is shown to be effective as a fitting parameter linking the model to experimental data, so it is generally used only in that way. The remaining two parameters are of more interest in terms of how they define the behaviour of the system.

The main excluded volume interaction model of interest in this work is the mvdW model, characterised by the excess chemical potential stated in Eq. (3.23), although comparison will be made in places to both the Bikerman and BMCSSL models for reference. The model provides a slightly simpler means to account for different ion sizes compared to the BMCSSL model and is a clear improvement over the Bikerman model, in which only one ion size is possible.

Some of the effects of ion polarisability on the double layer structure have been discussed previously in the work of Hatlo et al. (2012), along with similar models proposed by Ben-Yaakov et al. (2009; 2011). This section recapis some of these effects as they are of relevance to later discussions. In summary, subsection 5.1.1 examines the influence of the ion size on the double layer structure, then subsection 5.1.2 discusses the effect of the polarisability term. Finally, subsection 5.1.3 contains a comparison of the two terms and details of how they interact when both are accounted for.

5.1.1 The ion volume

Here, the influence of ion size on the structure of the electric double layer is examined. As a general introduction to the types of structures predicted by the mvdW (and all MF-LDA models), Fig. 5.1 (a) shows the counter-ion and co-ion concentrations as functions of the position for a selection of surface potentials, while the dependence of the potential itself on the position is shown in Fig. 5.1 (b). The electrolyte used in the example is a binary, symmetric, 1:1 electrolyte of 0.6 nm diameter ions with a bulk concentration of 0.01 M. As with all the systems discussed in this work, the solvent is water at 298 K, with a relative permittivity of 78, meaning the Bjerrum length $l_B$ is approximately equal to 7 Å.

Structurally, moving from the bulk at high $z$ to the electrode surface sees an increase in the concentration of counter-ions and a reduction in the concentration of co-ions, with both proper-
ties varying monotonically. A saturation of the counter-ion concentration at the electrode surface for the highest potential curves can be made out. This is the result of the excluded volume interaction, which defines the maximum concentration for this system to be $\bar{c}^{\text{max}} = 1/\bar{a}^3 = 1.7$ (where $\bar{a}$ is the dimensionless ion diameter). This saturation represents the fundamental difference between this and the GC model and leads to a widening of the double layer at high potentials. Although it is structurally different, the width of the double layer remains of the order of the Debye screening length, $\lambda_D$, calculated from Eq. 2.6 as

$$\lambda_D = \frac{1}{\kappa} = \left(4\pi l_B \sum_j z_j c_j^0\right)^{-1/2}$$

(5.1)

For this particular system, $\lambda_D \sim 4 l_B$. From the figures above it can be seen that most of the drop in the concentration and electrostatic potential is contained within this distance from the electrode surface.

The total charge density in the double layer is the sum of the co- and counter-ion charge densities. The removal of co-ions from the electrode region has the same effect on the charge as adding counter-ions. However, since most of the counter-charge comes from the increase in the counter-ion concentration rather than the removal of co-ions, it is the counter-ion concentration which predominantly defines the behaviour of the system. For this reason, throughout the remainder of this work, the double layer structure is almost always described in terms of the counter-ion concentration profiles. Fig. 5.2 shows a plot of the counter-ion concentration at the surface of the electrode against the potential as predicted by the three excess chemical potential terms introduced in Chapter 3. The hypothetical electrolyte is one in which there is no Stern layer, the bulk concentration is 0.01 M and the diameters of the ions are $a_1 = a_2 = 0.6$ nm.

In contrast to the GC model (the dashed curve in the figure), all mPB-theory curves converge on some maximum value, with the mvdW and Bikerman maximum values being equal and the BMCSL value being larger, due to differences in the way the excluded volume is calculated. Over much of the potential range shown, and in particular for potentials smaller than $\bar{\phi}^0 = 20$, which are the main area of interest for most of this work, the surface concentrations are
Figure 5.2: Comparison of the counter-ion surface concentration in the GC, Bikerman, BMCSL and mvdW models for a 0.01 M electrolyte with 0.6 nm diameter ions comparable in all three models. At very low $\theta^0$, in the range of validity of the GC model, all three mPB models show the same growth rate in $c(0)$. Once the concentration becomes large enough for crowding to have an impact, differences arise. The excluded volume interaction in the Bikerman model is much smaller for lower occupied volume fractions but grows rapidly as $\eta \to 1$ (see Fig. 3.3), which is reflected in the surface concentration being similar to the GC model over a wider potential range but converging much more rapidly than the other two models. The mvdW model, for which the excess energy is slightly larger at lower occupied volume fractions and does not have quite as rapid a divergence as $\eta \to 1$ shows a slower growth in the surface concentration and much more gradual convergence on it maximum. Finally, the BMCSL model, with the largest excess energy at lower occupied volume fractions both grows and converges at the slowest rate.

At equilibrium, the structure is defined by the fact that the electrochemical potential is constant in space, which means that throughout the double layer its value is equal to that in the bulk. An applied electrostatic potential lowers the energy of the counter-ions, allowing them to crowd, which causes an increase in the ideal gas and excess chemical potential terms. Equilibrium is achieved when these latter two terms balance the reduction in the energy due to the applied potential. Similarly for the co-ions, the applied potential increases their energy, and it is only by reducing their concentration relative to the bulk that the electrochemical potential may become constant in space and reach equilibrium.

The ideal and excluded volume contributions to the electrochemical potential ($\mu_{id}$ and $\mu_{ex}$ respectively) of the counter ions at the surface of the electrode are plotted in Fig. 5.3 as a function of the applied potential, using the mvdW model with two different ion diameters (0.6 nm and 0.8 nm) and a bulk electrolyte concentration of 0.01 M. It can be seen that for low potentials, when the surface concentration is low, the ideal term accounts for all of the growth in the energy balancing the electrostatic potential. However, the logarithmic dependence of this term would require the concentration to increase exponentially with the potential in order to balance it, and
this is clearly unrealistic. On the other hand, the excess term only requires a small increase in the concentration to grow very rapidly, as at higher potentials all growth in the balancing energy comes from the excess term. The potential at which the excess term begins to dominate is lower for larger ions, since the occupied volume fraction at a given concentration is larger.

Figure 5.3: Ideal and excluded volume components of the surface electrochemical potential in the mvdW model for a 0.01 M electrolyte with ion diameters of 0.6 nm (solid lines) or 0.8 nm (dotted lines)

The onset of the growth in the excess term at the electrode surface clearly does not mean that it dominates throughout the double layer. Instead, it makes a contribution very near to the electrode surface and vanishes rapidly with distance as the concentrations return to the bulk value (unless, of course, the bulk concentration is large). This is shown in Fig. 5.4 (a), in which the components of the electrochemical potential ($\mu_{id}$ in black, $\mu_{ex}$ in red and $\mu_\phi$ in green) are plotted as functions of the distance from the electrode at a selection of potentials, each of which is represented by a different line style.

Figure 5.4: (a) Components of the electrochemical potential in the mvdW model for $a = 0.6$ nm ions at potentials of $\phi = 1$ (solid lines), $\phi = 7.5$ ($\phi(C^{max})$) (dashed lines) and $\phi = 20$ (dash-double-dot lines) and (b) counter-ion profile at an applied potential $\phi = 5$ (solid lines) and $\phi = 20$ (dotted lines).
As mentioned above, the system is at equilibrium when the electrochemical potential throughout the domain is constant. In the figure, the sum of each component at each position is equal to the value of $\mu_j$ in the bulk or, equivalently, the sum of the positive components of the electrochemical potential ($\mu^{id}$ and $\mu^{ex}$) are equal in magnitude to the negative component ($\mu^{\phi}$). The excess term in part (a) of the figure can be seen to be significant only for $\bar{z} < 1$ and is only non-zero for the two larger applied potentials. At distances greater than $\bar{z} = 1$ from the surface, the local electrostatic potential energy is almost entirely balanced by the ideal term, so the electrolyte essentially behaves in an ideal manner in this region.

The plots in part (b) of the previous figure are the predictions of the double layer structure for each of the three excluded volume models at low and high potentials, together with the structure given by the GC model. At the lower of the two potentials the differences between the models are small, although it is clear that the stronger steric repulsion in the BMCSL model leads to lower concentrations. The differences are clearer at the higher potential. As well as having the largest surface concentration (excluding the GC model), the Bikerman model predicts a narrower but “squarer” double layer than the other models, but its shape shows that it contains more ions (i.e. the area beneath the curve is larger). In contrast, the BMCSL model has a lower concentration at the surface but decreases more slowly, making the double layer wider than predicted by the other models, although it contains the fewest ions. For the mvdW model at the potential shown, the concentrations and width of the double layer sit between each of the other two mPB models.

The shapes and numbers of ions predicted by the models are significant because they relate to the differences in the predicted electrical properties of the system, which can be measured. In all three models, the same potential drop occurs over the double layer. The distance over which the potential returns to the value in the bulk is dependent on its gradient, which is in turn dependent on the local charge density. If the local charge is larger (assuming no other properties change), the electric potential gradient is steeper and so the potential reaches the bulk value more quickly, explaining why the BMCSL double layer is wider than the mvdW double layer, and both are wider than the Bikerman double layer.

In addition to causing the width of the double layer to increase, the lower potential gradient at the electrode surface means that the surface charge density, $\sigma$, is also smaller, according to Eq. (3.79a). This feeds back in to the double layer structure because the electrode/electrolyte system must be neutral overall, so a smaller $\sigma$ means fewer ions in the double layer, also contributing to the differences in the double layer widths. As seen in Chapter 2, the effect of limiting the ion concentrations on the electrical properties of the system are significant, preventing the divergence of $\sigma$ with the applied potential, as demonstrated in Fig. 5.5 for the same hypothetical electrolyte system used above.

As with the surface concentrations, all models follow the GC model at low potentials which is again reasonable due to its validity in that region. As the increased concentration leads to ion crowding, there is an inflection point as the $\sigma$ curves move from exponential growth to convergent growth. As expected from the predicted double layer structures of the models, the
mvdW model predicts less charge than the Bikerman model and the BMCSL model predicts less than both other models. While the surface charge density is most easily accessible from the model, the differential capacitance, $C_d$, is more commonly measured experimentally and it also makes most clear the effect of the excluded volume interaction, as can be seen in part (b) of Fig. 5.5. The inflection point in the $\sigma$ curves manifests as a peak in $C_d$, which is typical for measured differential capacitance curves and something which cannot be predicted by the GC model.

The differential capacitance curves give an indication of the onset of crowding within the double layer, since it is these which limit the growth in $\sigma$, resulting in the peak and subsequent decrease in $C_d$ as the potential increases. Furthermore, the relationship between the differential capacitance and the double layer width stated in Eq. (2.8), namely that the width is inversely proportional to $C_d$, remains valid, meaning that the decrease in $C_d$ corresponds to a thickening of the double layer. Thus, the double layer behaves as a capacitor, but one in which the “plates” move further apart as the potential causes ion crowding and the double layer widens. It is this which causes the reduction in the differential capacitance.

Compared to the other two models, the significance of the mvdW model is that the peak in the differential capacitance is lower than the Bikerman model, which is too large when compared to experiment (Bazant et al. 2009), but that the rate of decay at higher potentials is slightly larger than the BMCSL model, which is too low (Bazant et al. 2009) (also see Fig. 5.25). While the mvdW and Bikerman models appear to converge, the former decays at a slightly faster rate than the latter and the lines cross, although the difference between them remains small.

In terms of the effect of varying the ion size, the general trends in the surface charge density and differential capacitance predicted by the mvdW model are summarised in Figs. 5.6(a) and (b). At the PZC the size of the ion has no effect and all curves converge identically on the GC solution. This is not simply a result of the low concentration used in the example or a unique feature of the mvdW model, but is rather a general consequence of the excluded volume interaction, as will be discussed further later.

Away from the PZC, the slower increase in the surface charge density with the potential at
higher ion volumes is a result of the fact that, for a particular ion concentration, the occupied volume fraction is larger for larger ions. As a result the excluded volume component of the electrochemical potential is larger and so increases to the concentration are more restricted. Because of this, there is a lower charge density as a function of the position in the electrolyte and so there is a lower potential gradient and a lower surface charge density. In terms of the differential capacitance, this manifests as $C_d$ being smaller at all potentials and also as a shift to lower potentials of the peak value.

### 5.1.2 Ion polarisability

As with accounting for the ion volume, the effect that the ionic excess polarisability has on the electrochemical potential has been shown to alter the double layer structure. If the polarisability is negative, as for most ions in water, this increases the energy of the ions and prevents ion crowding (Hatlo et al. 2012). For such systems, the polarisability energy leads to similar effects on the structural and electronic properties of the double layer, even in the absence of steric effects, although there are certain differences which arise due to the effect the ions have on the permittivity of the solvent.

In general, accounting for the polarisability leads to similar double layer structures as the excluded volume interaction, in that the concentration curves are monotonic and there is a saturation of the concentration with increasing potential, as demonstrated by Figs. 5.7(a) and (b), which both describe a 0.01 M binary, symmetric, 1:1 electrolyte with the stated ion polarisabilities and no excluded volume interactions.

Again, at low potentials, the concentration profiles and surface concentrations are similar to the GC model, but unlike the GC model they reach a maximum at higher potentials. The actual value on which the concentration converges is a function only of the bulk solvent permittivity and the ion excess polarisability, specifically taking the value $c^{\text{max}} = -\epsilon_w/8\pi\alpha$ (Hatlo et al. 2012). For polarisabilities larger than about $4\pi\alpha = -4 \, \text{M}^{-1}$, at which $c^{\text{max}} = 9.75 \, \text{M}$, the maximum concentration becomes comparable to that which results from accounting for the
ion volume. By comparison, a spherical hydrated ion of radius 0.6 nm has a maximum concentration at close packing (with packing fraction 0.74) of about 11 M. The similarities and differences between the effects of the excluded volume and polarisability will be discussed in more detail in the following section.

It can be seen from Fig. 5.7(a) that, as happened with the excluded volume, once the concentration at the surface nears the maximum allowed value, there is a thickening of the double layer. Again, this thickening is indicative of the differential capacitance decreasing above a certain potential, as shown in Fig. 5.8 (a). As with the excluded volume interaction, increasing the polarisability (i.e. reducing the maximum concentration) causes the peak in the differential capacitance to become smaller and occur at a lower potential.

Figure 5.7: Effect of increasing ion polarisability on the double layer structure: (a) the counter-ion concentration profile at potentials of $\bar{\phi} = 5$ (solid lines) and $\bar{\phi} = 20$ (dashed lines) and (b) the surface concentration as a function of potential.

Accounting for the ion polarisability has two main effects, these being a reduction in the solvent permittivity (see Fig. 5.8 (b)) and an increase in the energy of an ion as a function of the magnitude of the electric field. The reduction in the permittivity is a direct result of the increase
in the ion concentration, which in turn depends on the applied potential. In the same way as for the excluded volume interaction, the applied potential decreases the energy of the counterions and allows an increase in the concentration. At equilibrium this is balanced by the ideal gas term plus the polarisability term, provided $\alpha_j$ is negative. This can be seen in Fig. 5.9 (a), which shows the ideal, electrostatic and polarisability contributions to the total electrochemical potential for an electrolyte whose ions have an excess polarisability of $4\pi\alpha = -4\ \text{M}^{-1}$ at three different applied potentials. As with the similar data for the excluded volume interaction (Fig. 5.4), the electrostatic component, $\mu^\phi$, is balanced at all positions by the sum of the ideal component, $\mu^\text{id}$, and, in this case, the polarisability component, $\mu^\alpha$.

![Figure 5.9](image)

Figure 5.9: (a) Components of the electrochemical potential for $4\pi\alpha = -4\ \text{M}^{-1}$ polarisability ions at potentials of $\phi = 1$ (solid lines), $\phi = \phi(C_{\text{max}})$ (dashed lines), $\phi = 10$ (dotted lines) and $\phi = 20$ (double-dash-dot lines). (b) contributions of the ideal gas and excess polarisability terms to the electrochemical potential at the electrode surface for ion polarisabilities of $4\pi\alpha = -4\ \text{M}^{-1}$ (solid lines) and $4\pi\alpha = -8\ \text{M}^{-1}$ (dashed lines)

The polarisability term is small at low potentials, because the electric field is small, but grows to be dominant as the electric field grows. Near to the electrode surface, where the electric field is largest, the polarisability dominates the positive components of the energy balance, preventing an increase in the ideal term and thereby preventing the concentration from increasing beyond the maximum for the system.

The growth in the polarisability contribution to the total ion energy at the surface as a function of the potential is shown in part (b) of the above figure. The trend is the same as for the excluded volume term: the ideal gas term accounts for most of the increase in the total energy at low potentials and the polarisability term dominates at high potentials. Again, the latter term increases rapidly without a significant increase in the concentration, so the growth in ion numbers is heavily suppressed. At high potentials the result is that a maximum ion concentration is reached, producing an increase in the width of the double layer and hence a reduced growth rate to the surface charge density, causing the familiar peaked differential capacitance curves.

However, the situation is slightly more complex when modelling the polarisability compared to the excluded volume, because the permittivity of the electrolyte changes, as seen in Fig. 5.8 (b). This changes the screening length of the electrolyte and further affects the surface charge...
density as a result of Eq. (3.79a). The effect of reducing the permittivity is to allow larger electric fields for the same local charge density in the electrolyte. Hence the electric field initially grows more quickly than it would if the permittivity were constant, as can be seen in Fig. 5.10 (a). According to Eq. (3.79a) this should cause the electrode surface charge density to increase more quickly as the applied potential increases. However, the direct effect of the permittivity in that equation more than offsets the increased field as its value is significantly reduced over the same potential range, as shown in Fig. 5.10 (b).

![Figure 5.10: (a) Electric field at the surface as a function of the potential for a range of ion polarisabilities and (b) the variation in the surface permittivity as a function of the potential](image)

The surface permittivity varies little at low potentials, but then undergoes a region of rapid decrease before stabilising at half the permittivity of the pure solvent bulk phase. The fact that the permittivity is so much lower at higher potentials is the reason that the differential capacitance curves decrease much more steeply above the peak in the polarisability model than in the excluded volume models. In addition to the field growing more slowly with the potential because of the thickening of the double layer, the lower permittivity means that less charge is added for the same increase in the applied potential. It is also the reason for the differences between the effects of the polarisability and excluded volume models which will be explored in the following section.

There is one final point to note about the range of validity of the polarisability model, in that the $|\phi'|^2$ dependence in the electrochemical potential is only strictly valid for electric field strengths lower than about $0.25 \text{ V nm}^{-1}$ (Gavryushov and Linse 2003). As can be seen from Fig. 5.10 (b), the corresponding potential range over which the model is valid depends on the specific value of the permittivity, with lower values leading to larger electric fields at a given potential, and therefore a lower maximum potential. As a general rule, the maximum applied potentials considered in this work are about $\phi = 20$ ($\approx 0.5 \text{ V}$). While this does move the system out of the range of validity if only the polarisability term is considered, it will shortly be shown that the excluded volume term forces smaller electric fields, extending the potential range over which the polarisability model can be used when both properties are accounted for.
5.1.3 Comparison of the polarisability and excluded volume terms

Both the polarisability and excluded volume terms define a maximum concentration, and these maxima are similar for typical values of each property, so the question arises as to what differences are manifest when the maximum concentrations of two systems are the same but one maximum is due to steric effects and the other is due to the polarisability term. Shown in Fig. 5.11 is a plot of the maximum concentration as a function of the excess ion polarisability and the ion diameter.

![Graph showing the relationship between maximum concentration and ion diameter/polarisability](image)

Figure 5.11: Dependence of the maximum concentration on the ion diameter (black curve) and the polarisability (red curve)

The hydrated radius of many ions is in the region of $0.6 < a < 0.8 \text{ nm}$ (Nightingale 1959) while, as can be seen from Table 2.1, the polarisability for monovalent ions is usually smaller than $4\pi\alpha = -10 \text{ M}^{-1}$ (Hasted et al. 1948). Over this range of ion sizes and polarisabilities, either term can define the maximum concentration and it is in principle possible for an ion to have values of $a$ and $4\pi\alpha$ which yield the same maximum concentration. For the purposes of this section two hypothetical systems are compared: system one in which the maximum concentration is 9.5 M and system two in which it is 4.8 M. For the excluded volume interaction these maximum concentrations correspond to ion diameters of $a \approx 0.55 \text{ nm}$ and $a \approx 0.7\text{ nm}$ respectively, while for the excess polarisability term they correspond to polarisabilities of $4\pi\alpha = -4 \text{ M}^{-1}$ and $4\pi\alpha = -8 \text{ M}^{-1}$. For each system two cases are considered, one in which $c_{\text{max}}$ is defined by the excluded volume and the other in which it is defined by the polarisability. Plotted in Fig.5.12 are the differential capacitance curves for the four resulting cases, assuming a bulk ion concentration of 0.01 M.

At this low concentration, all cases behave similarly at low $\phi^0$, although $C_d$ is slightly smaller in the polarisability model, as will be discussed further in the following section. For each maximum concentration the pairs of curves exhibit very similar peak values of $C_d$, but those peaks occur at a lower potential in the polarisability model. Additionally, the peak is broader and the decay of the curve at higher potentials much more gradual in the excluded volume cases. It appears that for lower concentrations the peak in the differential capacitance is defined by the
Figure 5.12: Comparison of the differential capacitance curves for two systems with the same $c_{\text{max}}$, one due to the volume of the ions and the other due to the polarisability. Solid lines $c_{\text{max}} = 9.5 \, \text{M}$, dashed lines $c_{\text{max}} = 4.8 \, \text{M}$

maximum concentration rather than by the ion property which gives rise to that maximum, although differences do arise at higher concentrations, as will be discussed in Section 5.2.

The differences between the curves relate to how the excluded volume and polarisability energies change with the applied potential. Plotted in Fig.5.13 (a) are the contributions each makes to the electrochemical potential at the electrode surface for systems one and two, with the solid lines referring to the excluded volume interaction energies and the dashed lines referring to the polarisability energies. Shown in part (b) of the figure are the surface concentrations of the counter-ions in each case.

Figure 5.13: (a) Components of the surface electrochemical potential and (b) Surface concentration as a function of the potential. See text for details

In all four cases the ideal terms are limited, as expected, but within each system there are slight differences between the way that the excluded volume and polarisability energies change with the applied potential. While each pair of curves converge at high potentials, the excluded volume term grows slightly more quickly at low potentials and converges less quickly on the linear high potential growth than does the polarisability term. The more rapid switch that the
latter term makes from having little impact on the total energy to accounting for all of the total growth accounts for the difference in the way in which the surface concentration approaches the maximum. The initially weaker effect of the polarisability term means that the surface concentration more closely follows the exponential growth seen in the GC model, while the rapid growth in the polarisability energy at about $\bar{\phi} = 6$ causes the surface concentration to rapidly converge. The excluded volume interaction, by comparison, resists an increased concentration much more strongly at lower potentials and converges on the maximum at a much slower rate. Since the concentration is larger at lower potentials in the polarisability-only case, the total counter charge in the double layer is larger than in the excluded-volume case and so the surface charge density grows more quickly. However, once the maximum surface concentration is reached, the double layer has to increase in width, leading to the appearance of the peak.

At potentials above the peak in $C_d$, the double layer environments of the two systems are very different. While the surface concentrations of each are the same, the permittivity in the double layer differs, resulting in large differences in the the electric field and surface charge densities. This difference is the reason for the very different high-potential behaviours of the two cases in each system. Fig.5.14 (a) shows the electric field at the electrode surface for the four cases in question and, adjacent to it, are plots of the surface charge densities.

![Figure 5.14](image-url)

Figure 5.14: (a) Surface electric field and (b) Surface charge density as a function of the potential. In both figures solid lines correspond to $c_{\text{max}} = 9.5\,\text{M}$ and the dashed lines correspond to $c_{\text{max}} = 4.8\,\text{M}$

In the polarisability-only case the electric field is always larger, initially growing more quickly with the potential than it does in the excluded volume-only case. As seen in the previous section, the field initially grows more quickly than predicted by the GC model because of the slight drop in the local permittivity, something which does not happen when only steric effects are accounted for. However, this larger electric field does not translate into a larger surface charge density at high potentials, again because of the fact that the permittivity is so much reduced.

Having shown that the excluded volume and polarisability interactions both lead to the correct qualitative predictions for the shapes of the differential capacitance curves, it is evident that the shapes will be correct for a more realistic model system in which the ions have both a volume and a polarisability. The difference is in the specific values of the differential capacitance,
which are lower than when only one of the terms is accounted for. This follows from the fact that the applied potential energy is balanced by contributions from both the excluded volume and polarisability terms, meaning that the counter charge in the double layer grows more slowly.

To demonstrate this, Fig. 5.15 (a) shows the differential capacitance curve for a 0.01 M system with ions of diameter \( a = 0.7 \) nm and an excess polarisability of \( 4\pi\alpha = -8 \) M\(^{-1}\) compared to the two cases in system two, in which the ions have either the same diameter and zero polarisability or the same polarisability and zero diameter.

![Figure 5.15: (a) Differential capacitance when both the volume and polarisability are accounted for compared to when only one or the other is included and (b) breakdown of the contributions to the total surface electrochemical potential for when both terms are included. See text for details](image)

As with earlier plots, the low potential behaviour of the systems should be similar to the GC model predictions at this bulk concentration, but it can be seen that by accounting for both properties the differential capacitance peaks at a lower value, even though the maximum concentration for the ions is the same. With the energy from both the excluded volume and polarisability terms increasing with the applied potential (see Fig.5.15 (b)), the growth in the counter-ion concentration, and hence the counter-charge, is much slower, meaning that the surface charge density grows more slowly. While steric effects dominate the system at lower potentials, it can be seen that the polarisability term grows at a much greater rate at higher potentials. However, with both terms still being significant, the \( C_d \) behaviour at high \( \phi^0 \) of the joint model does not follow either curve exactly, showing a slightly slower decay with the potential than is observed in the polarisability-only case.

This shows that it is not simply whether the polarisability or the excluded volume interaction defines the maximum concentration which defines the behaviour of the system — one may dominate over a certain range and the other over a different range. The fact that the polarisability alters the environment means that they are not directly equivalent and also means that the predictions for the behaviour of the system are qualitatively different, particularly in mixed electrolytes, as will be discussed later.

A final, if self evident, point about real electrolytes is that the drop in the permittivity experienced in the double layer can only reach \( \epsilon_w/2 \) if the polarisability term defines the maximum
concentration. Additionally, the rate at which the permittivity approaches this value is dependent on the size of the ions, as shown in Fig. 5.16. Here, the permittivity at the surface is plotted as a function of the applied potential for systems combining ion diameters of either 0 nm, 0.55 nm or 0.7 nm with polarisabilities of either $-4 \text{ M}^{-1}$ or $-8 \text{ M}^{-1}$.

![Figure 5.16: Surface permittivity as a function of the potential when both the excluded volume and polarisability terms are included](image)

At low potentials the permittivity changes as it does if only the polarisability term is accounted for but, as the potential increases, differences arise. If the maximum concentration is determined by the polarisability term or if the two terms are equal, the permittivity does eventually decrease to half the value of that in the bulk solvent but at a rate which is determined by the size of the ion. However, if the maximum is determined only by the excluded volume term, the decrease in $\epsilon$ is limited, tending to a value of $\epsilon = \epsilon_w - 4\pi \alpha c^{\text{max}}$. In this case, the reduction in the permittivity has an impact on the electrical properties of the system, but the screening length will never change by as much as if the full permittivity drop were to be realised.

### 5.2 Varying the ion concentration

At low concentrations, the differential capacitance curves are characterised by a local minimum at the PZC, rising to a peak at some potential which depends on the value of the maximum concentration, followed by a decrease as the applied potential increases further. However, it is known from experimental data that increasing the bulk electrolyte concentration results in the peak occurring at progressively lower potentials until it coincides with $\phi^0 = 0$.

It has been demonstrated elsewhere (Bazant et al. 2009; Hatlo et al. 2012) that this behaviour is correctly predicted by both the excluded volume and polarisability interactions, but for completeness of this work this is shown again in Figs. 5.17 (a) and (b), wherein the differential capacitance is plotted as a function of the applied potential at several bulk concentrations. In part (a), the solid lines show the model predictions when only the excluded volume term is accounted for, with $a = 0.7 \text{ nm}$, and in part (b), they show the model predictions when only the
polarisability term is accounted for, with $4\pi\alpha = -8\text{ M}^{-1}$. In both parts, the dashed lines show the prediction for when both terms are included for reference.

Figure 5.17: The predicted differential capacitance as a function of the potential at selected bulk ion concentrations. Dashed lines in both figures show the case when both the ion volume and polarisabilities are accounted for (with $\alpha = 0.7\text{ nm}$ and $4\pi\alpha = -8\text{ M}^{-1}$). The solid lines in (a) are for when only the excluded volume interaction is accounted for and those in (b) are for when only the polarisability is accounted for.

In both cases, the systems have the same maximum ion concentration, but two things are evident. The first is that the peak moves to the PZC more slowly when the polarisability term alone is accounted for — when both properties are accounted for the peak reaches the y-axis when the bulk concentration is approximately 0.3 M while it is between 0.5 M and 1 M in the polarisability-only case. In contrast, accounting for the excluded volume interaction alone results in the peak of $C_d$ reaching the PZC at about 0.5 M. The second noticeable feature is that when both the excluded volume and polarisability terms are accounted for, the differential capacitance at the PZC is equal to the value predicted by the polarisability-only case whereas the excluded volume-only case is always larger. In fact, the differential capacitance at the PZC in the excluded volume-only case is always identical to that predicted by the GC model, and it is the polarisability term alone which defines deviations away from this value, as will be shown shortly.

The difference when the polarisability term is included is that the permittivity of the bulk electrolyte is reduced in proportion to the concentration. The reduction means the electrolyte is less able to resist an electric field even at very low field strengths. The result is that an infinitesimal change in the applied potential at the PZC will cause a different response in a system which accounts for the polarisability compared to one in which only the excluded volume is accounted for. Indeed, in the latter case, an infinitesimal change in the applied potential from $\phi^0 = 0$ will produce a response which is independent of the fact the ions have a volume, let alone what that volume is.

Based on the model which has been used to include the polarisability effects it is possible to derive an analytical expression for the differential capacitance at the PZC, the development of which is outlined below.
Analytical model for the differential capacitance at the Point of Zero Charge

There are a number of steps which need to be taken in the derivation of this model, the first of which is to develop an expression for the osmotic pressure difference between the surface and the bulk electrolyte. Starting from the Poisson equation and multiplying through by the gradient of the potential, the following steps can be taken:

\[- \frac{1}{4\pi} [\epsilon(z) \phi'(z)]' \phi'(z) = \sum_l z_l c_l(z) \phi'(z)\]

\[- \frac{1}{4\pi} [\epsilon(z) |\phi'(z)|^2]' - \epsilon(z) \phi'(z) \phi''(z) = \sum_l z_l c_l(z) \phi'(z)\]  \hspace{1cm} (5.2)

Subtracting \(\sum_l \alpha_l c_l(z) \phi''(z) \phi'(z)\) from both sides of the equation and noting from Eq. (3.45) that \(\epsilon_w = \epsilon(z) - 4\pi \sum_l \alpha_l c_l\), the above equation becomes

\[- \frac{1}{4\pi} \left[ \left( \epsilon(z) - 4\pi \sum_l \alpha_l c_l \right) |\phi'(z)|^2 \right]' = \sum_l \left[ -z_l \phi'(z) + \frac{\alpha_l}{2} |\phi'(z)|^2 \right] c_l(z)\]  \hspace{1cm} (5.3)

The system is at constant temperature, so the term on the right is related to the pressure gradient through the Gibbs-Duhem relation to give the following expression, which is exact in the MF-LDA:

\[\frac{1}{4\pi} \left\{ \epsilon(z) - \frac{\epsilon_w}{2} \right\} |\phi'(z)|^2 = p'(z)\]  \hspace{1cm} (5.4)

This leads to the following intermediate result for the pressure difference between a point and the bulk by integrating the above equation with respect to \(z\)

\[\frac{1}{4\pi} \left[ \epsilon(z) - \frac{\epsilon_w}{2} \right] |\phi'(z)|^2 = p(z) - p(\infty)\]  \hspace{1cm} (5.5)

It is now possible to derive a general expression for the differential capacitance, by setting the position to that of the Stern layer boundary and then taking the derivative with respect to the applied potential, \(\phi^0\). Note that because of the way the modelling domain is defined (see Fig. 3.1), the Stern layer boundary is always located at \(z = 0\) and the electrode is located at \(z = -s\). Because of this, the applied potential \(\phi^0 (= \phi(-s))\) should not be confused with the potential at the Stern layer boundary, \(\phi(0)\), although the two have the same value if the Stern
layer width is zero.

\[ \frac{1}{4\pi} \frac{d\epsilon(0)}{d\phi^0} |\phi'(0)|^2 + \frac{1}{4\pi} [2\epsilon(0) - \epsilon_w] \phi'(0) \frac{d\phi'(0)}{d\phi^0} = \frac{dp(0)}{d\phi^0} = -\sum_l \left[ z_l \frac{d\phi(0)}{d\phi^0} - \alpha_l \phi'(0) \frac{d\phi'(0)}{d\phi^0} \right] c_l(0) \]

\[ \frac{1}{4\pi} \frac{d\epsilon(0)}{d\phi^0} |\phi'(0)|^2 + \frac{1}{4\pi} \epsilon(0) \phi'(0) \frac{d\phi'(0)}{d\phi^0} = -\sum_l z_l \frac{d\phi(0)}{d\phi^0} c_l(0) \]

\[ \frac{\phi'(0)}{4\pi} \frac{d}{d\phi^0} [\epsilon(0) \phi'(0)] = -\sum_l z_l \frac{d\phi(0)}{d\phi^0} c_l(0) \]  

(5.6)

At this point Eq. (3.79a) is substituted for both the term in brackets and the \( \phi'(0) \) term on the left, and the derivative of Eq. (3.88) with respect to the boundary potential,

\[ \frac{d\phi(0)}{d\phi^0} = 1 - \frac{4\pi s}{\epsilon_s} \frac{d\sigma}{d\phi^0}, \]  

(5.7)

is used to substitute for the derivative term on the right hand side. The result can then be rearranged for the final expression for the differential capacitance

\[ \frac{4\pi \epsilon(0) \frac{d\sigma}{d\phi^0}}{\epsilon(0) \frac{d\phi(0)}{d\phi^0}} = -\sum_l z_l c_l(0) \left( 1 - \frac{4\pi s}{\epsilon_s} \frac{d\sigma}{d\phi^0} \right) \]

\[ \frac{d\sigma}{d\phi^0} = -\frac{\epsilon(0) \sum_l z_l c_l(0)}{4\pi \sigma \left( 1 - \frac{\epsilon(0)}{\epsilon_s} \frac{d\sigma}{d\phi^0} \right)} = C_d \]  

(5.8)

Eq. (5.8) states the differential capacitance, but in terms of several unknown quantities, so it is not immediately of use, but it is necessary for the aforementioned analytical solution for the differential capacitance at the PZC. At the PZC the modified Poisson equation can be linearised, leading to an analytical solution. From the electrochemical potential, Eq. (3.77), the dimensionless concentration of each species can be written

\[ c_j(z) = c_j(\infty) \exp \left[ -(\mu_j^{ex}(z) - \mu_j^{ex}(\infty)) - z_j \phi(z) + \frac{\alpha_j}{2\epsilon_w} |\phi'(z)|^2 \right] \]  

(5.9)

For small values of \( \phi \), the variation of the concentration with the the potential approximates to

\[ c_j(z) = c_j(\infty)(1 - z_j \phi(z)) \]  

(5.10)

The volumetric electrolyte charge density is \( \rho(z) = \sum_l z_l c_l(z) \) and, from the linearised equation above together with Eq. (3.45), the permittivity can be shown to be constant, taking the same value as it has in the bulk. Thus, the modified Poisson equation can be linearised as

\[ \phi''(z) = \frac{4\pi}{\epsilon(\infty)} \sum_j z_j^2 c_j(\infty) \phi(z) \]  

(5.11)

This has the general solution \( \phi(z) = \exp \left( -\sqrt{\frac{4\pi \sum_j z_j^2 c_j(\infty)}{\epsilon(\infty)}} \right) \) from which it can be seen that
the potential can be expressed in terms of its gradient as follows:

\[ \phi'(z) = - \left[ \frac{4\pi}{\varepsilon(\infty)} \sum_l z_l^2 c_l(\infty) \right]^{1/2} \phi(z) \] (5.12)

The final set of manipulations in the derivation commence with the substitution of Eq. (3.79a) for the potential gradient, after which the derivative is taken with respect to \( \phi^0 \) and Eq. (5.7) is used to rearrange the result:

\[
\frac{4\pi\sigma}{\epsilon(\infty)} = \left[ \frac{4\pi}{\epsilon(\infty)} \sum_l z_l^2 c_l(\infty) \right]^{1/2} \phi(z)
\]

\[
\frac{4\pi}{\epsilon(\infty)} \frac{d\sigma}{d\phi^0} = \left[ \frac{4\pi}{\epsilon(\infty)} \sum_l z_l^2 c_l(\infty) \right]^{1/2} \left( 1 - \frac{4\pi s}{\varepsilon_s} d\phi^0 \right)
\]

\[
\frac{4\pi}{\epsilon(\infty)} = \left[ \frac{4\pi}{\epsilon(\infty)} \sum_l z_l^2 c_l(\infty) \right]^{1/2} \left( 1 \right) \left( \frac{1}{C_d} - \frac{4\pi s}{\varepsilon_s} \right)
\]

\[
\frac{1}{C_d} = \frac{4\pi}{\epsilon(\infty)} \left[ \frac{4\pi}{\epsilon(\infty)} \sum_l z_l^2 c_l(\infty) \right]^{-1/2} + \frac{4\pi s}{\varepsilon_s}
\] (5.13)

From this equation the total differential capacitance can be seen to be the sum of two capacitances in series, much the same as for the GCS model. The second term on the left is the inverse of the Stern layer capacitance, dependent only on the permittivity in the Stern layer and its width as proposed by Helmholtz (see Eq. (2.2b)). The first term is similar to the inverse of the GC differential capacitance, Eq. (2.7), except that now the permittivity is replaced with the polarisability-dependent bulk permittivity as opposed to being the relative permittivity of the pure solvent. The term in brackets is equal to the Debye screening length of the bulk solvent, so the capacitance of the diffuse layer is equal to the product of this length with the effective dielectric constant of the solution.

Although the derivation of this expression commenced with the full electrochemical potential, including the excess term, it can be seen from the final expression that the excess term does indeed have no impact on the differential capacitance at the PZC. This confirms the observation which was made about Figs. 5.17 (a) and (b), wherein only the polarisability term affects the differential capacitance at the PZC because it alters the permittivity of the bulk electrolyte. Plotted in Fig. 5.18 is the variation of \( C_d \) at the PZC as a function of the ion excess polarisability for a selection of bulk concentrations and in the absence of a Stern layer which, although implicitly assumed during the development of the analytical expression, will be dealt with explicitly in the following section.

In part (a) of the figure, three different bulk electrolyte concentrations were considered and
for each concentration the analytical solution was compared to two runs of the full numerical model. In the first run, only the polarisability interaction was accounted for and in the second both the polarisability and excluded volume interactions (with \( \alpha = 0.7 \text{ nm} \)) were included. The three sets of data for each concentration are plotted in the figure so it is apparent that not only is the analytical solution exact, but the figure further confirms that the excluded volume interactions play no role in determining the differential capacitance at the PZC.

At lower concentrations there is little change in \( C_d \) at the PZC over the whole excess polarisability range shown — a range which extends up to some of the larger values measured for di- and tri-valent ions shown in Table 2.1. At higher concentrations there is a significant decrease in \( C_d \) at the PZC right across the polarisability range, however, and so significant deviations from the GC or excluded volume models arise. By holding the polarisability constant and altering the bulk concentration, as shown in Fig. 5.18 (b), it is possible to see the significance of the effect of the polarisability term on \( C_d \) at the PZC for a particular electrolyte species.

In the GC and excluded volume-only models for the double layer, the differential capacitance at the PZC is only a function of the bulk ion concentration, increasing in proportion to \( \sqrt{\sum_j z_j^2 c_j^0} \). It is therefore a monotonically increasing function over the possible concentration range. The polarisability term significantly alters this, causing a peak to appear in \( C_d \) beyond which the differential capacitance decreases with increasing concentration. This trend has been experimentally observed for aqueous solutions of ammonium nitrate and ethylammonium nitrate at mercury electrodes (Ammam et al. 2012) (see Fig. 8 therein). While the curves in that work do not follow the almost semi-circular lines in the above figure, the inclusion of the Stern layer (in the next section) qualitatively improves the shapes of the model curves and it is likely that the excess polarisabilities of the ions in the experiment play a significant role in determining the differential capacitance at the PZC.
5.3 Including the Stern layer

The Stern layer is the last remaining component of the model to be considered for its impact on the structural and electrical properties of the system before moving on to comparing the output with some real systems and then looking at the dynamics. The width of the Stern layer is, in principle, known — it is the point of closest approach of the hydrated ion to the electrode surface, equal to half the ion diameter, $a$. However, it has been shown (Hatlo et al. 2012) that the width of the Stern layer works well as a fitting parameter once ion interactions are accounted for and it is in this context that the term will be used.

The implementation of the Stern layer in the model has the basic effect of reducing the potential at the edge of the modelling domain relative to the applied potential at the surface. The electrolyte responds to the potential at the Stern layer boundary rather than the actual surface potential, so the smaller Stern layer potential means that the double layer which forms is correspondingly smaller. The extent to which the potential drops over the double layer depends not only on its size, but also on the ion-specific properties which are accounted for. Fig. 5.19 shows a plot of the Stern layer potential, $\phi(0)$, as a function of the applied potential $\phi^0$ for systems with only the excluded volume term (black curves, $a = 0.7$ nm) or only the polarisability term (red curves, $4\pi\alpha = -8$ M$^{-1}$), with both of these terms (blue curves) and with neither of them (i.e. the GCS model, green curves). The dotted straight line corresponds to $\phi^0 = \phi(0)$.

![Figure 5.19: Stern layer potential as a function of the surface potential for bulk concentrations of 0.01 M (solid lines) and 1 M (dashed lines). Dotted line represents $\phi(0) = \phi^0$, i.e. the Stern layer width is zero. See text for further details](image)

As has been demonstrated previously using a mPB model with a Bikerman-type excluded volume term (Lou and Yong Lee 2010) and also using Monte Carlo simulations (Fawcett and Smagala 2008), the potential drop across the diffuse part of the double layer (i.e. the potential at $z = 0$ in this model) is larger when the ion volume is accounted for. Additionally, it is shown here that the potential drop is also larger when the ion polarisability is accounted for.
The potential drop over the diffuse part of the double layer depends on the potential gradient/the electric field at the Stern layer boundary, which in turn depends on the local charge density and the permittivity at that point. The electric field grows more slowly over the whole potential range when only the excluded volume interaction is accounted for while, as seen previously, if only the polarisability is accounted for the field initially grows more rapidly but is constrained as the maximum concentration is reached, causing it to grow more slowly. These differences are reflected in the potential drop over the Stern layer, with $\phi(0)$ growing more quickly for the excluded volume interaction case and initially slightly more slowly in the polarisability case, although the growth rate in the latter increases slightly as the applied potential increases.

In keeping with the fact that the reduction in the permittivity results in a larger electric field when the polarisability term alone is accounted for, the Stern layer potential is commensurately smaller than when only steric interactions are modelled. These differences in the Stern layer potential may be relevant when considering reacting systems, since the reaction rate is a function of the Stern layer potential drop.

As mentioned, including the Stern layer effectively changes the potential which acts on the electrolyte. In general, since the Stern layer potential grows at a slower rate than the surface potential, the concentration at $z = 0$ at a particular surface potential is smaller, the amount of counter charge is smaller and therefore the surface charge density is smaller. The extent of the reduction differs depending on the ion properties accounted for and their values and the properties of the system. Shown in Figs. 5.20 (a) and (b), are the differential capacitance curves for the non-GCS curves in the previous figure.

Figure 5.20: The differential capacitance of systems with bulk concentrations of (a) $c^0 = 0.01 \text{ M}$ and (b) $c^0 = 1 \text{ M}$. Solid lines are with $s = 0 \text{ nm}$ and dashed lines are with $s = 0.35 \text{ nm}$.

In all cases the Stern layer causes $C_d$ to be suppressed significantly, although the extent of the suppression decreases at higher potentials and the specifics differ between the systems. For the excluded volume at low potentials, the reduction in $C_d$ is accompanied by a broadening of the peak and, at low concentrations, a shift in the maximum value to a higher potential. By contrast, the polarisability curve is suppressed much more strongly — the peak occurs at a much lower $C_d$ than that in the excluded volume case — but there is little movement of the potential at which
the peak occurs. When both properties are accounted for, the low concentration $C_d$ is actually reduced by a smaller amount than either of the other curves, except at high potentials when it matches the reduction in the polarisability curve. Additionally, at high concentrations the order of the polarisability-only and the full model curves is switched, possibly indicating that the excluded volume interactions in the latter are resisting an increased surface concentration (and so the double layer is forced to become wider) but that the reduced permittivity of the bulk enables a larger electric field, so the surface charge density can be larger. Without excluded volume effects, the ions crowd at their maximum value at the surface, reducing the permittivity there and forcing a smaller surface charge density as a result.

It can also be seen that, even with the Stern layer present, the differential capacitance at the PZC remains a function of the ion polarisabilities and not the excluded volume interactions, as indicated by Eq. (5.13). The influence of the Stern layer on $C_d$ at the PZC is plotted in Fig. 5.21 (a) and (b), recreating Fig. 5.18 with additional curves showing $C_d$ at the PZC for the same systems including a 0.35 nm Stern layer.

![Figure 5.21](image)

Figure 5.21: The impact of including a 0.35 nm Stern layer on the data presented in Fig. 5.18. Solid lines in both figures are the original data and dashed lines are for Stern layer modification.

The Stern layer always reduces the differential capacitance at the PZC, but the extent to which it does so depends on the bulk concentration: if this is small the effect is correspondingly small, but larger concentrations experience a much larger drop. This is because the increase in the concentration reduces the permittivity in the Stern layer, meaning a lower resistance to an electric field and therefore a lower surface charge to sustain a field of a given value.

The effect of the Stern layer on $C_d$ as a function of the concentration is both to reduce its value at a given potential and to shift the position of the maximum in $C_d$ to a lower concentration. The concentration at which the $C_d$ returns to zero is unchanged, being identical to that of the same system without a Stern layer, because this point is defined by the maximum concentration of the system, which is unaffected by the presence of the Stern layer.

The addition of the Stern layer, and the asymmetry to the $C_d$ vs $c^0$ curves which it brings, qualitatively shifts these curves towards the shapes seen experimentally. The differential capacitance at the PZC has been measured by Ammam et al for aqueous solutions of ammonium nitrate and ethylammonium nitrate (Ammam et al. 2012), finding an initial rapid increase to
a peak in $C_d$ at between 0.5 M and 1 M, followed by a slow decrease as the concentration increases further. It is possible to approximate the published data using the model, as shown in Fig. 5.22. The low-concentration trends can be fitted by adjusting the Stern layer width and the polarisability values of the two compounds. In the figure, the Stern layer width in both cases for the model data is 1.45 nm, the polarisability of ammonium nitrate is assumed to be $4\pi\alpha = -8 \, \text{M}^{-1}$ and that of ethylammonium nitrate is assumed to be $4\pi\alpha = -6 \, \text{M}^{-1}$. Note that these values are not measured values, rather they are those which best fit the low-concentration regions of the curves.

![Figure 5.22: Comparison of analytical model for $C_d$ at the PZC to the data of Ammam et al. (2012)](image)

For the low concentration region ($c^0 < 2 \, \text{M}$) the trends in the data agree, although at higher concentrations the measured values decrease at a much lower rate than predicted. The polarisability values are not unreasonably large, although the Stern layer width required is much larger than the size of the ions. Note from Eq. (2.2b) that increasing the size of the Stern layer is equivalent to decreasing its permittivity, so it is possible that in reality there is a much lower permittivity in the Stern layer which the model is accounting for by requiring an enlarged Stern layer.

The divergences of the models at higher concentrations are likely, in part, to be due to the assumption that the permittivity is a linear function of the concentration. While this is valid for lower concentrations, the dependence breaks down at higher concentrations (Hasted et al. 1948) and so deviations of the model from reality are likely. However, the fact that the reversal of the growth in $C_d$ at the PZC is predicted by the polarisability term but not the excluded volume term suggests that accounting for the ionic excess polarisability can be important in understanding the double layer behaviour near to the PZC.

As a final point in this section, the effect of the Stern layer on the surface permittivity in the polarisability-only model is plotted in Fig. 5.23. The slower growth in the concentration at the Stern layer boundary, which results from the slower growth in $\phi(0)$ and therefore the concentration, leads to the permittivity decreasing at a much slower rate as a function of the potential.
5.4 Comparison of the structural model and experimental data

The values of the differential capacitance which the model predicts show the correct qualitative trends and are in the correct order of magnitude to match experimental data. At this stage, it is pertinent to test how well the model agrees with specific experimental measurements beyond the PZC. In order to make this connection, data from the literature have been used to confirm that the model provides a reasonable estimate for the behaviour of the real world system.

The model does not include specific adsorption, hence the particular experimental data to which it is compared are those for systems in which the electrode has a low reactivity and the electrolyte is, as far as possible, comprised of two simple ions for which the size and polarisability are known. The first comparison is made to the data of Valette (1981), which has been used in several publications (Bazant et al. 2009; Hatlo et al. 2012; Zhao 2012). The experiment measured the differential capacitance of a KPF$_6$ electrolyte at the 110 crystal face of a silver electrode. A range of concentrations were used, the smallest and largest of which are reproduced in Fig. 5.24 below.

Owing to a lack of information as to the properties of the PF$_6^-$ ion, both ions are assumed to have the properties of the K$^+$ ion, with a diameter of 0.6 nm and a polarisability of $4\pi\alpha = -8$ M$^{-1}$. Two sets of simulated data are shown: one using a Stern layer width of 0.3 nm and the other with a larger width of 0.44 nm, showing how the Stern layer can be used as the fitting parameter in the same way as it is in Hatlo et al. (2012). The difference between this model and the one presented in that paper is that in this one the mvdW model is used for the excluded volume interaction, which is slightly stronger than the Bikerman model used in Hatlo et al. (2012). This explains why the necessary size of the Stern layer is slightly smaller than the 0.48 nm which those authors use.

The fit in the negative potential region, where K$^+$ is the counter-ion, is very good for the larger
Figure 5.24: Comparison of the model to experimental data from Valette (1981) using a single ion radius of 0.6 nm and excess ion polarisability of $4\pi\alpha = -8 \, \text{M}^{-1}$ with stern layer widths of $s = 0.3 \, \text{nm}$ (dashed lines) and $s = 0.44 \, \text{nm}$ (solid lines).

Stern layer width. The position of the negative potential peak is correct at both concentrations, although the value of $C_d$ at the PZC becomes slightly too large at higher concentrations. This is possibly because both ions are present at the electrode surface at the PZC, so the fact that the properties of the PF$_6^-$ ion may be incorrect could be causing the discrepancy. At larger negative potentials the differential capacitance predicted by the model appears to decrease at a slower rate than is observed experimentally. This can possibly be attributed to the fact that the field-dependent dielectric decrement is not accounted for, so the electric field in the double layer, and hence the surface charge density, is larger in the model than in reality. However, as will be seen in the following section, the proportionality of $C_d$ and $\phi^0$ at high potentials is correct, even if the specific values are not. A comparison of the mvdW and BMCSL models, both including the excess polarisability term, is shown in Fig. 5.25 below.

Figure 5.25: Comparison of the mvdW (solid lines) and BMCSL (double-dash-dot lines) models, both including the ion excess polarisability term, with reference to the data of Valette (1981).
This serves to demonstrate the point made previously as to the BMCSL model showing a slower decrease in the differential capacitance at high potentials than models which are ostensibly less accurate in their formalism. This has been attributed to a breakdown of the LDA framework at high potentials (Bazant et al. 2011), so rather than it being the case that the BMCSL model fails where the mvdW does not, it is more likely that the lower growth rate in the mvdW excess chemical potential with an increased concentration compensates somewhat for the breakdown of the framework itself.

A different set of experimental data, this time for a NaF electrolyte, is presented in Figs. 5.26 (a) and (b). In part (a) the electrode is surface is the 210 crystal face of a gold electrode, the experimental data for which is from Hamelin (1982), while in part (b) the electrode surface is the 311 crystal face of a silver electrode, for which the experimental data is from Veggini et al. (1994). The diameters of the ions for the model data were taken from their measured hydrated values, being 7.2 nm and 7.0 nm for the sodium and fluorine ions respectively, and their respective polarisabilities were set to $4\pi\alpha = -8 \text{ M}^{-1}$ and $4\pi\alpha = -5 \text{ M}^{-1}$ (Hasted et al. 1948).

![Figure 5.26](image_url)

**Figure 5.26:** Comparison of the model to experimental differential capacitance data for a NaF electrolyte at (a) an Au electrode with varying ion concentration (b) a 0.04 M NaF electrolyte at an Ag electrode with two different values for $s$. Solid lines are the model while crosses are the experimental data from (a) Hamelin (1982) and (b) Veggini et al. (1994).

As shown by Fig. 5.26(a), the model provides a reasonable fit for this electrolyte at the gold electrode, although, compared to the previous example, the differences between the model and experiment which arise at higher potentials are more apparent. While there are specific differences, all of the experimental trends are observed and the low potential values agree well considering the small number of parameters and that a single Stern layer width of 0.59 nm was used at all concentrations. In particular, the model captures entirely the merger of the positive and negative potential peaks as the concentration increases and also matches the shift of the single high concentration peak towards a positive potential, although extent of this shift is not as large in the model.

The model correctly shows that the negative potential peak in $C_d$ is smaller than the positive potential peak, as would be expected given the differences in the ion properties. It is possible
that a better fit could be achieved if each ion had its own Stern layer width, which would also be more realistic, but the model is not set up to handle this and it would also mean that two fitting parameters would be required. Finally, at higher potentials, while the differential capacitance does not decrease as quickly in the model, the ordering of the curves as a function of the concentration is correct. Again, this slower decay could be attributed to the fact that the field-dependence of the permittivity is not accounted for.

In contrast to Figs. 5.24 and 5.26 (a), Fig. 5.26 (b) demonstrates that the fact that the electrode material is not accounted for means that the model can struggle significantly in some situations. The electrolyte in this figure is the same as that for Fig. 5.26 (a), so the discrepancy between the model and experimental data lies with an electrode interaction property which is not accounted for, as no single Stern layer width can fit both peaks as well as the central minimum. Given that both Stern layer widths result in too small a $C_d$ at the PZC, even if each ion had its own Stern layer width the model would not be able to fit the entire data range.

The impact of the electrode is not only limited to the material, but also which crystal face of a material forms the electrode surface. Shown in Fig. 5.27 are Valette’s experimental data for a 0.04 M electrolyte at a the 110 face of a silver electrode (Valette 1981), making the system identical to that shown in Fig. 5.26 (b), apart from the crystal face of the electrode, which is also shown on the figure below.

![Figure 5.27: Experimentally measured differential capacitance curves for NaF at the 311 face (Veggini et al. 1994) (black crosses) and the 110 face (Valette 1981) (blue crosses) of a Ag electrode, together with the model output using the Na$^+$ and F$^-$ diameter and excess polarisability with Stern layer widths of $s = 0.22$ (red curve) and 0.45 nm (green curve).](image)

In general, the 110 face yields lower values for the peak in the differential capacitance while the 311 face gives a lower differential capacitance at the PZC. Since the electrolytes are identical in the two sets of experimental data, the differences in the data are entirely due to the electrode, probably in the way that the structure of the surface changes the energies of the interactions in the Stern layer. The model is not able to account for any of these effects as it simply treats the electrode as a flat charged surface with no other properties, although there are also problems with modelling F$^-$ ion at polycrystalline surfaces and in mixtures as discussed later. In terms
of the model, given the differences between the two sets of experimental data, it is actually
perhaps more surprising that the model predictions are not less accurate, particularly taking in
to account of how few parameters it uses.

It is apparent that the model reasonably describes the electrical properties of an electrode/electrolyte system, although there are evidently many factors which are beyond its capabilities and the fact that it has to be fitted to experiment limits its predictive power. As the direction of this work is in the dynamics of electrolyte systems, however, improvements on the accuracy are not considered here and the limited set of parameters which define the model remain. Prior to considering the dynamics, there are two further points of consideration. The first is how the model behaves at high potentials and the second is to consider electrolyte mixtures, as these arise when considering reacting systems and supported electrolytes in experiments.

5.5 High potential behaviour

At high potentials, the counter-ion concentration saturates at a maximum value and the behaviour of the system changes, as embodied in the decrease in the differential capacitance with the applied potential. The concentration maximum is defined by either the counter-ion volume, in which case it has the value \( c_{\text{max}} = \frac{1}{a^3} \), or by the counter-ion excess polarisability, in which case it takes the value \( c_{\text{max}} = -\frac{\epsilon_w}{8\pi\alpha} \) (Ben-Yaakov et al. 2011; Hatlo et al. 2012).

Once the surface concentration has saturated and the double layer begins to widen, the differential capacitance should decrease in proportion to the inverse square root of the potential. Such behaviour has been described as a universal property and should be independent of the model used to describe the system (Georgi et al. 2010). From the form of the chemical potential when the excess polarisability is included, it is possible to derive an approximate analytical solution for the high potential variation in \( C_d \). At equilibrium, the electrochemical potential must be constant with respect to the position and thus \( \mu_j(0) - \mu_j(\infty) = 0 \). From Eq. (3.77), therefore, the following statement holds:

\[
\ln \frac{\epsilon_j(0)}{\epsilon_j(\infty)} = -\left(\mu_j^{\text{ex}}(0) - \mu_j^{\text{ex}}(\infty)\right) - \left( z_j \phi(0) - z_j \phi(\infty) \right) + \frac{\alpha_j}{2\epsilon_w} \left( |\phi'(0)|^2 - |\phi'(\infty)|^2 \right)
\]

(5.14)

Only the counter-ion is present in any significant quantities at high potentials, so the equation can be approximated by neglecting the terms relating to the co-ion. The electrostatic potential and its gradient are zero in the bulk so the equation can be rearranged to

\[
|\phi'(0)|^2 \approx \frac{2\epsilon_w}{\alpha} \left( \ln \frac{\epsilon(0)}{\epsilon(\infty)} + \left( \mu^{\text{ex}}(0) - \mu^{\text{ex}}(\infty) \right) + z\phi(0) \right)
\]

(5.15)

where all values now refer only to the counter-ion. The above equation may rearranged to

\[
\phi'(0) \approx \left[ \frac{2\epsilon_w}{\alpha} \left( \ln \frac{\epsilon(0)}{\epsilon(\infty)} + \left( \mu^{\text{ex}}(\epsilon(0)) - \mu^{\text{ex}}(\epsilon(\infty)) \right) + z\phi(0) \right) \right]^\frac{1}{2}
\]

(5.16)
Using Eq. 3.79a to substitute the surface charge density for the term on the left and then differentiating with respect to the potential, the differential capacitance at high potentials can be derived:

\[ \frac{4\pi\varepsilon_w}{\varepsilon(0)} \sigma \approx \left[ \frac{2\varepsilon_w}{\alpha} \left( \ln \frac{c(0)}{c(\infty)} + \mu^{\text{ex}}(c(0)) - \mu^{\text{ex}}(c(\infty)) + z\phi(0) \right) \right]^\frac{1}{2} \]

\[ \frac{d\sigma}{d\phi} \approx -\frac{\varepsilon(0)}{8\pi} \frac{2\varepsilon_w}{\alpha} \left[ \frac{2\varepsilon_w}{\alpha} \left( \ln \frac{c(0)}{c(\infty)} + \mu^{\text{ex}}(c(0)) - \mu^{\text{ex}}(c(\infty)) + z\phi(0) \right) \right]^{-\frac{1}{2}} \] (5.17)

At high potentials, the permittivity at \( z = 0 \) converges on half the bulk value and so the final expression for the differential capacitance is

\[ C_d \approx -\frac{\varepsilon_w}{16\pi} \left[ \frac{\alpha}{2\varepsilon_w} \left( \ln \frac{c(0)}{c(\infty)} + \mu^{\text{ex}}(c(0)) - \mu^{\text{ex}}(c(\infty)) + z\phi(0) \right) \right]^\frac{1}{2} \] (5.18)

In the event that the maximum concentration is defined by the ion polarisability rather than the ion volume, the logarithm and \( \mu^{\text{ex}} \) terms become constant at high potential and hence the differential capacitance becomes proportional to \( \phi^{-1/2} \). This dependence is demonstrated in Fig. 5.28, showing \( 1/C_d \) as a function of the square root of the potential for systems which account for either the excluded volume or the polarisability, as well as a system which includes them both.

![Figure 5.28: High potential behaviour of the differential capacitance for a 0.01 M electrolyte. “n” represents the full numerical solution, “a” represents the analytical equation.](image)

If only the polarisability is accounted for, the analytical solution provides a good approximation to the numerical solution over the range shown, and improves further as the applied potential increases. The inclusion of steric effects modifies the inner bracket in Eq. (5.18). The analytical approximation assumes that \( \mu^{\text{ex}} \) is constant, having the value which it has when the concentration is equal to the maximum which results from the polarisability. In reality its value changes over the whole potential range, which is why the approximation fares less well at lower potentials. The two curves do however converge at higher potentials.
Also shown in the figure is the numerical solution for the case in which only steric effects are accounted for. In this case, the analytical solution does not apply, since the presence of the polarisability in the pre-factor to the inner bracket would make the differential capacitance zero. As with the case in which the polarisability dominates the system behaviour, the trend is the same, however, with $C_d$ varying as $\phi^{-1/2}$.

5.6 Supported electrolytes

In the context of experimental work, voltammetry is often conducted in the presence of a supporting electrolyte. The standard PB model of the double layer predicts that the ratio of ion concentrations in the double layer in this situation is simply equal to the ratio of the bulk concentrations (assuming the ions have the same charge), regardless of the applied potential. However, theoretical and experimental investigation of electrolyte mixtures shows this not to be the case. While at low potentials the predictions of the GC model are observed, at higher potentials the ratios of ion concentrations differ significantly, with one of the ions being preferentially found near the electrode surface (Biesheuvel and Soestbergen 2007; Shapovalov and Brezesinski 2006; Shapovalov et al. 2007).

The exclusion of one of the ions from the electrode surface has implications for modelling systems in which a supporting electrolyte is present. In particular, if the excluded ion is that which takes part in a reaction at the electrode surface, the rate of the reaction will be strongly affected. In this section, it will be demonstrated that both the excluded volume and excess polarisability interactions can lead to the exclusion of one of the ions, while accounting for both terms can lead to better agreement with experimental data than does the commonly used approach of accounting for the excluded volume interaction alone.

5.6.1 Different ion sizes

Previous studies using the BMCSL model have shown that the smaller ions in an electrolyte mixture are preferentially found near to the electrode surface at higher potentials (Biesheuvel and Soestbergen 2007). While the larger ion still forms part of the double layer, its concentration can be low at the surface, increasing to a maximum at some point away from the surface and then returning to the bulk value as the distance increases further. This is because it is energetically favourable for as much charge as possible to be adjacent to the surface. If the ionic charges on the counter-ions are the same, more counter-charge can be placed on the surface if it comes from the smaller ions. This sort of behaviour is also predicted by the mvdW model, as shown by Fig. 5.29 in which the equilibrium concentration profiles of the counter-ions for an equi-molar mixed electrolyte are plotted at two different potentials. Three cases are shown, one with equal ion diameters, with $a_1 = a_2 = 0.7$ nm, and two with unequal diameters, first with $a_1 = 0.7$ nm and $a_2 = 0.6$ nm and second with $a_1 = 0.7$ nm and $a_2 = 0.5$ nm. In all three cases the bulk concentration of each ion is 0.01 M.
It is evident that the smaller ion can significantly exclude the larger ion, even at moderate potentials — in the case with $a_2 = 0.5 \text{ nm}$ it can be seen that there is very little change in the surface concentration of the larger ion on doubling the applied potential. Should the system be such that the larger ion is able to react, this restriction on the surface concentration may significantly affect the reaction rate. In order to consider how the structure of the double layer changes in a mixed electrolyte, two properties are now considered. The first is the surface concentration of the two ions and the second is the overall composition of the double layer. This latter property is the ratio of the excess concentration of counter-ion $j$, $\Gamma_j$, to the total excess concentration of both counter-ions, relative to their bulk values. $\Gamma_{j+l}$ is calculated as the integral over the domain of the difference between the local and bulk concentrations of each species:

$$\Gamma_j(\phi) = \int_0^L dz (c_j(z) - c_j(L)),$$ (5.19)

Plots of the surface concentrations and the ratio of the excess concentrations of the smaller ion are shown in Figs. 5.30 (a) and (b) below.

As the applied potential increases, the surface concentration of the larger ion initially increases at the same rate as the smaller ion, and the proportion of the two ions in the whole double layer is the same. Beyond a certain threshold, dependent on the relative sizes of the ions, the smaller ion begins to dominate the surface concentration, pushing the larger ion out and causing its surface concentration to decrease. The larger the difference between the ion sizes, the lower the potential at which the smaller ion begins to dominate and the lower the potential at which the surface concentration of the larger ion tends to zero. Although the surface concentration of the larger ion tends to zero, it still contributes to the double layer but, as seen in Fig. 5.29, the peak concentration of that ion moves away from the electrode surface.

The surface concentrations of the ions and the composition of the double layer predicted by the mvdW model differs slightly from the BMCSL model, with the differences being more...
significant in the first property than the second, as demonstrated by Fig. 5.31.

Figure 5.31: Comparison of (a) the surface concentration and (b) the fraction of the total excess concentration belonging to the smaller counter ion as predicted by the mvdW and BMCSL models. Solid lines in part (a) represent the smaller ion.

It has already been seen in Fig. 5.2 that the surface concentration increases more slowly as a function of the potential for single electrolytes in the BMCSL model, so it is not unexpected for the surface concentrations of both ions to be smaller in this case than the mvdW model. There are two slight differences in the trends of the two model predictions. First is that the peak in the surface concentration of the larger ion occurs at a slightly larger surface potential in the BMCSL model, although this is only noticeable in the figures above for the 0.7 nm-0.6 nm case, where the peak moves from approximately $\bar{\phi}^0 = 8$ to $\bar{\phi}^0 = 9$. The second difference is that the mvdW model predicts a quicker approach to zero concentration for the larger ion at high potentials, although the numerical difference in the surface concentrations is small.

Along with the differences in the predicted surface concentrations, there are similarly slight
differences in the composition of the double layer. As would be expected, at low applied poten-
tials the double layer is comprised of equal amounts of both ions. For potentials in the range
$\phi_0 \sim 5$ to 12 the BMCSL model predicts that slightly more of the smaller ion is found in
the double layer than the larger one. From this point, however, there is little difference between
the predictions of the two models, although if the difference between the sizes of the ions is larger,
then the BMCSL model predicts a slightly larger component of the smaller ion.

Regardless of the model used to describe the excluded-volume effect, differences in the sizes
of the ions lead to quantitatively different electrolyte structures than can be predicted by ex-
cluded volume models which only account for one ion size. As will be seen in future sections,
these differences lead to differences in the equilibrium properties of the system and also lead to
differences in the dynamic properties. In particular, concentration-dependent processes such as
surface reactions will be significantly affected.

5.6.2 Different ion polarisabilities

Since the reason for the exclusion of the larger ion from near to the electrode surface when the
excluded volume interaction is accounted for can be attributed to the difference in the amount
of energy it takes to add a larger ion to an already crowded double layer compared to that of
a smaller ion, it can be expected that similar structures will arise for mixtures of ions with dif-
ferent polarisabilities, although this does not appear to have been demonstrated previously in
the literature. Shown in Fig. 5.32 is a plot of the double layer structure of a mixed electrolyte
double at two different potentials for three mixed electrolytes in which only the excess polar-
isability is accounted for. The data is presented in a similar format to Fig. 5.30; the colours
correspond to each of the electrolytes, for which the solid lines correspond to the ion with the
smaller polarisability. The polarisability combinations shown are: (i) $4\pi \alpha_1 = 4\pi \alpha_2 = -8 \text{ M}^{-1}$,
(ii) $4\pi \alpha_1 = -8 \text{ M}^{-1}$ and $4\pi \alpha_2 = -5 \text{ M}^{-1}$ and (ii) $4\pi \alpha_1 = -8 \text{ M}^{-1}$ and $4\pi \alpha_2 = -3 \text{ M}^{-1}$.

![Figure 5.32: Double layer structure for equimolar mixed electrolyte for different ion excess polarisabilities. See text for details](image-url)
As might be expected, the ions with the smaller polarisability in each pair are found closer to the electrode surface, with the extent of the difference in the concentrations increasing with both the applied potential and the relative difference between the ion excess polarisabilities. Again, the surface concentration of the higher excess polarisability ion is significantly reduced relative to that of the lower excess polarisability ion, tending to zero at high enough potentials. Meanwhile, the composition of the double layer overall also favours the lower polarisability ion, with the higher polarisability ion having a smaller presence. These two properties are plotted in Figs. 5.33 (a) and (b) respectively, for the same electrolyte mixtures whose concentration profiles are shown in the previous figure.

Figure 5.33: (a) the surface concentration of counter ions in a mixed electrolyte for ions with different excess polarisabilities and no excluded volume interaction (solid lines represent the lower polarisability counter-ion) and (b) the fraction of the total excess concentration belonging to the lower excess polarisability counter ion.

The particular ionic excess polarisabilities shown in the figures above have been chosen such that that the maximum species concentrations are approximately the same as for the excluded volume interactions in the previous section, so that some degree of comparison can be made. From the data in Section 5.1.3, it was seen that for single electrolytes the maximum concentration is approached much more rapidly in a system which only accounts for the polarisability than one which only accounts for the excluded volume, a trend which can be seen again here through comparison of Figs. 5.30(a) and Figs. 5.33(a). This more rapid convergence on the maximum concentration (of the smaller or lower excess polarisability ion) at the surface means that the larger polarisability ions are excluded from the surface at a lower potential in the polarisability-only case than the larger ions are excluded in the excluded volume-only case. As a result, the surface concentration of the larger-volume or higher-polarisability ion approaches zero at a lower applied potential in the polarisability-only case.

5.6.3 The effect of ion interactions in real electrolytes

In this section, two examples are used from the literature to elucidate some effects of accounting for both the excluded volume interaction and the excess polarisability in mixed electrolytes.
The composition of the double layer in CsCl-MgCl₂ at negatively charged Langmuir monolayers

The exclusion of one of the ions from the double layer has been observed experimentally through the use of X-ray reflectivity of ions near negatively charged Langmuir monolayers of the surfactant behenyl sulphate (Shapovalov and Brezesinski 2006). In the experiment, deviations of the ion concentration profiles from those predicted by the GC models were small in charge-symmetric electrolytes for surface charges smaller than 300 C m⁻² but significant differences occurred at higher surface charges or for charge-asymmetric electrolytes. First, for a mixed electrolyte system containing 9 mM LiCl and 1 mM CsCl, the Cs⁺ ion forms 50-60% of the double layer, as opposed to the 10% which is predicted by the GC theory. Second, for an equimolar mixture of CsCl and MgCl₂ ions, the Cs⁺ ion forms up to 66% of the double layer, some 70 times larger than the quantity predicted by the GC model. This is significant because the Mg ion has a valence of +2 and so should be more strongly attracted to the electrode surface.

Biesheuvel and Soestbergen (2007) have shown previously that the excluded volume interaction alone can explain the Cs⁺-Li⁺ data, since the Cs⁺ ion, with a hydrated ion diameter of 0.66 nm, is smaller than Li⁺ ion, with a diameter of 0.76 nm, so it is energetically favourable to increase the concentration of the smaller ion when the surface charge/potential increases. However, their model, which was based on BMCSL mPB theory, could not adequately explain the Mg²⁺ data, requiring a 20% increase in the Mg²⁺ ion radius in order to fit the data.

The inclusion of the polarisability term can provide a better route for explaining the experimental data. Shown in Fig. 5.34 are the predicted curves for the ratio of the Cs⁺ ion concentration to the total counter ion concentration (ΓCs⁺/(ΓCs⁺ + ΓMg²⁺)) in the double layer for the mvdW, BMCSL and GC models, both with and without the polarisability term. The ion diameters were set to values determined by Nightingale (1959) of 0.66 nm for Cs⁺, 0.86 nm for Mg²⁺ and 0.66 nm for Cl⁻ and the polarisability values for Mg²⁺ and Cl⁻ were set to 4πα = −24 M⁻¹ and −3 M⁻¹, the values measured by Hasted et al. (1948) and summarised in Table 2.1. Due to the lack of data for the polarisability of the Cs⁺ ion its value was estimated to be 4πα = −6 M⁻¹, following the trend in the polarisabilities which can be observed from moving down the column of group I elements in the periodic table.

Marked on the graph by the two crosses are the bounds for the composition ratio in the double layer as determined by experiment, from which it is clear that the polarisability term alone can account for the experimentally measured ratio of the ions. The inclusion of an expression for the excluded volume interaction acts to reduce slightly the ratio at the charge density measured in the experimental data, with the reduction being larger in the BMCSL+p case, although it remains just within the bounds. For lower charges, the differences between the GC+p, mvdW+p and BMCSL+p models are more pronounced, with the excluded volume interaction having a large effect on the ratio. If experimental data were available for this charge density range, it would provide an opportunity to better determine which of the models provides the best fit.

In the absence of the polarisability, the mvdW model shows the same behaviour as the full model at low surface charge densities but continues to decrease until about σ = 500 mC m⁻²,
Figure 5.34: Ratio of Cs\textsuperscript{+} concentration to the total counter ion concentration for a mixed Cs\textsuperscript{+}-Mg\textsuperscript{2+} double layer as a function of the surface charge density for the GC, mvdW and BMCSL models, with and without the polarisability interaction.

at which point it just begins to increase again. The BMCSL model likewise shows the same low charge behaviour but actually fares worse than the GC model at $\sigma = 600$ mC m\textsuperscript{-2}, relative to the experimental data. As shown by Biesheuvel and Soestbergen (2007), the BMCSL model can be made to agree with the experimental data, but only by increasing the size of the Mg\textsuperscript{2+} ion by 20%. As demonstrated here, this is unnecessary if the ion polarisabilities are accounted for.

The reason the ion volume does not need to be artificially enlarged is that it is not the excluded volume interaction which dominates for the Mg\textsuperscript{2+} ion. With a diameter of 0.86 nm, its volume limits the concentration to 2.61 M, which is much larger than the limit set by the polarisability term of 1.625 M. In contrast, the maximum Cs\textsuperscript{+} concentration is defined by its volume at 5.58 M, although this is not significantly smaller than the maximum set by the polarisability term, of 5.78 M.

The structure of the double layer which is predicted for a surface charge density of 600 mC m\textsuperscript{-2} follows the trend indicated in the previous sections, with the dominant ion having a monotonically decreasing profile with distance from the surface and the other ion having a concentration that initially rises with distance from the electrode before returning to the bulk value. In this case though there is almost a complete segregation of the ions in the double layer, as shown in Fig. 5.35.

The model suggests that the double layer is formed from approximately a single layer of Cs\textsuperscript{+} ions at the surface with a layer of Mg\textsuperscript{2+} ions adjacent to it. There is a slight difference between the mvdW and BMCSL models, in that the Cs\textsuperscript{+} ion concentration is slightly lower (although the overall width of the double layer is very similar) but the trends in the ion concentrations are the same and both show significant differences to the GC model, in which the order of the curves is reversed, with the Mg\textsuperscript{2+} ion being by far the dominant source of counter-charge.
Figure 5.35: Concentration profiles of Cs$^+$ and Mg$^{2+}$ ions at $\sigma = 600$ mC m$^{-2}$ for the mvdW+p (solid), BMCSL+p (dashed) and GC (dash-dot) models

The electrical properties of a NaF-NaCl mixed electrolyte

The exclusion of the larger or higher polarisability ion from the double layer as the potential increases leads to changes in the way that the electrode surface charge density changes as a function of the applied potential. In the previous section it was seen that the inclusion of the excess polarisability and allowing for different ion sizes improves on the predictions of the double layer composition. However, these changes to the standard models for the inclusion of ion-specific effects also lead to changes in the predictions of the electrical properties of the system. In Fig. 5.36 is shown the predicted differential capacitance curve for a NaF/NaCl electrolyte, to match experimentally measured data from Fig. 5 in Larkin et al. (1982), in which the differential capacitance for this mixed electrolyte is measured using a polycrystalline silver electrode. The total ionic concentration in all sets of data is 0.25 M, but the concentration of NaCl in the mixture is varied, as labelled. All ion properties take their measured values, specifically the diameters are $a_{Na^+} = 0.71$ nm, $a_{F^-} = 0.7$ nm and $a_{Cl^-} = 0.66$ nm, and the polarisabilities are $4\pi\alpha_{Na^+} = -8$ M$^{-1}$, $4\pi\alpha_{F^-} = -5$ M$^{-1}$ and $4\pi\alpha_{Cl^-} = -3$ M$^{-1}$. The Stern layer width was set to 0.6 nm in all cases.

The actual fit the experimental data is quite poor, and cannot be improved by changing the Stern layer width, so the experimental data is not overlaid on the graph, but the model does hint at some of the interplay between the ion-specific properties which may explain parts of the experimental data. The experimental data shows a peak in $C_d$ at the same potential as for a pure NaF electrolyte plus a second, much larger, peak at a more positive potential. This larger peak dominates the data, increasing in size as the concentration of the Cl$^-$ ions increases until the smaller peak is eventually consumed by it. As can be seen in the figure, this is not what the model predicts, since it suggests that the larger peak is at the more negative potential, although there are some similarities, discussed below.

There are two of significant reasons that the model and experiment do not match. The ex-
Experimental work was carried out using poly-crystalline electrodes and it was seen previously that the model does not very well describe single-electrolyte systems containing these types of electrode. Each crystal face behaves in a slightly different manner, leading to changes in properties such as the potential of the PZC, so the interaction and interference between each of the faces leads to changes in the system behaviour. The other problem is that the main electrolyte in the experimental system is NaF, for which it was challenging to attain a reasonable agreement with experiment even for single crystal electrodes in single electrolytes (see Fig. 5.26). There is, however, a lack of suitable experimental data, i.e. data for mixed electrolyte systems with known ionic diameters and excess polarisabilities at single crystal electrodes, with which to compare the model.

The model and experiment share agreement in the convergence of the differential capacitance curves at the negative end of the potential range, even if they do not agree in the actual values. This is because it is the positive ion which is attracted to the surface in this potential range and, since there is only one type of positive ion, there is effectively no mixed electrolyte in the double layer for negative potentials. At low NaCl concentrations the experiment shows two peaks in the differential capacitance curve, separated by between 0.6 V and 1.0 V, with larger values corresponding to smaller NaCl concentrations. While the model predicts two peaks at low concentrations, the potential separation is much larger, taking a value of 1.1 V for the 3.9 mM NaCl system and larger values for lower NaCl concentrations. Furthermore, while the model predicts an increase in the differential capacitance at the higher-potential peak with respect to the concentration, the extent of this rise is much, much smaller: in the experiment the peak at the higher potential dominates the $C_d$ curve, but in the model it remains small, becoming a shoulder on the lower potential peak as the chloride ion concentration is increased.

In their paper, Larkin et al attribute the peak at the higher potential to chloride adsorption and the peak at the lower potential to fluoride adsorption. This is in qualitative agreement with what
the model predicts for the surface concentrations of the two sets of ions, as shown in Fig. 5.37 (a), wherein the surface concentration of the chloride ion becomes larger than that of the fluoride ion at some NaCl-concentration dependent surface potential.

Figure 5.37: (a) the surface concentration of F\(^{-}\) ions (black) and Cl\(^{-}\) ions (red) and (b) the ratio of the number of ions over the bulk value to the total number of ions over the bulk value for F\(^{-}\) ions (black) and Cl\(^{-}\) ions (red). Legend the same for both figures

As seen previously for an equi-molar mixed electrolyte, the surface concentration of the smaller/lower excess polarisability (chloride) ion is much larger than would be predicted by the GC model and increases with the applied potential. Whether or not it is larger than the fluoride ion concentration depends on the bulk concentration and the actual applied potential, but this gives an indication of how the relative surface concentrations change. Fig. 5.37 (b) shows a plot of the composition of the double layer. Again, it can be seen that the chloride ion comprises an increasingly large proportion of the total counter-charge as the potential increases, representing a sizable (∼29%) fraction of the total counter-ion concentration in the double layer at \(\bar{\psi} = 50\) for the 17 mM NaCl solution, even though this only makes up ∼9% of the bulk counter-ion charge.

This replacement of the fluoride ions at the electrode surface is the same as predicted in models which only account for the excluded volume, but these do not predict a clear second peak in the differential capacitance at high potentials, away from the PZC, as shown by Figs. 5.38(a) and (b). The two figures show the predictions of the mvdW and BMCSL models for the highest and lowest NaCl concentrations respectively, both with and without the excess polarisability term (the former case denoted with “+p”), using the same ion volume and Stern layer width as was used in the full model above. Also shown is the model output when the excluded volume terms are omitted and the polarisability interaction alone is accounted for (denoted “p”).

In the absence of the polarisability term, neither excluded volume model predicts a second peak at high positive potentials (black and red lines). The BMCSL predicts a single peak at the PZC while the mvdW model predicts a twin peak near the same point. Given the absence of the polarisability term, the value of \(C_d\) at the PZC is slightly larger in the mvdW and BMCSL models, although this could be reduced by increasing the size of the Stern layer. Although there is
Figure 5.38: The differential capacitance predicted by different models for a NaCl-NaF electrolyte mixture with a total ionic strength of 0.25 M. NaCl concentration: (a) $4.5 \times 10^{-6}$ M and (b) 0.017 M. Comparison of the mvdW and BMCSL models with and without the polarisability interaction (“p”) and also the polarisability interaction alone.

No distinct peak at either concentration, the rate at which $C_d$ decreases in the non-polarisability models does change at higher Cl$^-$ concentrations, becoming slower as the bulk concentration of the smaller ion increases. This results from the fact that the energy cost of moving a smaller ion into the double layer is smaller than that of moving a larger ion at high potentials, so more of the smaller ions move inwards. As a result, the double layer charge increases slightly more quickly and the differential capacitance decreases slightly more slowly. It can be shown that if the size difference between the ions is larger, or ratio of the two ion concentrations smaller, the excluded volume terms alone will predict a second peak in the differential capacitance, but the difference between the sizes has to be larger than in the case shown here.

If the excluded volume interaction is not accounted for (green line), the polarisability term predicts a single peak at a small positive potential with a shoulder on the peak at a small negative potential. At higher potentials $C_d$ changes fairly significantly. For the lower concentration shown the curve remains monotonically decreasing, but the rate of decrease is reduced. For the higher concentration the curve just stops being monotonic, with the development of a small peak at about $\bar{\phi}^0 = 35$. This gives a clear indication that the presence of the second peak is in part the result of the relative excess polarisabilities of the two ions.

Of the two full models, the BMCSL+p predicts a smaller $C_d$ than the mvdW+p over the whole potential range, including the region in which the second peak develops. The fact that neither model predicts a large second peak (as observed in experiment) indicates that there must be a significant number of other processes occurring which alter the behaviour of the system but which are not described by any of the models discussed.

This particular case also highlights one of the effects of accounting for both the excluded volume and the polarisability in terms of how the permittivity of the double layer changes, showing that in one sense the excluded volume interaction can indirectly affect the permittivity of the system. As seen previous sections, both the excluded volume interaction and the polarisability term lead to a maximum concentration for the ions. For both the chloride and the fluoride ions...
the smaller of these maximum concentrations is that due to the excluded volume, for which the values are 4.69 M and 5.773 M, respectively. In contrast, the maxima due to the polarisabilities are 4.875 M for the fluoride ion and 13 M for the chloride ion.

For potentials near the PZC, when the fluoride ion makes up most of the double layer, the permittivity undergoes a rapid reduction due to the higher excess polarisability of that ion. However, as the potential becomes large and it becomes energetically favourable for additional counter-charge to be made up from the lower polarisability Cl\(^-\) ions, the displacement of the F\(^-\) ions means that the permittivity begins to increase again at the surface of the electrode, as shown in Fig. 5.39

Figure 5.39: Permittivity at \(z = 0\) for a mixed F\(^-\)-Cl\(^-\) double layer as a function of the applied potential.

For a single electrolyte system it was seen previously that the decrease in the permittivity once ion crowding had occurred caused the surface charge density to grow more slowly as a function of the potential. Here, the increase in the permittivity which occurs as the smaller ion moves in to the electrode surface has the opposite effect and the charge grows more quickly as a function of the applied potential. This effect is one which inherently cannot be predicted by models which do not account for the polarisability, but is one which is likely to play some role in determining the behaviour of these types of systems.

The differences between the experimental and model data can possibly be ascribed to the interactions of the two counter-ions and the electrode surface. If there are surface interactions which increase the energy of the fluoride ions near to the surface but which reduce the energy of the chloride ions, this could increase the extent to which the chloride ions are found at the electrode surface. Furthermore, the different sizes of the two ions means that the use of a single Stern layer width is not truly appropriate. The chloride ion is smaller, so when it is dominant in the double layer the Stern layer will be smaller, which would correspond to an increased differential capacitance.
5.7 Conclusions

The effect of the ion excess polarisability and excluded volume interactions on the equilibrium properties of an electrode/electrolyte system have been investigated, initially for single electrolytes. It has been shown that both terms individually lead to correctly shaped differential capacitance curves, while the use of both terms leads to reasonable agreement with experimental data in some situations, although the inherent simplicity of the models means that agreement is not always found.

An new analytical expression was developed for the differential capacitance at the PZC, showing that while the excluded volume interaction does not affect its value, the polarisability does. As a function of the concentration, the model predicts that increasing the concentration of an electrolyte results in a peak in the differential capacitance, in agreement with experimental data. Additionally, the high potential dependence of the differential capacitance was shown to vary as $\sqrt{1/\phi^0}$ in agreement with experimental observation and more detailed density functional theory models.

Finally, the effects of the excluded volume interaction and the ion excess polarisability were considered for mixed electrolytes. In agreement with other models and experiment, both types of interaction were able to describe the exclusion of the larger or higher polarisability ion in the mixture at high potentials. Attempts were made to model two sets of experimental data. In the first, the polarisability term was found to improve significantly the predictions for the double layer structure of a charge asymmetric mixed electrolyte, while in the second the interaction of the polarisability and excluded volume energies provides a hint of how these terms may interact in real systems to cause multiple peaks in the differential capacitance curves.
Chapter 6

Dynamics at blocking electrodes

In the previous chapter, the equilibrium state was discussed for electrolytes and electrolyte mixtures in terms of how accounting for either the ion excluded volume interactions or the excess polarisabilities leads to significant deviations from the standard GC model. Furthermore, by accounting for both properties, both single electrolytes and electrolyte mixtures can be reasonably approximated by using the width of the Stern layer as the only fitting parameter.

While the equilibrium properties provide useful information about electrochemical systems, the equilibrium properties do not provide information about how the ionic interactions lead to changes in the dynamics of these systems. Much of the information about these systems is derived from experiments in which a time-dependent potential is applied, for example through electrochemical impedance spectroscopy (EIS) or cyclic voltammetry (CV). Each of these can, under appropriate conditions, provide a wealth of information including, but not limited to, equilibrium properties such as the differential capacitance.

In this chapter the response of a non-reactive electrode/electrolyte system is considered in terms of the inclusion of ion interaction terms. Three types of time-dependent system are considered. First is the response of the electrolyte to a step change in the potential, second is the simulation of EIS and the third is the simulation of CV.

Throughout, the data are considered in terms of the equivalent circuit (EC) for the system, which is comprised simply of a resistor and a capacitor in series. ECs provide analogues to the processes occurring in the real system, but are not strictly models for the system. They are widely used in interpreting data, particularly in EIS, and their success in certain situations provides a starting point for understanding the effects of ion interactions upon the dynamics.

As with much of this work, the addition of the excess polarisability to a dynamic model of the electrolyte system sets it apart from previous work, as this effect does not appear to have been studied. In addition, the specific form of the excluded volume model has not previously been studied, although the similar Bikerman model has previously been applied in the context of the response of a system to a potential step (Kilic et al. 2007a), and time dependent applied potentials (Olesen et al. 2010; Wang and Pilon 2012b; Wang and Pilon 2012c).

For the application of a potential step, the response is observed to depend on the domain length, concentration and applied potential. The equilibration time generally follows the dif-
ferential capacitance, as would be expected given the EC for the system, but as the domain length or concentration are decreased or the potential increased, the equilibration time becomes longer than that predicted by the EC. This is attributed to depletion of ions from the bulk during the charging process. Slight differences between the polarisability and excluded volume terms arise once ion depletion becomes significant, although the exact reason for this is not clear. The response of the system when the Stern layer is accounted for is observed to be qualitatively different at higher potentials and shorter domains, depending on whether the excluded volume or the polarisability is accounted for.

In terms of modelling EIS, the output is not observed to differ from what is predicted by the EC for the system, again assuming that the correct differential capacitance is used when calculating the data from the EC. The system resistance is calculated from simulated EC data for systems which include the ion interactions and no deviation is observed to arise compared to either the GC model or the analytical expression for the ionic resistance of an electrolyte. For the most part, ion interactions seem to have little effect on EIS for blocking electrodes beyond the effect they have through the change in the differential capacitance. Likewise for CV, the model shows no new effects arising from the inclusion of ion interactions beyond those which arise from the change in $C_d$.

The remainder of this chapter is structured as follows: first, a description is given of the three techniques (the potential step response (PSR), EIS and CV), together with details of how they are modelled. A description is also given of the EC analogue for the system and of the results which the that method predicts for the model system. Subsequent sections will then consider in more detail the output of the numerical model for each type of input.

Unless otherwise stated, the diffusion coefficients for all ions are assumed to be equal and constant, being set to $1 \times 10^{-9}$ m$^2$ s$^{-1}$, a typical order of magnitude value for ions diffusing through water (Koneshan et al. 1998). The only exception to this is when considering capacitance dispersion in Section 6.3.1, when different values are considered for comparison.

### 6.1 Modelling PSR, EIS and CV and the equivalent circuit

In this section, a brief account is given of the three types of dynamic system which are considered. Each of them is applied by defining the boundary condition for the electrostatic potential at the electrode surface in a particular way.

#### 6.1.1 Potential step response

As the name implies, this technique involves applying a step change in the potential. This causes the ions to respond and the double layer to form, eventually reaching an equilibrium in which the potential drop across the double layer is equal to the applied potential. The boundary
condition for the potential in this case reads

$$\phi = \begin{cases} 
0 & \text{if } t < 0 \\
\phi^0 & \text{if } t \geq 0 
\end{cases} \quad (6.1)$$

Until $t = 0$, the system is assumed to be in the same initial state as described previously — the electrolyte concentrations throughout the domain are equal to their bulk values and the potential is zero. At $t = 0$ the potential is changed instantaneously and the system allowed to respond. As the system moves towards equilibrium, the electrode surface charge density changes, its rate of change being equal to the current in the external circuit, whose value is determined by how quickly the ionic current is able to flow in the electrolyte.

In all cases the equilibration time, $t_{eq}$, is defined as the length of time the surface charge density takes to reach 99.9% of the true equilibrium value. The generation of the equilibration time data therefore requires two runs: one to define the equilibrium point and a second to determine the value of $t_{eq}$. The first could be run quickly using a short domain and small value of the reference diffusion coefficient/diffusion coefficient scaling factor, $(D^c \approx 1 \times 10^{-13})$, while the second was run using the domain length of interest and a $D^c$ value more appropriate to that length. Longer domains mean larger values of $t_{eq}$, so smaller values of $D^c$ were used in order to maintain shorter run times. However, since reducing the value of $D^c$ effectively increases the size of each simulated time step, doing this reduces the precision of the calculated $t_{eq}$. Having said this, all data was calculated to a minimum of four significant figures, so this loss of precision introduces at most only a small relative error into the result.

### 6.1.2 Electrochemical impedance spectroscopy

This technique involves applying a small amplitude sinusoidal potential to the electrode and measuring the current density response. The amplitude and phase of the current depend on the amplitude and frequency of the potential and relate to how quickly elements of the system are able to respond to the changing potential. By considering how the response changes as a function of the frequency, the technique can be used experimentally for determining the properties of porous materials, measuring the dielectric and transport properties of materials and for investigating both passive surfaces and those at which electrochemical processes take place, in the latter case making it possible to gain insight into the mechanisms of the reactions (Macdonald 2006). EIS is also widely used for investigating the behaviours of fuel cells and electrochemical supercapacitors, for example, among many other types of electrochemical system (Taberna et al. 2003; Ktz and Carlen 2000; Ramya and Sangaranarayanan 2008; Nikonenko and Kozmai 2011; Gomadam and Weidner 2005).

A limitation to the technique is that it requires the response of the system to the input to be linear, i.e. that the input and output functions share the same frequency, although they may be of different phase and amplitude. As is well known, and can be seen throughout this work, the response of an electrode/electrolyte system over a large potential range is highly non-linear.
By limiting the amplitude of the potential to small values ($\phi \lesssim 10 \text{ mV}$), the response can be approximated as linear and the technique is valid.

In terms of modelling this type of system, it is the steady state which is of interest, once any transient waves have dissipated. Such transient waves may have a much longer decay time than the wavelength of the input potential. While for the PSR the value of $D^c$ can be reduced to increase the length of a (dimensionless) unit time step, this is not possible for EIS because this would mean that the oscillations of the potential at high frequencies could not be resolved. In order to reduce the overall simulation time, two runs were again made. In the first, the equilibrium state for the potential around which the oscillations occur (the bias potential, $\phi^0$) was calculated using the domain length of interest (generally $L = 5000 l_B$). This equilibrium state was then used as the initial condition for the second run, which was the actual EIS simulation, in which the potential oscillated about $\phi^0$. While there is still some transient decay of the mean current, it is much shorter than when the system is not pre-conditioned as described.

The boundary condition for the EIS component of the run is defined as:

$$\phi(t) = \begin{cases} 
\phi^0 & \text{if } t < 0 \\
\phi^0 + \Delta\phi^0 \sin(2\pi ft) & \text{if } t \geq 0
\end{cases}$$

(6.2)

where $f$ is the frequency of the input potential and $\Delta\phi^0$ is its amplitude. The assumption of a linear response allows the current to be linked to the voltage using the alternating current form of Ohm’s law, in which the resistance is replaced by the impedance, $Z$. We are only interested in the effects of the oscillations about the equilibrium potential, so the impedance can be written as

$$Z = \frac{\phi(t)}{I(t)A}$$

(6.3)

where $I(t)$ is the current density and $A$ is the cross-sectional area of the system. We then have

$$ZA = \frac{\phi(t)}{I(t)} = \frac{\Delta\phi^0 \sin(2\pi ft)}{\Delta I \sin(2\pi ft + \theta)} = |Z|A \frac{\sin(2\pi ft)}{\sin(2\pi ft + \theta)}$$

(6.4)

where $\Delta I$ is amplitude of the output current density signal, $\theta$ is the phase angle between the current and the voltage and $|Z|A = \Delta\phi^0/\Delta I$ is the ratio of the amplitudes of the current and potential signals. Specific values of the impedance are referred to throughout this work by the grouping $ZA$.

Practically, the output of the model gives the potential and the surface charge density as functions of time. The current was calculated from $\sigma$ at each time step using a backward difference formula, from which the magnitude of the impedance and the phase angle could be determined directly. However, since the output of the model is discrete, the exact position and value of the peak in the current density is not known, because it may not occur exactly at the output step. This problem is compounded by the fact that it is not possible to store all of the output data for every time step due to storage space limitations — a frequency of 0.01 Hz would generate
almost $2 \times 10^7$ data points per cycle if $D_c$ were set to $1 \times 10^{-9}$ m$^2$ s$^{-1}$. Even reducing $D_c$ by three or four orders of magnitude to increase the value of the unit dimensionless time would not resolve this problem. Instead, the code was set to output 500 regularly spaced data points for each cycle of each simulation. A cubic spline was then applied to interpolate between the points of the final cycle in the run to determine the position of the peak in the current density.

Analysis of EIS data is simpler in the Fourier (frequency) domain, in which the impedance is a frequency-dependent complex number of the general form

$$Z(j\omega) = Z'(\omega) - jZ''(\omega)$$

(6.5)

where $\omega = 2\pi f$ is the angular frequency, $Z'$ is the real component, $Z''$ is the imaginary component and $j = \sqrt{-1}$. If the input and output signals for the simulation consist of single-frequency signals, $Z(j\omega)$ can be determined in a straightforward manner by stating it in polar form, using the Euler formula:

$$Z = |Z| \exp(j\theta) = |Z|(\cos \theta + j \sin \theta)$$

(6.6)

where $|Z|$ and $\theta$ are the same as in Eqs. (6.4), and their values may be calculated using the following relationships:

$$|Z| = \sqrt{(Z')^2 + (Z'')^2} \quad \text{and} \quad \tan \theta = \frac{Z''}{Z'}, \quad (6.7)$$

EIS data are commonly interpreted using a Nyquist plot, a parametric plot of the complex plane ($Z''$ vs $Z'$). While this is particularly useful for fitting experimental data to that of an EC, this type of plot suffers in that it does not explicitly describe the frequency-dependence of the system properties, so they may be complimented by a Bode plot. This consists of a double plot of $|Z|$ as a function of $f$ and of $\theta$ as a function of $f$.

### 6.1.3 Cyclic voltammetry

Cyclic voltammetry is similar to EIS in that a cyclic time dependent potential is applied to the system and the current response is measured. In this case, however, the applied potential varies as a linear sweep between the maximum and minimum values, forming a triangular wave. Furthermore, the amplitude of the wave is much larger than in EIS and the frequency much lower, meaning that the entire non-linear response of the system is recorded. The technique is more relevant to electrochemically active surfaces, with changes in the output current occurring as the applied potential sweeps past the activation potentials of certain processes, but it is introduced in this chapter as preparation for the one which follows. Experimentally, CV is often conducted in a supporting electrolyte of a higher concentration than the electrolyte of interest in order to minimise the capacitive charging current, i.e. that which is attributable to the formation of the double layer, and focus only on the faradaic, or reaction, current.

The boundary condition for the potential when modelling CV is similar to that for EIS, but
with a linearly varying potential:

\[
\phi = \begin{cases} 
0 & \text{for } t < 0 \\
v(t - 4nt_{1/4}) & \text{for } 4nt_{1/4} \leq t < (4n + 1)t_{1/4} \\
\Delta \phi^0 - v(t - (4n + 1)t_{1/4}) & \text{for } (4n + 1)t_{1/4} \leq t < (4n + 3)t_{1/4} \\
-\Delta \phi^0 + v(t - (4n + 3)t_{1/4}) & \text{for } (4n + 3)t_{1/4} \leq t < 4(n + 1)t_{1/4}
\end{cases}
\]  \hspace{1cm} (6.8)

where \( v = \Delta \phi^0 / t_{1/4} \) is the scan rate, \( t_{1/4} \) is a quarter of the cycle period and \( n = (0, 1, 2, 3, \ldots) \) is the cycle number.

### 6.1.4 The equivalent circuit for the system

For the electrode/electrolyte system modelled, the basic EC is that of a resistor and a capacitor connected in series:

\[ \begin{array}{c}
r_e \quad | \quad C_e \\
\end{array} \]

Figure 6.1: The RC equivalent circuit.

The resistor represents the bulk electrolyte and the capacitor the double layer. Charging times in the numerical model are considered in terms of the surface charge density on the electrode, equivalent to the charge on the capacitor in the EC. As a function of time, if a potential step is applied at \( t = 0 \), the charge on the capacitor in the RC circuit is given by

\[
\sigma(t) = \sigma_{eq} \left[ 1 - \exp \left( -\frac{t}{RAC_d} \right) \right]
\]  \hspace{1cm} (6.9)

where \( \sigma_{eq} \) is the equilibrium surface charge density, \( R \) is the resistance of the capacitor, \( A \) is the electrode area and \( C_d \) is the specific differential capacitance as defined previously. Given that in the numerical model the charging time, \( t_{eq} \), is defined as the point at which \( \sigma(t) = 0.999\sigma_{eq} \), its value can be determined from the above expression as

\[
t_{eq} = -RAC_d \ln \left( 1 - \frac{0.999\sigma_{eq}}{\sigma_{eq}} \right) = 6.9RAC_d,
\]  \hspace{1cm} (6.10)

so it is apparent that the EC predicts that the equilibration time should be proportional to the resistance of the electrolyte and to the differential capacitance. The resistance is discussed in slightly more detail in the following section, but is assumed to be constant in EC models, while the differential capacitance depends on the applied voltage. Taking the GC model, for example, the differential capacitance can be seen from Eq. (2.7) to vary as \( \cosh(\bar{\phi}^0/2) \), so this is how the predicted equilibration time will vary in the EC analogue. Following on from this, the decrease in the differential capacitance at high potential, which is observed experimentally, and arises in more detailed structural models for the double layer, should lead to a decrease in the
equilibration time as the applied potential increases, which is one of the results of Kilic et al’s papers (Kilic et al. 2007a).

For time-dependent surface potentials, the analysis of the EC is carried out in the frequency domain, connecting directly to the EIS method. The complex impedances of the resistor and the capacitor, $Z_R$ and $Z_C$ respectively, are

$$Z_R = RA$$  \hspace{1cm} (6.11a)$$
$$Z_C = -\frac{j}{2\pi f C_d}$$  \hspace{1cm} (6.11b)

The total impedance of the RC circuit is the sum of these values. The magnitude of the impedance and the value of the phase are, respectively,

$$|Z| = \sqrt{(RA)^2 + \frac{1}{(2\pi f C_d)^2}}, \hspace{1cm} \theta = \arctan\left(-\frac{1}{2\pi f RAC_d}\right)$$  \hspace{1cm} (6.12)

It can be seen that for $|Z|$, at very high frequencies the resistive term dominates and at very low frequencies the capacitive term dominates. For the phase angle, its value varies between zero and $-\pi/2$ as the frequency is increased. The characteristic shapes of the Bode and Nyquist plots for the RC circuit with $R\bar{A} = 11000$ and $C_d = 0.1$ are shown in Fig. 6.2 below (the dimensionless unit conversions are as listed in Table 3.1)

Figure 6.2: (a) Bode and (b) Nyquist plots for a system with $C_d = 0.1$ and $RA = 11000$ according to the RC equivalent circuit

The Bode plot shows that the phase shift moves from being $-\pi/2$ rad out of phase to being in phase as the frequency increases and that $\ln(|Z|)$ is comprised of two distinct regions. In the low frequency region where the capacitor is dominant the line has a slope of $-1$ and at high frequency the slope is zero, having converged on the impedance of the resistor. As such, the resistance can be determined directly, while a plot of $|Z|A$ as a function of $1/(2\pi f)$ in the low frequency region will yield the inverse of the capacitance. The Nyquist plot for this EC is a vertical straight line which intercepts the real axis at the resistance of the resistor. This impedance does not show that much information for this type of system, but a plot of the admittance, defined as the inverse of the complex impedance can be used to determine the characteristic frequency of
the system and thereby also the capacitance. Mathematically, the complex admittance for the
RC circuit is
\[
Y = \frac{R}{|Z|^2} + \frac{j}{2\pi f C_d |Z|^2},
\]
(6.13)
a plot of which is shown in Fig. 6.3 below.

![Admittance for the RC circuit discussed in the text, indicating the point of the characteristic frequency](image)

Figure 6.3: Admittance for the RC circuit discussed in the text, indicating the point of the characteristic frequency

The admittance for the RC circuit has a semi-circular shape. The high-frequency intercept on the real axis corresponds to inverse of the system resistance and the frequency at which the apex occurs defines the characteristic frequency, the inverse of which is the characteristic time for the system, \( \tau_c = \frac{1}{RAC_d} \). This is the same as the characteristic charging time in the constant potential case, representing the amount time the surface charge density takes to reach \( \sim 0.74\sigma_{eq} \).

### 6.2 The response to a potential step

In this section, the predicted response of the system to a step change in the potential is considered. It was shown in the previous chapter that, by accounting for the interactions of ions with the solvent and each other, the equilibrium state is predicted to have a much lower surface charge density than that predicted by the GC model at the same \( \phi^0 \). For this reason alone it can be expected that the equilibration time should be smaller when either the excluded volume or excess polarisability are accounted for, since less material has to be moved into the double layer before equilibrium is reached. However, as shown by Kilic et al (Kilic et al. 2007a) for the Bikerman form of the excluded volume interaction (and also as implied by the simple EC analogue for a blocking electrode), the equilibration time is a function of the differential capacitance of the system. This means that it increases to a certain value as a function of the applied potential before decreasing again.
6.2.1 General features of the time evolution of the system

The basic response of any electrode/electrolyte system of the type described in Fig. 3.1 is largely the same, regardless of the inclusion of ion-specific effects, and is demonstrated by Figs. 6.4 (a) and (b). Plotted is the response of a 0.1 M monovalent 1:1 electrolyte in a 500 lB domain to an applied potential of $\bar{\varphi}(t) = 5$ using the GC (PNP) model, showing the concentration profiles of the counter- and co-ions (solid and dashed lines respectively) in the immediate vicinity of the electrode (part (a)) and across the whole domain (part (b)). In part (b), the arrows indicate the direction of increasing time and the inset shows the surface charge density as function of time, the crosses indicating the times at which the profiles are plotted.

In terms of the surface charge density, the response to the applied potential is an initially rapid growth in $\sigma$ giving way to a convergence on the equilibrium value, in much the same way as the charging occurs in a resistor-capacitor (RC) circuit. This rapid growth in $\sigma$ is driven by an initially rapid increase in the counter-ion surface concentration and an equally rapid decrease in the co-ion surface concentration, leading to much of the final double layer structure being formed in a short amount of time (black curves in Fig. 6.4(a)). The cost of doing this, however, is the formation of a depletion layer just outside the nascent double layer.

At early times this depletion layer grows rapidly, being narrow and deep (black curves in Fig. 6.4(b)), before gradually becoming wider and shallower as it is filled in by ions moving across the domain from the left hand boundary (red curves in Fig. 6.4(b)). The extent and depth of the depletion layer depends on the bulk ion concentrations and the amount of charge required in the fully formed double layer, being smaller at higher concentrations and lower potentials. Note that the extent of the depletion layer is small relative to that of the surface concentrations, so it is not visible at the sale of part (a) of the figure.

The figures also highlights one possible drawback to the model, which is that the finite nature of the domain means that the depletion layer cannot pass $z = L$, which is a fixed concentration point. This leads to changes in the concentration profiles, which are concave upwards at
earlier times but become concave downwards once the depletion layer extends to the right hand boundary. The result of this will be changes to the diffusive component of the flux, which is dependent on the concentration gradient, inevitably leading to changes in the overall equilibration time. Evidently, if the real system being modelled is this small (for example ions confined to pores), or there is some means of maintaining the concentration at a constant value at some distance from the electrode (such as by using a rotating disc electrode) then this is not a problem, but for larger real systems this artificial effect will impact on the system behaviour and longer domain lengths would be required for proper simulation.

The ion depletion, relative to the bulk, occurs for both the co- and counter-ions, with them having the same concentrations throughout most of the domain for all times — the concentration curves for both sets of ions in Fig. 6.4(b) overlap in most of the domain. Only in the immediate vicinity of the electrode is the electrostatic potential energy large enough to support a region of space-charge, with different ion concentrations. This equality of the co- and counter-ion concentration throughout most of the domain means that it remains charge neutral and that the potential remains a linear function of \(z\) as the double layer charges, as shown by Fig. 6.5(a).

The predicted flux is shown in Fig. 6.5(b) at the same time steps as the data in Figs. 6.4(a) and (b).

![Figure 6.5: (a) Electric potential and (b) counter- and co-ion fluxes in the domain plotted at the same times as the curves in Fig. 6.4](image)

In the basic PNP model the total flux of the ions is comprised of two components — a diffusion flux, due to concentration gradients, and an migration flux, due to the electric field. At \(t = 0\), when the potential is applied, the concentrations of the ions are uniform, so the field drives all initial ion motion — counter-ions towards the electrode and co-ions away from it. Since the electrode is impermeable, the counter-ions pile up at the surface and the co-ion concentration decreases, creating the region of space-charge which is the double layer. This space charge supports a larger electric field near the surface, which decreases the electric field across the rest of the domain. Since the migration flux depends on the electric field, this means that its value increases with time near to the electrode surface and decreases with time away from it, as can be inferred from Fig. 6.5(a).

The diffusive component to the flux is initially zero, but it grows as the migration flux changes.
the concentrations. At the surface, the growth in the counter-ion concentration and reduction in the co-ion concentration results in diffusive fluxes which counter the migration flux in that region. Beyond the forming double layer, the concentration gradients of both ions point towards the lowest point of the counter-ion concentration in the depletion layer, so the diffusive flux always acts towards the surface, complementing the counter-ion migration flux and counteracting the that of the co-ion.

The total flux profiles shown in Fig.6.5(b) reflect the competition between the two components. At \( \bar{z} = 0 \) both total fluxes are zero, as they must be to satisfy the boundary condition. As the time increases, the total fluxes across much of the domain are almost equal and opposite because the concentration gradient is small and the migration component dominates. The larger concentration gradients near the electrode surface, both within and without the region of space-charge, mean that the two total fluxes differ significantly. For the counter-ion, the two components complement each other, so the total flux is increased, while the opposite is true for the co-ion.

### 6.2.2 Equilibration time in the PNP model

The amount of time the system takes to reach equilibrium, \( t_{\text{eq}} \), in the PNP model can only depend on the limited number of parameters which describe the system. As the electrolyte is composed of monovalent ions, each with \( D_j = 10^{-9} \text{ m}^2 \text{ s}^{-1} \), the only remaining parameters are the electrolyte concentration, the domain length and the applied potential. Shown in Fig. 6.6 (a) is a plot of \( t_{\text{eq}} \) for a 0.1 M GC electrolyte as a function of the applied potential for a selection of domain lengths, and in part (b) is a plot of \( t_{\text{eq}} \) as a function of the applied potential for a 500 \( l_B \) domain at a selection of bulk ion concentrations. The highest potential applied in each case in the latter figure is the nearest whole number value for which the error in the equilibrium surface charge density remains smaller than 1\% at the grid spacings listed in Table 4.1.

![Equilibration time in the GC model](image)

Figure 6.6: Equilibration time in the GC model as a function of the applied potential; (a) 0.1 M solution at a selection of domain lengths and (b) 500 \( l_B \) domain at a selection of bulk ion concentrations.

Increasing either the potential or the domain length leads to an increase in \( t_{\text{eq}} \), while increasing the concentration causes \( t_{\text{eq}} \) to decrease. Qualitatively this is to be expected, since a longer
domain means that the electric field, and therefore the electromigration flux, is smaller, an increased potential means that more material has to be moved into the double layer before it reaches equilibrium, and increasing the concentration increases the number of charge carriers in the bulk, meaning a higher rate of charge transport and a lower equilibration time. However, the shapes of the curves differ from that which the EC for the system predicts. As discussed in Section 6.1.4, the equilibration time is a function of the differential capacitance and the resistance of the system. The differential capacitance has a \( \cosh(\bar{\phi}_0/2) \) dependence on the applied potential in the GC model and the resistance is assumed constant in the EC, so the RC equilibration time should also be proportional to \( \cosh(\bar{\phi}_0/2) \), which it is clearly not.

The reason for this is that the resistance is, in fact, not constant throughout the domain because there are fewer ions in the depletion layer than in the bulk. The resistance of an electrolyte depends on its conductivity, \( \kappa_c \), and its dimensions through the relationship

\[
R = \frac{L}{\kappa_c A} \tag{6.14}
\]

where \( L \) is the domain length and \( A \) its cross-sectional area. The conductivity is a function of the concentration and the mobility of the ions, defined as

\[
\kappa_c = \sum_j |z_j| e_0 \bar{c}_j^0 b_j \tag{6.15}
\]

where \( b_j \) is the electrical mobility of ion \( j \), related to the diffusion coefficient through the Einstein relation

\[
b_j = \frac{e_0 D_j}{k_B T} \tag{6.16}
\]

For a 1:1 symmetric monovalent electrolyte in which both ions have the same diffusion coefficient \( (D_1 = D_2 = D) \), the previous two equations combine with Eq. (6.14) to give the following expression for the product of the resistance and the area

\[
RA = \frac{k_B T L}{2 \sum_j |z_j| e_0^2 D c_0^0}, \tag{6.17}
\]

There is an inverse proportionality between the concentration and the resistance, so if the concentration drops, the resistance increases and charge will flow more slowly in response to an electric field. Such a reduction in the conductivity is what occurs in the example systems shown in the previous figures: the formation of the depletion layer as shown in Fig. 6.4, causes the local resistance to increase outside the developing double layer, reducing the ionic current and causing the equilibration time to be longer than it otherwise would be. The extent to which ions are depleted from the double layer depends on the concentration and the size of the initial electric field, itself a function of the domain length and the applied potential.

Considering in more detail the effect of the domain length on the behaviour of the system, Fig. 6.7 (a) shows \( t_{eq} \) a function of \( L \) for two electrolyte concentrations (0.01 M and 0.1 M) each at two potentials \( (\bar{\phi}_0^0 = 1 \text{ and } \bar{\phi}_0^0 = 5) \). Part (b) of the figure shows a normal-axes plot of the
0.1 M, $\bar{\phi}^0 = 5$ case, focusing on each of the numbered sections of the curves shown in part (a).

Figure 6.7: (a) GC model equilibration times as a function of domain length for 0.01 M and 0.1 M systems at applied potentials of $\bar{\phi}^0 = 1$ and $\bar{\phi}^0 = 5$ and (b) linear plot of the 0.1 M, $\bar{\phi}^0 = 5$ curve. Each sub-plot corresponds to the numbered region of the curve in part (a)

Fig. 6.7 (a) shows that there are three distinct regions in the growth of $t_{eq}$ with $L$ and that these regions are present for all systems regardless of their bulk concentration or the applied potential. The only difference between them is that the transition between the regions takes place at longer domain lengths when the applied potential is higher or the bulk concentration lower.

The third region is the most straightforward, with the normal-axes plot showing a linear relationship between $t_{eq}$ and $L$. In this region the depletion layer is sufficiently small that the ion concentrations do not deviate significantly from their bulk values at any point in the domain. As a result, the system behaves as predicted by the EC for the system and the charging time can be calculated according to Eq. (6.10).

It can be seen from part (a) of Fig. 6.7 that if the domain length and concentration are constant, increasing the potential moves the system out of region three, into region two and finally into region one, i.e. from the region in which Eq. (6.10) applies and into regions where it does not. From this it can be inferred that, for a given length and bulk concentration, there is a threshold potential below which the system should always exist in region three and so the RC circuit applies.

However, for the data shown in Fig. (6.6), the length is such that the transition from region three to region two occurs at very low potentials (of the order $\bar{\phi}^0 = 1$) which is why $t_{eq}$ deviates significantly from the $\cosh(\bar{\phi}^0/2)$ dependence predicted by the EC analogue for the system. Running the 0.1 M system from Fig. 6.6(b) again, this time with the domain length increased to $4 \times 10^6 l_B$, shows that this increases the range of potentials over which the EC remains valid. In the figure, the EC curve is plotted, using Eq. (6.17) to estimate the resistance of the electrolyte to be $RA = 0.03828 \Omega \text{m}^2$ and Eq. (6.10) to determine the equilibration time.

Until the potential reaches $\bar{\phi}^0 = 6$, the equilibration time from the numerical model is approx-
Figure 6.8: Comparison of the increase in equilibration times for a 0.1 M system with a $4 \times 10^6 \, l_B$ domain as predicted by a basic equivalent circuit model and the numerical solution.

imimately equal to that from the RC analogue, although it is very slightly smaller for the lower potentials, the possible reason for which will be discussed further in the following section. For potentials larger than $\phi^0 = 6$, the simulation predicts a longer equilibration time, in accordance with a shift of the system from region three to region two. As expected, the transition occurs at a larger potential in this longer domain than in the shorter one, but there will always be a potential which causes depletion of the ions to occur and so there will always be a potential above which the RC circuit does not apply.

### 6.2.3 Equilibration time in the mPNP model

From a simple consideration of the fact that accounting for ionic interactions reduces the number of ions required to form the double layer, it seems apparent that accounting for them in the structural model should cause a reduction in the equilibration time. Additionally, the reduction in the differential capacitance which ion interactions cause means that EC analogues also predict a reduction in $t_{eq}$. Running the full numerical model confirms that this is the case, as shown in Fig. 6.9, in which a comparison is made of a 0.1 M PNP system with two mPNP systems, all with the same domain length of $L = 4 \times 10^6 \, l_B$. In the first mPNP system, the excluded volume interaction is accounted for with $a = 0.7 \, nm$, and in the second, the polarisability term is accounted for with $4\pi\alpha = -8 \, M^{-1}$. In all cases the Stern layer is not accounted for.

The crosses show the data from the full runs of the numerical model and the solid lines show the EC result, using either the analytical solution for $C_d$ (for the GC model) or the calculated differential capacitance from the equilibrium data generated by the model (these data form part of Figs. 5.17 (a) and (b) and are also recreated in Fig. 6.12). The solution resistance in all cases was calculated using Eq. (6.17).

In accordance with the behaviour seen in the PNP model, $t_{eq}$ in the mPNP model again follows the differential capacitance. This means that, for potentials above that which gives the peak in the equilibrium $C_d$, the amount of time taken to reach equilibrium decreases, even though the
ends state contains more ions in the double layer and more charge on the electrode if the potential is larger. While this result has previously been demonstrated explicitly for the excluded volume interaction (Kilic et al. 2007a), it has not been modelled for the polarisability interaction. Furthermore, while there are differences between equilibration times predicted by the EC and numerical simulation results, these are much less significant over the entire potential range than in the GC model, indicating that the EC analogue provides a much better approximation to the system if the system is assumed to be non-ideal. This results from the fact that the formation of the double layer requires far fewer ions when deviations from ideal behaviour are accounted for, so the bulk is depleted to a much lesser extent during the charging process, meaning that the resistance of the electrolyte changes by a much smaller amount.

While the equilibration time is approximately the same in the EC and numerical solution results, there are distinct differences and trends. For very low potentials, the EC result is slightly larger than that of the numerical solution but as the potential moves above the peak the numerical model predicts the larger value. The low-potential discrepancy was not expected, since the system should approach EC-like behaviour as the potential tends to zero. In order to confirm that this was not a result of errors in the numerical solution, the number of grid points in the first three sub-domains was increased by 50% and the tolerance was reduced to $1 \times 10^{-10}$ and selected systems re-run, the result being a negligible (< 0.001% relative difference) in the predicted equilibration time. The discrepancy possibly due to a small contribution to the transport from diffusion. Although the length is such that there is no significant decrease in the concentration in the domain, leading to an increase in the solution resistance, a very small concentration gradient over the long equilibration time would cause a small reduction in the equilibration time.

The source of the difference between the model and the EC results at high potentials has been discussed previously; it is caused by a change in the electrolyte resistance during the charging process. However, the effect is evidently smaller for the mPNP systems than it is for the PNP
model, since the result from the numerical model follows the differential capacitance much more closely, rather than diverging from it as is the case for the PNP system (see Fig. 6.8).

As in the PNP model, the domain length has a significant impact on the equilibration time. Despite the fundamental change to the system wrought by accounting for ion interactions, \( t_{eq} \) as a function of the length still exhibits the three different regions of growth seen in Fig. 6.7, as shown in Fig. 6.10.

![Figure 6.10: Comparison of the equilibration times for the GC, excluded volume-only and polarisability-only cases for \( \phi_0 = 1, 5 \) and 9 and concentrations of \( c^0 = 0.01 \text{ M} \) (solid lines) and \( c^0 = 0.1 \text{ M} \) (dashed lines)](image)

While the three regions are still present, the ion interaction terms have an effect on which region the system is in at a given length and potential. Where for the PNP model increasing the applied potential has the effect only of increasing the equilibration time and thereby moving the transition points between the regions to longer lengths, the reduction in the equilibration time which results from the ion interactions leads to the transition points moving to lower lengths at higher potentials. In the case of the 0.1 M system shown in Fig. 6.9, the domain length of \( 4 \times 10^6 l_B \) means that the system remains in the third region throughout the potential range shown and so should show approximately RC circuit-like behaviour, as was observed. As with the PNP model, there is a change in the behaviour of the systems as the domain length is decreased, but the effect on the two systems is slightly different. Shown in Fig. 6.11 are the predicted equilibration times for the two mPNP systems for a range of domain lengths. The crosses represent the modelled data points, which have been interpolated using a cubic spline as a visual aid.

In shorter domains, the effects of the different ion interaction terms differ and seem depend on the domain length as well. The differential capacitance curves for the two electrolytes shown indicate that the peak for the excluded volume model should occur at about \( \bar{\phi}^0 \approx 4.5 \) and for the polarisability model should occur at about \( \bar{\phi}^0 \approx 3.6 \) but, in the same way as seen in Fig. 6.9,
the equilibration times peaks at a slightly higher potential. In addition to this, the peak of the differential capacitance curve is slightly higher for the polarisability case, but this is not always the case when considering the equilibration time.

It can be seen that the equilibration time peaks at a higher value in the polarisability model than it does in the excluded volume model both for very long domains (see Fig. 6.9) and for very short domains ($L \leq 1000$ curves in Fig. 6.11). However, for some intermediate lengths the polarisability model peaks at a lower value, the reason for which is not exactly clear. If we consider the excluded volume interaction, this will always act to attempt to fill the depletion layer, so this should offset some of the increase in the equilibration time caused by the reduction in the ion concentration. As the domain length is shrunk, the depletion layer becomes deeper and the excluded volume term makes a larger contribution, so it should slightly decrease the equilibration time relative to a system which has no excluded volume interaction (but which somehow has the same differential capacitance). The polarisability term, on the other hand, makes no contribution to the flux throughout most of the domain. It can be seen from Eq. (3.61) that the term depends on the gradient of the potential, and from Fig. 6.5 that the potential varies linearly with the position outside the double layer as it forms. The flux contribution, proportional to $\nabla \mu^\text{cl}$, is therefore zero except near to the double layer. It is possible that the reduced permittivity and corresponding increase in the electric field strength cause the ion flux to increase slightly as the ions approach the double layer region. This might compensate for the reduced resistance of the depletion layer to some extent but it has not been possible to show whether this is actually occurring or not.

6.2.4 The effect of the Stern layer

As seen previously, the Stern layer has the effect of reducing the differential capacitance at all concentrations and all applied potentials. The fact that there is a reduction in the differential
capacitance implies that the equilibration time should also decrease, which also follows from the physical fact that fewer ions are required to move from the bulk to form the double layer when the Stern layer is accounted for. However, there is a significant difference in the effect of the Stern layer on the excluded volume and polarisability models, particularly at higher potentials and shorter domains.

In order to discuss the effect of the Stern layer, the systems from the previous section which included ion interactions are again compared, this time with the same systems including a Stern layer. The width of the Stern layer in all cases is equal to 0.35 nm. For reference, the differential capacitance curves of the four systems are shown in Fig. 6.12(a). Part (b) of the figure shows the equilibration times of the four systems as a function of the potential for a domain length of $4 \times 10^6 \lambda_B$.

Along with the reduction in the differential capacitance introduced by the Stern layer, there is also a reduction in the equilibration time. There is also a smaller difference between the time calculated from the EC analogue and the numerical simulation when the Stern layer is accounted for, which is likely to result from a further reduction in the extent to which the ions are depleted from the electrolyte during the charging process.

As with the systems without the Stern layer, reducing the length reduces the equilibration time and leads to changes in the shapes of the $t_{eq}$ vs $\phi^0$ curves, but now the changes are much more significant, particularly for the polarisability term. Shown in Figs. 6.13(a) and (b) are plots of the same systems shown in Fig. 6.11 but this time including the Stern layer (symbols represent the modelled data points, the lines are cubic spline interpolations intended as a visual aid).

For both interaction terms, reducing the domain length has the same general effect of causing the peak in the equilibration time to shift to higher potentials and for the decay in the equilibration time to be slower than it would be in the EC analogue (i.e. $t_{eq}$ decays more slowly above the peak than does $C_d$). Since the decay of $C_d$ is already small at high potentials when
the Stern layer is included, the equilibration times become almost linear with respect to the potential in very short domains, with the decrease in $C_d$ apparently being offset by the increase in the solution resistance in the depletion layer.

The relative effects of increasing the potential on the equilibration times in the two models is also noticeable. The peak in the differential capacitance in the excluded volume model is approximately a factor of 1.2 larger than in the polarisability model, yet the peak in the equilibration time is approximately a factor of 2.5 larger (at $\bar{L} = 10000$). Additionally, $t_{eq}$ in the excluded volume model peaks about three units of potential higher than the peak in $C_d$, while for the polarisability model the difference is only about one unit of potential. The differences, again, are likely to be due to the difference in the extent to which ions are depleted from the bulk, being larger in the excluded volume model for which more ions are required to form the double layer at a given potential.

The inclusion of the Stern layer does not change the presence of the three growth regions identified in Fig. 6.7, but it does slightly change the lengths at which the systems transition between them, as shown in Fig. 6.14. The data presented shows a comparison of the data for the non-GC models shown in Fig. 6.10 with the same systems after a Stern layer of width 0.35 nm has been included.

At low potentials there remains very little difference between the two ion interaction models. In both cases there is a reduction in the equilibration time upon the addition of the Stern layer, commensurate with the decrease in the differential capacitance which accounting for the Stern layer causes. At the same time as undergoing a decrease in the equilibration time, the length at which the system moves between the three regions identified previously shifts to lower values.

There seems to be less of a shift in the transition points between the three regions at higher potentials, and at the same time it can be seen that the Stern layer has a much larger effect on the equilibration time in region two than it does in either regions one or three. Furthermore, the effect is greater when the polarisability term is accounted for.
6.3 Electrochemical impedance spectroscopy

In this section, the model is used to simulate the basic EIS experimental technique. A sinusoidal potential of the form stated in Eq. (6.2) is applied at the electrode boundary, the amplitude of which, for all runs, was $\Delta \bar{\phi} = 0.3$ ($\Delta \phi = 7.7 \text{mV}$), this being of a similar order to the values used in experiments. For the simple case of the PNP system with a 0.35 nm Stern layer, the simulated bode plots for a 1 M electrolyte in three domains of different lengths are shown in Figs. 6.15 (a) and (b).

The response of the system is as expected for the two longer lengths, with the characteristic opened L-shaped $|ZA|$ vs $f$ curves and s-shaped $\theta$ vs $f$ curves. The value of $|ZA|$ on which each of the lines converge at high frequency is equal to that given by Eq. (6.17), being approximately

Figure 6.14: Comparison of the equilibration times for the excluded volume-only and polarisability-only cases for $\bar{\psi}_0 = 1, 5$ and 9, concentrations of $c^0 = 0.01 \text{ M}$ (solid lines) and $c^0 = 0.1 \text{ M}$ (dashed lines), with and without a Stern layer

Figure 6.15: Simulated Bode plots for the standard PNP model at selected domain lengths (a) $|Z|$ and (b) $\theta$ as a function of the frequency
$|\bar{Z}\bar{A}| = 1120$ for the shortest length, 11230 for the middle length and 112300 for the longest length, showing that increasing the length by a factor of ten increases the resistance by the same factor. There is some variation in the exact value of the resistance predicted by the model at a given length, but for most of the data points the relative difference between the two extreme values is smaller than 1%, so this is within the range for the numerical error. The exception to this is for the $L = 5001_B$ domain, for which the phase angle seems to not quite tend to zero at high frequencies. This seems to be more a limitation of the model under the conditions of a short domain and high frequency rather than a physical effect, as it is not observed at longer domain lengths. In general, such combinations of high frequencies and short domains have been avoided throughout the rest of this work.

All three curves in the $|ZA|-f$ plots converge at low frequencies on a single line. This represents the region where the capacitor dominates the behaviour in the RC circuit and, since the ion concentration is the same in each system the differential capacitances are also the same. Based on the assumption that the RC analogue is valid, the differential capacitance in this simple system can be calculated from the complex part of the impedance using Eq. (6.11b) to give

$$C_d = \frac{1}{2\pi f Z''}$$

(6.18)

Applying this to the low frequency region of the Bode plot for any of the systems yields the result that the dimensionless differential capacitance is $\tilde{C}_d = 0.0874$. This is in very good agreement with the values calculated either using the equilibrium simulated data or by solving the equations for the GCS model, validating the numerical model for the low frequency dynamic response.

The Nyquist plots of the impedance and the admittance for the above systems are shown in Fig. 6.16.

![Figure 6.16: Simulated nyquist plots of (a) the impedance and (b) the admittance for the systems in Fig. 6.15](image)

The shapes of these curves are much as they should be — the impedances are vertical lines along $Z'\bar{A} = R\bar{A}$ and the points on the admittance plots trace out a semi-circular shape. The characteristic frequency for each system is the frequency of the apex of each curve, at which
point the frequency is equal to the inverse RC time of the equivalent circuit. Again, the values determined from the numerical simulation were found to be equal to those calculated directly from the resistance, given by Eq. (6.17), and the differential capacitance, from either of the calculation methods.

Accounting for the excluded volume or the polarisability of the ions in the solution has no discernible effect on the Nyquist plot of the impedance when the bias potential is zero; the result is the same series of vertical straight lines at the same values of $Z' A$, indicating that there is no change in the resistance of the electrolyte as a result of the interactions. Differences between the PNP and mPNP models do arise, but only in those properties which depend on the differential capacitance. Hence, while the excluded volume interaction leads to no changes to the Bode plots (since the system is at zero potential), the polarisability interaction does cause a slight shift upwards of the capacitive part of the $|Z| \text{vs} \ f$ curve as shown in Fig. 6.17(a), although the gradient of the line remains the same.

![Figure 6.17: (a) simulated $|Z| \text{vs} \ f$ component of the Bode plot (red and black lines coincide) and (b) Nyquist plot of the admittance for the GC and two mPNP cases Fig. 6.15](image)

Shown in part (b) of the figure above is the admittance for the three systems. Each set of frequencies plotted for the three systems are the same and it can be seen that all three models trace the same arc. However, while the two components of the admittance for the GC and excluded volume models are always the same, the points corresponding to the polarisability model are slightly retarded from the other two models as the frequency increases — for the points representing the same frequency, the polarisability point is the green symbol in the anti-clockwise direction from the black and red symbols of the other two models. This means that the value of the frequency when the polarisability reaches the apex is higher than the value when the other two models reach the apex. Through Eq. (6.18) this corresponds to the differential capacitance having a smaller value, as is expected.

### 6.3.1 Capacitance dispersion

It is well known that the capacitance of electrolyte materials changes with the frequency, an effect which has been attributed variously to the roughness of the electrode, anion adsorption and the porous properties of the electrode (Kerner and Pajkossy 2000; Pajkossy 1997; Pajkossy 175).
In addition to the these physical properties of the electrode surface, recent modelling by Wang and Pilon (Wang and Pilon 2012a) has demonstrated the effect to arise in the type of idealised system represented by the model in this work, namely an electrolyte adjacent to smooth planar electrode. In general the capacitance is constant up to some threshold frequency before decreasing at higher frequencies. The authors linked the capacitance dispersion effect to the inability of the ions to move quickly enough to follow the changing frequency. In essence, as the frequency is increased the electrolyte is unable to respond to the changing potential, meaning that the double layer charge, and therefore the electrode surface charge density, is smaller. Since the amplitude of the potential is the same at all frequencies, this reduced charge means that the differential capacitance must be smaller.

Through the construction of a model for a similar electrode/electrolyte system as that described in this work, but only accounting for the excluded volume interaction (through the Bikerman model), Wang and Pilon have discussed capacitance dispersion. Their results indicate that, beyond the change to the differential capacitance at $\phi \neq 0$ which the excluded volume interaction causes, there is no discernible effect on the rate at which the capacitance decreases with frequency. As will be shown below, the same is true of the polarisability interaction, despite the changes in the permittivity which arise when the polarisability is accounted for.

The way in which the differential capacitance changes as a function of the frequency is plotted in Fig. 6.18. The plot shows the value of the differential capacitance at the PZC (i.e. with zero bias potential) as calculated from simulated EIS for a system in which the polarisability is accounted for, at values of $4\pi\alpha = -8\,\text{M}^{-1}$ and $4\pi\alpha = -16\,\text{M}^{-1}$, at three different diffusion coefficients, $D = 1 \times 10^{-9}\,\text{m}^2\,\text{s}^{-1}$, $1 \times 10^{-8}\,\text{m}^2\,\text{s}^{-1}$ and $1 \times 10^{-7}\,\text{m}^2\,\text{s}^{-1}$.

![Figure 6.18: Simulated differential capacitance as a function of the frequency for two ion excess polarisabilities and three different diffusion coefficients](image)

In all cases at low frequency the differential capacitance converges on the value at the PZC, which is defined by the value of the polarisability, the Stern layer width and the bulk concentration. At high frequencies $C_d$ is seen to decrease, with the systems having the same diffusion coefficient converging on the same values of the differential capacitance at high frequencies. This further suggests that the polarisability has no impact on the bulk transport properties of the
electrolyte, otherwise there would likely be different rates of convergence at high frequency. If the time is rescaled to the characteristic diffusion time, \( \tau_d = \frac{L^2}{D} \) (Rubinstein et al. 2009), the curves with the same permittivity collapse on to a single line throughout the frequency range and all of the curves merge at high frequencies, as shown in Fig. 6.19.

When scaled in the manner shown in Fig. 6.19, the frequency at which the capacitance begins to decrease is independent of the value of the excess polarisability, occurring at \( \tau_D f \approx 100 \). This would suggest that the diffusion coefficient and domain length remain the sole determining factors on the capacitance dispersion. As discussed earlier in this section, the lack of an effect of the excluded volume on the capacitance dispersion has been previously demonstrated for the Bikerman excluded volume model although only a single ion volume was presented in that set of results. Both for completion of this work and in order to confirm that the ion volume does indeed have no effect, those results are recreated here using the mvdW model and two different ion diameters, as shown in Figs. 6.20(a) and (b). In these figures, the two ion diameters are \( a = 0.7 \) nm and \( a = 0.88 \) nm so that the maximum concentrations are the same as those shown in the polarisability case, and the same set of diffusion coefficients are used. Part (a) of the figure shows the data using the standard dimensionless units of this thesis, while part (b) shows the same data rescaled to the characteristic diffusion time-scale.

As expected, the excluded volume interaction has no effect on the capacitance dispersion, as shown by the fact that the six systems presented collapse on to a single line when the frequency is rescaled by the characteristic diffusion time. Furthermore, the point of onset for the dispersion is the same as that for the polarisability model.

As part of their work, Wang and Pilon proposed that the characteristic time-scale governing the frequency at which the system moves between being diffusion-limited and not diffusion-limited (i.e. the point at which capacitance dispersion begins) should be characterised by \( \tau_m = \frac{\lambda_m^2}{D} \), where \( \lambda_m \), is the Debye length at the maximum concentration, defined as

\[
\lambda_m = \sqrt{\frac{\epsilon_r k_B T}{4\pi \epsilon_0^2 \sum_j z_j^2 c_j^m}} \tag{6.19}
\]
Figure 6.20: Simulated capacitance as a function of frequency for a 1 M electrolyte with two different ion diameters ($a = 0.7$ nm and $a = 0.88$ nm). (a) in standard units and (b) with the time scaled to the characteristic time $\tau_D = L^2 / D$

where $c_m$ is the maximum concentration of the ions. However, the results above suggest that the diffusion time remains the more appropriate value. For the case with the excluded volume, the two systems have different values of $c_m$, meaning that they have different values of $\lambda_m$ and so the onset of the dispersion will occur at different values of $\tau_m$, whereas they are the same when the time is scaled to $\tau_D$. Additionally, comparing the excluded volume and polarisability models, there are two pairs of systems with the same maximum concentrations. These do not have the same values of $\lambda_m$ though, because the permittivity in the polarisability case is half of the bulk value when the concentration is at the maximum, meaning again that the systems have different values of $\tau_m$ for the same maximum concentration, so the onset of the capacitance dispersion will be different if the time is scaled to that value. Finally, capacitance dispersion can be observed when ion interactions are not accounted for, in which case there is no concentration limit and $\lambda_m \rightarrow 0$, making the that particular characteristic time zero.

Beyond the high concentration systems shown above, several runs were also made for systems at 0.1 M, both with and without a Stern layer, and also for systems in which the bias potential ($\phi_0$) was non-zero. In all cases the onset of the reduction of the capacitance occurred at the same value of $\tau_D f$, further indicating that neither the excluded volume nor ion polarisability affects capacitance dispersion even when a double layer is present. In all, the time-scale $\tau_m$ does not appear to be the most suitable for defining when the capacitance becomes diffusion-limited. Instead, the standard characteristic diffusion time-scale remains the more appropriate property.

It should be noted that, for the model systems shown above, the reduction in the capacitance occurs for frequencies in the kHz to MHz range and beyond, while it is experimentally observed to occur at much lower frequencies (Kerner and Pajkossy 2000). On the one hand, this is because of the very short simulated domain length, which leads to a correspondingly short characteristic time. Increasing the domain length would increase $\tau_D$ and so reduce the frequency range over which the capacitance dispersion occurs. However, while diffusion effects can be shown to influence the dispersion, it cannot recreate in detail the types of frequency-dependence which are measured experimentally, hence the influence of the factors mentioned at the beginning of this section remain significant.
6.4 Cyclic voltammetry

The final type of potential variation considered is that which is equivalent to cyclic voltammetry. As described in section 6.1.3, this entails the application of a triangular waveform potential to the electrode and measuring the current response. In this case, the amplitude of the applied waveform is much larger than is used in EIS, covering the whole range of interest in a particular system. As a result, the full non-linear response of the system is accounted for.

At this stage, given the fact that the system is simply an electrolyte at a blocking electrode, there is little which can be determined from the technique beyond a couple of remarks as to the effect of the ion interaction terms, although the model does provide insight into how the interior of the system behaves as the potential changes. In general the technique is of more relevance to reacting systems, which will be discussed in the following chapter.

Fig. 6.21 shows an example cyclic voltammogram for three systems, the first being the GCS model, the second the excluded volume model with \( a = 0.7 \text{ nm} \) and the third the polarisability model with \( 4\pi \alpha = -8 \text{ M}^{-1} \), each with a Stern layer of 0.35 nm width. The bulk concentration in all cases is 0.01 M, the amplitude of the applied potential is \( \Delta\phi^0 = 10 \) (the applied potential is shown in both parts of the figure in the black lines) and the sweep rate is 0.1 V s\(^{-1}\). The scan rate is slow compared to the amount of time which the system takes to come to equilibrium, so the system is in a quasi-steady state over the entire cycle. Part (a) shows the surface charge density for each system as a function of the time and part (b) the potential at various points in the domain.

Regardless of the system, at a given time the value of \( \sigma \) is equal to the value it would have in a constant potential system at the same potential as at the time of interest. From the previous chapter it is known that for the system parameters used in the examples, \( \sigma \) in the polarisability-only case (dotted line) peaks at a lower value than that of the excluded volume-only case (dashed line), and they both peak at a lower value than the GCS case (solid line). As the applied potential passes through zero, all \( \sigma \) values converge, again as they should.
Part (b) of the figure shows the potential at certain points in the domain for the three systems shown in part (a), with the different models again being represented by the same line styles. The black line is again the applied potential, the red curve is the potential drop across the Stern layer, the green curve is the potential drop across the diffuse layer and the blue curve is the potential drop across the bulk. The boundary between the double layer and the bulk is taken to be the first point, moving away from the electrode towards the bulk, at which the statement $\sum_j z_j c_j < 10^{-6}$ is true, i.e. it is the point at which the local charge density is sufficiently small that the point must be outside the double layer. From the way that the system develops in time (see Fig. 6.4), this is point is on the electrode side of the depletion layer, just before the concentrations of the co- and counter-ions converge as $z$ increases.

Again, the potentials over the three regions trace the equilibrium values, with the growth in the Stern layer accounting for a greater fraction of the total potential drop as the applied potential grows. The Stern layer potential drop is smallest in the excluded volume-only model and largest by a small margin for the polarisability-only model, due to the reduction in the permittivity associated with the increased ion concentration. In all three models the potential drop across the bulk barely deviates from zero, indicating a very small driving force for ionic electro-migration and also that the system is indeed in a quasi-steady state at all times.

Rather than plot the surface charge density as a function of time, CV experiments are considered in terms of the current as a function of the applied potential. Plotting these two values for the three systems in the previous figures gives the following result, where positive values of $I$ correspond to the forward sweep and negative values to the reverse sweep.

![Figure 6.22: Simulated cyclic voltammograms for the three systems shown in Fig. 6.21.](image)

In the GCS model the magnitude of the current can be seen to increase with the magnitude of the applied potential over the whole potential range, although the growth slows as the potential increases. The inclusion of the ion interaction terms leads to qualitatively different behaviour, however, with the introduction of peaks in the magnitude of the current. This type of behaviour has been demonstrated previously for the excluded volume interaction (Wang and Pilon 2012b),
but is included here in order to clearly show that the effect is identical for the polarisability interaction. Although this has not been explicitly shown before, the result is not a particularly surprising one, since the fact that the polarisability interaction leads to peaks in the differential capacitance means that the current must also peak during a linear potential sweep. For CV measurements, the current is directly related to the differential capacitance, since we can write

\[ C_d = \frac{d\sigma}{d\phi^0} = \frac{d\sigma/dt}{d\phi^0/dt} = \frac{I}{v} \]  

where \( v \) is the sweep rate (the sign differs between forward and reverse sweeps). This relationship shows that the differential capacitance is proportional to the measured current (assuming there are no surface reactions) and hence the \( I \text{ vs } \phi^0 \) curve traces the \( C_d \text{ vs } \phi^0 \) curve for the system.

Peaks in the \( I \text{ vs } \phi^0 \) curves from CV experiments are common (Chmiola et al. 2010; Inagaki et al. 2010; Konno et al. 2010; Li et al. 2007; Andreas and Conway 2006), often being attributed to processes such as adsorption, reactions or surface properties of the electrode. While it is not the intention to refute these other explanations here, it is clear from the figure above that it is possible for these peaks to arise naturally in systems for which these processes are not possible. Given that the \( I \text{ vs } \phi^0 \) curve simply follows the differential capacitance at sufficiently low frequencies, the extension of this to mixed electrolyte systems is that multiple peaks may arise, depending on the relative sizes and polarisabilities of the ions.

### 6.5 Comparison of the calculated differential capacitances

Between EIS, CV and the use of the equilibrium surface charge densities (as in the previous chapter), three methods have been outlined for calculating the differential capacitance of the system. As a final brief section to this chapter, it is shown that these three methods yield identical results. Fig. 6.23 shows the modelled differential capacitance for the mixed NaF/NaCl electrolyte system studied by Larkin et al (Larkin et al. 1982) and previously considered in Section 5.6.3. Only the data for the 17 mM NaCl case is shown, with the three different means for determining the differential capacitance overlaid.

The figure shows that there is no difference between calculating \( C_d \) using the equilibrium surface charge density data or using simulated CV measurements, with both curves being identical. For EIS, the amount of time taken to generate a single point makes it impractical to generate a full curve, and while the agreement between this and the other two methods remains good, it is not quite exact.

The frequency of the applied potential in the EIS simulation was set to 1000 Hz, the value used in Larkin et al’s original experiment. It can be seen from the figure that EIS predicts a very slightly lower differential capacitance as the potential is increased. The relative difference between this method and the other two is small — at \( \bar{\phi}^0 = 50 \) there is approximately a 0.9% relative difference between the values. Rather than being indicative of a difference in the cal-
calculated values of $C_d$, however, this can be attributed to the frequency not being small enough, so there is a small effect from the capacitance dispersion described above. By reducing $f$ by a factor of ten, the relative difference between the two sets of data reduces to approximately 0.15%, with further reductions likely with further reductions in the frequency.

In terms of generating differential capacitance curves, the equilibrium data should be the method which introduces the least error. This method only uses the equilibrium surface charge density data, the numerical error in which is only dependent on the grid spacing at the electrode surface boundary and how widely separated are the two potentials either side of the central value for which $C_d$ is calculated. The CV method should be the next most accurate, since $C_d$ in this method is directly determined by the time dependence of the system. However, the system is essentially at steady state throughout the cycle so any error introduced by the dynamics should be minimal. For EIS, there is the error in the simulated data and the additional error introduced by having to interpolate the results to determine values for the positions of the peaks in the measured current. Despite this, the three sets of data agree very well, indicating that the increase in the error from the two time-dependent methods is negligible.

In practical terms, determining $C_d$ through simulating CV is by far the best means. Each of the other methods requires individual data points to be simulated (two per point of interest if using the equilibrium data), which is time consuming — considerably more so for the EIS case, for which the system has to reach the steady state oscillation. However, simulated CV data does have the downside that not every simulation is guaranteed to run to completion because of the aforementioned problems with the code occasionally stopping mid-run without returning an error. However, this can usually be resolved through a small increase in the grid spacing or a reduction in the value of $D^c$, so it is not a significant problem.
6.6 Conclusions

In this chapter the effect of the two ion interactions terms upon the dynamic response of an electrolyte at a blocking electrode were presented through the simulation of three different commonly used experimental techniques. While the excluded volume interaction has previously been considered in such systems by several authors, the polarisability has not previously been accounted for in dynamic modelling. The work presented has largely served to demonstrate that in most situations the inclusion of ion interactions into dynamic models does not appear to alter significantly the dynamics of the system beyond the changes which would be expected from the variation in the differential capacitance which they cause.

For a step change in the applied potential, the time taken for the system to reach the new equilibrium was shown to vary in the same way as the differential capacitance of the system, with a peak in $t_{eq}$ as the applied potential increases. Deviations from the values predicted by the EC for the system were observed for all models at higher potentials, being attributed to changes in the electrolyte resistance due to ion depletion from the bulk. However, the deviations were much smaller in the mPNP models than in the basic PNP model, which can be attributed to the fact that the reduction in the number of ions required to form the double layer means that the bulk is depleted to a lesser extent and so there is a smaller reduction in the resistance. By looking at the equilibration time as a function of the potential for a range of lengths, small differences were observed between the effects of the two interaction terms for shorter domains, but no firm conclusions could be drawn from the data available to quantify this.

The model was also used to simulate EIS, again showing little difference between the EC for the system and the full numerical solution. Simulations of the capacitance dispersion effect were presented and, by rescaling the frequency by the inverse of the characteristic diffusion time-scale, it was shown that the two forms of ion interaction considered did not alter the dimensionless frequency at which the capacitance begins to decrease. Furthermore, it was found that this value was independent of the size of the ions or the value of the excess ion polarisability and also independent of the bias potential and bulk concentration.

Finally, the model was used to demonstrate the simulation of cyclic voltammetry. Given the idealised nature of the perfectly bocking electrode which the model represents, there is little additional behaviour which CV can elucidate. However, it was shown that the polarisability interaction is capable of introducing peaks into the $I$ vs $\phi^0$ curves in the same way as has been demonstrated previously for the excluded volume interaction. In the last part of this section it was shown that the three different means for determining the differential capacitance from the model yield identical results, so the three methods are equivalent.
Chapter 7

Reacting Systems

In most electrolyte systems, one or more of the species in the electrolyte is capable of undergoing an electrochemical reaction at the surface of the electrode. Such a reaction involves the transfer of electrons either to or from the electrode and so is measurable as an electric current, although the actual total current measured in an electrochemical experiment will contain both a Faradaic component, due to the reaction, and a non-Faradaic, or capacitive, component due to the charging of the double layer. In order to model the Faradaic component, a reaction model is required.

As discussed in Chapter 2, electrochemical reactions are most commonly modelled using the Butler-Volmer (BV) equation, a semi-empirical relationship between the overpotential and the current, although there also exists Marcus-Hush (MH) theory which is based more closely on the processes occurring during the course of the reaction. The latter is generally complex to use, which is why the BV model is more common, but neither of them account for the interactions between the ions in the environment in which the reaction takes place. Given the high concentrations of ions in the double layer, these interactions change the energies of the ions in the double layer and so could be expected to alter the rate of any reaction processes occurring.

In the following sections a model for the reaction rate is developed which accounts for the two ion interaction terms included in the earlier chapters of this work. The starting point is the affinity of the reaction, which is related to the ratio of the forward and reverse rates of the reaction, leading to an expression which is essentially a modified form of the generalised Frumkin-Butler-Volmer (gFBV) model (Biesheuvel et al. 2009; Van Soestbergen et al. 2010; Soestbergen 2012), wherein the rate is determined by the rate constants, ion concentrations, Stern layer potential drop and ion interactions. The gFBV model and the version derived herein naturally fit the structural model used to describe the electrolyte at the interface, being dependent only on local quantities at the surface. Furthermore, these two models also permit descriptions of an unsupported electrolyte, something which models that assume BV kinetics (a simple steady state form of which will be stated for comparison) cannot do.

The general types of reaction considered are purely electron transfer reactions of the form...
stated in Eq. (2.22), written here again for ease of reference:

\[ \text{Ox} + n_e e^- \rightleftharpoons \text{Re} \]  \hspace{1cm} (7.1)

where \( n_e \) is the number of electrons transferred in the reaction, equal to the magnitude of the stoichiometric coefficient. While the reaction theory is developed in general terms, the data throughout the chapter assumes a single electron transfer reaction in which the oxidised species is neutrally charged and the reduced species has a valence of \(-1\).

The remainder of the chapter is structured as follows: in the first section the reaction model is developed, commencing with a look at the equilibrium state before moving on to develop the kinetic expressions and describing how the expression is incorporated into the rest of the model. In Section 7.2 the variation of the equilibrium potential as a result of accounting for the ion volume is considered. Section 7.3 describes the work completed regarding the effect of the rate of the ion interactions on the steady state of the system and, finally, Section 7.4 contains the work thus far completed regarding the modelling of EIS for reacting systems.

### 7.1 Development of the reaction model

#### 7.1.1 Electrochemical reaction equilibrium

As discussed in Chapter 2, reactions are driven by a difference in the Gibbs free energies of formation of the reactants and products, although this does not determine the rate at which the reaction takes place. The starting point for developing the rate equation here is to use the reaction affinity. While this does not directly define the reaction rate, it can be used to link the electrochemical potentials to the ratio of the forward and reverse rates. The relationship between the affinity and the Gibbs free energy of reaction is defined as (IUPAC 1997)

\[ A_f = -\left( \frac{dG_{\text{RXN}}}{d\xi} \right)_{T,p} \]  \hspace{1cm} (7.2)

where \( \xi \) is the extent of the reaction, a measure of how far the reaction has proceeded. \( \xi \) links the number of reacting particles of type \( j \) at time \( t \) to the initial value through the expression

\[ n_j(t) = n_j(t = 0) + \nu_j \xi(t). \]  \hspace{1cm} (7.3)

where \( \nu_j \) is the stoichiometric coefficient of the species. An infinitesimal change in the Gibbs free energy is defined as

\[ dG = -SdT + Vdp + \sum_j \mu_j dn_j \]  \hspace{1cm} (7.4)

and by combining the previous two equations we get

\[ dG = -SdT + Vdp + \sum_j \nu_j \mu_j d\xi. \]  \hspace{1cm} (7.5)
For the particular system of interest, the temperature and pressure are constant at the reaction site, so the first two terms are zero. Furthermore, for an electrochemical reaction, the process can only take place at the reaction plane, where the ions and electrode are both present so that electron transfer can take place. The electrochemical potential which we are interested in is therefore the electrochemical potential at this reaction plane, denoted $\mu_j^R$. Making use of these properties of the system, the above expression can be substituted into Eq. (7.2) to define the affinity

$$A_f = -\sum_j n_j \mu_j^R$$  \hspace{1cm} (7.6)

As with $\Delta G_{RXN}$, the sign of the affinity determines the direction of the reaction, this time dependent on the species’ electrochemical potentials rather than their formation energies, but it does not determine the rate. If $A_f$ is positive, the reaction proceeds in the forwards direction (i.e. production of Re is favoured), while if it is negative it proceeds in the reverse direction.

Expressions for the electrochemical potential in the model have been defined in Chapter 3, so the affinity can be calculated using the data from the model. However, $\mu_j^R$ in the reaction model does not equal $\mu_j$ in the structural/dynamic model because for reactions the chemical potential is defined relative to the standard state, while for the structural/dynamic model it is defined relative to the bulk value. The relationship between the two is

$$\mu_j^R = \mu_j^{\oplus} + k_BT \ln \frac{c_j^R}{c_j^{\oplus}} + z_j e_0 \phi_j^R + \mu_{\text{res}, j}^R$$  \hspace{1cm} (7.7)

Here, the facts that the electrostatic potential and the residual chemical potential are both zero in the standard state have been used. This definition of $\mu_j^R$ is such that if the model is used to simulate a system which is actually in the standard state, i.e. $c_j^R = c_j^{\oplus}$ and $\mu_{\text{res}, j}^R = 0$, the electrochemical potential of the model system reduces to the electrochemical potential of the standard state, $\mu_j^{\oplus}$. Knowledge of the electrochemical potentials of the ion does not completely define the affinity, however, as the electrons are an integral component of the reaction. The chemical potential of an electron in the electrode is approximately equal to the electrode’s Fermi energy $E_f$; therefore, since the electron valence is $-1$, its electrochemical potential can be written (Girault 2004)

$$\mu_e = E_f - e_0 \phi^0$$  \hspace{1cm} (7.8)

Note that the electrons reside in the electrode itself, so the potential in this equation is equal to the electrode potential.

For the general reaction stated in Eq. (7.1), the stoichiometric coefficient of the oxidised species is $-1$, of the electron is $-n_e$ and of the reduced species is $+1$. Substituting these values, along with the electrochemical potentials for the species from Eq. (7.7) and (7.8), into
Eq. (7.6) yields the affinity for the reaction

$$A_f = \mu_{\text{Ox}} + k_BT \ln \frac{c_{\text{Ox}}^R}{c_{\text{Ox}}} + z_{\text{Ox}} e_0 \phi^R + \mu_{\text{Ox}} - \mu_{\text{Re}} - k_BT \ln \frac{c_{\text{Re}}^R}{c_{\text{Re}}} - z_{\text{Re}} e_0 \phi^R - \mu_{\text{Re}}^\ominus$$

$$+ n_e (E_f - e_0 \phi^0)$$

$$= - (\mu_{\text{Ox}}^\ominus + \mu_{\text{Re}}^\ominus - n_e E_f) - \left( k_BT \ln \frac{c_{\text{Re}}^R}{c_{\text{Ox}}} - \mu_{\text{Ox}}^\text{res} + \mu_{\text{Re}}^\text{res} \right) + (z_{\text{Ox}} - z_{\text{Re}}) \phi^R - n_e \phi^0$$

(7.9)

where the subscripts Ox and Re refer to the oxidised and reduced species, respectively. The first set of brackets is equal to the standard state Gibbs free energy of the reaction. The final two terms are the only ones dependent upon the electrostatic potential, and can be rearranged as follows:

$$A_f = -\Delta G_{\text{RXN}}^{\ominus} - \left( k_BT \ln \frac{c_{\text{Re}}^R}{c_{\text{Ox}}} - \mu_{\text{Ox}}^\text{res} + \mu_{\text{Re}}^\text{res} \right)$$

$$+ (z_{\text{Ox}} - z_{\text{Re}}) e_0 \phi^R - n_e e_0 \phi^R - n_e e_0 \phi^0$$

(7.10)

By accounting for the fact that $z_{\text{Ox}} - z_{\text{Re}} = n_e$, the affinity becomes

$$A_f = -\Delta G_{\text{RXN}}^{\ominus} - k_BT \ln \frac{c_{\text{Re}}^R}{c_{\text{Ox}}} - \mu_{\text{Ox}}^\text{res} - \mu_{\text{Re}}^\text{res} - n_e e_0 (\phi^0 - \phi^R)$$

(7.11)

The reaction plane in the model is assumed to be coincident with the Stern layer boundary, so $c_j^R = c_j(z = 0)$, $\phi^R = \phi_s = \phi(z = 0)$ and $\phi^0 - \phi^R = \Delta \phi_s$. From this, we finally arrive at the expression for the affinity in terms of the electrochemical potentials, which accounts for the ion interactions and the fact that the reaction does not occur at the electrode surface:

$$A_f = -\Delta G_{\text{RXN}}^{\ominus} - n_e e_0 \Delta \phi_s - k_BT \ln \frac{c_{\text{Re}}(z = 0)}{c_{\text{Ox}}(z = 0)} + \mu_{\text{Re}}^\text{res}(z = 0) - \mu_{\text{Re}}^\text{res}(z = 0)$$

(7.12)

7.1.2 Reaction kinetics

While the affinity of the reaction allows the equilibrium state to be defined in terms of the electrochemical potentials, it is not yet linked to the reaction rate away from equilibrium. For a reversible reaction, the rate can be defined both in terms of the extent of the reaction and also as the difference between the rate of the elementary reaction in the forward direction, $r_f$, and the rate of the elementary reaction in the reverse direction, $r_b$:

$$r = \frac{d\xi}{dt} = r_f - r_b$$

(7.13)

The affinity, while not determining the overall reaction rate, can be used to define the ratio of
the forward and reverse elementary reactions. It has been proposed that, provided the reaction takes place in a single step, as is assumed for the reaction stated in Eq. (7.1), the following relationship holds (Hall 1986; Hall 2002; Pekař 2009):

$$\frac{r_f}{r_b} = \exp(\beta A) \quad (7.14)$$

Combining the previous two equations yields an expression for the total rate in terms of the forward rate, which is

$$r = r_f \left(1 - e^{-\beta A}\right) \quad (7.15)$$

Substituting Eq. (7.11) into this (temporarily neglecting the \((z = 0)\)’s for notational clarity) yields the expression for the overall rate

$$r = r_f \left(1 - \frac{c_{Re} \exp(\mu_{Re}^{\text{res}})}{c_{Ox} \exp(\mu_{Ox}^{\text{res}})} \exp(n_e \beta c_0 \Delta \phi_s) \exp(\beta \Delta G^{\text{eq}}_{\text{RXN}})\right) \quad (7.16)$$

In order to determine the overall reaction rate, this equation still needs an expression for the forward rate, \(r_f\). However, since thermodynamics does not give any information about the rates of processes, such an expression has to be assumed. For the purposes of this work, the following form is proposed, in which it is assumed that the reaction is first order and that the residual chemical potential is accounted for:

$$r_f = k_f^{\ominus} c_{Ox}(z = 0) \exp(\mu_{Ox}^{\text{res}}) \exp(-\gamma n_e \beta c_0 \Delta \phi_s) \quad (7.17)$$

where \(k_f^{\ominus}\) is the forward rate constant in the standard state. Note that the rate is not directly dependent on the applied potential at the electrode, although this does determine the concentration, residual chemical potentials and Stern layer potential drop; therefore, the rate is indirectly determined by it. The \(\gamma\) term is essentially the symmetry factor in the Butler-Volmer (BV) and generalised Frumkin-Butler-Volmer (gFBV) models, and is used so that the exponent containing the \(\Delta \phi_s\) can be split between the forward and reverse reactions. It will henceforth assumed to take the value of a half.

Substituting this into Eq. (7.16) and then rearranging the result gives

$$r = k_f^{\ominus} c_{Ox}(z = 0) \exp(\mu_{Ox}^{\text{res}}) \exp\left(-\frac{n_e \beta c_0}{2} \Delta \phi_s\right) - k_b^{\ominus} c_{Re}(z = 0) \exp(\mu_{Re}^{\text{res}}) \exp\left(\frac{n_e \beta c_0}{2} \Delta \phi_s\right) \quad (7.18)$$

where \(K^{\ominus} = \exp(-\beta \Delta G^{\text{eq}}_{\text{RXN}}) = k_f^{\ominus}/k_b^{\ominus}\) is the equilibrium rate constant of the reaction. The above expression is of a similar form to standard chemical kinetics, but with concentrations which are dependent on the potential and some further potential dependence due to the \(\mu_j^{\text{res}}\)- and \(\Delta \phi_s\)-containing exponential terms. The values of \(k_f^{\ominus}\) and \(k_b^{\ominus}\) are unknown, but can be measured and are, in any event, the same as the values used in the BV model.

Note that in the absence of ion interactions, the \(\mu_j^{\text{res}}\) terms are equal to zero, and the expression
reduces to the gFBV model for the reaction rate.

7.1.3 The Nernst equation

In order to be thermodynamically correct, the reaction model should reduce to the Nernst equation, Eq. (2.25), at equilibrium. The overall rate of the reaction is equal to zero at this point, so Eq. (7.18) can be rearranged as

\[
\frac{k_f}{k_b} = \frac{c_{Re} \exp(\beta \mu_{Re}^{\text{res}})}{c_{Ox} \exp(\beta \mu_{Ox}^{\text{res}})} \exp \left( -n_e \beta e_0 \Delta \phi_s \right)
\]  

(7.19)

In terms of the structural model for the electrolyte, the electrochemical potentials at the Stern layer boundary relative to the values in the bulk can be written using Eq. (3.62) as

\[
z_{Ox} \beta e_0 \phi_s = - \ln \frac{c_{Ox}}{c_{Ox}^0} - \beta(\mu_{Ox}^{\text{res}} - \mu_{Ox}^{\text{res,0}})
\]

(7.20a)

\[
z_{Re} \beta e_0 \phi_s = - \ln \frac{c_{Re}}{c_{Re}^0} - \beta(\mu_{Re}^{\text{res}} - \mu_{Re}^{\text{res,0}})
\]

(7.20b)

Rearranging each of these for the group \( c_j \exp(\beta \mu_j^{\text{res}}) \) and substituting them into the previous equation gives

\[
\frac{k_f}{k_b} = \frac{c_{Re}^0 \exp(\beta \mu_{Re}^{\text{res,0}})}{c_{Ox}^0 \exp(\beta \mu_{Ox}^{\text{res,0}})} \exp \left( z_{Re}^0 \phi_s \right) \exp \left( n_e \beta e_0 \Delta \phi_s \right)
\]

\[
= \frac{c_{Re}^0 \exp(\beta \mu_{Re}^{\text{res,0}})}{c_{Ox}^0 \exp(\beta \mu_{Ox}^{\text{res,0}})} \exp \left( -z_{Ox} \beta \phi_s \right) \exp \left( n_e \beta e_0 (\phi^0 - \phi_s) \right)
\]

\[
= \frac{c_{Re}^0 \exp(\beta \mu_{Re}^{\text{res,0}})}{c_{Ox}^0 \exp(\beta \mu_{Ox}^{\text{res,0}})} \exp \left( n_e \beta e_0 \phi^0 \right)
\]

(7.21)

Given that \( k_f / k_b = K^\oplus = \exp(-\beta \Delta G_{\text{RXN}}^\oplus) = \exp(n_e \beta e_0 \Delta \phi^\oplus) \), taking the logarithm of the above expression and rearranging the result gives

\[
\phi^0 = \Delta \phi^\oplus + \frac{1}{n_e \beta e_0} \ln \frac{c_{Ox}^0 \exp(\beta \mu_{Ox}^{\text{res,0}})}{c_{Re}^0 \exp(\beta \mu_{Re}^{\text{res,0}})}
\]

(7.22)

which has the same form as Eq. (2.25), assuming that the activity coefficients are defined by the \( \exp(\mu_j^{\text{res}}) \) terms.

7.1.4 Incorporating the reaction model in the dynamic model

The reaction has two effects on the boundary conditions of the mPNP system. The first is that the flux of the reacting species at the surface is no longer zero and the second is that the surface charge density may be linked to the reaction rate, depending on the type of system being modelled. In terms of the Nernst-Planck equations, the expressions in the domain are
unaffected, but the boundary condition at the electrode surface becomes

\[ J_j = \nu_j r \]  \hspace{1cm} (7.23)

so if the reaction occurs in the forwards direction (\( \text{Ox} \rightarrow \text{Re} \)), the flux of the reactant is negative, i.e. towards to the electrode surface. The discretised form of the boundary condition (Eq. (4.14a)) remains the same, only now the value of \( J \) is no longer zero.

For the Poisson equation, the change to the boundary condition at the electrode surface depends on the nature of the system being modelled. If the potential is fixed, there is no change to the boundary condition, since the charge transferred cannot stay on the electrode; otherwise its charge, and therefore the potential, would change. In this case, the electrons are assumed to pass through the electrode from some source or to some sink as a pure reaction current which does not alter the electrode potential. If the electrode potential is not directly controlled, it is assumed that it is connected to a point of zero potential, such as a standard hydrogen electrode, through some resistance. In this case, the reaction will alter the charge on the electrode, changing the potential and thereby changing the electrolyte structure and altering the rate. However, the change of the potential also means that a current is driven between the point of zero potential and the electrode, the value of which depends on the potential of the reaction electrode and the resistance. The rate of change of charge density on the electrode at a given time is therefore defined in terms of the difference between the rate at which it is increased by the reaction and removed by the current density, \( I \), in the external circuit:

\[ \frac{d\sigma}{dt} = n_e e_0 r - I \]  \hspace{1cm} (7.24)

If the forward reaction is dominant, the electrode charge becomes more positive, while the reverse is true if the reverse reaction dominates. The current density represents the current flowing from the electrode to the point of zero potential through some resistance, \( R \), which arises due to an applied load, so the current density can be determined using Ohm’s law. In the discretised equations, the surface charge density is defined by Eq. (4.18a). Substituting that equation and Ohm’s law into the above expression yields the new boundary condition for the Poisson equation if the potential is not fixed:

\[ -\Delta \frac{1}{2} \sum_i \sum_j \frac{dz_i}{dz_j} \frac{d\varepsilon_{ij,0}}{dt} \frac{d\varepsilon_{ij}}{dt} (\epsilon_1 + \epsilon_0) (\phi_1 - \phi_0) = -\nu e_0 r + \phi_0 \]  \hspace{1cm} (7.25)

where \( \epsilon_i \) and \( \phi_i \) are respectively the permittivity and the potential at grid point \( i \).

### 7.2 Variation in the equilibrium potential

The Nernst equation as stated in Eq. (2.25) defines the relationship between the equilibrium potential, \( \phi^{eq} \), the bulk concentrations of the ions, \( c_{0j} \), and their bulk activities, \( a_{c,j}^0 \). Equation (7.22) explicitly states the Nernst equation in a form which defines the activity in the bulk in terms of
the known ion properties in the bulk, allowing the predicted effect of the ion interactions on the equilibrium potential to be calculated explicitly.

In the bulk, the gradient of the electrostatic potential must be zero, so the polarisability can have no effect on $\phi_{eq}$, but the ion volumes do change the bulk electrochemical potential and so will have an effect. Since the bulk concentrations and the ion sizes are known, the excess component of the electrochemical potential can be calculated allowing the change in $\phi_{eq}$ to be determined analytically. The result is plotted in Fig. 7.1, showing the equilibrium potential as a function of $\ln(c_{Ox}^0/c_{Re}^0)$. The concentration of the reduced species is held constant, at either 0.01 M, 0.1 M, or 1 M, and the concentration of the oxidised species is varied such that the concentration ratio increases from $c_{Ox}/c_{Re} = 0.01$ to $c_{Ox}/c_{Re} = 10$. The standard state potential is assumed to be $\Delta \bar{\phi}_{RXN} = 5$, so the reaction is such that it favours the production of the reduced species if the surface potential is smaller than $\phi^0 = 5$, which is the equilibrium potential. The ion diameters used in the example are either both $a_{Ox} = a_{Re} = 0$ (i.e. the GC case, black line) or $a_{Ox} = 0.5$ nm and $a_{Re} = 0.7$ nm (all coloured lines). Only one plot is shown for the zero diameter case since, for this, changing $c_{Re}$ has no effect on the value of $\phi_{eq}$ as long as the ratio of the ion concentrations is the same. The two line-styles in the figure correspond to the predictions of the mvdW model (dashed lines) and the BMCSL model (dashed-double-dot lines).

![Figure 7.1: Equilibrium potential as a function of the ratio of the bulk ion concentrations. Solid (black) line, no excluded volume, dashed lines, mvdW model and dashed-double-dot lines, BMCSL model](image)

The oxidised species being smaller than the reduced species causes the equilibrium potential to decrease relative to the GC case and, although not shown, it is increased if the sizes are the other way around. As would be expected, the deviation from the standard equilibrium potential is small when the total ion concentration is small, since the interaction energy is similarly small. Even when the total concentration is moderately large, the change in the equilibrium potential is still fairly small: taking the $c_{Re} = 0.1$ M mvdW case at the highest ratio ($c_{Ox}/c_{Re} = 10$), the equilibrium potential is decreased by just over 0.15 $\bar{\phi}$ ($\approx 3.9$ mV), a value which increases to approximately 0.30 $\bar{\phi}$ in the BMCSL case, as would be expected due to the stronger ion interactions in that model.
When \( c_{Re} = 1 \text{ M} \), there are larger changes in the equilibrium potential throughout the range, but they are particularly significant for high ratios, where the equilibrium potential can be seen to peak before decreasing sharply, a feature which occurs at a lower concentration ratio for the BMCSL model than for the mvdW model. This reduction in the equilibrium potential implies that the free energy of the system is such that it becomes less favourable for the reaction to proceed in the forward direction.

Increasing the concentration of the oxidised species increases the total concentration, so it increases the contribution to the electrochemical potential from the excluded volume interaction for both the oxidised and reduced forms of the species. The reduced form, being larger in this case, experiences a larger increase in its energy than does the smaller, oxidised, form. There comes a point, as the total occupied volume fraction approaches unity, when the growth in the excluded volume interaction energy in the bigger ion becomes larger than the growth in the sum of the ideal and excluded volume energies of the smaller ion (the ideal term also growing by virtue of the increased concentration for the smaller ion). At this point, it becomes less energetically favourable for the reaction to proceed in the expected direction, leading to a reduction in \( \phi_{eq} \). As indicated by the trend in the figure, this reduction can occur to the extent that the equilibrium potential becomes negative, i.e. the reaction will naturally run in the direction of forming the smaller, oxidised, species, contrary to the expected direction determined by the standard state reaction potential.

The changes in the equilibrium potential described above are effects which fundamentally cannot be predicted by accounting for the ion interactions using the Bikerman model, since this does not permit differences between the sizes of the ions. While the extent of the difference in size may be large in the example, changes to the diameter during the process of a reaction are likely, since the change in the charge of the ion will have both a direct effect and will also change the structure of the hydration shell, the size of which is included in the diameter of the ion.

### 7.3 Steady state reacting systems

In this section, the steady state of the system is considered in terms of the ion interaction terms. As seen in the Section 6.4, the steady state can be approximated by a sufficiently slow CV sweep, so this method is used to generate the data, rather than many single runs of the model at a constant potential. Again, only single electron transfer reactions are considered, with the oxidised form being neutral and the reduced form having a single negative charge.

In summary, the model predicts the development of the so-called “superlimiting” or “overlimiting” current at large positive potentials, a previously observed phenomenon (Rubinstein and Shtilman 1979; Chu and Bazant 2005) whereby more current is generated than the diffusion limitation permits, while at large negative potentials the current is shown either to converge on the diffusion limited current if ion interactions are not accounted for or initially to increase and then return to zero if they are. The differences between the effects of the two ion interaction
terms will be considered relative to the GCS/gFBV model for unsupported electrolytes. Supported electrolytes will also be considered, including the effects of the supporting electrolyte having different ion properties relative to the reacting species (also referred to herein as the reacting electrolyte).

Throughout, the variables considered are the ion diameters or polarisabilities, the bulk concentrations and the reaction rate constants, so a number of parameters are constant. These are the Stern layer width, set to $s = 0.35 \text{nm}$, the domain length, set to $\bar{L} = 10000$ and the diffusion coefficient, set to $1 \times 10^{-9} \text{m}^2 \text{s}^{-1}$. In some ways, the data presented represent preliminary findings, and it has so far only been possible to consider systems in which the standard state reaction potential is zero. This has the consequence that the forward and reverse rate constants in all cases are equal and are denoted in the figures simply as $\bar{k}^{\ominus}$. The specific values of the rate constants considered are $\bar{k}^{\ominus} = 10^{-3}, 10^{-4}$ and $10^{-5}$, corresponding to dimensional values of $5.1 \times 10^{-4} \text{m} \text{s}^{-1}, 5.1 \times 10^{-5} \text{m} \text{s}^{-1}$ and $5.1 \times 10^{-6} \text{m} \text{s}^{-1}$. The highest rate here is quicker than found experimentally, but the other two are of a similar order of magnitude to experimentally measured values (Tang et al. 2010; Meng et al. 2012), although they do represent quick reactions. Finally, in all systems considered the reactant and product have the same bulk concentrations.

### 7.3.1 Unsupported electrolytes

The systems considered in this section contain three species. The first two are those which take part in the reaction, which are a neutral species (Ox) and a negatively charged species (Re). In order to maintain bulk electroneutrality, a third, non-reactive, species with a single positive charge is added, having the same bulk concentration as the two reacting species.

**Butler-Volmer reference model**

For the purposes of comparison, a simple model for the current as a function of the potential is presented, using the Butler-Volmer model to define the reaction rate. The basic domain structure is similar to that of the main model, being a finite length domain with a fixed concentration at one end and the electrode surface at the other. However, the electrolyte is assumed to be electroneutral throughout the domain, implying the presence of an excess of supporting electrolyte. This assumption means that the double layer is always fully formed, so there is never a potential gradient across the domain. The Butler-Volmer reaction model is used to define the flux of the reacting species at the electrode boundary and, since there is no electric field in the domain, the species fluxes are dependent on diffusion alone, i.e. they are described by Fick’s law. Because the concentration gradient is linear, this can be written simply in terms of the two boundary concentrations. The systems which we are dealing with assume that the concentrations of the reactants in the bulk are equal, taking the value $c_{\text{Re}} = c_{\text{Ox}} = c^0$, so the fluxes become

$$J_j = -D \frac{dc_j}{dz} = -D \frac{c^0 - c_j(0)}{L} \quad (7.26)$$

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where it is assumed that both reacting species have the same diffusion coefficient. At the electrode boundary, the fluxes of the oxidised and reduced species must be equal, since their stoichiometric coefficients are equal but opposite, meaning that the surface concentration of the reduced species may be written in terms of the oxidised species:

\[ c_{\text{Re}}(0) = 2c^0 - c_{\text{Ox}}(0) \]  
(7.27)

The flux at \( z = 0 \), the electrode boundary, is defined by the reaction rate, which is calculated from the Butler-Volmer equation, the full form of which is stated in Eq. (2.29). Making the same assumption regarding the bulk ion concentrations, together with the further assumptions that the reaction involves a single electron transfer, so \( n_e = 1 \), and, to match the assumption made in the derivation of the mgFBV model, that \( \gamma = 1/2 \), the BV equation simplifies to

\[ I = I_0^0 \left[ c_{\text{Re}}(0) \exp \left( \frac{\beta e_0 \phi^0}{2} \right) - c_{\text{Ox}}(0) \exp \left( -\frac{\beta e_0 \phi^0}{2} \right) \right] \]  
(7.28)

Under the above-stated assumptions, the exchange current density, \( I_0^0 = n_e \epsilon_0 k^\oplus (\epsilon^0_{\text{Ox}})^1 - \gamma (\epsilon^0_{\text{Re}})^\gamma \) simplifies to \( I_0^0 = \epsilon_0 k^\oplus c^0 \). Substituting this and Eq. (7.27) into the BV equation, under the same assumptions regarding the bulk concentrations, we get

\[
    I = \epsilon_0 k^\oplus \left[ (2c^0 - c_{\text{Ox}}(0)) \exp \left( \frac{\beta e_0 \phi^0}{2} \right) - c_{\text{Ox}}(0) \exp \left( -\frac{\beta e_0 \phi^0}{2} \right) \right] \\
    = 2\epsilon_0 k^\oplus \left[ c^0 \exp \left( \frac{\beta e_0 \phi^0}{2} \right) - c_{\text{Ox}}(0) \cosh \left( \frac{\beta e_0 \phi^0}{2} \right) \right]  
\]  
(7.29)

The current is related to the flux through the reaction rate by the relationship

\[ J_j = \nu_j r = -\frac{\nu_j I}{n_e \epsilon_0} \]  
(7.30)

We are dealing with single electron transfer reactions (i.e. \( n_e = 1 \)) and, if we consider the flux of the oxidised species, \( \nu_j = -1 \), so the above expression becomes \( J_{\text{Ox}} = I/\epsilon_0 \). Rearranging this for \( I \) and substituting the result in to Eq. (7.29) we get

\[ J_{\text{Ox}} = k^\oplus \left[ c^0 \exp \left( \frac{\beta e_0 \phi^0}{2} \right) - c_{\text{Ox}}(0) \cosh \left( \frac{\beta e_0 \phi^0}{2} \right) \right]  
\]  
(7.31)

Equating this with Eq. (7.26) and rearranging the result, an analytical expression for \( c_{\text{Ox}} \) in terms of the applied potential can be derived:

\[ c_{\text{Ox}}(0) = \frac{D_{2k^\oplus L} + \exp \left( \frac{\beta e_0 \phi^0}{2} \right)}{D_{2k^\oplus L} + \cosh \left( \frac{\beta e_0 \phi^0}{2} \right)} \]  
(7.32)

This can be substituted back in to Eq. (7.29) and the result used to calculate the current as a function of the applied potential in this simplified BV model.
Comparison of BV and gFBV models

Prior to discussing the effects of ion interactions, the differences between the BV and gFBV models are presented. Figures 7.2(a) and (b) show the predicted current in each of the two models for systems with a bulk concentration of 0.1 M at three different rate constants, with part (b) showing, on an expanded $\phi^0$ scale, the detail in the region of the origin of part (a).

The first point to be noted from the curves is the minimal hysteresis between the forward and reverse sweeps in each of the simulated data sets (solid lines), indicating that the system is in a quasi-steady state throughout. The capacitive current in all cases was smaller than $I = 5 \times 10^{-11}$, so the current shown in the figures is almost entirely due to the reaction rate. This is the case for all curves shown throughout this section and, from this point onward, only a single sweep will be shown in the figures to avoid confusion in the line styles caused by the overlap of the two sweeps.

There are significant differences between the BV and gFBV models for both positive and negative potentials, many of which can be attributed to the assumption of the presence of a supporting electrolyte in the BV case. In general terms, the order of magnitude of the currents in the two cases is similar, indicating that nothing exceptionally different is taking place in the numerical model.

The assumption of a supporting electrolyte in the BV model means that a double layer is always present and thus the bulk electrolyte is fully shielded from the electrode surface charge. Under this assumption, only diffusion contributes to the total ion flux. The maximum value this can have is when the concentration of the reactant at the surface is zero, since this defines the steepest possible concentration gradient in the system. The value of this maximum flux is

$$J_{\text{max}} = -D \left( \frac{dc}{dz} \right)_{\text{max}} = -\frac{(c_j^0 - c_j(0))}{L}$$

(7.33)

The flux is related to current through Eq. (2.27), hence the previous equation defines a maxi-
mum current. For positive potentials, when Re is the reactant, this maximum current is

\[ I_{\text{max}}^{\text{max}} = -\nu_{\text{Re}} e_0 D \left( \frac{dc_{\text{Re}}}{dz} \right) \bigg|_{z=0} = -e_0 D \left( c_{\text{Re}}^0 - c_{\text{Re}}(0) \right) / L \]  

(7.34)

which is the diffusion limited current. In a similar manner, for large negative potentials, Re is repelled from the surface and the reaction is able to proceed through the diffusion of Ox to the surface. This has an equal but opposite maximum current to that for Re, again because of the maximum diffusion rate. The value of \( I_{\text{max}}^{\text{max}} \) at the high- and low-potential limits has the dimensionless value \( \bar{I}_{\text{max}}^{\text{max}} = \pm 2.2 \times 10^{-6} \), the value on which both models converge in the negative potential region and on which the BV model converges in the positive potential region.

The reason that the gFBV model converges on a higher value of \( I_{\text{max}}^{\text{max}} \) at large positive potentials is due to the lack of a supporting electrolyte. Since the counter-charge in the system is also the reacting species, it is consumed as it moves to the electrode surface, preventing the complete formation of the double layer. The result is that there is still be an electric field in the domain, as shown in Fig. 7.3(a), which drives a migration flux, making the total transport flux larger than that permitted by diffusion alone. This increase of the current above the diffusion limited value is known as the superlimiting current. Figure 7.3(b) shows the concentration profiles in the domain. It can be seen that the system still has the maximum allowable concentration gradient, with the concentration approaching zero, so the diffusive component of the flux remains largely the same in the superlimiting regime.

Figure 7.3: The superlimiting regime: (a) potential profile throughout the domain and (b) concentration profiles of the oxidised and reduced species near the electrode surface and (inset) throughout the domain. The system is the same as the \( \bar{k}^{\ominus} = 10^{-5} \) case in Fig. 7.2 at \( \bar{\phi}^0 = 15 \).

For negative potentials, the flux of the reactant, now Ox, is only dependent on diffusion, since it is uncharged. Thus, its maximum flux is defined by the maximum concentration gradient and the maximum current defined by Eq. (7.34). However, for lower negative potentials it can be seen from Fig. 7.2(a) that the gFBV current is always smaller than the BV current, something which can also be seen in Fig. 7.2(b) to be true for very small positive potentials. This is because the BV model also ignores the presence of the Stern layer, which affects the value of \( \phi_s \), the potential at the Stern layer boundary/the reaction plane and the relevant potential when
discussing how strongly ions are attracted to, or repelled from, the reaction surface.

The Stern layer shields the bulk from a fraction of the surface potential, the extent of this shielding depending on the applied potential (see Fig. 5.19). Increasing the applied potential increases the amount of counter charge at the surface, meaning that the electric field at the Stern layer boundary grows. The potential drop across the Stern layer, $\Delta \phi_s$, depends its width, the electric field across it and the permittivity within it (this can be seen by rearranging Eq. (3.87) for $\phi^0 - \phi(0)$): as the field grows, $\phi_s$ comprises a decreasing proportion of $\phi^0$ because $\Delta \phi_s$ increases. The result is that the ions in the electrolyte are less strongly attracted to (or repelled from) the reaction plane, changing the reaction rate. For positive potentials, the effect is overcome by the migration contribution to the flux, but for negative potentials the increasing counter-charge from the non-reactive species causes a much slower growth in $\phi_s$, meaning Re is repelled less strongly from the surface, resulting in a slower reaction rate at a given potential.

The effect of ion interactions on the reaction

Including each of the ion interaction terms in turn into the model, the effect on the rate of the reaction can be seen to be quite small, as shown by the $I$ vs $\phi^0$ plots in Figs. 7.4(a) and (b). In the first of these the ion volume alone is accounted for, using the mvdW model with both ions having a diameter of $0.7\,\text{nm}$, and in the second the polarisability alone is accounted for, with both ions having $4\pi\alpha = -8\,\text{M}^{-1}$.

![Figure 7.4](image.png)

Figure 7.4: Total current as a function of the electrode potential when ion interactions are accounted for (mgFBV kinetics). (a) mvdW with $a = 0.7\,\text{nm}$ and (b) polarisability with $4\pi\alpha = -8\,\text{M}^{-1}$. Bulk concentrations are 0.01 M (solid lines) and 0.1 M (dashed lines).

The general trends in each case are the same as for the system without ion interactions and the predicted current is similar in all cases. There are differences, however; for negative potentials the current can be seen to be slightly smaller than in the non-interacting case as the potential is made larger, while for positive potentials there are small differences in the way that the current grows with the potential, even though the final converged values are all very similar. These differences are more clearly seen by plotting the difference between the magnitudes of the mgFBV and gFBV currents, defined as $\Delta I^R = |I_{mg\text{FBV}}| - |I_{g\text{FBV}}|$, or in other words, the gFBV
data in Fig. 7.2 is subtracted from that in Figs. 7.4 (a) and (b) in turn. A plot of this parameter as a function of the potential is presented in Fig. 7.5.

![Graph](image)

**Figure 7.5**: Difference in the magnitudes of the current between the gFBV and mgFBV models. Solid lines account for the excluded volume ($a = 0.7$ nm), dashed lines account for the polarisability ($\pi \alpha = -8 \text{ M}^{-1}$). Inset shows detail of the positive potential region.

In the figure, negative values of $\Delta I^R$ represent the magnitude of the current being smaller (closer to zero) in the mgFBV case than in the gFBV case, regardless of the sign of the current. The change in the current is greatest for large negative potentials, with the current being significantly smaller than the gFBV case when the excluded volume interaction is accounted for (solid lines) compared to when the polarisability is accounted for (dashed lines). In fact, throughout the whole negative potential range the excluded volume modification to the model always reduces the current, while the polarisability modification increases the current at small negative potentials before causing it to decrease at larger negative potentials.

In contrast to the negative potential region, for positive potentials (inset) the two interaction terms always have the opposite effect to each other, with the polarisability making the current smaller and the excluded volume making it larger. The value of $\Delta I^R$ in each case rises to a peak/descends to a trough in the region at which gradient of the $I$ vs $\phi^0$ curve is changing most rapidly, at around $\bar{\phi}^0 = 5$, before appearing to converge again on the gFBV current. At the point of maximum deviation, the magnitude of the deviation in the excluded volume case is slightly larger than that of the polarisability case, although the differences are small by comparison with the actual value of the current.

The differences between the two interaction models and the gFBV case are due to similar reasons as were discussed for the difference between the gFBV and BV case, in that they relate to the potential drop across the Stern layer. As noted, this determines the potential at the Stern...
layer boundary/reaction plane relative to the bulk, and thus the extent to which the charged reactant is attracted to/repelled from the surface.

The interaction terms both cause the concentration of counter-charge near the electrode surface to be smaller than in the GCS/gFBV case. For the excluded volume interaction, this means that the electric field at the Stern layer boundary is smaller than in the GCS/gFBV case, so $\Delta \phi_s$ is smaller and $\phi_s$ correspondingly larger. For the polarisability interaction, the effect of constraining the counter charge concentration is initially counteracted by the reduction in the permittivity, so the electric field initially increases faster with the applied potential than in the GC case (see Fig. 5.19). As a result, $\Delta \phi_s$ is larger (for lower potentials) and $\phi_s$ correspondingly smaller. The increased value of $\phi_s$ in the excluded volume case increases the migration component of the flux relative to the GC case, allowing the reaction rate, and hence the current, to be larger, while the lower migration component in the polarisability model means that the reaction rate is smaller, as is the current.

The differences between the three models only apply until the diffusion component of the transport flux reaches the maximum value, however. Once this happens, increases to the reaction rate can only occur if there is an increase in the migration component to the transport flux. In order for this to happen, $\phi_s$ has to increase more rapidly with $\phi^0$ at higher potentials than it does at lower potentials. For this to happen, the growth in the electric field has to slow, which can only happen if the amount of counter charge at the surface stops increasing with $\phi^0$. As can be seen in Fig. 7.6(a), this is indeed what takes place: the concentration of Ox, which forms most of the counter-charge, reaches a plateau at higher potentials. Once this has happened, the electric field at the surface, and therefore $\Delta \phi_s$ become almost independent of the potential, which can be inferred from Fig. 7.6(b), showing $\phi_s$ as a function of $\phi^0$. $\phi_s$ becomes almost linear with the applied potential at high positive potentials, with a gradient of $\sim 1$, implying that $\Delta \phi_s$ has stopped growing.

![Figure 7.6](image-url)

Figure 7.6: (a) Surface concentration of the three species in the system as a function of the applied potential for a $0.1 \text{ M}$, $\bar{k} = 10^{-5}$ system. Black lines GC model, red lines mvdW model and blue lines polarisability model. (b) Stern layer potential as a function of the applied potential for the three cases shown in part (a).

That the value of $\phi_s$ in all cases becomes almost linear means that, as the applied potential
is increased, the relative differences between the migration components of the flux in the three models decrease. Since the diffusion component of the flux in all three cases is the same (i.e. the maximum), the convergence of the migration components means that that the currents must likewise converge, so $\Delta I^R$ returns to zero.

Returning to Fig. 7.5 to discuss the negative potential region, the current can be seen always to decrease relative to the GCS/gFBV case when the excluded volume term is accounted for, but to increase slightly at low potentials before decreasing at larger potentials in the polarisability case. In this region, the double layer is largely fully formed at a given potential because of the presence of the non-reactive positive ion. This has an effect on the electric field and also contributes to the crowding-out of the reacting species from the reaction plane.

As with the positive potential case, increasing the potential in the negative direction causes the amount of counter charge to increase near to the electrode, causing the electric field, and therefore the potential drop across the Stern layer to increase. Again, the GC model contains the most counter charge and the mvdW case the least (see Fig. 7.6(a)). Because of this, $|\phi_s|$ increases more quickly with the applied potential in the mvdW case. In the polarisability case the reduction in the permittivity causes the field initially to be larger than the GC case, leading to a smaller $|\phi_s|$, but at higher potentials ($\bar{\phi}^0 < -10$) the large field limits further growth of the counter charge and so further growth in its value is also limited, meaning $|\phi_s|$ grows more quickly than the GC case (see Fig. 7.6(b)).

In the small negative potential region, the rate of the reaction seems to be dominated by the actual electric field strength. The reaction takes place because Re is repelled from the surface, allowing Ox to diffuse to the surface to react. Provided the diffusion limitation to the transport flux is not reached, the flux of the product ions away from the surface is, in part, defined by the electric field across the double layer. If this is larger, the migration component of the flux across the double layer will be larger, meaning that a higher reaction rate can be supported because the ions are removed more quickly.

Increasing the potential in the negative direction causes the effects of the ion interactions and the diffusion limitation on the reaction flux to become apparent. The second of these only really affects the GC case, because the ion interactions in the other two cases actually reduce the current when the potential is increased beyond some limit. This can be seen in Fig. 7.7 (a), in which the data from Figs. 7.4(a) and (b) are re-plotted over a larger potential window together with the data for the gFBV model.

The gFBV case always reaches the diffusion limited current at high potentials, but the other two models always return to zero. The return to zero current occurs because the increased energy due to ion interactions in the double layer has to be offset in order for Ox to be able to cross the double layer so that it can react. The only means for doing this is to increase the concentration gradient across the double layer. This naturally occurs up to a point because Ox is consumed at the surface, but with the increase in the total surface concentration (in the excluded volume case) or the electric field (in the polarisability case), there is increased resistance to diffusion. In order to overcome this, Ox requires a larger concentration gradient across the double
layer than can be found in the domain. This can be achieved but, since the bulk concentration is fixed, it comes at the expense of a reduction in the concentration gradient across the domain. Evidently such a reduction in the concentration gradient across the domain is limited: once the required gradient across the double layer is such that the concentration just outside it is the same as the bulk concentration there can be no flux in Ox and the reaction must stop.

As a final comment in this section, the previous figure also gives an indication of the relative strengths of the excluded volume and polarisability interaction terms. In the excluded volume system the current in the negative potential region returns to zero at a much lower potential than in the polarisability system. This indicates that the energy cost of crossing the double layer increases more quickly as a function of the potential in the former system, even though the maximum concentrations in both are the same.

7.3.2 Supported electrolytes

The effect of ion interactions in supported electrolytes will now be considered. For the purposes of this section, the supporting electrolyte is taken to consist of the addition to the system of a fourth species of ion, which has the same charge as Re (i.e. \(-1\)). In order to maintain electroneutrality in the bulk, the concentration of the positively charged non-reactive species which is already present is also increased, such that its total concentration is equal to the sum of the concentrations of the two negatively charged ions.

The supporting electrolyte has opposite effects on the current in the positive and negative potential regions, significantly reducing the value in the former and slightly increasing the value in the latter. This can be seen in Fig. 7.8(a), which shows the \(I \text{ vs } \phi^0\) curves for each interaction type (GC, black, mvdW, red, and polarisability, blue) with different amounts of supporting electrolyte, together with the relevant data for the BV system (green). The bulk concentrations of the reacting species are 0.1 M in all cases and the rate constant is \(k^\ominus = 10^{-5}\). The three cases are comprised of no supporting electrolyte (i.e. the same as in the previous section), an equal
amount of supporting electrolyte (i.e. the addition of 0.1 M of non-reactive negative ions) and an excess of electrolyte, with the addition of 0.4 M of non-reacting negative ions. For the GC model, it was not possible to run the highest support concentration. Fig. 7.8(b) shows the detail near the origin of the curves in part (a).

![Diagram showing the effect of adding a supporting electrolyte to the systems shown in Fig. 7.7. Black lines GC model, red lines excluded volume, blue lines polarisability, green lines BV model. Line styles indicate the concentration of the non-reactive positively charged supporting species. Part (b) shows in more detail the behaviour near $\bar{\phi}^0 = 0$.]

The effect of the supporting electrolyte is to generally move the simulated results in the direction of the BV model, although it is only at large positive potentials in the high support case that the simulated system approaches the BV model. It was not possible to simulate larger concentrations of supporting electrolyte, for the previously described reason that the simulations would not run to completion, but there is no reason to suspect that the numerical and analytical solutions would not be identical if more supporting electrolyte were added. The reason for the convergence is simply that for high concentrations of supporting electrolyte the double layer is sufficiently well formed from non-reacting ions that there is no contribution to the transport flux from migration. For all other potentials, however, there remain many differences between the numerical and analytical models, even at the highest simulated support concentration. The supporting electrolyte means that these cannot be due to significant contributions to the transport flux from ion migration in the domain, but are instead thought to arise because of changes in the electric field in the double layer.

The presence of the supporting electrolyte increases the amount of counter charge in the double layer, meaning that the electric field is larger in that region at a given surface potential compared to the unsupported case. As with the unsupported case, an increased field near the electrode surface both increases the possible rate of ion transport across the double layer and reduces the potential at the Stern layer boundary, $\phi_s$.

For Re, increasing the field in the double layer reduces the amount of energy required for an ion to cross the double layer if the potential is positive and increases it if the potential is negative. For positive potentials, then, a smaller concentration gradient is required across the double layer to maintain a given flux, because of a larger migration component. In the opposite way to the
description of the rate at negative potentials for unsupported electrolytes, if the concentration
gradient across the double layer is smaller, the concentration gradient across the remainder of
the domain can be slightly larger. Thus, for all but the smallest and largest potentials, the rate of
the reaction will be increased relative to the BV system. For large positive potentials there still
exists the same maximum diffusion rate, so any changes to the transport rate at lower potentials
cannot increase the total flux above the diffusion limited value. Until the diffusion limitation is
reached, however, the rate can be increased above that of the BV model, as is observed.

For negative potentials, the addition of a supporting electrolyte increases the current in all
cases, including the GC case, so cannot be due only to the effects of the ion interaction terms.
As with positive potentials, the supporting electrolyte forms the double layer, resulting in a
larger electric field in the double layer. This supports a higher flux of the reduced species, as
they are pushed out of the double layer more readily.

It is unlikely that the ions in the supporting electrolyte will have the same size or polarisability
as the reacting species. As seen in Section 5.6.3, differences in the relative sizes or polarisabil-
ities of the ions in the two electrolytes can alter the relative equilibrium proportions of the two
ions in the double layer of a mixed electrolyte and, in particular, change the ratio of the surface
concentrations of the two ions relative to that predicted by the GC model, in which the ratio is
always equal to the ratio of the bulk concentrations (assuming the ions are all monovalent).

The effects of changing the relative properties of the reacting and supporting electrolytes
are shown in Figs. 7.9 and 7.10. The first of these shows the case when the excluded volume
interaction is accounted for, assuming the two reacting species to have a diameter of 0.7 nm.
Part (a) of the figure shows \( I \) as a function of \( \phi_0 \) for the cases of an equal amount of supporting
electrolyte (solid lines) and an excess (0.5 M) of supporting electrolyte (dashed lines). For each
supporting electrolyte concentration, a plot is made of the cases where the diameters of the
supporting electrolyte ions are of equal size to the reacting species (black lines), where they are
smaller (0.55 nm, red lines) and where they are larger (0.8 nm, blue lines). Part (b) of the figure
shows the deviation of the current in the latter two cases from the first, again presented as the
difference in the magnitudes of the current, so that negative values represent the current being
closer to zero regardless of the sign of the potential. The second figure shows a similar set of
data, but this time accounting for the polarisability. The reacting species have a polarisability of
\( 4\pi\alpha = -8 \text{ M}^{-1} \) and the polarisability of the supporting ions are either the same (black lines),
smaller (\( 4\pi\alpha = -4 \text{ M}^{-1} \)) (red lines) or larger (\( 4\pi\alpha = -12 \text{ M}^{-1} \)) (blue lines).

Defining the case in which the ion properties are all the same as the reference case for each
of the two systems, the extent of the deviations which result from differences in the relative
properties of the reacting and supporting species are relatively small. The changes, and the
reasons for them, are consistent with the reasons for most of the previously discussed variations
of the system behaviour from the BV or gFBV systems.

The differences are largely explained by the changes in the electric field (and the effect this
has on \( \phi_s \)) or the exclusion of reactant from the surface. The value of \( \phi_s \) as a function of \( \phi_0 \) is
shown in Fig. 7.11(a) for each of the six 0.5 M excess systems. Fig. 7.11(b) shows the difference
Figure 7.9: The impact of changing the ion diameter of the supporting electrolyte. (a) the current as a function of the potential for equal support and excess support and (b) the difference in the magnitude of the current relative to the case when all ion properties are equal. See text for further details.

Figure 7.10: The impact of changing the excess polarisability of the supporting electrolyte. (a) the current as a function of the potential for equal support and excess support and (b) the difference in the magnitude of the current relative to the case when all ion properties are equal. See text for further details.

between each of the cases with unequal ion properties and the respective reference case. This is plotted as the difference between the magnitudes of the Stern layer boundary potentials, \( \Delta \phi^R = |\phi_s| - |\phi^*_{reference}| \), so that negative values show \( \phi_s \) becoming smaller regardless of the sign of the potential.

For negative potentials, the rate of the reaction depends on how quickly Ox is able to diffuse to the surface. If the size of Ox is smaller, or it has a lower polarisability, than the reference case it will in general be easier for it to do so, as there is a smaller energy cost incurred in crossing the double layer, while the reverse is true if it is larger or has a higher polarisability. In accounting for the excluded volume interaction, the energy cost of crossing the double layer only ever increases with an increasing potential, because the concentration in the double layer only ever increases. If Ox is smaller than the supporting ions, it will be able to diffuse through more easily than if its is the same size, so the concentration gradient across the double layer can
be slightly smaller at a given potential, allowing the concentration gradient across the domain to be slightly larger, supporting an overall larger flux. The same limit on the gradient in the double layer as described previously still applies, however, in that there will always be a potential at which Ox is unable to form a sufficiently high concentration gradient across the double layer while still having a gradient in the domain. At this point the reaction stops and the current in all models becomes equal to zero (not shown). This explains the reduction in $\Delta I^R$ at a large negative potentials when the reacting species are smaller, which can be seen in the solid red curve in the excluded volume data in Fig.7.9(b). If the reacting species are larger than the supporting ions, the deviations in the current occur for the same reason, except this time the energy required to cross the double layer increases, so the transport rate across it is reduced.

The large negative potential trends in the polarisability data have the same basic explanation, but this time it is the field strength which prevents reacting ions approaching the surface at large potentials. The differences at low negative potential, where the current is reduced if the polarisability is smaller, are explained by the trends in the field in this region. If the polarisabilities of the supporting ions are smaller than that of the reacting species, Fig. 7.11(b) shows a slight increase in $\Delta \phi^R$, indicating a reduction in the field. This makes it relatively more easy for Ox to cross the double layer to the reaction plane, relative to the equal-polarisability case, so the rate is increased relative to the reference case.

For positive potentials, where the reactant is the negatively charged Re, the effect of the relative sizes of the reacting and supporting species is essentially reversed, with smaller or lower polarisability supporting ions reducing the current relative to the respective reference cases. In this case it is because the system, in attempting to move as much charge as possible to the surface to shield the surface potential, moves slightly more of the smaller ion, preventing the larger reacting species from approaching the surface. At sufficiently large potentials, the three systems converge because they all have the same limit to the diffusive flux of Re. Once this is reached, the current cannot increase further in any of the systems.

Finally, in the polarisability model there is an increase in the current at low positive potentials and a decrease at higher potentials if the supporting ions have a lower polarisability. Again, this
reflects the changes in the field strength, which can be inferred from $\Delta \phi^R$. The positive value of this parameter at low potentials indicates a smaller field, meaning that it is more likely that the reactant will be found at the surface compared to the reference case, so the current increases. Further increases to the potential cause the field to become larger, compared to the reference case, meaning that it is less likely that the higher polarisability ion will be found at the surface, so the relative current decreases.

### 7.3.3 Summary of steady state reactions

The reaction model has, to date, been used to consider some simple cases regarding how the effects of the ion interactions alter the rate of reaction in steady state systems, with comparison being made to a simple model based on the use of the BV equation and also to the gFBV equation, in neither of which are ion interactions accounted for. The reaction considered was a single electron transfer, with the oxidised form being charge neutral and the reduced form being negatively charged. The data is expected to be identical if the oxidised species is positively charged and the reduced species charge neutral, but in this case the effects described will occur at the opposite potential.

It was shown that even for supported electrolytes, the BV equation compares poorly to even the gFBV model, with the current in the latter case being larger for positive potentials and smaller for negative potentials, provided the diffusion limitation was not reached. The only exception to this was for very small positive potentials, in which case the current is larger in the BV case.

The inclusion of ion interactions (mgFBV case) was shown to cause small alterations the current, relative to the gFBV case, for positive potentials but to have a much larger effect for negative potentials. At large negative potentials, the current is predicted to return to zero when interactions are accounted for, where in the gFBV case it saturates at the diffusion limited current. This can be explained in terms of the energy required by the neutral reactant to cross the double layer increasing as the interaction energies grow, until their transport flux tends to zero.

For supported electrolytes, small deviations in the predicted current are observed depending on the properties of the supporting electrolyte relative to the reacting species. These are attributed to the way that changing the properties of the supporting species alter the electric field at the reaction plane and therefore the potential drop across the Stern layer.

### 7.4 Electrochemical impedance spectroscopy for a reacting system

In this final section, the effect of ion interactions upon the dynamics of a reacting system are briefly considered in the context of EIS. This data is considered relative to the simplest equivalent circuit for a reacting electrode/electrolyte system, which is the Randles-Ershler equivalent...
circuit (REEC), described below. The procedure for running the simulations was identical to
that discussed in the previous chapter, but with the changed boundary condition at the electrode
surface to allow for surface reactions to take place. As with the data presented in the first part of
this chapter, most of the systems considered assume that the reaction potential coincides with
the PZC for the system, i.e. $\Delta \phi_{\text{RXN}} = 0$. For most cases considered, the domain length is set
to $L = 5000$, the bulk concentration is 1 M and the rate constants are $k_f^\ominus = k_b^\ominus = 10^{-3}$. These
are quite short domains and fast reactions, but under certain conditions they do permit some
comparison and contrast with the results predicted by the REEC. In common with the previous
simulations of EIS, the amplitude of the applied potential is $\Delta \phi^0 = 0.3$.

7.4.1 The Randles-Ershler equivalent circuit

The simulated EIS has, to date, been considered only in terms of comparison to the REEC. The
circuit consists of a resistor in series with the Warburg element, both in parallel with a capacitor,
all in series with a second resistor, as shown in Fig. 7.12.

The components of the circuit represent the impedance of the bulk solution to ion transport
($Z_b$), the double layer capacitance ($C_d$), the impedance to charge transfer ($Z_{ct}$) and the Warburg
element ($W$), which accounts for the concentration impedance for a reaction (the effect of the
changing surface concentrations on the reaction rate). In terms of the physical assumptions
placed on the system which are required for the REEC to be valid, these are similar to those for
the BV model in Section 7.3.1: an excess of supporting electrolyte is assumed, such that the
system remains electroneutral at all times, and the surface flux of the reacting species is defined
by the BV equation. The equivalent circuit assumes that the capacitive (non-Faradaic) charging
current and reaction (Faradaic) current can be treated separately and that current flowing through
the bulk to the electrode may take either route. Applying Kirchoff’s laws to the circuit, the total
impedance takes the form

$$Z A = Z_b A + \frac{1}{2\pi j f C_d + \frac{1}{A(Z_{ct} + Z_W)}}$$  \hspace{1cm} (7.35)

where $Z_W$ is the impedance of the Warburg element. $Z_b$ is equal to $R_b$, stated in the previous
chapter and rewritten here:

$$Z_b A = R_b A = \frac{k_b T L}{2 z_j^c \phi_0^2 D e^0}$$  \hspace{1cm} (7.36)
Again, the property of interest is the product of the resistance and the area so that all the units match. The charge transfer impedance is another frequency independent resistance which is related to the exchange current density, $I^0$, for the system through the expression

$$Z_{ct}A = R_{ct}A = \frac{k_B T}{n_e e_0 I^0}$$

(7.37)

where $I^0 = n_e e_0 k\varphi (e_0^\varphi (c_0^R e_0^\varphi (1 - \gamma (c_0^O x_0^\gamma))^\gamma$. The symmetry factor has previously been assumed to be 0.5 and we are only considering single electron transfer reactions with equal bulk concentrations of the reactant and product species, so this expression may be rewritten more simply as $I^0 = e_0 k\varphi c_0^0$, where $c_0^0$ is the bulk ion concentration. Finally, the impedance for the Warburg element for finite length diffusion takes the form

$$Z_W A = \frac{k_B T}{n_e^2 e_0^2 \sqrt{2\pi j D} \text{tanh} \sqrt{\frac{2\pi j D}{2\pi j D} L}}$$

$$Z_W A = \frac{2k_B T}{e_0^2 c_0^0 \sqrt{2\pi j D} \text{tanh} \sqrt{\frac{2\pi j D}{2\pi j D} L}}$$

(7.38)

Where Nyquist plots for the EC are presented in the following sections, the Mathematica software package has been used to generate the data based on Eq. (7.35). The values of $Z_b$, $Z_{ct}$ and $Z_W$ were calculated using Eqs.(7.36), (7.37) and (7.38), and the value of the differential capacitance was taken from simulations of the non-reacting equivalent of the same model system.

### 7.4.2 Simulated EIS for systems with $\Delta \phi_{RXN} = 0$

In this section, data are presented regarding the simulation of EIS for systems similar to those discussed in Section 7.3, namely the standard state equilibrium potential is equal to zero, such that it coincides with the PZC of the system. The reaction remains the same as that described previously, which is to say it is a one-electron transfer process in which the reduced species has a single negative charge.

Two simulated Nyquist plots are shown in Figs. 7.13 (a) and (b), the first for a 1 M reacting unsupported electrolyte and the second for a 0.1 M reacting electrolyte in a 0.5 M supporting electrolyte (where the supporting ions have the same properties as the reacting species). In both, the domain length is $L = 5000$ and the standard reaction potential coincides with the PZC for the system, so the forward and reverse rate constants are equal, with $k_f = k_b = k = 10^{-3}$. In terms of the data, the symbols represent the GC, mvdW ($a = 0.7 \text{ nm}$) and polarisability ($4\pi \alpha = -8 \text{ M}^{-1}$) models for the system and the blue line represents the REEC result. For the REEC, the parameters $Z_{ct}$, $Z_b$ and $Z_W$ were calculated using the expressions defined in Section 7.4.1, while the values of $C_d$ were taken from previously simulated data.

In general terms, the shapes of the curves are the same, consisting of a small arc at higher frequencies (on the left) and a larger arc at lower frequencies. The high-frequency arc corresponds to the properties of the bulk electrolyte and the non-Faradaic electrode charging processes. The
high-frequency intercept on the real axis corresponds to the impedance of the bulk electrolyte, \( Z_b \) (\( \bar{Z}_b' \bar{A} \approx 0.2 \times 10^5 \) in Fig. 7.13(b)), and the point where the high-frequency arc would intercept the real axis, if it were continued in the clockwise direction, corresponds to the charge transfer impedance, \( Z_{ct} \) (\( \bar{Z}_{ct}' \bar{A} \approx 1 \times 10^5 \) in Fig. 7.13(b)). To the right of the central minimum is a linear region, corresponding to the frequency range in which the reaction dominates the generated current but in which it is not limited by the reactant transport rate. The transition from the linear region to the shape of the low-frequency arc is due to the transport limitation of the ions in the domain, and the low-frequency intercept of the curve with the real axis is denoted the transport impedance, \( Z_t \) (\( \bar{Z}_t' \bar{A} \approx 5.2 \times 10^5 \) in Fig. 7.13(b)).

The characteristic frequency for the processes taking place in each arc is the value at the apex. For the high-frequency arc, the characteristic frequency can be used to calculate the differential capacitance of the system using the equation

\[
C_d = \frac{1}{2\pi f A(Z_b' - Z_{ct}')} \quad (7.39)
\]

In both the simulated and REEC solutions, the calculated values of the differential capacitance using this equation agree well with all previously described means for its calculation in the absence of reactions. The frequency at the apex of the low-frequency curve is the same in all systems shown, being approximately \( \bar{f} = 1.5 \times 10^{-8} \).

Given the underlying assumption of electroneutrality in the REEC analogue, provided by an excess of supporting electrolyte, it is unsurprising that, of the two figures, it is the supported case which exhibits the better fit, with the total low-frequency resistance being equal in all the models. The lack of a supporting electrolyte in the 1 M system means that, as with the steady state systems, incomplete double layer formation results in a migration component to the total transport flux. The consequence of this is that the total transport impedance is smaller. In the supported case, the double layer is fully formed, resulting in no field being present in the domain and transport is limited by the diffusion rate across the domain, in line with the
underlying assumptions of the REEC.

Of the three numerically modelled sets of data, the GC and mvdW cases are identical at all points (the values of the frequencies in the three simulated cases are the same). At high frequencies this follows from the fact that the differential capacitance is identical in the GC and mvdW systems (see Section 5.3) and that there is a negligible difference in the reaction rate near $\phi^0 = 0$ between these systems (see Fig. 7.5). At lower frequencies, it was shown in Chapter 6 that accounting for the excluded volume interaction has little effect on the transport properties, so that, when the EIS simulation enters the transport limited regime, the mvdW model should not differ from GC model.

For the polarisability model, there is also no difference in the low-frequency arc, which again follows from the fact that the polarisability interaction has no effect on the transport properties. However, differences do arise between the polarisability model and the other two in the high-frequency arc. Given that the sets of frequencies simulated in the three cases were the same, the points corresponding to the polarisability data can be seen not to align with the other two sets of points. This is because of the reduction in the differential capacitance at the PZC which the ion polarisability causes relative to the GC model (see Section 5.2). In terms of EIS this corresponds to a shift in the impedance at a given frequency, in the same way as seen for the change in the admittance in Section 6.1.2. This can be seen more clearly in the Bode plots for the systems, the two parts of which are shown in Figs. 7.14(a) and (b).

Figure 7.14: Two parts of the Bode plot for the same systems shown in Fig. 7.13: (a) $|Z|$ and (b) $\theta$ as a function of the frequency

At high frequencies (between $1 \times 10^{-4}$ and $1 \times 10^{-3}$), it is just possible to see that the magnitude of the impedance is larger when the polarisability is accounted for, and that the change in the phase angle is shifted to a slightly higher frequency in the same range.

Returning to the two Nyquist plots in Figs. 7.13 (a) and (b), the charge transfer impedance can be seen in both cases to be smaller in the REEC than in the simulated data, regardless of the presence of the supporting electrolyte. These differences can be traced back to the fact that the steady state reaction rate in the BV model at small potentials near the PZC is slightly larger than that in the gFBV or mgFBV models (see Fig. 7.2), indicating that the reaction occurs more readily in the former case. This may have implications for the values of the rate constants
if they are determined using EIS, as this is interpreted using some form of equivalent circuit. Since the predicted values clearly differ between the REEC and models which account for the double layer structure in a more detailed manner, there will be differences in the rate constants when they are determined from the two different modelling methods. While it has not yet been possible to quantify the extent to which the rate constant differs between the BV and numerical models, the indication from the supported electrolyte data is that only the rate constants are altered, since the total impedance at very low frequencies appears to remain the same.

7.4.3 Simulated EIS for systems with $\Delta \phi_{RXN} \neq 0$

This section briefly considers some preliminary data regarding how the EIS spectra are predicted to change when the standard reaction potential is shifted from being zero, as in the previous section, to having the value $\Delta \bar{\phi} = 5$. The change in the reaction potential implies that the rate constants must also change, since their ratio must be equal to $\exp(\Delta \bar{\phi})$. In order to satisfy this, the values of the rate constants were set to $k_f = 10^{-5} \exp(2.5)$ and $k_b = 10^{-5} \exp(-2.5)$. The bulk concentrations of the reacting species were set to 0.1 M and, where a supporting electrolyte is present, the concentration of the negative ion was 0.4 M and that of the positive ion was 0.5 M, so that the bulk remains charge neutral.

The two plots in Fig. 7.15(a) and (b) show the predicted EIS spectra for the same GC, mvdW and polarisability systems as in the previous section (i.e. $a = 0.7$ nm and $4\pi\alpha = -8$ M$^{-1}$ where appropriate). Part (a) shows the unsupported system and part (b) shows the supported system.

![Figure 7.15: The predicted effect of ion interactions in the Nyquist plot for a 0.1 M electrolyte with $\Delta \phi = 5$. (a) unsupported case and (b) with 0.4 M support.](image)

The high-frequency arc in this case can be seen to be much larger than in the previous example, although it should be noted that the two cases are not directly comparable because the rate constants in this case are much smaller.

When the reaction potential is offset from the PZC for the system, it is apparent that more significant differences arise between the three models, regardless of the presence of the supporting electrolyte, with the high frequency arc being smallest in the mvdW system and largest
in the polarisability system. Although not particularly clear, it appears that the low-frequency arc does not change significantly, although this would need to be confirmed using a system in which this arc was larger (e.g., one with a longer domain).

The difference in the high-frequency arc size indicates a change in the relative values of the charge transfer resistance, with it being reduced in the excluded volume case relative to the GC case and increased in the polarisability case. This is true regardless of the presence of the supporting electrolyte. As with the case for $\Delta \phi_{\text{RXN}} = 0$, the effect of the supporting electrolyte is seen in an increase of the overall width of the two arcs, implying a larger system resistance. Again this is likely to be because the supporting electrolyte shields the reacting species in the domain from the changing potential, meaning that there is a smaller migration component to the reactant flux.

It has not yet been possible to investigate fully the reason for the ways in which the spectra change upon accounting for ion interactions. The interaction terms reduce the concentrations of the ions near to the electrode surface at the equilibrium potential, relative to the GC case, meaning that there will be differences in the diffusive components to the flux in the double layer as the potential varies during the oscillations. At the same time, the interactions alter the electric field, so the migration component to the flux will be similarly changed, although the different effects that the two interaction terms have on the field could be responsible for the fact that the polarisability interaction seems to reduce the predicted reaction rate. For a more complete investigation, the data for a range of $\Delta \phi_{\text{RXN}}$ and different ion properties would be needed.

Finally, in the same manner as for reactions in the steady state case, the relative properties of the species in the electrolyte also influence the impedance spectra. Again, it has not yet been possible to simulate a sufficient amount of data for detailed conclusions to be drawn, but there is some indication of the trends which occur. In a similar manner to Section 7.3.2, six supported systems with an excess of supporting ions are considered. For each of the two interaction terms, three cases are considered, in which the supporting ions have properties the same as, smaller than or greater than those of the associated reacting species. The reacting species were again assumed to either have a diameter of $a = 0.7 \text{ nm}$ or an excess polarisability of $4\pi\alpha = -8 \text{ M}^{-1}$, as in Fig. 7.15(b). The supporting species then had a diameter of either $0.55 \text{ nm}$, $0.7 \text{ nm}$ or $0.8 \text{ nm}$ in the excluded volume case, or otherwise an excess polarisability of $-4 \text{ M}^{-1}$, $-8 \text{ M}^{-1}$ or $-12 \text{ M}^{-1}$. The results are shown in Figs. 7.16(a) and (b), the former for the excluded volume interaction and the latter for the polarisability interaction.

The relative sizes of the ions in the excluded volume case can be seen to change the size of the low-frequency arc, but this is not the case for the polarisability interaction. Indeed, in the latter case, the three curves largely trace the same path, although the data points at a given frequency are either advanced or retarded relative to the case in which all polarisabilities are equal (the same set of frequencies were simulated in all cases). This effect is the same as seen several times previously, arising when the polarisabilities are changed because of the change this causes in the differential capacitance, the values of which were confirmed using simulated
Figure 7.16: The effect of the supporting electrolyte properties on the impedance spectra for (a) the excluded volume interaction (reacting species diameter is 0.7 nm) and (b) the polarisability interaction (reacting species polarisability is $-8 \text{ M}^{-1}$).

CV data.

The excluded volume interaction, on the other hand, in addition to undergoing a change in the differential capacitance, also experiences a change in the charge transfer impedance. If the supporting ions are larger, then $Z_{ct}$ is increased, and the reverse is true if the supporting ions are smaller. This trend in the behaviour is much as would be expected, given that when the reacting species are smaller they can pass through the double layer to the reaction plane more easily, meaning the reaction rate, and therefore the current, will be larger. Beyond the observations presented here, and as with differences between the models which account for interactions and the GC case, it has not yet been possible to determine exactly why the behaviour of the system changes in the way it does for supported electrolytes, particularly given the apparent lack of effect of the polarisability term.

### 7.5 Conclusions

In this chapter, a means was presented of deriving a modified form of the generalised Frumkin-Butler-Volmer (gFBV) rate equation which accounts for the interactions between the species that are present at the electrode surface (referred to as the mgFBV model). This was incorporated into the previously developed dynamic model for an electrode/electrolyte system and used to investigate how the excluded volume and polarisability interactions alter the reaction behaviour of steady state systems and also how they change the output of simulated electrochemical impedance spectroscopy.

For steady state systems, the numerical mgFBV model was compared to a simple analytical model based on Butler-Volmer kinetics. Significant deviations between the two were observed at large potentials with the the development of the superlimiting current at one extreme and a return to zero current at the other. The former of these was described in terms of incomplete double layer formation resulting in a significant migration contribution to the total flux of the
charged reactant, while the latter was ascribed to the exclusion of the neutral species from the electrode surface when ion interactions are accounted for.

The mgFBV model was further considered relative to the gFBV model (i.e. a system with no interactions). The differences which were observed were attributed to the way that the interactions alter the electric field in the double layer, altering how well the reactant can be replenished at the surface as it is consumed. The addition of a supporting electrolyte was shown to reduce the size of superlimiting current, as would be expected, but it did not entirely reduce the current to that of the BV model throughout the positive potential range. Furthermore, for negative potentials the rate was shown to be increased by the addition of a supporting electrolyte. Again, this was discussed in terms of the way that the supporting electrolyte alters the free energy of the species in the double layer, changing the rate at which reactant is able to pass through the double layer to the surface. The ion size and polarisability of the supporting ions relative to the reacting species were also shown to have an effect on the reaction rate.

The final part of the chapter considered how the use of the gFBV rate equation changes the predicted impedance spectra relative to the Randles-Ershler equivalent circuit (REEC), and then how this is further altered by accounting for ion interactions in the mgFBV case. For systems in which the equilibrium reaction potential is equal to the point of zero charge for the electrolyte, reasonable agreement between all models and the REEC was found for supported electrolytes. The impedance was observed to be smaller than in the REEC in the unsupported case, which was attributed to the contribution of migration to the total reactant transport flux increasing the overall rate/decreasing the charge transfer impedance.

Following the simulation of systems in which the equilibrium reaction potential is moved away from the point of zero charge, sizable differences were observed in the predicted spectra. The excluded volume interaction reduced the size of the high-frequency arc on the Nyquist plot of the impedance relative to the GC case, while the polarisability interaction was seen to increase it, whether or not a supporting electrolyte was present, but more work is required to determine the exact reasons for these changes. For systems in which the size of the supporting ions differed from that of the reacting species, further differences were seen to occur, with the high-frequency arc shrinking when the reacting species were smaller than the supporting ones. A similar effect was not seen in the polarisability case, which seems largely indifferent to the relative values of the species polarisabilities. Again, it was not possible to fully investigate the reasons for this.
Chapter 8

Conclusions and Future Work

In this final chapter, the main findings of the work are summarised and discussed, and the suggestions are made for further study.

8.1 Conclusions

In this work a dynamic model was developed to describe the behaviour of an electrolyte adjacent to a smooth planar electrode. The model was designed to account for the excluded volume interaction between ions, using a modified form of the van der Waals equation of state which permits difference in the sizes of the ions (Gorenstein et al. 1999). It was also designed to account for the change in the permittivity of the solvent which results from the interaction between the ions and the solvent (referred to as the polarisability interaction) by assuming a linear dependence of the permittivity on the ion concentration and a quadratic dependence of the electrochemical potential on the electric field strength (Netz 2001; Ben-Yaakov et al. 2009; Hatlo et al. 2012). The result was a modified form of the Poisson-Nernst-Planck equation, in which the motion of the ions is coupled to the Poisson equation (mPNP model). In addition, a modified version of the generalised Frumkin-Butler-Volmer (mgFBV) reaction model was developed in which ion interactions (the volume and polarisability) were accounted for, which was coupled to the mPNP model developed earlier.

In general, the work presented here goes some way to showing that ion interactions play a significant role in all aspects of the behaviour of an electrolyte, not just the equilibrium state, which is what a large proportion of current electrolyte modelling is aimed at. To a large extent, much non-equilibrium behaviour is inaccessible to the most detailed models (Molecular Dynamics, Monte Carlo, DFT, etc.), either because of limits to the size of the system, to the range of surface potentials which can be simulated, or to the growth of errors in the solution, among other reasons. What mean-field, local density approximation models offer is reasonably accurate solutions at the expense of some of the finer detail, which can then be used to complement simulation and experiment. Accounting for the various ion interactions is, with the exception of the excluded volume, still uncommon even for this type of modelling though. The work presented here represents a method for describing one such additional ion interaction which,
in combination with the excluded volume interaction, is discussed for single and mixed electrolytes, both at equilibrium and in reacting and non-reacting dynamic systems. The following sections summarise the main findings of the work.

8.1.1 Equilibrium properties

Individually, the mvdW and polarisability models were demonstrated to lead to the correct qualitative behaviour for the differential capacitance of an electrode/electrolyte system. Comparison of the two interactions showed that, if the parameters in each were set such that the maximum concentrations were the same, the differential capacitance peaked at a lower potential and decayed more rapidly at higher potentials when the polarisability was accounted for. This was linked to the fact that the permittivity in the double layer was significantly reduced at high potentials in the polarisability model, meaning that the surface charge density increased more slowly as a function of the potential, despite the observation that the electric field was larger than when the excluded volume interaction was accounted for.

An analytical expression was derived for the differential capacitance at the PZC for systems in which the polarisability was accounted for. This was used to show that the polarisability directly plays a role in determining the differential capacitance at that point, as a result of the fact that it changes the solvent permittivity. By contrast, the excluded volume interaction caused no deviations from the value predicted by the GC model. Furthermore, while in the GC and excluded volume models the differential capacitance at the PZC was a monotonically increasing function of the bulk ion concentration, it was predicted to peak and then decrease above a certain concentration when the polarisability was accounted for. This was shown to match experimentally observed trends for ammonium nitrate and ethylammonium nitrate.

The full model, accounting for both types of interaction, was shown to offer reasonable agreement with experimental data for several different electrode/electrolyte systems. The limitations were discussed, particularly for modelling NaF electrolytes, the specific reasons for which remain unclear.

Finally, systems of mixed electrolytes were considered, and this appears to be the first time a model which accounts of the polarisability interaction has been applied to such systems. A much improved agreement over models which only account for the excluded volume interaction was demonstrated for a MgCl/CsCl mixed electrolyte, the explanation being that the very high excess polarisability of the Mg\(^{2+}\) ion prevents its approach to the electrode surface at high potentials. The model was also used to consider the differential capacitance of a mixed NaF/NaCl electrolyte, but the agreement with the experimental data was much less convincing, indicating a number of shortcomings in the model. However, while the agreement was poor, accounting for the ion polarisability was shown to result in the appearance of a second peak in the differential capacitance at large applied potentials. This trend is observed experimentally, but the model was unable to predict the correct magnitude for the second peak. However, the excluded volume model alone was unable to predict any second peak over the range of systems tested (although it should be noted that, for a sufficiently large difference in ion diameter and bulk concentra-
tion, such a second peak is possible). It was suggested that the reason for the appearance of the second peak when both the excluded volume and the polarisability is accounted for lies in the way that the permittivity changes. The replacement of the larger, higher polarisability ion by a smaller, lower polarisability ion means that the permittivity in the double layer, having initially decreased, increase again. As a result, the surface charge density increases more quickly with the increased surface potential.

8.1.2 Electrolyte dynamics

The dynamic properties of the electrolyte were analysed in terms of the response to a potential step and through the capacitance dispersion effect. The main result was that that the interaction terms did not directly affect the way that the bulk electrolyte responded to gradients in the electrostatic potential.

The peak and then decrease in the differential capacitance which occurred at large potentials when interactions were accounted for led to improved agreement with the equivalent circuit analogue for the system. This was attributed to the fact that the reduction in the differential capacitance corresponded to a slower growth in the number of ions required in the double layer relative to the GC case. As a result, depletion of ions from the electrolyte in the domain was smaller and so the electrolyte resistance changed by a much smaller amount during the electrode charging process.

The change in the equilibration time as a function of the domain length was also qualitatively discussed. It was shown that the value of this parameter increased rapidly and non-linearly for short domain lengths, then entered a region of very minimal growth for a range of intermediate lengths, before finally becoming proportional to the domain length for long lengths. These trends were observed whether the ion interactions were accounted for or not, although the transition between the regions occurred at shorter domain lengths when they were accounted for. The Stern layer was also shown have a significant effect in reducing the lengths at which the transition between the types of growth occurred. The linear growth in the equilibration time at long domain lengths was identified with the system showing the type of behaviour predicted by the equivalent circuit, and could be explained in terms of the domain length becoming sufficiently long that the electric field was always small, so depletion of ions from the bulk was much smaller. The two types of growth seen at shorter domain lengths could not be quantitatively linked to a specific process occurring during the charging of the electrode, but they most likely arise from depletion of ions, causing the resistance of the bulk electrolyte to change.

The simulation of cyclic voltammetry was briefly presented in order to demonstrate that, in the absence of any other processes, both the excluded volume and the polarisability can give rise to peaks in the $I$ vs $\phi^0$ curves. The values of the differential capacitance were also demonstrated to be identical, regardless of which of the three methods described throughout the work (equilibrium calculations, EIS or CV) were used.
8.1.3 Reacting systems

The final chapter described a means for incorporating ion interactions into a reaction model derived from the reaction affinity, leading to a modified form of the generalised Frumkin-Butler-Volmer equation for the reaction rate (the mgFBV model). This model was then applied in the context of the dynamic model developed in the preceding chapters, looking at steady state reacting systems and simulated electrochemical impedance spectroscopy. In both cases only single electron transfer reactions were considered, with a neutral species reacting to form a negatively charged ion.

Under steady state conditions, significant deviations were observed relative to a simplified model which assumed Butler-Volmer (BV) kinetics and bulk electroneutrality, even in the presence of an excess of supporting electrolyte. For large positive potentials, the current generated was enhanced in unsupported or partially supported electrolytes, leading to currents in excess of that permitted by the diffusion flux of the reactant alone. This was explained in terms of the incomplete formation of the double layer allowing the presence of an electric field in the domain which could drive a migration flux. For large negative potentials the current was predicted to return to zero, and this was attributed to exclusion of reactant from the surface. Note that if the oxidised species in the reaction were positively charged and the reduced species neutral, the same effects would occur, but the potentials at which they occur would be reversed. For potentials near to the equilibrium potential, the rate of reaction was always larger in the BV model than the mgFBV model, regardless of whether ion interactions were accounted for. The specific effects of the two types of ion interaction were presented, relative to the gFBV model, with differences being observed across the entire potential range. The reasons for these differences were discussed in terms of the changes in the electric field at the reaction plane and the Stern layer potential that were caused by the ion interactions. These changes in the electric field were also taken to explain the variations in the predicted reaction current which arise when the ions in the supporting electrolyte have a different size or polarisability to that of the reacting species.

The final part of the thesis introduced the changes which are predicted to be observed in simulations of EIS when ion interactions are accounted for. It was not possible to analyse fully the reasons for the differences which arise, but some significant changes were seen. For a supported electrolyte in which the standard reaction potential is equal to the point of zero charge for the electrolyte, that is to say the type of system which should be reasonably accurately modelled by the Randles-Ershler equivalent circuit (REEC), the charge transfer impedance was seen to be smaller than that predicted by the REEC in both the gFBV and mgFBV models (which predicted largely the same results as each other), although the overall transport impedance at low frequency was seen to be the same. These results confirmed the notion developed earlier in the work that the ion interactions do not significantly affect the transport flux of the ions but that they do slightly reduce the rate of the reaction for very small potentials relative to the BV model on which the REEC is based.

By moving the equilibrium reaction potential away from the point of zero charge, the ion interactions were shown to have a marked effect on the predicted Nyquist plots, either in the
absence or presence of a supporting electrolyte. For the excluded volume interaction this man-
ifested as a reduction in the charge transfer impedance, leading to a smaller high frequency
arc, while for the polarisability interaction, the opposite effect was observed. In addition to
this, the relative properties of the ions in the supporting electrolyte compared to those of the
reacting species was shown to be significant only for variations in the ion volume. Differences
in the polarisabilities of the two sets of species appeared to have no effect on the sizes of the
arcs, although there was a shift in the positions of the points on those arcs due to the different
differential capacitances of the systems at the equilibrium potential.

8.2 Further work

Possible directions for further study are proposed in the following three sections. Given the
incomplete state of some of the data throughout this thesis, the first section discusses where the
results could benefit from the use of the model as it currently stands. The second section then
moves on to look at how the model could be developed in terms of properties and effects which
have not so far been included. The final section makes some discussion as to how the model
could be applied to real-world systems and the possible implications of some of the observed
behaviour seen in this work.

8.2.1 Development of the data and results

There are several parts of this work for which a greater range of data from the model could assist
the analysis of the results in terms of how the ion interactions alter the behaviour of the system.
Many of these could possibly be resolved by considering a range of different ion polarisabilities
or diameters, where it has so far largely only been possible to run one or two of each.

For non-reacting systems, the way in which the domain length and the ion interactions com-
bine to affect the equilibration time was not apparent from the data. The model is able to output
the position of the point of minimum counter-ion concentration (the minimum of the depletion
layer) and the value of the concentration, which may provide some insight into the changes in
the resistance of the solutions. It is also be possible to calculate the components of the flux
to determine exactly what drives the transport of the ions in the various parts of the modelling
domain. From this it should be possible to explain why the relative equilibration times in the
two interaction models differ as the length changes (i.e. why the peak in $t_{eq}$ is larger in the
polarisability model than in the excluded volume model at long and short domain lengths, but
smaller for intermediate lengths).

The effect of the ion concentration was also not considered in detail, with the concentration
being relegated to a parameter while investigating the effect of the domain length. A preliminary
run of the model was made for the equilibration time as a function of the concentration, in which
a similar set of three regions to those seen in Chapter 6 were observed in the growth of $t_{eq}$ with
the concentration. However, the fact that the bulk concentration changes both the conductivity
and the differential capacitance of the electrolyte means that significantly more data would be needed to discern the details of how the concentration alters the behaviour of the system.

For steady state reacting systems there are a number of properties whose effects were not considered. In particular, systems in which $\Delta \phi_{RXN} \neq 0$ were not considered. As such a system implies the presence of a fully formed double layer when the applied potential equals the equilibrium potential, there are likely to be changes in the way that the system responds when the potential does not equal the equilibrium value, in the same way that the predicted EIS data changes. Furthermore, it should be possible to quantify in more detail the extent to which the size or polarisability of the ions changes the reaction rate by simulating various systems with different ion sizes.

One of the areas most urgently needing to be addressed is some comparison with experimental data to try to validate the model. However, given the idealised nature of the model system, in particular the fact that the excluded volume and polarisability interactions are largely considered independently, it is not immediately apparent how best to investigate some of the results which the model predicts. For a particular reacting system, the reacting species will have fixed diameters and polarisabilities, and will also have a fixed $\Delta \phi_{RXN}$. Comparison of species with different diameters and polarisabilities also implies a system with a different $\Delta \phi_{RXN}$, so the effects of changing the former are wholly entangled with a change in the latter.

One aspect where it may be possible to link to experiment is the predicted change in the reaction rate as a function of the relative properties of the supporting electrolyte. By placing the reacting species in various supporting electrolytes it should be possible to discern any differences in the reaction rate, thereby possibly providing some degree of confirmation of the model predictions.

Since the model does not require the presence of a supporting electrolyte, it should also be possible to compare the results to data for similarly unsupported real systems. This, in particular, is an aspect which equivalent circuit models are largely unable to describe, since they cannot account for the depletion of ions from the bulk electrolyte.

### 8.2.2 Development of the model

One of the main effects that is missing from the model, given that it accounts for ion concentration dependence of the solvent permittivity, is the field-dependence of the permittivity. As discussed in Chapter 2, the large electric fields in the double layer should cause a significant reduction in the solvent permittivity. Since many of the changes observed in the behaviour of the system during the course of this work may be understood in terms of changes to the electric field, this neglected effect is expected to alter the system behaviour further. As indicated by the effects of the polarisability, a reduction in the permittivity causes a reduction in the differential capacitance, so accounting for the field-dependence of the permittivity should result in further reductions in the differential capacitance. However, since the permittivity is only significantly decreased at high field strengths, which require high potentials, it is only at these high potentials that the field-dependence should affect the differential capacitance. This could explain the dis-
crepancy which remains between the predicted and experimental differential capacitance curves seen in Fig. 5.26(a).

Another modification which may be relatively straightforward to make is to include a more accurate model for the polarisability interaction and how this alters the solvent permittivity. For simplicity, the model used in this work made the assumption that permittivity varies linearly with the ion concentration, which is only strictly valid in bulk electrolytes at low concentrations. In the double layer, the significantly increased ion concentrations are likely to invalidate this assumption, so a more accurate description, possibly using one of the types of model mentioned in Section 2.4.2, may yield different results.

A slightly more involved modification, which may yield qualitatively different results regarding the modelling of the mixed electrolyte system in Section 5.6.3, would be to account for different Stern layer widths for the ions in the system and also to account for specific adsorption. The first of these could be achieved by setting the nominal Stern layer width to that of the smallest ion in the system and then preventing the larger ions from moving past the grid point in the domain corresponding to the difference in the radii of the ions, although this would mean that the grid spacing would have to be equal to the difference in the ion sizes (or multiples thereof). The Stern layer width and specific adsorption of ions will have a significant effect on the electric field in the double larger. Setting up the model so that they can be accounted for may lead to changes in the predicted behaviour, leading to an improvement in the agreement of the model with experimental data in the systems for which it was found that the excluded volume and polarisability interactions alone were insufficient.

8.2.3 Model applications and adaptations

As presented in this work, the model developed represents an idealised interface rather than a particular real-world system, but given the structure of the model and the way in which the code is constructed, it would be possible to adapt the model to several such systems, albeit with some modifications. In this final section, an outline for some of these systems is discussed.

Electrochemical analysis

The use of cyclic voltammetry and electrochemical impedance spectroscopy (EIS) was discussed in Chapters 6 and 7, along with a description of the use of EC’s to analyse the data in the latter case. In both cases, the size and polarisabilities of the ions in the supporting electrolyte were shown to have an impact on the rate of the reaction, suggesting that the choice and quantity of supporting electrolyte can have some effect on the results obtained, something which may be possible to validate experimentally.

Additionally, since the model does not require the presence of a supporting electrolyte, it could prove useful for analysing EIS data for systems containing only a single electrolyte. By removing one of the species in the experimental system, its complexity is reduced as regards the various interactions in the system, possibly facilitating a better understanding of the processes
occurring within it through the use of modelling.

**Supercapacitors/pseudocapacitors**

Compared to a standard dielectric capacitor, these electrochemical devices contain an electrolyte sandwiched between two electrodes. The application of a potential difference across the electrodes causes the formation of a double layer at each electrode and, in the case of a pseudocapacitor, results in electrochemical reactions taking place at one or both surfaces. Because of the formation of the double layer, and the larger electric field which this enables, they are able to store much more energy than a standard capacitor, and are widely used in the electronics industry for a range of purposes.

In the simplest form, a supercapacitor or a pseudocapacitor can be represented by two parallel planar electrodes separated by an electrolyte, so the system is closed and the amount of electrolyte is finite. The changes to the model to account for this are simply a change to the boundary condition to the Nernst-Planck equation at $x = L$. Rather than having a fixed ion concentration, the boundary condition mirrors that at $x = 0$, i.e. the surface flux is defined. In a supercapacitor, this flux is zero, while in a pseudocapacitor charge transfer reactions can take place at the surface and the flux is non-zero. Aside from changing the boundary conditions, the grid spacing would also need to be redefined to account for the fact that steep concentration and potential gradients may occur at both boundaries.

Modelling may be useful for these devices to understand the amount of energy which can be stored as well as the charge/discharge behaviour. As seen throughout this work, these properties are affected by both the excluded volume interaction and the ion polarisability, particularly at larger potentials. In comparison to techniques such as DDFT or other dynamic statistical mechanical methods, the mean-field, local density approximation used here represents the simplest means to describe the dynamics of the system. While other methods may be more accurate, they are often also more limited, for example in only being valid at small surface charge densities. As discussed in Chapter 2, there also remain the problems of determining time-dependent correlation effects in those models, together with the requirement for increased computer power or longer simulation times, if this is a problem. Although not necessarily an inherent problem, this last point makes the type of model presented here useful as a relatively quick first approximation, possibly to guide further experiment or more detailed modelling.

One of the problems with using the model in its current form is that the porosity of the electrodes in supercapacitors plays a large role in determining the behaviour of the system. The high porosity is responsible for the increased surface area, but it also changes the transport behaviour of the ions, since this depends on the structure. Biesheuvel and Bazant (2010) and Biesheuvel et al. (2011) have previously studied porous electrodes using a model with a similar basis to that presented here, but without accounting for the ion volume or polarisability. It may be of interest to investigate how their conclusions are altered when the ion volume and polarisability are accounted for, although this would require some alterations to be made to the equations and thus to the program which runs the model.
Fuel cells

A fuel cell consists of an ion-permeable membrane sandwiched between two electrodes which are themselves sandwiched between two gas diffusion layers, as depicted in Fig. 8.1, which shows the basic structure of a polymer electrolyte membrane fuel cell (PEMFC). An electrolyte is present between the two electrodes, mediating ion transport between them across the membrane. Fuel, typically hydrogen, is provided to the anode, where it reacts electrochemically to release electrons to the electrode, leaving ions in the electrolyte. The membrane is permeable to the resulting ions so they are able to move to the opposite electrode, while the electrons, to which the membrane is impermeable, are pushed in to an external circuit where they can do useful work before returning to the opposite electrode. Once at that electrode, a second reaction uses the electrons to split oxygen molecules into two ions, which then combine with the hydrogen ions to form water, the waste product, which is expelled through the cathode gas diffusion layer.

As with supercapacitors, a simple model for the electrode-membrane part of the system could be formed from two planar electrodes bounding the membrane, which could be extended in the same way to model porous electrodes. Modelling the PEMFC membrane represents a challenge, since its permeability to the ions depends on its hydration (Weber and Newman 2003), but in a simple approximation it may be possible to set a particular level of hydration and thereby assume a diffusion coefficient. The ionic excluded volume and excess polarisability may play some role in the operation of a fuel cell through changes to the reaction rate, but also because of the limited available volume in the membrane and because the high polarisability of the hydrogen ion means a large reduction in the permittivity of the solvent.

More significant changes to the model would be required to include the gas diffusion layers, in which transport of water and fuel/exhaust occurs. The structure of the program is such that a suitable model could be incorporated relatively easily, either as a boundary condition or, if needs be, using part of the discretised domain to solve the equations which arise.

While the membrane requires water to function, too much of it can flood the gas diffusion
layers, preventing fuel/exhaust from entering/exiting the electrodes (Larminie and Dicks 2000). Water is produced at the cathode, so there is a concentration gradient across the membrane leading to a back-diffusion of water contrary to the direction of ion transport. At the same time, the motion of the ions causes electro-osmotic drag on the water molecules, offsetting some of this back-diffusion. The model as it stands cannot consistently account for either of these effects because the solvent is not directly described by the model. However, recent work by Dreyer et al. (2013) has provided the means to explicitly include the solvent in the Nernst-Planck equations, possibly providing a route to being able to describe these two properties. Doing this would require changes to the equations defined in the code, so represents a not insignificant amount of work. However, the aforementioned work uses the electrochemical potentials of the species in the system to determine the fluxes, so the excluded volume and polarisability could be included relatively easily. Furthermore, the model provides a value for the density of water throughout the system, so it may also provide a means for accounting for the electric-field dependence of the solvent permittivity, for which the number density of the water is required.

**Biology and ion Channels**

As noted in Chapter 1, biological cell membranes are formed from lipids, amphiphilic molecules with a hydrophobic tail and a polar head. The molecules self-assemble in to two parallel layers with the hydrophobic tails pointing in to the middle of the bilayer structure and the polar head group pointing outwards, as shown in Fig. 8.2.

![Lipid representation](a) Polar head group

![Bilayer structure](b) Hydrophobic tail

Figure 8.2: The arrangement of lipids in a cell membrane

The intra- and extra-cellular environment contains dissolved ions, such as potassium, sodium and calcium, which are essential to the function of an organism at the cellular level. An example of this is in the transmission of nerve impulses, which results from the movement of sodium and potassium ions across the membrane of a nerve cell. Ion selective channels across the membrane permit sodium ions to enter the cell and potassium cells to leave it, while a pump transfers sodium out of the cell and potassium in to it. At rest the channels are closed and there is a potential difference across the cell membrane (the interior is more negative) due to the difference in ion concentrations across the membrane, resulting from the action of the pump (Bezanilla 2011). As a result of this potential difference, the ions on either side of the
membrane will form a double layer, the structure of which determines the surface concentrations
of each species.

The transmission of a nerve impulse occurs through a number of stages. First, the sodium
channels are opened and sodium ions enter the cell under the influence of both a concentration
and potential gradient increasing the positive charge inside the cell and causing the potential
difference to become positive. Next, the sodium channels close and the potassium channels
open, allowing the potassium ions to exit the cell and the causing the potential to drop again
and become negative. Finally, the potassium channels close and the pump returns the potassium
ions to the cell interior and the sodium ions to the exterior. The full process generates a variation
in the cell potential, known as the action potential (Keynes et al. 2010).

The model presented in this work evidently cannot describe the full system, which is three-
dimensional, but may be able to provide some information about the environment and the select-
ivity of the ion channels. The membrane-electrolyte interface on either side of the lipid bilayer
is similar to the electrode/electrolyte interface presented in this work, so it may be possible to
use the model to determine the ion surface concentrations and from this make inferences as
to the concentration gradients across the ion channels and thus the driving forces which arise
when the channels open. The other result which may be of some significance can be inferred
from the way that ions with a higher polarisability are excluded from a highly charged surface
when in competition with ions of a lower polarisability. In the same way as the size of the ions
can be shown to determine the selectivity of ion channels because the double layer which forms
inside the channel excludes larger ions, a similar effect could be attributed to ions of different
polarisabilities. For the nerve cell example provided above, this is not directly applicable since
the sodium and potassium ions have the same polarisability (see Table 2.1), but it will make a
contribution to the selectivity between, for example, these two ions and the calcium ion which,
similar to the Mg^{2+} ion in Table 2.1, is likely to have a much larger polarisability since it is
divalent.
References


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