

Mathematical Modelling of Electric Double Layers in Electrolytes for Lithium-Ion Batteries

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Abstract

In this thesis we explore electric double layers (EDLs) in electrolytes for lithium-ion batteries using mathematical modelling tools. We review three standard continuum modelling approaches applied to model electrolytes: dilute theory, moderately concentrated theory, and thermodynamically consistent theory. We implement the thermodynamically consistent formulation to model a solid electrolyte whereby we investigate the structure of the EDLs both from numerical and asymptotic perspectives. We introduce an auxiliary variable to remove singularities from the domain, allowing for standard numerical methods and robust numerical simulations. In our non-dimensionalisation of the model we uncover a length scale representing the true width of these double charge layers. This informs an asymptotic reduction of the model whereby we reveal that the EDL is composed of two distinct regions: a boundary layer and an intermediate layer. The boundary layer exhibits polynomial behaviour while the intermediate layer exhibits exponential behaviour. We refer to the boundary layer as the strong space charge layer, and the intermediate layer as the weak space charge layer. Asymptotic matching between these two layers is non-standard, therefore we introduce a pseudo matching technique to complete the asymptotic solutions. We observe excellent agreement between our numerical simulations and asymptotics.

Motivated by these results we apply the thermodynamic formulation to a liquid electrolyte to investigate the differences between the two electrolytes; noting that throughout the literature it is posited that these double charge layers in solid electrolytes are wider than those of the liquid, and that the liquid exhibits exponential behaviour in these layers, without any reference to a polynomial region. Through our numerics we confirm that the layers are wider in the solid, however, via our asymptotics we determine that the structure of these layers in the liquid also displays both polynomial and exponential behaviour. We introduce a parameter into the model to reconcile this thermodynamic model with the standard Poisson-Nernst-Planck (PNP) model, which is widely associated to the observation of exponential behaviour in the double layers. We find that the PNP model becomes ill-posed under the prescribed boundary conditions and suggest ways to rectify that.

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Contents

Abstract	ii
Acknowledgements	iii
Table of Contents	iv
List of Tables	viii
List of Figures	ix
1 Introduction: Lithium-ion batteries and mathematical modelling	1
1.1 Overview	1
1.2 Lithium-ion batteries	2
1.2.1 Electrodes	4
1.2.2 Electrolytes	5
1.2.3 Electric double layers	6
1.3 Mathematical modelling	8
1.3.1 Modelling approaches and formulations	9
1.3.2 Modelling techniques at the macroscale level	10
1.3.3 Overview of modelling batteries at the macroscale level	11
1.3.4 Remarks	13
1.4 Thesis Summary and Novelty	13
2 Electrolyte modelling	16

2.1	History of continuum electrolyte modelling	16
2.2	Continuum modelling formulation	18
2.2.1	Modelling notation and conventions	19
2.2.2	Binary electrolyte	20
2.2.3	Dilute electrolyte	21
2.2.4	Concentrated electrolyte	28
2.2.5	Thermodynamic approach	44
2.3	Summary of models	57
2.4	Discussion	57
3	Solid electrolyte model	60
3.1	Problem motivation	60
3.2	Mathematical model	63
3.2.1	Model assumptions	63
3.2.2	Model equations	63
3.2.3	Non-dimensionalisation	73
3.2.4	Model simplifications and supplementations	76
3.2.5	Auxiliary variable	78
3.3	Numerical solution	78
3.3.1	Numerical details	78
3.3.2	Numerical results	79
3.4	Asymptotic reduction	81
3.4.1	Bulk	82
3.4.2	Boundary layers	84
3.4.3	Intermediate layers	87
3.4.4	Matching	89
3.4.5	SCL Summary	93
3.5	Comparison of asymptotics and numerics	94
3.5.1	Additional examples of asymptotic results	97
3.6	Integral approach	98
3.6.1	Analytical solution	102

3.6.2	Integral asymptotics	103
3.6.3	Comparisons	109
3.7	Discussion	109
4	Liquid electrolyte model	111
4.1	Problem Motivation	111
4.2	Mathematical model	112
4.2.1	Model equations	112
4.2.2	Non-dimensionalisation	115
4.2.3	Model simplifications and supplementations	117
4.2.4	Auxiliary variable	120
4.3	Numerical solution	121
4.3.1	Numerical details	121
4.3.2	Numerical results	122
4.4	Asymptotic reduction	125
4.4.1	Bulk	128
4.4.2	Boundary layers	130
4.4.3	Intermediate layers	136
4.4.4	Matching	140
4.4.5	Comparison of asymptotics and numerics	142
4.4.6	Observations	144
4.5	Reconciliation to PNP model	146
4.5.1	Asymptotic solution	147
4.5.2	Remarks	149
4.5.3	Comparisons	150
4.6	Discussion	151
5	Conclusions and future work	154
5.1	Conclusions	154
5.2	Future work	156
5.2.1	Capacitance	156

5.2.2	Knee regions	157
5.2.3	Full dynamic model formulation	157
5.2.4	PNP well-posedness	158
5.2.5	Non-uniform grid	159
5.2.6	Nanowire electrodes	160
A	Asymptotic matching	162
A.1	Boundary layer	163
A.2	Intermediate layer	164
A.3	Matching	165
	Bibliography	168

List of Tables

2.1	Final equations for dilute, concentrated, and thermodynamically consistent approaches to electrolyte modelling.	58
3.1	Summary of the solution obtained in each region of the solid electrolyte.	93

List of Figures

1.1	Diagram depicting the structure and operation of a battery cell.	4
1.2	Simple schematic of electric double layers in an electrolyte with an electrode on either end. .	6
3.1	Sketch of a solid electrolyte with lithium-metal blocks on either end. A fixed potential ΔV is applied across the electrolyte with Dirichlet boundary conditions prescribed for the electric potential and cation flux at the electrolyte-lithium interface.	74
3.2	Numerical results for the 1D steady-state problem (3.87) with (3.88) subject to $\phi(0) = 1$ and $\phi(1) = 0$ with parameter values: $z_c = 1$, $z_a = -1$, $m_c = 0.3$, $m_a = 0.7$, $n_a = 0.4$, $\nu = 0.6$ where $n = n_a + \nu = 1$, $m = m_a + m_c = 1$. We take $\lambda = 1.5 \times 10^{-3}$, $\delta^{-1} = 170$, and $\Delta V = 4V$. We show our solution and the solution obtained by Braun et al. (2015) for comparison, with ϕ shown dimensionally (in volts) as per convention. The shaded areas corresponds to the tail regions and the non-shaded area indicates the constant region. In the inset plot of Figure 3.2a we zoom in on the left tail region to highlight the difference between the two solutions. Similarly, in the inset of Figure 3.2b we zoom in on the constant region of the solution to highlight discrepancies between the solutions.	80
3.3	Profile of the electric potential as shown in Figure 3.2b with the addition of the light blue line which represents the $\mathcal{O}(1)$ component of the solution for ϕ [V].	83
3.4	Sketch of boundary layer structure.	88

3.5	Asymptotic solution from Section 3.4 versus numerical solution from Section 3.3 for both the lithium-ion concentration and electric potential [V]. Parameter values are as follows: $z_c = 1$, $z_a = -1$, $m_c = 0.3$, $m_a = 0.7$, $n_a = 0.4$, $\nu = 0.6$, with $\frac{\beta_1}{\beta_2} = 2 < \beta^*$, $\frac{\beta_2}{\beta_1} = \frac{1}{2} < \beta^*$. We also have $\lambda = 1.5 \times 10^{-3}$, $\delta^{-1} = 170$, and $\Delta V = 4V$. BL, BR refer to the left and right boundary-layer solutions, respectively; similarly IL, IR refer to the left and right intermediate layer solutions, respectively. z_L, z_R refer to the leading-order transition points from the boundary to the intermediate layers.	95
3.6	We zoom in on the boundary and intermediary regions of Figure 3.5a near $z = 0$, to highlight the agreement of the asymptotic and numerical solution approaches for steady-state profile for n_c	96
3.7	Solution profile of the number density of the lithium ions for both the asymptotics and the numerics shown for different applied voltages versus z in Figure 3.7a and different λ versus $\log(z)$ in Figure 3.7b.	97
3.8	Asymptotic versus numerical solution for n_c in the scenario where $F_L > 0, F_R < 0$: $z_a = -1, n_a = 0.45, \beta_1 = 0.45, \beta_2 = 0.1$. We also have $\lambda = 1.5 \times 10^{-3}$, $\delta^{-1} = 170$, and $\Delta V = 4V$. We include insets to show a close-up of the agreement at the two boundaries. BL, BR refer to the left and right boundary-layer solutions, respectively; similarly IL, IR refer to the left and right intermediate layer solutions, respectively. z_L, z_R refer to the leading-order transition points from the boundary to the intermediate layers.	99
3.9	Asymptotic versus numerical solution for n_c in the scenario where $F_L > 0, F_R < 0$: $z_a = -2, n_a = 0.3, \beta_1 = 0.6, \beta_2 = 0.1$. We also have $\lambda = 1.5 \times 10^{-3}$, $\delta^{-1} = 170$, and $\Delta V = 4V$. We include insets to show a close-up of the agreement at the two boundaries. BL, BR refer to the left and right boundary-layer solutions, respectively; similarly IL, IR refer to the left and right intermediate layer solutions, respectively. z_L, z_R refer to the leading-order transition points from the boundary to the intermediate layers.	100

3.10	Asymptotic versus numerical solution for n_c in the scenario where $F_R > 0, F_L < 0$. We take $z_a = -1, z_c = 1, \beta_1 = 0.2, \beta_2 = 0.6$. We also have $\lambda = 1.5 \times 10^{-3}, \delta^{-1} = 170$, and $\Delta V = 4V$. We include insets to show a close-up of the agreement at the two boundaries. BL, BR refer to the left and right boundary-layer solutions, respectively; similarly IL, IR refer to the left and right intermediate layer solutions, respectively. z_L, z_R refer to the leading-order transition points from the boundary to the intermediate layers.	101
3.11	Analytical versus numerical solutions for θ , the lithium concentration n_c , and electric potential ϕ [V]. Parameter values are as follows: $z_c = 1, z_a = -1, m_c = 0.3, m_a = 0.7, n_a = 0.4, \nu = 0.6$, with $\frac{\beta_1}{\beta_2} = 2 < \beta^*, \frac{\beta_2}{\beta_1} = \frac{1}{2} < \beta^*$. We also have $\lambda = 1.5 \times 10^{-3}, \delta = 170$, and $\Delta V = 4V$	103
3.12	Integral Asymptotic versus numerical solutions for lithium concentration and electric potential [V]. Parameter values are as follows: $z_c = 1, z_a = -1, m_c = 0.3, m_a = 0.7, n_a = 0.4, \nu = 0.6$, with $\frac{\beta_1}{\beta_2} = 2 < \beta^*, \frac{\beta_2}{\beta_1} = \frac{1}{2} < \beta^*$. We also have $\lambda = 1.5 \times 10^{-3}, \delta^{-1} = 170$, and $\Delta V = 4V$. BL, BR refer to the left and right boundary-layer solutions, respectively; similarly IL, IR refer to the left and right intermediate layer solutions, respectively. z_L, z_R refer to the leading-order transition points from the boundary to the intermediate layers. . .	108
3.13	ODE versus integral asymptotic versus numerical solutions for lithium concentration and electric potential [V]. Parameter values are as follows: $z_c = 1, z_a = -1, m_c = 0.3, m_a = 0.7, n_a = 0.4, \nu = 0.6$, with $\frac{\beta_1}{\beta_2} = 2 < \beta^*, \frac{\beta_2}{\beta_1} = \frac{1}{2} < \beta^*, \lambda = 1.5 \times 10^{-3}, \delta^{-1} = 170$, and $\Delta V = 4V$	109
4.1	Numerical results for the 1D steady-state problem (4.38) subject to (4.39) with parameter values: $z_c = 1, z_a = -2, \bar{y}_c = 0.24$. We take $\lambda = 5 \times 10^{-3}, \delta = 0.038$, and $\Delta V = 0.62V$. We have plotted the concentration of each species (n_c, n_a, n_s) and the profile for the electric potential, with ϕ shown dimensionally (in volts) as per convention.	123
4.2	Numerical results for the 1D steady-state problem (4.38) subject to (4.46) with parameter values: $z_c = 1, z_a = -2, \bar{y}_c = 0.24$. We take $\lambda = 5 \times 10^{-3}, \delta = 0.038$, and $\Delta V = 0.62V$. We show the solution profiles for the two auxiliary variables in the liquid problem, θ_c and θ_a . We also include inset plots for both figures whereby we zoom in on the boundaries near $z = 0$ and $z = 1$ to further highlight the solution profile in these regions.	124

4.3	Numerical results for the 1D steady-state problem (4.38) subject to (4.46) with parameter values: $z_c = 1$, $z_a = -1$, $\bar{y}_c = 0.4$, $\bar{y}_a = 0.4$, $\lambda = 1.5 \times 10^{-3}$, and $\Delta V = 4V$ to compare with the results presented in Figure 3.2 for the solid electrolyte. We include inset plots to more clearly display the variation in the two electrolyte models at the boundaries.	126
4.4	Asymptotic solution from Section 4.4 versus the numerical results from Section 4.3 for θ_c and θ_a . Parameter values are as follows: $z_c = 1$, $z_a = -2$, $\bar{y}_c = 0.24$. We take $\lambda = 5 \times 10^{-3}$, $\delta = 0.038$, and $\Delta V = 0.62V$. BL, BR refer to the left and right boundary layer solutions, respectively; similarly IL, IR refer to the left and right intermediate layer solutions, respectively. z_L, z_R refer to the leading-order transition points from the boundary to the intermediate layers.	144
4.5	Asymptotic solution from Section 4.4 versus the numerical results from Section 4.3 for n_c and n_a . Parameter values are as follows: $z_c = 1$, $z_a = -2$, $\bar{y}_c = 0.24$. We take $\lambda = 5 \times 10^{-3}$, $\delta = 0.038$, and $\Delta V = 0.62V$. BL, BR refer to the left and right boundary layer solutions, respectively; similarly IL, IR refer to the left and right intermediate layer solutions, respectively. z_L, z_R refer to the leading-order transition points from the boundary to the intermediate layers.	145
4.6	Asymptotic solution from Section 4.4 versus the numerical results from Section 4.3 for ϕ . Parameter values are as follows: $z_c = 1$, $z_a = -2$, $\bar{y}_c = 0.24$. We take $\lambda = 5 \times 10^{-3}$, $\delta = 0.038$, and $\Delta V = 0.62V$. BL, BR refer to the left and right boundary layer solutions, respectively; similarly IL, IR refer to the left and right intermediate layer solutions, respectively. z_L, z_R refer to the leading-order transition points from the boundary to the intermediate layers.	146
4.7	Asymptotic and numerical solutions for θ_c for varying values of α , $\alpha = 1, 0.75, 0.5, 0.25$. The arrows indicate the direction of the solution profiles for decreasing α . Parameter values are as follows: $z_c = 1$, $z_a = -2$, $\bar{y}_c = 0.24$. We take $\lambda = 5 \times 10^{-3}$, $\delta = 0.038$, and $\Delta V = 0.62V$	151
4.8	Asymptotic and numerical solutions for n_c for varying values of α , $\alpha = 1, 0.75, 0.5, 0.25$. The arrows indicate the direction of the solution profiles for decreasing α . Parameter values are as follows: $z_c = 1$, $z_a = -2$, $\bar{y}_c = 0.24$. We take $\lambda = 5 \times 10^{-3}$, $\delta = 0.038$, and $\Delta V = 0.62V$	152

4.9	Asymptotic and numerical solutions for ϕ (non-dimensional) for varying values of α , $\alpha = 1, 0.75, 0.5, 0.25$. The arrows indicate the direction of the solution profiles for decreasing α . Parameter values are as follows: $z_c = 1$, $z_a = -2$, $\bar{y}_c = 0.24$. We take $\lambda = 5 \times 10^{-3}$, $\delta = 0.038$, and $\Delta V = 0.62V$	153
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Chapter 1

Introduction: Lithium-ion batteries and mathematical modelling

1.1 Overview

Increasing global energy demands coupled with the ongoing climate change crisis is driving pressure for alternative, more sustainable energy sources over the widely used fossil fuels. In addition to energy sources, we require a means of storing energy generated by renewable energy sources; robust storage can assist with latency and intermittency issues associated to clean energy such as solar, wind, and hydro. We also need a means of powering our portable devices. Rechargeable batteries, and in particular, lithium-ion batteries (LIBs) have become the dominant energy storage technology for many of these purposes. The widespread adoption of LIBs is attributed to their high energy densities, long cycle life, and low self-discharge rates (Nishi (2001); Tarascon and Armand (2001)), which has driven extensive research across multiple disciplines and scientific domains, both experimental (Kennedy et al. (2014, 2017); Stokes et al. (2017)) and theoretical (Tasaki et al. (2003); Huang et al. (2020); Howey et al. (2020)), to continue to optimise and enhance the performance of LIBs.

LIBs are manufactured in a variety of different forms with examples including pouch cells (Cannarella and Arnold (2014); Harris et al. (2017); Günter and Wassiliadis (2022)), prismatic cells (Hatchard et al. (2001);

Cousseau et al. (2006); Inui et al. (2007)), cylindrical cells (Zhang (2011); Avdeev and Gilaki (2014); Baazouzi et al. (2023)), and coin cells (Marks et al. (2010); Kayyar et al. (2012); Chen et al. (2019)). Directing attention to the internal architecture of the battery components there is also a broad range of structure of electrodes, such as porous (Ogihara et al. (2012); Vu et al. (2012); Chen et al. (2022)), thin film (Bates et al. (2000); Sun et al. (2008); Zhou et al. (2013)), 3D structure (Ye et al. (2015); Li et al. (2017); Zhang and Ran (2021)), and nanowire (Mai et al. (2014); Kennedy et al. (2014, 2016)). The electrolyte can also take a variety of different forms such as liquid (Li et al. (1994); Xu (2004); Eftekhari (2018)), solid (Liu et al. (2011); Shen et al. (2018); Dixit et al. (2022)) and gel polymer (Stephan (2006); Liang et al. (2018); Du et al. (2019)). These attributes of versatility and flexibility in design also mean that LIBs can be scaled up or down for different applications, all of these factors contributing to why LIBs are widely used in many of the devices we use everyday, such as mobile phones and laptops, with other applications such as military and aerospace devices (Marsh et al. (2001); Ratnakumar et al. (2003); Puglia et al. (2006)) and electric vehicles (Kennedy et al. (2000); Chen et al. (2012)). Despite these many merits, there are outstanding issues to address before we can move toward a battery-powered society. The main limitations of LIB are related to the need for faster charging, thermal management, and preventing performance degradation (Goodenough and Kim (2010)). Remediating these challenges requires further research from many areas such as materials chemistry, cell design, and battery management systems.

1.2 Lithium-ion batteries

A typical LIB is made up of a cascade of individual battery cells; each battery cell is composed of the following primary components: a positive electrode, a negative electrode, and an electrolyte. The electrode is a material in which electrons are the mobile species and therefore the electrodes can be used to control the potential, defined as the electric potential energy per unit charge, of electrons. As such, the electrodes are electronic conductors. The electrolyte is a material where the mobile species are ions and free movement of electrons is blocked, therefore it is an ionic conductor and an electrical insulator. The two electrodes are separated by the electrolyte and are otherwise connected via an external electronic conductor (Newman and Thomas-Alyea (2012)). There can often be another component placed between the two electrodes, known aptly as the separator. The separator is typically a permeable membrane filled with electrolyte and is placed between the two electrodes to prevent short-circuiting, since it can conduct ions but not electrons (Flaim

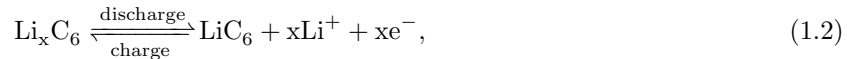
et al. (2004)).

When the battery discharges, the positive electrode receives lithium, while lithium leaves the negative electrode. This means that when the lithium atom leaves the negative electrode and as it enters the electrolyte it undergoes a chemical reaction at the electrode-electrolyte interface, being converted to a lithium ion and an electron. The lithium ions travel through the electrolyte and the electrons are released into the external circuit. The positive electrode then accepts the lithium ion from the electrolyte and the electron from the circuit, which undergo another chemical reaction to convert back to a lithium atom to complete the circuit. As the circuit is completed, the cell will discharge, *i.e.* the chemical energy from the movement (kinetic energy) of the species is converted to electrical energy to power the device. We note that in LIBs specifically, these processes can be referred to as intercalation, where lithium is absorbed from the electrolyte and inserted into the structure of the electrode, and deintercalation, where the lithium is expelled from the electrode material into the electrolyte. This reaction is reversible in LIBs. For the reverse reaction, a current must be applied to the cell, inducing an electrochemical potential greater than the cells own potential. This is because the electrochemical potential in the positive electrode is such that the chemical process is inclined to accept electrons and ions, while the reverse is true in the negative electrode.

For example, a common LIB chemistry involves the following half cell reactions occurring in the two electrodes (Doyle et al. (1996); Srinivasan and Wang (2002)):



and



where the subscript x corresponds to the amount of lithium that moves during charge/discharge, and subscript y is the maximum lithium content in the positive electrode (usually $y = 1$). This particular LIB cell consists of a manganese oxide positive electrode and a carbon negative electrode. We include an image in Figure 1.1 to depict this structure and operation of a typical LIB. For the purpose of the work undertaken in this thesis, the key component of the reaction is:



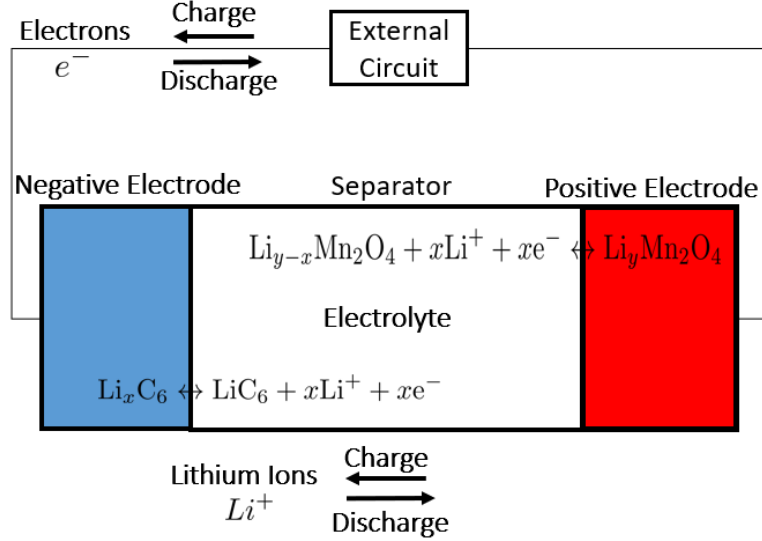


Figure 1.1: Diagram depicting the structure and operation of a battery cell.

1.2.1 Electrodes

To facilitate this movement of lithium to and from the electrode materials, the electrodes typically have crystal structures with paths through which lithium can move through freely. The chemical structure of the electrode material is not changed during the processes of intercalation and deintercalation; the materials used in electrodes are such that the electron in the outer shell of the lithium is loosely shared with the neighbouring electrode material atoms, which enables lithium to move throughout the electrode structure (Plett (2015)). As the focus of this thesis is concerned with the electrolyte component of LIBs, we do not discuss the electrodes in detail, but we acknowledge that there is a plethora of research surrounding the choice of materials used for each of the electrodes. There are a number of commercially viable material options for the positive electrode, the choice of which often depends on the application of the battery. Some common examples include cobalt (LCO; Mizushima et al. (1980)), manganese (LMO; Thackeray et al. (1983)), and iron phosphate (LFP; Padhi et al. (1997)). We remark that graphite is the ubiquitous choice for the negative electrode due to its stability and excellent lithium-ion intercalation properties (Xu et al. (2017); Li et al. (2019)), however, research is ongoing to address the limitations of graphite electrodes (Aurbach et al. (2002); Xu et al. (2022)). Silicon and germanium are two prospective candidates for negative electrode materials

(Casimir et al. (2016); Kennedy et al. (2016); Liu et al. (2020)), with a particular avenue of research related to the use of silicon or germanium nanowires having emerged as a major topic of interest ((Liu et al. (2011); Kennedy et al. (2014, 2016, 2017))), which we revisit briefly in our future work discussion in Chapter 5.

1.2.2 Electrolytes

The electrolyte is a crucial element of any electrochemical system. Many electrolytes are composed of a charge-neutral solute and a charge-neutral solvent, whereby the solute can dissociate into positively charged ions (cations), which are lithium ions in a lithium-ion battery, and negatively charged ions (anions). These terminologies (positive/cation/lithium, negative/anion) for the ions will be used interchangeably in this work¹. The electrolyte can conduct ions but not electrons (making it an electrically neutral substance), and thus facilitates the flow of ions between the two electrodes of the battery. Therefore, the electrolyte enables the electrochemical reactions that occur during battery charge and discharge, and hence, it is a key component contributing to battery operation and performance.

Many electrolytes use a liquid solvent as the main transport medium, and consequently, liquid electrolytes have been thoroughly studied and thus have established technology. The vast body of research concerning liquid electrolytes means that their performance and reliability are well understood, their use has been tested in a range of scenarios and so there exists a wide range of materials that are compatible with liquid electrolytes for use in the electrodes, and the manufacturing processes have been refined extensively. However, other types of electrolytes such as solid (Liu et al. (2011); Shen et al. (2018); Dixit et al. (2022)) and gel polymer (Stephan (2006); Liang et al. (2018); Du et al. (2019)) are used as well. Each category of electrolyte type can be further broken down into subcategories. For example, liquid electrolytes can be aqueous (Li et al. (1994); Wang et al. (1998); Eftekhari (2018)), non-aqueous (Xu (2004); Wang et al. (2018); Ouyang et al. (2024)), ionic liquid, or molten salt (Nakagawa et al. (2003); Galiński et al. (2006); Brutti et al. (2020)). In the case of a solid electrolyte, there are all-solid-state such as inorganic solid electrolytes which can be further

¹This terminology originated when batteries were just used to discharge; the negative electrode was referred to as the anode and the positive electrode was referred to as the cathode, because Faraday defined the anode to be the electrode where current enters, while the cathode is the electrode where current leaves (Faraday (1834); James (1991)). It then followed that the ions be referred to as anions and cations for the electrode to which they go to. For rechargeable batteries, the negative electrode is the anode when the cell discharges and theoretically it is the cathode when the cell is charging (Plett (2015)). To avoid confusion we do not use the anode/cathode terminology, but will use the anion/cation terminology as this not changed by the direction of current.

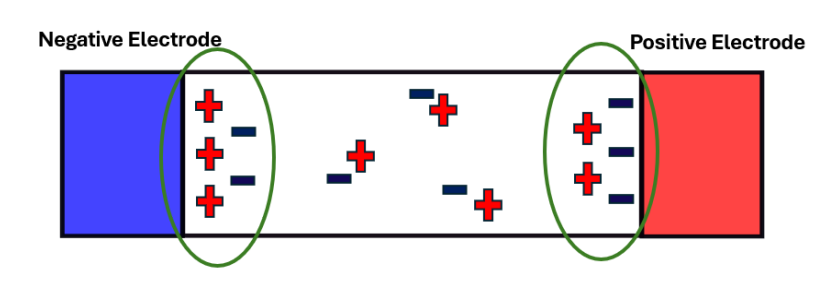


Figure 1.2: Simple schematic of electric double layers in an electrolyte with an electrode on either end.

categorised (Manthiram et al. (2017); Zheng et al. (2018); Famprikis et al. (2019)) and quasi-solid-state such as the gel polymer electrolytes (Song et al. (1999); Stephan (2006); Zhu et al. (2019)).

Each type of electrolyte has associated advantages and disadvantages, and each can impact many features of the battery such as safety, lifespan, and energy density. Due to the integral role the electrolyte plays in these systems, there is a plethora of research ongoing to optimise the choice of electrolyte. Stemming from this research, solid electrolytes (SEs) have emerged as a candidate warranting further exploration due to their improved safety, lower self-discharge, and higher power densities over their liquid counterparts (see Takada (2013); Manthiram et al. (2017); Zhao et al. (2019) and references therein).

1.2.3 Electric double layers

We have noted that the electrolyte is electrically neutral, so that the positive and negative charges balance each other. While this is true as a whole across the electrolyte, there are narrow regions where we have deviations from electroneutrality. These narrow regions are referred to as Electric Double Layers (EDLs), or electrostatic double charging layers, as they are composed of two thin parallel layers of charge. These layers form in the electrolyte at the electrode-electrolyte interface due to co- and countercharges being repelled and attracted at this interface (Newman and Thomas-Alyea (2012)). In liquid electrolytes these layers are commonly known as Debye layers, while in the case of solid state batteries they are more commonly referred to as space charge layers (SCLs). We include a simple depiction of these layers in Figure 1.2.

The two layers themselves are referred to as the Stern layer and the diffuse layer. The Stern layer occurs due to counterions being attracted to the charged surface of the electrode and thus adhering to the electrode

surface. As opposite charges attract, this Stern layer then attracts the oppositely charged ions to this surface charge layer, creating the diffuse layer. While the ions in the Stern layer are attached to the interface, the ions in the diffuse layer are free to move according to their electrical attraction. And so, as we move further away from the interface we can think of the diffuse layer as smoothly facilitating a transition from the Stern layer to the electroneutral bulk of the electrolyte.

From a modelling perspective, simplifications are frequently made to account for these layers due to their complexity, for example, models of full electrochemical systems will often assume charge neutrality thus neglecting the EDL. In general, because this is a very thin layer, charge neutrality can be assumed to hold in the bulk, while boundary conditions can be used to describe what is happening in these thin double layers. Here we provide a brief overview of the primary methods used to model the EDL in the electrolyte. We emphasise that these are approaches that are used to capture the effects of the EDL within a model structure, rather than an explicit model of the double charge layer dynamics themselves.

In general, the effects of the EDL are accounted for via differences in potential,

$$\phi_s - \phi_e = \Delta\phi_D + \Delta\phi_S, \quad (1.4)$$

which says that the difference in the potential between the electrode surface, ϕ_s , and the electrolyte solution, ϕ_e , is equal to the sum of the potential drops across the Stern and diffuse layers, where $\Delta\phi_S, \Delta\phi_D$ are the potential drops across the Stern and diffuse layer, respectively.

Helmholtz was one of the first to recognise and thus investigate this phenomena of double charge layers, formulating the Helmholtz model (Helmholtz (1853)), which assumes that the Stern layer is thicker than the diffuse layer. The Helmholtz model effectively sets $\Delta\phi_D = 0$ in (1.4) (Moyles et al. (2019)), as it ignores the diffuse layer by assuming that counter-ions form a compact, immobile layer adjacent to the electrode surface, neglecting any diffusive effects. The Helmholtz model predicted that the capacitance, defined as the ability of an object to store charge, was constant.

Following from the pioneering work of Helmholtz, Gouy (1910) and Chapman (1913) observed that the capacitance was not constant, culminating in the Gouy-Chapman model, which is considered a diffuse model of the EDL. This model assumes that the distribution of the ions near the interface follows the Boltzmann distribution (Boltzmann (1868)), which is related to the Debye-Huckel theory (Debye (1923); Newman and Thomas-Alyea (2012)) and indicates an exponential distribution of the ions near the interface.

The Stern model (Stern (1924)) effectively combines the Helmholtz and Gouy-Chapman models; the inner layer is described by the Helmholtz model akin to the Stern layer and the Gouy-Chapman model describes the diffuse part of the EDL. This then led to the classical terminology whereby inner and outer Helmholtz planes refer to the adsorbed ions and the diffuse layer can often be referred to as the Gouy-Chapman layer (Lück and Latz (2018); Newman and Thomas-Alyea (2012)). Other authors have since proposed modifications to these models, some examples include the work of Frumkin (1933); Bikerman (1942); Grahame (1947), and Bockris et al. (1965).

We note that there is increasing interest in trying to understand the dynamics occurring in these layers and the implications of the layers from a deeper perspective. The electric double layer is at the electrode-electrolyte interface and therefore the dynamics occurring in this layer can influence the kinetics and thermodynamics of reactions, making it a key component of the electrochemical interface (Swift et al. (2021)). Magnussen and Groß (2019) highlight the need for both experimental and theoretical development of our understanding of double layers, which is echoed by authors such as Groß and Sakong (2019) and Sakong et al. (2022) who point out that there is insufficient microscopic understanding of these double layers.

There is also evidence to suggest that these layers can have larger scale implications. For example, these layers may aid in understanding the formation of Solid Electrolyte Interphase (see Mozhzhukhina et al. (2020), Xu et al. (2021) and references therein), which is a passivation layer that is formed by the electrochemical reduction of the electrolyte at the surface of the electrode and a key contributor to performance degradation (Kennedy et al. (2016)). Swift *et al.* also note that the electrochemical interface can often influence the success of energy storage materials (Janek and Zeier (2016); Manthiram et al. (2017); Randau et al. (2020)).

We remark that Newman and Thomas-Alyea (2012) indicate that thermodynamics and continuum models are both important tools for studying the EDL. Thermodynamics is necessary in order to understand the relationships between different variables, while continuum-based models can help in understanding the structure of this layer, thus motivating the topic of this thesis.

1.3 Mathematical modelling

Mathematical modelling is a tool that can be used to aid in the design of next-generation battery technologies by providing a framework for understanding observed phenomena, supplementing testing, and for implemen-

tation of control mechanisms within battery management systems. There are various modelling approaches and formulations used throughout the literature, in this section we outline the common approaches used for modelling LIBs and introduce some of the key modelling tools that will be implemented in this thesis.

1.3.1 Modelling approaches and formulations

Modelling of electrochemical systems such as LIBs can span multiple length and time scales due to the interplay between physical, chemical, and electrochemical processes. The different spatial scales can be classified as microscale, mesoscale, and macroscale. Microscale models focus on what is happening at the particle level and thus require atomistic or electronic scale simulation. Examples of such approaches include Molecular Dynamics, Monte Carlo simulations, and Density Functional Theory. Molecular dynamics focuses on studying ionic systems at atomic levels, such as the study of individual ions or molecules and their motion over time (for examples, see Borodin et al. (2017); Park et al. (2018); Bedrov et al. (2019)). Monte Carlo simulations use a statistical approach to model the thermodynamic properties of electrolytes (c.f. Card and Valleau (1970); Valleau and Cohen (1980)). Density Functional Theory is a quantum mechanics modelling approach used to study electrostatic interactions between ions and solvent molecules (Qi et al. (2010); Zhang et al. (2013); He et al. (2019)). Microscale models can give insight into what happens within individual particles, but they can be difficult apply to full cell simulations as they are computationally expensive due to the fine resolution, and they often require knowledge of detailed material properties (Shi et al. (2015); Prentice et al. (2020)).

Mesosopic models provide an intermediate level of detail by considering the statistical behaviour of the ions, for example, the Lattice-Boltzmann Method and Brownian dynamics. The Lattice Boltzmann method is a computational fluid dynamics (CFD) approach that can be applied to ion transport in electrolytes by considering the motion of ions as a collection of particles on a grid (He and Li (2000); Lee et al. (2013)). Brownian dynamics uses the Langevin equation to describe the system dynamics in a diffusive regime, for example, Turq et al. (1977); Moy et al. (2000). This level of modelling can bridge the gap between the detailed particle level behaviour and larger scale battery performance, but can require accurate representations of the cell microstructure from experimental or imaging techniques (for example, see Ferraro et al. (2020) and references therein).

Macroscale models can vary in focus from the particle scale, to the single cell scale, and up to full batteries

of multiple cells in series. The most common approaches at the macroscale level are continuum models using partial differential equations (PDEs) (Newman and Tobias (1962); Newman and Tiedemann (1975); Farrell et al. (2000)) and more empirical models such as equivalent circuit models (Hu et al. (2011); Hu and Yurkovich (2011); Marcicki et al. (2013)). PDE models are physics-based models that can capture a wide range of the cell dynamics and operation. However, there is a trade off for this level of detailed physics; PDE models can be computationally intensive when incorporating all of the electrochemical processes and cell activity. Equivalent circuit models use a circuit to describe the cell behaviour by treating the cell as a series of resistors and capacitors. These models do not capture battery physics at the same resolution as PDE models but as a result they are much simpler and more computationally robust (Plett (2015)).

Each of these approaches has advantages and disadvantages, and the choice of which scale to choose depends on the level of detailed physics required, the accuracy desired, and the computational resources and time available. We note that a review of model formulations at these various scales can be found in Shi et al. (2015) and Howey et al. (2020). In this thesis we are concerned with modelling at the macroscale level and will therefore discuss this approach further in the context of battery modelling specifically. We note that we focus in particular on PDE and continuous models as we want to gain a deeper understanding of EDLs in electrolytes, which we have noted requires thermodynamics and continuum modelling.

1.3.2 Modelling techniques at the macroscale level

We briefly introduce some important concepts and techniques that are utilised in continuum modelling; numerical simulation, non-dimensionalisation, and asymptotic analysis. Numerical simulation involves using computer algorithms to approximate and solve mathematical models. The numerical methods that will be used in this work include discretisation via finite differencing, Newton’s method for non-linear problems, and the midpoint method for discretising an integral. For more detail see Strikwerda (2004) and Morton and Mayers (2005).

Non-dimensionalisation refers to the process of removing the physical dimensions of variables from a given equation or model by scaling each of the variables with characteristic quantities. Some typical examples of characteristic quantities are time, length, and mass. The resulting model is referred to as being dimensionless. The advantage of this process is in quantifying whether terms are large or small. It is a fundamental tool in mathematical modelling, by isolating the characteristic quantities into dimensionless parameters we can then

identify combinations of parameters that may be of significance, approximate solutions by neglecting terms that are small, and run numerical simulations more efficiently. For further detail we refer to the following texts; Lin and Segel (1988), Fowler (1997), and Howison (2005).

Asymptotic, or perturbation, analysis is a mathematical concept which is closely linked to non-dimensionalisation and involves limiting behaviour. Once an equation or model is in non-dimensional form we can more easily identify terms that are small or large, from which we can then make approximations. In scenarios whereby an equation cannot be solved exactly we can exploit the existence of these small or large parameters to determine the dominant solution behaviour. It can also be used to uncover length scales over which there is significant change in the model. We highlight Bender and Orszag (2013) and Nayfeh (2024) for more information.

We further note that the application of asymptotic techniques to PDE models enables us to identify the most important processes in the cell, which in turn can reduce the complexity of these models via neglecting the small parameters. In this way, the asymptotic approach increases the computational efficiency of the model while still retaining the dominant physics.

1.3.3 Overview of modelling batteries at the macroscale level

Macroscale modelling of LIBs requires a continuum description of conservation laws and charge transport in the electrodes and the electrolyte, the resulting equations are often referred to as the microscopic equations (Moyle et al. (2019); Richardson et al. (2022); Planella et al. (2022)), but serve as the foundation for much of continuum modelling at the macroscale. We remark that we refer to these equations as microscopic equations rather than the microscale model as they differ from the microscale modelling referred to Section 1.3.1. The associated equations for the electrolyte are derived in detail in Chapter 2 of this thesis and we refer the reader to Newman and Thomas-Alyea (2012); Plett (2015); Richardson et al. (2022) for the associated equations for the electrodes, which is outside the scope of this work. In this section we briefly outline some of the other key approaches and techniques applied in the battery modelling community, which are all underpinned by this set of microscopic continuum equations.

The porous electrode model is a physics-based continuum model that is used to describe species transport and reactions in batteries at the continuum level, pioneered by Newman (Newman and Tobias (1962); Newman and Tiedemann (1975)). Since its inception, this model has formed a basis for modelling a single cell of an

LIB (two electrodes and the electrolytes) throughout the literature. The microscopic equations contain all of the physical information, but are too detailed to be simulated efficiently for a full battery cell; therefore, in order to build a larger scale model from the physics-based model which can be more easily simulated, modifications are required. Homogenisation (Pavliotis and Stuart (2008); Bensoussan et al. (2011); Chapman and McBurnie (2015)) and volume averaging (Whitaker (2013); Plett (2015); Newman and Thomas-Alyea (2012)) are two closely related techniques which are often applied to the porous electrode model to describe the equations on a more macroscale level. Homogenisation is a formal approach which employs asymptotic expansions to derive macroscopic equations from the more detailed microscopic equations. Volume averaging involves averaging physical quantities, such as the behaviour of the particles, over the volume of the porous structure. While similar to homogenisation, the closure condition is often more ad hoc and can be empirically defined. Both approaches yield analogous results and primarily differ in the assumptions and formalisms (Davit et al. (2013)).

One particular implementation of these upscaling methodologies that is frequently used in the literature is the Doyle-Fuller-Newman (DFN) model (Doyle et al. (1993); Fuller et al. (1994a,b); Santhanagopalan et al. (2006); Newman and Thomas-Alyea (2012)), which is also referred to as the pseudo-2D (P2D) volume-averaged porous electrode model or the Newman model. The DFN model is itself often modified within the literature to formulate reduced order models which improve computational cost without sacrificing much of the vital physics. Particular examples include the Single Particle Model (SPM) and the SPM with electrolyte (SPMe) (cf. Atlung et al. (1979); Prada et al. (2012); Guo et al. (2010); Moura et al. (2016); Planella and Widanage (2023)).

Asymptotic approaches have also been applied to porous electrode models: for example, Moyles et al. (2019) utilises an asymptotic approach to determine a reduced model while identifying important features of cell voltage behaviour under different asymptotic regimes. Marquis et al. (2019) and Richardson et al. (2020) use asymptotic methods to reduce the DFN model to the simpler SPM and SPMc models, respectively. Other examples of model reduction applied to porous electrode models include the work of Foster et al. (2017), Hennessy and Moyles (2020), Planella et al. (2021), Timms et al. (2021), and Castle et al. (2022).

We highlight that a comprehensive review of continuum modelling applied to LIBs can be found in Planella et al. (2022). We note that these modelling approaches and techniques are also applied to other electrochemical systems and types of batteries. For example, lead acid batteries (Newman and Tiedemann (1975);

Sulzer et al. (2019); Sulzer (2019)), redox flow batteries (Vynnycky (2011); Assunção (2016); Vynnycky and Assunção (2019)), and fuel cells (Bernardi and Verbrugge (1992); Hajimolana et al. (2011)), to name a few.

1.3.4 Remarks

We note that comprehensive models of batteries often do not include comprehensive electrolyte models. For example, as noted in Section 1.2.3, many battery models assume electroneutrality holds in the entirety of the electrolyte. Alternatively, the Helmholtz model is often used to describe the charge separation between the electrode surface and the electrolyte solution (Safari and Delacourt (2011); Smith and Bazant (2017); Moyles et al. (2019)).

We note that other areas of electrolyte modelling, outside the battery community, often incorporate greater detail, particularly with respect to the EDL structure. For example, there has been extensive modelling of electrolytes in the contexts of capacitive deionization and ion channels. In models of deionization, diffuse layer effects are commonly included (see, *e.g.* Biesheuvel et al. (2011); Singh et al. (2018); He et al. (2018)). Similarly, in the study of ion channels, a distinct body of research has developed electroneutral electrolyte models that capture the electric double layer behaviour by using effective boundary conditions derived from matched asymptotic analysis (*e.g.* Song et al. (2018a,b)).

Furthermore, in the context of LIBs and electrolyte modelling, we have acknowledged that liquid electrolytes have been studied extensively. As such, most of the electrolyte modelling literature focuses on liquid electrolytes (Newman and Tobias (1962); Newman and Tiedemann (1975); Newman and Thomas-Alyea (2012); Plett (2015); Doyle et al. (1993); Fuller et al. (1994b) to name a few). However, with the emergence of solid electrolytes as an attractive alternative there has been progress in the modelling literature, with examples including the work of authors such as Li and Monroe (2019, 2021), Mistry and Mukherjee (2020), and Kim et al. (2022). Even so, solid electrolytes are not yet understood either experimentally or mathematically to the same level as liquid electrolytes.

1.4 Thesis Summary and Novelty

The remainder of this thesis is structured as follows. In Chapter 2 we begin with an overview of the history of continuum modelling for electrolytes to establish the foundations and rich background associated with modelling electrolytes. We provide a comprehensive derivation of continuum electrolyte modelling; in

particular, the dilute, moderately concentrated, and thermodynamically consistent approaches to modelling an electrolyte are included in this chapter. We note that these models are widely employed throughout the battery modelling literature. However, while aspects of these models have been previously explored, to the best of our knowledge, this work represents the first comprehensive study to rigorously derive all three of these models from first principles, elucidate their relations and differences, and provide context as to how and why one approach may be chosen over another.

Chapter 3 focuses on implementing the thermodynamic model derived in Chapter 2 to derive a model for a solid electrolyte, as first derived by Braun et al. (2015) and employing this model to investigate the electric double layers of a solid electrolyte. We carry out a non-dimensionalisation of the model, through which we uncover the true width of the boundary layers in solid electrolytes - a feature that has not been explicitly identified in previous studies. We acknowledge difficulties that other authors have encountered in numerically solving solid electrolyte models, whilst allowing for deviations from charge neutrality at the boundaries. To mitigate these issues we introduce an auxiliary variable in our model, enabling us to then proceed with standard numerical methods. We use our non-dimensionalisation to inform an asymptotic reduction of the model, whereby we identify two distinct boundary regions, each with their own characteristic behaviour - an insight which has not been rigorously derived in prior work. Specifically, we determine a strong SCL exhibiting polynomial behaviour at the boundary, and a weak SCL transitioning from the boundary to the bulk exhibiting exponential behaviour. We observe that matching between these two regions (quadratic and exponential) is non-standard and we therefore introduce a pseudo matching technique to accommodate this - which has not been previously applied in this setting. We also present an alternative formulation for the solid electrolyte model whereby we can determine a first integral solution to the problem and thus present a matched asymptotics of integrals approach.

In Chapter 4 we turn our attention to the liquid electrolyte. We again apply the thermodynamic model for an electrolyte, as derived in Chapter 2, to obtain the model first derived by Dreyer et al. (2013). Our objective in this chapter is to explore the differences between the EDLs of solid and liquid electrolytes. As highlighted in the literature, we observe that the EDLs of the solid electrolyte are wider than those of the liquid. However, in contrast to what is commonly observed in the literature, our findings reveal that the asymptotic structure of the two electrolyte types is the same, *i.e.* in both the solid and liquid electrolyte the EDL is composed of two regions, one which exhibits polynomial behaviour and the other exponential

behaviour. We remark that in the literature it is widely observed that the EDLs of liquid electrolytes display exponential behaviour, however there is no discussion of polynomial behaviour. We therefore investigate these double layer features more deeply by considering a reconciliation between this thermodynamically consistent model and the Poisson-Nernst-Planck (PNP) model, with which the exponential behaviour is often affiliated. Through our numerical and asymptotic approaches we identify a breakdown of the PNP model when Dirichlet boundary conditions are applied.

Finally, in Chapter 5 we summarise the key findings from this work and discuss a number of areas of future work.

Chapter 2

Electrolyte modelling

In this chapter we provide a historical overview of the development of continuum and thermodynamic electrolyte models. Continuum models use partial differential equations to study macroscopic properties and thermodynamic models are based on principles from equilibrium and non-equilibrium thermodynamics. We adopt this modelling framework to establish the background and groundwork for chapters 3 and 4. We note that this is not a comprehensive review of electrolyte modelling, but rather an overview to showcase the breadth and width of work that has been carried out to improve understanding and optimisation of electrolytes in electrochemical systems.

2.1 History of continuum electrolyte modelling

The study of electrochemistry began in the 19th century with the groundbreaking work of scientists such as Alessandro Volta, Luigi Galvani, and Michael Faraday, paving the way for future research through their work on understanding the behaviour of ions and electric currents in electrolytes (Shukla and Kumar (2008)). The work of these pioneering figures was largely empirical and experiment based; however, their insights laid the foundations for the development of theoretical models.

The onset of theoretical models occurred toward the end of the 19th century and the start of the 20th century. The early models were largely heuristic and rooted in classical electrostatics. Some notable discoveries around this period include Arrhenius' work on the concept of ionisation and dissociation theory (Arrhenius (1887,

1903, 1912, 1914)). This work explained the dissociation of electrolytes into their positive and negative ions, and that chemical reactions are caused by reactions between ions.

Nernst developed an equation based on a chemical thermodynamic relationship, which relates the equilibrium potential of ions across membranes to the concentrations of the reactants and products involved in the reaction (Nernst (1888, 1889, 1921, 1926, 2003)). It is a fundamental equation for understanding electrochemical potentials and concentration gradients. However, in arriving at the expression for the Nernst equation, approximations were made which involve ignoring liquid-junction potentials and the activity coefficients of the ionic species (Newman and Thomas-Alyea (2012)). The Debye-Huckel theory provides a framework for describing how ions move and interact in electric fields. In particular, this theory explains how activity coefficients in electrolytes behave due to the inert long-range coulombic interactions between ions. Debye and Huckel developed an electrostatic model which describes how ions in electrolyte solutions are distributed as a result of the attractive and repulsive forces between the ions (Debye (1923); Newman and Thomas-Alyea (2012)). We note that both the Nernst equation and Debye-Huckel theory are most applicable for certain electrolytes; their work did not account for ion-solvent interactions or short-range interactions between ions and thus electrolytes where this theory applied were called dilute electrolytes.

Fick carried out experiments to study diffusion in fluids, which culminated in Fick’s laws of diffusion, or Fickian diffusion (Fick (1855a,b)) which describes the movement of ions via concentration gradients; that is, the diffusive flux of particles is proportional to the particle’s concentration gradient. Fick’s work was largely focused on biological problems, with Fickian diffusion later being applied to electrolyte modelling by Nernst (1888, 1889) and Planck (1890). The Nernst equation provides a relationship between the concentration of ions and the electric potential, while Fick’s law relates the ion concentrations and the diffusive flux of the ions. Combining these principles led to the development of the Nernst–Planck equation, a continuity equation describing the movement of ions under the influence of electric fields, concentration gradients, and convection (Maex (2017)).

Poisson’s equation in the context of electrostatics is an elliptic partial differential equation which describes the electric field that is present due to the distribution of ions (Poisson (1826)). This relation governs many problems in the field of electrostatics (Griffiths (2023)). The Poisson equation combined with the Nernst–Planck equation is colloquially known as the Poisson–Nernst–Planck (PNP) model, a frequently used model for a comprehensive treatment of ion transport and electrostatics (Richardson et al. (2022)). The PNP model

is highly regarded for formulating a fundamental theoretical understanding of ion transport for electrolytes and is still widely used as a basis for present-day models (cf. Kilic et al. (2007b); Schmuck and Bazant (2015)).

Many of the aforementioned progressions in electrolyte modelling formulate the standard approach to continuum modelling of electrolytes, and in particular, the dilute theory for electrolyte modelling. Non-equilibrium thermodynamics was not yet established when dilute theory and the Poisson–Nernst–Planck model were first formulated. As the foundations for non-equilibrium thermodynamics were established, electrolyte modelling continued through concentrated electrolyte theory, whereby ion-solvent interactions and short-range interactions between ions are taken into account. In his seminal work, John Newman compiled a comprehensive resource for battery modelling (Newman and Thomas-Alyea (2012)). With regard to electrolyte modelling, Newman’s work outlines the foundations for dilute and concentrated electrolyte theory. Modern continuum modelling of electrolytes is generally adapted from the work outlined in Newman and Thomas-Alyea (2012). As the focus of this thesis is on understanding electric double layers in electrolytes, we first require a rigorous modelling framework for the electrolyte. Therefore, in this chapter we will summarize the derivation of different continuum electrolyte models.

2.2 Continuum modelling formulation

There are two standard approaches to continuum modelling of liquid electrolytes, the dilute electrolyte (or Poisson-Nernst-Planck) theory and moderately concentrated electrolyte theory. The dilute theory is defined by low ionic concentrations and considers ion/solvent interactions only, while the concentrated theory captures interactions by ionic species in addition to the ion/solvent interactions. Dilute theory is motivated by the fact that both the diffusivity and ionic conductivity do not change order of magnitude as the lithium salt concentration is varied (Valøen and Reimers (2005)). However, the diffusivity and conductivity do depend on the concentration, therefore moderately concentrated theory can be used to account for this non-ideal behaviour. This can be important because the mobility of the ions in the electric field is reduced due to the attraction between oppositely charged ions driving them towards each other (Richardson et al. (2022)), which has the effect of reducing the ionic conductivity.

The dilute and concentrated electrolyte models are largely phenomenologically driven, motivated by physical intuition and experimental evidence with varying degrees of a thermodynamic fashion. An alternative

approach is to begin from non-equilibrium thermodynamic principles and derive an electrolyte model consistent to this framework. Deriving the electrolyte model from a thermodynamic standpoint means that we first consider fundamental and established laws of nature, such as energy conservation, so that the resulting model is rooted in physics and can be then applied to any electrolyte.

In the following sections we present model derivations for the dilute, moderately concentrated, and thermodynamically consistent approaches to electrolyte modelling; highlighting similarities and differences between each. As these derivations are quite involved, we include a summary table with the final equations for each approach in Table 2.1 of Section 2.3 at the end of the chapter.

2.2.1 Modelling notation and conventions

Within the electrochemical literature there are often inconsistencies in modelling conventions and notations. The primary root of these distinctions relates to how one describes the amount of a substance, specifically, we are referring to concentration measures. For example, some authors will refer to a constituent part in terms of its molar volume concentration (molarity; $[\text{mol}/\text{m}^3]$, Newman and Thomas-Alyea (2012); Plett (2015)), its molar solid concentration (molality; $[\text{mol}/\text{kg}]$, Newman and Thomas-Alyea (2012); Plett (2015)), its number density ($[\text{1}/\text{m}^3]$, Dreyer et al. (2013); Braun et al. (2015)), or its mass concentration (density; $[\text{kg}/\text{m}^3]$, Dreyer et al. (2015)). In this section we discuss these discrepancies and summarize notations we will use throughout the thesis.

Molar concentration and number density refer to the number of moles or particles per unit volume of the solution respectively; the solution being composed of both the solvent and the dissolved ions. In the context of electrolyte modelling, molar concentration and number density are favoured over mass density. This is because ions are dissolved in the solvent, of which the volume does not change significantly when the solute is added, therefore using mass density would require more knowledge and detailed calculations related to both the solute and solvent volume and mass. Furthermore, it is the number of ions that influences solution properties such as conductivity, diffusion, and thermodynamic properties such as the chemical potential.

The convenience of molar concentration and number density relies on the fact that historically, most electrolytes have liquid solvents (Nazri (2009)). As such, we note that for uniformity; we adopt these conventions for the derivation of the dilute and concentrated electrolyte theories, but may use different notations as appropriate. When we build a general thermodynamic model in section 2.2.5, we utilise mass density ρ for

the initial derivations since we will be agnostic to the composition and phase of the electrolyte. However, we note that we can convert to concentrations c and number densities n as desired, for example, we relate mass density and number density via mass $\rho_k = m_k n_k$, where m_k is the atomic mass of species k . Molar concentration is related to number density via $c_k = \frac{n_k}{N_A}$ where N_A is the standard Avogadro's constant. It follows that molar mass M_k can be used to relate density and concentration via $\rho_k = m_k N_A c_k = M_k c_k$.

For a given concentration measure χ then we can define an average velocity $\mathbf{v}_\chi = \frac{1}{\chi T} \sum_k \chi_k \mathbf{v}_k$ where $\chi T = \sum_k \chi_k$ is the total concentration of the electrolyte solution and $\mathbf{v}_k$ denotes a species intrinsic velocity in a medium. Similarly we can define the flux of species k , which refers to the amount of the species that flow per unit area per unit time, as $\hat{\mathbf{J}}_k = \chi_k \mathbf{v}_k$ and its diffusive flux as that deviating from the concentration averaged velocity $\mathbf{J}_k = \chi_k (\mathbf{v}_k - \mathbf{v})$. For example, if $\chi = c$ then $\mathbf{v}$ is the molar averaged velocity and $\mathbf{J}_k$ is the molar diffusive flux whereas if $\chi = \rho$ then $\mathbf{v}$ is the mass averaged velocity and $\mathbf{J}_k$ the mass diffusive flux. We refer to Taylor and Krishna (1993) for further details.

Related to concentration measures we must also consider quantities used to describe the composition of a mixture. We let $\hat{n}$ and N denote number of moles and number of particles (molecules) respectively. We note that the number of molecules is related to number density via $N_k = n_k V$ where V is the total volume and is related to the number of moles via Avogadro's constant; $N_k = \hat{n}_k N_A$. These quantities influence our thermodynamic derivations in particular, and the units of the chemical potential. For example, in concentrated theory it is more common to use moles along with molar concentrations, whereas when number densities are used as the concentration measure it is more consistent to consider molecules; since $n_k = N_A c_k$ and $N_k = N_A \hat{n}_k$.

2.2.2 Binary electrolyte

For the purpose of the derivations we consider a binary electrolyte. That is, the electrolyte is composed of a charge-neutral solvent and a charge-neutral solute, where the solute is made up of two ionic species. We will have a positive ion with a molar concentration c_L , a negative ion with a concentration c_A , and a solvent with a concentration c_0 ; whereby we note that concentration is defined as the amount of substance of solute per unit volume of solution (or total volume), *i.e.* $V = V_L + V_A + V_0$. We note that the volumes themselves can change during mixing but a given mixture is made up of its constituent components.

The stoichiometric coefficient of a species, denoted ν_k , is defined as the number of ions produced as one

molecule of electrolyte dissociates. The charge neutral solution of the electrolyte will have a fixed mole ratio of positive and negative ions, corresponding to their ratio in the solute of which they originate (Plett (2015)). For example, if the total number of moles of electrolyte is $\hat{n}$ and the electrolyte dissociates into ν_L positive ions, then the number of moles of positive ions is $\hat{n}_L = \nu_L \hat{n}$.

We let z_k denote the charge state, with the solvent being neutral, i.e. $z_0 = 0$. Because the electrolyte is charge neutral, the total charge of the electrolyte must be zero; as it dissociates into ν_k ions of species k , each with charge z_k , this means that we must have

$$\sum_k z_k \nu_k = 0. \quad (2.1)$$

We note that in binary electrolytes, ion concentrations and their stoichiometric coefficients are proportional, $c_k \propto \nu_k$ (Plett (2015)) so that

$$c := \frac{c_L}{\nu_L} = \frac{c_A}{\nu_A}, \quad (2.2)$$

which is referred to as the concentration of the solute, which we denote c . This notation will be used consistently throughout this chapter. As a consequence of this proportionality in binary electrolytes, if we multiply (2.1) by c :

$$c(z_L \nu_L + z_A \nu_A) = \frac{c_L}{\nu_L} (z_L \nu_L) + \frac{c_A}{\nu_A} (z_A \nu_A) = 0, \quad (2.3)$$

and so, the ν_k will cancel, and we obtain

$$\sum_k z_k c_k = 0, \quad (2.4)$$

which is the charge neutrality condition which is used throughout the literature. From here, we will establish the equations for conservation of mass, the current density, and conservation of charge for each electrolyte model.

2.2.3 Dilute electrolyte

Model assumptions

The primary assumption associated with dilute electrolyte theory is that there is a low concentration of ions. Specifically, this means that the concentration of the ions is much smaller than the concentration of the solvent $c_k \ll c_0$. This assumption has a number of implications that influence the way dilute electrolytes are modelled. Because the ion concentration is small, the ions are spread out from each other within the

solution; as such, there is a lot of free space, and inter-ionic interactions are weak and minimal in frequency. As a result, the interactions between ions are neglected, implicitly assuming that the ions do not interact with each other.

As a consequence of the low ionic concentrations, the concentration of the solvent is approximately constant; if $c_k \ll c_0$ then the volumes $V_k \ll V_0$, so $V = V_L + V_A + V_0 \approx V_0$ and therefore $c_0 \sim \frac{1}{V}$ the molar volume of the solution and constant. In fact, because the ion concentrations are so small, the concentration of the solvent is approximately the same as the concentration of the solution ($c_0 \approx c_T$). Furthermore, if we consider the molar averaged velocity

$$\mathbf{v} = \frac{1}{c_T} \sum_k c_k \mathbf{v}_k = \frac{c_L}{c_T} \mathbf{v}_L + \frac{c_A}{c_T} \mathbf{v}_A + \frac{c_0}{c_T} \mathbf{v}_0 \approx \mathbf{v}_0, \quad (2.5)$$

that is, the average velocity is approximately the velocity of the solvent.

Conservation of ions

Since there are no sources or sinks, total mass of each species will be conserved, *i.e.*

$$\frac{dM_k}{dt} = 0 = \frac{d}{dt} \left(\int_{V(t)} c_k dV \right). \quad (2.6)$$

Following Reynold's transport theorem (Reynolds (1903)) applied to an arbitrary parcel of electrolyte, we can write this as

$$\frac{d}{dt} \left(\int_{V(t)} c_k dV \right) = \int_{V(t)} \frac{\partial c_k}{\partial t} dV + \int_{\partial V(t)} c_k \mathbf{v}_k \cdot \mathbf{n} dS = 0 \quad (2.7)$$

where $V(t)$ is the volume, $\partial V(t)$ is the boundary, and $\mathbf{n}$ is the outward facing normal. Applying Gauss' Divergence theorem we then arrive at the following equation for the conservation of molar concentration for each species $k = L, A$ ¹

$$\frac{\partial c_k}{\partial t} + \nabla \cdot (c_k \mathbf{v}_k) = 0. \quad (2.8)$$

In order to determine the species velocity we must first consider the flux. From Section 2.2.1 we define the molar diffusive flux by $\mathbf{J}_k = c_k (\mathbf{v}_k - \mathbf{v})$ with $\mathbf{v}$ as the molar average velocity, which we remark from (2.5) is

¹We must have a global conservation of mass, that is the mass of the total concentration of the electrolyte, c_T must be constant. For the solvent in the dilute case we have already shown that $c_0 \approx c_T$ and therefore $c_0 \approx \text{constant}$ so (2.8) is not needed for that constituent.

often taken to be the solvent velocity. From this we can rewrite (2.8) in terms of the molar averaged velocity to get

$$\frac{\partial c_k}{\partial t} + \nabla \cdot (\mathbf{v}c_k) = -\nabla \cdot (\mathbf{J}_k), \quad (2.9)$$

which tells us that the concentration of species c_k changes due to the flux of the species and the bulk motion of the fluid². To determine what this flux is, we note that transport of the ions is driven by both diffusion and migration (Newman and Thomas-Alyea (2012); Richardson et al. (2022)).

In dilute electrolytes we employ Fickian diffusion. Since the dilute assumption is that the relative concentrations of ions are small and their interaction negligible, *i.e.* the mixture is ideal, then we will assume that the mass diffusion is driven by concentration gradients in its own species. In other words, the ions will move from regions of high concentration to regions of low concentration. This can be written as

$$\mathbf{J}_{k,\text{diffusion}} = -D_k \nabla c_k, \quad (2.10)$$

where D_k is a diffusion coefficient and ∇c_k is the concentration gradient.

Aside from mass diffusion, species can migrate due to the presence of an electric field, $\mathbf{E}$. The induced velocity from the electric field can be defined in terms of the mobility of a species, u_k with units of mol s/kg, via $\mathbf{v}_{ek} = z_k F u_k \mathbf{E}$ where F is Faraday's constant ($F \approx 96487 \text{ C mol}^{-1}$) and is related to the standard Avogadro's constant via $F = eN_A$, where $e = 1.602176634 \times 10^{-19} \text{ C}$ is the elementary charge. We multiply $\mathbf{v}_{ek}$ by the concentration to get the migration flux

$$\mathbf{J}_{k,\text{migration}} = c_k z_k F u_k \mathbf{E}. \quad (2.11)$$

This can also be referred to as the advective velocity.

The total ion flux for each species will be the sum of the diffusive, migrative, and convective fluxes, putting this together we obtain

$$\frac{\partial c_k}{\partial t} = -\nabla \cdot \hat{\mathbf{J}}_k \quad (2.12)$$

with

$$\hat{\mathbf{J}}_k = -D_k \nabla c_k + z_k u_k F c_k \mathbf{E} + c_k \mathbf{v}, \quad (2.13)$$

²We note that $\mathbf{J}_{k,\text{convection}} = c_k \mathbf{v}$ is the convective flux.

where $-D_k \nabla c_k$ is the diffusion term, $z_k u_k F c_k \mathbf{E}$ is the migration term, and $c_k \mathbf{v}$ is the convection term. We note that (2.12) and (2.13) do not close the problem because $\mathbf{E}$ must be determined via conservation of charge³.

Current density and conservation of charge

Maxwell's equations are the fundamental mathematical descriptions for electric and magnetic fields. Batteries are typically charged and discharged over long timescales, this enables us to assume that magnetic effects are negligible and that the electric field, $\mathbf{E}$, is irrotational, therefore $\nabla \times \mathbf{E} = 0$ (Griffiths (2023)). As this is the case, and because mathematically the curl of the gradient of a scalar quantity is always zero, we can define the electric field, $\mathbf{E}$ in terms of a scalar electric potential, ϕ , by

$$\mathbf{E} = -\nabla \phi. \quad (2.14)$$

Gauss' law says that $\nabla \cdot (\epsilon_0 \mathbf{E}) = n_F^4$ where $n_F = F \sum_k z_k c_k$ is the free charge density and ϵ_0 is the permittivity of the free space (Griffiths (2023)). This equation tells us that the electric flux across any closed surface is proportional to the net electric charge enclosed by the surface. Substituting (2.14) into Gauss' law allows us to write Poisson's equation

$$\nabla \cdot (\epsilon_0 \nabla \phi) = -F \sum_k z_k c_k = -F(z_L c_L + z_A c_A). \quad (2.15)$$

Current in the electrolyte is due to motion of the charged species. Therefore, we can write the current as $\mathbf{i}_e = F \sum_k z_k \hat{\mathbf{J}}_k$. Specifically, in the binary electrolyte the current is given by

$$\mathbf{i}_e = F \left(z_L \hat{\mathbf{J}}_L + z_A \hat{\mathbf{J}}_A \right). \quad (2.16)$$

In most electrolytes it is found that charge neutrality, or electroneutrality, is a reasonable assumption to make (Newman and Thomas-Alyea (2012)). This means that the total charge in the electrolyte should be zero, which we express via the charge neutrality equation given by (2.4). We will refer to this charge neutrality

³The determination of the average velocity, $\mathbf{v}$, follows from conservation of momentum from the Navier-Stokes equation. However, the average velocity is often assumed constant (and typically taken to be zero) in electrolyte models for lithium-ion batteries. Therefore, we defer a discussion of the momentum equation to Section 2.2.5 and Chapters 3 and 4.

⁴In matter Gauss' law is proportional to the electric displacement field $\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}$ where $\mathbf{P}$ is the electric polarization. That is, $\nabla \cdot \mathbf{D} = n_F$, is the standard constitutive relation for electric fields. However, without loss of generality we consider the derivation whereby we assume that $\mathbf{P}$ is negligible, an assumption which works well for most electric fields.

equation as local charge neutrality, as it specifies a balance of charges at each point of the electrolyte. Considering (2.12), multiply across by Fz_k and then sum over k we obtain

$$\frac{\partial}{\partial t} F \sum_k z_k c_k = -\nabla \cdot F \sum_k z_k \hat{\mathbf{J}}_k. \quad (2.17)$$

Assuming that electroneutrality holds and given $\mathbf{i}_e = F \sum_k z_k \hat{\mathbf{J}}_k$ from (2.16), Equation (2.17) reduces to the charge conservation equation

$$\nabla \cdot \mathbf{i}_e = 0. \quad (2.18)$$

These equations, (2.12) for the continuity and (2.13) for the flux equation, (2.16) for the current density, and (2.18) for conservation of charge; close the model and thus the dilute electrolyte model is

$$\frac{\partial c_k}{\partial t} = -\nabla \cdot \hat{\mathbf{J}}_k, \quad k = L, A, \quad (2.19a)$$

$$\hat{\mathbf{J}}_k = -D_k \nabla c_k + z_k u_k F c_k \mathbf{E} + c_k \mathbf{v}, \quad (2.19b)$$

$$\mathbf{i}_e = F \left(z_L \hat{\mathbf{J}}_L + z_A \hat{\mathbf{J}}_A \right), \quad (2.19c)$$

$$\nabla \cdot \mathbf{i}_e = 0. \quad (2.19d)$$

We note that this can be simplified for a binary electrolyte under the assumptions of dilute theory and local charge neutrality from (2.4).

Simplifying the model

We simplify (2.19) to recover the set of equations commonly found in the literature. We note that in simplifying the equations in this manner, we rewrite (2.19) with effective diffusion coefficients, conductivities, and transference numbers. This can make these equations more user-friendly for those who implement models in practice, as these quantities can be measured experimentally.

Making use of charge neutrality, and the proportionality between concentrations and the stoichiometric coefficients, we recall $c := \frac{c_L}{\nu_L} = \frac{c_A}{\nu_A}$ from (2.2). From this we can eliminate one of the equations for conservation of concentration in (2.19a). Firstly, by definition $\mathbf{i}_e = F \sum_k z_k \hat{\mathbf{J}}_k$, if we substitute the expression for the flux (2.19b) into this equation we have

$$-\frac{\mathbf{i}_e}{F} = (z_L^2 u_L c_L + z_A^2 u_A c_A) F \nabla \phi + (z_L D_L \nabla c_L + z_A D_A \nabla c_A) - (z_L c_L + z_A c_A) \mathbf{v}. \quad (2.20)$$

By electroneutrality (2.4) we have $z_A c_A = -z_L c_L$, using this in (2.20) and noting that by definition $c_L = \nu_L c$ we obtain the following equation

$$-\frac{\mathbf{i}_e}{z_L \nu_L F} = F c (z_L u_L - z_A u_A) \nabla \phi + (D_L - D_A) \nabla c. \quad (2.21)$$

From this, we rearrange (2.21) to eliminate the electric potential

$$c \nabla \phi = -\frac{\mathbf{i}_e}{F^2 z_L \nu_L (z_L u_L - z_A u_A)} - \frac{(D_L - D_A) \nabla c}{F (z_L u_L - z_A u_A)}. \quad (2.22)$$

As we have $c = \frac{c_L}{\nu_L} = \frac{c_A}{\nu_A}$ we need only solve one conservation equation from (2.19a), *i.e.* taking

$$\frac{\partial c}{\partial t} = -\nabla \cdot (-D_L \nabla c - z_L u_L F c \nabla \phi + c \mathbf{v}). \quad (2.23)$$

Substituting (2.22) into (2.23) we will have the following equation for conservation of the ionic species

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = \nabla \cdot (D_{\text{eff}} \nabla c) - \frac{\mathbf{i}_e \cdot \nabla t_L}{F z_L \nu_L}, \quad (2.24)$$

where we define the effective diffusion coefficient

$$D_{\text{eff}} = \frac{z_L u_L D_A - z_A u_A D_L}{z_L u_L - z_A u_A} = \frac{D_L D_A (z_L - z_A)}{z_L D_L - z_A D_A}, \quad (2.25)$$

where the Einstein relation (Newman and Thomas-Alyea (2012)),

$$u_k = \frac{D_k}{RT}, \quad (2.26)$$

has been used to relate the mobility and diffusivity, with R as the ideal gas constant with a value of $8.3144621 \text{ J}(\text{mol K})^{-1}$ and T is temperature. We also define the transference number

$$t_L = 1 - t_A = \frac{z_L u_L}{z_L u_L - z_A u_A}, \quad (2.27)$$

which is the fraction of the electric current carried by the cation. The more mobile the anions are, the smaller the transference number. We note that we have used the charge conservation here, $\nabla \cdot (\mathbf{i}_e t_L) = t_L \nabla \cdot \mathbf{i}_e + \mathbf{i}_e \cdot \nabla t_L = \mathbf{i}_e \cdot \nabla t_L$ since $\nabla \cdot \mathbf{i}_e = 0$. Equation (2.24) is the general expression for non-constant transport properties. If the mobilities and diffusion coefficients are constant then this simplifies to

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = D_{\text{eff}} \nabla^2 c. \quad (2.28)$$

We can also obtain a version of Ohm's law by considering the expression for the current density given in (2.21), rewritten as

$$\frac{\mathbf{i}_e}{z_L \nu_L} = F^2 (z_A u_A - z_L u_L) c \nabla \phi + F (D_A - D_L) \nabla c. \quad (2.29)$$

We then use the Einstein relation (2.26) and can rearrange terms to write the following form of the current

$$\frac{\mathbf{i}_e}{z_L \nu_L} = -\hat{\kappa}(c) \left(\nabla \phi - \frac{RT}{F} \left(\frac{D_A - D_L}{z_L D_L} \right) t_L \frac{\nabla c}{c} \right), \quad (2.30)$$

where

$$\hat{\kappa}(c) = \frac{F^2}{RT} (z_L D_L - z_A D_A) c. \quad (2.31)$$

Here, $\hat{\kappa}$ is referred to as the electrical conductivity of the electrolyte. Therefore, a common form of the dilute electrolyte equations (2.19) found in the literature is given by (2.23) and (2.30), along with conservation of charge from (2.19d). We note that in the special case where $z_L = +1$, $z_A = -1$, and $\nu_L = +1$ (2.30) can be written as

$$\mathbf{i}_e = -\hat{\kappa}(c) \left(\nabla \phi - \frac{RT}{F} (1 - 2t_L) \frac{\nabla c}{c} \right), \quad (2.32)$$

as can be found in Richardson et al. (2022).

Poisson–Nernst–Planck

We note that the Poisson–Nernst–Planck (PNP) model is a subset of the dilute model for an electrolyte, therefore we will briefly outline the PNP model here, having derived the necessary concepts from dilute theory.

First, we consider the Nernst–Planck equation, which is our continuity equation (2.12) with the flux given by (2.13)

$$\frac{\partial c_k}{\partial t} = -\nabla \cdot \hat{\mathbf{J}}_k, \quad \hat{\mathbf{J}}_k = -D_k \nabla c_k + z_k u_k F c_k \mathbf{E} + c_k \mathbf{v}, \quad (2.33)$$

where our flux expression is composed of a diffusion term, an electromigration term, and an advective term.

We can write this in the conventional Nernst–Planck way as

$$\frac{\partial c_k}{\partial t} + \mathbf{v} \cdot \nabla c_k = \nabla \cdot \left(D_k \left(\nabla c_k + \frac{z_k F c_k}{RT} \nabla \phi \right) \right), \quad (2.34)$$

where we have used the Einstein relation (2.26).

Now we just need to address the electrostatic potential via the Poisson equation. Again, the steps mimic those outlined above to find (2.15)

$$\nabla \cdot (\epsilon_0 \nabla \phi) = -F \sum_k z_k c_k. \quad (2.35)$$

Therefore, the PNP equations are given by (2.34) and (2.35).

Failure of the dilute theory

Where the dilute theory falls short primarily resides with the flux equation (2.13), as it does not accurately define the transport properties, and from a practical point of view, the driving forces are not always readily measurable. The migration and diffusion of the ions must be defined with respect to the average velocity of the fluid and the flux relations should be consistent with these definitions (Newman and Thomas-Alyea (2012)). Furthermore, the driving forces should be gradients of the electrochemical potential.

The dilute assumption means that the flux equations can only account for interactions of the ions with the solvent, while interactions with other solute species are neglected. Of course, this expression for the flux is still valuable; it is commonly used in the electrochemical literature, and it conveys the physical phenomena occurring in a relatively straightforward manner. However, a more sophisticated and intricate approach is required in order to allow for the ionic species to interact with each other.

2.2.4 Concentrated electrolyte

The dilute electrolyte theory neglects interactions between different components within the electrolyte. These interactions can affect properties of an electrolyte such as the mobility and ionic conductivity due to the collisions between particles and the drag that they exert on each other (Samson et al. (1999); Valøen and Reimers (2005)). In concentrated electrolyte theory we relax the assumption that $c_k \ll c_0$ and thus we need to account for the inter-component effects in our conservation laws. In this section we introduce the equations for a concentrated electrolyte solution, however, if we consider (2.7), it is not immediately clear how the fluxes should be defined when $c_k \ll c_0$ fails.

We remark that in general, processes will move to minimise free energy (Friston et al. (2006); Friston (2010)). Furthermore, in the criticism of dilute electrolyte theory it is noted that the driving force for diffusion and migration should be related to the electrochemical potential, not the concentration gradient (Newman and Thomas-Alyea (2012)). In order to incorporate the electrochemical potential into our equations we first need to consider the chemical potential, defined to be the energy that can be absorbed or released as a result of the change in the number of particles of a species in the system. The first law of thermodynamics says that energy cannot be created or destroyed, but it can be converted from one form to another, therefore, to capture the more complex behaviour of the ions in a concentrated solution, we turn to thermodynamics. Thermodynamics provides a framework for accounting for interactions between ions, electrochemical potentials, and non-ideal

behaviour in solutions.

Gibbs free energy and the Gibbs-Duhem equation

Thermodynamics considers energy relations in systems. We first note that there are two types of thermodynamic properties; *intensive* and *extensive*. Intensive properties are uniform values independent of size or mass, for example, temperature, pressure, and chemical potential. Extensive properties depend on mass, for example, volume, entropy, and internal energy. Extensive properties can be made independent of size by dividing by mass to make them *specific* properties. These conventions will be applied as we explain and derive thermodynamic concepts throughout the subsequent sections.

The first law of thermodynamics can be written mathematically via

$$dU = T dS - p dV + \sum_k \mu_k d\hat{n}_k, \quad (2.36)$$

where U is the internal energy, p is pressure, V is volume, S is entropy, and T is temperature, with $\mu_k, \hat{n}_k$ denoting the chemical potential and number of moles of the substance respectively.⁵ Since U is a function of extensive variables $(S, V, \hat{n}_k)$ we can apply Euler's homogeneous function theorem to write

$$U = TS - pV + \sum_k \mu_k \hat{n}_k. \quad (2.37)$$

An important thermodynamic concept is free energy. The change in the free energy is the amount of energy (or potential) that can be used to do work provided that the temperature is kept constant. Free energy is used in understanding the direction of chemical reactions between various states of equilibrium, it tells us if a chemical change is thermodynamically possible (Plett (2015)). In many electrochemical systems, Gibbs free energy is commonly used because its natural state variables are pressure and temperature, which can often be held constant in these systems. The equation for Gibbs free energy can be derived from the first law of thermodynamics (2.36) as

$$dG = V dp - S dT + \sum_k \mu_k d\hat{n}_k \quad (2.38)$$

using a Legendre transformation. We will use this definition of the Gibbs free energy to derive an expression for the chemical potential of a species. We note that (2.38) can also be defined by

$$G = U + pV - TS, \quad (2.39)$$

⁵We note that the choice of $\hat{n}_k$ is arbitrary but in this formulation μ_k will then be of the form J/mol.

whereby taking the total differential of (2.39) and then substituting (2.36), we recover (2.38).

We start by considering an ideal gas which follows the ideal gas law⁶ (Clapeyron (1834)),

$$pV = \hat{n}RT. \quad (2.40)$$

For a fixed temperature and composition, the change in Gibbs free energy by (2.38) is reduced to

$$dG = V dp, \quad (2.41)$$

which means that

$$\left. \frac{dG}{dp} \right|_{T, \hat{n}} = V = \frac{\hat{n}RT}{p}, \quad (2.42)$$

from (2.40). Because the composition is fixed we can then integrate with respect to pressure to obtain

$$\begin{aligned} \int_{p_0}^p \frac{dG}{dx} dx &= \int_{p_0}^p \frac{\hat{n}RT}{x} dx \\ G(p) - G(p_0) &= \hat{n}RT(\log p - \log p_0). \end{aligned} \quad (2.43)$$

Rearranging the above expression, the specific Gibbs free energy, g , given by $G = \hat{n}g$ can then be defined by

$$g = g_0(T) + RT \log p, \quad (2.44)$$

where

$$g_0(T) = g(p_0) + RT \log p_0. \quad (2.45)$$

Substituting the first law given by (2.37) into (2.39)

$$G = (TS - pV + \sum_k \mu_k \hat{n}_k) + pV - TS = \sum_k \mu_k \hat{n}_k. \quad (2.46)$$

It follows that for specific Gibbs free energy

$$\begin{aligned} \hat{n}g &= \sum_k \mu_k \hat{n}_k \\ g &= \sum_k \mu_k \frac{\hat{n}_k}{\hat{n}}; \quad \hat{n} = \sum_k \hat{n}_k \\ g &= \sum_k \mu_k x_k; \quad x_k = \frac{\hat{n}_k}{\hat{n}}. \end{aligned} \quad (2.47)$$

⁶The use of the ideal gas law is for pedagogical purposes to derive the Guggenheim activity model for chemical potentials (Guggenheim (1959, 2002)).

We define the partial molar Gibbs free energy, g_k as

$$g_k = \frac{\partial G}{\partial \hat{n}_k}. \quad (2.48)$$

From this we can then see that the chemical potential μ_k can be interpreted as the partial molar Gibbs free energy g_k

$$g_k = \frac{\partial G}{\partial \hat{n}_k} = \frac{\partial(\hat{n}g)}{\partial \hat{n}_k} = \frac{\partial(\hat{n} \sum_k \mu_k x_k)}{\partial \hat{n}_k} = \frac{\partial(\sum_k \mu_k \hat{n}_k)}{\partial \hat{n}_k} = \mu_k. \quad (2.49)$$

We note that this is how the chemical potential is defined, $\mu_k = \left(\frac{dG}{d\hat{n}_k}\right)$ at constant temperature and pressure.

From here, if we assume that (2.44) holds for partial energies and partial pressures, assume the ideal gas law (2.40) holds for each gas $p_k = \frac{\hat{n}_k RT}{v_k}$ (where v_k is the specific volume), and use Dalton's law $p = \sum_k p_k$

$$\begin{aligned} g_k &= g_{k0}(T) + RT \log \frac{\hat{n}_k RT}{v_k} \\ &= g_{k0}(T) + RT \log \frac{\hat{n}_k}{\hat{n}} \frac{RT \hat{n}}{v_k} \\ &= g_{k0}(T, p) + RT \log \frac{\hat{n}_k}{\hat{n}} \end{aligned} \quad (2.50)$$

where we have defined $g_{k0}(T, p) = g_{k0}(T) + RT \log \frac{RT \hat{n}}{v_k}$ as the terms which do not depend on composition.

Because we can interpret μ_k as the partial molar Gibbs free energy

$$\mu_k = \mu_{k0}(T, p) + RT \log x_k. \quad (2.51)$$

This equation represents the ideal chemical potential, which we can assume will hold for any phase. If the phase is not ideal we consider that the chemical potential can be expressed as the sum of the ideal potential and an excess term representing the non-ideality, $\mu = \mu_{ideal} + \mu_{excess}$ where μ_{ideal} is given by (2.51) and the excess is given by $\mu_{excess} = RT \log \gamma$, thereby giving the following expression

$$\mu_k = \mu_{k0}(T, p) + RT \log \gamma_k x_k, \quad (2.52)$$

where γ_k is the activity coefficient, which describes the deviation of the chemical potential from that of an ideal solution. This expression for the chemical potential (2.52) is the general equation used for chemical potentials in concentrated electrolyte theory.

Coalescing all of these things together, $\mu_k = g_k$, $g = \sum_k \mu_k x_k$, and $G = \hat{n}g = \sum_k \mu_k \hat{n}_k$ we can take the total differential

$$dG = \sum_k \mu_k d\hat{n}_k + \sum_k \hat{n}_k d\mu_k, \quad (2.53)$$

setting this equal to (2.38) we obtain the Gibbs-Duhem equation

$$\sum_k \hat{n}_k d\mu_k = V dp - S dT. \quad (2.54)$$

The power of the Gibbs-Duhem relationship comes when pressure and temperature are fixed leading to

$$\sum_k \hat{n}_k \nabla \mu_k = \mathbf{0}, \quad (2.55)$$

which implies if there are N constituents then only $N - 1$ of the chemical potential gradients are independent. Equations (2.51), (2.52), and (2.55) will be used in the following sections to determine the concentrated electrolyte equations.

Conservation of ions

One of the primary differences between dilute and concentrated electrolyte theory is related to the inter-ionic reactions, or lack thereof in the dilute case. To define the flux to be used in the continuity equation for concentrated electrolyte theory we must first consider that the average velocity of the species can be determined by balancing the drag forces acting on a species with the gradients of electrochemical potential and pressure (Richardson et al. (2022)). Stefan-Maxwell theory describes transport by relating the drag acting on a species to its relative velocity with the other species; the Stefan-Maxwell equations are considered to be the cornerstone of concentrated electrolyte theory (Newman and Thomas-Alyea (2012); Richardson et al. (2022)). We also note that we can define force as the negative of the gradient in energy; if we take the Gibbs free energy as the energy driving the forces exerted on each particle, keeping other particles fixed, we can write

$$\mathbf{F}_k = -\nabla G_k, \quad (2.56)$$

where we let G_k be the Gibbs free energy of species k (*i.e.* $G_k = \mu_k \hat{n}_k$). Therefore, in this section we will consider Stefan-Maxwell theory and its relation to Gibbs free energy via the force to determine an expression for the average velocity. From here, we can determine the flux and then, implementing a conservation of each species, we can formulate the equations for modelling a concentrated electrolyte.

Stefan-Maxwell theory considers how changes in momentum, and therefore velocity, of species occur due to the collisions between the species. For simplicity of notation, we will derive these ideas by considering two particles, and will later generalise. Given two particles, of mass m_1, m_2 moving initially at velocities

$\mathbf{v}_1, \mathbf{v}_2$ which collide elastically, we can show (Present and Amdur (1959); Taylor and Krishna (1993)) that the average velocity of each species following the collision, $\bar{\mathbf{v}}_1, \bar{\mathbf{v}}_2$ is the centre of mass velocity

$$\bar{\mathbf{v}}_1 = \bar{\mathbf{v}}_2 = \frac{m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2}{m_1 + m_2}, \quad (2.57)$$

assuming that the particles masses are not affected by the collision. Deriving this involves conserving both momentum and kinetic energy, and then averaging over all possible collision directions. From this we can then determine the force per unit volume acting on each species. From Newton's second law, the force acted on a particle during a reaction is given by the change in momentum via $\mathbf{F}_k = \frac{d\mathbf{p}_k}{dt}$, where $\mathbf{F}_k$ is the force and $\mathbf{p}_k$ is the momentum of species k . We can approximate $\frac{d\mathbf{p}_k}{dt} \approx \Delta \mathbf{p}_k$, *i.e.* the instantaneous change in momentum can be approximated by the average change in momentum. Therefore, the force can be described by the average momentum loss

$$\mathbf{F}_1 = \Delta m_1 \mathbf{v}_1 = m_1(\mathbf{v}_1 - \bar{\mathbf{v}}_1) = \frac{m_1 m_2 (\mathbf{v}_1 - \mathbf{v}_2)}{m_1 + m_2}. \quad (2.58)$$

Dividing by volume and recalling $c_k = \frac{\rho_k}{M_k} = \frac{m_k}{VM_k}$ we can see that

$$\mathbf{F}_{1,v} \propto c_1 c_2 (\mathbf{v}_1 - \mathbf{v}_2), \quad (2.59)$$

where $\mathbf{F}_{1,v}$ denotes the force per unit volume. This can be generalised for multiple species

$$\mathbf{F}_{1,v} \propto \sum_j c_1 c_j (\mathbf{v}_1 - \mathbf{v}_j). \quad (2.60)$$

We can write this in the form

$$\mathbf{F}_{1,v} = \sum_j K_{1j} (\mathbf{v}_1 - \mathbf{v}_j), \quad (2.61)$$

thus giving an expression for species velocity in terms of the force, where K_{kj} is a proportionality constant known as a friction coefficient, and is related to the Stefan-Maxwell diffusivity by

$$D_{kj} = \frac{x_k x_j p}{K_{kj}} \text{ or } K_{kj} = \frac{RT c_k c_j}{c_T D_{kj}} \quad (2.62)$$

using the ideal gas law (Plett (2015)).

We then consider (2.56), so that we can express this force in terms of free energies and thus gradients of chemical potentials. We know that G can be defined by (2.49) and if we write $G = G(\mu_1, \mu_2)$, by the chain rule we can say

$$\nabla G = \frac{\partial G}{\partial \mu_k} \nabla \mu_k, \quad (2.63)$$

where we have assumed constant composition because of path independence⁷. Since G is a homogeneous function we can say

$$G(\mu) = \mu \cdot \nabla G(\mu) = \sum_k \mu_k \frac{\partial G}{\partial \mu_k}. \quad (2.64)$$

But $G = \sum_k \hat{n}_k \mu_k$ from (2.46), so with (2.64) we must have

$$\hat{n}_k = \frac{\partial G}{\partial \mu_k}. \quad (2.65)$$

Therefore, substituting this into (2.56) we have $\mathbf{F}_1 = -\nabla G_1 = -\hat{n}_1 \nabla \mu_1$, and we can rewrite (2.56) as the force per unit volume via

$$\mathbf{F}_{1,v} = -\frac{\hat{n}_1}{V} \nabla \mu_1 = -c_1 \nabla \mu_1, \quad (2.66)$$

where we define $c_k = \frac{\hat{n}_k}{V}$ as the molar concentration of species k and the following relation holds

$$x_k = \frac{\hat{n}_k}{\hat{n}} = \frac{\frac{\hat{n}_k}{V}}{\frac{\hat{n}}{V}} = \frac{c_k}{c_T} \quad (2.67)$$

where $c_T = \sum_k c_k$ is the total molar concentration so $c_k = x_k c_T$. Thus, equating the expression for the velocity in terms of the force given by (2.61) with (2.66) we find that

$$c_1 \nabla \mu_1 = \sum_j K_{1j} (\mathbf{v}_j - \mathbf{v}_1), \quad (2.68)$$

or more generally,

$$c_k \nabla \mu_k = \sum_j K_{kj} (\mathbf{v}_j - \mathbf{v}_k) = RT \sum_j \frac{c_k c_j}{c_T D_{kj}} (\mathbf{v}_j - \mathbf{v}_k), \quad (2.69)$$

this equation is referred to as the multicomponent diffusion equation (Newman and Thomas-Alyea (2012)). We highlight that this equation addresses the pitfalls of the flux equation determined for the dilute case. Specifically, the driving force in this case is the gradient of the chemical potential⁸, making this equation more practical than the dilute version (see footnote 7). Furthermore, this driving force is proportional to a linear combination of species interactions, not just an individual species reaction with the solvent thereby accounting for the inter-ionic interactions missing in the dilute case.

⁷We note that we take $\hat{n} \nabla \mu$ rather than $\mu \nabla \hat{n}$ in the Gibbs derivative because in practice the chemical potential is more readily measurable than gradients of concentration (Newman and Thomas-Alyea (2012)).

⁸We remark that the Gibbs free energy can also be defined to include the electric potential in the context where there is an electric field, in which case we have the electrochemical potential as the driving force for the fluxes.

Having (2.69) we now need to determine expressions for the flux of each species. For a binary electrolyte, where we have cations, anions and solvent, (2.69) yields two independent equations

$$c_L \nabla \mu_L = K_{LA}(\mathbf{v}_A - \mathbf{v}_L) + K_{L0}(\mathbf{v}_0 - \mathbf{v}_L), \quad (2.70)$$

$$c_A \nabla \mu_A = K_{LA}(\mathbf{v}_L - \mathbf{v}_A) + K_{A0}(\mathbf{v}_0 - \mathbf{v}_A), \quad (2.71)$$

whereby we can use the Gibbs-Duhem relation, (2.55), written in terms of concentration as

$$\sum_k c_k \nabla \mu_k = \mathbf{0}, \quad (2.72)$$

to eliminate the chemical potential for the solvent. These equations ((2.70) and (2.71)) can be rearranged to determine the fluxes for the concentrated electrolyte, $\hat{\mathbf{J}}_L = c_L \mathbf{v}_L$ and $\hat{\mathbf{J}}_A = c_A \mathbf{v}_A$, via the following steps. We define the chemical potential of the electrolyte by

$$\mu_e = \nu_L \mu_L + \nu_A \mu_A \quad (2.73)$$

since the neutral electrolyte dissociates into ν_L cations with chemical potential μ_L and ν_A anions with chemical potential μ_A (Newman and Thomas-Alyea (2012); Plett (2015)). As was the case in the dilute derivation, for a binary electrolyte we define $c = \frac{c_L}{\nu_L} = \frac{c_A}{\nu_A}$ from (2.2). Therefore, by taking the gradient of μ_e and multiplying by c we find

$$c \nabla \mu_e = c_L \nabla \mu_L + c_A \nabla \mu_A. \quad (2.74)$$

Using (2.70) and (2.71), and writing $K_{kj} = \frac{RT c_k c_j}{c_T D_{kj}}$ we obtain

$$c \nabla \mu_e = \frac{RT c_0}{c_T} \left(\frac{c_L}{D_{0L}} (\mathbf{v}_0 - \mathbf{v}_L) + \frac{c_A}{D_{0A}} (\mathbf{v}_0 - \mathbf{v}_A) \right), \quad (2.75)$$

where we have omitted the terms with the K_{LA} coefficient as they cancel each other out. Isolating for $c_L \mathbf{v}_L$

$$c_L \mathbf{v}_L = -\frac{D_{0L} c_T c}{RT c_0} \nabla \mu_e + D_{0L} \left(\frac{c_L}{D_{0L}} + \frac{c_A}{D_{0A}} \right) \mathbf{v}_0 - \frac{c_A D_{0L} \mathbf{v}_A}{D_{0A}}. \quad (2.76)$$

Now, from the definition of the current density (2.16) and since $\hat{\mathbf{J}}_L = c_L \mathbf{v}_L$ and $\hat{\mathbf{J}}_A = c_A \mathbf{v}_A$, we can eliminate $\mathbf{v}_A$ via

$$\mathbf{v}_A = \mathbf{v}_L - \frac{\mathbf{i}_e}{F z_L c_L}, \quad (2.77)$$

due to electroneutrality ($z_A c_A = -z_L c_L$). Rearranging and using $c_A = -\frac{z_L c_L}{z_A}$

$$c_L \mathbf{v}_L \left(\frac{z_A D_{0A} - z_L D_{0L}}{z_A D_{0A}} \right) = -\frac{D_{0L} c_T c}{RT c_0} \nabla \mu_e + D_{0L} \left(\frac{c_L}{D_{0L}} + \frac{c_A}{D_{0A}} \right) \mathbf{v}_0 + \frac{c_A D_{0L}}{c_L D_{0A}} \frac{\mathbf{i}_e}{F z_L}. \quad (2.78)$$

We can simplify the above expression to isolate for $\hat{\mathbf{J}}_L = c_L \mathbf{v}_L$ and rearrange, where we rewrite $-z_A$ as

$$-z_A = \frac{\nu_L}{\nu} (z_L - z_A); \quad \nu = \nu_L + \nu_A \quad (2.79)$$

using $z_L \nu_L + z_A \nu_A = 0$ by electroneutrality from (2.1) and $c\nu_k = c_k$ by definition for a binary electrolyte. Making use of these relations and electroneutrality we can then write (2.78) as

$$\hat{\mathbf{J}}_L = c_L \mathbf{v}_L = -\frac{\nu_L \mathcal{D}_{cT}}{\nu RT c_0} c \nabla \mu_e + c_L \mathbf{v}_0 + \frac{\mathbf{i}_e t_{0L}}{z_L F}, \quad (2.80)$$

where

$$\mathcal{D} = \frac{D_{0L} D_{0A} (z_L - z_A)}{z_L D_{0L} - z_A D_{0A}}, \quad t_{0L} = 1 - t_{0A} = \frac{z_L D_{0L}}{z_L D_{0L} - z_A D_{0A}} \quad (2.81)$$

are the diffusion coefficient and transference number in the concentrated electrolyte framework. Similarly we find for the anion flux

$$\hat{\mathbf{J}}_A = c_A \mathbf{v}_A = -\frac{\nu_A \mathcal{D}_{cT}}{\nu RT c_0} c \nabla \mu_e + c_A \mathbf{v}_0 + \frac{\mathbf{i}_e t_{0A}}{z_A F}. \quad (2.82)$$

Now we would like to write $\nabla \mu_e$ in terms of concentrations to align with what is conventionally presented in the literature. To do so, we first recall that in general chemical potentials can be defined using (2.52). However, we note that in this expression $\mu_{k0}(T, p)$ depends on c , therefore we rewrite (2.52) as

$$\mu_k = RT \left(\mu_k^* + \log \left(\frac{c_T}{c_0} \right) + \log \gamma_k x_k \right), \quad (2.83)$$

so that μ_k^* has no compositional dependence. Noting the definition of the chemical potential of the electrolyte in (2.73) and using (2.83) for μ_L, μ_A

$$\begin{aligned} \mu_e &= \nu_L \mu_L + \nu_A \mu_A \\ &= \nu_L RT \log (x_L \gamma_L) + \nu_A RT \log (x_A \gamma_A) + RT (\nu_L + \nu_A) \log \left(\frac{c_T}{c_0} \right) + RT \mu_e^*, \quad \mu_e^* = \mu_L^* + \mu_A^* \\ &= \nu_L RT \log \left(\frac{c \nu_L \gamma_L}{c_T} \right) + \nu_A RT \log \left(\frac{c \nu_A \gamma_A}{c_T} \right) + RT (\nu_L + \nu_A) \log \left(\frac{c_T}{c_0} \right) + RT \mu_e^* \\ &= \nu RT \left(\log \left(\frac{c}{c_0} \right) + \log \gamma_{LA} \right) + \nu_L RT \log \nu_L + \nu_A RT \log \nu_A + RT \mu_e^*, \end{aligned} \quad (2.84)$$

where we have used that $\nu = \nu_L + \nu_A$ and we define $\gamma_{LA}^\nu = \gamma_L^{\nu_L} \gamma_A^{\nu_A}$ to be the mean activity coefficient. From the above expression for μ_e we have

$$\nabla \mu_e = \nu RT \nabla \left(\log \left(\frac{c}{c_0} \right) + \log \gamma_{LA} \right). \quad (2.85)$$

From this we can use the chain rule to determine $\nabla\mu_e$ in terms of concentration c . Firstly,

$$\nabla \log \left(\frac{c}{c_0} \right) = \frac{1}{c} \left(1 - \frac{\partial \log c_0}{\partial \log c} \right) \nabla c. \quad (2.86)$$

We remark that γ_{LA} is dimensionless, hence we define $y = \frac{c}{c_0}$ to be the ratio of the electrolyte to the solvent and obtain

$$\nabla \log \gamma_{LA} = \frac{\partial \log \gamma_{LA}}{\partial y} \nabla y = \frac{1}{c} \frac{\partial \log \gamma_{LA}}{\partial \log y} \left(1 - \frac{\partial \log c_0}{\partial \log c} \right) \nabla c. \quad (2.87)$$

Therefore, combining (2.86) and (2.87), $\nabla\mu_e$ can be expressed as

$$\nabla\mu_e = \frac{\nu RT}{c} \left(1 + \frac{\partial \log \gamma_{LA}}{\partial \log y} \right) \left(1 - \frac{\partial \log c_0}{\partial \log c} \right) \nabla c. \quad (2.88)$$

Defining the diffusion coefficient of the salt to be⁹

$$D_e = \mathcal{D} \frac{c_T}{c_0} \left(1 + \frac{\partial \log \gamma_{LA}}{\partial \log y} \right), \quad (2.89)$$

we arrive at the following form for the flux equation

$$\hat{\mathbf{J}}_L = c_L \mathbf{v}_L = -\nu_L D_e \left(1 - \frac{d \log c_0}{d \log c} \right) \nabla c + c_L \mathbf{v}_0 + \frac{\mathbf{i}_e t_{0L}}{z_L F}. \quad (2.90)$$

We must have conservation of concentration of each species, therefore we must have (2.12) hold for $k = L$.

Substituting (2.90) into (2.12), using the fact that $c_L = c\nu_L$ and

$$\nabla \cdot (\mathbf{i}_e t_{0L}) = \mathbf{i}_e \cdot \nabla t_{0L} + t_{0L} \nabla \cdot \mathbf{i}_e = \mathbf{i}_e \cdot \nabla t_{0L}, \quad (2.91)$$

because of conservation of charge ($\nabla \cdot \mathbf{i}_e = 0$), the continuity equation for the concentrated binary electrolyte is given by

$$\frac{\partial c}{\partial t} = \nabla \cdot \left(D_e \left(1 - \frac{d \log c_0}{d \log c} \right) \nabla c \right) - \frac{\mathbf{i}_e \cdot \nabla t_{0L}}{z_L \nu_L F} - \nabla \cdot (c \mathbf{v}_0). \quad (2.92)$$

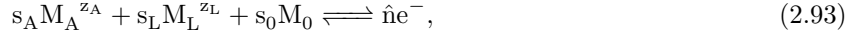
Current density and conservation of charge

To incorporate the electric potential as a driving force for the current we must first consider the thermodynamic principles facilitating the electrode reaction and thus, the role that the electric and chemical potentials

⁹We note that in the classic definition of this diffusion coefficient of the salt, m is used in place of y (Newman and Thomas-Alyea (2012); Plett (2015)). Mathematically this is inconsistent in our formulation since γ_{LA} is dimensionless while m is not, but this can be rectified by carefully retaining other constants, *i.e.* if one had mM_0 instead, this is dimensionless and $mM_0 = \frac{cM_0}{c_0M_0} = y$.

have in the reaction. In doing so, we will be able to derive an expression for the current density in terms of the electric and chemical potentials.

The general form for the electrode reaction involving a solvent and a binary electrolyte is



where M_k represents the chemical formula for the species (anion, cation, solvent) involved in the reaction, s_k is the signed stoichiometric coefficient of the species, and we have $\hat{n}$ moles of electrons e^- . For example, in a lithium ion cell we would have a reaction of the form



where M is a metal oxide, we have that $s_A = s_0 = 0$ since no anions or solvent take part in the reaction, $s_L = -1$, and $\hat{n} = 1$.

The energy change for reactions is given by the change in Gibbs free energy

$$\Delta G = \left(\sum_k s_k \mu_k \right) \Big|_{\text{forward}} - \left(\sum_k s_k \mu_k \right) \Big|_{\text{backward}}. \quad (2.95)$$

At equilibrium we expect that $\Delta G = 0$, and therefore from (2.93) and (2.95) we must have

$$\sum_k s_k \mu_k = \hat{n} \mu_{e^-}, \quad (2.96)$$

that is, the electrode reaction must balance the electrolyte reaction in terms of chemical potential equilibrium.

On the other hand, the maximum amount of work that be done by an electrochemical cell is the product of the total charge ($\hat{n}F$) and the cell potential (ϕ). Because the change in Gibbs free energy represents the thermodynamic potential for a reaction to occur, the following relation also holds for the total electrical work $\Delta G = -\hat{n}F\phi$ (Newman and Thomas-Alyea (2012)). The minus sign arises as the electrons want to move to the electrode where electrons have a lower electrochemical potential. Therefore, we have that $\mu_{e^-} = -F\phi$.

Thus, the equilibrium condition for the reaction can be written as

$$\underbrace{\sum_k s_k \mu_k}_{\text{Total change in Gibbs free energy}} = \underbrace{-\hat{n}F\phi}_{\text{electrical work done per mole of the reaction}} \quad (2.97)$$

Taking the gradient of (2.97)

$$s_L \nabla \mu_L + s_A \nabla \mu_A + s_0 \nabla \mu_0 = -\hat{n}F \nabla \phi. \quad (2.98)$$

We can use the Gibbs Duhem relationship (2.72) to eliminate μ_0

$$\nabla\mu_0 = \frac{-c_L\nabla\mu_L - c_A\nabla\mu_A}{c_0} \quad (2.99)$$

then using $c\nu_k = c_k$

$$\nabla\mu_0 = -\frac{c}{c_0} (\nu_L\nabla\mu_L + \nu_A\nabla\mu_A). \quad (2.100)$$

We then use the definition of μ_e (2.73) to rewrite (2.98) as

$$s_L\nabla\mu_L + s_A\nabla\mu_A - s_0\frac{c}{c_0}\nabla\mu_e = -\hat{n}F\nabla\phi. \quad (2.101)$$

In order to balance charge in (2.97) we must have

$$s_L z_L + s_A z_A = -\hat{n}. \quad (2.102)$$

Using (2.102) to eliminate s_A from (2.101) we have

$$s_L \left(\nabla\mu_L - \frac{z_L}{z_A} \nabla\mu_A \right) - \frac{\hat{n}}{z_A} \nabla\mu_A - \frac{s_0 c}{c_0} \nabla\mu_e = -\hat{n}F\nabla\phi, \quad (2.103)$$

and using that $\nu_A z_A = -\nu_L z_L$ from (2.1) to rewrite the first expression in terms of μ_e we can then say

$$\left(\frac{s_L}{\nu_L} - s_0 \frac{c}{c_0} \right) \nabla\mu_e - \frac{\hat{n}}{z_A} \nabla\mu_A = -\hat{n}F\nabla\phi. \quad (2.104)$$

We can eliminate μ_A so that (2.104) only depends on the chemical potential of the electrolyte similar to conservation of mass. To do this, we must consider (2.71) written in terms of the expressions we determined for the lithium (2.80) and anion (2.82) fluxes. Rearranging the expressions for the fluxes from (2.80) and (2.82), we can write $c_k \mathbf{v}_k - c_k \mathbf{v}_0$ in terms of $\nabla\mu_e$ and $\mathbf{i}_e$ for both equations as

$$c_L \mathbf{v}_L - c_L \mathbf{v}_0 = -\frac{\nu_L \mathcal{D} c_T}{\nu R T c_0} c \nabla\mu_e + \frac{\mathbf{i}_e t_{0L}}{z_L F}, \quad (2.105)$$

$$c_A \mathbf{v}_A - c_A \mathbf{v}_0 = -\frac{\nu_A \mathcal{D} c_T}{\nu R T c_0} c \nabla\mu_e + \frac{\mathbf{i}_e t_{0A}}{z_A F}. \quad (2.106)$$

Dividing each equation by c_k

$$\mathbf{v}_L - \mathbf{v}_0 = -\frac{\nu_L \mathcal{D} c_T}{\nu R T c_0 c_L} c \nabla\mu_e + \frac{\mathbf{i}_e t_{0L}}{z_L c_L F}, \quad (2.107)$$

$$\mathbf{v}_A - \mathbf{v}_0 = -\frac{\nu_A \mathcal{D} c_T}{\nu R T c_0 c_A} c \nabla\mu_e + \frac{\mathbf{i}_e t_{0A}}{z_A c_A F}. \quad (2.108)$$

Now, for (2.71) we want expressions for $\mathbf{v}_0 - \mathbf{v}_A$ and $\mathbf{v}_L - \mathbf{v}_A$, which we can obtain from the two equations above. The first of these is the negative of (2.106). For the second, we subtract the two expressions to obtain

$$\mathbf{v}_L - \mathbf{v}_A = \frac{\mathbf{i}_e}{F} \left(\frac{t_{0L}}{z_L c_L} - \frac{t_{0A}}{z_A c_A} \right) - \frac{\mathcal{D} c_T}{\nu R T c_0} \left(\frac{\nu_L}{c_L} - \frac{\nu_A}{c_A} \right) c \nabla\mu_e \quad (2.109)$$

where the second term will be zero since $c_k = \nu_k c$. The first term can also be simplified recalling that $c_L z_L = -c_A z_A$ by electroneutrality, and $t_{0A} = 1 - t_{0L}$ by definition of the transference numbers, reducing to

$$\mathbf{v}_L - \mathbf{v}_A = \frac{\mathbf{i}_e}{F z_L c_L}. \quad (2.110)$$

Therefore, substituting these relations for $\mathbf{v}_0 - \mathbf{v}_A$ and $\mathbf{v}_L - \mathbf{v}_A$ into (2.71) we have that

$$\frac{\nabla \mu_A}{z_A} = \frac{1}{c_A z_A} \left(K_{LA} \left(\frac{\mathbf{i}_e}{F z_L c_L} \right) + K_{A0} \left(\frac{\nu_A \mathcal{D} c_T}{\nu R T c_0 c_A} c \nabla \mu_e - \frac{\mathbf{i}_e t_{0A}}{z_A c_A F} \right) \right). \quad (2.111)$$

To simplify this expression we first consider the two terms multiplying $\mathbf{i}_e$, noting that applying $c_L z_L = -c_A z_A$, followed by (2.62), we can write

$$\frac{1}{c_A z_A} \left(K_{LA} \left(\frac{\mathbf{i}_e}{F z_L c_L} \right) - K_{A0} \left(\frac{\mathbf{i}_e t_{0A}}{z_A c_A F} \right) \right) = \frac{\mathbf{i}_e R T}{F c_T z_A z_L} \left(\frac{1}{D_{LA}} + \frac{c_0 t_{0A}}{c_L D_{0A}} \right). \quad (2.112)$$

For the $\nabla \mu_e$ term we again use (2.62), followed by the definitions of $\frac{\mathcal{D}}{D_{0A}}$ and t_{0L} from (2.81), and the relations $\nu = \nu_L + \nu_A$; $\nu_A z_A = -\nu_L z_L$ and $c_L z_L = -c_A z_A$; $c = \frac{c_L}{\nu_L}$ to write

$$\frac{K_{A0}}{c_A z_A} \left(\frac{\nu_A \mathcal{D} c_T}{\nu R T c_0 c_A} c \right) = -\frac{t_{0L}}{\nu_L z_L} \quad (2.113)$$

Putting these two expressions together we rewrite (2.111) as

$$\frac{\nabla \mu_A}{z_A} = -\frac{t_{0L}}{\nu_L z_L} \nabla \mu_e - \frac{F \mathbf{i}_e}{\kappa} \quad (2.114)$$

with κ being the ionic conductivity of the electrolyte, given by

$$\frac{1}{\kappa} = \frac{-R T}{c_T z_L z_A F^2} \left(\frac{1}{D_{LA}} + \frac{c_0 t_{0A}}{c_L D_{0A}} \right). \quad (2.115)$$

Substituting this into (2.104) and isolating for $\mathbf{i}_e$, we have the following equation for the current density

$$\mathbf{i}_e = -\kappa \nabla \phi - \frac{\kappa}{F} \left(\frac{s_L}{\hat{n} \nu_L} + \frac{t_{0L}}{z_L \nu_L} - \frac{s_0 c}{\hat{n} c_0} \right) \nabla \mu_e, \quad (2.116)$$

noting that we have $\nabla \mu_e$ in terms of concentration in (2.88). We still require conservation of charge to hold in the concentrated electrolyte case,

$$\nabla \cdot \mathbf{i}_e = 0. \quad (2.117)$$

Reduction of concentrated to dilute case

We take, for the concentrated electrolyte, the continuity equations and the current density, given by (2.92) and (2.116) respectively, with the multicomponent diffusion equation (2.69). For the dilute case, we had (2.24) and (2.30) with the fluxes given by (2.13).

Going from a concentrated solution to a dilute solution, we implement the assumption that the ion concentrations are small, so that $c_k \ll c_0$ and $c_T \approx c_0$. This then implies that

$$\frac{d \log c_0}{d \log c} \approx 0. \quad (2.118)$$

Furthermore, we remark that the transport properties - such as diffusion coefficients, transference numbers and conductivity - differ between the two theories. This is because interactions between ionic species are not explicitly accounted for in the dilute case, whereas the concentrated theory incorporates these effects through coupled transport relations. The transport properties associated with the concentrated theory equations are much more intricate than those of the dilute theory equations. In dilute theory, effective diffusion coefficients and transference numbers are defined as simple combinations of the individual species' diffusion coefficients and charge numbers. In contrast, concentrated theory requires the Stefan-Maxwell framework and a consideration of the solvent more explicitly in order to capture multi-species interaction and non-ideal solution behaviour. In this limit of low ionic concentration, ion-ion interactions and inter-species coupling become negligible; meaning that the transport properties from the concentrated theory equations simplify and the chemical potentials reduce to the ideal case - thus recovering the dilute theory transport relations. We can therefore see how the concentrated electrolyte equations reduce to the dilute solution equations in the limit of low ionic concentration.

Note on potentials

Having derived concepts such as the chemical potential for the concentrated electrolyte equations, we use these to reconcile the potentials in the dilute theory equations. We first acknowledge a distinction between chemical and electrochemical potentials. Both are a measure of the energy of a species; however, the chemical potential will depend on temperature, pressure, and composition, while the electrochemical potential also depends on the electric state. That is, neutral species will have a chemical potential, while charged species, such as ions and electrons, will have an electrochemical potential. The electrochemical potential, φ_k is related to the chemical potential μ_k , as derived and given by (2.51) via

$$\varphi_k = \mu_k + z_k F \phi = \mu_{k0}(T, p) + RT \log x_k + z_k F \phi, \quad (2.119)$$

where $z_k F \phi$ is the electrostatic potential and the chemical potential can be written as given by (2.51).

We note that the expression for the current density for the dilute electrolyte (2.30) differs from the form found in Newman's work (Newman and Thomas-Alyea (2012)). As highlighted by Richardson et al. (2022)

and other authors, this is as a result of how the electric potential is defined. Here we have considered, in a general sense, the electric potential of the electrolyte. This is distinct from the more commonly measured electric potential with respect to a reference electrode, which is also used in models, such as that of Newman and Thomas-Alyea (2012). This distinction arises since the electric potential of the electrolyte, ϕ , is more conceptual as it is not a readily measured quantity. We note that by definition, the electric potential is the energy needed per unit of charge to move the charge from a reference point to a specific point in the electric field. Therefore, in practice, because potential needs a reference point, a reference electrode is used. The reference electrode is usually made from a pure compound, for example, a lithium reference electrode is normally used in lithium-ion battery applications. Following Richardson et al. (2022) we define Φ to denote the electric potential with respect to a reference electrode.

In order to convert between the two forms of the potential we consider the following reversible reaction that occurs at the electrode-electrolyte interface



which says that at the interface, lithium ions and electrons react to form lithium, and vice versa. We can assume that this reaction is in quasi-equilibrium and therefore, the electrochemical potentials of both sides of the reaction must be equal

$$\varphi_{\text{Li}^+} + \varphi_{\text{e}^-} = \varphi_{\text{Li}}, \quad (2.121)$$

where φ_{Li^+} , φ_{e^-} , and φ_{Li} are the electrochemical potentials of the lithium ion, electron, and lithium atom, respectively. Considering our definition of the electrochemical potential in (2.119) and the chemical potential in (2.51) we can expand out the expressions for each of these electrochemical potentials. The lithium atom is neutral (no charge) and the activity coefficient of lithium metal is equal to one, therefore

$$\varphi_{\text{Li}} = \mu_{\text{Li}} = \mu_{\text{Li}}^0, \quad (2.122)$$

which is a constant. The electron has a negative charge (-1), so we obtain

$$\varphi_{\text{e}^-} = \mu_{\text{e}^-} + (z_{\text{e}} F \Phi) = \mu_{\text{e}^-}^0 - F \Phi, \quad (2.123)$$

where $\mu_{\text{e}^-}^0$ is related to the Fermi energy and there is no activity term for the electron because it is not a species in the electrolyte solution. Since the electrolyte does not conduct electrons, the electron resides in the electrode and is governed by electronic structure rather than thermodynamics. The lithium ion has a

positive charge (+1), leading to the expression

$$\varphi_{L+} = \mu_{L+} + (z_L F \phi) = \mu_{L+}^0 + RT \log\left(\frac{c_L}{c}\right) + F \phi. \quad (2.124)$$

Substituting (2.122), (2.123), and (2.124) into (2.121):

$$\mu_{L+}^0 + RT \log\left(\frac{c_L}{c}\right) + F \phi + \mu_{e-}^0 - F \Phi = \mu_{Li}^0. \quad (2.125)$$

Now, μ_{L+}^0 and μ_{e-}^0 are also constant, therefore we must have

$$\phi = \Phi - \frac{RT}{F} \log\left(\frac{c_L}{c_T}\right) + \text{constant}. \quad (2.126)$$

We can use this relation for ϕ in (2.30) to obtain the following alternate form for the current density in an Ohm's law format,

$$\frac{\mathbf{i}_e}{z_L \nu_L} = -\hat{\kappa}(c) \left(\nabla \Phi - \frac{RT}{F} \left(1 + \frac{u_A - u_L}{z_L u_L} t_L \right) \frac{\nabla c}{c} \right), \quad (2.127)$$

where we have again used $c_L = c \nu_L$ and the Einstein relation (2.26). We note that this is how the current density is presented by Newman and Thomas-Alyea (2012). We also remark that this can be written as

$$\mathbf{i}_e = -\hat{\kappa}(c) \left(\nabla \Phi - 2 \frac{RT}{F} (1 - t_L) \frac{\nabla c}{c} \right), \quad (2.128)$$

when $z_L = +1$, $z_A = -1$, and $\nu_L = +1$ as presented in Richardson et al. (2022).

Comments on concentrated theory

We note that the concentrated electrolyte equations provide a detailed description of the ionic behaviours in electrolytes, however, there are still criticisms of the model to address. Concentrated electrolyte theory draws on principles from thermodynamics, however not all thermodynamics laws are satisfied. For example, it has been observed that the concentrated equations violate the Onsager relation (Casimir (1945), Rajagopal and Srinivasa (2004)), and therefore may not satisfy the necessary condition that entropy production is strictly positive (Taylor and Krishna (1993); Latz and Zausch (2011)). We note that having a thermodynamically consistent model is important in the context of batteries, particularly if local heat production is to be included in the model (Latz et al. (2010)). Therefore, we will address this by considering a fully thermodynamic derivation of the equations for an electrolyte model.

2.2.5 Thermodynamic approach

We reiterate that in thermodynamics there is a focus on understanding energy and equilibrium states. The primary variables reflect this: free energies, entropy, and chemical potentials. Thermodynamic and continuum models can be complementary; implementing thermodynamic principles in the derivation of a continuum model will lead to a thermodynamically consistent model, which can help to achieve a more complete understanding of electrolyte behaviour in electrochemical systems. While the concentrated electrolyte model from the previous section relies on thermodynamics principles, it is not entirely derived from a thermodynamic standpoint. Therefore, in this section, we will first provide a background for non-equilibrium thermodynamics and the concepts therein that will be used in deriving the electrolyte equations from first principles. We note that this differs from the previous sections as the dilute and concentrated models are derived specifically for the purpose of modelling an electrolyte. However, here we derive the thermodynamic equations in a general sense and then apply these generalised equations to the specific scenario of modelling an electrolyte.

Non-equilibrium thermodynamics

Thermodynamics is concerned with transport processes, rates of chemical reactions, and the energy relationship between systems. A system is said to be in thermodynamic equilibrium if its properties do not change when isolated. Most systems in nature are not in thermodynamic equilibrium but are near enough to be described by nonequilibrium thermodynamics. The difference between equilibrium and nonequilibrium thermodynamics is in the treatment of time. Equilibrium thermodynamics mostly accounts for the initial and final states of the system, like a quasi-static process, whereas nonequilibrium thermodynamics attempts to describe the time courses of a system in continuous detail (De Groot and Mazur (2013)).

In thermodynamics an equation of state is used to relate the state variables, which describe the state of matter of the system under particular conditions. Equations of state typically relate the properties of pressure, temperature, density, and internal energy. Furthermore, all thermodynamic quantities can be written in terms of temperature, pressure, and volume (De Groot and Mazur (2013)). The general form of an equation of state is

$$f(p, V, T) = 0, \tag{2.129}$$

where p is pressure, V is volume, and T is temperature. One equation of state that we have encountered in

our derivation of the Gibbs-Duhem relationship is the ideal gas law, given by

$$pV = \hat{n}RT. \quad (2.130)$$

Thermodynamic properties can be extended using the concept of a local thermodynamic equilibrium. If we assume that a system can be partitioned into small homogeneous volume elements, where individual volumes are small enough to be in thermodynamic equilibrium but large enough to be described by thermodynamic quantities (Di Vita (2022)). In this case, the intensive variables are often used as the independent variables. For example, consider the equation of state $\rho = \rho(T, p)$ where ρ is density

$$\begin{aligned} d\rho &= \left. \frac{\partial \rho}{\partial T} \right|_p dT + \left. \frac{\partial \rho}{\partial p} \right|_T dp \\ &= \rho \left(\frac{1}{\rho} \left. \frac{\partial \rho}{\partial T} \right|_p dT + \frac{1}{\rho} \left. \frac{\partial \rho}{\partial p} \right|_T dp \right) \\ &= \rho (-\alpha_t dT + X dp), \end{aligned} \quad (2.131)$$

where α_t is the coefficient of thermal expansion and X is the isothermal compressibility (De Groot and Mazur (2013)). If we apply the assumption of local thermodynamic equilibrium, then the thermodynamic quantities hold in the new fields (De Groot and Mazur (2013)):

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= \rho(x, t) \left(-\alpha_t \frac{\partial T(x, t)}{\partial t} + X \frac{\partial p(x, t)}{\partial t} \right) \\ \nabla \rho &= \rho (-\alpha_t \nabla T(x, t) + X \nabla p(x, t)). \end{aligned} \quad (2.132)$$

These concepts will be used in the derivations for the following sections. We will derive conservation of mass, momentum, and energy, which will be necessary to arrive at the relevant equations for the electrolyte.

Conservation of mass

As considered earlier in the dilute limit derivation, we consider an arbitrary volume element ΔV , where we now assume local thermodynamic equilibrium applies. Any change in mass in this volume element must be due to mass moving through the boundary ∂V

$$\frac{d}{dt} \int_{\Delta V} \rho(x, t) dV = - \int_{\partial V} \rho \mathbf{v} \cdot \mathbf{n} dS, \quad (2.133)$$

here $\mathbf{n}$ is the outward facing normal and $\mathbf{v} = \mathbf{v}(x, t)$ represents a centre of mass velocity. Assuming that ΔV is constant and applying the divergence theorem we have

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0. \quad (2.134)$$

For a multicomponent system, where each species k has density ρ_k and velocity $\mathbf{v}_k$, (2.134) applies for each species,

$$\frac{\partial \rho_k}{\partial t} + \nabla \cdot (\rho_k \mathbf{v}_k) = 0 \quad (2.135)$$

where the centre of mass velocity and the total density of the mixture are given by

$$\mathbf{v}(x, t) = \frac{\sum_k \rho_k \mathbf{v}_k}{\rho}, \quad \rho = \sum_k \rho_k. \quad (2.136)$$

We can define a diffusive flux by

$$\mathbf{J}_k = \rho_k (\mathbf{v}_k - \mathbf{v}); \quad (2.137)$$

rewriting (2.135) in terms of the flux, we will have

$$\frac{\partial \rho_k}{\partial t} + \nabla \cdot (\rho_k \mathbf{v}) = -\nabla \cdot \mathbf{J}_k, \quad (2.138)$$

which we note is analogous to our earlier equation relating to the dilute electrolyte (2.12).

Conservation of momentum

In order to conserve momentum we must consider body forces $\mathbf{f}$ and surface forces σ , σ will be a second order tensor with component σ_{kj} representing force in direction k of a surface with normal j . The force acting on the surface can then be given by $dF_s = -\sigma \cdot \mathbf{n} dS$ (De Groot and Mazur (2013)). Applying the divergence theorem

$$dF_s = -\nabla \cdot \sigma^T dV. \quad (2.139)$$

Usually, for fluids, torques will cause symmetry so that $\sigma^T = \sigma$ (De Groot and Mazur (2013)). In general, the surface forces take the form (De Groot and Mazur (2013))

$$\sigma = p\mathbf{I} - \mathbf{D}_s, \quad (2.140)$$

where $\mathbf{I}$ is the identity tensor and $\mathbf{D}_s$ is the component of the surface forces that causes movement and is known as the deviatoric stress tensor. The minus sign arises because $\mathbf{n}$ is the outward facing normal, while forces (such as pressure) act inwards – opposite to $\mathbf{n}$. If a fluid is at rest then the only force to consider is pressure, $\sigma = p\mathbf{I}$.

The conservation of momentum can be written as:

$$\frac{d}{dt} \int_{\Delta V} \rho \mathbf{v} dV = \int_{\Delta V} \mathbf{f} dV - \int_{\Delta V} \nabla \cdot \sigma dV. \quad (2.141)$$

Applying Reynold's Transport Theorem we obtain

$$\int_{\Delta V} \left(\frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) \right) dV = \int_{\Delta V} \mathbf{f} dV - \int_{\Delta V} \nabla \cdot \boldsymbol{\sigma} dV \quad (2.142)$$

$$\implies \frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) = \mathbf{f} - \nabla p + \nabla \cdot \mathbf{D}_s \quad (2.143)$$

in the centre of mass framework. To simplify the expression we expand the terms on the left-hand side and recall the conservation of mass (2.134) to obtain the following equation for conservation of momentum

$$\rho \frac{d\mathbf{v}}{dt} = \mathbf{f} - \nabla p + \nabla \cdot \mathbf{D}_s = \mathbf{f} - \nabla \cdot \boldsymbol{\sigma}, \quad (2.144)$$

where the derivative on the left-hand side is the material derivative, defined by

$$\frac{d\mathbf{y}}{dt} = \left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right) \mathbf{y}. \quad (2.145)$$

We note that body forces are proportional to mass and can therefore be written as $\mathbf{f} = \rho \mathbf{b}$, where $\mathbf{b}$ is the body force per unit mass. In an isothermal steady case, if we have $\mathbf{v}=0$, then $\nabla p = \mathbf{f}$, from the conservation of momentum equation (2.144). Therefore, we assume that body forces are conservative, *i.e.* $\mathbf{b} = -\nabla \psi$ for some scalar potential field ψ , and thus $\mathbf{f}$ can further be written in terms of a scalar field as¹⁰

$$\mathbf{f}(\mathbf{x}, t) = -\rho(\mathbf{x}, t) \nabla \psi(\mathbf{x}), \quad (2.146)$$

or for a multicomponent system

$$\mathbf{f} = - \sum_k \rho_k(\mathbf{x}, t) \nabla \psi_k(\mathbf{x}), \quad (2.147)$$

where ψ is the mass-averaged potential energy

$$\psi(\mathbf{x}, t) = \frac{\sum_k \rho_k \psi_k}{\rho}. \quad (2.148)$$

Conservation of energy

Total energy in a system should be locally conserved, where total energy is given by ρe with

$$\rho e = \frac{1}{2} \rho \mathbf{v}^2 + \rho \psi + \rho u, \quad (2.149)$$

where the right-hand side terms correspond to kinetic energy, potential energy and internal energy, respectively. Since $\psi_k = \psi_k(x)$ and from (2.148) we can take the time derivative of the potential energy to get

$$\frac{\partial (\rho \psi)}{\partial t} = \sum_k \frac{\partial \rho_k}{\partial t} \psi_k. \quad (2.150)$$

¹⁰The minus sign arises because the force acts in the direction of decreasing potential.

Applying conservation of mass from (2.138) to $\rho_k \psi_k$ and expanding

$$\nabla \cdot (\rho_k \psi_k \mathbf{v}) = \psi_k \nabla \cdot (\rho_k \mathbf{v}) + \rho_k \mathbf{v} \cdot \nabla \psi_k \quad (2.151)$$

and

$$\nabla \cdot (\psi_k \mathbf{J}_k) = \mathbf{J}_k \cdot \nabla \psi_k + \psi_k \nabla \cdot \mathbf{J}_k, \quad (2.152)$$

which we can then rearrange to determine an expression for $\frac{\partial \rho_k}{\partial t} \psi_k$. From here we combine (2.150), (2.151), (2.152), sum over k , and recall (2.147), to define conservation of potential energy

$$\frac{\partial (\rho \psi)}{\partial t} + \nabla \cdot \left(\rho \psi \mathbf{v} + \sum_k \psi_k \mathbf{J}_k \right) = \sum_k \mathbf{J}_k \cdot \nabla \psi_k - \mathbf{f} \cdot \mathbf{v}. \quad (2.153)$$

For kinetic energy we first consider that

$$\frac{d(\rho \mathbf{v} \cdot \mathbf{v})}{dt} = \mathbf{v}^2 \frac{d\rho}{dt} + \rho \frac{d(\mathbf{v} \cdot \mathbf{v})}{dt} = 2\rho \mathbf{v} \cdot \frac{d\mathbf{v}}{dt} + \mathbf{v}^2 \frac{d\rho}{dt}. \quad (2.154)$$

Writing conservation of mass (2.134) in terms of the material derivative, we have that $\frac{d\rho}{dt} = -\rho \nabla \cdot \mathbf{v}$ and using conservation of momentum (2.144), we can rewrite (2.154) for conservation of kinetic energy as

$$\frac{d(\frac{1}{2} \rho \mathbf{v}^2)}{dt} = -\frac{1}{2} \rho \mathbf{v}^2 \nabla \cdot \mathbf{v} + \mathbf{f} \cdot \mathbf{v} - \mathbf{v} \cdot (\nabla \cdot \sigma). \quad (2.155)$$

Expanding the expression for the material derivative,

$$\frac{\partial(\frac{1}{2} \rho \mathbf{v}^2)}{\partial t} + \mathbf{v} \cdot \nabla \left(\frac{1}{2} \rho \mathbf{v}^2 \right) = -\frac{1}{2} \rho \mathbf{v}^2 \nabla \cdot \mathbf{v} + \mathbf{f} \cdot \mathbf{v} - \mathbf{v} \cdot (\nabla \cdot \sigma). \quad (2.156)$$

Then, noting that $\nabla \cdot (\frac{1}{2} \rho \mathbf{v}^2 \mathbf{v}) = \mathbf{v} \cdot \nabla (\frac{1}{2} \rho \mathbf{v}^2) + \frac{1}{2} \rho \mathbf{v}^2 \nabla \cdot \mathbf{v}$ and that $\nabla \cdot (\sigma \cdot \mathbf{v}) = (\nabla \cdot \sigma) \cdot \mathbf{v} + \sigma : \nabla \mathbf{v}$, where we define $\sigma : \nabla \mathbf{v} = \sum_{kj} \sigma_{kj} \frac{\partial \mathbf{v}_k}{\partial x_j}$, the final expression for conservation of kinetic energy can be written as

$$\frac{\partial(\frac{1}{2} \rho \mathbf{v}^2)}{\partial t} = -\nabla \cdot \left(\frac{1}{2} \rho \mathbf{v}^2 \mathbf{v} + \sigma \cdot \mathbf{v} \right) + \mathbf{f} \cdot \mathbf{v} + \sigma : \nabla \mathbf{v}. \quad (2.157)$$

Adding potential and kinetic energy gives us an expression for conservation of mechanical energy:

$$\frac{\partial(\frac{1}{2} \rho \mathbf{v}^2 + \rho \psi)}{\partial t} = -\nabla \cdot \left(\left(\frac{1}{2} \rho \mathbf{v}^2 + \rho \psi \right) \mathbf{v} + \sigma \cdot \mathbf{v} + \sum_k \psi_k \mathbf{J}_k \right) + \sum_k \mathbf{J}_k \cdot \nabla \psi_k + \sigma : \nabla \mathbf{v}. \quad (2.158)$$

We notice from expression (2.158) that mechanical energy, $\frac{1}{2} \rho \mathbf{v}^2 + \rho \psi$, is not locally conserved, as there are source terms outside of the divergence. In fact, mechanical energy need not be locally conserved, but rather the total energy. For the total energy to be conserved, the equation for the conservation of the internal energy, u , must take the form

$$\rho \frac{du}{dt} = -\nabla \cdot \mathbf{Q} - \sigma : \nabla \mathbf{v} - \sum_k \mathbf{J}_k \cdot \nabla \psi_k, \quad (2.159)$$

where $\nabla \cdot \mathbf{Q}$ represents the transfer of thermodynamic energy that is not associated to flow. Expanding the material derivative and adding u times conservation of mass gives, for the left-hand side of (2.159),

$$\rho \frac{du}{dt} = \rho \left(\frac{\partial u}{\partial t} + \mathbf{v} \cdot \nabla u \right) + u \left(\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) \right), \quad (2.160)$$

noting that since conservation of mass is equal to zero, the equation is unchanged. Writing the left-hand side in this way allows us to rearrange terms to write

$$\rho \frac{du}{dt} = \frac{\partial(\rho u)}{\partial t} + \nabla \cdot (\rho u \mathbf{v}). \quad (2.161)$$

Then, using this expression, (2.161), the equation for conservation of internal (thermodynamic) energy from (2.159) can be written as:

$$\begin{aligned} \frac{\partial(\rho u)}{\partial t} &= -\nabla \cdot (\rho u \mathbf{v} + \mathbf{Q}) - \sigma : \nabla \mathbf{v} - \sum_k \mathbf{J}_k \cdot \nabla \psi_k \\ &= -\nabla \cdot (\rho u \mathbf{v} + \mathbf{Q}) - p \nabla \cdot \mathbf{v} + \mathbf{D}_s : \nabla \mathbf{v} - \sum_k \mathbf{J}_k \cdot \nabla \psi_k. \end{aligned} \quad (2.162)$$

Thermodynamic laws

The first law of thermodynamics is a version of conservation of energy; it is written as

$$dU = T dS - p dV + \sum_k \mu_k d\hat{n}_k, \quad (2.163)$$

where U is the internal energy, S is the entropy, μ_k is the chemical potential of species k and $\hat{n}_k$ is the number of moles of species k . We consider a fixed volume and divide by mass, m ¹¹

$$du = T ds - p dv + \sum_k \frac{\mu_k M_k}{M_k} \frac{d\hat{n}_k}{m} = T ds - p dv + \sum_k \bar{\mu}_k dw_k, \quad (2.164)$$

where M_k is the molar mass of species k , $\bar{\mu}_k = \frac{\mu_k}{M_k}$, $w_k = \frac{\rho_k}{\rho}$, $M_k \hat{n}_k = m_k$, and $\rho_k = \frac{m_k}{V}$. Then entropy can be written as

$$T ds = du + p dv - \sum_k \bar{\mu}_k dw_k. \quad (2.165)$$

Using the assumption of local thermal equilibrium and noting that since v is a volume per mass, $dv = d\left(\frac{1}{\rho}\right) = -\frac{1}{\rho^2} d\rho$, we must have that

$$T \frac{\partial s}{\partial t} = \frac{\partial u}{\partial t} - \frac{p}{\rho^2} \frac{\partial \rho}{\partial t} - \sum_k \bar{\mu}_k \frac{\partial w_k}{\partial t}, \quad (2.166)$$

$$T \nabla s = \nabla u - \frac{p}{\rho^2} \nabla \rho - \sum_k \bar{\mu}_k \nabla w_k. \quad (2.167)$$

¹¹An extensive property, X , can be made specific by dividing by mass, m , whereby the specific property is then denoted x with $x = \frac{X}{m}$.

Then multiplying (2.166) by ρ and (2.167) by $\rho \mathbf{v}$ and adding these together

$$T\rho \left(\frac{\partial s}{\partial t} + \mathbf{v} \cdot \nabla s \right) = \rho \left(\frac{\partial u}{\partial t} + \mathbf{v} \cdot \nabla u - \frac{p}{\rho^2} \left(\frac{\partial \rho}{\partial t} + \mathbf{v} \cdot \nabla \rho \right) - \sum_k \bar{\mu}_k \left(\frac{\partial w_k}{\partial t} + \mathbf{v} \cdot \nabla w_k \right) \right). \quad (2.168)$$

Next, for each term (except density), we will add zero in the form of a conservation of mass term (2.134), that is, for each variable we can write the following

$$\rho \left(\frac{\partial x}{\partial t} + \mathbf{v} \cdot \nabla x \right) + x \left(\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) \right) = \frac{\partial(\rho x)}{\partial t} + \nabla \cdot (\rho x \mathbf{v}), \quad x = s, u, w_k. \quad (2.169)$$

For the density terms we will use conservation of mass again as follows:

$$\frac{\partial \rho}{\partial t} + \mathbf{v} \cdot \nabla \rho = \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) - \rho \nabla \cdot \mathbf{v} = -\rho \nabla \cdot \mathbf{v}. \quad (2.170)$$

Using these substitutions in (2.168), noting that $\rho w_k = \rho_k$, $\frac{\partial \rho_k}{\partial t} + \nabla \cdot (\rho_k \mathbf{v}) = -\nabla \cdot \mathbf{J}_k$ from (2.138), and using the expression for the internal energy given by (2.162), we obtain

$$\frac{\partial(\rho s)}{\partial t} = -\nabla \cdot (\rho s \mathbf{v}) + \frac{1}{T} \left(-\nabla \cdot \mathbf{Q} + \mathbf{D}_s : \nabla \mathbf{v} - \sum_k \mathbf{J}_k \cdot \nabla \psi_k + \sum_k \bar{\mu}_k \nabla \cdot \mathbf{J}_k \right). \quad (2.171)$$

Finally, if we rewrite the $\mathbf{Q}$ and $\bar{\mu}_k$ terms using

$$\nabla \cdot \left(\frac{\mathbf{Q}}{T} \right) = \frac{1}{T} \nabla \cdot \mathbf{Q} - \frac{\mathbf{Q}}{T^2} \cdot \nabla T \quad (2.172)$$

and

$$\nabla \cdot \left(\frac{\bar{\mu}_k \mathbf{J}_k}{T} \right) = \nabla \cdot \left(\frac{\bar{\mu}_k}{T} \right) \cdot \mathbf{J}_k + \frac{\bar{\mu}_k}{T} \nabla \cdot \mathbf{J}_k \quad (2.173)$$

we have

$$\frac{\partial(\rho s)}{\partial t} = -\nabla \cdot \left(\rho s \mathbf{v} + \frac{1}{T} (\mathbf{Q} - \bar{\mu}_k \mathbf{J}_k) \right) + \xi \quad (2.174)$$

where we define the entropy production ξ as

$$\xi = -\frac{\mathbf{Q} \cdot \nabla T}{T^2} + \frac{\mathbf{D}_s : \nabla \mathbf{v}}{T} - \frac{1}{T} \sum_k \mathbf{J}_k \cdot \left(T \nabla \left(\frac{\bar{\mu}_k}{T} \right) + \nabla \psi_k \right). \quad (2.175)$$

We note that the second law of thermodynamics says that $\xi \geq 0$. For more information on the entropy production and its derivation we refer to chapter 2 of Taylor and Krishna (1993).

According to the Onsager reciprocal relations (Casimir (1945), Rajagopal and Srinivasa (2004)), the entropy production can be written as the sum of the dot product of each of the operating fluxes with the gradient of the corresponding thermodynamic forces. Defining the dissipative function $\Psi = T\xi$, we then have:

$$\Psi = \sum_k \mathbf{L}_k \mathbf{X}_k, \quad (2.176)$$

where $\mathbf{L}_k$ are the dissipative fluxes – such as $-\mathbf{Q}$, $\mathbf{D}_s$, and $\mathbf{J}_k$; and $\mathbf{X}_k$ are the gradients of the corresponding thermodynamic forces – such as $\frac{\nabla T}{T}$, $\nabla \mathbf{v}$, $T \nabla \left(\frac{\mu_k}{T} \right)$, and $\nabla \psi_k$. We note that as the system approaches equilibrium, the entropy production can be described by a linear relation between the forces and fluxes (Taylor and Krishna (1993)),

$$L_j = \sum_k M_{jk} X_k, \quad (2.177)$$

which then tells us that

$$\Psi = \sum_{jk} M_{jk} X_j X_k = \mathbf{X}^T \mathbf{M} \mathbf{X}. \quad (2.178)$$

Furthermore, following the second law ($\xi \geq 0$), we must have that $\Psi \geq 0$, therefore $\mathbf{M}$ must be positive semi-definite. In addition, $\mathbf{M}$ must be symmetric due to time reversal invariance, or the Onsager reciprocal relation (Onsager (1931)). We also note that from the Curie-Prigogine principle, thermodynamic forces of different tensorial components are uncoupled (De Groot and Mazur (2013)).

Thermodynamic derivation of electrolyte equations

In this section we implement the thermodynamic laws and principles presented in the previous sections to derive a thermodynamically consistent model for an electrolyte, under isothermal conditions. For the purpose of generality we assume that we have an electrolyte composed of three species: cations (c), anions (a), and solvent (s). We then use these equations as a basis for more specific models in Chapters 3 and 4.

We have a conservation of mass equation (2.138) for each species $k = c, a, s$,

$$\frac{\partial \rho_c}{\partial t} + \nabla \cdot (\rho_c \mathbf{v}_c) = 0, \quad (2.179a)$$

$$\frac{\partial \rho_a}{\partial t} + \nabla \cdot (\rho_a \mathbf{v}_a) = 0, \quad (2.179b)$$

$$\frac{\partial \rho_s}{\partial t} + \nabla \cdot (\rho_s \mathbf{v}_s) = 0, \quad (2.179c)$$

where $\rho_k = m_k n_k$ is the mass density of each species, m_k is the atomic mass, n_k is the number density, and $\mathbf{v}_k$ is the species velocity. We define the total density by $\rho = \sum_k \rho_k$ and the mass averaged velocity by $\mathbf{v} = \frac{1}{\rho} \sum_k \rho_k \mathbf{v}_k$. For each species we have a diffusive flux defined by an equation of the form (2.137),

$$\mathbf{J}_k = \rho_k (\mathbf{v}_k - \mathbf{v}). \quad (2.180)$$

We note that, as a result of conservation of total mass in the system,

$$\sum_k \mathbf{J}_k = \sum_k \rho_k (\mathbf{v}_k - \mathbf{v}) = \sum_k \rho_k \mathbf{v}_k - \sum_k \rho_k \mathbf{v} = 0. \quad (2.181)$$

We derived an expression for entropy production from nonequilibrium thermodynamics, which we now implement for the electrolyte. Substituting $\mathbf{D}_s = 0$, constant temperature T , and taking the general form of the electrochemical potential (2.119) as $\mu_{\text{electrochemical}} = \mu_{\text{chemical}} + zF\nabla\phi$ for each species, we can write the entropy production equation from (2.175) as

$$\xi = -\frac{1}{T} \sum_k (\nabla\mu_k + z_k \nabla\phi) \cdot \frac{\mathbf{J}_k}{m_k}, \quad (2.182)$$

where we have z_k as species charge, μ_k is species chemical potential, and ϕ is the electric potential. It then follows from (2.178) that, assuming the fluxes depend linearly on the thermodynamic driving forces, $\nabla(\mu_k + z_k \phi)$ (see Onsager (1931); Prigogine and Van Rysselberghe (1963); De Groot and Mazur (2013); Rajagopal and Srinivasa (2004)), we can write

$$\mathbf{J} = \begin{bmatrix} \frac{\mathbf{J}_a}{m_a} \\ \frac{\mathbf{J}_c}{m_c} \\ \frac{\mathbf{J}_s}{m_s} \end{bmatrix} = - \underbrace{\begin{bmatrix} N_{aa} & N_{ac} & N_{as} \\ N_{ca} & N_{cc} & N_{cs} \\ N_{sa} & N_{sc} & N_{ss} \end{bmatrix}}_{\mathbf{M}} \underbrace{\begin{bmatrix} \nabla\mu_a + z_a \nabla\phi \\ \nabla\mu_c + z_c \nabla\phi \\ \nabla\mu_s + z_s \nabla\phi \end{bmatrix}}_{\mathbf{X}} \quad (2.183)$$

It appears that we have nine constants of proportionality here, but find that they are not all unique based on the following principles. Physically, we need entropy production to be positive so the matrix must be positive semi-definite, Onsager (1931) tells us that the matrix should be symmetric so we must have $N_{ij} = N_{ji}$, and the Curie-Prigogine principle (also referred to as *Curie's law*) says that thermodynamic forces of different tensorial components are uncoupled (De Groot and Mazur (2013)), *i.e.* only symmetry-allowed coupling between the forces and fluxes can exist; thus,

$$\mathbf{J} = \begin{bmatrix} \frac{\mathbf{J}_a}{m_a} \\ \frac{\mathbf{J}_c}{m_c} \\ \frac{\mathbf{J}_s}{m_s} \end{bmatrix} = - \begin{bmatrix} N_{aa} & N_{ac} & N_{as} \\ N_{ac} & N_{cc} & N_{cs} \\ N_{as} & N_{cs} & N_{ss} \end{bmatrix} \begin{bmatrix} \nabla\mu_a + z_a \nabla\phi \\ \nabla\mu_c + z_c \nabla\phi \\ \nabla\mu_s + z_s \nabla\phi \end{bmatrix}. \quad (2.184)$$

Now, because $\sum_k \mathbf{J}_k = 0$, only two of the fluxes are independent and we can write

$$\frac{\mathbf{J}_s}{m_s} = -\frac{\mathbf{J}_a}{m_s} - \frac{\mathbf{J}_c}{m_s}. \quad (2.185)$$

From (2.184),

$$\begin{aligned} \frac{\mathbf{J}_a}{m_s} &= \frac{m_a}{m_s} \left(\frac{\mathbf{J}_a}{m_a} \right) \\ &= \frac{m_a}{m_s} (-N_{aa} (\nabla\mu_a + z_a \nabla\phi) - N_{ac} (\nabla\mu_c + z_c \nabla\phi) - N_{as} (\nabla\mu_s + z_s \nabla\phi)) \end{aligned} \quad (2.186)$$

and

$$\begin{aligned}\frac{\mathbf{J}_c}{m_s} &= \frac{m_c}{m_s} \left(\frac{\mathbf{J}_c}{m_c} \right) \\ &= \frac{m_c}{m_s} (-N_{ac} (\nabla \mu_a + z_a \nabla \phi) - N_{cc} (\nabla \mu_c + z_c \nabla \phi) - N_{cs} (\nabla \mu_s + z_s \nabla \phi)).\end{aligned}\quad (2.187)$$

If we substitute (2.186) and (2.187) into (2.185) and equate this with the expression for $\mathbf{J}_s$ from (2.184), *i.e.*

$$\begin{aligned}\frac{\mathbf{J}_s}{m_s} &= -\frac{m_a}{m_s} \left(\frac{\mathbf{J}_a}{m_a} \right) - \frac{m_c}{m_s} \left(\frac{\mathbf{J}_c}{m_c} \right) \\ &= -N_{as} (\nabla \mu_a + z_a \nabla \phi) - N_{cs} (\nabla \mu_c + z_c \nabla \phi) - N_{ss} (\nabla \mu_s + z_s \nabla \phi),\end{aligned}\quad (2.188)$$

we can find relations between the N_{ij} ;

$$N_{as} = -\frac{m_a}{m_s} N_{aa} - \frac{m_c}{m_s} N_{ac}, \quad (2.189a)$$

$$N_{cs} = -\frac{m_a}{m_s} N_{ac} - \frac{m_c}{m_s} N_{cc}, \quad (2.189b)$$

$$N_{ss} = -\frac{m_a}{m_s} N_{as} - \frac{m_c}{m_s} N_{cs}. \quad (2.189c)$$

Therefore, upon rearranging terms, we will write our fluxes as follows

$$\frac{\mathbf{J}_a}{m_a} = -N_{aa} \left(\nabla \left(\mu_a - \frac{m_a}{m_s} \mu_s \right) + \left(z_a - \frac{m_a}{m_s} z_s \right) \nabla \phi \right) - N_{ac} \left(\nabla \left(\mu_c - \frac{m_c}{m_s} \mu_s \right) + \left(z_c - \frac{m_c}{m_s} z_s \right) \nabla \phi \right), \quad (2.190a)$$

$$\frac{\mathbf{J}_c}{m_c} = -N_{ac} \left(\nabla \left(\mu_a - \frac{m_a}{m_s} \mu_s \right) + \left(z_a - \frac{m_a}{m_s} z_s \right) \nabla \phi \right) - N_{cc} \left(\nabla \left(\mu_c - \frac{m_c}{m_s} \mu_s \right) + \left(z_c - \frac{m_c}{m_s} z_s \right) \nabla \phi \right), \quad (2.190b)$$

$$\frac{\mathbf{J}_s}{m_s} = -\frac{\mathbf{J}_a}{m_s} - \frac{\mathbf{J}_c}{m_s}, \quad (2.190c)$$

where the $N_{i,j}$'s are empirical constants such as mobility coefficients, which are determined via constitutive relations; for an example, see below in the next section. Comparing these flux equations with those derived in (2.90) for concentrated theory and (2.13) for dilute theory, we observe that the expressions for the flux are where the primary distinctions between the various modelling approaches (dilute, concentrated, thermodynamic) arise. We note that the driving forces for these thermodynamic flux equations (2.190) are the chemical and electric potentials, as is the case for the concentrated electrolyte equations, while we remarked that the driving forces in the dilute case were gradients of concentration and electric potentials. Furthermore, the thermodynamically derived expressions for the flux are based on upholding particular laws of thermodynamics such as that of Onsager and the Curie-Prigogine principle, which are not explicitly guaranteed in the concentrated or dilute fluxes.

The general form of the chemical potential for each species k is

$$\mu_k = \mu_{k0}(T, p) + k_B T \log \left(\frac{n_k}{n} \gamma_k \right) = \mu_{k0}(T, p) + k_B T \log \left(\frac{n_k}{n} \right) + k_B T \log (\gamma_k), \quad (2.191)$$

where $n = \sum_k n_k$, γ_k is the non ideality, and μ_{k0} is the reference chemical potential.¹²

Relating concentrated and thermodynamic approaches

We take the equations derived from thermodynamic principles and show how they relate to the equations for concentrated electrolyte theory. Again, we consider a binary electrolyte composed of solvent, cations, and anions. We use the subscript L for the cations, A for the anions, 0 for the solvent to align with the concentrated equations notation.

As in the concentrated theory case, the solvent can be eliminated as an independent variable using the Gibbs-Duhem relationship (2.72). We have:

$$c_0 d\mu_0 + c_L d\mu_L + c_A d\mu_A = 0, \quad (2.192)$$

and recalling that we can write $\mu_k = RT \log x_k = \log \frac{c_k}{c_T}$, we can rewrite the above equation. Dividing across by RT and multiplying by N_A (Avogadro's number), we obtain:

$$dn_0 + dn_L + dn_A = 0, \quad (2.193)$$

which we can use to eliminate the solvent.

We note that we did not make any assumptions about electroneutrality in the thermodynamic derivations, however, we do so now, assuming local electroneutrality (*i.e.* (2.4))

$$z_L c_L + z_A c_A = 0. \quad (2.194)$$

Due to electroneutrality we have the relation $c_A = -\frac{z_L c_L}{z_A}$, and since $N_A c_k = n_k$, we can write $n_A = -\frac{z_L n_L}{z_A}$ so that

$$\begin{aligned} dn_0 &= -dn_L - dn_A \\ &= -dn_L + \frac{z_L}{z_A} dn_L. \end{aligned} \quad (2.195)$$

¹²We note that here it is more consistent to use k_B instead of R ($R = N_A k_B$), as used in (2.51), in our definition of the chemical potential since we are using number density here, while in the dilute and concentrated theory equations, we use concentration as our variable for the amount of each species ($n = N_A c$).

We define effective chemical potentials:

$$\bar{\mu}_L = \mu_L - \mu_0 \quad (2.196)$$

$$\bar{\mu}_A = \mu_A - \mu_0 \quad (2.197)$$

$$\bar{\mu} = \bar{\mu}_L - \frac{z_L}{z_A} \bar{\mu}_A. \quad (2.198)$$

These effective chemical potentials can then be used to eliminate the solvent from the entropy equation because we can rewrite

$$\sum_{k=0,L,A} \mu_k \, dn_k = \bar{\mu} \, dn_L. \quad (2.199)$$

We will assume isothermal conditions, $\mathbf{D}_s = 0$, and we allow for the effects of the external electric field explicitly. Using our entropy production equation (2.182), we will have the following relation:

$$\xi = -\frac{1}{T} \sum_k (\nabla \bar{\mu}_k + z_k \nabla \phi) \cdot \mathbf{J}_k = -\frac{1}{T} (\mathbf{J}_A \cdot (\nabla \bar{\mu}_A + z_A \nabla \phi) + \mathbf{J}_L \cdot (\nabla \bar{\mu}_L + z_L \nabla \phi)). \quad (2.200)$$

Writing $\mathbf{J}_A$ in terms of $\mathbf{i}_e$ and $\mathbf{J}_L$ using the definition of the current density $\mathbf{i}_e = F(z_L \mathbf{J}_L + z_A \mathbf{J}_A)$ and using our definitions of the effective chemical potentials, we rewrite this as

$$\xi = -\frac{1}{T} \left(\mathbf{J}_L \cdot (\nabla \bar{\mu}) + \frac{\mathbf{i}_e}{F} \cdot \left(\nabla \phi + \frac{1}{z_A} \nabla \bar{\mu}_A \right) \right). \quad (2.201)$$

With this, we can then use the linearity assumption discussed in Section 2.2.5 to obtain the following expression for the fluxes:

$$\begin{bmatrix} \mathbf{J}_L \\ \mathbf{i}_e \end{bmatrix} = \begin{bmatrix} N_{11} & N_{12} \\ N_{21} & N_{22} \end{bmatrix} * \begin{bmatrix} \nabla \bar{\mu} \\ \nabla \varphi_e \end{bmatrix}, \quad (2.202)$$

here, we define $\varphi_e = \frac{\phi}{F} + \frac{\bar{\mu}_A}{F z_A}$ to be a normalized effective electrochemical potential (Latz et al. (2010)). Due to the symmetry, we must have $N_{12} = N_{21}$, and N_{11} must be negative to ensure negative definiteness, which is required for $\xi \geq 0$. Recall also that we can express the chemical potential in terms of the concentration $\nabla \bar{\mu} = \frac{\partial \bar{\mu}}{\partial c} \nabla c$. Using this we can rewrite

$$\begin{bmatrix} \mathbf{J}_L \\ \mathbf{i}_e \end{bmatrix} = \begin{bmatrix} N_{11} & N_{12} \\ N_{12} & N_{22} \end{bmatrix} * \begin{bmatrix} \frac{\partial \bar{\mu}}{\partial c} \nabla c \\ \nabla \varphi_e \end{bmatrix} \quad (2.203)$$

From the above expression and the relationship between $\mathbf{i}_e$ and the fluxes, we can write $\mathbf{J}_A$ as

$$\begin{aligned} \mathbf{J}_A &= \frac{\mathbf{i}_e}{F z_A} - \frac{z_L}{z_A} \mathbf{J}_L \\ &= \left(\frac{N_{12}}{F z_A} - \frac{z_L N_{11}}{z_A} \right) \frac{\partial \bar{\mu}}{\partial c} \nabla c + \left(\frac{N_{22}}{F z_A} - \frac{z_L N_{12}}{z_A} \right) \nabla \varphi_e. \end{aligned} \quad (2.204)$$

Looking at the $\nabla\varphi_e$ term we can write this coefficient in the form $\frac{N_{22}}{Fz_A}(1 - \hat{\beta})$ where we define $N_{12} = \frac{N_{22}\hat{\beta}}{z_L F}$. We define $\tilde{t}_L = \hat{\beta}$ and $\tilde{\kappa} = -N_{22}$ where $\tilde{t}_L, \tilde{\kappa}$ are the transference number and the conductivity, respectively. Given this we then obtain the following expressions for the fluxes:

$$\mathbf{J}_L = -\tilde{D}_e \nabla c + \frac{\tilde{t}_L}{Fz_L} \mathbf{i}_e, \quad (2.205)$$

$$\mathbf{i}_e = -\tilde{\kappa} \nabla \varphi_e - \tilde{\kappa} \frac{\tilde{t}_L}{Fz_L} \frac{\partial \bar{\mu}}{\partial c} \nabla c = -\tilde{\kappa} \nabla \varphi_e - \tilde{\kappa} \frac{\tilde{t}_L}{Fz_L} \nabla \bar{\mu}, \quad (2.206)$$

where $\tilde{D}_e = -\left(N_{11} + \tilde{\kappa} \left(\frac{\tilde{t}_L}{Fz_L}\right)^2\right) \frac{\partial \bar{\mu}}{\partial c}$.

Considering our continuity equations (2.179) and the definition of the flux (2.180), we have (in terms of concentration)

$$\frac{\partial c_L}{\partial t} = -\nabla \cdot \mathbf{J}_L - \nabla \cdot (c_L \mathbf{v}). \quad (2.207)$$

Recalling from equation (2.2) that, for a binary electrolyte under the assumption of local electroneutrality, we define the concentration of the solute as

$$c := \frac{c_L}{\nu_L} = \frac{c_A}{\nu_A}. \quad (2.208)$$

Substituting (2.205) and using (2.208) in (2.207), we obtain the following expression for the continuity equation:

$$\frac{\partial c}{\partial t} = \nabla \cdot \left(\frac{\tilde{D}_e}{\nu_L} \nabla c \right) - \frac{\mathbf{i}_e \cdot \nabla \tilde{t}_L}{Fz_L \nu_L} - \nabla \cdot (c \mathbf{v}). \quad (2.209)$$

We note that these equations ((2.205), (2.206), and (2.209)) bear a strong resemblance to those derived in the concentrated case, (2.90), (2.92) and (2.116); however, there are some notable differences. For example, the potential: the concentrated theory derivation involves directly the electric potential ϕ while the thermodynamic case instead involves the electrochemical potential φ_e of the electrolyte. While we noted a similar commentary after deriving the dilute theory equations, and acknowledged this by writing the current density in terms of the electric potential plus the chemical potential to account for this in the concentrated theory equations, Latz et al. (2010) indicate that the entropy production is not guaranteed to always be strictly positive in this case. Furthermore, we note that the coefficient of the $\nabla\mu_e$ term in (2.116) is derived based on a general electrode reaction, while the coefficient for (2.206) is an inherent property of the gradients in the independent field variables. This distinction causes asymmetry in the relations for the fluxes, which violates the Onsager reciprocal relation (Onsager (1931)). Finally, we highlight the difference in velocity:

in the concentrated equations derivation we circumvent a discussion on average or reference velocities by using the velocity difference in the multicomponent diffusion equation (2.69), this results in the reference velocity being the solvent velocity in (2.92). Similarly, we avoid this in the dilute case due to the assumption that the low concentration of ions means that the average fluid velocity is equal to the solvent velocity, and is frequently taken to be zero in (2.13). In this thermodynamic derivation, we must specifically define our choice of reference velocity. In general, this choice is arbitrary but the velocity chosen must be consistent with the diffusion velocities and must be characteristic of the bulk motion (Newman and Thomas-Alyea (2012)). As solutions become more dilute the mass average, molar average, and solvent velocity all become the same due to the low ion concentrations.

2.3 Summary of models

For ease of comparison, we include the final equations for each of the three approaches for continuum modelling of electrolytes discussed in this chapter, shown in Table 2.1. We have noted that in the dilute formulation, the driving forces for the flux are concentration and potential gradients, while in the concentrated and thermodynamic formulations the flux is driven by gradients in chemical and electric potentials. We summarise that the dilute and concentrated theory approaches to modelling an electrolyte are more heuristic than the thermodynamic framework. In the thermodynamic approach we do not explicitly choose the form for the flux, rather the thermodynamic principles such as the Onsager reciprocal relation inform what form the fluxes should take. We also emphasise that the thermodynamic approach is more rooted in physics and is agnostic to the electrolyte type.

2.4 Discussion

In Chapter 1 we acknowledge that there is a vast body of research dedicated to enhancing the performance, safety, efficiency, and lifespan of rechargeable batteries such as lithium-ion batteries. Due to the key role the electrolyte plays in LIBs, we also have extensive research focused on understanding the behaviours and dynamics occurring in electrolytes and on optimising the choice of electrolyte in different electrochemical systems. In addition, we discussed how mathematical modelling is a crucial tool that can contribute to advancing battery technology.

Table 2.1: Final equations for dilute, concentrated, and thermodynamically consistent approaches to electrolyte modelling.

Equations for electrolyte models	
Dilute equations	
(2.24)	$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = \nabla \cdot (D_{\text{eff}} \nabla c) - \frac{\mathbf{i}_e \cdot \nabla t_L}{F z_L \nu_L}$
(2.30)	$\frac{\mathbf{i}_e}{z_L \nu_L} = -\hat{\kappa}(c) \left(\nabla \phi - \frac{RT}{F} \left(\frac{D_A - D_L}{z_L D_L} \right) t_L \frac{\nabla c}{c} \right)$
Concentrated equations	
(2.92)	$\frac{\partial c}{\partial t} = \nabla \cdot \left(D_e \left(1 - \frac{d \log c_0}{d \log c} \right) \nabla c \right) - \frac{\mathbf{i}_e \cdot \nabla t_{0L}}{z_L \nu_L F} - \nabla \cdot (c \mathbf{v}_0)$
(2.116)	$\mathbf{i}_e = -\kappa \nabla \phi - \frac{\kappa}{F} \left(\frac{s_L}{\tilde{n} \nu_L} + \frac{t_{0L}}{z_L \nu_L} - \frac{s_0 c}{\tilde{n} c_0} \right) \nabla \mu_e$
Thermodynamically derived equations	
(2.209)	$\frac{\partial c}{\partial t} = \nabla \cdot \left(\frac{\tilde{D}_e}{\nu_L} \nabla c \right) - \frac{\mathbf{i}_e \cdot \nabla \tilde{t}_L}{F z_L \nu_L} - \nabla \cdot (c \mathbf{v})$
(2.206)	$\mathbf{i}_e = -\tilde{\kappa} \nabla \varphi_e - \tilde{\kappa} \frac{\tilde{t}_L}{F z_L} \nabla \bar{\mu}$

In this chapter, we have explored some of the primary approaches taken and methods used to model electrolytes, with a particular focus on continuum modelling and thermodynamics. Specifically, we introduced the dilute, concentrated, and thermodynamically derived electrolyte models. While these models are widely used in the literature, this chapter contributes a comprehensive mathematical derivation of each of the models from first principles, along with a systematic demonstration of how these models are connected. We recognise the dilute electrolyte model as a model which is widely used and regarded as it can capture many of the key features of transport in an electrolyte without being too cumbersome to derive or understand. From here we highlighted that the primary flaw associated with the dilute model lies in the absence of interactions between the ionic species in the electrolyte and some ambiguity regarding the driving forces for ionic transport. Hence, we introduced concentrated electrolyte theory, which builds on the dilute theory by incorporating a more in-depth treatment of the inter-ion and ion-solvent interactions occurring and a more rigorous treatment of the driving forces. This derivation was more lengthy and involved than the dilute case in order to carefully account for these additional interactions and transport properties. The concentrated electrolyte equations rely on principles from thermodynamics, however, on closer inspection it is found that there are some laws of thermodynamics that not necessarily obeyed in this framework. Therefore, we present a complete derivation of the necessary equations from thermodynamics in order to construct a

thermodynamically-consistent model from first principles.

We remark that the thermodynamically-consistent model represents the most comprehensive and physically rigorous framework for electrolyte modelling at the continuum level. However, additional effects such as temperature dependence (*e.g.* Latz and Zausch (2015)) and finite ion size (some examples in PNP type models include Borukhov et al. (1997); Jia et al. (2016); Horng et al. (2017); Song et al. (2019); Kilic et al. (2007a)) can be incorporated. The electrolyte model can also be coupled with other physical processes such as mechanics, to capture chemo-mechanical interactions (*e.g.* Kilchert et al. (2024)). Furthermore, the thermodynamic approach provides a macroscopic description; for more microscopic detail, statistical mechanics and quantum effects could be considered via molecular dynamics or density functional theory (briefly discussed in Section 1.3.1 of Chapter 1).

In the following chapters we will build on the knowledge from this chapter. In particular, we will implement a thermodynamically-consistent model for an electrolyte in order to apply further mathematical techniques to gain insight into the feature of electrolytes known as electric double layers.

Chapter 3

Solid electrolyte model

This chapter outlines the work published in Keane and Moyles (2024).

3.1 Problem motivation

From our discussions in Chapter 1, it is clear that optimising performance, safety, and efficiency of lithium-ion batteries is paramount to reaching societal goals of reducing our dependence on fossil fuels. We have emphasised that the electrolyte is an important component of all electrochemical systems, including LIBs. As a result of ongoing research concerning battery materials, solid electrolytes (SEs) are emerging as a popular alternative to the more commonly used liquid electrolytes for a variety of reasons (Takada (2013); Manthiram et al. (2017); Zhao et al. (2019)). Despite this, much of the existing literature, in particular, the modelling literature, surrounds liquid electrolytes.

Investigating the existing literature on SE, there is a common theme that a better understanding of SCLs is crucial for advancing battery research and development. In particular, many authors indicate that the SCL can have a considerable influence on ion and electron transport. For example, Zhang et al. (2022) stress the importance of understanding the formation, structure, and effect of the SCL, referring to it as one of the most important influences on ion transport due to its proximity to the electrode-electrolyte interface. Solid-phase reactions have been shown to be influenced by SCLs and the electrochemical performance of materials can be impacted by the physical and chemical properties of the SCL (Wu et al. (2022)). There is

also research showing that the SCL can contribute to high interfacial resistance, which is considered a major hindrance of solid state batteries (Xia et al. (2019); Liu et al. (2022); Ahmad et al. (2022)).

However, the SCL can be complex to model, which can lead to issues in analytics and numerical implementation of models; therefore, simplifications are often made. Zhang et al. (2022, 2023) insinuate that theoretical simulation calculation cannot fully understand or predict the behaviour of SCLs. These authors suggest that both numerical simulations and analytical calculations are required in parallel to characterise the SCL. A number of authors have considered mathematical models for SE and SCL, some notable examples include: Landstorfer et al. (2011); Braun et al. (2015); Swift et al. (2021); Becker-Steinberger et al. (2021); Katzenmeier (2022). However, due to the complexity of these SCLs this work often involves semi-analytical solutions or is numerically driven, in line with the observations made by Zhang et al. (2022, 2023). We note that the model simplifications and assumptions employed by these authors are not without compromise. Semi-analytical solutions of the model can be used to derive approximate numerical solutions, however, this can add error and therefore limit the interpretability of the results. Contrastingly, numerically-driven models can be derived and simulated without much consideration for the driving mechanisms.

On further examination of the modelling simplifications applied to study SE and SCL, common challenges arise throughout the literature. Many authors suggest that they encountered difficulties when numerically solving a model for a SE with SCLs. We recall the general expression for the chemical potential (2.191), derived in Chapter 2, noting that these chemical potentials have a logarithmic structure and therefore this will limit the domain, as the logarithm is only continuous (and defined) for positive arguments, which can cause numerical challenges. In particular, as we will observe, these difficulties occur as the electrolyte can become exponentially close to fully lithiated or depleted of lithium ions, leading to near singularities in the domain. Numerical methods struggle with the computations as we near these two limits.

To circumvent these difficulties many authors employ approaches to avoid direct computation. Landstorfer et al. (2011) describe the electrode/electrolyte interface as numerically problematic, requiring a priori knowledge of the interfaces to generate the lattice for their numerical solutions. Semi-analytic approaches are used by Braun et al. (2015) and Swift et al. (2021) to approximate and supplement some of their numerics. In Swift et al. (2021) the authors acknowledge numerical difficulties arise due to the proximity to the depleted (or zero) limit when charge neutrality is reached. Katzenmeier (2022) implements the model derived by Braun et al. (2015) for their simulations in COMSOL Multiphysics, however, they utilise an empirical

equation with Sigmoid functions to compensate for singularities at the boundaries.

Aside from the numerical difficulties encountered, we also highlight that many authors observe that the double charge layers in a solid electrolyte are wider than those of a liquid electrolyte (Braun et al. (2015); Knauth (2009); Li and Monroe (2019, 2021); Yamada et al. (2013)). However, within the literature there is no unified consensus as to how much wider these layers are in the solid electrolyte, with variations from twice as thick (Yamada et al. (2013)) to ten times as thick suggested (Braun et al. (2015); Li and Monroe (2019, 2021)). In addition to determining the widths of these layers, insight into the behaviour of these layers is also required. For example, Li and Monroe (2019) observe that the SCL becomes more dilated as the applied voltage increases, in contrast to the contraction of the Debye length typically observed in liquid diffuse layers. Furthermore, in Swift et al. (2021) the authors observe a combination of quadratic behaviour at the boundaries and exponential behaviour between the boundaries and the bulk. We therefore remark that understanding the double layer structure of the solid electrolyte beyond numerics warrants investigation to discern these behaviours and uncover the true widths of these layers.

The purpose of this chapter is to present a model of a SE and apply mathematical modelling techniques to help enhance our knowledge of the SCL. We want to construct a generalized numerical framework that can be used in standard numerical solving techniques without much pre-processing. We will utilise asymptotic methods to quantify these layers and to gain deeper insight into the underlying mechanisms and behaviours occurring within.

This chapter is organised as follows. We first discuss some of the peculiarities associated with SE, in particular, highlighting the primary differences between liquid and solid electrolytes to account for when modelling. We refer back to the equations derived in Chapter 2 in order to present a thermodynamically consistent model for a SE, first derived by Braun et al. (2015). We non-dimensionalise the SE model and identify the important parameters in the model. Before we solve the model numerically, we introduce an auxiliary variable which maps the concentration of ions into another domain to avoid any singularities arising. We use the non-dimensionalisation to inform an asymptotic reduction of the model. We then compare the results of our numerical and asymptotic approaches. We also present an integral approach to solving the SE model. Finally, we conclude and discuss areas for future work.

3.2 Mathematical model

3.2.1 Model assumptions

In Chapter 2 we discuss several approaches to modelling electrolytes; in each scenario, the model derivation is based on the assumption that the electrolyte solution is composed of two ionic species, dissolved in some solvent. In this characterisation, both ionic species diffuse in the solvent; this is not the case when modelling a solid electrolyte. Nevertheless, in Chapter 2 we also discussed that the general framework from thermodynamics does not require any specification of the electrolyte properties, making the thermodynamic approach a robust modelling framework, which we can apply in accordance with the properties of the chosen electrolyte.

When considering SE, typically the anion is much larger than the cation (lithium), so it is usually assumed that the anion is immobile. This immobility can be rationalised by the fact that only the lithium intercalates. As a result, the anions form a fixed lattice structure and the lithium ions diffuse through this structure by hopping between sites, leaving vacant sites behind as they move. In order for this to occur, there are gaps in the lattice which effectively have a negative charge from the anion, and these gaps are referred to as vacancies. This can be modelled chemically as $\text{LiA} \rightleftharpoons \text{Li}^+ + \text{vacancy} + \text{A}^-$. The vacancies are considered to be massless and chargeless; however, since the lithium ion creates a vacancy whenever it moves, the vacancies also move. We assume that the vacancies are based on Schottky-type defects, so that each time a cation leaves a spot, it leaves exactly one vacancy behind (Kittel (2005)). Therefore, we still have three species to account for in the model; cations, anions, and vacancies. As such, the fixed anion lattice plays the role of the solvent, enabling the lithium ions to diffuse as they hop between the vacant sites. Furthermore, it is assumed that the fixed anion lattice is incompressible; thus by the nature of Schottky defects, the sum of the cations and the vacancies should be constant (Braun et al. (2015)).

3.2.2 Model equations

In this section we use the equations derived in Section 2.2.5 of Chapter 2 for a thermodynamically consistent model for an electrolyte, recalling that in Section 2.2.1 we indicate that we use mass density, ρ , as our concentration measure in the initial derivations of these equations. Here we provide additional details specific to the solid electrolyte in order to arrive at the model first derived by Braun et al. (2015). We consider a solid electrolyte composed of three species; cations c , stationary anions a , and massless vacancies

v .

The conservation equation for each species as given by (2.179) is modified as follows for $k = c, a, v$:

$$\frac{\partial \rho_c}{\partial t} + \nabla \cdot (\rho_c \mathbf{v}_c) = 0, \quad (3.1a)$$

$$\frac{\partial \rho_a}{\partial t} + \nabla \cdot (\rho_a \mathbf{v}_a) = 0, \quad (3.1b)$$

$$\frac{\partial n_v}{\partial t} + \nabla \cdot (n_v \mathbf{v}_v) = 0. \quad (3.1c)$$

We conserve mass for both the cations and anions, however because the vacancies are massless, we instead conserve the number density of the vacancies in (3.1c). Furthermore, because the anion is assumed to be stationary, we must have that $\mathbf{v}_a = 0$. Therefore, we can reduce (3.1b) to

$$\frac{\partial \rho_a}{\partial t} = 0. \quad (3.2)$$

Considering the general expression for the diffusive fluxes (2.180), we note that in the case of the solid electrolyte we have mass diffusive fluxes given by

$$\mathbf{J}_c = \rho_c(\mathbf{v}_c - \mathbf{v}), \quad \mathbf{J}_a = \rho_a(\mathbf{v}_a - \mathbf{v}), \quad (3.3)$$

and because of the masslessness of the vacancies,

$$\mathbf{J}_v = \mathbf{0}. \quad (3.4)$$

Total conservation of mass, $\sum_k \mathbf{J}_k = \mathbf{0}$, then implies that $\mathbf{J}_a = -\mathbf{J}_c$. We note that rewriting (3.1c) with $n_v \mathbf{v}_v = n_v \mathbf{v} + n_v (\mathbf{v}_v - \mathbf{v})$, thereby introducing a number density flux ($n_v (\mathbf{v}_v - \mathbf{v})$), we can also express $\mathbf{J}_v$ in terms of $\mathbf{J}_c$. In order to see this, firstly, we recall from Chapter 2 that it is more convenient to write the continuity equation for each species in terms of number densities,

$$\frac{\partial n_c}{\partial t} + \nabla \cdot (n_c \mathbf{v}_c) = 0, \quad (3.5a)$$

$$\frac{\partial n_a}{\partial t} = 0, \quad (3.5b)$$

$$\frac{\partial n_v}{\partial t} + \nabla \cdot (n_v \mathbf{v}_v) = 0, \quad (3.5c)$$

since $\mathbf{v}_a = 0$. Adding the three equations together gives

$$\frac{\partial n}{\partial t} + \nabla \cdot (n_c \mathbf{v}_c + n_v \mathbf{v}_v) = 0, \quad (3.6)$$

where $n = n_c + n_a + n_v$. We must have a global conservation of mass, which means that $\int_V n \, dV$ must be constant, therefore

$$0 = \frac{d}{dt} \left(\int_V n \, dV \right) = \int_V \frac{\partial n}{\partial t} \, dV. \quad (3.7)$$

It follows that

$$\nabla \cdot (n_c \mathbf{v}_c + n_v \mathbf{v}_v) = 0, \quad (3.8)$$

thus $n_c \mathbf{v}_c + n_v \mathbf{v}_v = \nabla \times \mathbf{B}$ for some $\mathbf{B}$ which we set to zero. Rewriting (2.180) in terms of the number density for $\mathbf{J}_v, \mathbf{J}_c$

$$\frac{\mathbf{J}_v}{m_v} + n_v \mathbf{v} = n_v \mathbf{v}_v, \quad \frac{\mathbf{J}_c}{m_c} + n_c \mathbf{v} = n_c \mathbf{v}_c, \quad (3.9)$$

we add these together and noting that $n_c \mathbf{v}_c + n_v \mathbf{v}_v = \mathbf{0}$ we can write

$$\frac{\mathbf{J}_v}{m_v} + \frac{\mathbf{J}_c}{m_c} + (n_v + n_c) \mathbf{v} = \mathbf{0}. \quad (3.10)$$

Similarly, the anion flux $\mathbf{J}_a = \rho_a (\mathbf{v}_a - \mathbf{v})$, can be rewritten as

$$\frac{\mathbf{J}_a}{m_a} = -n_a \mathbf{v} \quad (3.11)$$

since $\mathbf{v}_a = 0$. Rewriting $\mathbf{v}$ in (3.10) using (3.11), and rearranging with $\mathbf{J}_a = -\mathbf{J}_c$, $\mathbf{J}_v$ can be expressed in terms of $\mathbf{J}_c$ as

$$\frac{\mathbf{J}_v}{m_v} = -\kappa \frac{\mathbf{J}_c}{m_c} \quad (3.12)$$

where we define

$$\kappa = 1 + \left(\frac{n_c + n_v}{n_a} \right) \left(\frac{m_c}{m_a} \right). \quad (3.13)$$

Given these relationships between the variables, the cation flux is the only independent flux, therefore we can solve the continuity equation for the cations and use the solution to determine the vacancy concentration. As such, we note that the continuity equation for the cation from (3.1) can be rewritten using the relationship between the diffusive fluxes. Furthermore, noting that $\rho_c \mathbf{v}_c = \rho \mathbf{v} = \frac{\rho}{(\rho - \rho_c)} \mathbf{J}_c$, we obtain the following continuity equation for the cation:

$$\frac{\partial n_c}{\partial t} = -\frac{1}{m_c} \nabla \cdot \left(\frac{m_c n_c + m_a n_a}{m_a n_a} \mathbf{J}_c \right). \quad (3.14)$$

The equation for entropy production is given by (2.182). We then employ the same assumptions and properties used in deriving (2.184) to rewrite the flux in terms of the driving forces, $\nabla \mu_k + z_k \nabla \phi$. However,

here, instead of solvent, we have massless and chargeless vacancies, so there is no potential term in the third row of the driving forces vector:

$$\begin{bmatrix} \frac{\mathbf{J}_c}{m_c} \\ \frac{\mathbf{J}_a}{m_a} \\ \frac{\mathbf{J}_v}{m_v} \end{bmatrix} = - \begin{bmatrix} N_{cc} & N_{ac} & N_{cv} \\ N_{ac} & N_{aa} & N_{av} \\ N_{cv} & N_{av} & N_{vv} \end{bmatrix} \begin{bmatrix} \nabla\mu_c + z_c \nabla\phi \\ \nabla\mu_a + z_a \nabla\phi \\ \nabla\mu_v \end{bmatrix} = \begin{bmatrix} -N_{cc} & -N_{ac} & -N_{cv} \\ \frac{m_c}{m_a} N_{cc} & \frac{m_c}{m_a} N_{ac} & \frac{m_c}{m_a} N_{cv} \\ \kappa N_{cc} & \kappa N_{ac} & \kappa N_{cv} \end{bmatrix} \begin{bmatrix} \nabla\mu_c + z_c \nabla\phi \\ \nabla\mu_a + z_a \nabla\phi \\ \nabla\mu_v \end{bmatrix}, \quad (3.15)$$

where we have used $\mathbf{J}_a = -\mathbf{J}_c$ and $\frac{\mathbf{J}_v}{m_v} = -\kappa \frac{\mathbf{J}_c}{m_c}$ to rewrite the constants of proportionality. We recall that the remaining coefficients N_{cc} , N_{ac} , and N_{cv} can be found from the following; physically, we need entropy production to be positive so the matrix must be positive semi-definite and Onsager (1931) tells us that the matrix should be symmetric. These conditions then tell us that $N_{cc} = M > 0$, $N_{ac} = -\frac{m_c}{m_a} N_{cc}$, and $N_{cv} = -\kappa N_{cc}$, where M is a free positive constant; furthermore, the Curie-Prigogine principle says that there is only coupling between thermodynamic forces via the symmetry (De Groot and Mazur (2013)), leading to the reduced expression for the flux equation

$$\frac{\mathbf{J}_c}{m_c} = -M \left(\nabla\mu_c - \frac{m_c}{m_a} \nabla\mu_a - \kappa \nabla\mu_v + \left(z_c - \frac{m_c}{m_a} z_a \right) \nabla\phi \right). \quad (3.16)$$

For the chemical potentials we have the general form given by (2.191); however here only n_c and n_v mix under the assumptions for the solid electrolyte, so we write the individual species chemical potentials as

$$\mu_c = \mu_{c0}(T, p, n) + k_B T \log \left(\frac{n_c}{n_c + n_v} \gamma_c \right) \quad (3.17a)$$

$$\mu_v = \mu_{v0}(T, p, n) + k_B T \log \left(\frac{n_v}{n_c + n_v} \gamma_v \right) \quad (3.17b)$$

$$\mu_a = \mu_{a0}(T, p, n), \quad (3.17c)$$

i.e. for the solid electrolyte $x_k = \frac{n_k}{n_c + n_v}$ and the anion chemical potential has no term related to mixing. We refer to $k_B T \log(x_k \gamma_k)$ as the energy of mixing and therefore, $\mu_{k0}(T, p, n)$ represents the chemical potential of species k with no mixing.

We note that in classic models for liquid electrolyte in lithium-ion batteries, the average velocity is frequently taken to be zero (for example, Doyle et al. (1993); Fuller et al. (1994b)). As a result, the conservation of momentum equation, which is an equation for velocity in this case, is implicitly accounted for. However, in considering SEs this is not the case. As anions are considered stationary, the species velocity for anions is zero. The vacancies cannot contribute to a mass-averaged velocity because they are massless; therefore, a

zero average velocity would imply that the lithium does not move, and is therefore only permissible when the lithium is stationary (in the zero flux case). Therefore, an equation for the velocity is required, and as such we must explicitly retain the momentum equation. We have conservation of momentum coming from (2.144) in Chapter 2, where we further assume that the deviatoric stress tensor $\mathbf{D}_s$ is zero and that temperature is constant; therefore, there are no external forces apart from the electric field and we have the following form for conservation of momentum

$$\frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) + \nabla p = -n^F \nabla \phi, \quad (3.18)$$

where n^F is the free charge given by $n^F = \sum_k z_k n_k$ with z_k being the charge of the species and ϕ is the electric potential. In a solid electrolyte the free charge is given by

$$n^F = z_c n_c + z_a n_a, \quad (3.19)$$

since the vacancies are chargeless.

For the electric potential, we have conservation of charge from Gauss' law

$$\nabla \cdot (\epsilon_0 (1 + \chi) \mathbf{E}) = n^F, \quad (3.20)$$

where $\epsilon_0 = 8.854 \times 10^{-12} \text{F/m}$ is the permittivity of free space, χ is the electric susceptibility (assumed constant), and $\mathbf{E}$ is the electric field with $\mathbf{E} = -\nabla \phi$. To close the problem we need an equation of state,

$$p = p_r + K \left(\frac{n}{n_r} - 1 \right), \quad (3.21)$$

where K is the bulk modulus coming from the assumption of the electrolyte being linearly elastic and the subscript r indicates a reference variable.

Chemical potentials

As we have an equation of state, we then need to understand the (T, p) dependence in the chemical potentials given in (3.17) more explicitly. We will therefore consider free energies and non-equilibrium thermodynamics to formally address the non-ideality and to determine a way to express this non-mixing energy term, we note that we follow the approach of Dreyer et al. (2013).

For the free energy we take the Helmholtz free energy, as we have a system with constant temperature, given by

$$\psi = \psi(T, V) = U - ST = -pV + \sum_k \mu_k n_k V, \quad (3.22)$$

where U is the internal energy of the system, given by

$$U = ST - pV + \sum_k \mu_k n_k V, \quad (3.23)$$

V is volume, S is entropy, and $G = \sum_k \mu_k n_k V = \sum_k \mu_k N_k$ is the Gibbs free energy with $N_k = n_k V$ being the number of molecules. Using (3.22), if M is the total mass of the system, the free energy per mass can be written as

$$\bar{\psi} = \frac{\psi}{M} = -\frac{p}{\rho} + \frac{\sum_k \mu_k n_k}{\rho}, \quad (3.24)$$

thus making this an intensive property. This can be rewritten as

$$\rho \bar{\psi} = -p + \sum_k \mu_k n_k = -p + \sum_k \bar{\mu}_k \rho_k, \quad (3.25)$$

where we define $\bar{\mu}_k = \frac{\mu_k}{m_k}$ with m_k denoting the atomic mass. From (3.25) we can express the chemical potential in terms of the free energy per mass via

$$\bar{\mu}_k = \left. \frac{\partial (\rho \bar{\psi})}{\partial \rho_k} \right|_{(\rho_j, j \neq k)}. \quad (3.26)$$

If we rewrite the Gibbs free energy (2.46) of the system using the general expression for the chemical potentials (2.191) we have

$$G = \sum_k \mu_k N_k = \sum_k (g_k^* + k_B T N_k \log(x_k \gamma_k)) = \sum_k (g_k^* + k_B T N x_k \log(x_k \gamma_k)), \quad (3.27)$$

which we can also write in terms of the number density:

$$G = \sum_k \mu_k n_k = \sum_k (g_k^* + k_B T n x_k \log(x_k \gamma_k)). \quad (3.28)$$

We therefore define the energy of mixing to be

$$\rho \psi_m = \sum_k k_B T n x_k \log(x_k \gamma_k). \quad (3.29)$$

We have that $\rho \bar{\psi} = -p + \sum_k \bar{\mu}_k \rho_k$ and $\bar{\mu}_k = \frac{\partial (\rho \bar{\psi})}{\partial \rho_k}$. Because energies are additive we can write the free energy as

$$\rho \bar{\psi} = \sum_k \rho_k \psi_k^* + \rho \psi_m + \rho \psi_p, \quad (3.30)$$

where ψ_k^* is the energy from the pure substance and ψ_p is the pressure component. Therefore, we can write

$$\bar{\mu}_k = \frac{\partial (\rho \bar{\psi})}{\partial \rho_k} = \psi_k^* + \frac{\partial (\rho \psi_m)}{\partial \rho_k} + \frac{\partial (\rho \psi_p)}{\partial \rho_k} = \psi_k^* + \frac{1}{m_k} \frac{\partial (\rho \psi_m)}{\partial n_k} + \frac{1}{m_k} \frac{\partial (\rho \psi_p)}{\partial n_k}, \quad (3.31)$$

which we can express as

$$\bar{\mu}_k = \psi_k^* + \frac{k_B T}{m_k} \frac{\partial}{\partial n_k} \left(n \sum_j x_j \log(x_j \gamma_j) \right) + \frac{1}{m_k} \frac{\partial p}{\partial n_k} \frac{\partial (\rho \psi_p)}{\partial p}, \quad (3.32)$$

using (3.29) and again noting that temperature is fixed. We want to simplify this derivative of the energy from mixing, using the product rule we can find

$$\frac{\partial}{\partial n_k} \left(n \sum_j x_j \log(x_j \gamma_j) \right) = \sum_j x_j \log(x_j \gamma_j) + n \sum_j \frac{\partial x_j}{\partial n_k} \log(x_j \gamma_j) + n \sum_j \frac{\partial x_j}{\partial n_k} + \frac{x_j}{\gamma_j} \frac{\partial \gamma_j}{\partial n_k}, \quad (3.33)$$

whereby

$$\frac{\partial x_j}{\partial n_k} = \frac{\partial}{\partial n_k} \frac{n_j}{n} = \frac{1}{n} \frac{\partial n_j}{\partial n_k} - \frac{n_j}{n^2} \frac{\partial n}{\partial n_k} = \begin{cases} \frac{1}{n} - \frac{n_k}{n^2} = \frac{1}{n} - \frac{x_k}{n} & \text{if } j = k \\ 0 - \frac{n_j}{n^2} = -\frac{x_j}{n} & \text{if } j \neq k \end{cases}, \quad (3.34)$$

so that

$$\frac{\partial}{\partial n_k} \left(n \sum_j x_j \log(x_j \gamma_j) \right) = \log(x_k \gamma_k) + n \sum_j \frac{x_j}{\gamma_j} \frac{\partial \gamma_j}{\partial n_k} \quad (3.35)$$

since $x_k + \sum_{j \neq k} x_j = \sum_j x_j = 1$ and $x_k \log(x_k \gamma_k) + \sum_{j \neq k} x_j \log(x_j \gamma_j) = \sum_j x_j \log(x_j \gamma_j)$. Therefore, returning to (3.32) we have

$$\bar{\mu}_k = \psi_k^* + \frac{1}{m_k} \frac{\partial p}{\partial n_k} \frac{\partial (\rho \psi_p)}{\partial p} + \frac{k_B T}{m_k} \left(\log(x_k \gamma_k) + n \sum_j \frac{x_j}{\gamma_j} \frac{\partial \gamma_j}{\partial n_k} \right). \quad (3.36)$$

Now we turn our attention to the pressure component. Firstly, we note that we can rewrite the following

$$p = -\rho \bar{\psi} + \sum_k \bar{\mu}_k m_k n_k = -\rho \psi_p + \frac{d(\rho \psi_p)}{dp} \sum_k n_k \frac{\partial p}{\partial n_k} + k_B T n^2 \sum_k x_k \sum_j \frac{x_j}{\gamma_j} \frac{\partial \gamma_j}{\partial n_k} \quad (3.37)$$

where we highlight that the last term, $\sum_k x_k \sum_j \frac{x_j}{\gamma_j} \frac{\partial \gamma_j}{\partial n_k}$, is related to non-ideal mixing and therefore must vanish for ideal mixtures, *i.e.*

$$\sum_k x_k \sum_j \frac{x_j}{\gamma_j} \frac{\partial \gamma_j}{\partial n_k} = 0. \quad (3.38)$$

We note that Braun et al. (2015) use Margules activity coefficients (Margules (1895); Gokcen (1996)) to model the non-ideality. This means that the excess free energy is expressed as a power series of the mole fractions which yields

$$\ln \gamma_c = (A_{12} + 2(A_{21} - A_{12})x_c) x_v^2 = A x_v^2, \quad (3.39a)$$

$$\ln \gamma_v = (A_{21} + 2(A_{12} - A_{21})x_v) x_c^2 = A x_c^2, \quad (3.39b)$$

where we have taken $A_{12} = A_{21} = A$. We note that using these Margules expressions for the non-ideality term of (3.36) will yield (3.38). For example, if we consider

$$\sum_j \frac{x_j}{\gamma_j} \frac{\partial \gamma_j}{\partial n_k} = \sum_j x_j \frac{\partial \log \gamma_j}{\partial n_k}, \quad (3.40)$$

with $\log(\gamma_j) = Ax_k^2 = \frac{An_k^2}{(n_k + n_j)^2}$, we have

$$\begin{aligned} x_c \frac{\partial \log(\gamma_c)}{\partial n_c} + x_v \frac{\partial \log(\gamma_v)}{\partial n_c} &= x_c \frac{\partial}{\partial n_c} \left(\frac{An_v^2}{(n_c + n_v)^2} \right) + x_v \frac{\partial}{\partial n_c} \left(\frac{An_c^2}{(n_c + n_v)^2} \right) \\ &= \frac{-2A}{(n_c + n_v)} (x_c x_v^2 - x_v x_c^2 + x_c^2 x_v - x_c x_v^2) \\ &= 0, \end{aligned} \quad (3.41)$$

and similarly for the other terms in the sum in (3.38).

Therefore, assuming Margules activity coefficients for the excess energy, and since

$$\frac{\partial p}{\partial n_k} = \frac{dp}{dn} \frac{\partial n}{\partial n_k}, \quad \frac{\partial n}{\partial n_k} = 1, \quad (3.42)$$

we obtain

$$p = -\rho\psi_p + \frac{d(\rho\psi_p)}{dp} \sum_k n_k \frac{dp}{dn} = -\rho\psi_p + n \frac{dp}{dn} \frac{d\rho\psi_p}{dp} \quad (3.43)$$

which is a differential equation for $\rho\psi_p$. Taking the derivative of the equation of state (3.21) with respect to the number density, we must then have

$$\frac{dp}{dn} = \frac{K}{n_r} \quad (3.44)$$

and we can rearrange the equation of state as

$$n = \frac{n_r}{K} (p - p_r + K). \quad (3.45)$$

We can then rewrite the differential equation for $\rho\psi_p$

$$\frac{d(\rho\psi_p)}{dp} - \frac{\rho\psi_p}{p - p_r + K} = \frac{p}{p - p_r + K} \quad (3.46)$$

which has solution

$$\rho\psi_p = K - p_r + (p - p_r + K) (C_0 + \log(p - p_r + K)) = K - p_r + \frac{Kn}{n_r} \left(C_0 + \log(K) + \log\left(\frac{n}{n_r}\right) \right) \quad (3.47)$$

where C_0 is an arbitrary constant of integration. We note that the base energy is captured by ψ^* , therefore we take $\rho\psi_p(p_r) = 0$, noting that when $p = p_r$, $n = n_r$ from our equation of state (3.21), meaning we can find

$$C_0 + \log(K) = \frac{p_r - K}{K}. \quad (3.48)$$

Thus we have that

$$\rho\psi_p = (K - p_r) \left(1 - \frac{n}{n_r}\right) + \frac{Kn}{n_r} \log\left(\frac{n}{n_r}\right) \quad (3.49)$$

as our pressure component of the free energy, and it follows that, on taking the derivative with respect to n_k we obtain

$$\frac{d(\rho\psi_p)}{dn_k} = \frac{p_r}{n_r} + \frac{K}{n_r} \log\left(\frac{n}{n_r}\right). \quad (3.50)$$

Thus, using this expression for the pressure part and again assuming ideality in (3.36), we can express $\bar{\mu}_k$ as

$$\bar{\mu}_k = \psi_k^* + \frac{1}{m_k} \frac{d(\rho\psi_p)}{dn_k} + \frac{k_B T}{m_k} \log(x_k \gamma_k) = \psi_k^* + \frac{p_r}{m_k n_r} + \frac{K}{m_k n_r} \log\left(\frac{n}{n_r}\right) + \frac{k_B T}{m_k} \log(x_k \gamma_k). \quad (3.51)$$

Recalling that $\bar{\mu}_k = \frac{\mu_k}{m_k}$ and rearranging the expression for the equation of state, we can write the chemical potentials as

$$\mu_k = \mu_k^*(T) + \frac{K}{n_r} \log\left(\frac{p - p_r}{K} + 1\right) + k_B T \log\left(\frac{n_k}{n}\right), \quad (3.52)$$

whereby under the assumption of ideality, we take $\gamma_k = 1$. As a result, the species specific chemical potentials from (3.17) can then expressed as

$$\begin{aligned} \mu_c &= \mu_c^*(T) + \frac{K}{n_r} \log\left(\frac{p - p_r}{K} + 1\right) + k_B T \log\left(\frac{n_c}{n_c + n_v}\right), \\ \mu_v &= \mu_v^*(T) + \frac{K}{n_r} \log\left(\frac{p - p_r}{K} + 1\right) + k_B T \log\left(\frac{n_v}{n_c + n_v}\right), \\ \mu_a &= \mu_a^*(T) + \frac{K}{n_r} \log\left(\frac{p - p_r}{K} + 1\right), \end{aligned} \quad (3.53a)$$

with μ^* denoting the reference chemical potential. We take the incompressibility limit $K \rightarrow \infty$ in the chemical potentials to obtain

$$\begin{aligned} \mu_c &= \mu_c^* + \frac{p - p_r}{n_r} + k_B T \log\left(\frac{n_c}{n_c + n_v}\right), \\ \mu_v &= \mu_v^* + \frac{p - p_r}{n_r} + k_B T \log\left(\frac{n_v}{n_c + n_v}\right), \\ \mu_a &= \mu_a^* + \frac{p - p_r}{n_r}. \end{aligned} \quad (3.54a)$$

Model summary

Therefore, the overall model for an SE under isothermal conditions involving three species can be defined by the following set of equations:

$$\frac{\partial n_c}{\partial t} = -\frac{1}{m_c} \nabla \cdot \left(\left(1 + \frac{m_c n_c}{m_a n_a} \right) \mathbf{J}_c \right), \quad (3.55a)$$

$$n^F = -\epsilon_0 (1 + \chi) \nabla^2 \phi, \quad (3.55b)$$

$$-n^F \nabla \phi = \frac{\partial(\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) + \nabla p, \quad (3.55c)$$

$$\frac{\mathbf{J}_c}{m_c} = -M \left(\nabla \mu_c - \frac{m_c}{m_a} \nabla \mu_a - \left(1 + \frac{n_c + n_v}{n_a} \frac{m_c}{m_a} \right) \nabla \mu_v + \left(z_c - \frac{m_c}{m_a} z_a \right) \nabla \phi \right), \quad (3.55d)$$

and the chemical potentials are given by

$$\mu_c = \mu_c^* + \frac{1}{n_r} (p - p_r) + k_B T \log \left(\frac{n_c}{n_c + n_v} \right), \quad (3.56a)$$

$$\mu_v = \mu_v^* + \frac{1}{n_r} (p - p_r) + k_B T \log \left(\frac{n_v}{n_c + n_v} \right), \quad (3.56b)$$

$$\mu_a = \mu_a^* + \frac{1}{n_r} (p - p_r). \quad (3.56c)$$

We focus on the one-dimensional problem, so that (3.55) becomes

$$\frac{\partial n_c}{\partial t} = -\frac{1}{m_c} \frac{\partial}{\partial z} \left(\left(1 + \frac{m_c n_c}{m_a n_a} \right) J_c \right), \quad (3.57a)$$

$$n^F = -\epsilon_0 (1 + \chi) \frac{\partial^2 \phi}{\partial z^2}, \quad (3.57b)$$

$$-n^F \frac{\partial \phi}{\partial z} = \frac{\partial(\rho v)}{\partial t} + \frac{\partial(\rho v^2)}{\partial z} + \frac{\partial p}{\partial z}, \quad (3.57c)$$

$$\frac{J_c}{m_c} = -M \left(\frac{\partial \mu_c}{\partial z} - \frac{m_c}{m_a} \frac{\partial \mu_a}{\partial z} - \left(1 + \frac{n_c + n_v}{n_a} \frac{m_c}{m_a} \right) \frac{\partial \mu_v}{\partial z} + \left(z_c - \frac{m_c}{m_a} z_a \right) \frac{\partial \phi}{\partial z} \right), \quad (3.57d)$$

with chemical potentials unchanged from (3.56). We remark that the unknowns are n_c , ϕ , p , and v , recalling that our equation of state, given by (3.21), closes the system. Since the anion lattice is fixed and incompressible, n_a is constant, and the sum of the lithium ions and vacancies is also constant. Therefore, once n_c is found, n_v can be determined.

Finally, we supplement the problem with boundary and initial conditions: for (3.57a) we need an initial condition for n_c and two boundary conditions for J_c , for (3.57b) we require two boundary conditions on ϕ , and for (3.57c) we need initial and boundary conditions for v . We are interested in investigating the SCL;

therefore, we assume lithium-metal electrodes on either end of the electrolyte and a fixed voltage condition applied across the electrolyte. We impose constant boundary conditions for the electric potential

$$\begin{aligned}\phi(z=0) &= \Delta V, \\ \phi(z=L) &= 0,\end{aligned}\tag{3.58}$$

and the flux

$$\begin{aligned}J_c(z=0) &= J_0, \\ J_c(z=L) &= J_L,\end{aligned}\tag{3.59}$$

as well as

$$v = 0\tag{3.60}$$

at the boundaries (no-slip). We also have initial conditions of the form

$$v(t=0) = v_0(z)\tag{3.61}$$

for v and

$$n_c(t=0) = n_{c0}(z)\tag{3.62}$$

for n_c , which should satisfy

$$\int_0^L n_{c0}(z,0) \, dz = n_a L\tag{3.63}$$

for charge neutrality. A sketch of the geometry of this setup can be found in Figure 3.1.

3.2.3 Non-dimensionalisation

We non-dimensionalise the model given by (3.57) with the following scales

$$\begin{aligned}z &= Lz', \quad t = t_0 t', \quad \mu_k = k_B T \mu'_k, \quad v = \frac{L}{t_0} v', \quad J_c = \frac{\Delta V q m_c M}{L} J'_c, \\ n &= n_r n', \quad z_k = q z'_k, \quad p = p_r p', \quad \rho = \rho_0 \rho', \quad \phi = \Delta V \phi'\end{aligned}$$

where L is a reference length scale corresponding to the width of the solid electrolyte and $q = \frac{F}{N_A} = 1.602 \times 10^{-19}$ Coulombs is the elementary charge. To balance the two velocity terms of (3.57c), we chose

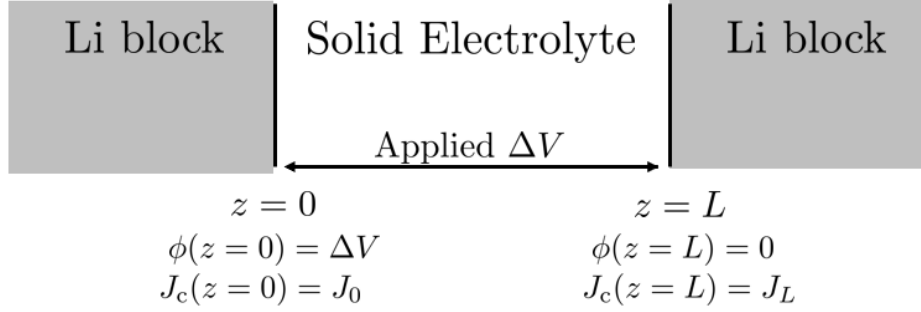


Figure 3.1: Sketch of a solid electrolyte with lithium-metal blocks on either end. A fixed potential ΔV is applied across the electrolyte with Dirichlet boundary conditions prescribed for the electric potential and cation flux at the electrolyte-lithium interface.

the velocity scale to be $\frac{L}{t_0}$, where t_0 is still to be determined. The scales for μ_k , ϕ , and J_c are chosen from balancing the flux and potential terms in (3.57d). The scaled potential conditions are given by

$$\begin{aligned}\phi'(z' = 0) &= 1, \\ \phi'(z' = 1) &= 0,\end{aligned}\tag{3.64}$$

and scaled flux conditions by

$$\begin{aligned}J'_c(z' = 0) &= j_0, \\ J'_c(z' = 1) &= j_1.\end{aligned}\tag{3.65}$$

Since we have conservation of total mass,

$$n' = n'_c + n'_v + n'_a = 1,\tag{3.66}$$

and based on the assumption of a stationary and incompressible anion lattice, we have that n'_a is constant.

It then follows that

$$n'_c + n'_v = 1 - n'_a := \nu,\tag{3.67}$$

which is also a constant.

For the timescale we first consider the non-dimensional form of the conservation of mass equation (3.57a)

$$\frac{\partial n'_c}{\partial t'} = -\frac{t_0 \Delta V M q}{n_r L^2} \frac{\partial}{\partial z'} \left(\left(\frac{m_c n'_c}{m_a n'_a} + 1 \right) J'_c \right),\tag{3.68}$$

and the conservation of charge equation (3.57b)

$$n^{F'} = -\frac{\Delta V \epsilon_0 (1 + \chi)}{q n_r L^2} \frac{\partial^2 \phi'}{\partial z'^2}. \quad (3.69)$$

If we differentiate the equation for $n^{F'}$ in (3.69) with respect to time, noting that from our definition of free charge in (3.19), and since z_a, z_c , and n'_a are constant, we must have:

$$\frac{\partial n^{F'}}{\partial t'} = z_c \frac{\partial n'_c}{\partial t'}. \quad (3.70)$$

Substituting (3.68) and (3.69) into (3.70), it follows that:

$$\frac{\partial n^{F'}}{\partial t'} = -\frac{\Delta V \epsilon_0 (1 + \chi)}{q n_r L^2} \frac{\partial^2}{\partial z'^2} \left(\frac{\partial \phi'}{\partial t'} \right) = -z_c \frac{t_0 \Delta V M q}{n_r L^2} \frac{\partial}{\partial z'} \left(\left(\frac{m_c n'_c}{m_a n'_a} + 1 \right) J'_c \right). \quad (3.71)$$

Therefore, the appropriate scale for time to balance these two expressions in (3.71) is

$$t_0 = \frac{\Delta V \epsilon_0 (1 + \chi) n_r L^2}{\Delta V z_c M q^2 n_r L^2} = \frac{\epsilon_0 (1 + \chi)}{q^2 M z_c}, \quad (3.72)$$

which has units of seconds and is a mobility time scale relative to free space.

Therefore, dropping the primes, we have the following non-dimensional problem:

$$\frac{\partial n_c}{\partial t} = -\frac{\delta^{-1} \lambda^2}{z_c} \frac{\partial}{\partial z} \left(\left(1 + \frac{m_c n_c}{m_a n_a} \right) J_c \right), \quad (3.73a)$$

$$n^F = -\delta^{-1} \lambda^2 \frac{\partial^2 \phi}{\partial z^2}, \quad (3.73b)$$

$$-\delta^{-1} n^F \frac{\partial \phi}{\partial z} = a^2 \frac{\partial p}{\partial z} + \eta \left(\frac{\partial(\rho v)}{\partial t} + \frac{\partial(\rho v^2)}{\partial z} \right), \quad (3.73c)$$

$$J_c = -\frac{\partial}{\partial z} \left(\delta \left((\mu_c - \mu_v) - \frac{m_c}{m_a} \left(\mu_a + \frac{n_c + n_v}{n_a} \mu_v \right) \right) + \left(z_c - \frac{m_c}{m_a} \right) \phi \right), \quad (3.73d)$$

subject to $\phi(0) = 1$, $\phi(1) = 0$, $J_c(0) = j_0$, $J_c(1) = j_1$, $v(0) = 0$, and $v(1) = 0$, with chemical potentials given by

$$\mu_c = a^2(p-1) + \log \left(\frac{n_c}{n_c + n_v} \right) + \mu_c^*, \quad \mu_v = a^2(p-1) + \log \left(\frac{n_v}{n_c + n_v} \right) + \mu_v^*, \quad \mu_a = a^2(p-1) + \mu_a^*, \quad (3.74)$$

subject to $n = n_c + n_v + n_a = 1$ from (3.66). We also have scaled initial conditions for the concentration of lithium ions

$$n_c(z, t = 0) = n_{c0}(z), \quad (3.75)$$

and the velocity

$$v(z, t = 0) = v_0(z). \quad (3.76)$$

In (3.73) and (3.74) we have defined four non-dimensional parameters;

$$a^2 = \frac{p_r}{n_r k_B T}, \quad \eta = \frac{\rho_0 L^2 q^4 M^2 z_c^2}{n_r k_B T \epsilon_0^2 (1 + \chi)^2}, \quad \lambda^2 = \frac{\epsilon_0 (1 + \chi) k_B T}{q^2 n_r L^2}, \quad \delta = \frac{k_B T}{\Delta V q}, \quad (3.77)$$

where a represents the ratio of the reference pressure to the ideal gas pressure; η denotes a momentum ratio; λ is similar to the Debye length of liquid electrolytes, and δ is the ratio of the thermal voltage to the applied voltage and typically (see, for example, Braun et al. (2015)) $\delta \ll 1$. We will define one additional non-dimensional parameter:

$$\epsilon^2 = \lambda^2 \delta^{-1}, \quad (3.78)$$

which will then appear in (3.73a) and (3.73b) above. Since $\lambda \ll 1$ and $\delta \ll 1$, ϵ is a combination of the small λ and the large δ^{-1} . However, we note that using the parameter values of Braun et al. (2015) $\lambda = 1.5 \times 10^{-3}$ and $\delta \approx 5.88 \times 10^{-3}$, which leads to $\epsilon \approx 1.96 \times 10^{-2} \ll 1$. Therefore, we will formally assume the distinguished limit that $\epsilon \ll 1$.

3.2.4 Model simplifications and supplementations

Based on the assumption of a stationary anion lattice (n_a constant) and conservation of total mass, we have $n_c + n_v = \nu$, as given in (3.67). It follows that we need only solve for n_c , since n_v can be determined from $n_v = \nu - n_c$, where ν is a known constant for a given n_a . From this, we note that we can combine the chemical potentials from (3.74) to find

$$\begin{aligned} \mu_c - \mu_v &= \log\left(\frac{n_c}{\nu}\right) - \log\left(\frac{n_v}{\nu}\right) + \mu_c^* - \mu_v^* = \log\left(\frac{n_c}{n_v}\right) + \mu_c^* - \mu_v^*, \\ \mu_a + \frac{\nu}{n_a} \mu_v &= \left(1 + \frac{\nu}{n_a}\right) a^2 (p - 1) + \frac{\nu}{n_a} \log\left(\frac{n_v}{\nu}\right) + \mu_a^* + \frac{\nu}{n_a} \mu_v^*, \end{aligned} \quad (3.79)$$

after performing some algebraic operations. Substituting these expressions into the flux equation (3.73d) we can rewrite this as

$$J_c = -\frac{\partial}{\partial z} \left(\delta \left(\log\left(\frac{n_c}{\nu - n_c}\right) - \frac{m_c}{m_a} \frac{n_a + \nu}{n_a} a^2 p - \frac{m_c}{m_a} \frac{\nu}{n_a} \log\left(\frac{\nu - n_c}{\nu}\right) \right) + \left(z_c - \frac{m_c}{m_a} z_a \right) \phi \right), \quad (3.80)$$

where the μ_k^* have vanished under the gradient.

We note that a manufactured battery would have a set amount of material, and hence charge, so we will assume that there is no build up of charge. This then imposes constraints on the flux prescribed at the boundaries. Because we are taking the Laplacian and the flux conditions are homogeneous Neumann-type

boundary conditions, this will then lead to uniqueness issues. Specifically, the Laplacian with Neumann boundary conditions has a nullspace consisting of constant functions, *i.e.* any constant satisfies the homogeneous Laplacian. Therefore, an additional condition, often referred to as a nullspace constraint, is required to ensure uniqueness of the solution. A natural condition to take is charge neutrality. Here, as we are concerned with the deviations from charge neutrality in the EDL we impose a global charge neutrality condition, which will allow for deviations while still preserving the overall electrolyte charge neutrality, expressed by the integral constraint

$$\int_0^1 n^F dz = 0. \quad (3.81)$$

For simplicity, we take the no flux limit, $J_c = 0$, and furthermore, we focus on the steady state, $\frac{\partial n_c}{\partial t} = 0$. We note that under the steady-state assumption, the average velocity must be constant; in this work, we take $v = 0$. This enables us to further simplify the problem by neglecting the dynamic and convective terms in the momentum equation (3.73c), reducing this equation to

$$-\delta^{-1} n^F \frac{d\phi}{dz} = a^2 \frac{dp}{dz}. \quad (3.82)$$

Following from this, we can eliminate pressure in the flux equation by substituting (3.82) into (3.80), thus rewriting the flux equation as

$$J_c = - \left(1 + \frac{m_c n_c}{m_a n_a} \right) \frac{d}{dz} \left(\delta \log \left(\frac{n_c}{\nu - n_c} \right) + z_c \phi \right). \quad (3.83)$$

Therefore, we can reduce the full non-dimensional problem (3.73) in this limit with $v = 0$ and $J_c = 0$ so that our final model is

$$n^F = -\epsilon^2 \frac{d^2 \phi}{dz^2}, \quad (3.84a)$$

$$c = \delta \log \left(\frac{n_c}{\nu - n_c} \right) + z_c \phi, \quad (3.84b)$$

with our potential boundary conditions $\phi(0) = 1$ and $\phi(1) = 0$, and our integral constraint (3.81). Here c is a yet unknown constant of integration. In the full time-dependent problem we would have (3.73a) and that the integral of the initial condition is preserved, *i.e.*

$$\int_0^1 n_c(z, t) dz = \int_0^1 n_c(z, t = 0) dz. \quad (3.85)$$

When we go to the steady-state problem we lose this condition and so, mathematically, we need another condition in order to compensate for the additional unknown, c . In this limit we see the explicit need for the integral condition as the nullspace constraint used to determine c .

3.2.5 Auxiliary variable

At the beginning of this chapter, we acknowledged that other authors have previously encountered difficulties when numerically solving a SE model with SCL (Katzenmeier et al. (2022); Swift et al. (2021); Landstorfer et al. (2011)). We commented that these difficulties arise as a result of the lithium-ion number density, $n_c \in (0, \nu)$, becoming exponentially close to its two singular limits of 0 and ν . From (3.84b) we can immediately see how this will cause issues in the logarithmic term. We will introduce an auxiliary variable, θ , to simplify the relationship between n_c and ϕ and to avoid this issue of near singularities. To do so, we define θ by

$$e^\theta = \frac{n_c}{\nu - n_c} \quad (3.86)$$

which maps $n_c \in (0, \nu)$ to $\theta \in (-\infty, +\infty)$, thus avoiding numerical artifacts of near singularity by transforming to a smooth domain. Rewriting the problem (3.84) using (3.86) leads to

$$\epsilon^2 \frac{d^2 \phi}{dz^2} = -n^F = -\frac{z_c \nu}{1 + e^{-\theta}} - z_a n_a, \quad (3.87a)$$

$$c = \delta \theta + z_c \phi. \quad (3.87b)$$

The integral constraint (3.81) can be written in terms of θ as

$$\int_0^1 \frac{1}{1 + e^{-\theta}} dz = -\frac{z_a n_a}{z_c \nu}. \quad (3.88)$$

3.3 Numerical solution

3.3.1 Numerical details

The main advantage of the auxiliary variable is that the domain is now smooth and therefore we can use standard numerical methods. To solve the zero flux steady-state problem (3.87) with (3.88) subject to $\phi(0) = 1$, $\phi(1) = 0$ we use cell centered finite differences for the derivatives, the midpoint rule for the integral, and Newton's method. We use the same parameter values as used in Braun et al. (2015)

$$z_c = 1, \quad z_a = -1, \quad m_c = 0.3, \quad m_a = 0.7, \quad n_a = 0.4, \quad \nu = 0.6,$$

where $n = n_a + \nu = 1$ and $m = m_a + m_c = 1$ from our non-dimensionalisation.

Simulations were implemented in MATLAB (Inc. (2023)) and run on a standard Dell laptop equipped with an 11th Gen Intel Core i5-1135G7 @ 2.40GHz and 8 GB of RAM, running Windows 11. A uniform grid of

$N = 10,000$ nodes is used to compute the solution over the domain $z \in (0, 1)$, with an elapsed computational time of approximately 1 second. The following constant initial conditions are applied:

$$\phi = 0.65, \quad \theta = \log \left(\frac{-z_a n_a}{z_c \nu + z_a n_a} \right), \quad c = 0.5, \quad (3.89)$$

where ϕ and c are chosen arbitrarily within reasonable bounds ($\phi \in [0, 1]$, $c = \mathcal{O}(1)$), and θ was chosen to satisfy the integral constraint (3.88). The numerical scheme has been tested for various other $\mathcal{O}(1)$ constant initial conditions and exhibits robust, consistent results across these choices.

Various grid sizes were investigated and mesh independence has been verified: for fixed parameter values, the numerical error scales with $h = \frac{1}{N+1}$, and the solution stabilizes with grid refinement. The boundary layer width remains independent of h , but fine spatial resolution is necessary to resolve the steep gradients in the narrow boundary layers.

The code has also been tested for varying ϵ and δ values. As these parameters decrease, the problem becomes increasingly stiff, and in such cases, solutions computed on coarser grid can serve as initial data for more refined computations.

3.3.2 Numerical results

Both the lithium ion concentration and electric potential solution profiles for the zero flux steady-state case are presented in Figure 3.2. In general, the numerical solutions yield two regions, a “constant” region where both the concentration and electric potential profiles appear to be approximately constant, and a “tail” region where the solution profiles divert from the constant solution in a narrow area to meet the required boundary conditions. In this figure we also include the solutions obtained by Braun et al. (2015) for comparison, whereby these authors determine their solutions by first computing a semi-analytical solution to their steady state zero flux equivalent of (3.73) and then solving the resulting equations numerically in Mathematica. We note that the overall behaviour agrees between our numerical approach and their semi-analytic approach in both plots of Figure 3.2, however, we observe some discrepancies between the two, which we highlight below.

Considering the inset plot of Figure 3.2a we observe some disparity in the tail regions (shaded regions) between our solution (solid blue line) and that of Braun et al. (2015) (in red dotted lines) for the lithium-ion concentration distribution. In particular, the two solutions diverge from each other as we move farther away from the constant (non-shaded) region. On closer inspection, we also notice some differences near the ends

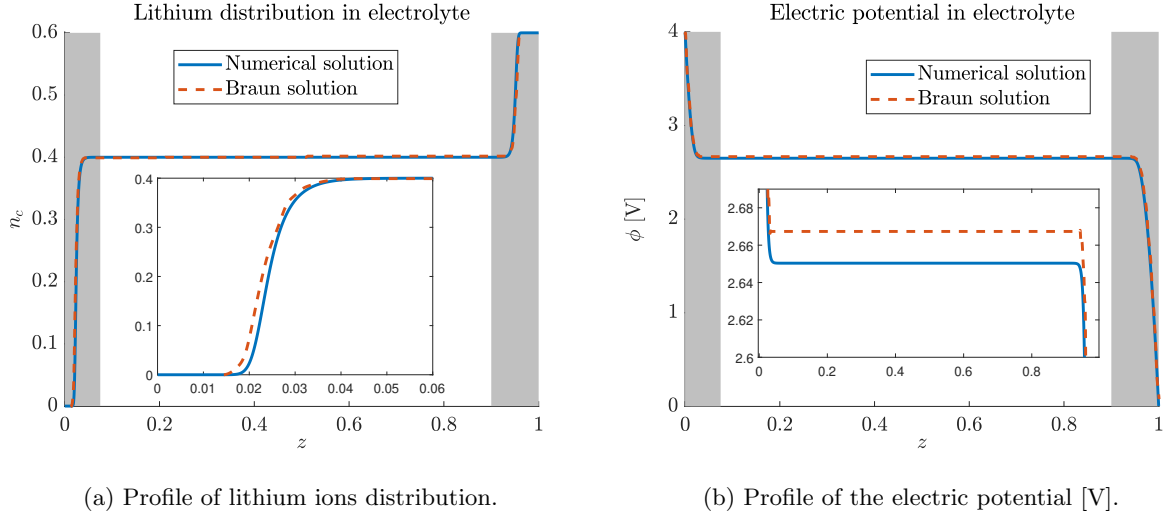


Figure 3.2: Numerical results for the 1D steady-state problem (3.87) with (3.88) subject to $\phi(0) = 1$ and $\phi(1) = 0$ with parameter values: $z_c = 1$, $z_a = -1$, $m_c = 0.3$, $m_a = 0.7$, $n_a = 0.4$, $\nu = 0.6$ where $n = n_a + \nu = 1$, $m = m_a + m_c = 1$. We take $\lambda = 1.5 \times 10^{-3}$, $\delta^{-1} = 170$, and $\Delta V = 4V$. We show our solution and the solution obtained by Braun et al. (2015) for comparison, with ϕ shown dimensionally (in volts) as per convention. The shaded areas corresponds to the tail regions and the non-shaded area indicates the constant region. In the inset plot of Figure 3.2a we zoom in on the left tail region to highlight the difference between the two solutions. Similarly, in the inset of Figure 3.2b we zoom in on the constant region of the solution to highlight discrepancies between the solutions.

of tails of the solutions as we approach the boundary. The solution in solid blue gets exponentially close to the limiting value of 0, while the red dotted solution seems to terminate much sooner – likely because Braun et al. (2015) do not resolve the logarithmic singularity.

Turning our attention to the potential profile in the inset plot of Figure 3.2b, we observe that the two solutions appear to differ by a constant within the non-shaded region of the main plot. As we will see in Section 3.4, this difference can be attributed to asymptotic corrections. We note that a similar correction also applies to the tail regions of Figure 3.2b. These observations suggest that the semi-analytic approach may be a coarse first-order approximation to the problem while the addition of the auxiliary variable removes the issues surrounding singularities and thus enables us to solve the full problem.

Overall, from our numerical simulation results shown in Figure 3.2, we observe that the profiles of both the

lithium ions and the electric potential are constant throughout the bulk (non-shaded, constant region) of the electrolyte and that there are narrow boundary layers (shaded, tail regions) on either side of the bulk. We remark that these narrow boundary layers are the SCL of the electrolyte, corresponding to the regions in which the solution deviates from electroneutrality. Considering (3.87a), since we have an ϵ^2 coefficient on $\frac{d^2\phi}{dz^2}$, this suggests that ϵ is the appropriate scaling for the boundary layer. This choice maintains $\mathcal{O}(1)$ potentials, consistent with the prescribed boundary conditions for ϕ . From the parameter values used by Braun et al. (2015) we have $\epsilon = \sqrt{\lambda^2\delta^{-1}} = 0.0196 \approx 10\lambda$, which aligns with qualitative observations made by Braun et al. (2015) regarding the SCL width. We note that similar comments on these wider SCL lengths have been stipulated in work by other authors, such as Li and Monroe (2019, 2021). This indicates that the scaling and non-dimensional numbers we have introduced (ϵ, δ) provide a quantifiable measure of these double-layer widths.

3.4 Asymptotic reduction

We remark that there are two pathways in undertaking an asymptotic analysis of this solid electrolyte model; matched asymptotics of Ordinary Differential Equations (ODEs) (which we present here) and matched asymptotics of integrals which we present as an alternative formulation in section 3.6.

From our numerical simulation results in Figure 3.2, we observe distinct behaviour in the tail (shaded) and constant (non-shaded) regions of the solution profiles for the lithium-ion concentrations and the electric potential. Motivated by this behaviour, we perform an asymptotic reduction of the ODE model, which will allow us to formally define these regions and the structure of the layers, explore the asymptotic limits, and gain a deeper understanding of the double charge layer thickness.

Before we proceed with the asymptotic reduction, we note that we can further simplify the calculations by eliminating ϕ from the problem. We consider the 1D zero flux steady-state problem given by (3.87), (3.88) and subject to $\phi(0) = 1$, $\phi(1) = 0$. Under steady-state conditions we remark that (3.87b) can be used to

write ϕ in terms of θ ; therefore the zero flux steady-state problem can be written as

$$\frac{\epsilon^2 \delta}{z_c} \frac{d^2 \theta}{dz^2} = \frac{\beta_1 + \beta_2}{1 + e^{-\theta}} - \beta_1 \quad (3.90a)$$

$$\int_0^1 \frac{1}{1 + e^{-\theta}} dz = \frac{\beta_1}{\beta_1 + \beta_2} \quad (3.90b)$$

$$\theta(0) = \frac{c - z_c}{\delta}, \quad \theta(1) = \frac{c}{\delta}, \quad (3.90c)$$

where we define

$$\beta_1 = -z_a n_a, \quad \beta_2 = z_a n_a + z_c \nu. \quad (3.91)$$

We observe that while the boundary conditions for θ are large, the problem is appropriately scaled for ϕ (where the original boundary conditions are applied) and we have chosen a scaling that maintains $\theta \sim \mathcal{O}(1)$ in the bulk region.

3.4.1 Bulk

The constant (non-shaded) regions of Figure 3.2 correspond to the bulk of the solution, *i.e.* the region of the solution where we expect all of the variables to be approximately $\mathcal{O}(1)$ constants and the small parameters are notionally zero. Therefore, we take $z \sim \mathcal{O}(1)$ and since $\epsilon, \delta \ll 1$, (3.90a) becomes

$$0 = \frac{\beta_1 + \beta_2}{1 + e^{-\theta}} - \beta_1 \quad (3.92)$$

which we solve for the bulk value of θ , denoted θ^*

$$\theta^* = \log \left(\frac{\beta_1}{\beta_2} \right). \quad (3.93)$$

We can then refer to (3.87b) to determine the corresponding solution for the potential in the bulk

$$\phi^* = \frac{c}{z_c} - \delta \frac{\theta^*}{z_c}, \quad (3.94)$$

where the constant c is currently unknown and will later be determined from asymptotic matching. We note from (3.92) that any corrections to θ will be exponentially small, meaning there is no formal power series correction of $\mathcal{O}(\delta)$. However, ϕ does have an $\mathcal{O}(\delta)$ correction, which depends on the bulk solution for θ . From this, we notice that if we peel off the $\delta\theta^*/z_c$ term from our numerical solution for ϕ and plot the remaining $\mathcal{O}(1)$ component (shown via the light blue dotted line) in Figure 3.3, essentially neglecting the $\mathcal{O}(\delta)$ correction, we observe that it aligns with the solution from Braun et al. (2015), confirming our earlier

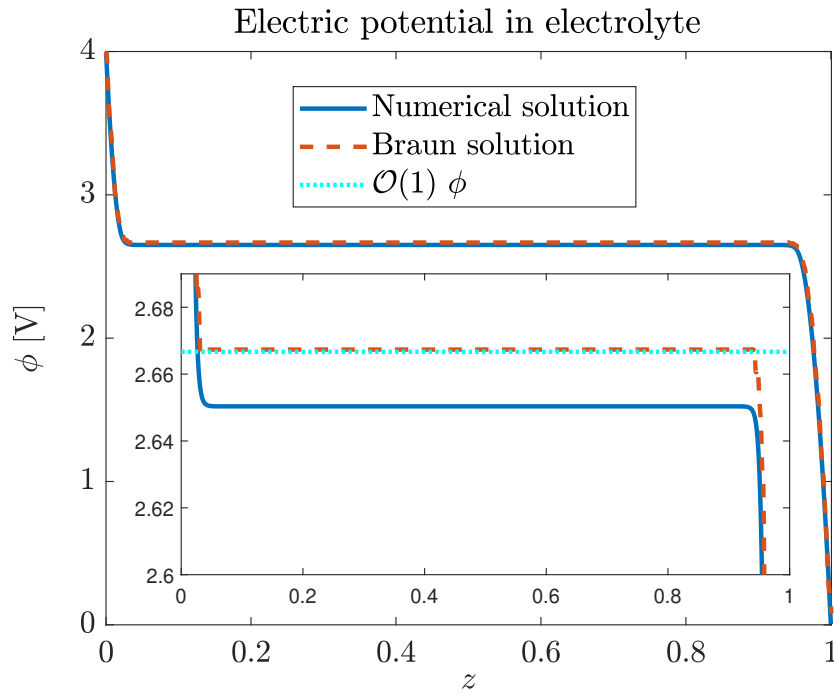


Figure 3.3: Profile of the electric potential as shown in Figure 3.2b with the addition of the light blue line which represents the $\mathcal{O}(1)$ component of the solution for ϕ [V].

hypothesis in Section 3.3 regarding the possibility of a missed asymptotic correction. Moreover, we note that (3.87b) indicates that $\mathcal{O}(1)$ changes in θ have $\mathcal{O}(\delta)$ impacts on ϕ everywhere in the domain.

Clearly, this bulk solution is constant and therefore cannot satisfy both boundary conditions (*i.e.* the two prescribed values of ϕ). While we could choose ϕ^* to satisfy one of the boundary conditions, thereby determining a value for c , there is no reason a priori to know where the boundary layer is. Given the structure of the problem, and considering the shaded regions of the solution profiles in Figure 3.2, it is likely that there is a boundary layer on both sides. As a result, ϕ^* does not satisfy either boundary condition. We therefore proceed with a boundary-layer analysis on either side of the bulk.

3.4.2 Boundary layers

To investigate what is happening in the tail (shaded) regions of Figure 3.2 we will need to rescale the problem to identify the terms that play a dominant role near these boundaries. At the left boundary, near $z = 0$, z is small (since it is close to zero) and therefore we will scale $z = \epsilon x_{\text{BL}}$. From the boundary condition (3.90c), we expect $c < z_c$ since $n_c \rightarrow 0$ near the left boundary. This implies that θ is large and negative near $z = 0$; therefore, we scale $\theta = -\delta^{-1}\psi_{\text{BL}}$. We use the subscript BL to indicate the left boundary layer. We can then rewrite (3.90a) as

$$\frac{d^2\psi_{\text{BL}}}{dx_{\text{BL}}^2} = z_c\beta_1 - z_c\frac{\beta_1 + \beta_2}{1 + e^{+\delta^{-1}\psi_{\text{BL}}}} \approx z_c\beta_1 \quad (3.95)$$

near this boundary. We want to solve for each variable to at least $\mathcal{O}(1)$, so we will expand ψ_{BL} up to $\mathcal{O}(\delta)$ as

$$\psi_{\text{BL}} = \psi_{\text{BL}}^0 + \delta\psi_{\text{BL}}^1 \quad (3.96)$$

in order to ensure that θ_{BL} has an $\mathcal{O}(1)$ component for matching to the bulk solution θ^* . Substituting (3.96) into (3.95) and looking at each order we have the following problems and associated boundary conditions

$$\mathcal{O}(1) : \quad \frac{d^2\psi_{\text{BL}}^0}{dx_{\text{BL}}^2} = z_c\beta_1, \quad \psi_{\text{BL}}^0(0) = z_c - c, \quad (3.97a)$$

$$\mathcal{O}(\delta) : \quad \frac{d^2\psi_{\text{BL}}^1}{dx_{\text{BL}}^2} = 0, \quad \psi_{\text{BL}}^1(0) = 0 \quad (3.97b)$$

which, on integrating, yields the following solutions for θ

$$\mathcal{O}(1) : \quad \psi_{\text{BL}}^0 = \frac{z_c\beta_1 x_{\text{BL}}^2}{2} + A_0 x_{\text{BL}} + z_c - c \quad (3.98a)$$

$$\mathcal{O}(\delta) : \quad \psi_{\text{BL}}^1 = A_1 x_{\text{BL}}, \quad (3.98b)$$

where A_0 and A_1 are unknown constants to be determined.

The right boundary, near $z = 1$, can be solved in a similar manner; here z is close to one and so we scale $z = 1 - \epsilon x_{\text{BR}}$. We expect θ to be large and positive from our boundary condition (3.90c) hence we scale $\theta = \delta^{-1} \psi_{\text{BR}}$. We use the subscript BR to denote the boundary layer near 1. Rewriting (3.90a) with these scales gives

$$\frac{d^2 \psi_{\text{BR}}}{dx_{\text{BR}}^2} = -z_c \beta_1 + z_c \frac{\beta_1 + \beta_2}{1 + e^{-\delta^{-1} \psi_{\text{BR}}}} \approx z_c \beta_2. \quad (3.99)$$

We expand $\psi_{\text{BR}} = \psi_{\text{BR}}^0 + \delta \psi_{\text{BR}}^1$ and substitute into (3.99) to find

$$\mathcal{O}(1): \quad \psi_{\text{BR}}^0 = \frac{z_c \beta_2 x_{\text{BR}}^2}{2} + B_0 x_{\text{BR}} + c \quad (3.100a)$$

$$\mathcal{O}(\delta): \quad \psi_{\text{BR}}^1 = B_1 x_{\text{BR}}, \quad (3.100b)$$

for unknown constants B_0 and B_1 .

We observe that if we apply the integral constraint from (3.90b) to (3.73b)

$$\lambda^2 \delta^{-1} \int_0^1 \frac{d^2 \phi}{dz^2} dz = -z_c \int_0^1 n_c dz - z_a n_a = 0, \quad (3.101)$$

which then implies that

$$\left. \frac{d\psi_{\text{BL}}}{dx_{\text{BL}}} \right|_{(x_{\text{BL}}=0)} = \left. \frac{d\psi_{\text{BR}}}{dx_{\text{BR}}} \right|_{(x_{\text{BR}}=0)} \quad (3.102)$$

and therefore, considering our two boundary layer solutions for θ ((3.98) and (3.100)), it follows that

$$B_0 = A_0, \quad B_1 = A_1. \quad (3.103)$$

Typically, we determine the unknown constants when we do our asymptotic matching between the various regions. Specifically, we would find the values for A_0 and A_1 through the integral condition (3.90b), which is a global constraint on the problem. However, this involves matching together asymptotic solutions which likely introduces error. Instead, we can take advantage of the fact that the full problem (3.90a) has a first integral. If we multiply both sides of (3.90a) by $\frac{d\theta}{dz}$ and then integrate with respect to z , we obtain

$$\begin{aligned} \frac{\epsilon^2 \delta}{2z_c} \left(\frac{d\theta}{dz} \right)^2 &= (\beta_1 + \beta_2) \log(1 + e^{-\theta}) - \beta_1 \theta + \beta_1 \log\left(\frac{\beta_1}{\beta_2}\right) \\ &\quad - (\beta_1 + \beta_2) \log\left(\frac{\beta_1 + \beta_2}{\beta_2}\right), \end{aligned} \quad (3.104)$$

where we have determined the constant of integration from the bulk since we know that $\frac{d\theta}{dz} = 0$ when $\theta = \theta^*$. From our boundary condition at $z = 0$ (3.90c) we know that $\theta(0) = \frac{c - z_c}{\delta}$, and our left boundary

layer solution (3.98) says that $\frac{d\theta}{dz} = -\frac{1}{\epsilon\delta} (z_c\beta_1\frac{z}{\epsilon} + A_0 + \delta A_1)$ since $z = \epsilon x$ in this layer. Therefore we must have the following local condition, substituting this expression for $\frac{d\theta}{dz}$ and our boundary condition into (3.104):

$$\begin{aligned} \frac{\epsilon^2\delta}{2z_c} \left(-\frac{1}{\epsilon\delta} \left(z_c\beta_1\frac{z}{\epsilon} + A_0 + \delta A_1 \right) \right)^2 \Big|_{z=0} &= (\beta_1 + \beta_2) \log \left(1 + e^{-\frac{c-z_c}{\delta}} \right) - \\ &\quad \beta_1 \left(\frac{c-z_c}{\delta} \right) + \beta_1 \log \left(\frac{\beta_1}{\beta_2} \right) - \\ &\quad (\beta_1 + \beta_2) \log \left(\frac{\beta_1 + \beta_2}{\beta_2} \right). \end{aligned} \quad (3.105)$$

We can expand this expression in orders of $\mathcal{O}(\delta)$ and match terms to find A_0, A_1 , noting that $e^{-\frac{c-z_c}{\delta}}$ is asymptotically small. At $\mathcal{O}(\delta^{-1})$,

$$A_0 = -\sqrt{2z_c\beta_1(z_c - c)}, \quad (3.106)$$

and at $\mathcal{O}(1)$,

$$A_1 = \frac{z_c}{A_0} \left(\beta_1 \log \left(\frac{\beta_1}{\beta_2} \right) - (\beta_1 + \beta_2) \log \left(\frac{\beta_1 + \beta_2}{\beta_2} \right) \right). \quad (3.107)$$

For the remaining unknown constant c we will have to revert to the standard matching procedure between each region for it to be determined. Before we can proceed with matching we observe that θ^* , the bulk solution for θ is an $\mathcal{O}(1)$ constant. Therefore, we require our boundary layer solutions to approach $\theta \sim \mathcal{O}(1)$ as we move away from the boundaries and towards the bulk in order to match there. However, if we consider the boundary layer solution on the left, (3.98) is quadratic and therefore does not plateau; furthermore the quadratic solution reaches it's maximum and begins to decrease before reaching the bulk value. In particular, if we said that ψ_{BL} reached it's maximum at some $x^* = x_0^* + \delta x_1^*$, we would solve for x^* by solving

$$\frac{d\psi_{\text{BL}}^0}{dx} \Big|_{x_0^*} + \delta \left(\frac{d^2\psi_{\text{BL}}^0}{dx^2} \Big|_{x_0^*} x_1^* + \frac{d\psi_{\text{BL}}^1}{dx} \Big|_{x_0^*} \right) = 0, \quad (3.108)$$

using our solution $\theta_{\text{BL}} = -\delta^{-1}\psi_{\text{BL}}$ from (3.98). Hence, we would determine

$$x_0^* = \frac{-A_0}{z_c\beta_1}, \quad x_1^* = \frac{-A_1}{z_c\beta_1}. \quad (3.109)$$

Substituting these values back into our boundary layer solution (3.98) and using our solutions for A_0, A_1

from (3.106) and (3.107) respectively;

$$\begin{aligned}
\theta_{\text{BL}}(x^*) &= -\delta^{-1}\psi_{\text{BL}}(x^*) \approx -\delta^{-1} \left(\psi_{\text{BL}}^0(x_0^*) + \delta \left(\frac{d\psi_{\text{BL}}^0}{dx} \Big|_{x_0^*} x_1^* + \psi_{\text{BL}}^1(x_0^*) \right) \right) \\
&= \frac{A_0 A_1}{z_c \beta_1} = \log \left(\frac{\beta_1}{\beta_2} \right) - \frac{\beta_1 + \beta_2}{\beta_1} \log \left(\frac{\beta_1 + \beta_2}{\beta_2} \right) \\
&< \log \left(\frac{\beta_1}{\beta_2} \right) = \theta^*,
\end{aligned} \tag{3.110}$$

since $\beta_1 + \beta_2 = z_c \nu > 0$, $\beta_1 > 0$, and $\beta_1 + \beta_2 > \beta_1$ from (3.91) and our given parameter values. We note that we have a similar issue at the right boundary layer, in which case the minimum of the quadratic overshoots the bulk value. This indicates that there must be some other region connecting the boundary to the bulk.

We revisit (3.90a), noting that there are in fact two possible scalings which preserve the derivative when $z \sim \epsilon$:

$$\theta \sim \delta^{-1} \text{ or } x \sim \sqrt{\delta}.$$

Therefore, we must have some intermediate layer where $\theta \sim \mathcal{O}(1)$ and $x \sim \sqrt{\delta}$ which facilitates a transition for θ from large (at the boundary) to $\mathcal{O}(1)$ (in the bulk) and to ensure that we have continuity between the bulk and boundary layers.

3.4.3 Intermediate layers

To investigate this intermediate region connecting the boundary and bulk regions we must then rescale $x \sim \sqrt{\delta}$. We consider the left boundary first, where we have $z = \epsilon x_{\text{BL}}$ and we rescale

$$x_{\text{BL}} = \xi_{\text{L}} + \sqrt{\delta} y_{\text{IL}}, \tag{3.111}$$

where we define ξ_{L} to be the point of continuity between the boundary and the intermediate layer solutions on the left. Here the subscript IL denotes this left intermediate layer. In this region we will let the solution for θ be given as

$$\theta_{\text{IL}}(y_{\text{IL}}) = \theta(\xi_{\text{L}} + \sqrt{\delta} y_{\text{IL}}). \tag{3.112}$$

We include a schematic of this boundary layer structure in Figure 3.4, noting that this is not representative of the width of each region, but rather to give a visual representation of where these regions are.

Substituting these expressions into (3.90a) yields the following equation for θ in this layer:

$$\frac{d^2 \theta_{\text{IL}}}{dy_{\text{IL}}^2} = -z_c \beta_1 + z_c \frac{\beta_1 + \beta_2}{1 + e^{-\theta_{\text{IL}}}}. \tag{3.113}$$

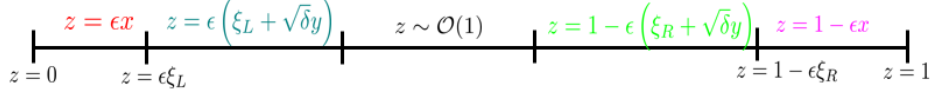


Figure 3.4: Sketch of boundary layer structure.

We observe that this equation for θ is equivalent to the full non-linear problem, albeit with the rescaled length variables. Now, if this was straightforward to solve we would have done so already, however this is not the case and therefore, we will have to make some approximation in order to gain analytic insight. To do so, we first notice that this intermediate layer is not needed to resolve the leading-order problem for the electric potential. Recalling from (3.87b) which tells us that $z_c \phi + \delta \theta = c$, while the intermediate layer has $\mathcal{O}(1)$ effects in θ , its strongest effect in ϕ will be at $\mathcal{O}(\delta)$. In other words, $\phi_{\text{IL}} = \frac{c}{z_c} - \frac{\delta}{z_c} \theta_{\text{IL}}$; so the intermediate layer behaviour is a correction to ϕ . In fact, if we recall our bulk solution for ϕ given by (3.94), it follows that the intermediate solution for ϕ is some correction to the solution in the bulk region. We therefore make the assumption that the intermediate solution for θ is also close to its bulk value, taking

$$\theta_{\text{IL}} = \theta^* + \Theta_{\text{IL}}, \quad (3.114)$$

where $\Theta_{\text{IL}} \ll 1$ is the intermediate solution correction to the bulk value. We note that this linearisation approach can be justified as the dominant singularity component of an integral (see section 3.6).

Substituting this expression for θ_{IL} into (3.113) and Taylor-expanding about the correction term, *i.e.* $\theta_{\text{IL}} = \theta^*$ with $\Theta_{\text{IL}} \ll \theta^*$, we will have

$$\begin{aligned} \frac{d^2 \Theta_{\text{IL}}}{dy_{\text{IL}}^2} &= -z_c \beta_1 + z_c \frac{\beta_1 + \beta_2}{1 + e^{-\theta^* - \Theta_{\text{IL}}}} \\ &\approx -z_c \beta_1 + z_c (\beta_1 + \beta_2) \left(\frac{1}{1 + e^{-\theta^*}} + \frac{e^{-\theta^*}}{(1 + e^{-\theta^*})^2} \Theta_{\text{IL}} \right) \\ &= -z_c \beta_1 + z_c (\beta_1 + \beta_2) \left(\frac{\beta_1}{\beta_1 + \beta_2} + \frac{\beta_1 \beta_2}{(\beta_1 + \beta_2)^2} \Theta_{\text{IL}} \right) \\ &= \frac{\beta_1 \beta_2}{\nu} \Theta_{\text{IL}}. \end{aligned} \quad (3.115)$$

Solving (3.115) is straightforward and we write the solution for Θ_{IL} as

$$\Theta_{\text{IL}} = (\theta_1 - \theta^*) e^{-\sqrt{\frac{\beta_1 \beta_2}{\nu}} y_{\text{IL}}} = (\theta_1 - \theta^*) e^{-\sqrt{\frac{\beta_1 \beta_2}{\delta \nu}} (x_{\text{BL}} - \xi_L)} = (\theta_1 - \theta^*) e^{-a \frac{(z - z_L)}{\epsilon \sqrt{\delta}}}, \quad (3.116)$$

for some constant θ_1 which we determine later. We define $z_L = \epsilon \xi_L$ and we let $a = \sqrt{\frac{z_c \beta_1 \beta_2}{\beta_1 + \beta_2}} = \sqrt{\frac{\beta_1 \beta_2}{\nu}}$. Therefore, our left intermediate layer solution for θ is

$$\theta_{IL} = \theta^* + \Theta_{IL} = \theta^* + (\theta_1 - \theta^*) e^{-a \frac{(z - z_L)}{\epsilon \sqrt{\delta}}}. \quad (3.117)$$

We note that $\Theta_{IL} \rightarrow 0$ as $y_{IL} \rightarrow \infty$, thus the intermediate solution tends to the bulk solution ($\theta_{IL} \rightarrow \theta^*$) as we move toward the bulk region in z , as required. As a consequence of the choice to linearise the intermediate layer problem, which we do in order to gain analytical insight into the structure of this layer, we determine this exponential intermediate layer solution. As a result, we cannot match at both $y_{IL} \rightarrow \pm\infty$. Therefore, noting the translational invariance of the intermediate layer problem, we instead truncate at $y_{IL} = 0$. It follows that, matching at $y_{IL} = 0$ and $y_{IL} \rightarrow +\infty$, the coefficient of the $e^{a \frac{(z - z_L)}{\epsilon \sqrt{\delta}}}$ must be equal to zero.

The intermediate layer near the right boundary layer at $z = 1$ yields analogous expressions. In this layer we have $z = 1 - \epsilon x_{BR}$, we rescale $x_{BR} = \xi_R + \sqrt{\delta} y_{IR}$, and we let $\theta_{IR} = \theta^* + \Theta_{IR}$ to find the following solution for θ in the right intermediate layer, which we denote as θ_{IR} ,

$$\theta_{IR} = \theta^* + (\theta_2 - \theta^*) e^{-\sqrt{\frac{\beta_1 \beta_2}{\delta \nu}} (x_{BR} - \xi_R)} = \theta^* + (\theta_2 - \theta^*) e^{-a \frac{(z_R - z)}{\epsilon \sqrt{\delta}}}, \quad (3.118)$$

for some constant θ_2 with $z_R = 1 - \epsilon \xi_R$.

3.4.4 Matching

Before we proceed with the asymptotic matching we note that the approach taken here follows from the linearisation of the intermediate layer problem. We have included an alternative matching technique in Appendix A whereby we consider the full intermediate layer problem, thus losing the analytical solution for this region, but enabling a consideration of matching at both $y_{IL} \rightarrow \infty$ and $y_{IL} \rightarrow -\infty$, with the use of an alternative front-centering condition.

In order to complete our asymptotic solution and determine any remaining constants we must match the solutions between the various regions (boundary, intermediate, and bulk). We note that by construction, the intermediate layer solution is a far-field expansion of the bulk solution $\theta = \theta^*$, and therefore continuity between these two regions is an automatic consequence of the approximation made. Thus, it remains to match between the boundary and intermediate layers. Typically, enforcing continuity and differentiability between the boundary and intermediate solutions at z_L and z_R would furnish the remaining conditions to solve the problem. However, as a consequence of deriving the intermediate layer solutions from a far-field expansion

near the bulk, the boundary and intermediate layers need not necessarily agree at z_L and z_R . We note that the monotonicity of the intermediate layer provides a mechanism for continuity, but differentiability can, in general, not be satisfied¹. The boundary layer structure here necessitates matching between two asymptotic solutions, each of which diverges, thereby complicating the matching process. Instead, we will perform a pseudo-matching technique, where we minimize the error in differentiability between the two layers. There is another layer where the full non-linear problem must be realized, but since we are seeking an approximation of these layer locations, we will proceed with the minimisation and pseudo matching approach.

Starting with the left-hand side; we prescribe continuity at z_L between the solution for ψ_{BL} in the boundary layer and the solution for θ_{IL} in the intermediate layer, which will take the form

$$\theta_{BL}(z_L) = -\delta^{-1}\psi_{BL}(z_L) = \theta_{IL}(z_L). \quad (3.119)$$

Substituting the relevant solutions, (3.98) and (3.117), at $z = z_L$ we will have

$$-\delta^{-1} \left(\frac{z_c \beta_1}{2} \left(\frac{z_L}{\epsilon} \right)^2 + A_0 \frac{z_L}{\epsilon} + z_c - c + \delta A_1 \frac{z_L}{\epsilon} \right) = \theta_1, \quad (3.120)$$

since $x_L = \frac{z_L}{\epsilon}$. For our differentiability condition we first define $F_L = F_L(z_L)$ to be the difference in the derivatives, given by

$$\begin{aligned} F_L(z_L) &= \frac{d\theta_{BL}}{dz} \Big|_{z_L} - \frac{d\theta_{IL}}{dz} \Big|_{z_L} \\ &= -\frac{1}{\delta\epsilon} \left(z_c \beta_1 \frac{z_L}{\epsilon} + A_0 + \delta A_1 \right) + \frac{a}{\sqrt{\delta\epsilon}} (\theta_1(z_L) - \theta^*), \end{aligned} \quad (3.121)$$

where we substitute θ_1 from the continuity condition (3.120) into (3.121). We note that $F_L(z_L)$ is convex; thus,

$$\frac{d^2 F_L}{dz_L^2} = -\frac{az_c \beta_1}{\lambda^3} < 0. \quad (3.122)$$

Normally, from here we would match term by term in orders of δ to enforce differentiability so that $F_L = 0$. There will be cases where differentiability is possible, as well as cases where it is not; in the latter scenario we determine the value of z_L that minimises $|F_L|$.

¹Since the original problem is smooth, it must be continuous and differentiable everywhere. If we could solve (3.113) analytically in the intermediate layer, we could apply standard smooth matching. However, we simplify the full non-linear problem to an analytical approximation valid near the bulk far-field. This approximation loses validity as we approach the boundary layer creating a situation where smooth matching may no longer be feasible.

We have equivalent matching conditions for the right-hand side. Continuity at $z = z_R$ means that

$$\theta_{BR}(z_R) = \delta^{-1} \psi_{BR}(z_R) = \theta_{IR}(z_R), \quad (3.123)$$

which, from (3.100) and (3.118), is written as

$$\delta^{-1} \left(\frac{z_c \beta_2}{2} \left(\frac{1 - z_R}{\epsilon} \right)^2 + A_0 \frac{1 - z_R}{\epsilon} + c + \delta A_1 \frac{1 - z_R}{\epsilon} \right) = \theta_2, \quad (3.124)$$

since $x_R = \frac{1 - z_R}{\epsilon}$. Similar to the left side, we define F_R as

$$\begin{aligned} F_R(z_R) &= \frac{d\theta_{BR}}{dz} \Big|_{z_R} - \frac{d\theta_{IR}}{dz} \Big|_{z_R} \\ &= -\frac{1}{\delta \epsilon} \left(z_c \beta_2 \left(\frac{1 - z_R}{\epsilon} \right) + A_0 + \delta A_1 \right) - \frac{a}{\sqrt{\delta} \epsilon} (\theta_2(z_R) - \theta^*), \end{aligned} \quad (3.125)$$

which we note is also convex:

$$\frac{d^2 F_R}{dz_R^2} = -\frac{a z_c \beta_2}{\lambda^3} < 0. \quad (3.126)$$

Since we have that both F_i are convex, $F_i'' < 0$, if $F_i(z_i^*) > 0$, where z_i^* is the critical point, then the parabola will have a root and we can enforce differentiability. When differentiability holds, we solve for the root by setting $F_i(z_i) = 0$, noting that we take the root closer to the intermediate layer (*i.e.* the larger z_i). If we cannot enforce differentiability we then minimise the difference between the two derivatives. That is, we let z_i^* be the value of z_i that minimises $|F_i|$. Setting $F_L' = 0$ and solving for z_L^*

$$z_L^* = -\epsilon \left(\frac{A_0}{z_c \beta_1} + \frac{\sqrt{\delta}}{a} + \frac{\delta A_1}{z_c \beta_1} \right), \quad (3.127)$$

We remark that this value for z_L^* is similar to the maximum point of the quadratic in (3.109) since $z^* = \epsilon x^*$, except for this additional $\sqrt{\delta}$ term. Similarly, setting $F_R' = 0$ and solving for z_R^* we find

$$z_R^* = 1 - \epsilon \left(-\frac{A_0}{z_c \beta_2} - \frac{\sqrt{\delta}}{a} - \frac{\delta A_1}{z_c \beta_2} \right). \quad (3.128)$$

Substituting z_L^* from (3.127), A_0 from (3.106), and A_1 from (3.107) into (3.121), we obtain

$$F_L(z_L^*) = \frac{z_c \beta_2}{2\epsilon \sqrt{\delta}} \sqrt{\frac{\beta_1 + \beta_2}{z_c \beta_1 \beta_2}} \left(\frac{\beta_1}{\beta_2} - 2 \log \left(1 + \frac{\beta_1}{\beta_2} \right) \right). \quad (3.129)$$

We observe that we can determine whether differentiability holds or we proceed with the minimisation of F_i based on the values of β_i :

$$\frac{\beta_1}{\beta_2} - 2 \log \left(1 + \frac{\beta_1}{\beta_2} \right) = 0 \text{ when } \frac{\beta_1}{\beta_2} = 2.51286 = \beta^*. \quad (3.130)$$

That is, β^* is the critical value since we will have $F_L(z_L^*) < 0$ whenever $\frac{\beta_1}{\beta_2} < \beta^*$ and $F_L(z_L^*) > 0$ otherwise; if $F_L(z_L^*) < 0$, then there are no roots and differentiability is not permissible since F_L is convex. Similarly, substituting z_R^* from (3.128), A_0 from (3.106), and A_1 from (3.107) into (3.125), we obtain

$$F_R(z_R^*) = \frac{z_c \beta_1}{2\epsilon \sqrt{\delta}} \sqrt{\frac{\beta_1 + \beta_2}{z_c \beta_1 \beta_2}} \left(\frac{\beta_2}{\beta_1} - 2 \log \left(1 + \frac{\beta_2}{\beta_1} \right) \right), \quad (3.131)$$

and we find that $F_R > 0$ when $\frac{\beta_2}{\beta_1} - 2 \log \left(1 + \frac{\beta_2}{\beta_1} \right) > 0$, which occurs when $\frac{\beta_2}{\beta_1} > \beta^*$.

Thus, to complete our solution and determine the values of any outstanding unknown constants, we use the values for z_L and z_R obtained from the differentiability conditions ($F(z_i) = 0$ or minimising $|F_i|$) in equations (3.120) and (3.124) to find the values of θ_1 and θ_2 . As an example, we consider the scenario where both $F_i(z_i^*) < 0$ and we therefore take $z_L = z_L^*, z_R = z_R^*$. Taking (3.127) for z_L in the continuity condition (3.120) at $\mathcal{O}(1)$ gives the following expression for the constant θ_1

$$\theta_1 = -\frac{\beta_1 + \beta_2}{2\beta_2} + \frac{A_0 A_1}{z_c \beta_1}, \quad (3.132)$$

where we have only taken the leading-order solution for θ . Similarly, using (3.128) for z_R , we will have

$$\theta_2 = \frac{\beta_1 + \beta_2}{2\beta_1} - \frac{A_0 A_1}{z_c \beta_2}. \quad (3.133)$$

Finally, using z_R from (3.128) and θ_2 from (3.133) in the continuity condition (3.124), with the value determined for A_0 from (3.106), and matching at orders of δ we find that

$$c = \frac{\beta_1}{\nu}, \quad (3.134)$$

completing our solution. We note that, using the definitions of β_1 and β_2 from (3.91), we have $\beta_1 + \beta_2 = z_c \nu$. Substituting this into (3.134), the expression for c can be rewritten as

$$c = \frac{\beta_1}{\nu} = \frac{z_c \beta_1}{\beta_1 + \beta_2} < z_c, \quad (3.135)$$

which is consistent with our earlier expectation that $c < z_c$.

We acknowledge that the points of continuity between the boundary and intermediate layers, ξ_L and ξ_R , are not equal ($\xi_L \neq \xi_R$), which indicates that the left and right boundary layers have different widths, and thus the problem is not perfectly symmetric. This has also been highlighted by Braun et al. (2015), where the authors suggest that this is as a result of the fixed anion lattice since the free charge density, $n^F \in [-n_a, \nu - n_a]$, can only be symmetric if $\nu = 2n_a$.

3.4.5 SCL Summary

In this section we provide a summary of the solutions for the auxiliary variable, θ , obtained in each region in Table 3.1. We again note that the corresponding solutions for the lithium-ion concentration n_c and the electric potential ϕ for each region can then be determined by substituting the relevant expression for θ into (3.86) and (3.87b). The complete solution is composed of two boundary layers (left and right), two

Table 3.1: Summary of the solution obtained in each region of the solid electrolyte.

Summary of the solutions obtained in each of the regions	
Region	Solution for θ
Left boundary layer	$\theta_{\text{BL}} = -\frac{1}{\delta} \left(\frac{z_c \beta_1}{2} \left(\frac{z}{\epsilon} \right)^2 + A_0 \frac{z}{\epsilon} + z_c - c + \delta A_1 \frac{z}{\epsilon} \right)$
Left intermediate layer	$\theta_{\text{IL}} = \theta^* + (\theta_1 - \theta^*) e^{-a \frac{(z - z_L)}{\epsilon \sqrt{\delta}}}$
Bulk	$\theta^* = \log \left(\frac{\beta_1}{\beta_2} \right)$
Right intermediate layer	$\theta_{\text{IR}} = \theta^* + (\theta_2 - \theta^*) e^{-a \frac{(z_R - z)}{\epsilon \sqrt{\delta}}}$
Right boundary layer	$\theta_{\text{BR}} = \frac{1}{\delta} \left(\frac{z_c \beta_2}{2} \left(\frac{1-z}{\epsilon} \right)^2 + A_0 \frac{1-z}{\epsilon} + c + \delta A_1 \frac{1-z}{\epsilon} \right)$

intermediate layers (left and right), and a bulk layer. The left boundary meets the left intermediate layer at z_L , the right intermediate layer joins the right boundary layer at z_R , and the bulk solution connects the two intermediate layer solutions. The constants $A_0, A_1, z_L, z_R, \theta_1, \theta_2$ and c have all been determined and are given by (3.106), (3.107), (3.127), (3.128), (3.132), (3.133), and (3.134) respectively. We have also defined the parameter $a = \sqrt{\frac{\beta_1 \beta_2}{\nu}}$.

From our asymptotic solution to this problem, we can also characterise the space-charge-layer widths in the solid electrolyte. We note that the boundary layers have a width of ϵ , while the intermediate layers are of width λ . Upon examining these solution profiles, we observe that the boundary layers exhibit quadratic behaviour and that there is rapid change in these regions. We therefore refer to the boundary layer as a strong SCL. The intermediate layer solutions exhibit exponential behaviour, with the solution in these regions involving a rapidly decaying exponential. These intermediate layers facilitate the transition between the boundaries which are fully lithiated/depleted of cations and the constant bulk concentration, therefore we will refer to this region as the weak SCL.

3.5 Comparison of asymptotics and numerics

Having solved the one-dimensional zero flux steady-state problem for a solid electrolyte, given by (3.84), both numerically (in Section 3.3) and via an asymptotic approach (in Section 3.4), we now compare the results of the two approaches. In each plot we show the solution for n_c , obtained from the solution for θ via the auxiliary relation (3.86) and we plot ϕ dimensionally (in volts) as per convention. We include vertical lines in grey in both plots to indicate the leading-order point where the solutions transition between the boundary and intermediate layers. We remark that for the given parameter values

$$z_c = 1, \quad z_a = -1, \quad m_c = 0.3, \quad m_a = 0.7, \quad n_a = 0.4, \quad \nu = 0.6,$$

with $\beta_1 = -z_a n_a$ and $\beta_2 = z_a n_a + z_c \nu$, we will have the scenario whereby

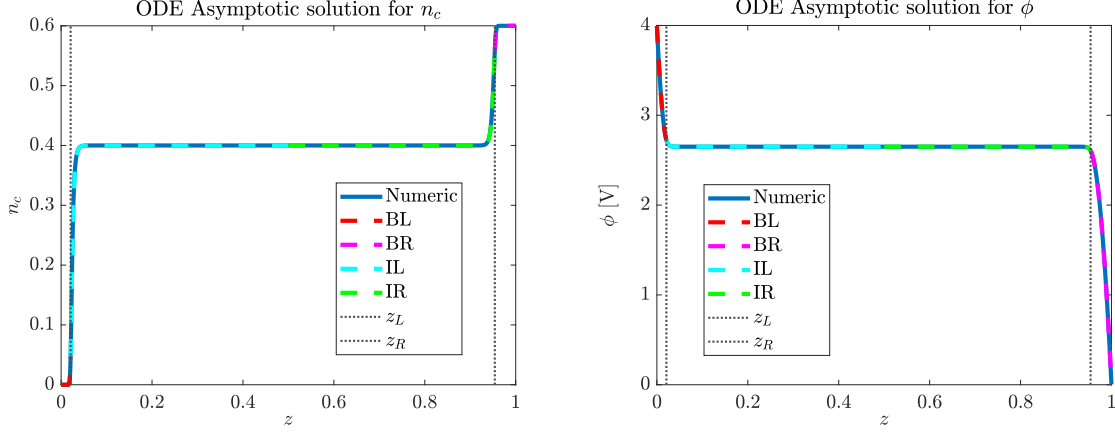
$$\frac{\beta_1}{\beta_2} = 2 < \beta^*, \quad \frac{\beta_2}{\beta_1} = \frac{1}{2} < \beta^*,$$

and hence, neither F_L nor F_R has a root and so we minimise both $|F_i|$. We plot the solutions obtained from both the numerics and the asymptotics for this set of parameters in Figure 3.5 and we observe fantastic agreement between our asymptotic regimes and the numerical solutions, and we remark how the intermediate layer solutions merge seamlessly into the bulk solution. To demonstrate the agreement between the asymptotic and numeric approaches, we have computed the L2 norm via

$$L_{2\text{error}} = \sqrt{\frac{1}{N} \sum_j \left(u_j^{\text{numeric}} - u_j^{\text{asymptotic}} \right)^2}, \quad (3.136)$$

where N is the number of cell centres in our discretisation and $u_j^{\text{numeric}}, u_j^{\text{asymptotic}}$ are the solution values at the points $j, j = 1..N$, for both n_c and ϕ . For n_c , the L2 norm for the asymptotics versus the numerics is 8.46×10^{-4} and for ϕ , the error is 1.77×10^{-4} , which are both $\mathcal{O}(\epsilon^2)$ as expected from an asymptotic perspective.

To emphasize the agreement between the different asymptotic regimes with the numerical solution, we zoom in on the boundary and intermediate layer regions near the left boundary and demonstrate these results in Figure 3.6. We note that comparable results can be seen at the right boundary, near $z = 1$. In these plots we have included the semi-analytic solution obtained by Braun et al. (2015) in dashed blue lines and we plot the numerical solution of solving the full model ((3.87) with (3.88) subject to $\phi(0) = 1, \phi(1) = 0$) in black markers. Figure 3.6a displays our boundary layer solution (3.98) in red with the vertical grey line indicating the transition point, z_L as given by (3.127), between boundary and intermediate layers. There is



(a) Lithium concentration asymptotics versus numerics (b) Electric potential [V] asymptotics versus numerics

Figure 3.5: Asymptotic solution from Section 3.4 versus numerical solution from Section 3.3 for both the lithium-ion concentration and electric potential [V]. Parameter values are as follows: $z_c = 1$, $z_a = -1$, $m_c = 0.3$, $m_a = 0.7$, $n_a = 0.4$, $\nu = 0.6$, with $\frac{\beta_1}{\beta_2} = 2 < \beta^*$, $\frac{\beta_2}{\beta_1} = \frac{1}{2} < \beta^*$. We also have $\lambda = 1.5 \times 10^{-3}$, $\delta^{-1} = 170$, and $\Delta V = 4V$. BL, BR refer to the left and right boundary-layer solutions, respectively; similarly IL, IR refer to the left and right intermediate layer solutions, respectively. z_L, z_R refer to the leading-order transition points from the boundary to the intermediate layers.

exceptional agreement between the asymptotic and numerical solutions in this region. As noted earlier in Section 3.3, we observe some discrepancy between the semi-analytic solution and our two approaches in this boundary layer. Figure 3.6b presents our intermediate layer solution, given by (3.117), shown in teal. The asymptotic solution shows excellent agreement with the numerical results, with the agreement worsening as we move further from the bulk, which is expected from this far-field expansion. Once again, we observe that the asymptotic solution outperforms the semi-analytic solution from Braun et al. (2015).

The results presented in Figures 3.5 and 3.6 validate the characterisation of the SCL into these two distinct layers: the strong and weak SCLs, via our asymptotic approach. Having defined these layers as such, we now proceed to use these results to provide further insight into and clarify observations made by other authors. For example, Braun et al. (2015) include additional results in their work in order to carry out a deeper investigation of the SCL. The authors use their semi-analytic solution to gain insight into how the SCL changes with varying applied potential difference ΔV . We follow suit and present our numerical

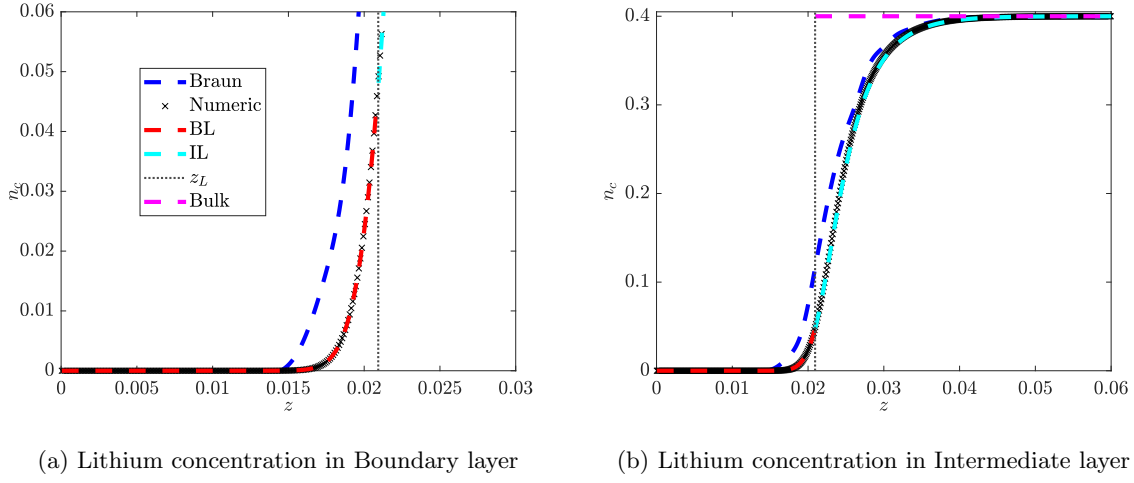
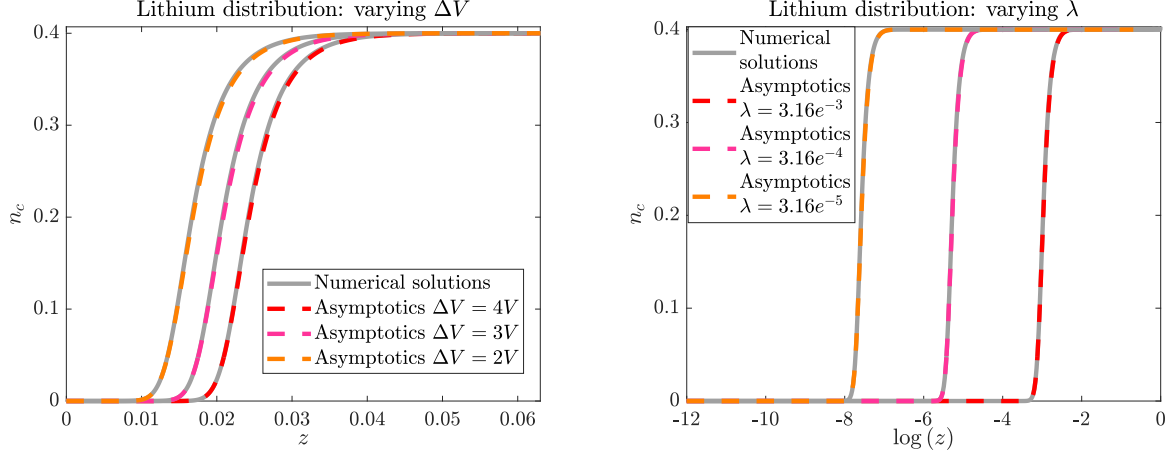


Figure 3.6: We zoom in on the boundary and intermediary regions of Figure 3.5a near $z = 0$, to highlight the agreement of the asymptotic and numerical solution approaches for steady-state profile for n_c .

and asymptotic results for three different values of ΔV in Figure 3.7a. Braun et al. (2015) conclude that increasing ΔV increases the width of the boundary layers, but does not impact the region of transition between the boundary layer and the bulk. In other words, a larger ΔV results in the regions which are either depleted or saturated with cations being wider. We can elucidate this observation using our characterisation of the layers. We have identified the strong SCL as the region of width $\epsilon = \lambda\sqrt{\delta^{-1}}$, while the weak SCL is the region of width λ . We note that from our scaling, ΔV directly affects δ and thus will influence the width of the strong SCL. However, ΔV does not impact λ , thus explaining why the transition (or weak SCL) width is not impacted by a change in ΔV . We also observe that this resolves the finding of Li and Monroe (2019) concerning the dilation of the SCL for an increase in voltage bias, which the authors noted as not typically observed in liquid electrolytes.

Braun et al. (2015) also explore the role that the parameter λ plays in the thickness of the SCL. In Figure 3.7b we perform a similar analysis, plotting the numerical and asymptotic solutions for three different values of λ . Braun et al. (2015) note that increasing λ increases the width of both the boundary layer and the transition region between the boundary and the bulk. Again, this observation aligns with our description of both the strong and weak SCL exhibiting dependence on the parameter λ . We can therefore conclude that our chosen scaling and asymptotic reduction of the model is a useful tool in explaining observed space

charge layers widths and behaviours.



(a) We have fixed $z_c = 1, z_a = -1, m_c = 0.3,$
 $m_a = 0.7, n_a = 0.4, \nu = 0.6, \lambda = 1.5 \times 10^{-3}$ as before.

(b) We have fixed $z_c = 1, z_a = -1, m_c = 0.3,$
 $m_a = 0.7, n_a = 0.4, \nu = 0.6, \Delta V = 4V$ as before.

Figure 3.7: Solution profile of the number density of the lithium ions for both the asymptotics and the numerics shown for different applied voltages versus z in Figure 3.7a and different λ versus $\log(z)$ in Figure 3.7b.

3.5.1 Additional examples of asymptotic results

In this section we present some additional examples of the results from our asymptotic approach; in particular, we provide examples of results for scenarios whereby one of $F_i, i = L, R$ has a root and the other is minimised as before.

We first present the scenario where we have

$$\frac{\beta_1}{\beta_2} > \beta^*, \quad \frac{\beta_2}{\beta_1} < \beta^*, \quad (3.137)$$

under which conditions F_L has a root but F_R does not. Therefore we will solve $F_L(z_L) = 0$ and use the value of z_R^* that minimises $|F_R|$. We illustrate two examples of this scenario and present the results for the lithium concentration profile from both the asymptotic and numerical approaches in Figures 3.8 and 3.9. We need to ensure we retain $\beta_i > 0$ so we take $\beta_1 = 0.45, \beta_2 = 0.1$ by choosing $z_a = -1, n_a = 0.45$ with the results shown in Figure 3.8. We also include an example in Figure 3.9 where we take $z_a = -2, n_a = 0.3$ to obtain

$\beta_1 = 0.6, \beta_2 = 0.1$. In both cases we see similar agreement between the asymptotics and the numerics as was observed in the case presented in Figure 3.5a. In the insets of both plots we have zoomed in on the two boundary layers to further demonstrate the agreement.

We also show an example of the scenario where F_L is minimised and F_R has a root, corresponding to

$$\frac{\beta_1}{\beta_2} < \beta^*, \quad \frac{\beta_2}{\beta_1} > \beta^*. \quad (3.138)$$

To demonstrate this we take $\beta_1 = 0.2, \beta_2 = 0.6$ as shown in Figure 3.10. Again, we zoom in on the boundaries as seen in the inset plots and we observe good agreement between the numerics and asymptotics.

3.6 Integral approach

In this section we present an alternative formulation to the ODE matched asymptotic approach taken in the preceding sections, whereby we exploit the existence of a first integral. We remark that the two approaches yield analogous results, but we present the ODE version first in order to present an approach that could be generalised to other scenarios such as the liquid electrolyte or non-zero flux extensions of the model.

We rewrite the one-dimensional steady-state problem in terms of θ , *i.e.* (3.90) in Section 3.4, here; thus,

$$\frac{\epsilon^2 \delta}{z_c} \frac{d^2 \theta}{dz^2} = \frac{\beta_1 + \beta_2}{1 + e^{-\theta}} - \beta_1, \quad (3.139a)$$

$$\int_0^1 \frac{1}{1 + e^{-\theta}} dz = \frac{\beta_1}{\beta_1 + \beta_2}, \quad (3.139b)$$

$$\theta(0) = \frac{c - z_c}{\delta}, \quad \theta(1) = \frac{c}{\delta}, \quad (3.139c)$$

and we recall that in Section 3.4 we determined the values of A_0 and A_1 by making use of the fact that (3.139a) has a first integral and using this to generate a local matching condition. In this section we further exploit this first integral property of the equation, as we notice that the resulting problem is separable; therefore we can write down an analytical solution which will hold across the whole domain. In this section we present the analytical solution and we also perform an asymptotic reduction of the first integral problem, which reiterates the various regimes we described in Section 3.4.

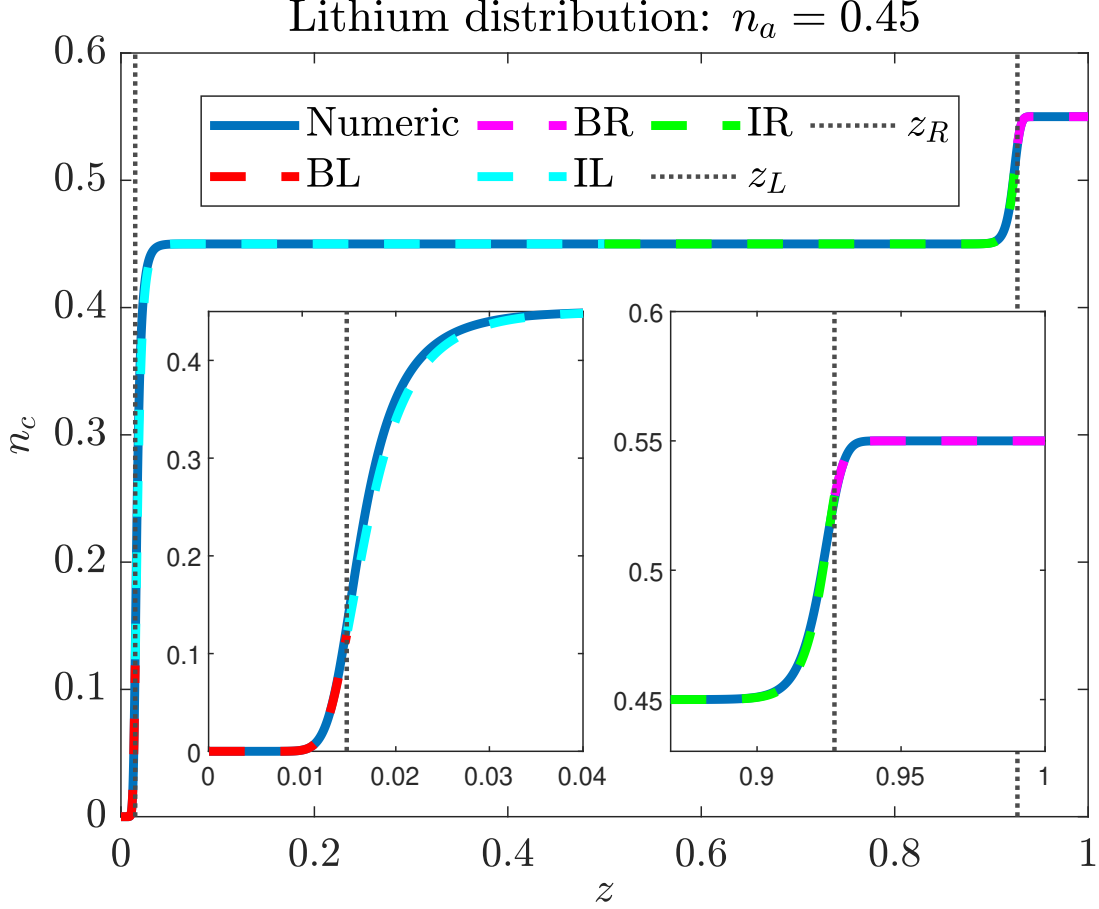


Figure 3.8: Asymptotic versus numerical solution for n_c in the scenario where $F_L > 0, F_R < 0$: $z_a = -1, n_a = 0.45, \beta_1 = 0.45, \beta_2 = 0.1$. We also have $\lambda = 1.5 \times 10^{-3}$, $\delta^{-1} = 170$, and $\Delta V = 4V$. We include insets to show a close-up of the agreement at the two boundaries. BL, BR refer to the left and right boundary-layer solutions, respectively; similarly IL, IR refer to the left and right intermediate layer solutions, respectively. z_L, z_R refer to the leading-order transition points from the boundary to the intermediate layers.

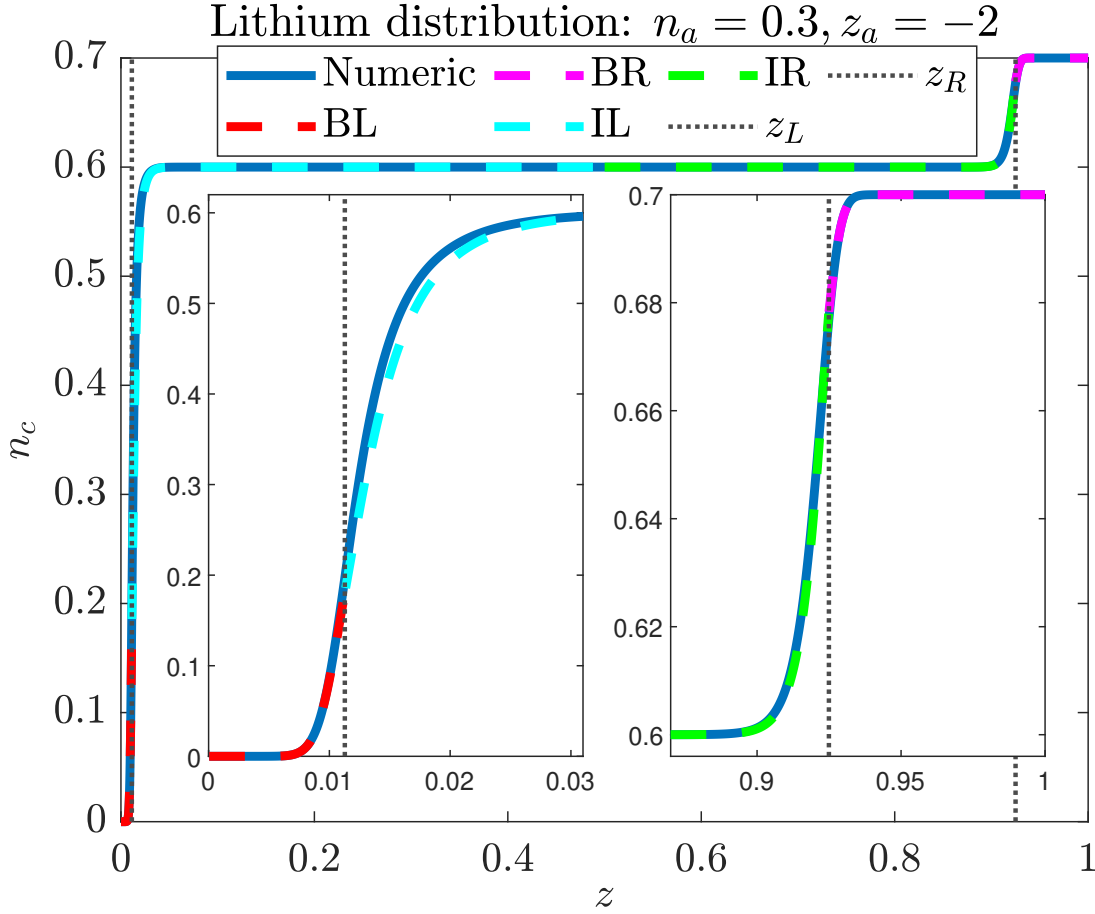


Figure 3.9: Asymptotic versus numerical solution for n_c in the scenario where $F_L > 0, F_R < 0$: $z_a = -2, n_a = 0.3, \beta_1 = 0.6, \beta_2 = 0.1$. We also have $\lambda = 1.5 \times 10^{-3}$, $\delta^{-1} = 170$, and $\Delta V = 4V$. We include insets to show a close-up of the agreement at the two boundaries. BL, BR refer to the left and right boundary-layer solutions, respectively; similarly IL, IR refer to the left and right intermediate layer solutions, respectively. z_L, z_R refer to the leading-order transition points from the boundary to the intermediate layers.

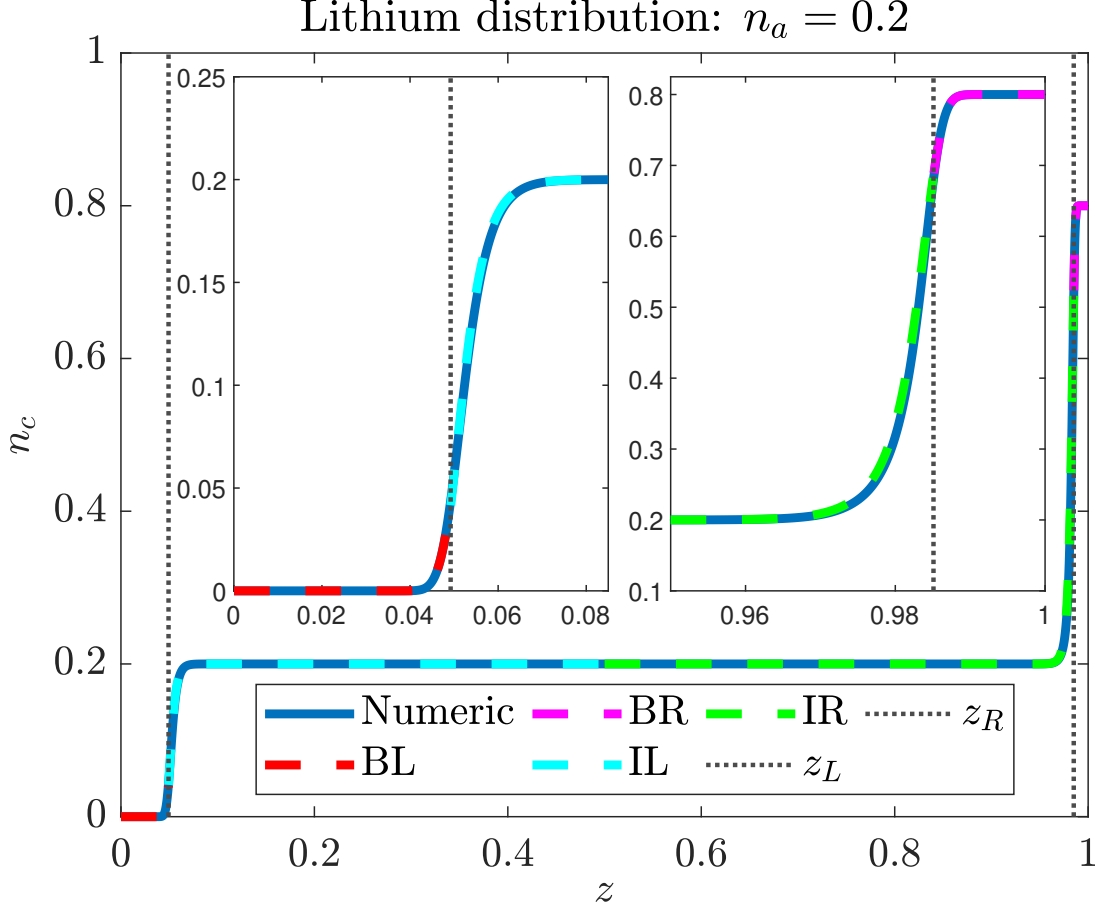


Figure 3.10: Asymptotic versus numerical solution for n_c in the scenario where $F_R > 0, F_L < 0$. We take $z_a = -1, z_c = 1, \beta_1 = 0.2, \beta_2 = 0.6$. We also have $\lambda = 1.5 \times 10^{-3}$, $\delta^{-1} = 170$, and $\Delta V = 4V$. We include insets to show a close-up of the agreement at the two boundaries. BL, BR refer to the left and right boundary-layer solutions, respectively; similarly IL, IR refer to the left and right intermediate layer solutions, respectively. z_L, z_R refer to the leading-order transition points from the boundary to the intermediate layers.

3.6.1 Analytical solution

To determine the first integral we multiply (3.139a) by $\frac{d\theta}{dz}$ and note that

$$\frac{d}{dz} \log(1 + e^\theta) = (1 + e^{-\theta})^{-1} \frac{d\theta}{dz}, \quad (3.140)$$

so that we can then rewrite this equation as

$$\frac{\delta\epsilon^2}{2z_c} \frac{d}{dz} \left(\frac{d\theta}{dz} \right)^2 = \frac{d}{dz} ((\beta_1 + \beta_2) \log(1 + e^\theta) - \beta_1 \theta). \quad (3.141)$$

We solve for an expression for θ using separation of variables and integrating, defining $F(\theta)$ by

$$F(\theta) = \int_{\frac{c-z_c}{\delta}}^{\theta} \frac{du}{\sqrt{(\beta_1 + \beta_2) \log(1 + e^u) - \beta_1 u - C_0}} = \sqrt{\frac{2z_c}{\delta\epsilon^2}} z, \quad (3.142)$$

where we take the positive root so that θ increases with increasing z , as we expect from our boundary conditions on θ from (3.139c), and we have that C_0 is some constant of integration. As we encountered in Section 3.4, a consequence of the integral constraint is that $\frac{d\theta}{dz}(z=0) = \frac{d\theta}{dz}(z=1)$ and from our boundary conditions $\theta(0) = \frac{c-z_c}{\delta}$, $\theta(1) = \frac{c}{\delta}$. We can apply these conditions to (3.141) to find that

$$(\beta_1 + \beta_2) \log(1 + e^{\frac{c-z_c}{\delta}}) - \beta_1 \left(\frac{c-z_c}{\delta} \right) = (\beta_1 + \beta_2) \log(1 + e^{\frac{c}{\delta}}) - \beta_1 \left(\frac{c}{\delta} \right) \quad (3.143)$$

must hold, which can then be used to solve for c exactly:

$$c = \delta \log \left(\frac{1 - e^{z_c \beta_1 / \delta(\beta_1 + \beta_2)}}{e^{-z_c \beta_2 / \delta(\beta_1 + \beta_2)} - 1} \right) = \frac{z_c \beta_1}{\beta_1 + \beta_2} + \delta \log \left(\frac{1 - e^{-z_c \beta_1 / \delta(\beta_1 + \beta_2)}}{1 - e^{-z_c \beta_2 / \delta(\beta_1 + \beta_2)}} \right). \quad (3.144)$$

Noting that $\delta \ll 1$ so we then approximate

$$c \approx \frac{z_c \beta_1}{\beta_1 + \beta_2} = \frac{\beta_1}{\nu}, \quad (3.145)$$

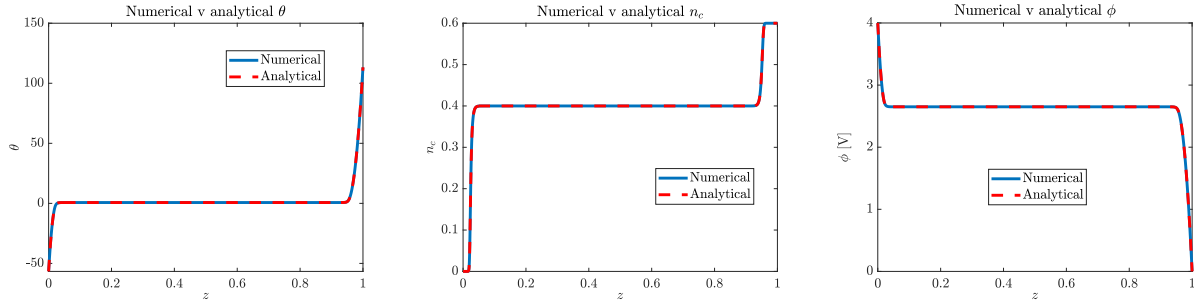
which agrees with our solution for c in (3.134) of Section 3.4.4. From (3.144) we note that any corrections to c beyond leading order are exponentially small. To find C_0 we recall that $\theta(1) = \frac{c}{\delta}$, so that $F(\frac{c}{\delta}) = \sqrt{\frac{2z_c}{\delta\epsilon^2}}$ to close the problem. Practically, determining C_0 can be difficult because the bulk value is near a singularity of the integral; however we can exploit this to approximate C_0 by using the fact that $\delta\epsilon^2 \ll 1$ so that there is a bulk value for θ when $\frac{\beta_1 + \beta_2}{1 + e^{-\theta}} = \beta_1$, corresponding to

$$\theta = \log \left(\frac{\beta_1}{\beta_2} \right), \quad (3.146)$$

which is what we find from the ODE approach. Now, in the bulk, the derivative in (3.141) is approximately zero, therefore we approximate C_0 by

$$(\beta_1 + \beta_2) \log \left(\frac{\beta_1 + \beta_2}{\beta_2} \right) - \beta_1 \log \left(\frac{\beta_1}{\beta_2} \right) = C_0, \quad (3.147)$$

completing the analytical solution to the zero flux steady-state problem. We note that here the constant $z_c C_0$ is equivalent to A_1 from the ODE approach to the asymptotics in Section 3.4, given by (3.107). In Figure 3.11a we plot the analytical solution for θ in comparison with the numerical solution obtained in Section 3.3. Using the solution for θ we also compute the analytical solutions for n_c and ϕ . We present these solutions, with their numerical counterparts in Figures 3.11b and 3.11c. In all three figures we have outstanding agreement between the analytics and the numerics.



(a) Numerical versus analytical θ solution so- (b) Numerical versus analytical n_c solution (c) Numerical versus analytical ϕ [V] solution

Figure 3.11: Analytical versus numerical solutions for θ , the lithium concentration n_c , and electric potential ϕ [V]. Parameter values are as follows: $z_c = 1$, $z_a = -1$, $m_c = 0.3$, $m_a = 0.7$, $n_a = 0.4$, $\nu = 0.6$, with $\frac{\beta_1}{\beta_2} = 2 < \beta^*$, $\frac{\beta_2}{\beta_1} = \frac{1}{2} < \beta^*$. We also have $\lambda = 1.5 \times 10^{-3}$, $\delta = 170$, and $\Delta V = 4V$.

3.6.2 Integral asymptotics

Having a full analytic solution as outlined in the last section can be useful, however there are drawbacks. For example, we do not gain insight into the behaviour in the different regimes of the solution as we do from the asymptotic approach. We note that using the approximation (3.147) for C_0 introduces a singularity in the integral at $\theta = \theta^* = \log \left(\frac{\beta_1}{\beta_2} \right)$ which leads us to consider splitting the integral. In addition, from our boundary conditions in (3.139) we see that $\theta \sim \mathcal{O}(\delta^{-1})$ at the two limits, therefore we have four cases for an asymptotic approximation to the solution. We will outline the first two cases, and then briefly overview

the solutions for the last two, which are symmetric to the first two. We further note that this section echoes that of Section 3.4.

Case 1: $\theta < \log\left(\frac{\beta_1}{\beta_2}\right)$, $\theta \sim \mathcal{O}(\delta^{-1})$

The boundary value of θ is $c - z_c < 0$, so θ must be large and negative in this region. We introduce the scale $u = -\delta^{-1}w$, $du = -\delta^{-1}dw$. With this change of variable, when

$$u = \frac{c - z_c}{\delta}, \quad w = z_c - c \quad (3.148)$$

and when

$$u = \theta, \quad w = -\delta\theta = \psi \quad (3.149)$$

with $\theta = -\delta^{-1}\psi$. Using this substitution in (3.142) and noting that

$$\log\left(1 + e^{-\delta^{-1}w}\right) \approx 0, \quad (3.150)$$

(3.142) can be approximated as

$$\begin{aligned} -\delta^{-1} \int_{z_c - c}^{-\delta\theta} \frac{dw}{\sqrt{(\beta_1 + \beta_2) \log(1 + e^{-\delta^{-1}w}) + \beta_1 \delta^{-1}w - C_0}} &\approx \sqrt{\delta^{-1}} \int_{-\delta\theta}^{z_c - c} \frac{dw}{\sqrt{\beta_1 w - \delta C_0}}, \\ &= \sqrt{\frac{2z_c}{\delta}} \frac{z}{\epsilon}, \end{aligned} \quad (3.151)$$

where we have just set the simplified integral equal to the right hand side of (3.142) in the last line. Simplifying and solving (3.151) yields

$$\theta = -\delta^{-1} \left(\frac{z_c \beta_1}{2} \frac{z^2}{\epsilon^2} - \sqrt{2z_c(\beta_1(z_c - c) - \delta C_0)} \frac{z}{\epsilon} + z_c - c \right). \quad (3.152)$$

We can then expand about $\delta \ll 1$ to get

$$\theta \sim -\delta^{-1} \left(\frac{z_c \beta_1}{2} \frac{z^2}{\epsilon^2} - \sqrt{2z_c \beta_1 (z_c - c)} \frac{z}{\epsilon} + z_c - c \right) - \frac{z_c \delta C_0}{\sqrt{2z_c \beta_1 (z_c - c)}} \frac{z}{\epsilon} + \mathcal{O}(\delta^{3/2}). \quad (3.153)$$

We rewrite to highlight our $\mathcal{O}(1)$, $\mathcal{O}(\delta)$ solutions

$$\mathcal{O}(1) : \psi_0 = \frac{z_c \beta_1}{2} \left(\frac{z}{\epsilon} \right)^2 - \sqrt{2(z_c - c)z_c \beta_1} \frac{z}{\epsilon} + z_c - c, \quad (3.154)$$

$$\mathcal{O}(\delta) : \psi_1 = \frac{z_c C_0}{\sqrt{2z_c \beta_1 (z_c - c)}} \frac{z}{\epsilon}, \quad (3.155)$$

with $\theta = -\delta^{-1}(\psi_0 + \delta\psi_1)$. We note that this expression (3.154) for ψ_0 matches the solution we recover from the ODE approach (3.98) with A_0 given as (3.106). We can see that we lose asymptotic consistency when $\frac{z}{\epsilon} \sim \delta^{-1}$. This region is valid up to some $\hat{z}_1$ ($\hat{\psi} = \psi(\hat{z}_1)$) where θ transitions to $\mathcal{O}(1)$, and as this is an $\mathcal{O}(1)$ value we would expect $\hat{\psi} = 0 + \delta\hat{\psi}_1$ ($\hat{\theta} = \hat{\theta}_1$), which then leads us into Case 2.

Case 2: $\theta < \log\left(\frac{\beta_1}{\beta_2}\right), \theta \sim \mathcal{O}(1)$

We want to exploit the singularity when $\theta = \theta^* = \log\left(\frac{\beta_1}{\beta_2}\right)$. We define $u = \theta^* - y$ and we will integrate from the point where the previous solution terminates, which we call $\hat{\theta}_1$. This will give us

$$\int_{\hat{\theta}_1}^{\theta} \frac{du}{\sqrt{(\beta_1 + \beta_2) \log(1 + e^u) - \beta_1 u - C_0}} = \sqrt{\frac{2z_c}{\delta\epsilon^2}} (z - \hat{z}_1). \quad (3.156)$$

If $u = \theta^* - y$, $du = -dy$, then when $u = \hat{\theta}_1$, $y = \theta^* - \hat{\theta}_1$, and $u = \theta$, $y = \theta^* - \theta$. With this we can expand about the singularity

$$\begin{aligned} (\beta_1 + \beta_2) \log(1 + e^u) - \beta_1 u - C_0 &= (\beta_1 + \beta_2) \log(1 + e^{\theta^* - y}) - \beta_1 (\theta^* - y) - C_0 \\ &\approx \frac{\beta_1 \beta_2}{2(\beta_1 + \beta_2)} y^2 \end{aligned} \quad (3.157)$$

since

$$(\beta_1 + \beta_2) \log(1 + e^{\theta^*}) - \beta_1 \theta^* - C_0 = 0 \quad (3.158)$$

as it corresponds to the bulk solution,

$$\frac{(\beta_1 + \beta_2) e^{\theta^*}}{1 + e^{\theta^*}} - \beta_1 = \beta_1 - \beta_1 = 0, \quad (3.159)$$

and

$$\frac{(\beta_1 + \beta_2) y^2 e^{\theta^*}}{2(1 + e^{\theta^*})^2} = \frac{\beta_1 \beta_2}{2(\beta_1 + \beta_2)} y^2. \quad (3.160)$$

Substituting back into the left hand side of (3.156) we then have

$$\int_{\hat{\theta}_1}^{\theta} \frac{du}{\sqrt{(\beta_1 + \beta_2) \log(1 + e^u) - \beta_1 u - C_0}} = \sqrt{\frac{2(\beta_1 + \beta_2)}{\beta_1 \beta_2}} \int_{\theta^* - \theta}^{\theta^* - \hat{\theta}_1} \frac{dy}{y} = \sqrt{\frac{2(\beta_1 + \beta_2)}{\beta_1 \beta_2}} \log\left(\frac{\theta^* - \hat{\theta}_1}{\theta^* - \theta}\right). \quad (3.161)$$

Therefore,

$$\sqrt{\frac{2(\beta_1 + \beta_2)}{\beta_1 \beta_2}} \log\left(\frac{\theta^* - \hat{\theta}_1}{\theta^* - \theta}\right) = \sqrt{\frac{2z_c}{\delta\epsilon^2}} (z - \hat{z}_1), \quad (3.162)$$

which we rearrange to obtain the following solution for θ

$$\theta = \theta^* - \left(\theta^* - \hat{\theta}_1\right) e^{-\sqrt{\frac{z_c \beta_1 \beta_2}{(\beta_1 + \beta_2) \delta\epsilon^2}} (z - \hat{z}_1)}. \quad (3.163)$$

We note that because of the singularity at $\theta = \theta^*$ this will go to θ^* as $z \rightarrow \infty$. We observe that this also agrees with the intermediate solution found in (3.117).

Left matching

We can now look to determine $\hat{z}_1$ and $\hat{\theta}_1$. Ideally we would impose both continuity and differentiability at $\hat{z}_1$, however as the boundary layer is concerned with $\theta \sim \delta^{-1}$ and the intermediate layer is based on $\theta \sim \theta^*$ there may be no natural single point for matching. We impose continuity

$$\theta(\hat{z}_1) = -\delta^{-1} \left(\frac{z_c \beta_1}{2} \left(\frac{\hat{z}_1}{\epsilon} \right)^2 - \sqrt{2z_c \beta_1 (z_c - c) - 2z_c \delta C_0} \left(\frac{\hat{z}_1}{\epsilon} \right) + z_c - c \right) = \hat{\theta}_1. \quad (3.164)$$

We define

$$\begin{aligned} F_L &= \left. \frac{d\theta}{dz} \right|_{\hat{z}_{\text{case 1}}} - \left. \frac{d\theta}{dz} \right|_{\hat{z}_{\text{case 2}}} \\ &= -\frac{1}{\delta\epsilon} \left(z_c \beta_1 \left(\frac{\hat{z}_1}{\epsilon} \right) - \sqrt{2z_c \beta_1 (z_c - c) - 2z_c \delta C_0} \right) - \frac{a}{\sqrt{\delta\epsilon}} (\theta^* - \hat{\theta}_1), \end{aligned} \quad (3.165)$$

where $a = \sqrt{\frac{z_c \beta_1 \beta_2}{\beta_1 + \beta_2}}$. Ideally we would choose $\hat{z}_1$ so that $F_L = 0$, but instead we minimise $|F_L|$. Note that $F_L'' = -\frac{az_c \beta_1}{\lambda^3} < 0$ so F_L is convex. Using the continuity constraint (3.164) in F_L (3.165) and setting this equal to zero

$$F_L' = -\frac{z_c \beta_1}{\delta\epsilon^2} - \frac{az_c \beta_1 \hat{z}_1}{\delta^{3/2} \epsilon^3} + \frac{a \sqrt{2z_c \beta_1 (z_c - c) - 2z_c \delta C_0}}{\delta^{3/2} \epsilon^2} = 0, \quad (3.166)$$

is satisfied for

$$\hat{z}_1 = \frac{\left(a \sqrt{2z_c \beta_1 (z_c - c) - 2z_c \delta C_0} - z_c \beta_1 \sqrt{\delta} \right)}{az_c \beta_1} \epsilon. \quad (3.167)$$

This gives us that

$$\theta(\hat{z}_1) = -\left(\frac{\beta_1 + \beta_2}{2\beta_2} + \frac{C_0}{\beta_1} \right). \quad (3.168)$$

Case 3: $\theta > \log\left(\frac{\beta_1}{\beta_2}\right)$, $\theta \sim \mathcal{O}(\delta^{-1})$

We now consider the symmetric cases on the other side of the singularity. On this side we redefine the integral as

$$\int_{\hat{\theta}}^{\frac{\zeta}{\delta}} \frac{du}{\sqrt{(\beta_1 + \beta_2) \log(1 + e^u) - \beta_1 u - C_0}} = \sqrt{\frac{2z_c}{\delta\epsilon^2}} (1 - z) = \sqrt{\frac{2z_c}{\delta\epsilon^2}} \zeta, \quad (3.169)$$

where $\zeta = 1 - z$. As before we scale $u = \delta^{-1} w$, $du = \delta^{-1} dw$, $\theta = \delta^{-1} \xi$. We proceed with the same step as taken in Case 1 to find the following solution

$$\theta = \delta^{-1} \left(\frac{z_c \beta_2}{2} \left(\frac{\zeta}{\epsilon} \right)^2 - \sqrt{2z_c \beta_2 c - 2z_c C_0 \delta} \left(\frac{\zeta}{\epsilon} \right) + c \right). \quad (3.170)$$

As before, we expand about $\delta \ll 1$ to obtain

$$\theta \sim \delta^{-1} \left(\frac{z_c \beta_2}{2} \frac{\zeta^2}{\epsilon^2} - \sqrt{2z_c \beta_2 c} \frac{\zeta}{\epsilon} + c \right) + \frac{z_c \delta C_0}{\sqrt{2z_c \beta_2 c}} \frac{\zeta}{\epsilon} + \mathcal{O}(\delta^{3/2}) \quad (3.171)$$

again, highlighting our $\mathcal{O}(1)$, $\mathcal{O}(\delta)$ solutions

$$\mathcal{O}(1): \quad \xi_0 = \frac{z_c \beta_2}{2} \left(\frac{\zeta}{\epsilon} \right)^2 - \sqrt{2z_c \beta_2 c} \left(\frac{\zeta}{\epsilon} \right) + c, \quad (3.172a)$$

$$\mathcal{O}(\delta): \quad \xi_1 = \frac{C_0}{\sqrt{2z_c \beta_2 c}} \frac{\zeta}{\epsilon}, \quad (3.172b)$$

corresponding to (3.100) from the ODE approach. As on the other side, this will be valid up to some $\hat{\zeta}$ where $\xi(\hat{\zeta}) = \hat{\xi} = 0 + \delta \hat{\xi}_1$, thus leading us into the final scenario, Case 4.

Case 4: $\theta > \log\left(\frac{\beta_1}{\beta_2}\right)$, $\theta \sim \mathcal{O}(1)$

We split the integral based on where the solution is valid. θ in case 3 will be valid to some $\theta = \hat{\theta}_2$ and

$$\int_{\theta}^{\hat{\theta}_2} \frac{du}{\sqrt{(\beta_1 + \beta_2) \log(1 + e^u) - \beta_1 u - C_0}} = \sqrt{\frac{2z_c}{\delta \epsilon^2}} (\zeta - \hat{\zeta}) \quad (3.173)$$

We let $u = \theta^* + y$, $du = dy$ so that when $u = \theta$, $y = \theta - \theta^*$ and when $u = \hat{\theta}_2$, then $y = \hat{\theta}_2 - \theta^*$. We proceed as in (3.157), expanding about the singularity and taking the leading order to obtain

$$\begin{aligned} \int_{\theta}^{\hat{\theta}_2} \frac{du}{\sqrt{(\beta_1 + \beta_2) \log(1 + e^u) - \beta_1 u - C_0}} &= \sqrt{\frac{2(\beta_1 + \beta_2)}{\beta_1 \beta_2}} \int_{\theta - \theta^*}^{\hat{\theta}_2 - \theta^*} \frac{dy}{y} = \sqrt{\frac{2(\beta_1 + \beta_2)}{\beta_1 \beta_2}} \log \left(\frac{\hat{\theta}_2 - \theta^*}{\theta - \theta^*} \right) \\ \Rightarrow \sqrt{\frac{2(\beta_1 + \beta_2)}{\beta_1 \beta_2}} \log \left(\frac{\hat{\theta}_2 - \theta^*}{\theta - \theta^*} \right) &= \sqrt{\frac{2z_c}{\delta \epsilon^2}} (\zeta - \hat{\zeta}) \\ \theta &= \theta^* + (\hat{\theta}_2 - \theta^*) e^{-\sqrt{\frac{z_c \beta_1 \beta_2}{(\beta_1 + \beta_2) \delta \epsilon^2}} (\zeta - \hat{\zeta})}, \end{aligned} \quad (3.174)$$

We observe that this agrees with the intermediate solution found in (3.118).

Right matching

We proceed similarly as for matching between case 1 and 2. We first enforce continuity where $\hat{\zeta} = 1 - \hat{z}_2$

$$\theta(\hat{\zeta}) = \delta^{-1} \left(\frac{z_c \beta_2}{2} \left(\frac{\hat{\zeta}}{\epsilon} \right)^2 - \sqrt{2z_c \beta_2 c - 2z_c \delta C_0} \left(\frac{\hat{\zeta}}{\epsilon} \right) + c \right) = \hat{\theta}_2. \quad (3.175)$$

We define

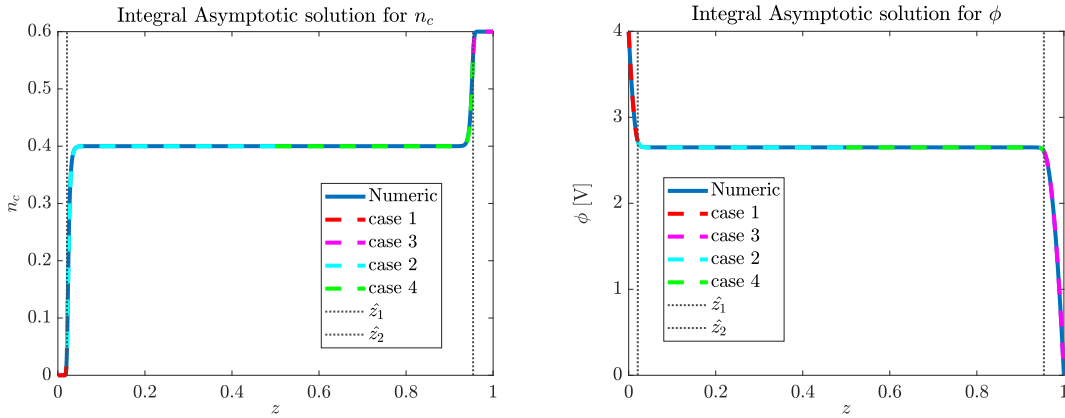
$$F_R = \frac{d\theta}{d\zeta} \Big|_{\hat{\zeta}_{\text{case 3}}} - \frac{d\theta}{d\zeta} \Big|_{\hat{\zeta}_{\text{case 4}}} = \frac{1}{\epsilon\delta} \left(z_c \beta_2 \left(\frac{\hat{\zeta}}{\epsilon} \right) - \sqrt{2z_c \beta_2 c - 2z_c \delta C_0} \right) + \frac{a}{\epsilon\sqrt{\delta}} (\hat{\theta}_2 - \theta^*). \quad (3.176)$$

Similar to the left hand side matching we find that $F'_R = 0$ for

$$\hat{\zeta} = \frac{(a\sqrt{2z_c \beta_2 c - 2z_c \delta C_0} - z_c \beta_2 \sqrt{\delta})}{az_c \beta_2} \epsilon. \quad (3.177)$$

Which corresponds to

$$\theta(\hat{\zeta}) = \left(\frac{\beta_1 + \beta_2}{2\beta_1} + \frac{C_0}{\beta_2} \right). \quad (3.178)$$

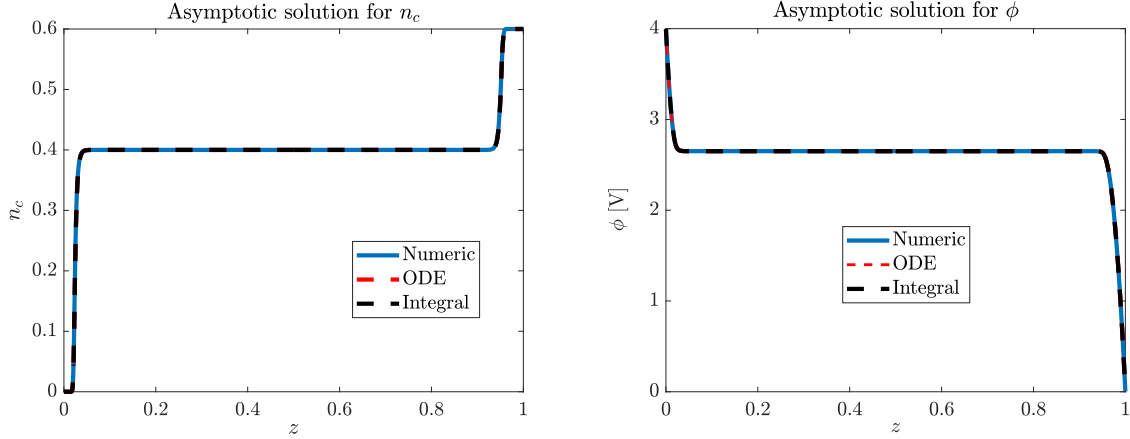


(a) Lithium concentration asymptotics versus numerics (b) Electric potential [V] asymptotics versus numerics

Figure 3.12: Integral Asymptotic versus numerical solutions for lithium concentration and electric potential [V]. Parameter values are as follows: $z_c = 1$, $z_a = -1$, $m_c = 0.3$, $m_a = 0.7$, $n_a = 0.4$, $\nu = 0.6$, with $\frac{\beta_1}{\beta_2} = 2 < \beta^*$, $\frac{\beta_2}{\beta_1} = \frac{1}{2} < \beta^*$. We also have $\lambda = 1.5 \times 10^{-3}$, $\delta^{-1} = 170$, and $\Delta V = 4V$. BL, BR refer to the left and right boundary-layer solutions, respectively; similarly IL, IR refer to the left and right intermediate layer solutions, respectively. z_L, z_R refer to the leading-order transition points from the boundary to the intermediate layers.

3.6.3 Comparisons

In this section we show that both asymptotic solution approaches are equivalent and we show the agreement between the integral asymptotic solution and the numerical solution. In Figure 3.12 we plot the integral asymptotic solution versus the numerical solution for both n_c in Figure 3.12a and ϕ in Figure 3.12b. As with the ODE asymptotics, we see very good agreement between the two solutions. Figure 3.13a shows the solution for n_c obtained via all three methods: the numerical solution is shown in blue, the ODE asymptotics are shown in red and the integral asymptotics are shown in black. We observe that the two asymptotic solutions are indistinguishable, and both show excellent agreement with the numerics. We see similar results for the ϕ profile as shown in Figure 3.13b.



(a) Lithium concentration ODE versus integral asymptotics versus numerics (b) Electric potential [V] ODE versus integral asymptotics versus numerics

Figure 3.13: ODE versus integral asymptotic versus numerical solutions for lithium concentration and electric potential [V]. Parameter values are as follows: $z_c = 1$, $z_a = -1$, $m_c = 0.3$, $m_a = 0.7$, $n_a = 0.4$, $\nu = 0.6$, with $\frac{\beta_1}{\beta_2} = 2 < \beta^*$, $\frac{\beta_2}{\beta_1} = \frac{1}{2} < \beta^*$, $\lambda = 1.5 \times 10^{-3}$, $\delta^{-1} = 170$, and $\Delta V = 4V$.

3.7 Discussion

The purpose of this chapter was to review a thermodynamic model for a solid electrolyte and to carry out a deeper investigation into the SCLs. The key questions that had been raised by other authors were related to the numerical issues encountered and the double charge layers in solid electrolytes being wider than their

liquid counterparts.

Our non-dimensionalisation and subsequent rewriting of the model, for example, the flux expression in (3.80), highlight the underlying issue faced by other authors when solving the model numerically (Braun et al. (2015); Katzenmeier et al. (2022); Katzenmeier (2022); Swift et al. (2021)). That is, the near singularities arising via the logarithmic term. The introduction of the auxiliary variable allows us to overcome these numerical issues by transforming the problem to a smooth domain, thus avoiding numerical difficulties associated with the proximity to singularities in the true domain. Furthermore, this approach enables us to implement standard numerical techniques to solve the problem, meaning that we do not have to rely on more intricate pre-processing. This can be advantageous computationally when implementing the model in higher dimensional problems and full battery problems.

The non-dimensionalisation and our asymptotic approach also reveal insights into the characterisation of the SCLs. In particular, we uncover the true length scale of these double layers in comparison with previous literature; we observe that the SCL is composed of two distinct regions; the boundary layer of width ϵ , and the intermediate layers of width λ . Moreover, the two regions demonstrate quadratic and exponential behaviour respectively. Consequently, we refer to the quadratic layer as the strong SCL and the exponential layer as the weak SCL. We acknowledge that Swift et al. (2021) also observe these two behaviours (quadratic and exponential) occurring in the boundaries of the solid electrolyte, however we have characterised this behaviour in a formal manner.

We note that these insights address and clarify many of the observations made by other authors regarding the widths of these SCLs (Knauth (2009); Yamada et al. (2013); Braun et al. (2015); Li and Monroe (2019, 2021)). However, these results then raise the question as to which feature of the solid electrolyte model leads to these wider layers. Moreover, the layers are not simply just wider, but rather are composed of two separate layers, each with a distinct behaviour. As indicated, liquid electrolytes have been studied to a much greater extent than solid electrolytes and it is widely accepted that liquid electrolytes exhibit exponential behaviour, via the Boltzmann distribution, in the double charge layers (Attard (1993); Newman and Thomas-Alyea (2012); Groß and Sakong (2019)); there is no indication of a quadratic region. Therefore, in the next chapter we will further investigate and elucidate this distinction between the boundary layer behaviours observed in solid versus liquid electrolytes.

Chapter 4

Liquid electrolyte model

4.1 Problem Motivation

In Chapter 3 we discuss and investigate a model for the electric double layers (EDLs) in a solid electrolyte, known as the space charge layers (SCLs) in that context. We noted that this work was motivated by observations that were made by a number of authors about the width of these layers, in particular, that these layers are wider in a solid electrolyte than that which is observed in a liquid electrolyte. Furthermore, regarding these wider layers, there was no consensus or explicit characterisation of the scale of this width. In Chapter 3 we uncover the true width of these double charge layers via an asymptotic approach. Specifically, we determine that these double charge layers are made up of two distinct boundary layers: a strong layer and a weak layer. The strong SCL is characterised by a width which is wider than the standard liquid electrolyte Debye width, and the weak is characterised by a width equal to the Debye width. These two distinct layers also exhibit particular behaviour; quadratic behaviour is observed in the strong layer while exponential behaviour is observed in the weak layer.

We recall our discussions in Chapters 1 and 2 regarding the fact that liquid electrolytes have been well-established from a modelling perspective. We noted that the literature surrounding EDLs is more limited, but it is widely accepted that the double layers in liquid electrolytes exhibit exponential behaviour and that these layers are characterised by the Debye width (Debye and Falkenhagen (1928); Kilic et al. (2007a); Newman and Thomas-Alyea (2012)). To the best of our knowledge, there is no indication of the existence

of another layer exhibiting quadratic behaviour in liquid electrolyte EDLs. However, from a general model perspective, there are no apparent mathematical reasons as to why these double layers differ between the solid and the liquid. We are therefore interested in uncovering which features of the solid electrolyte model favour this additional component of the double layer.

Therefore, motivated by the results of our solid model, we take a deeper look at the double charge layers in a liquid electrolyte in order to compare and contrast with the solid electrolyte equivalent. In this chapter, we take the same approach as that of Chapter 3 to study the liquid electrolyte double charge layer model. Our focus here is not on developing a new model, but taking a similar investigative approach to an existing model in order to better understand and explain the differences in the electric double layers between liquid and solid electrolytes.

This chapter will largely follow the same structure as Chapter 3; we begin by referring to the thermodynamically derived equations in Chapter 2 to form the basis for the liquid electrolyte model which we will study. We non-dimensionalise the model and introduce auxiliary variables for the ion concentrations. We then proceed with computing numerical solutions, an asymptotic reduction, and a comparison between the numerical and asymptotic results. We compare our results with those obtained in Chapter 3, as well as establishing a connection between the results obtained in this chapter and the standard convention for liquid electrolytes.

4.2 Mathematical model

We present a mathematical model of liquid electrolytes following Dreyer et al. (2013), which is based on the thermodynamic approach derived in Chapter 2.

4.2.1 Model equations

For the liquid electrolyte model we proceed with an electrolyte composed of three species; cations c , anions a , and the solvent s . We will have the conservation of mass equation for each species $k = c, a, s$ as given by (2.179). If we sum all three equations in (2.179) we obtain the usual conservation of total mass equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0. \quad (4.1)$$

We will have a diffusive flux for each species given by (2.180), whereby we have that $\sum_k \mathbf{J}_k = 0$. We note that we can rearrange (2.180) to write

$$\rho_k \mathbf{v}_k = \mathbf{J}_k + \rho_k \mathbf{v}. \quad (4.2)$$

Using this expression, and the definition of the mass density ($\rho_k = m_k n_k$), we can rewrite the conservation equation (2.179) for each species as

$$\frac{\partial (m_k n_k)}{\partial t} + \nabla \cdot (\mathbf{J}_k + m_k n_k \mathbf{v}) = 0. \quad (4.3)$$

We take the equation for entropy production (2.182), which we use to rewrite our expressions for the diffusive fluxes in terms of the thermodynamic driving forces as shown in (2.190) as

$$\frac{\mathbf{J}_a}{m_a} = -N_{aa} \left(\nabla \left(\mu_a - \frac{m_a}{m_s} \mu_s \right) + \left(z_a - \frac{m_a}{m_s} z_s \right) \nabla \phi \right) - N_{ac} \left(\nabla \left(\mu_c - \frac{m_c}{m_s} \mu_s \right) + \left(z_c - \frac{m_c}{m_s} z_s \right) \nabla \phi \right), \quad (4.4a)$$

$$\frac{\mathbf{J}_c}{m_c} = -N_{ac} \left(\nabla \left(\mu_a - \frac{m_a}{m_s} \mu_s \right) + \left(z_a - \frac{m_a}{m_s} z_s \right) \nabla \phi \right) - N_{cc} \left(\nabla \left(\mu_c - \frac{m_c}{m_s} \mu_s \right) + \left(z_c - \frac{m_c}{m_s} z_s \right) \nabla \phi \right), \quad (4.4b)$$

$$\frac{\mathbf{J}_s}{m_s} = -\frac{\mathbf{J}_a}{m_s} - \frac{\mathbf{J}_c}{m_s}. \quad (4.4c)$$

From here, the remaining model equations reflect those outlined in Chapter 3 for the solid electrolyte; the conservation of momentum equation is given by (3.18) and Gauss' law for conservation of charge is given by (3.20). We note that the chemical potentials are derived in the same way as before, although more generally we take (3.38) without explicitly choosing a particular model such as Margules for the activity coefficients. The chemical potential for each species is then given by (3.52) and we will also have the equation of state (3.21), as before. We again take the incompressibility limit $K \rightarrow \infty$ in the equation of state (3.21), leading to $n = n_r$ to prevent infinite pressure. Therefore $\log \left(\frac{p-p_r}{K} + 1 \right) \approx \frac{p-p_r}{K}$, and we have the following expression for the chemical potentials

$$\mu_k = \mu_k^* + \frac{p-p_r}{n_r} + k_B T \log \left(\frac{n_k}{n} \right). \quad (4.5)$$

Therefore, our thermodynamically consistent model for the liquid electrolyte is given by the following

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \quad (4.6a)$$

$$\frac{\partial (m_k n_k)}{\partial t} + \nabla \cdot (\mathbf{J}_k + m_k n_k \mathbf{v}) = 0, \quad (4.6b)$$

$$\frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) + \nabla p = -n^F \nabla \phi, \quad (4.6c)$$

$$-\epsilon_0 (1 + \chi) \nabla^2 \phi = n^F, \quad (4.6d)$$

$$p_r + K \left(\frac{n}{n_r} - 1 \right) = p, \quad (4.6e)$$

$$\mu_k^* + \frac{p - p_r}{n_r} + k_B T \log \left(\frac{n_k}{n} \right) = \mu_k, \quad (4.6f)$$

$$- \sum_{j=a,c} N_{k,j} \left(\nabla \left(\mu_j - \frac{m_j}{m_s} \mu_s \right) + \left(z_j - \frac{m_j}{m_s} z_s \right) \nabla \phi \right) = \frac{\mathbf{J}_k}{m_k} \quad (4.6g)$$

We have omitted the flux equation for $\mathbf{J}_s$ as this can be determined from (4.4c). We remark that here the $N_{k,j}$ does not collapse to a single $M = N_{c,c}$ as is the case for the solid model in Equation 3.16, which was conveniently done through massless vacancies and stationary anions.

We will follow the approach taken for the solid electrolyte and thus we focus on the one-dimensional problem ($\nabla \rightarrow \frac{\partial}{\partial z}$), whereby (4.6) becomes

$$\frac{\partial \rho}{\partial t} + \frac{\partial (\rho v)}{\partial z} = 0, \quad (4.7a)$$

$$\frac{\partial (m_k n_k)}{\partial t} + \frac{\partial}{\partial z} (J_k + m_k n_k v) = 0, \quad (4.7b)$$

$$\frac{\partial (\rho v)}{\partial t} + \frac{\partial (\rho v^2)}{\partial z} + \frac{\partial p}{\partial z} = -n^F \frac{\partial \phi}{\partial z}, \quad (4.7c)$$

$$-\epsilon_0 (1 + \chi) \frac{\partial^2 \phi}{\partial z^2} = n^F, \quad (4.7d)$$

$$p_r + K \left(\frac{n}{n_r} - 1 \right) = p, \quad (4.7e)$$

$$\mu_k^* + \frac{p - p_r}{n_r} + k_B T \log \left(\frac{n_k}{n} \right) = \mu_k, \quad (4.7f)$$

$$- \sum_{j=a,c} N_{k,j} \left(\frac{\partial}{\partial z} \left(\mu_j - \frac{m_j}{m_s} \mu_s \right) + \left(z_j - \frac{m_j}{m_s} z_s \right) \frac{\partial \phi}{\partial z} \right) = \frac{J_k}{m_k}. \quad (4.7g)$$

We require boundary and initial conditions to supplement the problem. For comparative purposes, we will impose conditions in line with those imposed for the solid electrolyte problem in Chapter 3. We impose

Dirichlet boundary conditions for the electric potential

$$\begin{aligned}\phi(z=0) &= \Delta V, \\ \phi(z=L) &= 0,\end{aligned}\tag{4.8}$$

the flux $k = a, c$

$$\begin{aligned}J_k(z=0) &= J_{k0}, \\ J_k(z=L) &= J_{kL},\end{aligned}\tag{4.9}$$

as well as

$$v = 0\tag{4.10}$$

at the boundaries (no-slip). Initial conditions take the form

$$v(t=0) = v_0(z)\tag{4.11}$$

for v and for the n_k we have

$$n_k(t=0) = n_{k0}(z).\tag{4.12}$$

4.2.2 Non-dimensionalisation

For our non-dimensionalisation we will take the following scales,

$$\begin{aligned}z &= Lz', \quad t = t_0t', \quad \mu_k = k_B T \mu'_k, \quad v = \frac{L}{t_0} v', \quad J_k = J_{0k} J'_k, \\ n_k &= n_r n'_k, \quad z_k = qz'_k, \quad p = p_r p', \quad \rho = \rho_0 \rho', \quad \phi = \Delta V \phi', \quad m_k = m_r m'_k,\end{aligned}$$

and we proceed in the same way as for the solid electrolyte model. We will then have the following non-dimensional model (where we have dropped the primes):

$$\frac{\partial \rho}{\partial t} + \frac{\partial (\rho v)}{\partial z} = 0, \quad (4.13a)$$

$$\frac{\partial n_k}{\partial t} + \frac{\partial}{\partial z} (\delta^{-1} \lambda^2 J_k + n_k v) = 0, \quad (4.13b)$$

$$\eta \left(\frac{\partial \rho v}{\partial t} + \frac{\partial (\rho v^2)}{\partial z} \right) + a^2 \frac{\partial p}{\partial z} = -\delta^{-1} n^F \frac{\partial \phi}{\partial z}, \quad (4.13c)$$

$$-\lambda^2 \delta^{-1} \frac{\partial^2 \phi}{\partial z^2} = n^F, \quad (4.13d)$$

$$\mu_k^* + \log \left(\frac{n_k}{n} \right) + a^2 (p - 1) = \mu_k, \quad (4.13e)$$

$$- \sum_{j=a,c} M_{k,j} \left(\delta \frac{\partial}{\partial z} \left(\mu_j - \frac{m_j}{m_s} \mu_s \right) + \left(z_j - \frac{m_j}{m_s} z_s \right) \frac{\partial \phi}{\partial z} \right) = J_k, \quad (4.13f)$$

where we have used the equation of state in the chemical potential equation. We note that, in the above balances, we have chosen the scales

$$J_{0k} = \frac{N_{c,c} m_r m_k q \Delta V}{L}, \quad N_{k,j} = N_{c,c} M_{k,j}, \quad \text{and } t_0 = \frac{\epsilon_0 (1 + \chi)}{q^2 N_{c,c}}, \quad (4.14)$$

i.e. the flux for each species is scaled proportionally to its mass (as we had in the solid model in Chapter 3) and we have chosen $N_{c,c}$ as the mobility scale, in line with the scale for the solid electrolyte model. Therefore, $M_{k,j}$ is a ratio of species mobility with respect to the lithium-ion mobility. These equations are then supplemented with scaled initial conditions and the non-dimensional boundary conditions for the potential

$$\begin{aligned} \phi(z=0) &= 1, \\ \phi(z=1) &= 0, \end{aligned} \quad (4.15)$$

the fluxes

$$\begin{aligned} J_k(z=0) &= j_{k0}, \\ J_k(z=1) &= j_{k1}, \end{aligned} \quad (4.16)$$

and the no-slip velocity condition $v = 0$. Correspondingly, we have defined the following non-dimensional parameters

$$a^2 = \frac{p_r}{n_r k_B T}, \quad \eta = \frac{\rho_0 L^2}{k_B T n_r t_0^2}, \quad \lambda^2 = \frac{\epsilon_0 (1 + \chi) k_B T}{q^2 n_r L^2}, \quad \delta = \frac{k_B T}{\Delta V q}, \quad (4.17)$$

as before for the solid electrolyte model in (3.77). We observe that, in this set of equations (4.13), we have the same combination of non-dimensional parameters emerging as in (3.73), with minor differences in the time and flux scales as a result of having two mobile ionic species. This then prompts us to again define ϵ as the combination of λ and δ given by

$$\epsilon^2 = \lambda^2 \delta^{-1}. \quad (4.18)$$

In Chapter 3 we noted that $\lambda \ll 1$, $\delta \ll 1$, and $\epsilon \ll 1$ for the parameter values being considered. We note that Dreyer et al. (2013) do not explicitly address the length scale λ in their work as they decompose their domain in order to consider the boundary regions separately. We therefore use parameter values consistent with Dreyer *et al.*, while also being consistent with the values used in Chapter 3 for comparative purposes. That is, we consider parameter values where we retain the distinguished limit with λ , δ , and ϵ all being small.

4.2.3 Model simplifications and supplementations

Similar to (3.81) in section 3.2.4 of Chapter 3, we impose a global charge neutrality condition, via the following integral constraint

$$\int_0^1 n^F dz = 0. \quad (4.19)$$

This condition prevents build up of charge over time via (4.13b), acts as a nullspace constraint, and upholds the electroneutrality property of the electrolyte while allowing for departures from electroneutrality in the EDL.

We again adhere to the approach taken in Chapter 3, that is, we consider zero charge flux ($J_k = 0$) and the steady state limit $\frac{\partial n_k}{\partial t} = 0$. In this steady state, we must have constant average velocity, therefore allowing us to neglect the dynamic and convective terms in the momentum equation (4.13c). Implementing these simplifications, the model will reduce to the following set of equations

$$a^2 \frac{dp}{dz} = -\delta^{-1} n^F \frac{d\phi}{dz}, \quad (4.20a)$$

$$-\epsilon^2 \frac{d^2 \phi}{dz^2} = n^F, \quad (4.20b)$$

$$\mu_k^* + \log\left(\frac{n_k}{n}\right) + a^2(p - 1) = \mu_k, \quad (4.20c)$$

$$-\sum_{j=a,c} M_{k,j} \left(\delta \frac{d}{dz} \left(\mu_j - \frac{m_j}{m_s} \mu_s \right) + \left(z_j - \frac{m_j}{m_s} z_s \right) \frac{d\phi}{dz} \right) = 0, \quad (4.20d)$$

supplemented with the integral constraint and boundary conditions on ϕ .

We make the standard assumption that the solvent is charge neutral and therefore we take $z_s = 0$, and from the Gibbs-Duhem relation (2.55) we have that $\frac{d\mu_s}{dz} = 0$. As a result, the flux equation becomes

$$-\sum_{j=a,c} M_{k,j} \left(\delta \frac{d\mu_j}{dz} + z_j \frac{d\phi}{dz} \right) = 0. \quad (4.21)$$

Now, taking the gradient of the chemical potential equation and replacing the gradient of the pressure with (4.20a) we will have

$$\frac{d\mu_k}{dz} = \frac{d}{dz}(\log(n_k)) - \delta^{-1} n^F \frac{d\phi}{dz}. \quad (4.22)$$

We can also simplify the flux expressions further using the fact that $J_a = J_c = 0$ and $J_s = -J_a - J_c = 0$ to get the following equations

$$\delta \frac{d\log(n_a)}{dz} + (z_a - n^F) \frac{d\phi}{dz} = 0, \quad (4.23a)$$

$$\delta \frac{d\log(n_c)}{dz} + (z_c - n^F) \frac{d\phi}{dz} = 0. \quad (4.23b)$$

Then, because we have (4.20b), we can rewrite these two equations to eliminate the product term involving the concentrations and the potential as

$$\delta \frac{d\log(n_k)}{dz} + z_k \frac{d\phi}{dz} + \frac{\epsilon^2}{2} \frac{d}{dz} \left(\left(\frac{d\phi}{dz} \right)^2 \right) = 0 \quad (4.24)$$

for $k = a, c$.

We have an additional condition required for the liquid model, which is a prescribed mass condition. We did not require these mass conditions in the solid electrolyte problem due to the fixed anion concentration and the Schottky defect properties. We note that this mass condition can be derived from the differential form of the conservation of mass equation, that is, if we consider (4.1), then by definition of mass in terms of density; thus,

$$\frac{dM}{dt} = \frac{d}{dt} \int \rho \, dV = 0, \quad (4.25)$$

where M is the total mass, which is the sum of all the masses in the system and therefore does not change over time. This then implies that

$$\int_0^L \rho_k \, dz = M_k, \quad (4.26)$$

which we refer to as the prescribed mass condition. Now we must non-dimensionalise this; given the scales used in Section 4.2.2 we obtain

$$\int_0^1 n_k \, dz = \frac{M_k}{m_k m_r n_r L} = \bar{y}_k, \quad (4.27)$$

where we have defined the non-dimensional $\bar{y}_k$ by

$$\bar{y}_k = \frac{M_k}{m_k m_r n_r L}. \quad (4.28)$$

From our non-dimensionalisation and conservation of total mass we will have

$$\sum_k n_k = n_a + n_c + n_s = 1. \quad (4.29)$$

We know that by definition $\rho_k = m_k n_k = m_r m_k n_r n_k$ using our scales for the non-dimensionalisation. If we integrate this and use (4.26)

$$\int_0^1 \rho_k dz = m_r m_k n_r \int_0^1 n_k dz = \frac{M_k}{L} \quad (4.30)$$

whereby, rearranging we recover (4.27), then summing over k and using (4.29) it also follows that

$$\sum_k \bar{y}_k = \bar{y}_a + \bar{y}_c + \bar{y}_s = 1. \quad (4.31)$$

Therefore, the reduced model for the liquid electrolyte is

$$-\epsilon^2 \frac{d^2 \phi}{dz^2} = n^F, \quad (4.32a)$$

$$\frac{d}{dz} \left(\delta \log(n_k) + z_k \phi + \frac{\epsilon^2}{2} \left(\frac{d\phi}{dz} \right)^2 \right) = 0, \quad (4.32b)$$

$$\int_0^1 (z_a n_a + z_c n_c) dz = 0, \quad (4.32c)$$

$$\int_0^1 n_c dz = \bar{y}_c, \quad (4.32d)$$

$$n_a + n_c + n_s = 1, \quad (4.32e)$$

subject to the fixed potential boundary conditions

$$\phi(z=0) = 1, \quad (4.33a)$$

$$\phi(z=1) = 0. \quad (4.33b)$$

We note that the second prescribed mass condition (for the anion) is not required to solve the problem as it is accounted for via the integral constraint for charge neutrality (4.32c).

4.2.4 Auxiliary variable

In Chapter 3 we noted that numerical issues arise in the problem due to the concentrations becoming exponentially close to singular limits. We will have a similar issue here where n_a, n_c approach zero (depleted of negative/positive ions). We define our auxiliary variables, θ_a and θ_c in this scenario by

$$n_a = e^{\theta_a}, \quad (4.34a)$$

$$n_c = e^{\theta_c}. \quad (4.34b)$$

By doing this, we can map $n_c, n_a \in (0, 1)$ to $\theta_c, \theta_a \in (-\infty, 0)$ avoiding any numerical issues near singularities. In the solid electrolyte problem we also have an upper limit (saturated with positive ions), however this will not be the case here; as both the cations and anions are free to move, we have an equation for each species and from (4.32b) we will only encounter numerical issues near the lower limit. We note that physically, we still require all $0 \leq n_k \leq 1$ but this upper limit is thus reflected via (4.32c).

Rewriting (4.32) in terms of these auxiliary variables we will have

$$-\epsilon^2 \frac{d^2 \phi}{dz^2} = z_a e^{\theta_a} + z_c e^{\theta_c} = n^F, \quad (4.35a)$$

$$\frac{d}{dz} \left(\delta \theta_k + z_k \phi + \frac{\epsilon^2}{2} \left(\frac{d\phi}{dz} \right)^2 \right) = 0, \quad (4.35b)$$

$$\int_0^1 (z_a e^{\theta_a} + z_c e^{\theta_c}) dz = 0, \quad (4.35c)$$

$$\int_0^1 e^{\theta_c} dz = \bar{y}_c, \quad (4.35d)$$

$$e^{\theta_a} + e^{\theta_c} + n_s = 1. \quad (4.35e)$$

We also integrate (4.35b) for $k = a, c$

$$\delta \theta_c + z_c \phi + \frac{\epsilon^2}{2} \left(\frac{d\phi}{dz} \right)^2 = c_1, \quad (4.36a)$$

$$\delta \theta_a + z_a \phi + \frac{\epsilon^2}{2} \left(\frac{d\phi}{dz} \right)^2 = c_2. \quad (4.36b)$$

Expressing the equations in this form we again observe the explicit need for the two integral conditions (charge neutrality (4.32c) and prescribed mass (4.35d)) in order to compensate for the two additional unknown constants c_1, c_2 .

We note that in order to limit the number of equations with non-linearities to solve, we can look at combinations of (4.36). For example, subtracting the equation for θ_c from the equation for θ_a to get

$$\delta(\theta_a - \theta_c) + (z_a - z_c)\phi = c_1 - c_2 := c_3. \quad (4.37)$$

Our final non-dimensional model is as follows (as presented in the code);

$$\epsilon^2 \frac{d^2 \phi}{dz^2} = -z_a e^{\theta_a} - z_c e^{\theta_c}, \quad (4.38a)$$

$$\delta \theta_c + z_c \phi + \frac{\epsilon^2}{2} u^2 = c_1, \quad (4.38b)$$

$$\delta(\theta_a - \theta_c) + (z_a - z_c)\phi = c_3, \quad (4.38c)$$

$$\int_0^1 (z_a e^{\theta_a} + z_c e^{\theta_c}) dz = 0, \quad (4.38d)$$

$$\int_0^1 e^{\theta_c} dz = \bar{y}_c, \quad (4.38e)$$

$$u = \frac{d\phi}{dz}, \quad (4.38f)$$

$$e^{\theta_a} + e^{\theta_c} + n_s = 1, \quad (4.38g)$$

where we have defined $u = \frac{d\phi}{dz}$ for numerical ease and efficiency. We solve this subject to

$$\phi(z = 0) = 1, \quad (4.39a)$$

$$\phi(z = 1) = 0. \quad (4.39b)$$

We note that the variables we must solve for here are θ_c , θ_a , and ϕ . We further note that this problem is analogous to the solid electrolyte problem (3.87), except here we have one additional equation (for n_a) and correspondingly an additional integral condition (the prescribed mass for the additional constant).

4.3 Numerical solution

4.3.1 Numerical details

We take the same approach as used in Chapter 3, solving (4.38) subject to (4.39) numerically using MATLAB (Inc. (2023)). We use cell-centred finite differences for the derivatives, the midpoint rule for the integral conditions, and Newton's method. For parameter values we take the following (similar to those used by

Dreyer et al. (2013)):

$$z_c = 1, \quad z_a = -2, \quad \bar{y}_c = 0.24, \quad \bar{y}_a = 0.12,$$

where $\bar{y}_c + \bar{y}_a + \bar{y}_s = 1$ from our non-dimensionalisation.

Simulations were performed on the same machine as specified earlier, with a uniform grid of $N = 10,000$ nodes over the domain $z \in (0, 1)$. The elapsed computational time was approximately 90 seconds. The following constant initial conditions were applied:

$$\phi = 0.5, \quad u = 0, \quad \theta_c = \log(\bar{y}_c), \quad \theta_a = \log(\bar{y}_a), \quad c_1 = 0.5, \quad c_2 = -1.5, \quad (4.40)$$

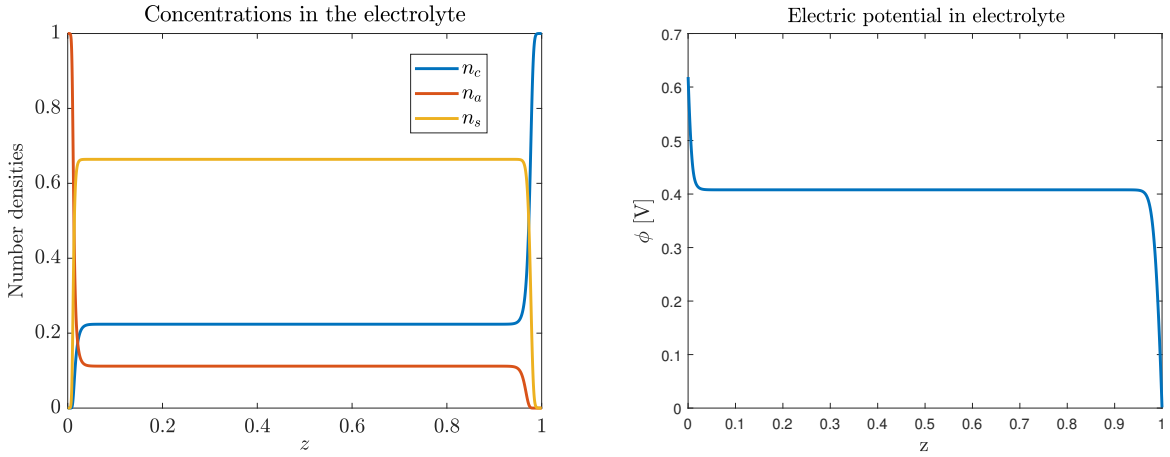
where ϕ , c_1 , and c_2 are chosen arbitrarily within reasonable bounds ($\phi \in [0, 1]$, $c_1, c_2 = \mathcal{O}(1)$). The initial value for u is taken to be zero because we expect $\frac{d\phi}{dz}$ to be approximately zero in the bulk. Initial values for θ_c and θ_a were chosen to satisfy the prescribed mass condition (4.27). The numerical scheme has been tested for various other $\mathcal{O}(1)$ constant initial conditions and exhibits consistent results.

Mesh independence and parameter sensitivity studies were conducted, yielding similar results to that of section 3.3.1 of Chapter 3. We remark that the liquid electrolyte problem is more stiff than the solid electrolyte problem. For example, while values of ϵ are of the same order in both problems - $\epsilon \approx 0.02567$ in the liquid model versus $\epsilon \approx 0.01958$ in Chapter 3 - the computational time is significantly higher for the liquid electrolyte problem. We also provide results for the liquid electrolyte using parameter values to match that of the solid problem, confirming this increased stiffness, necessitating the use of coarse-grid solutions as initial guesses.

4.3.2 Numerical results

In Figure 4.1 we plot the results of solving the model numerically. The profiles of the concentrations of all three species (n_c, n_a, n_s) are shown in Figure 4.1a and the electric potential profile is presented in Figure 4.1b. In general, we note that these results resonate qualitatively with those presented by Dreyer *et al.* in their work. Moreover, the profiles demonstrate behaviour similar to that for the solid electrolyte model, under the conditions of a zero flux steady-state. That is, we observe that the concentration profiles are constant in the bulk of the electrolyte, with narrow boundary layers near $z = 0$ and $z = 1$. We also note that, similar to the profile for n_c in Figure 3.2a, the boundary layers are not symmetric on either side of the bulk. In particular, the boundary layer near $z = 1$ appears to be wider than the boundary layer near $z = 0$.

We remark that n_c and n_a display opposite behaviour; as expected according to the nature of double charge layers, one species is attracted to the charge at the boundary, with the concentration of the other species then increasing as we move into the diffuse layer of the EDL and then the bulk, with the reverse occurring at the other side of the bulk. We further note that the solvent concentration is constant in the bulk and then also exhibits boundary layers near $z = 0, 1$. Taking a closer look at the figures, we observe that the bulk of each of the concentration profiles is approximately the same value as the prescribed mass ($\bar{y}_k$) for that species.



(a) Profile of ionic concentrations for all three species.

(b) Profile of the electric potential.

Figure 4.1: Numerical results for the 1D steady-state problem (4.38) subject to (4.39) with parameter values: $z_c = 1$, $z_a = -2$, $\bar{y}_c = 0.24$. We take $\lambda = 5 \times 10^{-3}$, $\delta = 0.038$, and $\Delta V = 0.62\text{V}$. We have plotted the concentration of each species (n_c, n_a, n_s) and the profile for the electric potential, with ϕ shown dimensionally (in volts) as per convention.

We also plot the auxiliary variable solutions in Figure 4.2 for both θ_c (in Figure 4.2b) and θ_a (in Figure 4.2b). The inset plots of both figures zoom in on the two boundaries to highlight what is happening in these regions. We observe that θ_c becomes very large and negative near the boundary at $z = 0$, which is similar to the solid model scenario, while near $z = 1$ it appears to approach 0. The opposite can be seen for θ_a . From these inset plots we also observe a distinct “knee” region in the solutions, that is, there appears to be a superlinear type of behaviour occurring in the boundaries.

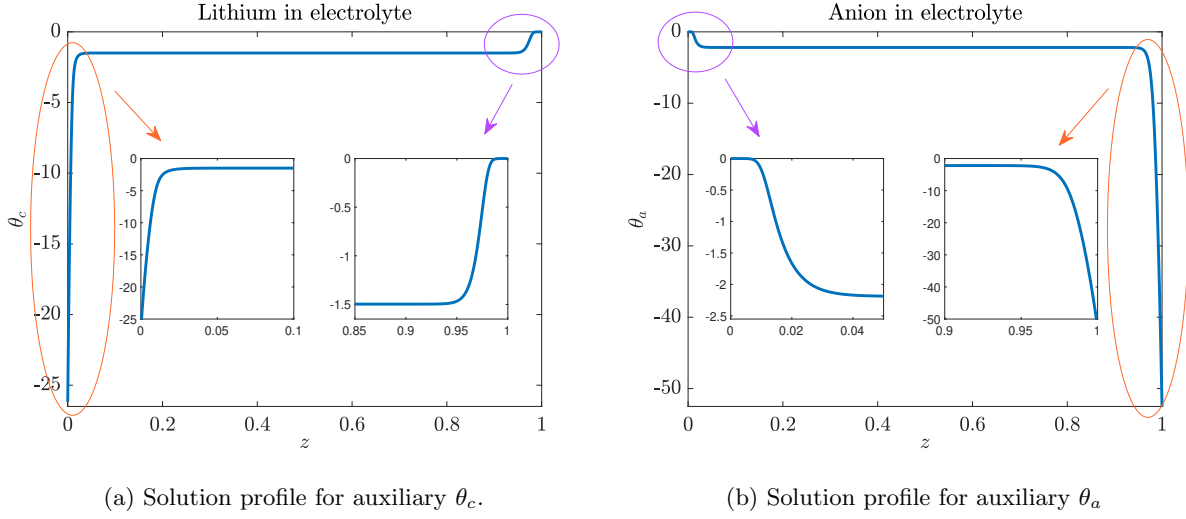


Figure 4.2: Numerical results for the 1D steady-state problem (4.38) subject to (4.46) with parameter values: $z_c = 1$, $z_a = -2$, $\bar{y}_c = 0.24$. We take $\lambda = 5 \times 10^{-3}$, $\delta = 0.038$, and $\Delta V = 0.62V$. We show the solution profiles for the two auxiliary variables in the liquid problem, θ_c and θ_a . We also include inset plots for both figures whereby we zoom in on the boundaries near $z = 0$ and $z = 1$ to further highlight the solution profile in these regions.

Comparison with solid

To carry out this comparison we will leave the parameters for the solid electrolyte model in Chapter 3 unchanged and we take the following for this liquid electrolyte model:

$$z_c = 1, \quad z_a = -1, \quad \bar{y}_c = 0.4, \quad \bar{y}_a = 0.4, \quad \Delta V = 4V, \quad \lambda = 1.5 \times 10^{-3}.$$

We note that $\bar{y}_a$ is chosen to be 0.4 in order to align with the fixed anion concentration of 0.4 in the solid electrolyte model, however, this value is only an estimate of the bulk value of n_a in the liquid, while it is prescribed in the solid electrolyte model. We note that variations are expected even so as a result of the mobile anion in the liquid model and we remind the reader that an exact equivalence between the two solution profiles would not occur due to the assumption of a stationary anion in the solid electrolyte model. The plots for both n_c and ϕ are shown in Figure 4.3.

In Figure 4.3a we note, by construction, that the bulk values agree (likely to within some $\mathcal{O}(\delta)$ correction in the bulk of the liquid). The boundary values near $z = 0$ align reasonably well, while there seems to be a

larger distinction between the boundary layers near $z = 1$. We note that part of this difference near $z = 1$ can be attributed to the modelling differences, *i.e.* in the liquid model the electrolyte can become saturated with lithium ions here, while this is not the case in the solid model with the constant anion concentration; whereby the lithium ions saturate at a maximum of $n - n_a$. We have included inset plots to zoom in on the two boundaries. As we look more closely, we note that the transition region between the boundaries and the bulk are sharper, or more “knee-like” in the liquid model, in comparison to the solid electrolyte. Furthermore, it is apparent that at both boundaries the width of the boundary layer in n_c for the solid is wider than that for the liquid, supporting the claims and observations noted by other researchers, as discussed and referenced in Chapter 3.

We note that similar remarks can be made for the electric potential in Figure 4.3b; the boundary layer regions for the solid solution appear to be wider than those for the liquid and the transition into the bulk solution is sharper for the liquid than for the solid. We also acknowledge that the bulk values for the potential are substantially different, but again, this distinction can be associated to the treatment and mobility of the anion.

These numerical simulation results suggest that the solid electrolyte model exhibits wider EDLs than the liquid electrolyte model. However, due to the inherent differences between the two models, it is not immediately clear why the liquid model leads to thinner layers, nor the extent to which the solid model yields wider layers; thus necessitating a closer look at this model. We therefore follow the approach taken in Chapter 3 and undertake an asymptotic reduction of the liquid model.

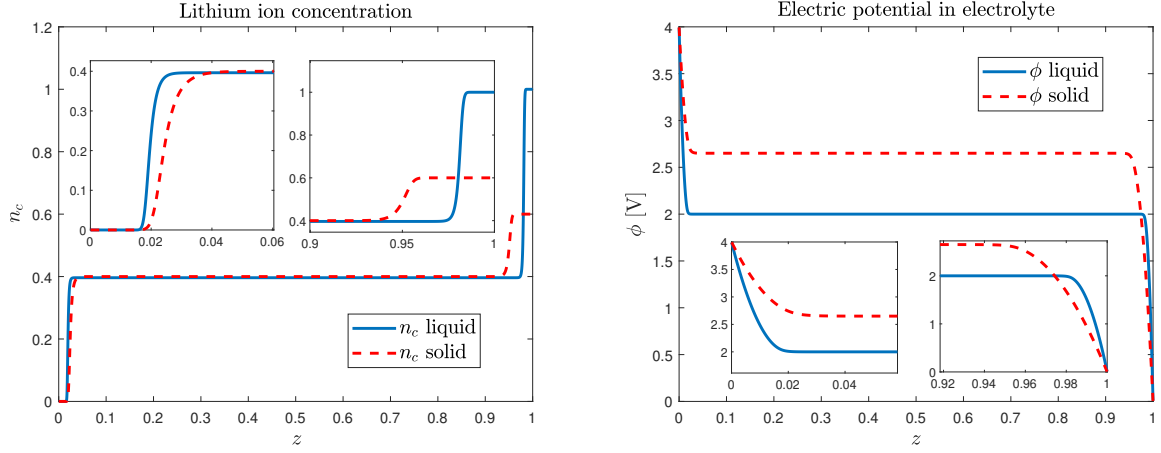
4.4 Asymptotic reduction

We first restate the set of equations for which we carry out the asymptotic reduction; we have

$$\epsilon^2 \frac{d^2 \phi}{dz^2} = -z_a e^{\theta_a} - z_c e^{\theta_c}, \quad (4.41a)$$

$$\delta \theta_c + z_c \phi + \frac{\epsilon^2}{2} u^2 = c_1, \quad (4.41b)$$

$$\delta \theta_a + z_a \phi + \frac{\epsilon^2}{2} u^2 = c_2, \quad (4.41c)$$



(a) Solution profile for n_c for both the solid and liquid models. (b) Solution profile for ϕ [V] for both the solid and liquid models.

Figure 4.3: Numerical results for the 1D steady-state problem (4.38) subject to (4.46) with parameter values: $z_c = 1$, $z_a = -1$, $\bar{y}_c = 0.4$, $\bar{y}_a = 0.4$, $\lambda = 1.5 \times 10^{-3}$, and $\Delta V = 4V$ to compare with the results presented in Figure 3.2 for the solid electrolyte. We include inset plots to more clearly display the variation in the two electrolyte models at the boundaries.

with

$$u = \frac{d\phi}{dz}, \quad (4.42)$$

$$e^{\theta_a} + e^{\theta_c} + n_s = 1, \quad (4.43)$$

$$\int_0^1 (z_a e^{\theta_a} + z_c e^{\theta_c}) dz = 0, \quad (4.44)$$

$$\int_0^1 e^{\theta_c} dz = \bar{y}_c, \quad (4.45)$$

and subject to

$$\phi(z = 0) = 1, \quad (4.46a)$$

$$\phi(z = 1) = 0. \quad (4.46b)$$

Before we proceed with the asymptotics, we identify some connections between the variables from the given set of equations (4.41) that will be useful throughout this section. We note that, if we apply (4.44) to (4.41a),

we must have that

$$\left. \frac{d\phi}{dz} \right|_{z=0}^{z=1} = 0, \quad (4.47)$$

from which it follows from our definition of u , (4.42), that

$$u(z=0) = u(z=1). \quad (4.48)$$

In addition, because (4.41b) and (4.41c) are pointwise conditions we can write the following relations

$$\delta\theta_c(0) + z_c\phi(0) + \frac{\epsilon^2}{2}u^2(0) = c_1, \quad (4.49a)$$

$$\delta\theta_c(1) + z_c\phi(1) + \frac{\epsilon^2}{2}u^2(1) = c_1, \quad (4.49b)$$

$$\delta\theta_a(0) + z_a\phi(0) + \frac{\epsilon^2}{2}u^2(0) = c_2, \quad (4.49c)$$

$$\delta\theta_a(1) + z_a\phi(1) + \frac{\epsilon^2}{2}u^2(1) = c_2. \quad (4.49d)$$

We can further simplify these relations by applying our boundary conditions on ϕ (4.46) and subtracting combinations of these. For example, subtracting (4.49a) and (4.49b)

$$\delta(\theta_c(1) - \theta_c(0)) - z_c = 0 \quad (4.50)$$

using (4.48). Similarly, subtracting (4.49c) and (4.49d), (4.49b) and (4.49c), and (4.49a) and (4.49d) we have the following set of associations between the variables:

$$\delta(\theta_a(1) - \theta_a(0)) - z_a = 0, \quad (4.51)$$

$$\delta(\theta_c(1) - \theta_a(0)) - z_a = c_1 - c_2, \quad (4.52)$$

$$\delta(\theta_a(1) - \theta_c(0)) - z_c = c_2 - c_1. \quad (4.53)$$

From our boundary condition (4.46) we know that $\phi(0) = 1$, thus following the solid electrolyte problem and from our numerical solutions for θ_k in Figure 4.2, we expect that $\theta_c(0) = \mathcal{O}(\delta^{-1})$ and likewise, $\theta_a(1) = \mathcal{O}(\delta^{-1})$. We note that the premise of the EDL is a higher concentration of one species dominating near the boundary, with the inverse at the opposite boundary. Therefore, it is reasonable to expect that $\theta_c(1) \sim \theta_a(0) \sim \mathcal{O}(1)$, which is also indicated by the numerical profiles in Figure 4.2. Following the results we observe

in Chapter 3, we then pose the following expansions in δ ,

$$c_1 = c_{10} + \delta c_{11}, \quad (4.54a)$$

$$c_2 = c_{20} + \delta c_{21}, \quad (4.54b)$$

$$\phi = \phi_0 + \delta \phi_1, \quad (4.54c)$$

$$\theta_c = \theta_{c0} + \delta \theta_{c1}, \quad (4.54d)$$

$$\theta_a = \theta_{a0} + \delta \theta_{a1}, \quad (4.54e)$$

so that we have each variable to at least $\mathcal{O}(1)$. Substituting these expansions into the conditions above (eqs. (4.50) to (4.53)), we will have the following relations:

$$c_{20} - c_{10} = z_a, \quad (4.55a)$$

$$\theta_{c0}(1) - \theta_{a0}(0) = c_{11} - c_{21}, \quad (4.55b)$$

$$\theta_{c0}(0) = -\delta^{-1} z_c, \quad (4.55c)$$

$$\theta_{c0}(1) - \delta \theta_{c1}(0) = 0, \quad (4.55d)$$

$$\theta_{a0}(1) = \delta^{-1} z_a, \quad (4.55e)$$

$$\delta \theta_{a1}(1) - \theta_{a0}(0) = 0; \quad (4.55f)$$

we will refer to these in the following sections.

4.4.1 Bulk

In the bulk we expect $z, \phi, \theta_c, \theta_a \sim \mathcal{O}(1)$. Therefore, taking $z \sim \mathcal{O}(1)$ and noting that $\epsilon \ll 1$ and $\delta \ll 1$, (4.41) in the bulk is then given by

$$z_a e^{\theta_a^*} + z_c e^{\theta_c^*} = 0, \quad (4.56a)$$

$$\delta \theta_c^* + z_c \phi^* = c_1, \quad (4.56b)$$

$$\delta \theta_a^* + z_a \phi^* = c_2, \quad (4.56c)$$

where we use the superscript $*$ to denote the bulk solution. Expanding each variable as shown in (4.54), we obtain

$$z_a e^{\theta_{a0}^* + \delta \theta_{a1}^*} + z_c e^{\theta_{c0}^* + \delta \theta_{c1}^*} = 0, \quad (4.57a)$$

$$\delta(\theta_{c0}^* + \delta \theta_{c1}^*) + z_c(\phi_0^* + \delta \phi_1^*) = c_{10} + \delta c_{11}, \quad (4.57b)$$

$$\delta(\theta_{a0}^* + \delta \theta_{a1}^*) + z_a(\phi_0^* + \delta \phi_1^*) = c_{20} + \delta c_{21}. \quad (4.57c)$$

From the leading-order terms of (4.57a), we can determine θ_{a0}^* in terms of θ_{c0}^* to be

$$\theta_{a0}^* = \theta_{c0}^* + \log\left(\frac{-z_c}{z_a}\right). \quad (4.58)$$

We can subtract the leading order (4.57b) and (4.57c) to solve for ϕ_0^* :

$$\phi_0^* = \frac{c_{20} - c_{10}}{z_a - z_c} = \frac{-z_a}{z_c - z_a} \quad (4.59)$$

where we have used (4.55a). Then, from the leading order of (4.57b) and (4.57c),

$$c_{10} = z_c \phi_0^* = \frac{-z_c z_a}{z_c - z_a} \quad (4.60)$$

and

$$c_{20} = z_a \phi_0^* = \frac{-z_a^2}{z_c - z_a}. \quad (4.61)$$

We notice that since $z_c > 0$ and $z_a < 0$, we have that $c_{10} > 0$, and from (4.55a) it also follows that $c_{20} - z_a = c_{10} > 0$. We use the prescribed mass integral constraint (4.45) to determine θ_{c0}^* ; we have

$$\int_0^1 e^{\theta_c} dz = \underbrace{\int_0^{\hat{z}_L} e^{\theta_c} dz}_{\text{left boundary}} + \underbrace{\int_{\hat{z}_L}^{\hat{z}_R} e^{\theta_c} dz}_{\text{bulk}} + \underbrace{\int_{\hat{z}_R}^1 e^{\theta_c} dz}_{\text{right boundary}}, \quad (4.62)$$

$$\approx \underbrace{\int_{\hat{z}_L}^{\hat{z}_R} e^{\theta_c} dz}_{\text{bulk}} \approx \int_0^1 e^{\theta_c^*} dz \quad (4.63)$$

since $\int_0^{\hat{z}_L} e^{\theta_c} dz \ll 1$ since we expect that $\theta_c \sim \mathcal{O}(\delta^{-1})$ and $\theta_c < 0$ here, and $\int_{\hat{z}_R}^1 e^{\theta_c} dz \ll 1$ since $\theta_c \sim \mathcal{O}(1)$ here, but $1 - \hat{z}_R \ll 1$ by virtue of it being a narrow boundary layer. Therefore, we must have

$$\int_0^1 e^{\theta_c^*} dz = e^{\theta_{c0}^*} = \bar{y}_c. \quad (4.64)$$

And so, our leading-order bulk solution will be

$$\theta_{c0}^* = \log(\bar{y}_c), \quad (4.65a)$$

$$\theta_{a0}^* = \log(\bar{y}_c) + \log\left(\frac{-z_c}{z_a}\right) = \log\left(\frac{-z_c \bar{y}_c}{z_a}\right), \quad (4.65b)$$

$$\phi_0^* = \frac{-z_a}{z_c - z_a}, \quad (4.65c)$$

with c_{10} and c_{20} as given in (4.60) and (4.61), respectively.

At the next order, $\mathcal{O}(\delta)$, we have

$$\theta_{c0}^* + z_c \phi_1^* = c_{11}, \quad (4.66)$$

$$\theta_{a0}^* + z_a \phi_1^* = c_{21}. \quad (4.67)$$

Subtracting (4.67) from (4.66), we obtain

$$\phi_1^* = \frac{c_{11} - c_{21} + \log\left(\frac{-z_c}{z_a}\right)}{z_c - z_a}, \quad (4.68)$$

where we have used (4.58). We note that we currently do not have enough information to determine the constants c_{11} and c_{12} .

Unlike the solid electrolyte problem, the corrections in the bulk are not all exponentially small, and we can determine corrections in orders of δ . We acknowledge that this confirms our speculation in Figure 4.3a regarding the approximate bulk value of $\bar{y}_c$ being within $\mathcal{O}(\delta)$ of the actual value. However, since our goal focuses on understanding the similarities and differences between the solid and liquid models, we will proceed with the $\mathcal{O}(1)$ solutions in both θ_k and ϕ , as well as the $\mathcal{O}(\delta)$ corrections to ϕ to be consistent with the work in Chapter 3. We remind the reader that in Chapter 3 we observe that we require the solution to $\mathcal{O}(\delta)$ in ϕ in order to determine θ to $\mathcal{O}(1)$ in the boundary layers.

4.4.2 Boundary layers

Of course, the solutions in the bulk (4.65) do not satisfy either of the boundary conditions (4.46), necessitating a boundary layer rescaling. We note that the contribution of the derivatives is negligible in determining the bulk solution, but become crucial in order to facilitate the transition between the boundary conditions for ϕ . Therefore, we require a rescaling that will reintroduce the derivative terms into our boundary layer equations. We will consider the layers to the left and to the right of the bulk separately.

Left boundary layer

As in Chapter 3, we use the subscript BL to indicate the left boundary layer. Near $z = 0$, we scale $z = \epsilon x_{\text{BL}}$ since z is small here and from (4.41a) ϵ is the small parameter of the boundary layer. We note that using this scaling in $\epsilon^2 \frac{d^2 \phi}{dz^2}$ we retain $\phi \sim \mathcal{O}(1)$, which is in agreement with our $\mathcal{O}(1)$ boundary conditions on ϕ . We scale $\theta_c = -\delta^{-1} \psi_c$ as we expect θ_c to be large and negative near $z = 0$ and we retain $\theta_a = \theta_{a_{\text{BL}}}$ as $\mathcal{O}(1)$. We also let $u = \epsilon^{-1} U_{\text{BL}}$ where $U_{\text{BL}} = \frac{d\phi_{\text{BL}}}{dx_{\text{BL}}}$. Our boundary layer problem is then given by

$$\frac{d^2 \phi_{\text{BL}}}{dx_{\text{BL}}^2} = -z_a e^{\theta_{a_{\text{BL}}}} - z_c e^{-\delta^{-1} \psi_c}, \quad (4.69a)$$

$$-\psi_c + z_c \phi_{\text{BL}} + \frac{1}{2} U_{\text{BL}}^2 = c_1, \quad (4.69b)$$

$$\delta \theta_{a_{\text{BL}}} + z_a \phi_{\text{BL}} + \frac{1}{2} U_{\text{BL}}^2 = c_2. \quad (4.69c)$$

From the leading order of (4.69c) we can write the following equation for ϕ

$$z_a \phi_{\text{BL}}^0 + \frac{1}{2} \left(\frac{d\phi_{\text{BL}}^0}{dx_{\text{BL}}} \right)^2 = c_{20}, \quad (4.70)$$

which we can rewrite as

$$\frac{d\phi_{\text{BL}}^0}{dx_{\text{BL}}} = -\sqrt{2(c_{20} - z_a \phi_{\text{BL}}^0)} \quad (4.71)$$

where we have taken the negative square root as ϕ_{BL}^0 should decrease monotonically ($\phi(0) = 1 \rightarrow \phi(1) = 0$).

We can integrate this to solve for ϕ_{BL}^0

$$\int_1^{\phi_{\text{BL}}^0} \frac{d\phi_{\text{BL}}^0}{\sqrt{(c_{20} - z_a \phi_{\text{BL}}^0)}} = - \int_0^{x_{\text{BL}}} \sqrt{2} dx_{\text{BL}} \quad (4.72)$$

obtaining

$$\phi_{\text{BL}}^0 = \frac{-z_a}{2} x_{\text{BL}}^2 - \sqrt{2(c_{20} - z_a)} x_{\text{BL}} + 1. \quad (4.73)$$

From here we have

$$U_{\text{BL}}^0 = \frac{d\phi_{\text{BL}}^0}{dx_{\text{BL}}} = -z_a x_{\text{BL}} - \sqrt{2(c_{20} - z_a)}, \quad (4.74)$$

$$\frac{d^2 \phi_{\text{BL}}^0}{dx_{\text{BL}}^2} = -z_a. \quad (4.75)$$

Therefore, returning to (4.69a) using (4.75) we must have

$$-z_a = -z_a e^{\theta_{a_{\text{BL}}}}, \quad (4.76)$$

since $\delta \ll 1$ so $e^{-\delta^{-1}\psi_c} \ll 1$ and thus

$$\theta_{a_{BL}}^0 = \log 1 = 0. \quad (4.77)$$

Now we can use (4.69b) to determine ψ_c^0 as

$$-\psi_c^0 + z_c \phi_{BL}^0 + \frac{1}{2} \left(\frac{d\phi_{BL}^0}{dx_{BL}} \right)^2 = c_{10}, \quad (4.78)$$

whereby we find

$$\psi_c^0 = \frac{-z_a(z_c - z_a)}{2} x_{BL}^2 - (z_c - z_a) \sqrt{2(c_{20} - z_a)} x_{BL} + z_c, \quad (4.79)$$

where we have used $c_{20} - c_{10} = z_a$ from (4.55a).

We note that if $\theta_{a_{BL}}^0 = 0$ from (4.77) then $\theta_{a_{BL}}^0(0) = 0$, and by symmetry we assume that $\theta_{c_{BR}}^0(1) = 0$ also; therefore, from (4.55b)

$$\theta_c^0(1) - \theta_a^0(0) = 0 = c_{11} - c_{21}, \quad (4.80)$$

i.e. we must have

$$c_{11} = c_{21}. \quad (4.81)$$

From this, we now have enough information to complete our bulk solution, substituting this into (4.68)

$$\phi_1^* = \frac{\log\left(\frac{-z_c}{z_a}\right)}{z_c - z_a}. \quad (4.82)$$

It follows that

$$c_{11} = c_{21} = \theta_c^* + \frac{z_c \log\left(\frac{-z_c}{z_a}\right)}{z_c - z_a}. \quad (4.83)$$

Returning to the left boundary layer now at $\mathcal{O}(\delta)$,

$$\frac{d^2 \phi_{BL}^1}{dx_{BL}^2} = -z_a \theta_{a_{BL}}^1 e^{\theta_{a_{BL}}^0}, \quad (4.84a)$$

$$-\psi_c^1 + z_c \phi_{BL}^1 + U_{BL}^0 U_{BL}^1 = c_{11}, \quad (4.84b)$$

$$\theta_{a_{BL}}^0 + z_a \phi_{BL}^1 + U_{BL}^0 U_{BL}^1 = c_{21} = c_{11}. \quad (4.84c)$$

Considering (4.84c) and substituting our leading-order boundary layer solutions for $\theta_{a_{BL}}^0$ given by (4.77) and ϕ_{BL}^0 given by (4.73), we can rewrite this as an equation for ϕ_{BL}^1 and integrate

$$\int_0^{\phi_{BL}^1} \frac{d\phi_{BL}^1}{z_a \phi_{BL}^1 - c_{11}} = \int_0^{x_{BL}} \frac{dx_{BL}}{z_a x_{BL} + \sqrt{2(c_{20} - z_a)}}, \quad (4.85)$$

where $\phi(0) = \phi^0(0) + \delta\phi^1(0) = 1$ so we must have that $\phi^1(0) = 0$. Integrating we have the following solution for ϕ_{BL}^1 :

$$\phi_{\text{BL}}^1 = \frac{-c_{11}}{\sqrt{2(c_{20} - z_a)}} x_{\text{BL}}. \quad (4.86)$$

It follows that

$$U_{\text{BL}}^1 = \frac{d\phi_{\text{BL}}^1}{dx_{\text{BL}}} = \frac{-c_{11}}{\sqrt{2(c_{20} - z_a)}}, \quad (4.87)$$

$$\frac{d^2\phi_{\text{BL}}^1}{dx_{\text{BL}}^2} = 0. \quad (4.88)$$

As before, using (4.88) in (4.84a) we find

$$\theta_{a\text{BL}}^1 = 0. \quad (4.89)$$

It remains to use (4.84b) to solve for ψ_c^1 :

$$\psi_c^1 = z_c \phi_{\text{BL}}^1 + U_{\text{BL}}^0 U_{\text{BL}}^1 - c_{11}. \quad (4.90)$$

Substituting (4.86) and (4.87) we find

$$\psi_c^1 = \frac{-c_{11}(z_c - z_a)}{\sqrt{2(c_{20} - z_a)}} x_{\text{BL}}. \quad (4.91)$$

Therefore, the left boundary-layer solution is given as

$$\phi_{\text{BL}} = \frac{-z_a}{2} x_{\text{BL}}^2 - \sqrt{2(c_{20} - z_a)} x_{\text{BL}} + 1 + \delta \frac{-c_{11}}{\sqrt{2(c_{20} - z_a)}} x_{\text{BL}}, \quad (4.92a)$$

$$\theta_{c\text{BL}} = -\delta^{-1} \psi_c = -\delta^{-1} \left(\frac{-z_a(z_c - z_a)}{2} x_{\text{BL}}^2 - (z_c - z_a) \sqrt{2(c_{20} - z_a)} x_{\text{BL}} + z_c + \delta \left(\frac{-c_{11}(z_c - z_a)}{\sqrt{2(c_{20} - z_a)}} x_{\text{BL}} \right) \right), \quad (4.92b)$$

$$\theta_{a\text{BL}} = 0, \quad (4.92c)$$

$$c_{11} = c_{21} = \theta_c^* + \frac{z_c \log\left(\frac{-z_c}{z_a}\right)}{z_c - z_a}. \quad (4.92d)$$

We note that from (4.55d)

$$\theta_c^0(1) - \delta\theta_c^1(0) = 0, \quad (4.93)$$

and from (4.91) we have $\psi_c^1(0) = 0$, therefore we must also have that $\theta_c^0(1) = 0$, confirming our earlier assumption in determining c_{11}, c_{21} .

Right boundary layer

We proceed in exactly the same way for the boundary near $z = 1$, where we take the subscript BR for solutions in this region. Here we scale $z = 1 - \epsilon x_{\text{BR}}$ and $u = \epsilon^{-1} U_{\text{BR}}$. At this boundary we expect θ_a to be large and negative, $\theta_a = -\delta^{-1} \psi_a$, and $\theta_c = \theta_{c_{\text{BR}}} \sim \mathcal{O}(1)$.

Implementing these scales in (4.41) we will have the following at the right boundary

$$\frac{d^2 \phi_{\text{BR}}}{dx_{\text{BR}}^2} = -z_a e^{-\delta^{-1} \psi_a} - z_c e^{\theta_{c_{\text{BR}}}}, \quad (4.94a)$$

$$\delta \theta_{c_{\text{BR}}} + z_c \phi_{\text{BR}} + \frac{1}{2} U_{\text{BR}}^2 = c_1, \quad (4.94b)$$

$$-\psi_a + z_a \phi_{\text{BR}} + \frac{1}{2} U_{\text{BR}}^2 = c_2. \quad (4.94c)$$

We take the same steps as used for the left boundary, noting that the leading order of (4.94b) can be used to determine ϕ_{BR}^0

$$z_c \phi_{\text{BR}}^0 + \frac{1}{2} \left(\frac{d\phi_{\text{BR}}^0}{dx_{\text{BR}}} \right)^2 = c_{10}, \quad (4.95)$$

which we can express as

$$\frac{d\phi_{\text{BR}}^0}{dx} = \sqrt{2(c_{10} - z_c \phi_{\text{BR}}^0)}, \quad (4.96)$$

where this time we take the positive square root since ϕ increasing in x_{BR} means ϕ is decreasing in z as required ($z = 1 - \epsilon x_{\text{BR}}$). We again integrate to find ϕ_{BR}^0

$$\int_0^{\phi_{\text{BR}}^0} \frac{d\phi_{\text{BR}}^0}{\sqrt{(c_{10} - z_c \phi_{\text{BR}}^0)}} = \int_0^{x_{\text{BR}}} \sqrt{2} dx_{\text{BR}} \quad (4.97)$$

which has solution

$$\phi_{\text{BR}}^0 = \frac{-z_c}{2} x_{\text{BR}}^2 - \sqrt{2c_{10}} x_{\text{BR}}. \quad (4.98)$$

Following from (4.98),

$$U_{\text{BR}}^0 = \frac{d\phi_{\text{BR}}^0}{dx_{\text{BR}}} = -z_c x_{\text{BR}} + \sqrt{2c_{10}}, \quad (4.99)$$

$$\frac{d^2 \phi_{\text{BR}}^0}{dx_{\text{BR}}^2} = -z_c. \quad (4.100)$$

Given (4.100) and $e^{-\delta^{-1} \psi_a} \ll 1$, (4.94a) becomes an equation for $\theta_{c_{\text{BR}}}^0$,

$$-z_c = -z_c e^{\theta_{c_{\text{BR}}}^0}, \quad (4.101)$$

and thus

$$\theta_{\text{cBR}}^0 = 0. \quad (4.102)$$

Now we can use the leading order (4.94c) to solve for ψ_a^0

$$\begin{aligned} \psi_a^0 &= z_a \phi_{\text{BR}}^0 + \frac{1}{2} \left(\frac{d\phi_{\text{BR}}^0}{dx_{\text{BR}}} \right)^2 - c_{20}, \\ &= \frac{z_c(z_c - z_a)}{2} x_{\text{BR}}^2 - (z_c - z_a) \sqrt{2c_{10}} x_{\text{BR}} - z_a. \end{aligned} \quad (4.103)$$

From this $\psi_a^0(0) = -z_a$, which agrees with $\theta_a^0(z=1) = -\delta^{-1}\psi_a^0(x_{\text{BR}}=0) = \delta^{-1}z_a$ from (4.55e).

At $\mathcal{O}(\delta)$ the right boundary-layer problem is given by

$$\frac{d^2 \phi_{\text{BR}}^1}{dx_{\text{BR}}^2} = -z_c \theta_{\text{cBR}}^1 e^{\theta_{\text{cBR}}^0}, \quad (4.104a)$$

$$\theta_{\text{cBR}}^0 + z_c \phi_{\text{BR}}^1 + U_{\text{BR}}^0 U_{\text{BR}}^1 = c_{11}, \quad (4.104b)$$

$$-\psi_a^1 + z_a \phi_{\text{BR}}^1 + U_{\text{BR}}^0 U_{\text{BR}}^1 = c_{21} = c_{11}. \quad (4.104c)$$

We solve this set of equations in the same manner as the left hand side; from (4.104b) we find

$$\phi_{\text{BR}}^1 = \frac{c_{11}}{\sqrt{2c_{10}}} x_{\text{BR}}, \quad (4.105)$$

from which

$$U_{\text{BR}}^1 = \frac{d\phi_{\text{BR}}^1}{dx_{\text{BR}}} = \frac{c_{11}}{\sqrt{2c_{10}}}, \quad (4.106)$$

$$\frac{d^2 \phi_{\text{BR}}^1}{dx_{\text{BR}}^2} = 0. \quad (4.107)$$

From (4.104a) we then have

$$\theta_{\text{cBR}}^1 = 0. \quad (4.108)$$

We then use (4.104c) to find

$$\psi_a^1 = \frac{-c_{11}(z_c - z_a)}{\sqrt{2c_{10}}} x_{\text{BR}}, \quad (4.109)$$

and $\psi_a^1(0) = 0$.

Our right boundary-layer solution is then

$$\phi_{\text{BR}} = \frac{-z_c}{2}x_{\text{BR}}^2 + \sqrt{2c_{10}}x_{\text{BR}} + \delta \frac{c_{11}}{\sqrt{2c_{10}}}x_{\text{BR}}, \quad (4.110\text{a})$$

$$\theta_{c\text{BR}} = 0, \quad (4.110\text{b})$$

$$\theta_{a\text{BR}} = -\delta^{-1}\psi_a = -\delta^{-1} \left(\frac{z_c(z_c - z_a)}{2}x_{\text{BR}}^2 - (z_c - z_a)\sqrt{2c_{10}}x_{\text{BR}} - z_a + \delta \left(\frac{-c_{11}(z_c - z_a)}{\sqrt{2c_{10}}}x_{\text{BR}} \right) \right). \quad (4.110\text{c})$$

We observe that the structure of the solution, for both the left and right boundary layers ((4.92) and (4.110)), is similar to the solutions of the boundary layer of the solid model ((3.98) and (3.100)). Specifically, the electric potential and the ionic species that are depleted at a given boundary demonstrate quadratic behaviour, while the abundant species is constant.

4.4.3 Intermediate layers

We note that the boundary layer solutions for θ are $\mathcal{O}(\delta^{-1})$ and zero as found in (4.92) and (4.110), however, the bulk solutions (4.65) are $\mathcal{O}(1)$ constants. Therefore, we must have some intermediate region between the boundary and the bulk to facilitate this change from something large (or something equal to zero) to the constant bulk values.

Left intermediate layer

We note that the boundary layer solution will break down as x_{BL} grows; when x_{BL} becomes large z is no longer $\mathcal{O}(\epsilon)$ and the boundary layer solution violates $\theta_c \gg 1$. Furthermore, the boundary layer solution (4.92) is quadratic and can only grow to its maximum.

Here we will determine the maximum of the quadratic, *i.e.* where $\frac{d\theta_c}{dz} = 0$, or equivalently, where $\frac{d\psi_c}{dx} = 0$. Because $\psi_c = \psi_c^0 + \delta\psi_c^1$, we want to find the point whereby

$$\frac{d\psi_c}{dx} = \frac{d\psi_c^0}{dx} + \delta \frac{d\psi_c^1}{dx} = 0. \quad (4.111)$$

If we let $x_L = x_L^0 + \delta x_L^1$ be the point where we have a maximum then x_L should satisfy

$$\left. \frac{d\psi_c}{dx} \right|_{x_L} \approx \left. \frac{d\psi_c^0}{dx} \right|_{x_L^0} + \delta \left(\left. \frac{d^2\psi_c^0}{dx^2} \right|_{x_L^0} x_L^1 + \left. \frac{d\psi_c^1}{dx} \right|_{x_L^0} \right) = 0. \quad (4.112)$$

From (4.79)

$$\left. \frac{d\psi_c^0}{dx} \right|_{x_L^0} = -z_a (z_c - z_a) x_L^0 - (z_c - z_a) \sqrt{2(c_{20} - z_a)}; \quad (4.113)$$

therefore

$$x_L^0 = \frac{-\sqrt{2(c_{20} - z_a)}}{z_a}. \quad (4.114)$$

Given this and (4.91) it follows that

$$\left. \frac{d^2\psi_c^0}{dx^2} \right|_{x_L^0} x_L^1 + \left. \frac{d\psi_c^1}{dx} \right|_{x_L^0} = \frac{-c_{11}(z_c - z_a)}{\sqrt{2(c_{20} - z_a)}} - z_a (z_c - z_a) x_L^1 = 0, \quad (4.115)$$

and thus

$$x_L^1 = \frac{-c_{11}}{z_a \sqrt{2(c_{20} - z_a)}}. \quad (4.116)$$

Substituting x_L^0 from (4.114) into ψ_c^0 from (4.73) we find $\psi_c^0(x_L^0) = 0$. Therefore,

$$\psi_c(x_L) \sim \psi_c^0(x_L^0) + \delta \left(\left. \frac{d\psi_c^0}{dx} \right|_{x_L^0} x_L^1 + \psi_c^1(x_L^0) \right) = \delta \psi_c^1(x_L^0) = \delta \left(\frac{(z_c - z_a) c_{11}}{z_a} \right), \quad (4.117)$$

where we have used (4.114) in (4.91). This suggests a rescaling of the form $x_{BL} = x_L + \omega(\delta)y_{IL}$, where y_{IL} is our intermediate layer spatial variable, with $\delta \ll \omega \ll 1$, since if $\omega \ll \delta$ then the previous expansion dominates, and $\theta_c \sim \mathcal{O}(1)$. If we expand ψ_c about small δ

$$\begin{aligned} \psi_c(x_L + \omega(\delta)y_{IL}) &\sim \psi_c(x_L) + \omega \left. \frac{d\psi_c}{dx} \right|_{x_L} y_{IL} + \omega^2 \left. \frac{d^2\psi_c}{dx^2} \right|_{x_L} y_{IL}^2 \\ &= \psi_c^0(x_L^0) + \omega \left. \frac{d\psi_c^0}{dx} \right|_{x_L^0} y_{IL} + \omega^2 \left. \frac{d^2\psi_c^0}{dx^2} \right|_{x_L^0} y_{IL}^2 + \delta \left(\left. \frac{d\psi_c^0}{dx} \right|_{x_L^0} x_L^1 + \psi_c^1(x_L^0) \right) \\ &= \omega^2 \left. \frac{d^2\psi_c^0}{dx^2} \right|_{x_L^0} y_{IL}^2 + \delta \psi_c^1(x_L^0) \end{aligned} \quad (4.118)$$

since $\psi_c^0(x_L^0) = \left. \frac{d\psi_c^0}{dx} \right|_{x_L^0} = 0$. Therefore, we must have $\omega = \sqrt{\delta}$, as was the case in the solid problem in Chapter 3.

Thus, the intermediate layer we will be characterised by the rescaling $x_{BL} = x_L + \sqrt{\delta}y_{IL}$. It follows that we will also have the rescaling $U_{BL} = \frac{1}{\sqrt{\delta}}\hat{U}_{IL}$ where $\hat{U}_{IL} = \frac{d\phi_{IL}}{dy_{IL}}$. Our intermediate layer problem can then be written as

$$\frac{1}{\delta} \frac{d^2\phi_{IL}}{dy_{IL}^2} = -z_a e^{\theta_{aIL}} - z_c e^{\theta_{cIL}}, \quad (4.119a)$$

$$\delta\theta_{cIL} + z_c\phi_{IL} + \frac{1}{2} \frac{\hat{U}_{IL}^2}{\delta} = c_1, \quad (4.119b)$$

$$\delta\theta_{aIL} + z_a\phi_{IL} + \frac{1}{2} \frac{\hat{U}_{IL}^2}{\delta} = c_2. \quad (4.119c)$$

We note that if we subtract (4.119c) from (4.119b)

$$\delta(\theta_{c_{\text{IL}}} - \theta_{a_{\text{IL}}}) + (z_c - z_a)\phi_{\text{IL}} = c_1 - c_2. \quad (4.120)$$

At leading order we will have

$$\hat{U}_{\text{IL}}^0 = 0, \quad (4.121)$$

$$\phi_{\text{IL}}^0 = \frac{c_{10} - c_{20}}{z_c - z_a} = \phi_0^* \quad (4.122)$$

i.e. the leading order solution for ϕ is the leading order bulk solution. Looking at the next order, the problem is

$$\frac{d^2 \phi_{\text{IL}}^1}{dy_{\text{IL}}^2} = -z_a e^{\theta_{a_{\text{IL}}}} - z_c e^{\theta_{c_{\text{IL}}}}, \quad (4.123a)$$

$$\theta_{c_{\text{IL}}} + z_c \phi_{\text{IL}}^1 + \frac{1}{2} \left(\hat{U}_{\text{IL}}^1 \right)^2 = c_{11}, \quad (4.123b)$$

$$\theta_{a_{\text{IL}}} + z_a \phi_{\text{IL}}^1 + \frac{1}{2} \left(\hat{U}_{\text{IL}}^1 \right)^2 = c_{21}. \quad (4.123c)$$

Similar to the solid problem, we cannot solve (4.123) directly; instead we assume that the solution can be approximated by linearizing around the bulk solution

$$\theta_{c_{\text{IL}}} = \theta_c^* + \Theta_c, \quad (4.124)$$

$$\theta_{a_{\text{IL}}} = \theta_a^* + \Theta_a, \quad (4.125)$$

$$\phi_{\text{IL}}^1 = \phi_1^* + \Phi, \quad (4.126)$$

$$\hat{U}_{\text{IL}}^1 = 0 + \bar{U}_{\text{IL}}, \quad (4.127)$$

where we assume that the intermediate correction terms are asymptotically small, $\Theta_c, \Theta_a, \Phi, \bar{U}_{\text{IL}} \ll 1$.

We rewrite (4.123a) using these linearised variables and our intermediate layer scales

$$\begin{aligned} \frac{d^2 \Phi}{dy_{\text{IL}}^2} &= -z_a e^{\theta_a^* + \Theta_a} - z_c e^{\theta_c^* + \Theta_c} \\ &= -z_a e^{\theta_a^*} - z_a \Theta_a e^{\theta_a^*} - z_c e^{\theta_c^*} - z_c \Theta_c e^{\theta_c^*}, \end{aligned} \quad (4.128)$$

noting that from the bulk equation (4.56a) this becomes

$$\frac{d^2 \Phi}{dy_{\text{IL}}^2} = -z_a \Theta_a e^{\theta_a^*} - z_c \Theta_c e^{\theta_c^*}. \quad (4.129)$$

We do the same for (4.123b) obtaining

$$\theta_c^* + \Theta_c + z_c(\phi_1^* + \Phi) + \frac{1}{2}\bar{U}_{\text{IL}}^2 = c_{11} \quad (4.130)$$

again noting that from the bulk equation (4.56b) and the fact that $\bar{U}_{\text{IL}} \ll 1$ so that $\bar{U}_{\text{IL}}^2$ is negligibly small; leaving us with the leading order problem

$$\Theta_c + z_c\Phi = 0. \quad (4.131)$$

Similarly, (4.123c) becomes

$$\Theta_a + z_a\Phi = 0 \quad (4.132)$$

at leading order. From (4.131) and (4.132) we find

$$\Theta_c = -z_c\Phi, \quad (4.133)$$

$$\Theta_a = -z_a\Phi, \quad (4.134)$$

which we can then substitute into (4.129)

$$\frac{d^2\Phi}{dy_{\text{IL}}^2} = \left(z_a^2 e^{\theta_a^*} + z_c^2 e^{\theta_c^*}\right)\Phi = \beta^2\Phi, \quad (4.135)$$

where we define

$$\beta^2 = z_a^2 e^{\theta_a^*} + z_c^2 e^{\theta_c^*}. \quad (4.136)$$

This equation, (4.135), has solution

$$\Phi = A_0 e^{-\beta y_{\text{IL}}} \quad (4.137)$$

since Φ should be decaying, and A_0 is a constant to be determined. Therefore, our left intermediate layer solution is

$$\theta_{c\text{IL}} = \theta_c^* - z_c A_0 e^{-\beta y_{\text{IL}}}, \quad (4.138a)$$

$$\theta_{a\text{IL}} = \theta_a^* - z_a A_0 e^{-\beta y_{\text{IL}}}, \quad (4.138b)$$

$$\phi_{\text{IL}} = \phi_0^* + \delta(\phi_1^* + A_0 e^{-\beta y_{\text{IL}}}). \quad (4.138c)$$

We note that the right intermediate layer is analogous, the maximum of the quadratic boundary layer solution will occur at some $x_R = x_R^0 + \delta x_R^1$ which satisfies

$$\frac{d\psi_a}{dx} = \frac{d\psi_a^0}{dx} \Big|_{x_R^0} + \delta \left(\frac{d^2\psi_a^0}{dx^2} \Big|_{x_R^0} x_R^1 + \frac{d\psi_a^1}{dx} \Big|_{x_R^0} \right) = 0. \quad (4.139)$$

Taking the derivative of (4.103) at x_R^0 and setting this equal to zero, we find

$$x_R^0 = \frac{\sqrt{2c_{10}}}{z_c}. \quad (4.140)$$

Computing $\left. \frac{d^2 \psi_a^0}{dx^2} \right|_{x_R^0} x_R^1 + \left. \frac{d\psi_a^1}{dx} \right|_{x_R^0} = 0$ from (4.103) and (4.109) we find

$$x_R^1 = \frac{c_{11}}{z_c \sqrt{2c_{10}}}. \quad (4.141)$$

We observe that $\psi_a^0(x_R^0) = 0$ and hence

$$\psi_a(x_R) \sim \delta \psi_a^1(x_R^0) = \delta \left(\frac{-c_{11}(z_c - z_a)}{z_c} \right), \quad (4.142)$$

again indicating the need for an intermediate layer rescaling. We take $z = 1 - \epsilon x_{\text{BR}}$ and we rescale $x_{\text{BR}} = x_R + \sqrt{\delta} y_{\text{IR}}$ and proceed in exactly the same manner as for the left intermediate layer to determine

$$\theta_{c_{\text{IR}}} = \theta_c^* - z_c B_0 e^{-\beta y_{\text{IR}}}, \quad (4.143a)$$

$$\theta_{a_{\text{IR}}} = \theta_a^* - z_a B_0 e^{-\beta y_{\text{IR}}}, \quad (4.143b)$$

$$\phi_{\text{IR}} = \phi_0^* + \delta (\phi_1^* + B_0 e^{-\beta y_{\text{IR}}}), \quad (4.143c)$$

where B_0 is a constant yet to be determined.

4.4.4 Matching

In order to determine the values of the remaining constants (A_0, B_0) which furnish our asymptotic solution, we will need to match between the layers: we require continuity between the boundary and intermediate layers and between the intermediate layers and the bulk. We refer to Figure 3.4 for a sketch of these layers. We note that by construction, the intermediate layer solution is a far-field expansion of the bulk, and so, as $y_{\text{IL}} \rightarrow \infty$ and $y_{\text{IR}} \rightarrow \infty$, the left and right intermediate layers will naturally tend to the bulk solution. Consequently, formally, we just match between the boundary and intermediate layers. We note that, similar to Chapter 3, we truncate at $y_{\text{IL}} = 0, y_{\text{IR}} = 0$ for continuity, and we match at zero because of the exploitation of this far-field expansion of the bulk solution.¹

¹We note that, as presented in Appendix A for the solid electrolyte problem, as an alternative to this linearisation and truncation approach, we could proceed with the full non-linear problem. Considering the full intermediate layer problem with a different front-centering condition, we can obtain smooth matching as $y_{\text{IL}} \rightarrow \pm\infty$ and $y_{\text{IR}} \rightarrow \pm\infty$.

We note that matching in this case is more straightforward than that encountered in the solid problem. Here we have two outstanding unknowns; and will therefore require two matching conditions. The natural choice is to require continuity between the boundary and intermediate solutions. As we have both θ_c and θ_a , enforcing continuity of both variables will furnish the remaining two unknowns without the need for enforcing differentiability. We recall that in Chapter 3 we had two remaining unknowns but only one variable, so continuity and differentiability were both required. The difficulties in matching are related to differentiability, which is not explicitly needed here to complete the asymptotic solution. Certainly, differentiability is desirable, but we remark that the issues indicated in Chapter 3 still prevail here, *i.e.* differentiability cannot be satisfied in general due to the linearisation assumptions we make in the intermediate region. We remark that we could have chosen to enforce continuity and differentiability in either θ_c or θ_a , which would result in continuity not being enforced in the other; which we note could lead to unphysical results such as $\theta > 0 \implies n > 1$. Therefore, we choose to enforce continuity in both θ_c and θ_a .

Considering the left hand side, we will require the following conditions to be satisfied when $x_{BL} = x_L$

$$\theta_{aBL} = \theta_{aIL}, \quad (4.144a)$$

$$\theta_{cBL} = \theta_{cIL}. \quad (4.144b)$$

From (4.92c) we have that $\theta_{aBL} = 0$ and therefore given (4.138b) and imposing the continuity condition (4.144a) at $x_{BL} = x_L (y_{IL} = 0)$

$$\theta_{aIL} = \theta_a^* - z_a A_0 = 0, \quad (4.145)$$

which tells us that we must have

$$A_0 = \frac{\theta_a^*}{z_a}. \quad (4.146)$$

Given this, substituting back into (4.138a), we can then write

$$\theta_{cIL} (y_{IL} = 0) = \frac{-(z_c - z_a)}{z_a} \theta_c^* - \frac{z_c}{z_a} \log \left(\frac{-z_c}{z_a} \right). \quad (4.147)$$

For perfect continuity, we also need $\theta_{cIL} (y_{IL} = 0) = -\delta^{-1} \psi_c (x_L)$. From (4.147) and (4.117),

$$\begin{aligned} \theta_{cIL} (y_{IL} = 0) &= -\delta^{-1} \psi_c (x_L), \\ \frac{-(z_c - z_a)}{z_a} \theta_c^* - \frac{z_c}{z_a} \log \left(\frac{-z_c}{z_a} \right) &= - \left(\frac{(z_c - z_a) c_{11}}{z_a} \right). \end{aligned} \quad (4.148)$$

Recalling from (4.92d) that $c_{11} = \theta_c^* + \frac{z_c \log \left(\frac{-z_c}{z_a} \right)}{z_c - z_a}$, these two expressions are already equal, and thus we have that continuity holds.

We do the same on the right hand side, requiring

$$\theta_{a_{\text{BR}}} = \theta_{a_{\text{IR}}}, \quad (4.149\text{a})$$

$$\theta_{c_{\text{BR}}} = \theta_{c_{\text{IR}}} \quad (4.149\text{b})$$

when $x_{\text{BR}} = x_R$.

Setting $\theta_{c_{\text{BR}}} = \theta_{c_{\text{IR}}}$ ($y_{\text{IR}} = 0$) we have, from (4.110b) and (4.143a), that

$$\theta_c^* - z_c B_0 = 0 \quad (4.150)$$

and therefore

$$B_0 = \frac{\theta_c^*}{z_c}. \quad (4.151)$$

Following from this, substituting back into (4.143b), we have

$$\theta_{a_{\text{IR}}}(y_{\text{IR}} = 0) = \frac{(z_c - z_a)}{z_c} \theta_c^* + \log \left(\frac{-z_c}{z_a} \right). \quad (4.152)$$

Hence, taking (4.152) and (4.142), for continuity in θ_a we must have

$$\begin{aligned} \theta_{a_{\text{IR}}}(y_{\text{IR}} = 0) &= -\delta^{-1} \psi_a(x_R), \\ \frac{(z_c - z_a)}{z_c} \theta_c^* + \log \left(\frac{-z_c}{z_a} \right) &= \left(\frac{(z_c - z_a) c_{11}}{z_c} \right), \end{aligned} \quad (4.153)$$

which are again equal, and thus, continuity is satisfied and our asymptotic solution is complete.

4.4.5 Comparison of asymptotics and numerics

In this section we compare the results of solving the one-dimensional zero-flux steady-state problem for a liquid electrolyte both numerically (in Section 4.3) and asymptotically (in Section 4.4). In each plot the numerical solution will be shown in solid blue and the asymptotics will be shown in dashed lines, with a different colour used to distinguish each of the components of the asymptotic solution (left/right boundaries and left/right intermediate layer). We note that we do not explicitly plot the bulk solution as this is captured from the two intermediate layer solutions. The points of transition between boundary and intermediate layers ($z_L := \epsilon x_L$ and $z_R := 1 - \epsilon x_R$) are also shown in each of the plots.

The solutions for the two auxiliary variables, θ_c and θ_a , are shown in Figure 4.4. Overall we observe good agreement between the two solution approaches. We include inset plots to take a closer look at the

agreement near the boundaries. For the lithium ion variable, θ_c , we consider the insets in Figure 4.4a. We remark that at the left boundary there is excellent agreement between the asymptotic and numerical solutions. Specifically, we note that the boundary layer solution (shown in red) agrees very closely with the numerical solution and begins to diverge slightly around $z = 0.01$, with the intermediate solution (light blue) taking over at $z = z_L$ and displaying fantastic agreement with the numerical solution. In the second inset plot, near the boundary at $z = 1$, we see a little more discrepancy between the two approaches. As before, the boundary layer solution (in pink) agrees with the numerical solution close to the boundary and the intermediate layer solution (in green) agrees well near the bulk. We remark that the bulk region of the numerical and asymptotic solutions do not match perfectly, they differ by $\mathcal{O}(\delta)$ since we know that in this problem we can obtain $\mathcal{O}(\delta)$ corrections to θ_k in the bulk. Furthermore, at this boundary we notice both solutions diverging from the numerical solution either side of the transition point z_R . On closer inspection of this inset plot we note that there is a change in concavity of the numerical solution in this region. However, the boundary asymptotic solution is constant (and more specifically, zero) in this region, therefore there is no mechanism for an adjustment of the profile. Similarly, the intermediate solution is exponential and thus there is no mechanism for the change in concavity here either. This suggests that there is another “knee” region bridging the intermediate and boundary layer solutions. The inset plots in Figure 4.4b show corresponding results, on opposite sides of the electrolyte. We note that undertaking further analysis into the nature of this knee-region is outside the scope of this work, but does form part of the future work.

We also include the plots for n_c and n_a , obtained via the auxiliary relation in (4.34), in Figure 4.5. These plots further echo the results noted by the auxiliary variable plots in Figure 4.4. We note in particular that the difference between the bulk solutions for the numerics and the asymptotics, of $\mathcal{O}(\delta)$ due to the missing correction term to the asymptotic bulk solutions, is more apparent in these plots. We reiterate that this extra order in δ is omitted in order to be consistent with the steps taken in Chapter 3. Determining the next order of corrections to each variable would proceed in a similar manner as outlined in this section.

Finally, we plot the electric potential ϕ in Figure 4.6. In this plot, the numerical and asymptotic solutions are closely aligned. We recall that we have determined the solution for ϕ to $\mathcal{O}(\delta)$, as such, the bulk solutions match extremely well. We note that the boundary and intermediate layer solutions also demonstrate fantastic agreement with the numerical solution in these regions. However, we again observe that both solutions start to peel away from the numerical solution as we approach z_L, z_R as shown in the inset plots.

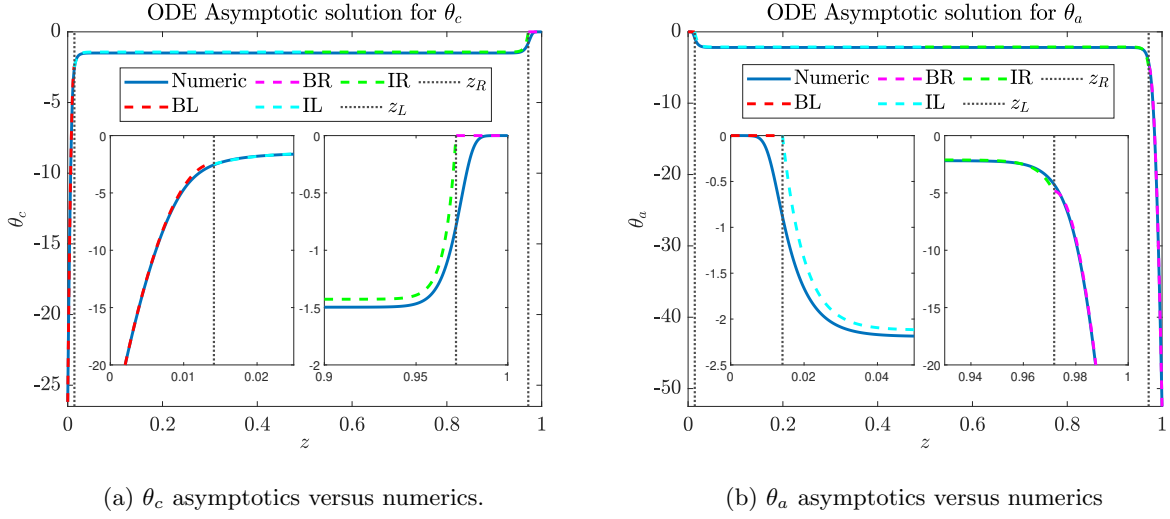


Figure 4.4: Asymptotic solution from Section 4.4 versus the numerical results from Section 4.3 for θ_c and θ_a . Parameter values are as follows: $z_c = 1$, $z_a = -2$, $\bar{y}_c = 0.24$. We take $\lambda = 5 \times 10^{-3}$, $\delta = 0.038$, and $\Delta V = 0.62V$. BL, BR refer to the left and right boundary layer solutions, respectively; similarly IL, IR refer to the left and right intermediate layer solutions, respectively. z_L, z_R refer to the leading-order transition points from the boundary to the intermediate layers.

4.4.6 Observations

From our asymptotics and the comparison between the asymptotic and numerical solutions, we observe that we have two distinct regions in the double charge layers, which we refer to as the boundary and intermediate layers, or strong and weak layers. This is in agreement with the results obtained for our solid electrolyte model. We note that in the literature for liquid electrolytes, it is commonly known that the electric double layer exhibits exponential behaviour (for example, Attard (1993); Newman and Thomas-Alyea (2012); Groß and Sakong (2019)), which coincides with our intermediate layer. However, there is no reference to the quadratic behaviour. This prompts the question as to why we still observe the quadratic boundary layer behaviour emerging from this electrolyte model when this does not appear in any literature to the best of our knowledge.

Our hypothesis is that the solid electrolyte model is the limit of the thermodynamic liquid electrolyte model, in the limit where the anion concentration is constant. That is, we speculate that when the anion concentration is not constant and we increase the applied voltages, the boundary layers become so narrow as

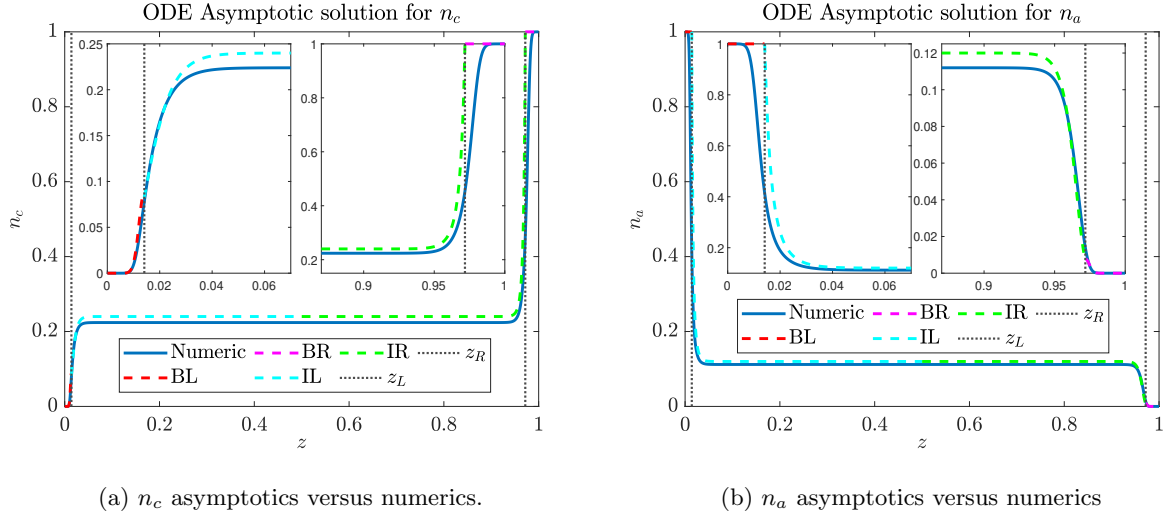


Figure 4.5: Asymptotic solution from Section 4.4 versus the numerical results from Section 4.3 for n_c and n_a . Parameter values are as follows: $z_c = 1$, $z_a = -2$, $\bar{y}_c = 0.24$. We take $\lambda = 5 \times 10^{-3}$, $\delta = 0.038$, and $\Delta V = 0.62V$. BL, BR refer to the left and right boundary layer solutions, respectively; similarly IL, IR refer to the left and right intermediate layer solutions, respectively. z_L, z_R refer to the leading-order transition points from the boundary to the intermediate layers.

to be difficult to resolve, thus leaving the intermediate layer as the dominant behaviour. Although, from our analysis, the intermediate layer can never satisfy the required boundary conditions, thus necessitating a very narrow boundary layer. We recall from our comparison between the solid and liquid models in Figure 4.3 that there are indeed differences between the EDL of the two electrolytes, but even so, the strong (quadratic) layer is still needed to capture the solution at the boundaries.

These observations then motivate carrying out further examination of these models. In particular, we note that many of the liquid electrolyte models that talk about exponential behaviours in the electric double layer are based on the PNP framework. Therefore, we speculate that a comparison between the thermodynamic liquid model and the standard PNP model (as discussed in Chapter 2) for a liquid electrolyte may elucidate this matter further. Therefore, in the next section we will modify the liquid electrolyte model with the aim of pursuing this comparison.

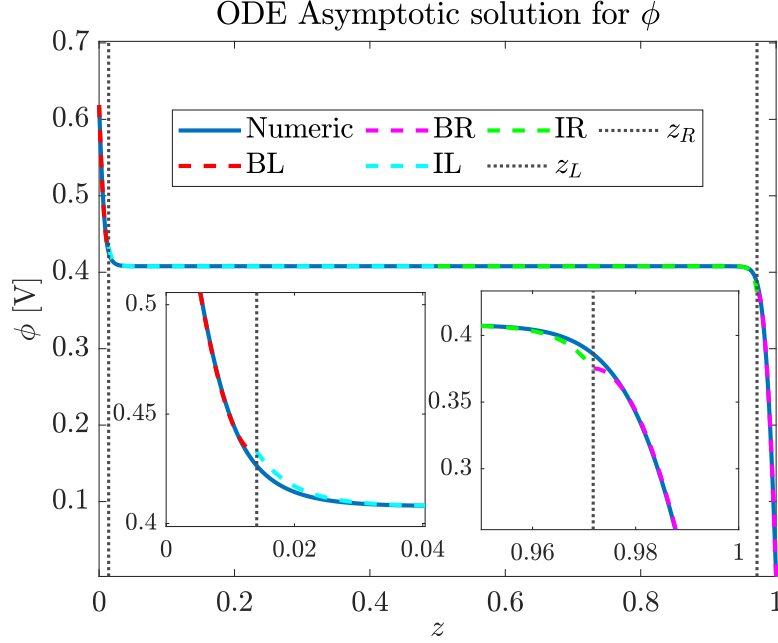


Figure 4.6: Asymptotic solution from Section 4.4 versus the numerical results from Section 4.3 for ϕ . Parameter values are as follows: $z_c = 1$, $z_a = -2$, $\bar{y}_c = 0.24$. We take $\lambda = 5 \times 10^{-3}$, $\delta = 0.038$, and $\Delta V = 0.62\text{V}$. BL, BR refer to the left and right boundary layer solutions, respectively; similarly IL, IR refer to the left and right intermediate layer solutions, respectively. z_L, z_R refer to the leading-order transition points from the boundary to the intermediate layers.

4.5 Reconciliation to PNP model

We note that Dreyer et al. (2013) highlight the $\left(\frac{d\phi}{dz}\right)^2$ term as being of particular importance in their model. In fact, they comment that their model will reduce to the Nernst-Planck (or Poisson-Nernst-Planck PNP) model in the absence of this particular term, with some underlying assumptions and implications. Dreyer et al. (2013) remove this term, and in doing so, observe that the model blows up toward the boundaries and that the boundary layers are more narrow (see figures 8 and 9 of Dreyer et al. (2013)).

We investigate this further whereby we observe that the PNP limit of the Dreyer model, as we will refer to it, is actually only applicable to the bulk of the electrolyte and cannot properly account for the boundary layers. That is, neglecting the $\left(\frac{d\phi}{dz}\right)^2$ term in $\delta\theta_k + z_k\phi + \frac{\lambda^2\delta^{-1}}{2}\left(\frac{d\phi}{dz}\right)^2 = c_i$ of (4.38) is inconsistent. To do so would require us to also neglect the $\frac{d^2\phi}{dz^2}$ term in $\lambda^2\delta^{-1}\frac{d^2\phi}{dz^2} = -z_a e^{\theta_a} - z_c e^{\theta_c}$, *i.e.* these terms are neglected

if $\lambda = 0$, which then reduces the model to the charge neutral bulk. Therefore, it is true that neglecting both terms will recover the PNP model, but only under the assumption of electroneutrality everywhere; there is no longer a mechanism to consider the EDL.

To gain a deeper understanding of the differences between these models, we artificially introduce a new variable α into the model, therefore (4.41) becomes

$$\epsilon^2 \frac{d^2 \phi}{dz^2} = -z_a e^{\theta_a} - z_c e^{\theta_c}, \quad (4.154a)$$

$$\delta \theta_c + z_c \phi + \frac{\alpha \epsilon^2}{2} u^2 = c_1, \quad (4.154b)$$

$$\delta \theta_a + z_a \phi + \frac{\alpha \epsilon^2}{2} u^2 = c_2, \quad (4.154c)$$

$$\int_0^1 (z_a e^{\theta_a} + z_c e^{\theta_c}) dz = 0, \quad (4.154d)$$

$$\int_0^1 e^{\theta_c} dz = \bar{y}_c, \quad (4.154e)$$

$$u = \frac{d\phi}{dz}, \quad (4.154f)$$

$$e^{\theta_a} + e^{\theta_c} + n_s = 1, \quad (4.154g)$$

that is, the only equations that are directly modified are (4.154b) and (4.154c). We do this in order to analyse the transition between this thermodynamically consistent model Dreyer ($\alpha = 1$) and the PNP model ($\alpha = 0$), while still incorporating the $\frac{d^2 \phi}{dz^2}$ in order to capture the impact on the EDL. We note that $0 < \alpha < 1$ does not have any physical relevance, but is rather a tool to help us to better understand the role of the $\left(\frac{d\phi}{dz}\right)^2$ term and why simply taking $\alpha = 0$ is problematic. We proceed directly with the asymptotic approach in this case but will present the associated numerical solutions alongside the asymptotics in plots when we present the results.

4.5.1 Asymptotic solution

We note much of the analysis replicates that of the case where $\alpha = 1$ and so we will highlight the changes in the solutions but will not go through all of the details.

From the combinations of the pointwise conditions ((4.154b) and (4.154c)), and expanding to $\mathcal{O}(\delta)$ as in (4.54) we note that the relations highlighted in (4.55) all hold independently of α . We also note that the

bulk solution is independent of α and thus remains unchanged:

$$\theta_c^* = \log(\bar{y}_c), \quad (4.155a)$$

$$\theta_a^* = \log(\bar{y}_c) + \log\left(\frac{-z_c}{z_a}\right) = \log\left(\frac{-z_c \bar{y}_c}{z_a}\right), \quad (4.155b)$$

$$\phi^* = \phi_0^* + \delta \phi_1^* = \frac{-z_a}{z_c - z_a} + \delta \frac{\log\left(\frac{-z_c}{z_a}\right)}{z_c - z_a}, \quad (4.155c)$$

with

$$c_{10} = \frac{-z_c z_a}{z_c - z_a}, \quad (4.156)$$

$$c_{20} = \frac{-z_a^2}{z_c - z_a}, \quad (4.157)$$

$$c_{11} = c_{21} = \theta_c^* + \frac{z_c \log\left(\frac{-z_c}{z_a}\right)}{z_c - z_a}. \quad (4.158)$$

In the boundary layer we are rescaling to explicitly account for the derivatives, therefore, we will notice a dependency on α throughout the boundary layer solution. We find, following the same steps as before that the left boundary layer has solution

$$\phi_{\text{BL}} = \frac{-z_a}{2\alpha} x_{\text{BL}}^2 - \sqrt{\frac{2(c_{20} - z_a)}{\alpha}} x_{\text{BL}} + 1 + \delta \frac{\log\left(\frac{1}{\alpha}\right) - c_{11}}{\sqrt{2\alpha(c_{20} - z_a)}} x_{\text{BL}}, \quad (4.159a)$$

$$\begin{aligned} \theta_{\text{cBL}} &= -\delta^{-1} \psi_c \\ &= \frac{-1}{\delta} \left(\frac{-z_a(z_c - z_a)}{2\alpha} x_{\text{BL}}^2 - (z_c - z_a) \sqrt{\frac{2(c_{20} - z_a)}{\alpha}} x_{\text{BL}} + z_c + \delta \left(\frac{(\log\left(\frac{1}{\alpha}\right) - c_{11})(z_c - z_a)}{\sqrt{2\alpha(c_{20} - z_a)}} x_{\text{BL}} - \log\left(\frac{1}{\alpha}\right) \right) \right), \end{aligned} \quad (4.159b)$$

$$\theta_{\text{aBL}} = \log\left(\frac{1}{\alpha}\right), \quad (4.159c)$$

and the right boundary layer is given by

$$\phi_{\text{BR}} = \frac{-z_c}{2\alpha} x_{\text{BR}}^2 + \sqrt{\frac{2c_{10}}{\alpha}} x_{\text{BR}} + \delta \frac{c_{11} - \log\left(\frac{1}{\alpha}\right)}{\sqrt{2\alpha c_{10}}} x_{\text{BR}}, \quad (4.160a)$$

$$\theta_{\text{cBR}} = \log\left(\frac{1}{\alpha}\right), \quad (4.160b)$$

$$\begin{aligned} \theta_{\text{aBR}} &= -\delta^{-1} \psi_a \\ &= \frac{-1}{\delta} \left(\frac{z_c(z_c - z_a)}{2\alpha} x_{\text{BR}}^2 - (z_c - z_a) \sqrt{\frac{2c_{10}}{\alpha}} x_{\text{BR}} - z_a + \delta \left(\frac{(\log\left(\frac{1}{\alpha}\right) - c_{11})(z_c - z_a)}{\sqrt{2\alpha c_{10}}} x_{\text{BR}} - \log\left(\frac{1}{\alpha}\right) \right) \right). \end{aligned} \quad (4.160c)$$

Consequently, the maximum of the boundary layer quadratics also exhibit an α dependence with

$$x_L = x_L^0 + \delta x_L^1 = \frac{-\sqrt{2\alpha(c_{20} - z_a)}}{z_a} + \delta \frac{\sqrt{\alpha}(\log(\frac{1}{\alpha}) - c_{11})}{z_a \sqrt{2(c_{20} - z_a)}} \quad (4.161)$$

and

$$x_R = x_R^0 + \delta x_R^1 = \frac{\sqrt{2\alpha c_{10}}}{z_c} + \delta \frac{\sqrt{\alpha}(c_{11} - \log(\frac{1}{\alpha}))}{z_c \sqrt{2c_{10}}}. \quad (4.162)$$

Finally, for the intermediate layer, we note that the intermediate layer is a far-field expansion of the bulk solution and so the α dependence is much weaker than that observed in the boundary layer. In particular, our left intermediate layer solution is

$$\theta_{c_{\text{IL}}} = \theta_c^* - z_c A_0 e^{-\beta y_{\text{IL}}}, \quad (4.163a)$$

$$\theta_{a_{\text{IL}}} = \theta_a^* - z_a A_0 e^{-\beta y_{\text{IL}}}, \quad (4.163b)$$

$$\phi_{\text{IL}} = \phi_0^* + \delta(\phi_1^* + A_0 e^{-\beta y_{\text{IL}}}), \quad (4.163c)$$

whereby β is unchanged from (4.136),

$$\beta^2 = z_a^2 e^{\theta_a^*} + z_c^2 e^{\theta_c^*}. \quad (4.164)$$

and here we have

$$A_0 = \frac{\theta_a^* - \log(\frac{1}{\alpha})}{z_a}. \quad (4.165)$$

Similarly, for the right intermediate layer,

$$\theta_{c_{\text{IR}}} = \theta_c^* - z_c B_0 e^{-\beta y_{\text{IR}}}, \quad (4.166a)$$

$$\theta_{a_{\text{IR}}} = \theta_a^* - z_a B_0 e^{-\beta y_{\text{IR}}}, \quad (4.166b)$$

$$\phi_{\text{IR}} = \phi_0^* + \delta(\phi_1^* + B_0 e^{-\beta y_{\text{IR}}}), \quad (4.166c)$$

with

$$B_0 = \frac{\theta_c^* - \log(\frac{1}{\alpha})}{z_c}. \quad (4.167)$$

4.5.2 Remarks

From this asymptotic solution we can make the following observations. Firstly, the bulk solution (4.155) remains unchanged, aligning with our initial comment that the omission of the $\left(\frac{d\phi}{dz}\right)^2$ term from the thermodynamically derived model reduces this to the PNP model under the assumption of electroneutrality everywhere *i.e.* no EDL.

Considering our boundary layer solutions in (4.159) and (4.160) we can immediately see why the model fails if we simply take $\alpha = 0$, we see our boundary layer solutions go to ∞ as $\alpha \rightarrow 0$. We also highlight that the maximum of the quadratic, as portrayed in (4.161) and (4.162), is proportional to $\sqrt{\alpha}$, so as $\alpha \rightarrow 0$, the point where the quadratic reaches its maximum approaches zero, which also corresponds to the width of the boundary layer approaching zero. Hence as $\alpha \rightarrow 0$, the magnitude of the boundary layer solutions becomes unbounded and the width of the solutions approaches zero. That is, the solutions become infeasible at the edge and we lose physical insight as this violates the physics of the problem.

This may also explain why the exponential behaviour is widely taken to represent the EDL; we have noted that the addition of α has less of an impact on the intermediate layer solutions. Of course, the solutions for A_0 in (4.165) and B_0 in (4.167), are also problematic as α approaches zero. However, we remark that these constants are determined by matching the intermediate layer to the boundary layers; and thus if the boundary layers are of negligible width, one can see how the exponential intermediate layers are the dominating behaviour. Nevertheless, this does not address the inability of the exponential solutions to satisfy the prescribed boundary conditions.

4.5.3 Comparisons

In this section we plot the numerical and asymptotic solution profiles for the variables for different values of α . We take $\alpha = 1, 0.75, 0.5$, and 0.25 in each of the plots. In this case, the numerical solutions are shown in solid lines and the asymptotic solutions are shown in dashed lines. We also include $z_L := \epsilon x_L$ and $z_R := 1 - \epsilon x_R$ for each value of α in the plots. We have used arrows to indicate the movement of the solution as α is decreased from $\alpha = 1$ towards $\alpha = 0$.

In Figure 4.7 we have plotted θ_c at the left and right boundaries. We observe in both plots that as $\alpha \rightarrow 0$, $z_L \rightarrow 0$ and $z_R \rightarrow 0$. In both figures we also observe that θ_c at, and near, the boundary increases (both from the numerics and the asymptotics). These observations are all in line with the role of α in the asymptotic solutions derived in this section.

We have plotted $n_c = e^{\theta_c}$ in Figure 4.8. In this case we further observe that close to the boundary, n_c is increasing, however there is a change in concavity before we reach the bulk of the solution and here we observe the solution magnitude decreasing as α decreases. We acknowledge that in Figure 4.8b, the maximum values of n_c exceeds 1. In fact, as α decreases below one we immediately see this maximum of n_c increase beyond

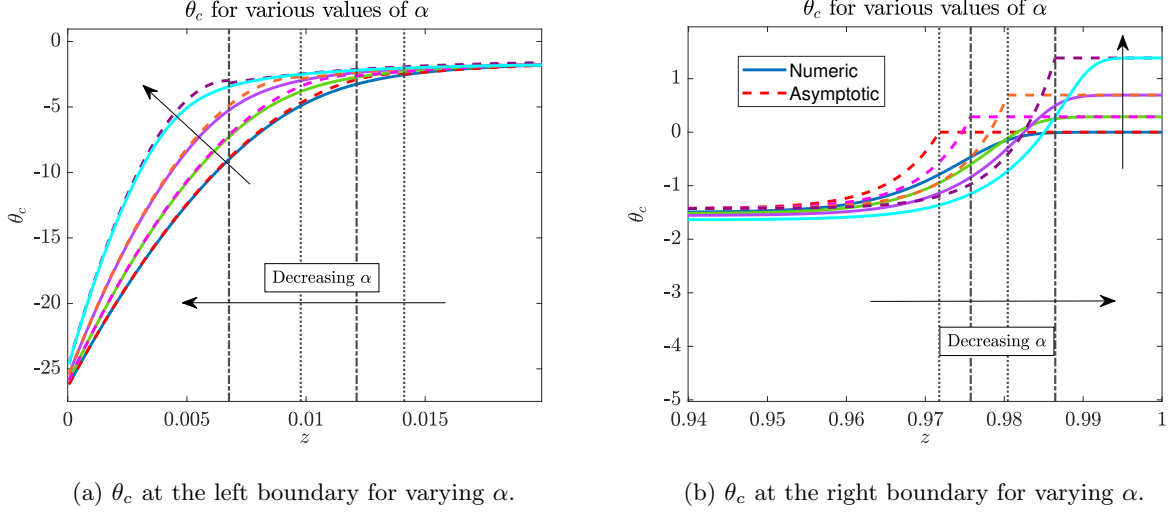


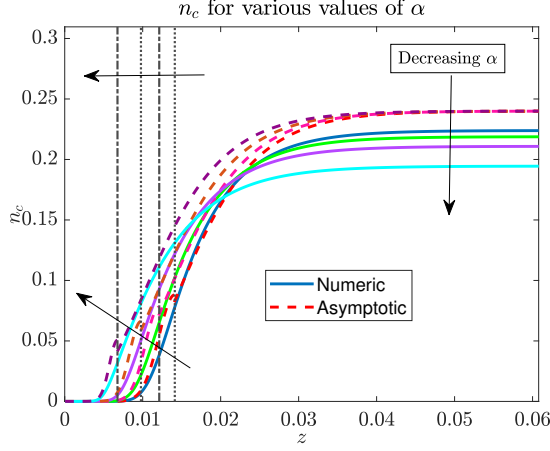
Figure 4.7: Asymptotic and numerical solutions for θ_c for varying values of α , $\alpha = 1, 0.75, 0.5, 0.25$. The arrows indicate the direction of the solution profiles for decreasing α . Parameter values are as follows: $z_c = 1$, $z_a = -2$, $\bar{y}_c = 0.24$. We take $\lambda = 5 \times 10^{-3}$, $\delta = 0.038$, and $\Delta V = 0.62V$.

1. This of course is non-physical as we non-dimensional so that $n = n_c + n_a + n_s = 1$; therefore this implies that one of the other number densities must be negative; violating physicality. We remark that n_s becomes negative in these scenarios.

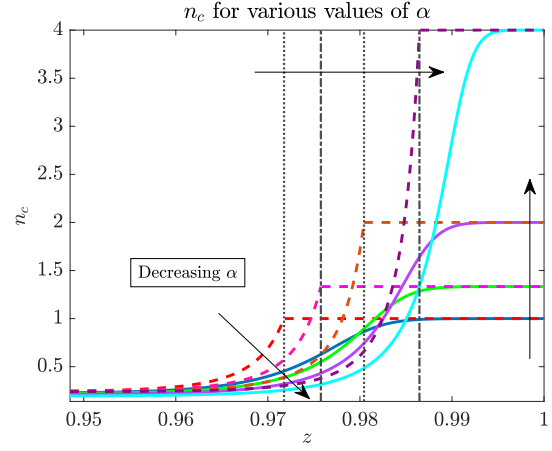
We also show the results for ϕ in Figure 4.9. In this case, we leave the potential in non-dimensional form so that it is normalised for improved visual clarity. In Figure 4.9a we see that the solutions progressively compress closer to the boundary as $\alpha \rightarrow 0$, and in Figure 4.9b the profiles expand out further (again, closer to the boundary). The differences in ϕ on the surface appear less problematic than those of the concentrations, however, we recall that ϕ is constrained to obey the two boundary conditions.

4.6 Discussion

In this chapter, our goal was to investigate and compare the width of the double charge layers between those of the solid electrolyte model in Chapter 3 and those of the thermodynamically derived liquid model, *i.e.* this model derived by Dreyer et al. (2013). Following the same approach as taken in Chapter 3 we uncover firstly that the EDLs of the solid electrolyte do in fact appear to be wider than that of the liquid electrolyte as



(a) n_c at the left boundary for varying α .



(b) n_c at the right boundary for varying α .

Figure 4.8: Asymptotic and numerical solutions for n_c for varying values of α , $\alpha = 1, 0.75, 0.5, 0.25$. The arrows indicate the direction of the solution profiles for decreasing α . Parameter values are as follows: $z_c = 1$, $z_a = -2$, $\bar{y}_c = 0.24$. We take $\lambda = 5 \times 10^{-3}$, $\delta = 0.038$, and $\Delta V = 0.62V$.

indicated in the literature. However, the difference is not significant, therefore we carry out an asymptotic reduction of the model to ascertain the differences between the solid and the liquid. The asymptotics reveal that the liquid electrolyte model also exhibits both strong and weak charge layers, similar to the solid electrolyte. Therefore, it is possible that the solid electrolyte exhibits wider EDLs, but structurally the layers are the same between the two electrolytes and further, the two layers we have identified have the same scale in both the liquid and solid cases.

As this has not been acknowledged in the liquid electrolyte modelling or electrochemical literature, that is, the liquid electrolyte EDLs are largely associated with exponential behaviour and the Debye length, we investigated further. We hypothesize that the exponential behaviour widely associated with the EDL of liquid electrolytes comes primarily from models akin to the Poisson-Nernst-Planck (PNP) model for liquid electrolytes (Debye and Falkenhagen (1928); Kilic et al. (2007a); Newman and Thomas-Alyea (2012)). Correspondingly, we note that Dreyer et al. (2013) highlight the $\left(\frac{d\phi}{dz}\right)^2$ term as a key component of their model; remarking that the model reduces to the PNP model in the absence of this term. We therefore introduce the parameter α to gain a deeper understanding of the distinction between the commonly used PNP model (with exponential behaviour in the boundary layers) and the liquid electrolyte model derived

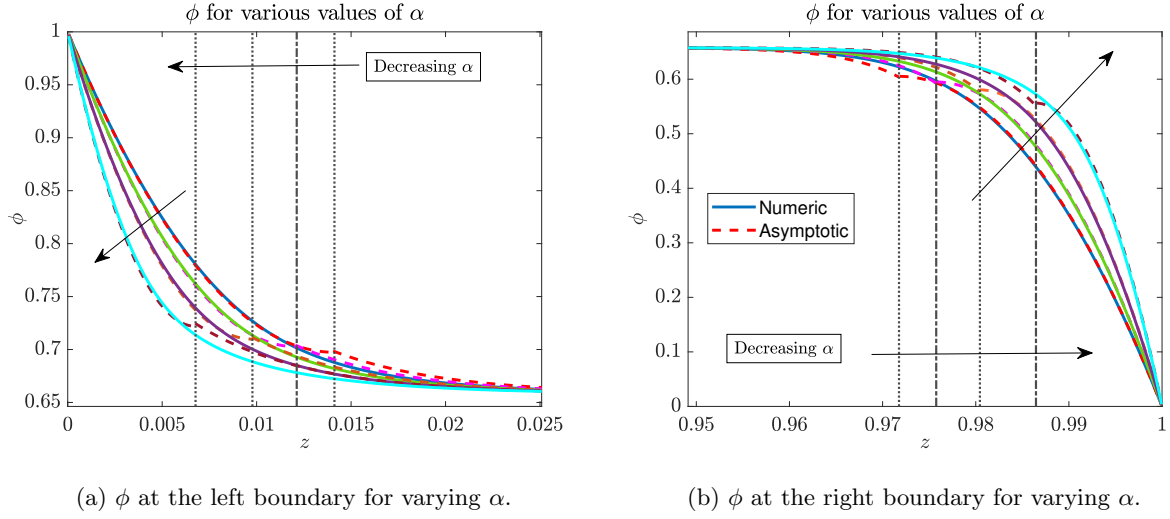


Figure 4.9: Asymptotic and numerical solutions for ϕ (non-dimensional) for varying values of α , $\alpha = 1, 0.75, 0.5, 0.25$. The arrows indicate the direction of the solution profiles for decreasing α . Parameter values are as follows: $z_c = 1$, $z_a = -2$, $\bar{y}_c = 0.24$. We take $\lambda = 5 \times 10^{-3}$, $\delta = 0.038$, and $\Delta V = 0.62V$.

from thermodynamic principles (with both exponential and quadratic behaviour in the boundary layers). In doing so, we conclude that as $\alpha \rightarrow 0$, the quadratic layers approach zero width and infinite magnitude; thus explaining why exponential behaviour is largely associated with the boundary layers. However, from our analysis, the quadratic layer is still needed in order to satisfy the boundary conditions. We therefore conclude that in the absence of the $\left(\frac{d\phi}{dz}\right)^2$ term, the problem is ill-posed. This raises some questions, which are outside the scope of this current work but will form part of our future work. In particular, from our analysis and simulations we hypothesize that the PNP model itself is only applicable/well posed under particular boundary conditions, which has been alluded to within the literature (Bazant et al. (2004)).

Overall we remark that the results presented in this chapter indicate that the asymptotic structure is the same for both the solid and liquid electrolytes, due to the thermodynamic formulation of the models. However, the actual boundary layer width realized will depend on the electrolyte type as we do observe some width differences between the liquid and solid models in Figure 4.3.

Chapter 5

Conclusions and future work

In this thesis we have investigated Electric Double Layers (EDLs) in electrolytes for lithium-ion batteries using mathematical modelling tools. In particular, we implement numerical simulations and asymptotic analysis to gain insight into this feature of electrolytes. In this chapter we provide a summary of the results of this work and highlight avenues for extensions to these results and other future work.

5.1 Conclusions

The overarching aim of this work is to develop a clear understanding of the behaviour in the electric double layers of LIBs. Through our auxiliary variable, numerical simulations, and asymptotic analysis of the double layers in both solid and liquid electrolytes we have identified a number of important features of the double layer structure, we have implemented a pseudo-matching technique to reconcile between different asymptotic regimes, and our auxiliary variable approach facilitates robust numerical simulations using standard methods.

The introduction of the auxiliary variable enables our numerical framework to robustly compute concentration and electric potential profiles in EDLs, which we commented was an issue encountered by other authors throughout the literature. Our asymptotic analysis of these electrolyte models has elucidated the double-layer structure of both solid and liquid electrolytes. We have characterised the width of these EDLs and identified two distinct boundary layer behaviours, which we refer to as strong and weak layers due to their associated polynomial and exponential solution behaviours respectively. Throughout the literature it is

remarked that the EDL of a solid electrolyte is wider than its liquid counterpart; we have shown that while the solid electrolyte EDL does appear wider, the two electrolytes exhibit the same asymptotic structures, which is where the width difference had been discussed. We note that in determining the intermediate layer we make an approximation, linearising about the bulk solutions in order to derive some analytic insight into the behaviour in this region. This approximation has a trade off whereby we lose the ability to enforce differentiability between the two regions; therefore we implement a pseudo-matching technique to complete our asymptotic solution, yielding excellent agreement between our asymptotic and numerical solutions.

We have noted that the exponential behaviour observed is widely associated to liquid electrolyte EDLs, but the polynomial behaviour has not previously been identified as part of the liquid EDL. We hypothesize that the asymptotic structure is a consequence of the thermodynamic formulation rather than the type of electrolyte. This led to further exploration of the liquid electrolyte model; noting that the thermodynamically consistent model can be reduced to a version of the more heuristic PNP model for liquid electrolytes, which we note is often associated with the exponential EDL. We introduce a parameter, α , to bridge these two model formulations. When $\alpha = 1$ we are in the thermodynamic model and when $\alpha = 0$ we have recovered the PNP type model. Values of α between 0 and 1 are somewhat artificial and for the purpose of understanding the mathematical behaviour and differences between these two models. From this analysis we observe that the asymptotic structure is not unchanged but the quadratic regions become of negligible width as we approach the PNP model. At the same time, these quadratic boundary layers tend toward infinite magnitude, coinciding with a breakdown in the physics of the model. This then poses the question of the PNP model being ill-posed with Dirichlet boundary conditions, which will form part of the future work. We also identify that there is a more pronounced knee region existing between the boundary and intermediate regions of the liquid electrolyte. Characterisation of this region and reconciling whether or not this exists in the solid electrolyte, and to what extent, was outside the scope of this work but investigating this further is part of the future work.

We must also acknowledge some limitations of the analysis carried out in this work, in particular, this thermodynamic approach to a continuum model applies to the concentrated limit where mean-field theory still holds, and consequently omits the contribution of particle effects. Authors such as Bikerman (1942) and Gavish et al. (2018) find that this approach can be oversimplified and the role of the finite size of ions should be incorporated in highly concentrated electrolytes and ionic liquids. We note that the continuum

model framework can be modified to consider molecular effects, such as charge sizes, for example see the work of Kilic et al. (2007b). We also remark that de Klerk and Wagemaker (2018) identify coulombic interactions between the vacancies as playing a significant role in the impact of SCL and the effects in solid state batteries. Therefore, incorporating these interactions could form part of the future work. We remark that contemporary modelling often takes a hybrid approach, using tools from various modelling approaches such as continuum modelling, atomistic simulations, and statistical methods to build models which can accurately predict the dynamic behaviour of the electrochemical system while maintaining computational efficiency and also accounting for molecular level effects. Incorporating analysis from these other approaches is beyond the scope of this thesis, but is worth acknowledging for future work.

5.2 Future work

Here we outline the most immediate areas of future work, some of which are underway to varying degrees with some preliminary insights.

5.2.1 Capacitance

Capacitance is defined as the ability of an object to store electric charge per unit electric potential (voltage), and is given by:

$$C = \frac{q}{V}, \tag{5.1}$$

where q is the electric charge and V is the potential difference. Capacitance can be measured experimentally using a variety of techniques, including electrochemical impedance spectroscopy (EIS) and cyclic voltammetry. In the context of batteries and electrolytes, the differential capacitance— that is, the capacitance per unit area—is commonly used to characterise the structure and behaviour of the electric double layer.

However, existing mathematical models of EDLs often exhibit discrepancies when compared to experimental measurements for capacitance (see Section 1.2.3). Consequently, part of our future work involves computing the capacitance using both our numerical solutions and our asymptotic solutions for each of the regimes and comparing these predictions to both existing models and experimental data.

5.2.2 Knee regions

We note that in Chapter 4 we observe a distinct “knee” region between the boundary and intermediate regions for the thermodynamic liquid electrolyte model in Figures 4.4, 4.5, and 4.6. Between the boundary and the intermediate layers, there is a region which is not captured by the polynomial or exponential behaviours, leading to less agreement between these two asymptotic solution regimes. This region appears to exhibit a superlinear type of behaviour, which can be referred to a “knee” (Attia et al. (2022)). To investigate this further we would look at possible rescalings to capture this additional region between the boundary and intermediate regions. Furthermore, we hypothesise that the existence of this region is not isolated to the liquid electrolyte and that this region is also present in the solid, albeit to a much lesser degree. Although a mathematical characterisation of the behaviour in this knee region is outside the scope of this thesis, it forms part of the future work.

5.2.3 Full dynamic model formulation

The results presented in this thesis have been focused on one-dimensional zero charge flux and steady state scenarios, a natural next step would involve extending these models to consider non-zero flux conditions. In particular, Butler-Volmer (Doyle et al. (1993); Newman and Thomas-Alyea (2012)) boundary conditions are frequently used in battery modelling, and thus incorporating prescribed flux conditions would enable us to better model real problems and to connect to a full battery model.

The Butler-Volmer equation has the general form

$$i_n = i_0 \left(\exp \left(\frac{\alpha_a F \eta_s}{RT} \right) - \exp \left(\frac{-\alpha_c F \eta_s}{RT} \right) \right), \quad (5.2)$$

where i_0 is the exchange current density and is analogous to the rate constant used in chemical kinetics (Newman and Thomas-Alyea (2012)), η_s is the surface overpotential, and α_a, α_c are kinetic parameters referred to as transfer anodic and cathodic coefficients respectively. The surface overpotential is defined by

$$\eta_s = \phi_s - \phi_e - U, \quad (5.3)$$

where ϕ_s is the potential at the electrode surface, ϕ_e is the potential in the electrolyte, and U is the open circuit potential. For this electrolyte potential, many battery models only consider bulk electrolyte mechanics (Bazant et al. (2004); Biesheuvel et al. (2011)). From our model we would instead incorporate the potential at the edge of the boundary layer, comparing the results with those which use the bulk solution, and determine

how this affects overall battery dynamics. Therefore, the next step would be to work on a full battery model with the electrolyte model built into the Butler-Volmer kinetics.

Naturally, achieving a more complete battery model which can be applied to more real world scenarios, we must also extend the work in Chapters 3 and 4 to the dynamic scenario. From a numerical perspective, this is relatively straightforward; we can adapt our existing numerical codes to apply a Method of Lines approach via a MATLAB solver such as *ode15s* for the time derivatives. Preliminary results to this effect suggest that the boundary layer solutions quickly adjust to their steady-state values for $t \sim \mathcal{O}(1)$, while the bulk reaches its steady-state for $t \sim \mathcal{O}(\epsilon^{-2})$. This timescale distinction between the bulk and boundary layer regions indicates that an asymptotic reduction of the time dependent problem would also be an interesting direction for future work. We note that Becker-Steinberger et al. (2021) extend the work of Braun et al. (2015) for the solid electrolyte model to consider time dependency in their model, however, the authors do not examine the timescale for the development of the solution profiles.

5.2.4 PNP well-posedness

Adjacent to the non-zero flux boundary condition extensions to this work, in Chapter 4 we highlight that the PNP reduction of the thermodynamically derived liquid electrolyte model is not well-posed. We observe that the Dirichlet boundary conditions, as used in the thermodynamic solid and liquid models, become problematic when we are in the PNP limit; we encounter a breakdown in the physicality of the solutions with mass no longer conserved (and thus negative solvent concentrations) and asymptotes at the boundaries. Therefore it would be of value to carry out further investigation into the feasibility of different boundary conditions that can retain physically sensible solutions for this model. We remark that within the literature other authors acknowledge similar observations with the boundary conditions for the use of the PNP model (Bazant et al. (2004); Kilic et al. (2007a,b)).

We also acknowledge some other avenues worth investigating related to this issue. For example, the PNP model is frequently used under the assumption of local electroneutrality, while we instead enforce global electroneutrality in order to gain insight into the boundary layer behaviour. In Chapter 4 we remark that under the assumption of local electroneutrality across the electrolyte this break down in the physics does not occur. However, it remains that the solution cannot satisfy the fixed potential boundary conditions, again indicating the need for further analysis into the appropriate boundary conditions.

Finally, we note that the PNP model is most often considered in the context of a 1:1 binary electrolyte, whereby the solvent is not considered or rather treated as a constant. In Chapter 4 we allow the solvent concentration to vary, however we note that we obtain our solution for the solvent concentration directly from Equation (4.38g) and so the treatment of n_s (ignored, constant, allowed to vary) should not impact this non-physical scenario when we transition from the thermodynamic model to the PNP model. Regardless, the role of the solvent concentration should be examined further as part of future work.

5.2.5 Non-uniform grid

In this thesis we have considered solely the electrolyte to better understand EDLs. Naturally, incorporating the EDL in full battery models is an important future work so that the role of the EDL in these more complete battery models can also be better understood. However, in Chapter 3 we commented that many authors have indicated numerically solving models of solid electrolytes which incorporate SCL can be challenging and cumbersome, noting that often pre-processing is required to ensure reliable numerical results. This issue is further heightened once the electrolyte is coupled with electrodes in a full battery model. In Section 5.2.3 we suggest that our asymptotic solutions near the boundary could be implemented directly in the Butler-Volmer conditions to enhance accuracy and reduce computational time, here we also propose the use of a non-uniform grid approach. Motivated by the distinct behaviour exhibited in the double charge layers in both Chapters 3 and 4, we can construct a new discretisation grid to exploit these distinct behaviours and thus streamline the numerical computations. This approach allows us to focus the computational power in the regions of the most rapid change, that is, the double charge layers. To implement this we would follow the work on non-uniform grids by Wang et al. (2011) and Veldman and Rinzema (1992).

In particular, based on our results and observations in Chapters 3 and 4, we would proceed in the following manner. In the boundary layers we could use a polynomial grid, reflecting the quadratic growth that we observe in our solutions here. We could then switch to an exponential grid in the intermediate layer to mirror the exponential form of the solution for θ , before transitioning to a sparse uniform grid in the bulk of the solution. Or alternatively, for simplicity, we could consider creating an exponential grid, as the focus is to concentrate more points where the solution is rapidly changing (Boundary and Intermediate layer) and have a more sparse grid where there is little change, *i.e.* as we approach the bulk. An exponential grid will facilitate this by creating a grid whereby the stepsize exponentially increases from the left boundary to the bulk, and similarly exponentially increases moving from the right boundary layer to the bulk. In both

scenarios this enables us to have a large number of points near the boundaries, with points becoming more spread out as we approach the bulk from either side, thus allocating computational resources toward the regions which evolve more significantly.

5.2.6 Nanowire electrodes

Each of the next steps mentioned thus far in this future work section are concerned with extending the electrolyte models so that these models can be utilised in a more complete battery model. Here we outline an area of future work going beyond the electrolyte which will require the electrolyte models and the extensions to these models. From a bigger picture perspective, one particular direction for the extension of these electrolyte models to more complete battery models is the use of nanowire electrodes.

Nanowire electrodes have emerged as a point of interest in the battery community due to factors such as good conductivity, increased rate capabilities, and low capacity fade (Liu et al. (2011); Kennedy et al. (2014, 2016, 2017)). However, the performance of these electrodes are very sensitive to experimental conditions and early charge behaviour (Liu et al. (2011); Kennedy et al. (2016); Sarra et al. (2023)) and thus it is important to understand the lithium transport processes in these systems, prompting the use of mathematical modelling to help shed light on these mechanisms and dynamics.

For example, motivated by the experimental work carried out by Liu et al. (2011), we would consider an LIB composed of a single cylindrical nanowire electrode and a solid electrolyte, which also acts as the separator, and piece of lithium metal acting as the reference electrode. Their experiments reveal aspects such as the formation of nanopores during delithiation, expansion and contraction of the nanowire morphology during cycling, and a lithiation and delithiation front, whereby the authors use a phase field model approach to determine this front follows a logarithmic time law. We would create a mathematical model to thoroughly describe the electrochemical processes occurring in the single nanowire electrode with a solid electrolyte and further investigate these observations from a theoretical perspective. Furthermore, in Liu et al. (2011) the authors study a nanowire with a lithium oxide solid electrolyte; we note that lithium oxide is also a common component of the solid electrolyte interphase (SEI), and thus, we could use this model as a starting point to study the development and growth of the SEI layer, which is a large contributor to diminishing performance of LIBs over time. For examples of other modelling work regarding SEI formation we refer to Pinson and Bazant (2012); Single et al. (2017).

Following the nanowire-solid electrolyte model we would then consider a cylindrical nanowire in an electrolyte bath in order to lend mathematical insight into the experimental observations of K.M. Ryan and authors in work such as Kennedy et al. (2014, 2016, 2017); Stokes et al. (2017); Kim et al. (2017); Sarra et al. (2023). More long term future work stemming from these model extensions and experimental observations would involve developing more intricate models to include features such as the structural mechanics of a swelling nanowire (for example, Devine et al. (2022) consider a model for the deformation of silicon nanowires during lithiation and delithiation), homogenized network of nanowire cylinders, the breakdown of these cylinders to networks, and the impact of this nanowire network on reducing capacity fade.

Overall, we have shown through asymptotic and numerical methods how to characterise the width and the solution behaviours in the EDLs of both solid and liquid electrolyte models derived from a thermodynamic standpoint. Through future work, we have clearly outlined how there are many impactful avenues for this research.

Appendix A

Asymptotic matching

In this Appendix, we present an alternative approach to asymptotic matching, that does not rely on the pseudo-matching technique introduced in Chapter 3.

We note that in Chapters 3 and 4 we linearise the intermediate layer problem about the bulk, in order to gain analytic insight into the behaviour in this region. In doing so, we obtain an exponential solution for θ in the intermediate layer. Normally, when we match between these regions we must match as $y_{\text{IL}}, y_{\text{IR}} \rightarrow \pm\infty$, however the exponential solution cannot match at both $\pm\infty$. Therefore, we take a front-centering condition at $y_{\text{IL}}, y_{\text{IR}} = 0$, due to the translational invariance of the intermediate layer problem. As a result, we can still enforce continuity between the layers, but not differentiability; thus introducing the pseudo-matching approach.

Here, instead of linearising the intermediate layer problem, we will retain the full equation for this layer and we will consider matching conditions for both $y \rightarrow \pm\infty$: $y \rightarrow -\infty$ to match the intermediate layer to the boundary layer, and $y_{\text{IL}} \rightarrow \infty$ to match to the bulk. The translational invariance will still necessitate a front-centering condition which we detail below.

A.1 Boundary layer

Consider the problem, already scaled in the boundary layer where $z = \epsilon x$:

$$\frac{\delta}{z_c} \frac{d^2 \theta}{dx^2} = \frac{\beta_1 + \beta_2}{1 + e^{-\theta}} - \beta_1, \quad (\text{A.1})$$

subject to

$$\theta(0) = \frac{c - z_c}{\delta}, \quad (\text{A.2})$$

so that

$$\frac{\delta}{2z_c} \left(\frac{d\theta}{dx} \right)^2 \Big|_{x=0} = (\beta_1 + \beta_2) \log \left(1 + e^{\theta(0)} \right) - \beta_1 \theta(0) - \hat{A}, \quad (\text{A.3})$$

where we determine that

$$\hat{A} = (\beta_1 + \beta_2) \log \left(\frac{\beta_1 + \beta_2}{\beta_2} \right) - \beta_1 \log \left(\frac{\beta_1}{\beta_2} \right). \quad (\text{A.4})$$

Near the boundary we let $\theta = -\delta^{-1}\psi$:

$$\frac{1}{z_c} \frac{d^2 \psi}{dx^2} = \beta_1 - \frac{\beta_1 + \beta_2}{1 + e^{\delta^{-1}\psi}} \sim \beta_1 \quad (\text{A.5})$$

with

$$\psi(0) = c - z_c, \quad (\text{A.6})$$

so that

$$\frac{1}{2z_c} \left(\frac{d\psi}{dx} \right)^2 \Big|_{x=0} = (\beta_1 + \beta_2) \log \left(1 + e^{-\delta^{-1}\psi(0)} \right) + \beta_1 \psi(0) - \delta \hat{A} \sim \beta_1 \psi(0) - \delta \hat{A}. \quad (\text{A.7})$$

We expand $\psi \sim \psi_0 + \delta \psi_1$

$$\frac{d^2 \psi_0}{dx^2} = z_c \beta_1 \implies \psi_0 = \frac{z_c \beta_1 x^2}{2} + A_0 x + z_c - c, \quad (\text{A.8})$$

$$\frac{d^2 \psi_1}{dx^2} = 0 \implies \psi_1 = A_1 x, \quad (\text{A.9})$$

where

$$A_0 = -\sqrt{2z_c \beta_1 (z_c - c)} \quad (\text{A.10})$$

and

$$A_1 = -\frac{z_c \hat{A}}{A_0}. \quad (\text{A.11})$$

A.2 Intermediate layer

We let $x = x_0 + \sqrt{\delta}y$ and $\Theta(y) = -\delta\psi(x_0 + \sqrt{\delta}y)$, leading to

$$\frac{1}{z_c} \frac{d^2\Theta}{dy^2} = \frac{\beta_1 + \beta_2}{1 + e^{\delta^{-1}\psi}} - \beta_1 \quad (\text{A.12})$$

with $\Theta \rightarrow \theta_0$ as $y \rightarrow \infty$ and Θ matches to the boundary layer as $y \rightarrow -\infty$. We take a first integral, noting that $\dot{\Theta} \rightarrow 0$, $\Theta \rightarrow \theta_0$ as $y \rightarrow \infty$,

$$\frac{d\Theta}{dy} = \sqrt{2z_c \left((\beta_1 + \beta_2) \log(1 + e^\Theta) - \beta_1\Theta - \hat{A} \right)}. \quad (\text{A.13})$$

We cannot solve this explicitly, but can get the result from the first integral and then note where we choose $\hat{\Theta}$ by the value of Θ at $y = 0$. This is the general front-centering condition. In Chapter 3 we took this to match from the bulk, resulting in the pseudo-matching approach. Here instead we can preserve derivative matching with an alternative choice which we will make clear. Taking a first integral:

$$\int_{\hat{\Theta}}^{\Theta} \frac{dz}{\sqrt{(\beta_1 + \beta_2) \log(1 + e^z) - \beta_1 z - \hat{A}}} = \sqrt{2z_c} y, \quad (\text{A.14})$$

as $y \rightarrow -\infty$ and $\Theta \rightarrow -\infty$ we need to match to the boundary layer. For $z < 0$, $|z| \gg 1$:

$$\sqrt{(\beta_1 + \beta_2) \log(1 + e^z) - \beta_1 z - \hat{A}} \sim \sqrt{-\beta_1 z - \hat{A}}. \quad (\text{A.15})$$

For simplicity, we will take

$$\hat{\Theta} = -\frac{\hat{A}}{\beta_1} \quad (\text{A.16})$$

so that (A.15) is zero when $z = \hat{\Theta}$. This is now the front-centering choice. We just make this choice (and it is our choice, nothing in the problem requires it) to simplify the integral. Thus, for $y \rightarrow -\infty$

$$\int_{\hat{\Theta}}^{\Theta} \frac{dz}{\sqrt{(\beta_1 + \beta_2) \log(1 + e^z) - \beta_1 z - \hat{A}}} \sim \int_{\hat{\Theta}}^{\Theta} \frac{dz}{\sqrt{-\beta_1 z - \hat{A}}} - c_1 \quad (\text{A.17})$$

where we define

$$-c_1 = \int_{\hat{\Theta}}^{-\infty} \left(\frac{1}{\sqrt{(\beta_1 + \beta_2) \log(1 + e^z) - \beta_1 z - \hat{A}}} - \frac{1}{\sqrt{-\beta_1 z - \hat{A}}} \right) dz. \quad (\text{A.18})$$

For the parameter values used in Chapter 3: $\beta_1 = 0.4, \beta_2 = 0.2$ we have $c_1 \sim 1.45$ and

$$\int_{\hat{\Theta}}^{\Theta} \frac{dz}{\sqrt{-\beta_1 z - \hat{A}}} = -\frac{2}{\beta_1} \sqrt{-\beta_1 \Theta - \hat{A}}, \quad (\text{A.19})$$

justifying the choice of $\hat{\Theta}$ so that the integral evaluates to zero at $\hat{\Theta}$. Therefore, as $y \rightarrow -\infty$

$$\sqrt{2z_c}y \sim -\frac{2}{\beta_1}\sqrt{-\beta_1\Theta - \hat{A} - c_1}. \quad (\text{A.20})$$

We rearrange to find

$$\Theta \sim -\frac{\beta_1}{4}(c_1 + \sqrt{2z_c}y)^2 - \frac{\hat{A}}{\beta_1} \quad (\text{A.21})$$

as $y \rightarrow -\infty$.

A.3 Matching

To match the boundary and intermediate layers we use an intermediate variable

$$x = x_0 + \eta\omega, \quad y = \frac{\eta}{\sqrt{\delta}}\omega, \quad \sqrt{\delta} \ll \eta \ll 1. \quad (\text{A.22})$$

For the boundary layer

$$\theta \sim -\delta^{-1} \left(\frac{z_c\beta_1}{2}x_0^2 + A_0x_0 + z_c - c + \delta A_1x_0 + \eta\omega(z_c\beta_1x_0 + A_0 + \delta A_1) + \frac{z_c\beta_1\eta^2\omega^2}{2} \right) \quad (\text{A.23})$$

and the intermediate layer

$$\Theta \sim -\frac{\beta_1}{2} \frac{z_c\eta^2\omega^2}{\delta} - \frac{\beta_1}{2} c_1 \sqrt{2z_c} \frac{\eta\omega}{\sqrt{\delta}} - \frac{\beta_1 c_1^2}{4} - \frac{\hat{A}}{\beta_1}. \quad (\text{A.24})$$

We expand $x_0 \sim x_{00} + \sqrt{\delta}x_{01}$ and at $\mathcal{O}(\delta^{-1})$ we have

$$\left(\frac{z_c\beta_1}{2}x_{00}^2 + A_0x_{00} + z_c - c \right) = 0 \quad (\text{A.25})$$

and

$$z_c\beta_1x_{00} + A_0 = 0, \quad (\text{A.26})$$

therefore we have

$$A_0x_{00} = -z_c\beta_1x_{00}^2 \quad (\text{A.27})$$

and

$$-\frac{z_c\beta_1}{2}x_{00}^2 + z_c - c = 0, \quad (\text{A.28})$$

so that

$$x_{00} = \sqrt{\frac{2(z_c - c)}{z_c\beta_1}} = -\frac{A_0}{z_c\beta_1}. \quad (\text{A.29})$$

At the next order, $\mathcal{O}(\delta^{-\frac{1}{2}})$ we have

$$(z_c \beta_1 x_{00} + A_0) x_{01} - \eta \omega z_c \beta_1 x_{01} = -\frac{\beta_1}{2} c_1 \sqrt{2z_c} \eta \omega, \quad (\text{A.30})$$

therefore

$$z_c \beta_1 x_{01} = \frac{\beta_1}{2} c_1 \sqrt{2z_c}, \quad (\text{A.31})$$

so that

$$x_{01} = \frac{c_1}{\sqrt{2z_c}}, \quad (\text{A.32})$$

noting that the η^2 terms already match. Thus, we have smooth matching. Importantly, we note that both this alternative matching approach and the pseudo-matching method yield the same leading-order transition point between the two regions. In the approach taken here, $\hat{\Theta}$ is arbitrarily chosen; we highlight that variations in its value only influence higher-order corrections to x_0 . For example, in the pseudo-matching approach, $\hat{\Theta}$ was chosen to front-center at $y = 0$. Both choices are somewhat arbitrary, but any choice will lead to an $\mathcal{O}(\sqrt{\delta})$ difference in the front position.

For $y \rightarrow \infty$ we write

$$\int_{\hat{\Theta}}^{\Theta} \frac{dz}{\sqrt{(\beta_1 + \beta_2) \log(1 + e^z) - \beta_1 z - \hat{A}}} \sim -\sqrt{2z_c} \int_{\hat{\Theta}}^{\Theta} \frac{dz}{a(z - \theta_0)} - c_2 \quad (\text{A.33})$$

where we define

$$-c_2 = \int_{\hat{\Theta}}^{\theta_0^-} \left(\frac{1}{\sqrt{(\beta_1 + \beta_2) \log(1 + e^z) - \beta_1 z - \hat{A}}} + \frac{\sqrt{2z_c}}{a(z - \theta_0)} \right) dz. \quad (\text{A.34})$$

For $\beta_1 = 0.4$ and $\beta_2 = 0.2$ we have $c_2 \approx 0.1278$;

$$\int_{\hat{\Theta}}^{\theta} \frac{dz}{a(z - \theta_0)} = \frac{1}{a} \log \left(\frac{\theta_0 - \theta}{\theta_0 - \hat{\Theta}} \right) \quad (\text{A.35})$$

since $\theta < \theta_0$. Therefore, for $y \rightarrow \infty$

$$\sqrt{2z_c} y \sim -\frac{\sqrt{2z_c}}{a} \log \left(\frac{\theta_0 - \Theta}{\theta_0 - \hat{\Theta}} \right) - c_2 \quad (\text{A.36})$$

and rearranging

$$-ay - \frac{c_2}{\sqrt{2z_c}} = \log \left(\frac{\theta_0 - \Theta}{\theta_0 - \hat{\Theta}} \right), \quad (\text{A.37})$$

and so

$$\Theta = \theta_0 - (\theta_0 - \hat{\Theta}) e^{-a \left(y + \frac{c_2}{\sqrt{2z_c}} \right)} \quad (\text{A.38})$$

which already matches to θ_0 as $y \rightarrow \infty$. This is the form we had before in Chapter 3, obtained via the linearisation approach.

Although this method follows a more traditional matching framework, we sacrifice the analytical form for the intermediate behaviour - obtained as a result of the linearisation. As such, the linearisation and pseudo-matching approach are featured in the main body of this thesis, as it allows us to characterise the electric double layers analytically.

In this Appendix we have presented an alternative approach to asymptotic matching for the left-hand side of the solid electrolyte problem from Chapter 3. We note that the results for the right-hand side will be analogous. Rather than employing pseudo-matching, we get smooth matching with a different front-centering condition.

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