

Interfacial Nanostructure of Solvate Ionic Liquids and Ionic Liquid Solutions

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Doctor of Philosophy



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Abstract

The technology employed by human beings for the generation, storage and usage of energy is presently undergoing the fastest and most profound change since the industrial revolution. The changes in the generation and usage of energy necessitate the development of new methods of energy storage. In these systems, electrochemical energy storage will play a crucial role and to this end new electrolytes need to be explored to complement these changes.

One such class of liquids is ionic liquids, a class of salts that are molten at room temperature. These liquids have a broad applicability to batteries and supercapacitors. This thesis details work where molecular dynamics simulations have been used to explore the nanostructure of ionic liquids and their mixtures with various molecular solvents at simplistic electrodes.

The thesis has two broad sections. The first is covered in Chapter 3, and explores the nanostructure of ionic liquid propylene carbonate solutions, developing a framework through which these nanostructures can be understood. The section concludes that the increasing dilution of ionic liquids decreases the surface charge at which the characteristic ionic liquid oscillatory interfacial structure gives way to a different structure featuring monotonic charge decay. The behaviour of ionic liquids at interfaces is found to be correlated to ion size and type, as well as concentration. A wide divergence in the observed behaviour is shown at positive and negative electrodes due to the asymmetry of propylene carbonate.

The second section, consisting of two chapters, explores the interfacial nanostructure of solvate ionic liquids using two different boundary conditions to model the electrode. This work is the first simulation of solvate ionic liquids at electrified interfaces. This section will explore the effect of electrode model on the behaviour of these ionic liquids at the electrode. Chapter 4 uses a fixed charge

electrode, whereas Chapter 5 uses one with a fixed potential. The section concludes that regardless of electrode model, the idealised portrait of a solvate ionic liquid - one where the liquid behaves exactly as an aprotic ionic liquid - is not applicable. In Chapter 4's exploration of fixed charged electrodes, the formation of 2 glyme to lithium complexes contradicts the idealised portrait of the liquid. A different change is observed in Chapter 5's exploration of fixed potential electrodes, with both lithium glyme and lithium anion clusters forming at the interface. The key difference between the two studies is that lithium does not coordinate to the electrode in the fixed charge simulations, while in the fixed potential case it does. At the end of Chapter 5 the results are compared against experimental data, with the efficacy of the two models discussed.

The aim of both studies is to look at the nanostructure of ionic liquids, when the symmetry between co-ion and cation repulsion - and related effects - is broken by the presence of a non ionic constituent in the liquid.

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Declaration

This thesis is submitted for the degree of Doctor of Philosophy in Physical and Theoretical Chemistry at the University of Oxford. No part of this thesis has been accepted or is currently being submitted for any degree, diploma, certificate or other qualification in this University or elsewhere. This thesis is wholly my own work, except where indicated.

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Chapter 1

Introduction

The pressures of climate change and diminishing oil supply are fundamentally changing the energy sector, with a transition taking place from fossil fuels to renewable energy. There has been a large amount of progress in this direction with less than 50 % of the UK National Grid's energy coming from fossil fuels on Wednesday 6th of June 2017 [3]. While there are many competing ways forward it is highly unlikely that the future of the energy grid, and automotive energy sector do not include electrochemical devices such as batteries and supercapacitors. These new electrochemical devices will need new electrolytes, which will likely include one such class of electrolyte: ionic liquids.

This thesis explores the interfacial nanostructures of solutions of conventional ionic liquids and solvate ionic liquids. These new classes of ionic liquids have potential applications in the next generation of electrochemical devices.

This chapter will introduce the key scientific themes discussed in this thesis. It will start by discussing ionic liquids, before moving on to discuss the electrochemical devices to which ionic liquids are being applied. This will be followed by discussion of the experimental studies of ionic liquid at interfaces. Finally the state of the art in simulations of ionic liquids and lithium-based electrolytes at interfaces will be discussed.

1.1 Ionic Liquids

Ionic liquids are a class of liquids that are comprised solely of ions, with melting points below 100°C [4]¹. However, a large number of known ionic liquids can be found to have melting points far below room temperature, and in general ionic liquids have a wide liquidus range which is beneficial for many applications.

The existence of ionic liquids is somewhat surprising from the viewpoint of more conventional chemistry. When first introduced to the idea of salts the archetypical example is sodium chloride, a material with an exceptionally high melting point. The thermodynamics by which ionic liquids have such a low melting temperature are interesting, consisting of both entropic and enthalpic effects. Firstly, the electrostatic attraction between ions is diminished due to the larger size of the ions, weakening the interaction between the ions.

Further to this, entropic effects also contribute to a decreased melting point. Most ionic liquids have long aliphatic tails. These tails introduce a large number of degrees of freedom. On freezing, these tails become less able to move, decreasing the entropy of the system. This effect leads to a far larger entropy change of fusion, and thus further decreases the melting point [4].

Ionic liquids are comprised solely of ions, and therefore have properties that are somewhat unique. The subsequent paragraphs will start by introducing the many classes of ionic liquids, followed by discussion of their properties and finally their non-electrochemical applications.

1.1.1 Classes of Ionic Liquids

A number of classes of ionic liquids have been synthesised. There are four principle types of ionic liquids: aprotic ionic liquids, protic ionic liquids, inorganic ionic liquids,

¹This temperature is somewhat arbitrary and was largely chosen due to the demands of organic synthesis.

and solvate ionic liquids. This section will make an introduction of the types and classes of ionic liquids.

As a general rule there is a far wider array of ionic cations, which are in general the larger, more exotic ion within the ionic liquids. Fig. 1.1 shows five of the most prominent types of aprotic ionic liquid cations. There are two classes of cations shown in Fig. 1.1. The first class are those based around tetrahedral phosphonium, and ammonium ions (both aliphatic and alicyclic). While the second consists of those based around aromatic heterocycles.

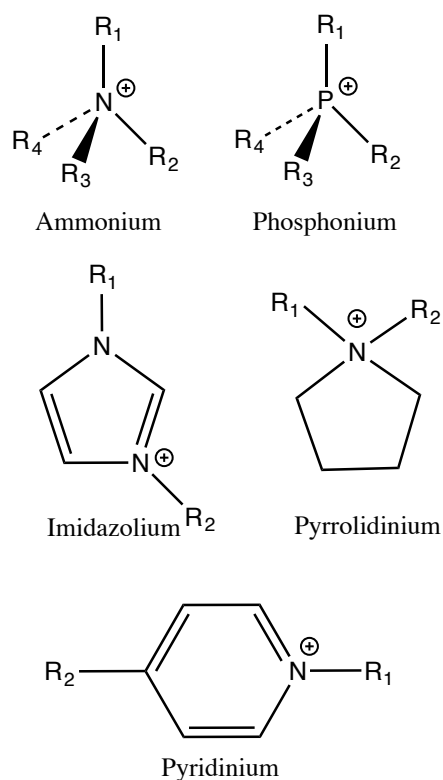


Figure 1.1: Structural formula of common aprotic cations.

The most prominent anions in ionic liquids, examples of which are shown in Fig. 1.2, can be more conventional, however some examples such as bistriflimide and

tris(perfluoroalkyl)trifluorophosphate (FAP) are specifically chosen to produce ionic liquids with particular properties, such as hydrophobicity and chemical stability.

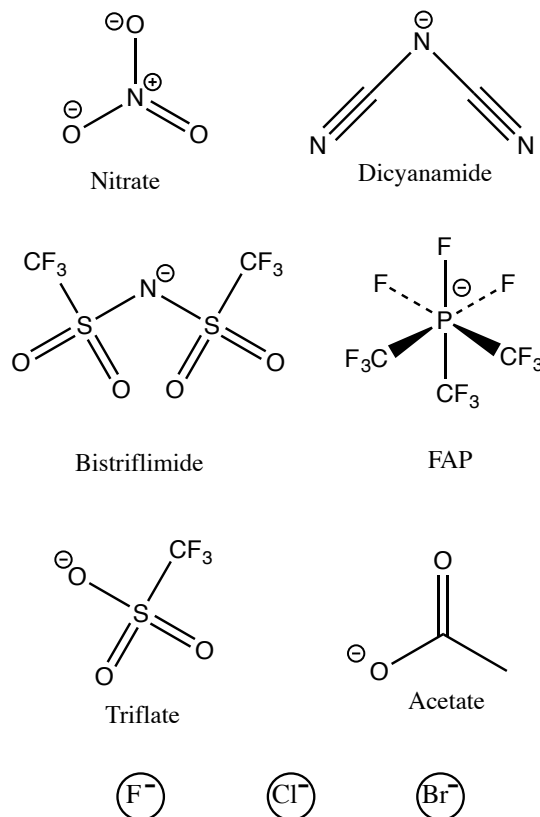


Figure 1.2: Structural formula of common ionic liquid anions.

Cations in protic ionic liquids are normally similar in structure to aprotic ionic liquids, but with one of the alkyl groups replaced with a hydrogen atom. They are more simple to synthesise than aprotic ionic liquids as they can be produced by a proton transfer reaction from a Brønsted acid to a Brønsted base, leading to a lower cost of production [5].

Solvate ionic liquids, which are the focus of Chapters 4 and 5 of this thesis have a coordination complex cation formed by coordination of a solvent molecule to a metal cation [6], as shown in Fig. 1.3. They are formed by the dissolution of a metal salt in a solvent in a molar ratio equal to that of the solvent salt ratio in the desired complex ion. If a very high percentage of ions are fully coordinated and the lifetime of the

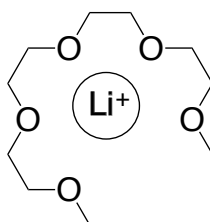


Figure 1.3: Structure of the complex cation of a solvate ionic liquid. This particular structure is a chelation complex formed from tetraglyme and lithium.

complex ion is sufficiently long the solution can be viewed as a liquid comprised near solely of ions, this is called a good solvate ionic liquid [7]. In the case where there are still a large number of complex ions present, but some properties of the bulk solvent are still observed then the substance is called a poor solvate ionic liquid [6].

The final class of ionic liquids are the inorganic ionic liquids. One such example of this are the compounds based around aluminium halide anions such as $[\text{Na}][\text{Al}_2\text{Cl}_7]$ [8]. Like solvate ionic liquids this field has gained more interest recently. This class of ionic liquids is sure to have many novel applications [9], however this thesis does not investigate this class at all and therefore subsequent sections will feature limited discussion of these compounds in the interest of brevity.

Across all classes of ionic liquids properties can be tuned by choice of cation and anion leading to an ability to create designer liquids. However, there are an array of properties which are common across nearly all ionic liquids in nearly all classes. The subsequent paragraphs will discuss some important characteristics of ionic liquids.

1.1.2 Thermochemical Properties of Ionic Liquids

In general ionic liquids have high temperatures of decomposition and vapourisation. This is due to the strong electrostatic interactions between ions leading to temperatures of vapourisation far in excess of those seen for molecular materials which are liquid at room temperature [10, 11].

Some component ions cause ionic liquids to decompose at a reduced temperature. For instance the acetate anion and the dicyanamide anion lead to reduced temperature of decomposition due to specific chemical pathways [10]. Like many systems ionic liquids exhibit some difference in thermal stability and thermoxidative stability. For instance tetrafluoroborate ionic liquids are known to have a higher thermal stability than bistriflimide based ionic liquids [10], but a poorer thermoxidative stability [12].

Ionic liquids have a low vapour pressure owing to very similar reasons as their high thermal stability. The vapour pressure of most ionic liquids is low even in the range of 110°C to 120°C where it is measurable for some ionic liquids, it is far lower than traditional low vapour pressure solvents [13], for instance the vapour pressure of glycerol is 92.1 Pa at 120°C, whereas the ionic liquid [BMIm][TFSI] has a vapour pressure of 0.004 Pa at the same temperature [13].

1.1.3 Viscosity of Ionic Liquids

Ionic liquids typically have a far higher viscosity than conventional liquids. This is due to the strong electrostatic interactions between the components of the liquids, which increases molecular friction [14]. The viscosity of ionic liquids was found to be hugely dependent on the cations and anions in the liquid [15–18]. And as a general rule ionic liquids composed of larger ions will have a higher viscosity due to the greater van der Waals interactions. However in the case of cations with alkyl chains viscosity is minimised for an ion where alkyl constituents are roughly four carbons in length, with viscosity rising with increasing and decreasing length. Larger chains increase van der Waals interactions, while shorter chains allow for closer approach of ions leading to increased Coulombic interactions [15–18].

Viscosity is also increased when the ion charge is localised on a single atom. This means the cations and anions which have ionic charge delocalised, such as dicyanamide, imidazolium, and bistriflimide have low viscosity, while viscosity is higher

for liquids comprised of ions where charge is localised on a single atom, such as tri-flate and pyrrolidinium [19]. Finally fluorination of side chains leads to a decrease in viscosity due to diminished van der Waals interactions [19].

1.1.4 Tribological Properties of Ionic Liquids

Ionic liquid's high viscosity and thermal stability has lead to them being considered as lubricants [20, 21]. For many commercial applications the lubricant must play multiple roles, beyond simply reducing friction. A lubricant is often required to prevent wear, and oxidation of the surfaces, protect from other unwanted chemical processes, and control friction within a certain range. Ionic liquids have been successful in many applications due to their combination of non-volatility and chemical stability, as well as reducing friction.

Aprotic ionic liquids, which are not susceptible to hydrolytic decomposition, typically have strong anti-wear properties [22]. Ionic liquids that have some fluorinated components are also particularly effective. X-ray Photoelectron Spectroscopy (XPS) analysis of steel tribological contacts has shown the liquids undergo tribochemical reactions with the metal leading to the fluorination of the metal surface protecting it from other forms of tribochemical wear [23].

Surface force experiments of the friction of ionic liquids confined on the order of nanometres have found friction to be quantised based on the number of confined liquid layers [24, 25], a result, which has been replicated by molecular dynamics simulations [26].

1.1.5 Electrochemical Properties of Ionic Liquids

Ionic liquids are conductive compared to other liquids with similar thermochemical properties. Ions act as charge carriers and the density of ions in ionic liquids is far higher than for more conventional electrolytes. However the conductivity of

ionic liquids is surprisingly low [27–29]. The high viscosity, and associated low speed of ion migration is the limiting factor decreasing the conductivity of ionic liquids. Conductivity of ionic liquids can be improved by mixing the ionic liquid with a small quantity of a suitable solvent [30]. The concentrated electrolytes produced in this way are not yet well understood in terms of interfacial structure or dynamics. This is the motivation for the simulations reported in Chapter 3 [28, 30]. Broadly, the trends in conductivity are related to changes in viscosity with bistriflimide [31] and dicyanamide [32] based ionic liquids showing some of the highest conductivities. Other properties of ionic liquids, such as the size of ions or the length of aliphatic chains can also affect the conductivity of an ionic liquid, however, as many of these properties also affect the viscosity of an ionic liquid it can be hard to divine causality in an absolute sense [28].

A significant benefit of ionic liquid electrolytes is that aprotic ionic liquids also have broad electrochemical windows [33–35]. Generally, the electrochemical window of ionic liquids, i.e. the range of voltage accessible without electrochemical decomposition, based around aromatic systems, such as imidazolium rings, is narrower than for systems based around non aromatic systems, such as quaternary ammonium salts [36–39]. Further to this, changing the substituents attached to the molecular ion can have a large effect on the electrochemical window. Protic ammonium salts generally exhibit a far narrower electrochemical window than aprotic ones [40], and in most cases increasing the length of alkyl chains attached to ionic liquids increases stability [36], however this is not universal. For example replacing the methyl unit on an 1-Ethyl-3-Methyl-imidazolium cation with a second ethyl tail, creating 1,3-Diethyl-imidazolium, will narrow the electrochemical window [34].

1.2 Supercapacitors and Batteries

One area in which ionic liquids have seen widespread interest is in electrochemical devices. This application is particularly prescient at the present time due to two key demands of a carbon free energy grid: the output of non-carbon energy sources is not as controllable or reliable as fossil fuels and therefore methods of energy storage are needed for the energy grid. Secondly, they have applications to storage devices in electric vehicles. Ionic liquids have an applicability in a number of exciting novel electrochemical devices. The following paragraphs will discuss three particularly interesting types of devices: redox flow batteries, lithium-sulfur batteries, and supercapacitors.

1.2.1 Redox Flow Batteries

Redox flow batteries are applicable to use as an energy storage mechanism in a future smart grid. They have on average a very low energy density, which makes them inapplicable for weight specific applications, however they do allow for operation at higher current and power densities [41].

Redox flow batteries operate by maintaining two reservoirs of electrolyte that can be pumped in and out of the cell. These two electrolytes, the catholyte which solvates and reacts with the cathode, and the anolyte which solvates and reacts with the anode, are separated within the cell by a charge carrier permeable membrane. The liquids are reduced or oxidised at their respective electrode but are otherwise kept separate from one and other [41]. The form of a redox flow battery is shown in Fig. 1.4.

Ionic liquids have been applied to the next generation of redox flow batteries in a number of ways. For example; work by Ejigu *et al.* has used an ionic liquid solvent to stabilise charge carrying transition metal complexes [42], and work by Takechi *et al.*

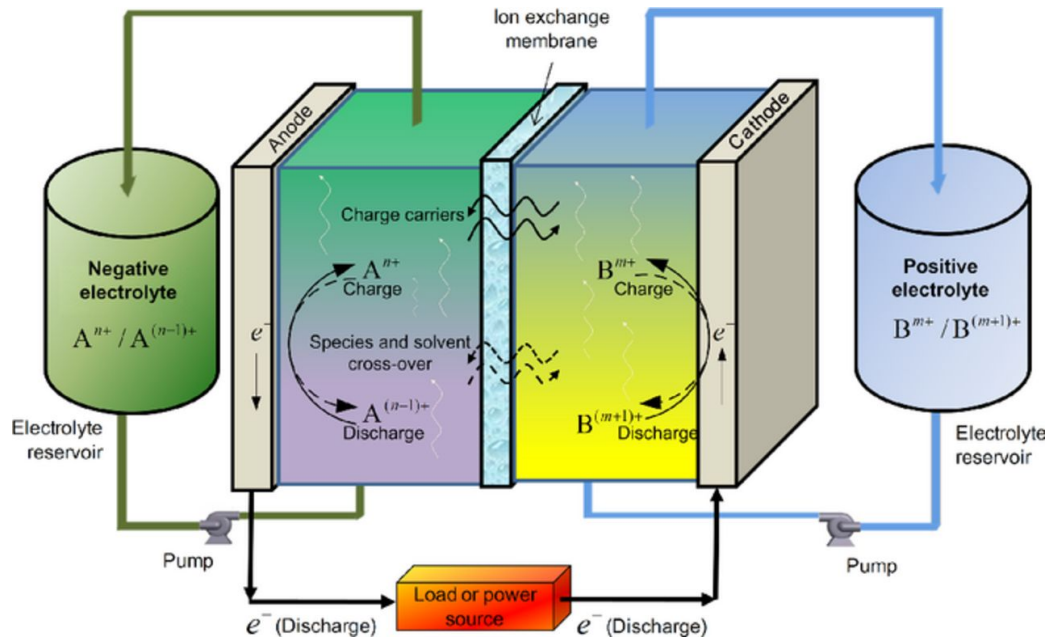


Figure 1.4: Diagram of a redox flow battery reproduced from Perry *et al.* [41]

has used a solvate ionic liquid to synthesise a highly concentrated catholyte with a far greater energy density than conventional electrolytes [43].

1.2.2 Lithium Sulfur Batteries

Lithium sulfur batteries, alongside lithium air batteries, are the main candidate for a high energy density automotive battery. Lithium sulfur batteries are in many ways seen as successors to the currently dominant lithium ion batteries. Unlike in lithium ion batteries where the lithium ions intercalate into the cathode the lithium ions react with the sulfur at the cathode forming lithium sulfides [44]. The two key challenges with lithium sulfur batteries are: firstly the relatively poor conductivity of sulfur. This is usually countered by the use of a specially designed, highly novel, cathode,

such as sulfur graphene oxide composites [45]. Secondly the solubility of lithium sulfides leading to a rapid decrease in capacity [46].

Lithium glyme solvate ionic liquids are particularly applicable to lithium sulfur batteries due to the ionic liquids suppression of lithium sulfides [46, 47]. Dissolution of the solvate ionic liquids in fluorinated ether leads to an even higher power density, and no break up of the lithium glyme complex [46, 47]. Conversely, conventional ionic liquids have also been used as electrolytes for lithium sulfur batteries, however, this was less successful for multiple reasons including anion side reactions [48].

1.2.3 Supercapacitors

Supercapacitors are an alternative energy storage device to batteries. Unlike batteries most supercapacitors do not store energy through means of chemical reactions, but instead by the polarisation of electrochemical cells. Supercapacitors are a high performing subclass of capacitors. Supercapacitors are based on two subclasses of capacitor: pseudo-capacitors and double layer capacitors [49].

Double-layer capacitors store energy by means of a potential being generated between the two capacitors separated by liquid media. Pseudo-capacitors feature faradic energy storage at the two electrodes in the capacitor. Hybrids of the two forms can also be created. In all cases when a potential is applied between the two electrodes the system is polarised with counter-ions moving towards the relevant electrode, as shown in Fig. 1.5. Most energy storage in these capacitors takes place in the first interfacial layer at the electrodes [49].

The primary difference between pseudo-capacitors and double layer capacitors is the presence of charge transfer. In a double-layer capacitor the ions at the electrodes are bound by electrostatic forces, whereas in pseudo-capacitors there is some charge transfer between the electrodes and the ions [49].

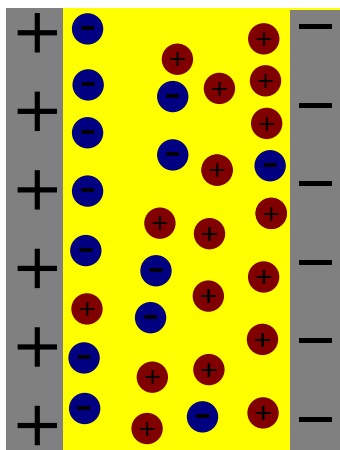


Figure 1.5: A cartoon of a capacitor

The energy density of capacitors is directly proportional to the surface area of the electrodes. Therefore, traditionally, nano-porous electrodes are used in order to obtain a very high energy density. A wide variety of aprotic ionic liquids have been applied to use in these supercapacitors [50–55]. They are favoured over protic ionic liquids due to their wider electrochemical window [56].

Ionic liquids and ionic liquid-based electrolytes are the main candidate for modern supercapacitors, so high-level molecular dynamics simulations have been performed for these systems. Simulations of both pure ionic liquids and ionic liquid acetonitrile mixtures have been performed by Merlet *et al.* [57, 58]. This, along with ionic liquids application as novel lubricants, has driven a large amount of research looking at the interfacial behaviour of ionic liquids.

1.3 The Interfacial Nanostructure of Ionic Liquids.

The interfacial nanostructure of ionic liquids has been a hugely active topic over the last decade. The structure of these liquid interfaces has been studied by: molecular dynamics simulations [26, 59–62], atomic force microscopy [63–66], surface force experiments [24, 25, 67], sum frequency generation spectroscopy [68, 69], scattering

experiments [70–72] and quartz crystal microbalance [73]. Further to this, a set of theoretical frameworks have been developed to describe the behaviour of these liquids at interfaces [74].

Ionic liquids have been found to differ from conventional electrolytes in how the charge of an immersed electrode is screened. In solution surface charge is screened by the formation of a double layer. A charged electrode in an electrolyte solution will repel co-ions while attracting counter-ions. The nature of this double layer was slowly elucidated in studies, by: Helmholtz [75], Stern [76], Gouy, and Chapman. Fig. 1.6 shows both the physical form of the double layer, and a plot of potential versus distance arising from it. Closest to the electrode there is a layer of strongly electrostatically attracted counter-ions. This layer is commonly known as a Stern layer or a Helmholtz layer. Beyond this layer there is a diffuse layer consisting of an exponentially decaying excess of counter-ions. The electric potential within the double-layer declines linearly within the Stern layer, before declining exponentially in the diffuse layer.

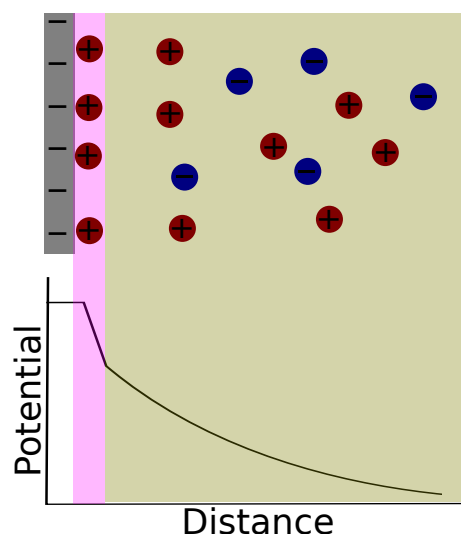


Figure 1.6: A cartoon of a double layer (top), and sketch of potential with distance (bottom). Within the cartoon cations are shown in red and anions are Shown in blue. The cartoon does not feature solvent molecules which can be assumed to surround all ions. The Stern layer component of the plot and cartoon is coloured pink while the diffuse layer is coloured in brown.

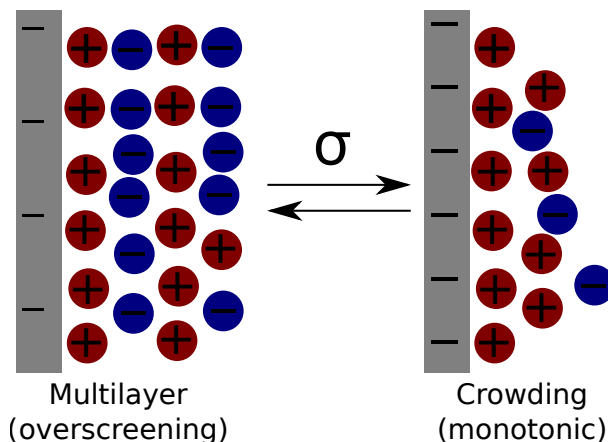


Figure 1.7: An cartoon showing the transition from the multilayer to the crowded structure.

At higher concentrations, and for ionic liquids, this portrait does not reflect the reality of the system. This leads to an array of interfacial nanostructures that are not observed in conventional solutions [74]. The form of these nanostructures is the primary focus of much of the work in this thesis, and is discussed in detail over the course of the rest of the chapter.

If an uncharged metallic electrode is placed into an ionic liquid the near-surface layer of liquid contains (in an ideal case) equal numbers of cations and anions (as illustrated in Fig 1.8.D). Increasing the charge (or potential) of the electrode leads to counter-ions being enriched in the near electrode region, and co-ions being enriched in a layer behind the counter-ions, this can be followed by layers of counter-ion and co-ions as shown in Fig.1.7, this structure is called a multilayer structure. Ever increasing surface charge leads to a formation of a structure with net counter-ion density beyond one ion diameter and monotonic counter-ion decay. This structure is known as the crowded structure.

This contrasts with the simple Guoy-Chapmann picture in diluted electrolytes, because for concentrated electrolytes the polarisation of the electrolyte in response to polarisation of the electrode can potentially lead to several qualitatively different structures. Some of these are illustrated in Figs.1.7 and 1.8: alternating layers of

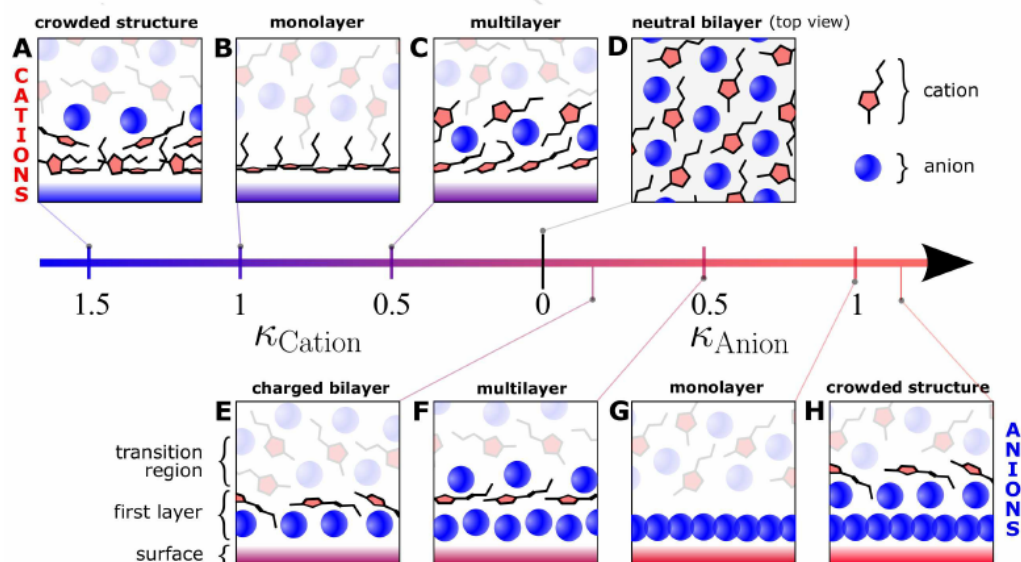


Figure 1.8: A cartoon of changing interfacial structure with surface charge from Ivaništšev *et al.* [59]. The transition to the monolayer takes place at reduced surface charge where $\kappa = 1$.

cations and anions can form, either a single bilayer (Fig. 1.8.E), or the previously described multilayer structure (Fig. 1.8.C) (which is related to the broader concept of overscreening). Under different conditions multiple layers of counter-ions form, in a structure previously introduced as crowding (Fig. 1.8). The transition between the multilayer and crowding structures takes place via an intermediate monolayer structure (Fig. 1.8.B). This system has been described by a number of researchers using a number of different schemes, including mathematical approaches from first principles. One description, which will be evoked in this thesis is provided by Ivaništšev and co-workers [59, 77, 78]. This approach defines the structural transitions in terms of the surface charge at which the monolayer occurs. This method, which will provide a basis to the work presented in Chapter 3, defines a reduced surface charge κ , which is the charge density of the interface normalised by the charge density of a monolayer of counter-ions, such that,

$$\kappa_{ion} = \left| \frac{\sigma}{\theta_{ion}^{max}} \right|, \quad (1.1)$$

where σ is the surface charge, and θ_{ion}^{max} is the charge density of a monolayer of ions.

At a surface charge of $\kappa = 1$ the monolayer structure is observed, below this charge the multilayer structure is observed, while above this charge the crowded structure is observed. This effect is summarised in Fig. 1.8, which shows the change in structure with increasing and decreasing κ .

While the most relevant structural description to the work described in this thesis is the portrait of Ivaništšev *et al.* [59] which arises from molecular dynamics simulations, there have been other theoretically robust descriptions of the interfacial nanostructure of ionic liquids. In particular the work of Kornyshev and Bazant provides an appropriate mathematical framework to the structural transitions of ionic liquids at interfaces [79]. And a series of molecular dynamics simulations performed by Merlet *et al.* which suggested a set of transitions within the plane of the electrode showing a crystallisation of interfacial ions at a certain surface potential [80].

The interfacial capacitance, of prime importance to the energy storage applications described previously, is entirely determined by the molecular details of the ion arrangements. The key starting point in this field was the prediction of a maximum or two-peak (“camel shaped”) capacitance versus voltage in ionic liquids [81], as shown in Fig. 1.9. This has been observed in simulations [82] and experiments [83] but remains controversial.

1.4 Simulations of Ionic Liquids at Interfaces

Ionic liquids’ potential use as electrolytes and lubricants as well as their high surface activity has lead to a large number of computational studies being performed to study the behaviour of these liquids at interfaces.

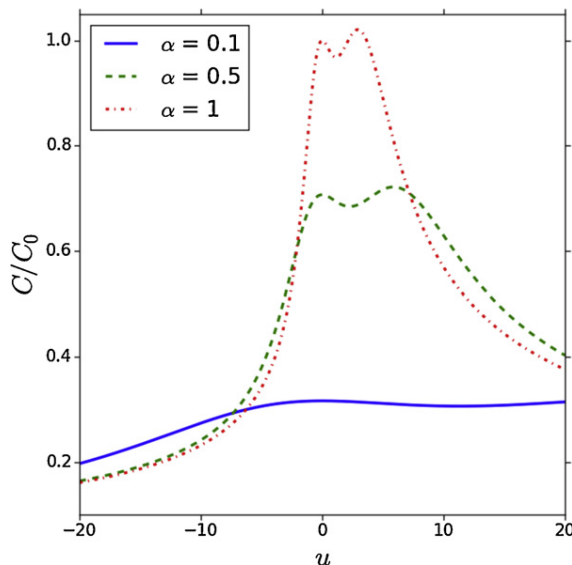


Figure 1.9: A figure taken from the work of Goodwin *et al.* showing change in capacitance with electrode potential for three cases of ion symmetry [84]. The value of α is indicative of the difference in ion size. $\alpha = 1$ is the case for symmetric ions. Notice that in most cases there is a camel shaped form to the peak.

Work using simple electrode models has allowed for the study of a wide variety of liquids, at a variety of interfaces including: graphene [62, 77, 78], amorphous carbon [85, 86], carbon nanotubes [87, 88], silica nanopores [89] and metals [90]. These simulations have allowed for a set of broad principles regarding the interfacial behaviour of ionic liquids to be explored. The relative simplicity of models used has also allowed for steered molecular dynamics simulations to be performed allowing for the study of the nano-frictional and nano-rheological properties of ionic liquids by means of simulations [85, 90]. With a number of studies being able to simulate the behaviours observed in surface force experiments [26, 91, 92].

On the other side, studies with more sophisticated fixed potential electrode models have been able to perform more accurate simulations of supercapacitors. These studies first looked at the behaviour of ionic liquids at planar electrodes before moving on to perform accurate simulations of the behaviour of ionic liquids at nanoporous electrodes [60, 80, 82, 93–95]. These simulations have used a slightly more simplistic

family of electrolyte models, but do appear to be highly successful in providing a broad understanding of ionic liquid structure in supercapacitors. These electrode models can also be used to study solutions of conventional lithium electrolytes at interfaces, with a large amount of success in simulating the double layer capacitance of lithium solutions at electrified interfaces [96].

1.5 Aim of Study

The work in this thesis aims to look at the fundamental properties of ionic liquid derived electrolytes at interfaces. This thesis will focus on two different types of electrolyte: a solvate ionic liquid, and solutions of ionic liquids in propylene carbonate (a polar solvent).

The third chapter of this thesis will aim to develop a broad understanding of the interfacial nanostructure in mixtures of ionic liquid with propylene carbonate. This will be explored from the perspective of several different variables: electrode surface charge, ion size, and solvent mole fraction.

Chapters 4 and 5 present the first simulations of solvate ionic liquids at interfaces. The goal of this work is to provide context to previous AFM studies of the nanostructure of solvate ionic liquids at interfaces, and to look at how the coordination structure of the complex cation within the solvate ionic liquid changes at interfaces. The fourth Chapter of the thesis looks at behaviour of one of these liquids at a simple fixed charge electrode, while in the fifth Chapter a more complex fixed potential electrode will be studied.

Together the aim of these two concurrent pieces of work, i.e. ionic liquid with molecular solvent (Chapter 3), and solvate ionic liquids (Chapters 4 and 5), is to use molecular dynamics simulations to study how the interfacial nanostructure of salts changes when other species are added to the solution. The common features, and

deficiencies, between electrolytes consisting of salt and solvent, and salt and chelating solvent, will be addressed in the concluding chapter.

1.6 Afterword

This chapter started by introducing ionic liquids, a class of salts which are liquid at room temperature. The properties of these liquids were defined, before a more general in depth discussion of their behaviour at electrified interfaces, and finally previous interfacial molecular dynamics simulations were discussed. The last section of this chapter presented the aims of the work in this thesis, and discussed briefly the simulations performed. Prior to presenting the results of these simulations the next chapter will introduce the basis of molecular dynamics, and explain some of the key techniques used in the simulations presented in this thesis.

Chapter 2

Simulation Methodology

The simulation of chemical systems allows for the rationalisation and prediction of chemical properties seen in experiment. Simulation of a chemical system thus provides a bridge between theoretical chemistry and experimental chemistry, allowing the examination of theoretical predictions in a significantly simplified system, or the contextualisation of experimental results. The rise in both computational power, and the expansion in available techniques has made simulations more ubiquitous and widened their scope.

This chapter starts by looking at the range of methods adopted in order to simulate chemical systems, before discussing in close detail the specific simulation technique used in this thesis: molecular dynamics. First the general assumptions of molecular dynamics investigations will be discussed followed by the introduction of the general simulation methods employed in order to generate accurate data efficiently. Having established the fundamentals of classical molecular dynamics, the discussion will move on to the techniques specifically applied to the field of liquids at interfaces. This chapter will finish by presenting the specific simulation methods used in this thesis.

2.1 Computer Simulations of Molecular Scale Systems

Computational chemistry has emerged over the past century in parallel to development of ever more powerful computers. A wide variety of computational methods have been developed for a wide variety of different layers of theory. Larger scale methods such as the finite element method being used to explicitly model experimental systems on a macroscopic scale [97]. Other simulation methods study systems

on the molecular level. There are essentially two sub-classes of these molecular scale simulations: computational quantum chemistry, and simulations which model molecular systems. This thesis is primarily concerned with the latter and most of this chapter will focus on this field. However force field parameterisation, a critical part of molecular dynamics simulation, takes place via the use of computational quantum chemistry.

A number of methods have emerged to apply computational methods to quantum calculations. The first calculations of quantum chemical orbitals were performed on diatomics using the Hartree-Fock method, and a set of Slater orbitals [98]. Subsequently a number of other *ab initio* methods were applied to calculation of the electronic structure of increasingly large chemical systems, including Møssler-Plesset perturbation theory [99, 100] and *ab initio* density functional theory (DFT) calculations [85, 101] which both have a particular relevance to the parameterisation of molecular dynamics force fields [85, 100]. Special care should be taken when referring to DFT calculations as *ab initio* calculations of electronic structure. While some functionals are indeed *ab initio* others are parameterised to produce results equivalent to true *ab initio* calculations, or even to reproduce empirical results [101].

2.2 Molecular Dynamics

This section will discuss molecular dynamics, with a particular focus on classical molecular dynamics. It will start by discussing the history of the technique before moving on to discuss the fundamentals of its operation. It will then discuss in detail the calculation of forces acting on components and the calculation of trajectories from these forces. Sections subsequent to this will discuss the handling of long range electrostatics in molecular dynamics simulations and the thermostats and barostats used to regulate the temperature and pressure of simulations.

2.2.1 The History of Molecular Dynamics Simulation

A research team working under Fermi at Los Alamos National Laboratory first pioneered the use of molecular dynamics simulations. However a subsequent independent study by Rahman has perhaps been more influential than the work of Fermi and his co-workers, due to its more widespread publication [102]. The popularity and power of molecular dynamics simulations rose with increasing computational power, not to mention the expansion of the variety of the available methods. The emergence of open source molecular dynamics software has spurred the widespread growth in the field. Programs like Gromacs [103], Lammmps [104], and Amber [105] have facilitated a huge expansion in molecular dynamics simulation. Even more recently, research programs have started using the home computational facilities of volunteers to increase computational power and perform molecular dynamics simulations of protein folding [106].

2.2.2 The Fundamental Characteristics of Molecular Dynamics

Molecular dynamics describes a range of computational chemistry simulation mechanisms. All of these mechanisms have at their root a procedure for calculating the trajectories of atoms within a system over a period of time. A highly generic scheme of such simulations is shown in Fig.2.1. First, initial positions of atoms or other bodies within the system are read into the program. Then the forces acting on the atoms are calculated. From these forces the movement of atoms is calculated over the course of a small time-step. This process is repeated for newly calculated positions for a preset number of time-steps. At the end of this process a trajectory of the atoms in the system has been calculated. If the trajectory is of significant length, the frames at the end of the trajectory can be considered to be independent of those at

the beginning of the trajectory leading to sampling of a large number of states in a manner similar to a ‘perfect’ Monte Carlo simulation¹.

At its core, molecular dynamics works by iterative calculations of the forces acting on a set of atoms, and the calculation of the locations of atoms under the influence of these forces after a set period of time. These two calculations can be performed through a number of different methods, which will be summarised in the next sections. First, however, it is important to discuss the geometry of simulations.

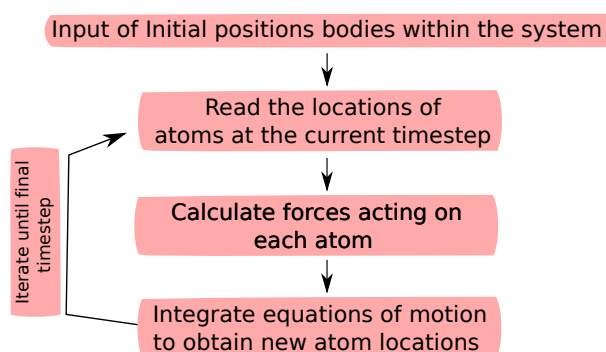


Figure 2.1: Flow diagram showing the basic anatomy of molecular dynamics simulations.

2.2.3 System Geometry and Boundary Conditions

Most molecular dynamics simulations are performed in either a cubic or octahedral box, with octahedral boxes particularly popular for the simulation of a single protein with lowest possible box size. To minimise edge effects, and to ease calculation of long range electrostatics, periodic boundary conditions are used [107]. In a system with periodic boundary conditions when an atom passes beyond the boundary it reappears on the other side of the box, with all interactions taking place across the boundary.

¹In some cases it is too computationally expensive to run a simulation of significant timescale and so some states are either insufficiently sampled or not sampled at all. Techniques have been developed to increase sampling such as RESPA or Umbrella Sampling can be employed.

2.2.4 Calculation of Forces Acting on Atoms

The forces acting on atoms can be calculated using an array of different methods. The main methods used, are to use classical potentials (classical molecular dynamics), or *ab initio* methods, commonly density functional theory, (*ab initio* molecular dynamics). Classical molecular dynamics is far less computationally expensive than *ab initio* molecular dynamics, while *ab initio* molecular dynamics makes far fewer assumptions about the nature of the chemical system than classical molecular dynamics. This thesis focuses solely on classical molecular dynamics and so will neglect to discuss the calculation of forces in *ab initio* molecular dynamics further². However, the thermostats, barostats, and integrators described in subsequent sections can also be used in *ab initio* molecular dynamics simulations.

Classical molecular dynamics seeks to convert the forces that act on systems at the molecular level to a classical analogue. By its very nature this process is reductive as at this length scale the potentials acting on bodies have their origins in quantum mechanics. However, a good approximation can be made for most species. In general forces acting on atoms in a chemical system can be split into those forces that arise from bonding related interactions and those that do not. The following paragraphs discuss how these forces are modelled. Special consideration is given to the potentials employed in the OPLS-AA (Optimised Potential for Liquid Simulations- All Atom) force field which is employed in the simulations presented in subsequent chapters.

2.2.4.1 Non-bonding Interactions

Within the frameworks of classical molecular dynamics non-bonding interactions can be split into two subsets, uncharged interactions, and electrostatic interactions.

²A good introduction to *ab initio* molecular dynamics is available in the book of Frenkel and Smit [108]

While some simulations have used potentials featuring multi-body electrostatic interactions, for instance Tersoff's early work on the modelling of metaloids in the solid state [109], most molecular dynamics studies use electrostatic potentials that are modelled as the summation of pairwise interactions. The most common potential used for this calculation is the pairwise Coulomb potential V_c between atoms i and j described as,

$$V_c(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_r\epsilon_0 r_{ij}}, \quad (2.1)$$

where ϵ_r is the relative permittivity, ϵ_0 is the permittivity of free space, and r_{ij} is the distance between the two charges. This leads to a force ($\mathbf{F}_{c,i}(r_{ij})$) acting on ion i due to its interaction with ion j being defined as,

$$\mathbf{F}_{c,i}(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_r\epsilon_0} \frac{\hat{\mathbf{r}}_{ij}}{|\mathbf{r}_{ij}|^2}. \quad (2.2)$$

However, pairwise summation of all electrostatic potentials within a simulation is computationally expensive; and therefore a cutoff distance between atoms is set beyond which the force acting between these atoms is set equal to zero. If the cutoff is set at a separation where the Coulomb potential has not converged closely enough to zero there will be a noticeable change in potential at the point of the cutoff. This problem can be overcome by use of a reaction field which models the area outside the cutoff as an implicit dielectric with a relative permittivity set so as to nullify this change in potential. In real systems longer range electrostatic potentials can have a large effect on a system, therefore electrostatic interactions beyond the cutoff must also be considered; a matter which will be discussed in detail later in this chapter.

Modeling of uncharged interactions is achieved empirically. Dispersion interactions arise from induced polarisation of electron density within a body. As electrons are not explicitly modeled in classical molecular dynamics a potential that mirrors the effect of dispersion is required. However, the dispersion attraction is not the only non

charge based interaction between atoms. At the closest separation, a ‘hard-wall’ repulsion is observed between the atoms due to the Pauli repulsion between the atoms’ electrons. A number of simple potentials have been used to describe non-charged interactions ranging from hard spheres [110] (which model only the Pauli repulsion), to square well potentials [111], and purely repulsive deformable spheres [26]. However by far the most popular are those based on the Lennard Jones potential ($V_{LJ}(r_{ij})$). The OPLS-AA force field [112] uses the most common, the 6-12 version, which has the form,

$$V_{LJ}(r_{ij}) = 4\epsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right), \quad (2.3)$$

where σ_{ij} is a coefficient related to the radii of the two atoms, and ϵ_{ij} is the potential at the minimum of the attractive well between the two atoms. The form of this potential is shown Fig. 2.2. The Lennard Jones potential models the attractive nature of dispersion forces, and the eventual hard-wall caused by the Pauli repulsion. However, it does not model polarisability. While polarisable force fields do exist they must employ an additional element, such as classical Drude oscillators [113], in order to render the atom polarisable. However these methods are far more computationally expensive, and often do not lead to an exceptional improvement in results.

2.2.4.2 Bonding Interactions

Covalent bonds are fundamentally a quantum phenomenon based around the molecular orbitals that form between valence electrons. However it is possible to analogue the vibrations of bonds as classical oscillators.

The simplest model is the harmonic oscillator, which is used to model bonds in many common force fields, such as OPLS-AA [112] and Amber [115], the form of the harmonic oscillator equation is as follows,

$$V_b(r_{ij}) = \frac{1}{2}k_{ij}^b(r_{ij} - b_{ij})^2, \quad (2.4)$$

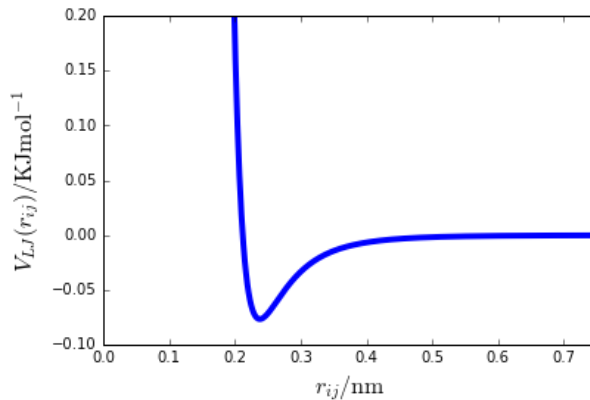


Figure 2.2: Lennard Jones potential between two lithium ions (parametrised using the Åqvist force field [114]), where $\sigma_{Li-Li} = 0.212$ nm and $\epsilon_{Li-Li} = 0.0765$ KJmol^{-1}

where b_{ij} is the equilibrium bond length and k_{ij}^b the force constant of the bond. Angles, 1,3 bonded interactions, (equivalent to the interaction between oxygen atoms and the hydrogen atoms they are not bonded to in the hydrogen peroxide molecule, shown in Fig. 2.3) also play a large role in maintaining the structure of molecules in molecular dynamics. Again there are a number of ways of modelling angle potentials, however the most common is to model this as a harmonic oscillator as well. The form of the potential is as follows,

$$V_a(\theta_{ijk}) = \frac{1}{2}k_{ijk}^\theta(\theta_{ijk} - \theta_{ijk}^0)^2, \quad (2.5)$$

where θ_{ijk}^0 is the equilibrium bond angle, k_{ijk}^θ the force constant, and θ_{ijk} is the angle between the two bonds. These bond and angle parameters are parameterised to try to both replicate the ideal gas phase thermodynamic properties of sample systems, and to match as closely as possible the spectroscopic data for these sample systems [116].

The form of the potential for modelling dihedral, 1,4 bonded, interactions (equivalent to the interactions between the hydrogen atoms in the hydrogen peroxide molecule shown in Fig. 2.3) are conventionally more complex than that for angle

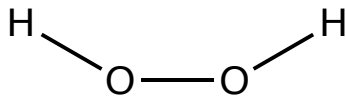


Figure 2.3: The structure of hydrogen peroxide, which is used as a guide to the type of interactions discussed in this chapter.

and bond interactions. In the case of the OPLS-AA force field the dihedral potential has the form,

$$V_{\text{OPLS}}(\phi_{ijkl}) = \frac{1}{2}C_1 [1 + \cos(\phi_{ijkl})] + \frac{1}{2}C_2 [1 + \cos(2\phi_{ijkl})] \\ + \frac{1}{2}C_3 [1 + \cos(3\phi_{ijkl})] + \frac{1}{2}C_4 [1 + \cos(4\phi_{ijkl})], \quad (2.6)$$

where C_n are the constants for the n^{th} term of the potential. These 1,4 dihedral interactions are only one type of dihedral interaction, a second type of dihedral interaction also exists, the improper dihedral. Improper dihedrals model areas of molecules where a number of atoms are required to sit in the same plane, for instance in aromatic rings. All forms of bonded potentials are shown in Fig. 2.4.

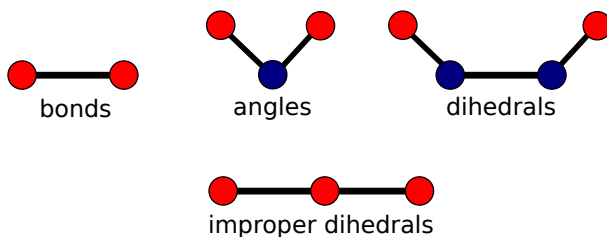


Figure 2.4: Cartoons showing the four types of non bonded interaction. Atoms which the experience the potential are shown in red, other atoms are shown in blue.

The previous sections have described the different potentials that model the forces acting on atoms in classical mechanical simulations. The next section will discuss the algorithms, which compute the movement of atoms within these systems.

2.2.5 Computing Atom Trajectories

In order to calculate the atom trajectories it is necessary to solve the equations of motion for the atoms within the system. While Langevin's equations of motion are sometimes used, owing to inbuilt control of temperature in the equations of motion, most molecular dynamics simulations are performed through the algorithmic integration of Newtons equations of motion [117]. These algorithms are produced by performing a Taylor expansion of the position of an atom in time, which, truncated beyond the fourth derivative of the position in time, has the form,

$$r(t + \Delta t) = r(t) + \dot{r}(t) \cdot \Delta t + \frac{\ddot{r}(t) \cdot (\Delta t)^2}{2!} + \frac{\dddot{r}(t) \cdot (\Delta t)^3}{3!} + \frac{\ddddot{r}(t) \cdot (\Delta t)^4}{4!}, \quad (2.7)$$

where $r(t)$ is the time dependent position of particles, and Δt is the timestep. This can be rewritten as,

$$r(t + \Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}(\Delta t)^2 + \frac{(\Delta t)^3}{3!}\ddot{r} + \mathcal{O}(\Delta t)^4, \quad (2.8)$$

where $f(t)$ is a function in time, $v(t)$ is the velocity as a function of time, $\mathcal{O}(\Delta t)^4$ is a function of timestep, $\ddot{r}$ is the third derivative of the position. Making the assumption that it is possible to neglect terms beyond the second order of the expansion the Euler formulation is obtained. The Euler formulation is however an inadequate solution to this problem as it leads to widespread propagation of errors through the simulation [117].

The Verlet algorithm is a more accurate algorithm. It can be obtained via the summation of the Taylor expansions of $r(t + \Delta t)$ in (2.8) with $r(t - \Delta t)$ which is defined as,

$$r(t - \Delta t) = r(t) - v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 - \frac{\Delta t^3}{3!}\ddot{r} + \mathcal{O}(\Delta t^4) \quad (2.9)$$

which yields the Verlet equation,

$$r(t + \Delta t) \approx 2r(t) - r(t - \Delta t) + \frac{f(t)}{m} \Delta t^2 \quad (2.10)$$

The Verlet algorithm has the necessary accuracy for the performance of accurate molecular dynamics simulations [117]. More efficient algorithms based on the Verlet algorithm have been described. Two such algorithms are used in the simulations described in this thesis; the Gromacs based simulations employ the leapfrog Verlet algorithm, which has the form,

$$r(t + \Delta t) = r(t) + \Delta t v(t + \Delta t/2) \quad (2.11)$$

with velocity at time $t + \Delta t/2$ defined as,

$$v(t + \Delta t/2) = v(t - \Delta t/2) + \Delta t \frac{f(t)}{m}. \quad (2.12)$$

The Leapfrog algorithm outputs velocity and locations offset by a value of half a timestep. This in turn leads to potential and kinetic energies being calculated offset by a value of half a timestep.

The LAMMPS based simulations use the velocity Verlet algorithm, which is closely related to the leapfrog algorithm. Unlike the Leapfrog algorithm energies and positions are calculated for the same timestep. The trade off for this is however that the velocity must be calculated during integration, which has a slight computational cost.

2.3 Electrostatics in Classical Molecular Dynamics

The simulations in this thesis are based around the behaviour of charged particles at interfaces. In order to avoid artefacts and to mirror as closely as possible the

experimental behaviour of these systems, correct handling of electrostatic interactions is required. While the Coulomb potentials discussed in section 2.2.4.1 are effective at simulating the pairwise interactions within the cutoff they are far too computationally expensive to be used to simulate all the electrostatic interactions in the system. However unlike dispersion forces long range electrostatic interactions have a large effect on charged particles. To this end a number of methods have been created to calculate the electrostatic potentials acting on charged particles beyond the cutoff. The subsequent section briefly discusses the three methods used in this thesis: Ewald summation, the Particle Mesh Ewald method, and the Particle-Particle Particle-Mesh solver.

2.3.1 Ewald Summation

The most conceptually simplistic mechanism for calculation of long range forces is the Ewald summation. In a periodic and net-neutral system with N particles the Coulomb contribution to potential energy is defined as

$$V_{\text{coul}} = \frac{1}{2} \sum_{i=1}^N q_i \phi(r_i), \quad (2.13)$$

where $\phi(r_i)$ is the global electrostatic potential, acting at position of ion i ,

$$\phi(r_i) = \sum_{j, \mathbf{n}}' \frac{q_j}{|\mathbf{r}_{ij} + \mathbf{n}L|}, \quad (2.14)$$

where $\mathbf{n}$ is the number of periodic representations between particles i and j , $\mathbf{r}_{ij}$ is the distance between the particles, and L is the length of the periodic box. Charged particles interact with their periodic image but crucially do not interact with themselves, (which is implied by the prime sum in Eq. (2.14)). The fundamental problem with using this version of the Coulomb summation is that this sum is only conditionally convergent, and is therefore inappropriate for usage in molecular dynamics

simulations. Ewald summation is a method by which the single non-converging sum is replaced with two converging sums³. Ewald's genius was to realise that performing the summation of an array of screened charges was simpler than the performing the summation for an array of point charges. Eq. (2.14) can be split into a summation of screened charges and the inverse of the screening field. This can be converted into a Fourier series of charges. The resulting Coulomb potential can be treated as summation of three parts. A Fourier component for computation of the long-range electrostatic interactions, a short-range term for calculation of the interaction between screened charges, and a correction for the fact that Ewald summation includes a term for the interaction of a charge with itself. Which gives it the form,

$$\begin{aligned}
 V_{coul} &= \frac{1}{2V} \sum_{\mathbf{k} \neq 0} \frac{4\pi}{k^2} |\rho(\mathbf{k})|^2 \exp(-k^2/4\alpha) \\
 &- \sqrt{\frac{\alpha}{\pi}} \sum_{i=1}^N q_i^2 \\
 &+ \frac{1}{2} \sum_{i \neq j}^N \frac{q_i q_j \operatorname{erfc}(\sqrt{\alpha} r_{ij})}{r_{ij}},
 \end{aligned} \tag{2.15}$$

where the first term is the long range part of the Ewald sum, the second the self correction, and the third the short range term. In Eq. (2.15), α is the screening Gaussian charges' width, erfc is the complementary error function, and $\mathbf{k}$ is defined as,

$$\mathbf{k} = \frac{2\pi}{L} \mathbf{l} \tag{2.16}$$

where $\mathbf{l}$ are the lattice vectors in Fourier space and L is the box length. Finally $\rho(\mathbf{k})$ is defined as,

$$\rho(\mathbf{k}) = \sum_{i=1}^N q_i \exp i\mathbf{k} \cdot \mathbf{r}_i \tag{2.17}$$

³This thesis gives an abridged description of Ewald summation. A full mathematical description of Ewald summation can be found in any comprehensive molecular dynamics textbook, such as *Understanding Molecular Simulation* by Frenkel and Smit [108].

Despite its efficacy Ewald summation is computationally expensive, particularly in larger systems. The computational effort required to perform a Ewald summation is proportional to $N^{3/2}$ where N is the number of particles. For most systems studied in this thesis there are well over 10,000 particles. In order to more efficiently calculate the long-range electrostatic interactions in the studied systems mesh based calculations are used in all cases in this thesis, except for the potential calculations fixed potential simulations. The computational effort required for these mesh based methods is proportional to $N \log N$ making them more appropriate for larger systems. Particle Mesh Ewald (PME) [118] method and the Particle-Particle Particle-Mesh (PPPM) [119] method are described in the next section.

2.3.2 Mesh Based Methods

For large systems the converging Fourier sum used to calculate long range electrostatics in the Ewald summation is not computationally efficient, particularly if a fixed cutoff is used for the short range pairwise interactions. However, if charge is assigned to the discrete lattice points in a mesh the solution of this long-range term becomes far easier: fast Fourier transforms can be used to solve the converging sum when charges are interpolated to mesh lattice points. This hugely increases the efficiency of the calculation. A detailed mathematical explanation of these methods is beyond the scope of this thesis. Here a qualitative and abridged explanation is provided.

Firstly charges that are interspersed throughout the system must be assigned to discrete points on the mesh. This can proceed via a number of methods, however the most popular, and the one used in both the mesh methods in this thesis, treats this as an interpolation problem.

Secondly the potential term must be solved. This is the difference between the PME Method and the PPPM methods. The expressions by which this is achieved

are discussed in detail by Deserno and Holm in the case of PPPM [120, 121] and by Petersen [122] for the PME method.

Finally the resulting field is used to calculate the forces acting on the particles in the system. There are a number of methods by which this can be achieved when using the PPPM solver⁴

These methods allow for more efficient calculation of the long range electrostatics in a system. However all of these methodologies were originally designed for systems that are periodic in all directions⁵. These methods can be adapted to allow for systems with a slab geometry such as lipid bilayers and the capacitors simulated in later chapters of this thesis; slabs are not periodic in the z direction, but periodic in the other two directions. The system can be made periodic by placing a vacuum slab between the two discrete surfaces of the slab. However, this alone is not enough as the two sides of the slab can interact with one and other discretely polarising the slab and creating interaction between periodic images in the z direction. Work by Yeh and Berkowitz showed that some of this error can be corrected for by inclusion of some additional terms [124]. However, the thickness of the vacuum slab being studied is a matter of importance. Generally a vacuum slab three to five times the size of the system is appropriate [124]. However, in the specific case of the fixed charge capacitor type systems studied in Chapters 3 and 4, a previous study by Lynden-Bell *et al.* found that a far smaller vacuum slab is effective [62].

⁴The methods by which this is achieved is detailed in the literature. As for the PPPM solver there are a number of different methods by which this can be achieved.

⁵Long range Coulomb potentials can be calculated for systems which are non periodic using other methods. One such method is the MSM solver developed by Hardy a mesh based method which does not involve the use of fast Fourier transforms. [123]

2.4 Maintaining Temperature and Pressure in Molecular Dynamics Simulations

The previous sections have looked at the calculation of forces in molecular dynamics simulations and the computation of the motion particles over the course of the simulation timestep. However one key issue with regards to molecular dynamics simulations has as of yet not been discussed. For molecular dynamics simulations to model real systems certain thermodynamic conditions may need to be applied. In particular the maintenance of a constant temperature in the canonical (NVT) ensemble and a constant pressure and temperature in the isothermal-isobaric (NPT) ensemble. There are wide variety of methods by which this can be done. A detailed discussion of each of these methods, or all the methods used in this thesis would be too exhaustive for this brief introduction. However the next two paragraphs will briefly introduce some of the methodologies by which pressure and temperature are controlled in molecular dynamics simulations.

Thermostats range from the relatively simplistic weakly coupling Berendsen [125] and V-rescale [126] thermostats which function by coupling the simulation box to an external heat bath, to replacing Newton's laws of motion with Langevin's version, which includes a frictional drag on all the components of the system. This specific yet random drag can be applied to the particles in the system allowing for the maintenance of system temperature within the integration step itself, as opposed to other thermostats where velocities are rescaled at the end of each step. The No se-Hoover thermostat operates via a Hamiltonian which adds an additional set of terms for an external heat bath [127, 128], and can be viewed as being between the weak coupling thermostats, and Langevin dynamics in terms of complexity.

Barostats aim to maintain a constant pressure through the course of a simulation. The Berendsen barostat works by means of weak coupling of the dimensions of the simulation box to the pressure. While the other two commonly used barostats, Nosé-Hoover [127] and Parinello–Rahman [129, 130], are extensions of the Nosé-Hoover thermostat with an additional dimension added for pressure. The key difference between these two more complex barostats is primarily that for the Nosé-Hoover barostat the three box dimensions are coupled whereas for the Parinello–Rahman the three box dimensions can move independently of one another.

2.5 Afterword

This chapter briefly discussed the basic history of computer simulations in chemical science before moving on to discuss the basic methods used in the molecular dynamics simulations in subsequent chapters. More information regarding specific simulation methodologies will be provided in subsequent chapters.

Chapter 3

Propylene Carbonate and Ionic Liquid Mixtures at Charged Interfaces

Chapter 1 of this thesis put forward the many reasons for which ionic liquids are considered to be an exciting, if underutilised, class of electrolytes. However, there is a problem. Ionic liquids consist solely of charged species, meaning the species interact strongly with one another through electrostatic interactions. These strong interactions cause ionic liquids to have a high viscosity, which in turn causes diminished ionic conductivity. It is possible to boost the conductivity of ionic liquids, including the solvate ionic liquids studied in Chapters 4 and 5, by dissolving the ionic liquid in a suitable solvent. These ionic liquid solvent mixtures have reduced viscosity, and thus an increased conductivity. These solutions are applicable as electrolytes in electrochemical devices, which has led to much interest in their nanostructure. This chapter explores the nanostructures of ionic liquid mixtures in one particular solvent, propylene carbonate. This chapter will attempt to explain the structural basis behind the experimental results previously observed by Smith *et al.* [131] (which are described in detail in Section 3.3).

This chapter starts by exploring the properties of mixtures of propylene carbonate with ionic liquid and previous simulations of ionic liquid solutions at interfaces, followed by discussion of the recent experimental results from Smith *et al.* [131]. The main part of this chapter will then present simulation results looking at mixtures of ionic liquid and propylene carbonate at interfaces.

3.1 Properties of Ionic Liquid Solutions

Ionic liquid solutions is a term that will be used in this thesis to describe solutions formed by the dissolution of a room temperature ionic liquid in a solvent. These ionic liquid solutions are distinct from standard inorganic electrolyte solutions in water in some ways and similar in others. The key difference arises from (i) the fact that ionic liquids in solvent can exhibit nanostructure and other properties arising from the complex nature of the molecular ions, and (ii) the interest in very high concentrations, i.e. small fractions of molecular species dissolved in large quantities of salt.

As mentioned in Chapter 1 ionic liquids' high viscosity leads to a diminished conductivity. Dissolution of an ionic liquid in a solvent can cause a decrease in viscosity and thus an increase in conductivity. However, this is something of a balancing act. While concentrated ionic liquids may be poorly conducting due to their viscosity if they are excessively diluted the number of charge carriers becomes the limiting factor. It can be seen in Fig 3.1, which shows change in conductivity with increasing ionic liquid concentration, that there is a maximum in conductivity of concentrations roughly equal to 10% to 20% salt. This curve is typical for ionic liquid solvent mixtures and is shown here for solutions in: acetonitrile, dichloroethane, and propylene carbonate.

Solutions of ionic liquids, with the strong exception of those solutions containing a large amount of water, normally maintain the relatively broad electrochemical window of conventional ionic liquids. However unlike solvate ionic liquids the thermophysical properties of these solutions still exhibit behaviours owing to the pure solvent. For instance ionic liquid solutions will exhibit mass loss on heating above the boiling point of the solvent [6].

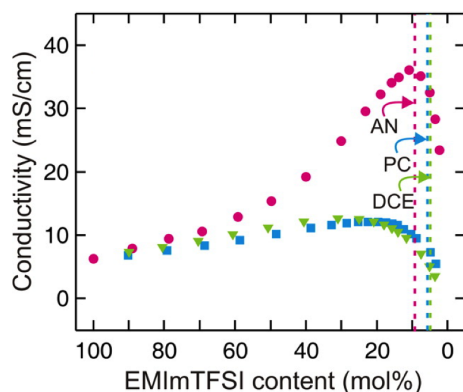


Figure 3.1: A plot from the work of Bozym *et al.* [30] Change in conductivity with concentration for solutions of ethyl-methyl-imidazolium bistriflimide in three solvents: acetonitrile (AN), propylene carbonate (PC), and dichloroethane (DCE). Copyright 2015 American Chemical Society.

3.2 Simulations of Ionic Liquid Solutions at Interfaces

There have been a number of simulations of ionic liquid solutions at interfaces. A number of studies have been performed looking at the effect of the dissolution of ionic liquids in water on the observed interfacial nanostructure. A study by Docampo-Alvarez *et al.* showed the startling effect that the dissolution of a small amount of water in ionic liquids can have on interfacial nanostructure [132].

Further to this, two key papers have been produced on the subject of ionic liquid solutions at charged electrodes. The first study performed by Merlet *et al.* showed a decrease in the extended nature of layering of positive and negative ions with increasing dilution, however the standard structure of positive and negative layers of cations and anions observed in conventional ionic liquid remains [133]. Another study was performed by Vatamanu *et al.* investigating acetonitrile ionic liquid mixtures at electrodes in a ratio of 1 set of ion pairs to 9 solvent molecules [94]. In this study it was reported that there was largely diminished layering with the majority of screening taking place within the first nanometre of the liquid, but with an overscreening like structure still being observed. However in the case of the positive electrode when ionic liquids containing the PF_6 cation are used a differential capacitance more akin

to that observed for the crowded structure was observed. The authors state that this structural effect is due to the incorporation of a large amount of solvent into the interfacial layer and an energy penalty that comes from exchange of a solvent molecule for an anion. Most recently a study by Uralclan *et al.* has shown a decrease in charge density oscillations with increasing dilution, but made little discussion of the interfacial nanostructure [82].

While these pioneering studies provide insight into the nanostructure of ionic liquid solutions, all show continuation of the overscreening regime at negatively charged electrodes, and therefore none of the papers provide a definitive explanation for the results presented by Smith *et al.* [131]. Further to this prior to work described in this thesis there appears to have been no work simulating the interfacial nanostructure of ionic liquid propylene carbonate mixtures, in spite of these liquids possible usage in supercapacitors.

3.3 Surface Force Balance Studies of Ionic Liquid Solutions

The rest of this chapter will seek to explain and expand on the experimental results obtained by Smith *et al.* [131]. This study presented Surface force balance (SFB) measurements on mixtures of the ionic liquid butyl-methyl-pyrrolidinium bistriflimide ([BMPyr][TFSI]) and Propylene Carbonate. SFB experiments measure the forces between two surfaces with a nano-confined liquid between them. By use of white light interferometry the SFB is able to measure surface separation on the order of Ångstroms. The surfaces normally consist of atomically smooth Muscovite mica. The force between the surfaces is measured by placing a spring of known stiffness behind one surface. By measuring the deflection of this spring the force between the surfaces can be measured using Hooke's law. When the surfaces are separated on the order of single nanometres application of force leads to jumps in distance on the order of 0.1 to 15 nm. These jumps are due to the "squeezing out" discrete layers of liquid.

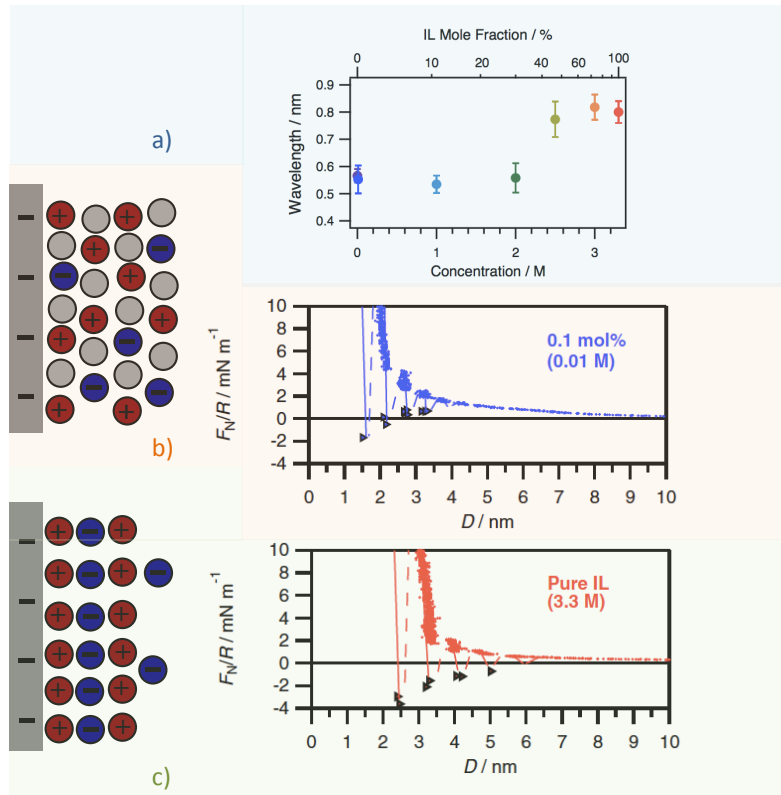


Figure 3.2: Plots adapted from Smith *et al.* [131]. panel b) shows the SFB force profiles for $x_{\text{IL } 0.1} = 0.1$, while panel c) is for the force profile for pure ionic liquids. The two cartoons on the left show the specific interfacial structures suggested to be causing the different layer thicknesses in these force profiles. These plots show the two regimes of layer thickness with the upper plot showing a layer thickness of 0.55 nm and the lower plot showing a layer thickness of roughly 0.8 nm. The bottom plot shows the discontinuity in layer thickness observed by Smith *et al.* which is the feature this chapter seeks to explain.

Due to the dissolution of the potassium ions on the mica surface in the ionic liquid mica has a strongly negative surface charge in these experiments. While the exact value of the surface charge is highly dependent on the liquid in the gap it has been estimated for ionic liquids that it is equal to $-19 \mu\text{C}/\text{cm}^2$ [1]. At this surface charge ionic liquids exhibit the overscreening type structure which consists of layers of counter-ions and co-ions discussed in the introductory chapter, and shown in Fig. 1.7. When an SFB force profile of an ionic liquid in the overscreening regime is recorded the layers of liquid squeezed out have a thickness of two ionic radii, as shown in Fig. 3.2. Smith *et al.* [131] found that as the ionic liquid was dissolved in propylene

carbonate, and the ionic liquid mole fraction is decreased, at first the thickness of layers did not change, as shown in Fig. 3.2, however at a certain concentration of ionic liquid, somewhere between 2.0 mol/dm^3 and 2.2 mol/dm^3 , the layer thickness suddenly decreased. Smith *et al.* proposed that this was due to a transition from layering defined by the width of two ion pairs, to layering defined by the width of a single molecule.

The cartoons on the left side of Fig. 3.2 present a basic portrait of the interfacial nanostructure which could cause such force profiles. This chapter aims to see to what extent this portrait is true while going further to understand the underlying behaviours with varying surface charge. This will be achieved by the use of high throughput molecular dynamics simulations.

3.4 Methodology

The rest of this chapter presents simulations looking at the effect of dissolution of ionic liquids in propylene carbonate on the observed nanostructures. This section discusses the methodology used for the simulations. The section will start by discussion of the chosen force field, including a brief look at the bulk interactions in these liquids.

After this the section will move on to discussing the methodology used for the interfacial simulations presented in the rest of this chapter.

3.4.1 Force field Choice

Simulations in this chapter use force fields based on the OPLS-AA parameters [112]. For the ionic liquids the OPLS-AA derived CL&P force field is used [100, 134]. While for propylene carbonate standard OPLS-AA parameters are used. The partial charges on the propylene carbonate molecule are set to be the same as a previous study by You *et al.* [135, 136], which successfully replicated the experimental dielectric constant. The exact forms of the force fields used in these simulations are detailed in

the Appendix A, the simulations are run with $\varepsilon_r = 1.6$ to model the effects of polarisability of ions [137], the charges on propylene carbonate molecules are scaled up to maintain the same dielectric constant.

3.4.2 Bulk Simulations

In order to verify the force field choice and develop a stronger understanding of the nature of the ionic liquid nanostructure bulk simulations of the ionic liquids were performed for mixtures of the ionic liquid [BMPyr][TFSI] and propylene carbonate, the same salt and solvent used by Smith *et al.* [131]. The simulations were performed for mole fractions of ionic liquid, x_{IL} , of: 1.0, 0.8, 0.6, 0.5, 0.4, and 0.2. The upcoming paragraphs will present the methodology used for these simulations, followed by discussing the results obtained in these bulk simulations. These paragraphs will both justify the use of this force field to study the interfacial nanostructure of ionic liquid propylene carbonate mixtures, and provide a degree of context to the interfacial simulations.

3.4.2.1 Bulk Simulation Methodology

The bulk simulations were performed using the Gromacs 2016 molecular dynamics software [103, 138–143]. The number of ions in each bulk box are described in Table 3.1, the specific number of each species are packed into simulation boxes using the Packmol algorithm [144]. The simulation is then stabilised by means of steepest decent energy minimisation, followed by performance of a brief equilibration run of 0.5 ns using the V-rescale thermostat and the Berendsen barostat [125].¹ The system is then annealed over the course of 3 ns from 300 K to 500 K and back. This is followed by a 2 ns equilibration run and a 18 ns² production run at 300 K. For all steps

¹The Berendsen barostat is used for the first brief period of simulation due to its greater stability over the more accurate Parinello-Rahman barostat used in subsequent steps.

²A length of time roughly an order of magnitude greater than the relaxation time of pure ionic liquids.

after the first 0.5 ns run the timestep used is 2 fs and the simulations are run using the Parinello-Rahman Barostat [129, 130] and the V-rescale thermostat [126]. For all runs a timestep of 2 fs is used.

Electrostatic and van der Waals cutoffs of 1.2 nm were employed throughout the simulations while long range electrostatics were calculated by means of the Particle Mesh Ewald (PME) method with a Fourier spacing of 0.16 nm and a PME order of 4 [124, 145]³.

Table 3.1: Table showing the composition of bulk simulation boxes studied.

X_{IL}	N_{cations}	N_{anions}	N_{PC}
1	200	200	0
0.8	200	200	50
0.6	200	200	100
0.5	200	200	200
0.4	200	200	300
0.2	100	100	400

3.4.2.2 Bulk Simulation Results

There are three main results of these simulations which are of interest: the simulated density, the correlation functions of cations, anions, and propylene carbonate molecules with themselves and each other, and finally the mean square displacement of each species within each system. Each of these will now be discussed in turn.

The density of the simulated mixtures of [BMPyr][TFSI] is reported in Table 3.2. These values are within 4% of the experimentally achieved values [146], which is about standard for force fields of this kind. These densities will later be used in order to produce simulation boxes.

The mean square displacement of molecules and ions in the liquid are reported in Fig. 3.3, and the calculated diffusion coefficient are shown in Table 3.3. All the plots in Fig. 3.3 show a progressive linear increase, and hence show that the solutions are

³A PME order of 4 corresponds to cubic interpolation of charges onto grid points.

Table 3.2: Table showing the simulated densities of solutions of [BMPyr][TFSI] in propylene carbonate.

$x_{IL}/$	Density g/cm ³
1	1.45
0.8	1.44
0.6	1.42
0.5	1.40
0.4	1.39
0.2	1.35

all in the liquid state in the simulations. However, there are two further points to be taken from the transport properties of these solutions. Firstly, increasing dilution leads to an increase in the diffusion constant of every component of the solution by roughly the same factor, a fact that is evident on inspection of the diffusion constants in Table 3.3. This is the reasoning behind the dissolution of ionic liquids in polar solvents for the use in electrochemical devices, the decreased viscosity leads to an increased conductivity. Secondly it can be noticed that the diffusion constant for the propylene carbonate molecules is roughly double the value observed the ionic component in each solution. This is not unexpected, as in most solutions the charged ions are likely to interact more strongly with the other components of the solution causing them to diffuse more slowly.

Table 3.3: Table showing the diffusion constants of each component within each of the studies solutions.

x_{IL}	$D_{BMPyr}/1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	$D_{TFSI}/1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	$D_{PC}/1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
1	0.0017	0.0024	
0.8	0.0023	0.0022	0.0060
0.6	0.0036	0.0032	0.0075
0.5	0.0073	0.0064	0.0131
0.4	0.0099	0.0113	0.0212
0.2	0.0261	0.0305	0.0543

The pair correlation functions for species in these mixtures are reminiscent of those observed for conventional molten salts such as lithium chloride for which the

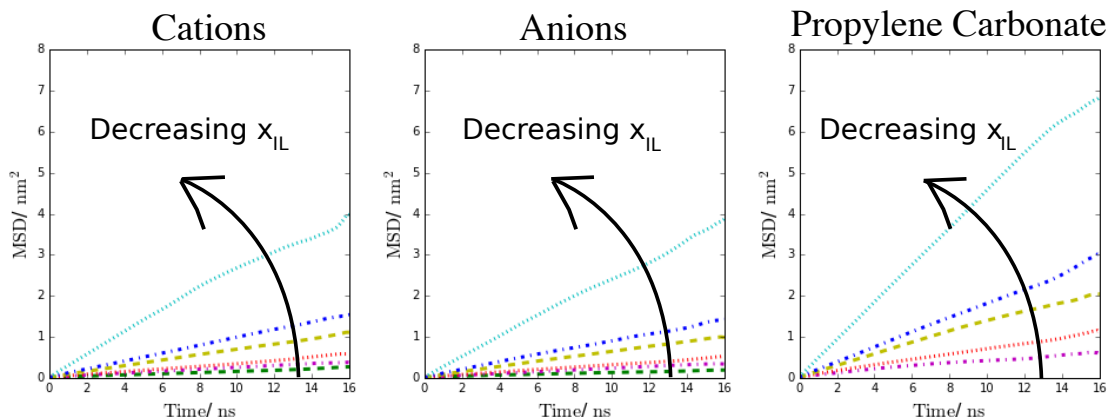


Figure 3.3: Plots showing the simulated mean square displacement of constituent components in the [BMPyr][TFSI] propylene carbonate solutions. The plot for $x_{IL} = 1$ is shown in green, The plot for $x_{IL} = 0.8$ is shown in magenta, $x_{IL} = 0.6$ is shown in red, $x_{IL} = 0.5$ is shown in yellow, $x_{IL} = 0.4$ is shown in dark blue, and $x_{IL} = 0.2$ is shown in cyan.

neutron diffraction determined pair distribution function is shown in Fig. 3.4. Looking at the forms of the pair correlation functions it is possible to see the peaks in the Li-Cl correlation function occur at the same distance as the troughs in the Li-Li and Cl-Cl correlation functions (indicated by the red lines). In the contrary case the troughs in the Li-Cl correlation function occur at the same distances as the peaks in the Li-Li and Cl-Cl correlation function (indicated by blue lines). The reason for the first peak occurring at a shorter distance in the Li-Cl plot is due to the electrostatic attraction between unlike charged ions and occurs at a distance of two ionic radii, the first peak in the Li-Li and Cl-Cl plots occurs at a distance equivalent to four ionic radii, and is representative of a chain of co-ion, counter-ion, co-ion, an arrangement that is favourable due to electrostatic interactions.

Fig 3.5 shows pair correlation functions between cations and cations, anions and anions, and cations and anions in the studied ionic liquid propylene carbonate solutions. As with the molten salt in the pure ionic liquid the oscillations in the cation-cation pair distribution function, $g(r_{cc})$, and the anion pair distribution function, $g(r_{aa})$, are located in the same location, with peaks and troughs occurring with a

periodicity equivalent to two ionic radii. However, unlike with the LiCl pair distribution function the oscillations in $g(r_{aa})$, and $g(r_{cc})$ have roughly the same magnitude. As with the LiCl $g(r_{ca})$, is offset so that peaks in $g(r_{ca})$ occur at the location of troughs in the other two pair distribution functions, and vice versa.

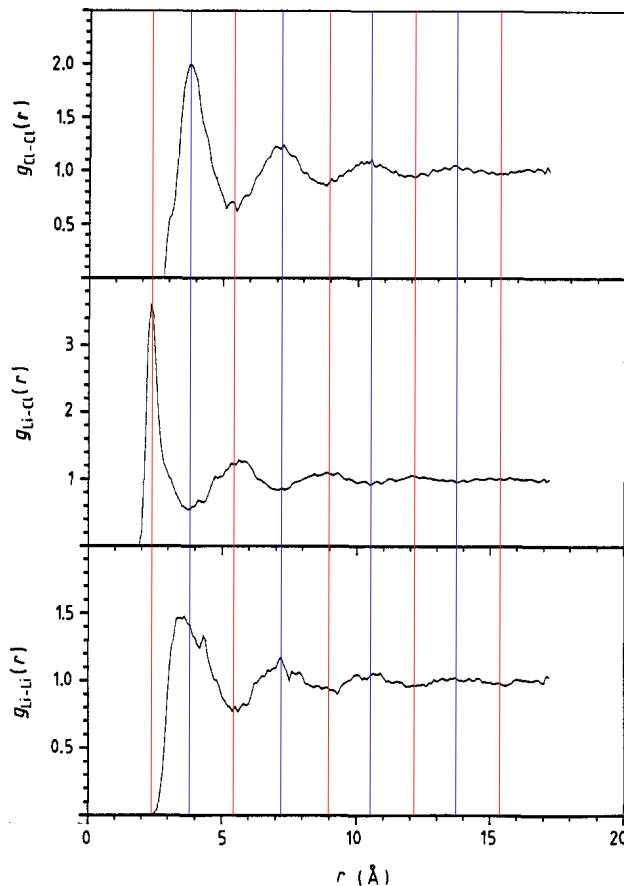


Figure 3.4: Pair correlation functions, $g(r_{ij})$, experimentally obtained before by McGreevey *et al.* [147]. The red and blue lines indicate the periodicity of the peaks and troughs in the pair correlation function.

Looking now to the effect of increasing dilution. In Fig.3.5 increasing dilution leads to little to no changes in the locations at which the peaks and troughs occur. The oscillations in the pair correlation functions are damped, and as pair correlation functions are normalised with respect to the density of the second species within the system, the decrease in order is not an effect of a decrease in the absolute number of ions, but in fact a decline in the ordered nature of the coordination shell. This

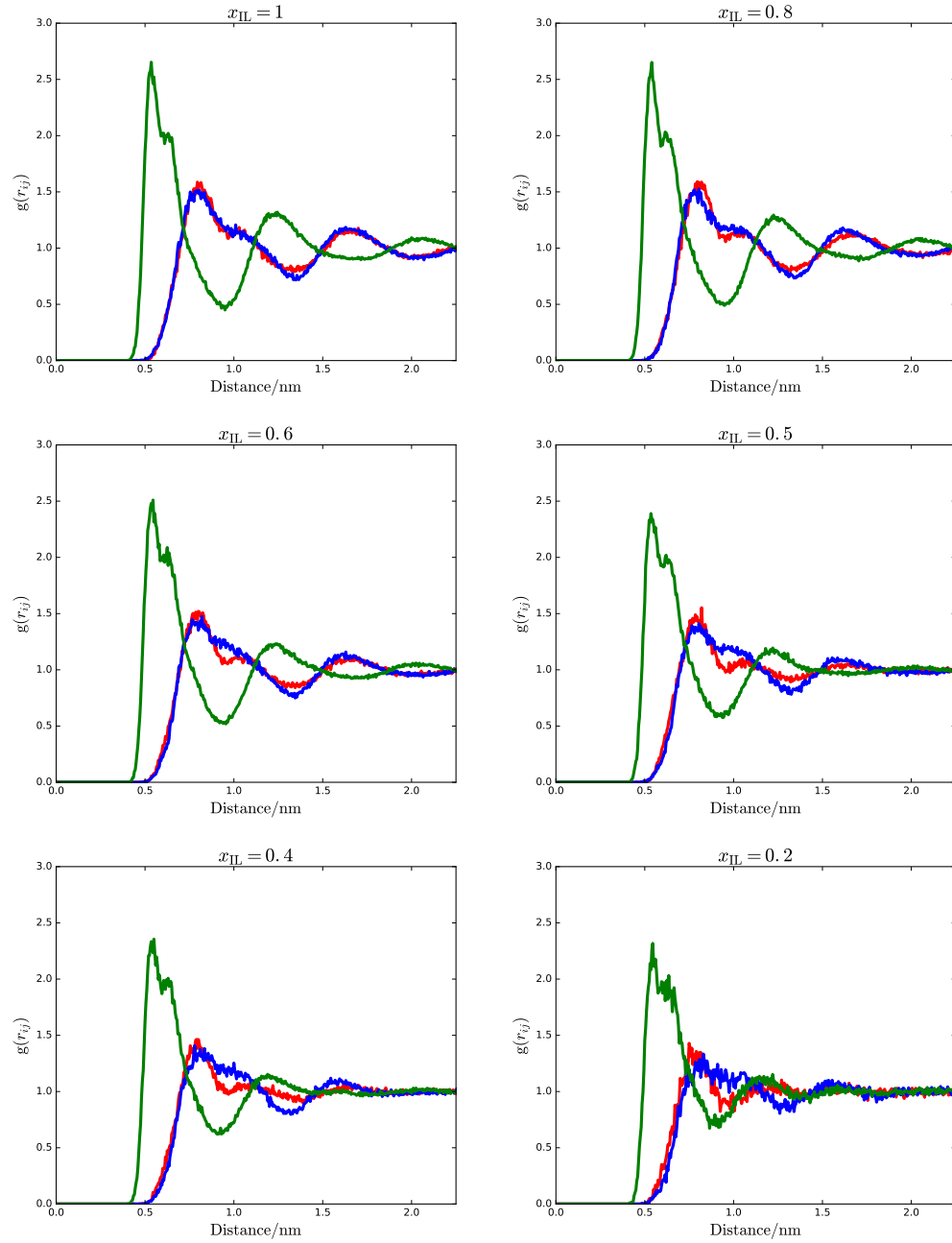


Figure 3.5: Pair correlation functions, $g(r_{ij})$, for cations and cations, shown in red, anions and anions, shown in blue, and cations and anions shown in green. The location is taken as its centre of geometry. Each panel corresponds to a different studied ionic liquid solution mole fraction.

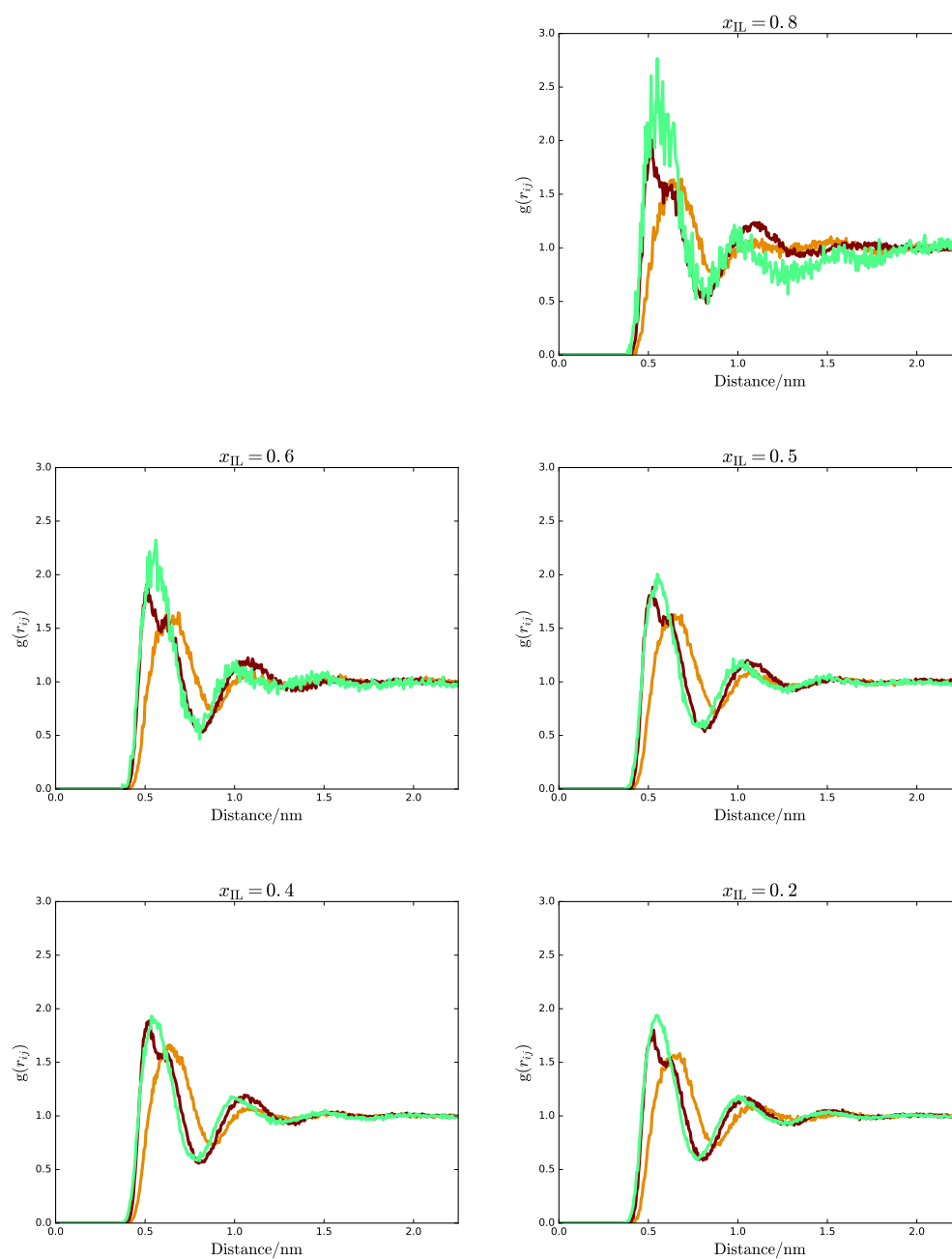


Figure 3.6: Pair correlation functions, $g(r_{ij})$, for propylene carbonate and cations, shown in gold, propylene carbonate and anions, shown in claret, and propylene carbonate and propylene carbonate shown in leaf green for each mole fraction studies. The location of each species is taken as its centre of geometry.

dampening is so great that for the highest propylene carbonate mole fraction in Fig. 3.5 oscillations are damped completely before reaching the end of the plot.

Fig 3.6 shows the pair correlation functions between propylene carbonate molecules in the mixtures, and each of the three species in the solution. Study of this graph shows little change in the form of the plots with increasing dilution between propylene carbonate and any other species in the liquid. This suggests that the propylene carbonate is distributed evenly throughout the liquid. Suggesting propylene carbonate does not specifically gravitate towards either cations or anions; or phase separate into nanoscopic domains separate from other components.

3.4.3 Methodology for Interfacial Simulations

Two different sorts of simulation were performed to study the nano-structure of propylene carbonate ionic liquid mixtures. Firstly, interfacial simulations of the model capacitor were performed for a variety of liquids at a range of surface charges. Secondly two specific mole fractions were chosen for a further study by means of calculation of the potential of mean force between a probe particle, diluted in ionic liquid solution, and the interface. These potentials of mean force provide a potential energy environments which are indicative of the liquid surroundings of the probe in each system. The two different methodologies are described below in further detail.

Simulations of ionic liquid propylene carbonate solutions were performed using the Gromacs 2016 molecular dynamics software [103, 138–143]. The structure of the simulated system, shown in Fig. 3.7, is similar to previous simulations [59, 62]. It consists of two graphene interfaces 12.6410 nm apart. Each interface has dimensions of 3.4080 nm by 3.4433 nm. The carbon molecules in these electrodes are frozen in space for the duration of the simulation.

The number of ion pairs and propylene carbonate ions used in simulations for each molefraction are listed in Table 3.4. Systems were packed at bulk density using the

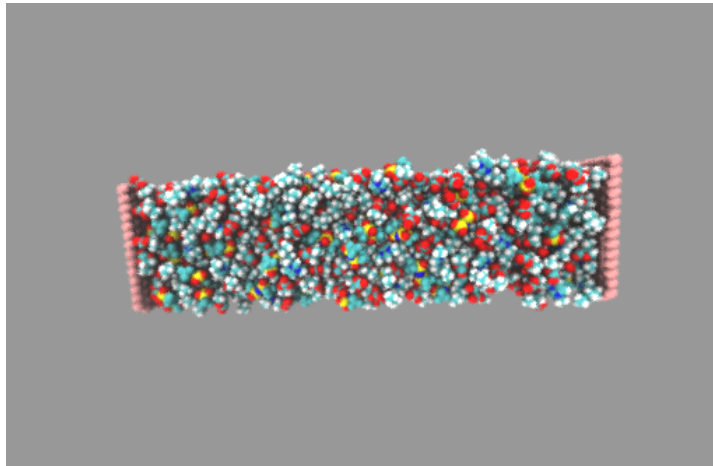


Figure 3.7: Snapshot of the simulated system. The snapshot shows a slab of liquid confined between two graphenes, which have a peach colouration in the image.

Packmol algorithm [144] followed by steepest descent energy minimisation, and a low timestep run of 20,000 steps to create stable initial starting configurations. At this point the electrodes within the system are charged equally and oppositely. The two electrodes have an equal and opposite charge applied to them in order to maintain charge neutrality. Box dimensions are chosen in order to allow for the potential and charge density oscillations to tend to zero at the centre of the box. With charges from $0 \mu\text{C}/\text{cm}^2$ to $\pm 37 \mu\text{C}/\text{cm}^2$ in steps of $1 \mu\text{C}/\text{cm}^2$ are applied. Each replica is annealed from a temperature of 300 K to 450 K and back over the course of 2 ns. A further 1 ns equilibration run is performed at 300 K. A production run was performed at a temperature of 300 K for 2 ns with this process. All timesteps after charging are of 1 fs in length. The temperature is maintained using the V-rescale thermostat [126]. The Coulomb and van der Waals cutoffs were set to 1 nm. Long-range electrostatics are performed using the Particle Mesh Ewald Method, with a slab geometry with a Fourier Spacing of 0.14 nm and a PME order of 4 and using a slab correction to allow for the use of a three dimensional PME [124, 145]. The vacuum between the electrodes has a width of 5.2 nm. This process is performed for three replicas.

Potentials of mean force were calculated using a related, but not wholly identical method. The box is generated with the same number of cations and anions, however, one of the cations in the system is replaced with a single positive probe particle in a manner similar to previous work [62]. This probe has a σ value of 0.5 nm and an ε value of 0.619 kJmol⁻¹ and a charge of +1 e. The probe particle is initially held at a fixed distance of 5 nm from the electrode. The simulation systems are again created through means of Packmol algorithm [144] followed by steepest descent energy minimization, and a low timestep equilibration run. The system is annealed from 300 K to 450 K and back over the course of 5 ns. At this point centre of mass pulling is used to pull the probe from its starting location to the interface over the course of 4.85 ns. The probe is pulled with a speed of 0.001 nm/ps. Snapshots are taken every 0.05 ns generating a set of snapshots with probes with distances from the interfaces from 0.15 nm to 5 nm in steps of 0.05 nm. A 1 ns production run is then produced for each of the snapshots. The forces acting on the probe every picosecond are recorded and averaged. A potential of mean force acting on the probe is then calculate by integrating the forces acting on the probe as it approaches an interface.

In all calculations of number density of the species from the simulated trajectories in this section a bin size of 0.01 nm is used, while the bin size for charge density calculations is 0.001 nm.

Table 3.4: Table showing the composition of interfacial simulation boxes studied.

x_{IL}	N_{cations}	N_{anions}	N_{PC}
1	300	300	0
0.8	284	284	71
0.6	256	256	169
0.5	238	238	238
0.4	214	214	321
0.2	143	143	572

3.5 Proposal of a Framework for Understanding Ionic Liquid Solutions at Interfaces

In Section 1.3 the interfacial nanostructures adopted by ionic liquids at electrified interfaces were introduced. It was described that the structure goes through a number of different transitions with changing surface charge, further to this, this section introduced a quantity κ_{ion} , a reduced surface charge which has a value of 1 when the interfacial nanostructure transitions from a charged multilayer structure to a crowded structure. For conventional ionic liquids the value of κ is calculated by means of the equation,

$$\kappa_{ion} = \left| \frac{\sigma}{\theta_{ion}^{max}} \right| \quad (3.1)$$

where σ is the absolute surface charge, and θ_{ion}^{max} is the maximum counter-ion density in the first interfacial layer of the ionic liquid nanostructure. However the presence of an additional component, the propylene carbonate molecules, leads to a more complex situation and thus an extended version of this equation is required,

$$\tilde{\kappa}_{ion} = \left| \frac{\sigma}{\theta_{ion}^{layer}} \right|, \quad (3.2)$$

where $\tilde{\kappa}_{ion}$ is an expanded version of κ_{ion} , and θ_{ion}^{layer} is the density of counter-ions in the first interfacial layer at that surface charge. Later in this chapter it will be shown that θ_{ion}^{layer} can be assumed to be dependent on both the amount of propylene carbonate incorporated in the first interfacial layer and the charge dependence of cation density. Allowing θ_{ion}^{layer} to be written as,

$$\theta_{ion}^{layer} = \theta_{ion}(\sigma) \cdot (1 - f_{v,PC}), \quad (3.3)$$

where $\theta_{ion}(\sigma)$ is the surface charge dependent density of counter-ions in the first interfacial layer, and $f_{v,PC}$ is the volume fraction of propylene carbonate molecules in the first interfacial layer. The necessity and effect of each of these terms will be described in detail in the coming sections.

3.6 The Interfacial Nanostructure of [BMPyr][TFSI] Propylene Carbonate Mixtures

The interfacial nanostructure of pure [BMPyr][TFSI] is described in Fig. 3.8. The liquid-solid interface was studied over a range of surface charges between $-37 \mu\text{C}/\text{cm}^2$ and $+37 \mu\text{C}/\text{cm}^2$. The colourmap in this figure, as well as all other colourmaps in this Chapter, plot the value $\Delta\rho$ which is defined as,

$$\Delta\rho = \rho_+ - \rho_-, \quad (3.4)$$

where ρ_+ is the number density of cations, and ρ_- is the number density of anions. The plots on the right hand side of the figures are traces of the number density of the three components of the ionic liquid mixtures, ρ_+ , ρ_- , and ρ_{pc} . Propylene carbonate density is shown in green, cation density is shown in red, and anion density is shown in blue. The bin width for all the linear density plots in this section is 0.01 nm. The ion locations are taken as the weighted location of certain heteroatoms within the liquid, which are highlighted in the graphical legend of Fig. 3.8 and all subsequent figures.⁴ The structure of the pure ionic liquid will be described before moving on to discuss the effect of dilution.

There are strong blue and red bands at the closest distance from the electrode in the colourmap in Fig. 3.8. This is correlated with a strong excess of counter-ions in

⁴Weighted number densities of individual atoms within ions are used to locate ions instead of centroids owing to blurring of the first interfacial layer caused by centroiding.

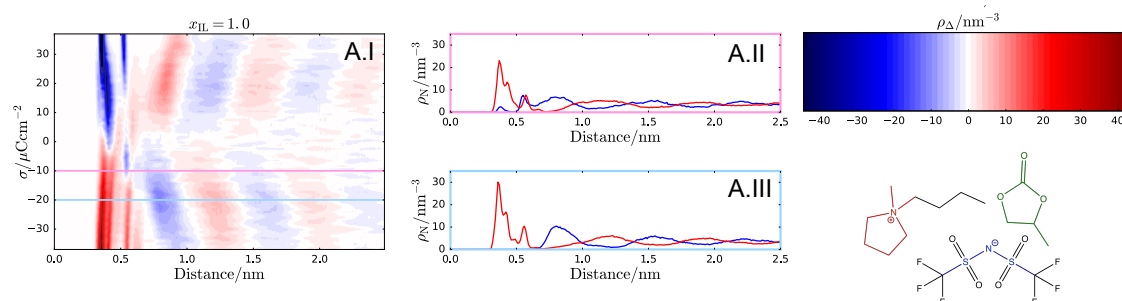


Figure 3.8: Plots demonstrating the interfacial nanostructure of pure [BMPyr][TFSI]. The colourmap on the left show the variation of $\Delta\rho$ with distance from the surface and for varying surface charge between $-37 \mu\text{C}/\text{cm}^2$ to $+37 \mu\text{C}/\text{cm}^2$. Negative values, (anionic surplus) shown in blue and positive values (cationic surplus) shown in red. On the right hand side exemplar traces of number density of each component with distance are shown. The number density of propylene carbonate is shown in green, cations ring atoms are shown in red and the core of the anion are shown in blue. The exemplar traces are taken for a surface charge of $-10 \mu\text{C}/\text{cm}^2$, in the pink box, and $-20 \mu\text{C}/\text{cm}^2$ in the blue box. The graphical legend shows which atoms are used to indicate each component: the cation ring is shown in red, the anion core is shown in blue, and the propylene carbonate is shown in green.

the first interfacial layer (as has been shown in the previous studies discussed in Section 1.3). For systems where $\sigma \approx 0 \mu\text{C}/\text{cm}^2$ these bands appear to have disappeared to be replaced by a mixture of blue and red, which could be indicative of a mixed interfacial layer. These structures in the first interfacial layer are closely correlated with two different long range structures. For the cases with strong counter-ion enrichment in the first interfacial layer, indicated by the strong blue and red bands closest to the interface, there are normally alternating blue and red bands with increasing distance from the interface. This is indicative of the multilayer structure, which is characteristic for conventional ionic liquids. For the case of $\sigma \approx 0 \mu\text{C}/\text{cm}^2$ this extended layering is not observed as in previous simulations. The traces to the side of the main plot show that this structure arises from oscillations of cation and anion number density. Looking specifically at panel A.III which shows the nanostructure at $-20 \mu\text{C}/\text{cm}^2$. The surface charge which has previously be shown to be the estimated surface charge of mica in these liquid mixtures [131]. This oscillatory structure is

correlated with the measured SFB layering with a magnitude of two ion diameters. It is worth noting that for the pure liquid the crowded structure is not observed in the range of surface charges studied.

Moving on to look at the effect of the variation of ionic liquid mole fraction on the interfacial nanostructure, which is reported in Fig. 3.9 for pure liquids and solutions with $x_{\text{IL}} = 0.8$, and $x_{\text{IL}} = 0.6$, and in Fig. 3.10 for solutions with $x_{\text{IL}} = 0.5$, $x_{\text{IL}} = 0.2$, and $x_{\text{IL}} = 0.4$, there are a number of key facts to observe. First and foremost the magnitude of the oscillations in the areas where the multilayer structure (indicated by the alternate bands of blue and red in the colourmap) is observed to decline with decreasing ionic liquid mole fraction. For instance the oscillations in the traces for panels A-F.II decline with decreasing ionic liquid mole fraction. This is somewhat to be expected because as the ionic liquid is diluted, the absolute density of ions in the capacitor decreases. This effect can be related to the decrease in the experimentally measured decay length in the related overscreening repulsion with increasing dilution of the ionic liquid observed in SFB experiments [131]. Further to this however the number of oscillations observed in the multilayer regime also decreases with increasing dilution for similar reasons. For instance there is a large collapse in the number of oscillations in traces A.III, B.III, and C.III with increasing dilution. This effect can also be observed in the colourmaps where the structure of consecutive blue and red bands can be visibly seen to weaken with decreasing mole fraction of ionic liquid. The reasons for this are multiple, however one effect, which also leads to the smaller oscillations with the layering structure, is the role of propylene carbonate in screening charges within all layers, and in particular the first interfacial layer, which will be discussed in more detail in Sections 3.8 and 3.11.

There is an even more striking trend observed for higher surface charges. It was previously stated that the crowded structure is not observed for the pure ionic liquid at the studied surface charges. For ionic liquid mixtures a nanostructure somewhat

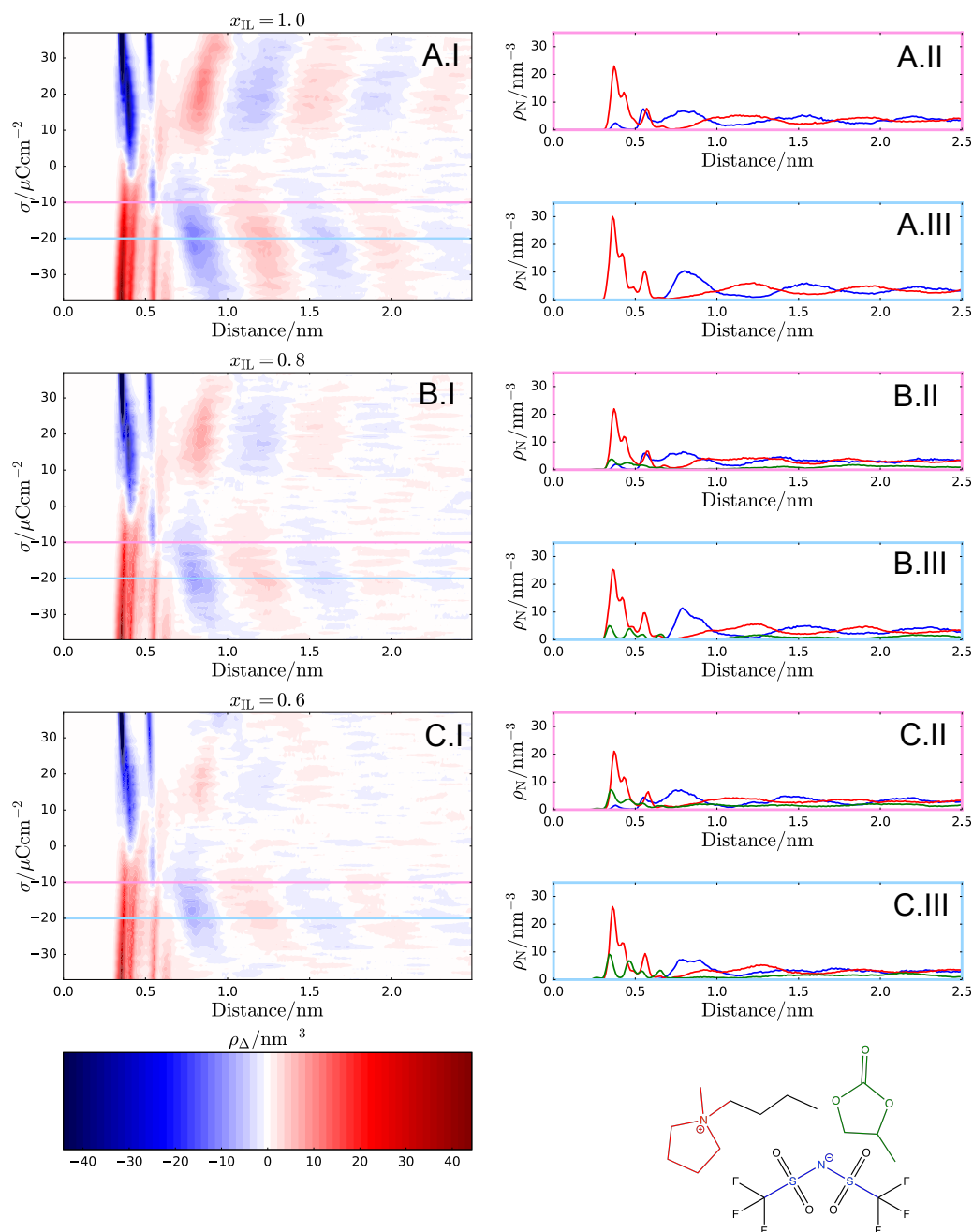


Figure 3.9: Plots demonstrating the interfacial nanostructure of [BMPyr][TFSI] propylene carbonate solutions for ionic liquid mole fractions of $x_{IL} = 1$, $x_{IL} = 0.8$, and $x_{IL} = 0.6$. The colourmaps on the left show the variation of $\Delta\rho$ with distance from the surface and for varying surface charge between $-37\mu\text{C}/\text{cm}^2$ to $+37\mu\text{C}/\text{cm}^2$. Negative values, (anionic surplus) shown in blue and positive values (cationic surplus) shown in red. On the right hand side exemplar traces of number density of each component with distance are shown. The number density of propylene carbonate is shown in green, cations ring atoms are shown in red and the core of the anion are shown in blue. The exemplar traces are taken for surface charges of $-10\mu\text{C}/\text{cm}^2$, in the pink box, and $-20\mu\text{C}/\text{cm}^2$ in the blue box. The graphical legend shows which atoms are used to indicate each component: the cation ring is shown in red, the anion core is shown in blue, and the propylene carbonate is shown in green.

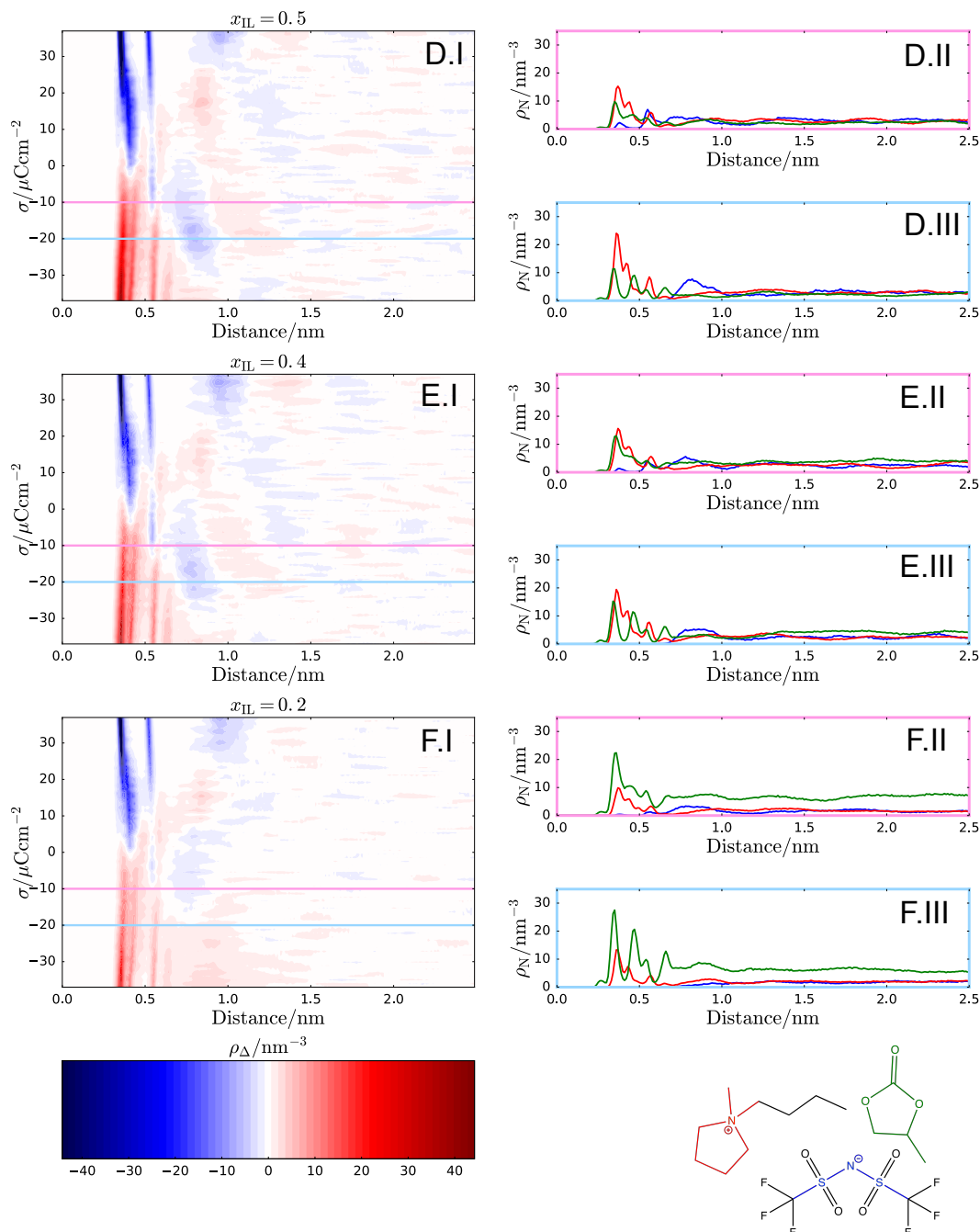


Figure 3.10: Plots demonstrating the interfacial nanostructure of [BMPyr][TFSI] propylene carbonate solutions for ionic liquid mole fractions of $x_{\text{IL}} = 0.5$, $x_{\text{IL}} = 0.4$, and $x_{\text{IL}} = 0.2$. The colormaps on the left show the variation of $\Delta\rho$ with distance from the surface and for varying surface charge between $-37\ \mu\text{C}/\text{cm}^2$ to $+37\ \mu\text{C}/\text{cm}^2$. Negative values, (anionic surplus) shown in blue and positive values cationic surplus shown in red. On the right hand side exemplar traces of number density of each component with distance are shown. The number density of propylene carbonate is shown in green, cations ring atoms are shown in red and the core of the anion are shown in blue. The exemplar traces are taken for surface charges of $-10\ \mu\text{C}/\text{cm}^2$, in the pink box, and $-20\ \mu\text{C}/\text{cm}^2$ in the blue box. The graphical legend shows which atoms are used to indicate each component: the cation ring is shown in red, the anion core is shown in blue, and the propylene carbonate is shown in green.

reminiscent of the crowded structure can be seen within the studied range of surface charges⁵. This can be observed in the colourmaps in Fig. 3.10. In these colourmaps at the most negative charges there are no oscillations in $\Delta\rho$, which is observed as an extended area of pure red in the colourmap. This is observed for charges in excess of $-15 \mu\text{C}/\text{cm}^2$ for $x_{\text{IL}} = 0.2$ (as shown in panel F.I Fig. 3.10), surface charges of over $-20 \mu\text{C}/\text{cm}^2$ for $x_{\text{IL}} = 0.4$ (as shown in panel E.I Fig. 3.10), and at surface charges of about $-30 \mu\text{C}/\text{cm}^2$, for $x_{\text{IL}} = 0.5$. Looking at the traces in panel F.III there is an area of persistent cation excess for at least two molecular diameters from the interface. The relationship between mole fraction of ionic liquid, surface charge, and interfacial structure is made clear by the phase diagram in Fig 3.11. The surface charge at which the multilayer structure gives way to this crowding like structure appears to be dependent on a number of factors.

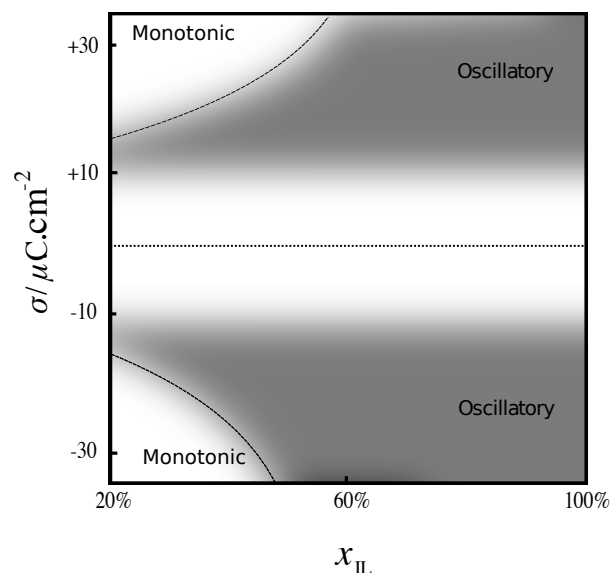


Figure 3.11: A surface charge versus composition phase diagram for [BMPyr][TFSI] propylene carbonate solutions at charged electrodes. The regions are marked to indicate either oscillatory or monotonic decay of the charge distribution away from the electrode. The diagram was constructed directly from Figs. 3.9 and 3.10. The lines between the oscillatory and monotonic regions correspond to the point at which the transition is observed in the simulation.

⁵It is not clear whether an interfacial nanostructure in a two component system can be described as the crowded structure, therefore in this thesis structures that look like the crowded structure with ionic liquid mixtures will be described as being pseudo-crowded, or exhibiting monotonic decay

Looking at Fig. 3.11 from the perspective of Eq. (3.2) and Eq. (3.3), certain additional information can be understood. The black lines between the monotonic and oscillatory regions are the values of surface charge for which $\kappa = 1$. From Eq. (3.2),

$$\tilde{\kappa}_{ion} = \left| \frac{\sigma}{\theta_{ion}^{layer}} \right|, \quad (3.2)$$

and it can be understood that this must be due to a changing value of θ_{ion}^{layer} with increasing dilution of the ionic liquid mixture. If this is the case there should be a visible change in counter-ion density in the first interfacial layer.

To understand how θ_{ion}^{layer} changes with mole fraction, it is useful to look at the interfacial density of cations and anions with changing surface charge. Fig. 3.12 shows the number density of cations and anions present in the first interfacial layer of ionic liquid⁶. There are a number of features in the interfacial density of anions and cations that deviate from that for a pure ionic liquid. Firstly, in all cases the number density of all ionic species in the interfacial region declines with increasing mole fraction of propylene carbonate. Secondly, there is, with a notable exception, relatively little change in the form of the curves with increasing mole fraction of propylene carbonate. This data mostly fits the simplified model in Eq. (3.2) decreasing ionic liquid mole fraction is correlated with a decrease in θ_{ion}^{layer} which would in turn lead to the previously observed decrease in absolute surface charge for which κ is equal to one.

The notable exception to this is the curve for solutions where $x_{IL} = 0.2$, which appears to have a form which consists of two plateaus and two sharp rises. The reason for this shape is unknown, but may be due to the charge dependence of ion packing density, which will be discussed later in this chapter.

The density of cations in the interfacial layer is higher than for anions at the equal and opposite charge (with the partial exception of systems where $x_{IL} = 0.2$). This

⁶The propylene carbonate incorporation in the interfacial layers is more complex due to the ambiguity in where the cutoff should be placed and is therefore not presented.

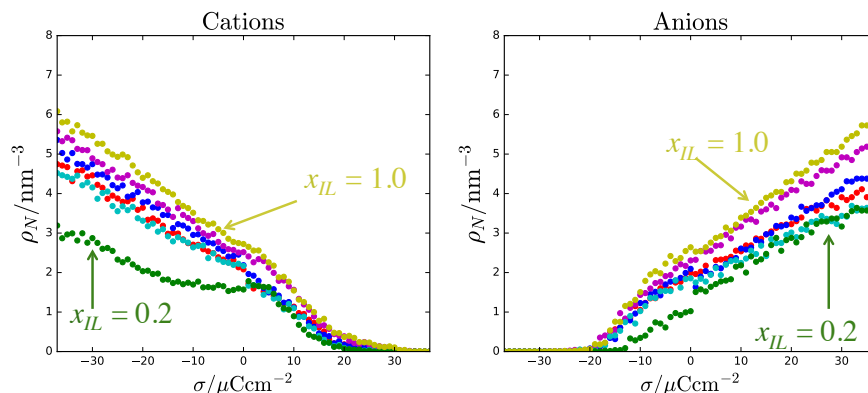


Figure 3.12: The interfacial number density of cations and anions within 0.7 nm of the interface for all surface charges studied. $x_{IL} = 1$ is shown in gold, $x_{IL} = 0.8$ is shown in magenta, $x_{IL} = 0.6$ is shown in dark blue, $x_{IL} = 0.5$ is shown in red, $x_{IL} = 0.4$ is shown in cyan, and $x_{IL} = 0.2$ is shown in green.

runs counter to the smaller size of the anions compared to cations. There could be a number of reasons for this, however, it is likely due to either the greater favourability of mixing of propylene carbonate with anions compared with pyrrolidinium cations, or the strong interactions between the propylene carbonate molecule and the positive electrode, which will be described later in this chapter.

This section has discussed the interfacial structure of solutions of [BMPyr][TFSI] in propylene carbonate. The results presented here provided a tantalising glimpse as to the possible structure adopted by mixtures of [BMPyr][TFSI] and propylene carbonate. And the changes in this structure with increasing dilution of ionic liquid. While these results are interesting it is possible to look at this structure by means of another method generating a potential of mean force (an environmentally dependent version of a pair potential). The next section will discuss how this result mirrors the SFB results of Smith *at al.* [131] with respect to the free energy of a charged particle approaching the negative electrode.

3.7 The Effect of Dilution on the Interfacial Potential Energy Environment

The results of Smith *at al.* [131] showed a transition in layer thickness with increasing dilution of ionic liquids. In previous ionic liquid simulations transitions in SFB layer thickness have been related to the potential of mean force of a charged particle approaching an electrode [62]. Potentials of mean force for a positive probe particle approaching a negative are shown in Fig. 3.13 for solutions with $x_{IL} = 0.2$ and $x_{IL} = 0.8$ and surface charges of $-10 \mu\text{C}/\text{cm}^2$ and $-20 \mu\text{C}/\text{cm}^2$.

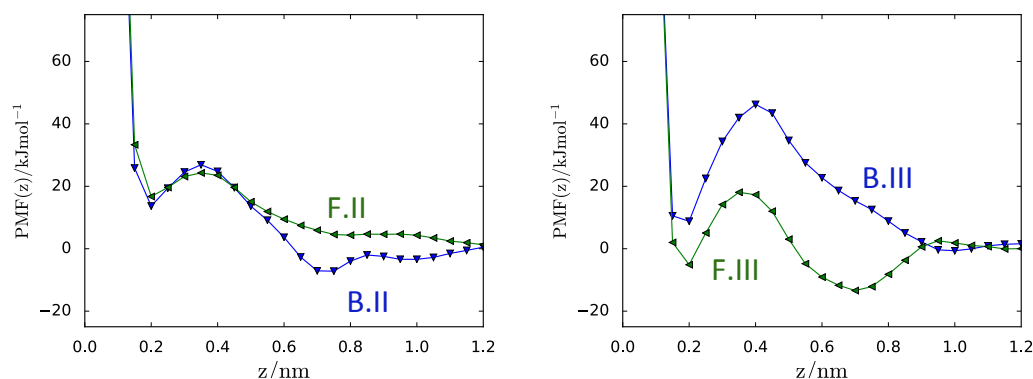


Figure 3.13: The potential of mean force of positive probe particles approaching an interface for two charges: $-10 \mu\text{C}/\text{cm}^2$ (left) and $-20 \mu\text{C}/\text{cm}^2$ (right) and two propylene carbonate mole fractions ($x_{IL} = 0.2$ (green) and $x_{IL} = 0.8$ (blue)).

In all cases there is a minimum observed adjacent to the interface at approximately 0.2 nm. This is indicative of the cation rich first interfacial layer observed for all ionic liquid structures. While its presence does show the attraction between a positive probe and a negative wall, as can be seen in Fig. 3.14, it has less relevance to the comparative nanostructure than the rest of the plot.

The key difference between the potentials of mean force is the presence of a minimum, or otherwise at a position of 0.75 nm. Presence of a minimum at this location would not be observed for the multilayer regime, but will be observed for both a

crowding like structure and for surface charges below which a multilayer type structure is observed.

For $x_{\text{IL}} = 0.8$ at a surface charge of $-10 \mu\text{C}/\text{cm}^2$ there is a minimum at this location. Study of panel B.II of Fig. 3.9 shows that while oscillatory order has started to arise there is still substantial mixing of layers, in a system where a small number of cations are observed in this location there will also be some stabilisation of a positive probe. For systems with $x_{\text{IL}} = 0.2$, at $\sigma = -10 \mu\text{C}/\text{cm}^2$, a small minimum is also observed.

At a higher charge, $-20 \mu\text{C}/\text{cm}^2$ for systems where $x_{\text{IL}} = 0.8$, this minimum is no longer observed due to the presence of a fully oscillatory structure, as would be observed for conventional ionic liquids. The panel of the cartoons in Fig. 3.14 for 0.5 nm for this ionic liquid mole fraction show the positive probe in a layer of anions leading to the lack of a minimum at this location⁷. For systems where $x_{\text{IL}} = 0.2$ there is a minimum at 0.7 nm. This minimum is more pronounced than at lower charge. The reason for the minima's presence is that, as previously shown, at these surface charges this liquid exists in the monotonic regime, and therefore there are multiple layers of cation excess in the near interfacial region, as can be seen in Fig. 3.14. This leads to the intervals in the PMF existing with a periodicity of 0.5 nm.

The results obtained by means of a potential of mean force appear to provide a degree of corroboration to the conclusions drawn from the plots of interfacial nanostructure. In previous studies potentials of mean force between a probe particle and an interface has been able to be related to results obtained by means of surface force experiments. Experimental data recorded by Hausen and Smith [1] has supported the idea that the surface charge of mica in this variety of solution is approximately equal to $-20 \mu\text{C}/\text{cm}^2$. Inspection of the data presented in Fig. 3.13 shows that the

⁷This may at first appear to be a low energy state for the positive probe as it is surrounded by negative ions, however the same thermodynamic driving force that drove away all the cations is now acting on the probe. This leads to a probe being in this location being hugely unfavourable.

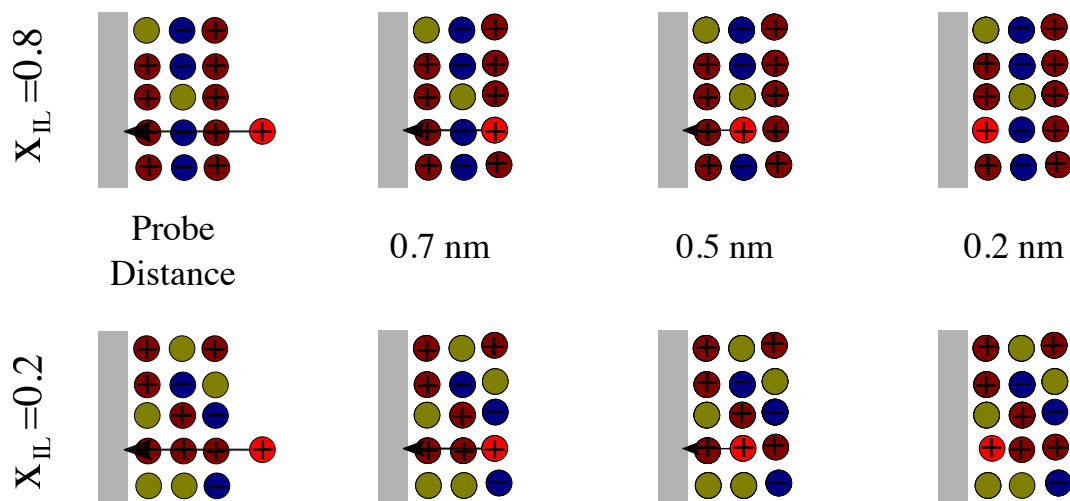


Figure 3.14: The potential of mean force of positive probe particles approaching an interface for two charges ($-10 \mu\text{C}/\text{cm}^2$ and $-20 \mu\text{C}/\text{cm}^2$) and two propylene carbonate mole fractions ($x_{\text{IL}} = 0.2$ and $x_{\text{IL}} = 0.8$).

gaps between the first and second minimum are 0.55 nm and 0.8 nm for $x_{\text{IL}} = 0.2$ and $x_{\text{IL}} = 0.8$ successively. This is exceptionally similar to results observed in SFB experiments, and suggests that these simulations are reflecting the behaviour observed in these experiments. However, the motivation of these simulations goes beyond demonstrating the structure that gives rise to the experimental results observed by Smith *et al.*, and extends to understanding the nature of the interfacial structure adopted by these liquid mixtures. To develop a further understanding of this structure the electrostatic potential of the interface was studied to provide a comparison to pure ionic liquids.

3.8 Electrostatic Potentials in [BMPyr][TFSI] Propylene Carbonate Solutions

In order to better understand the electrostatic interactions in the capacitor a Poisson potential can be calculated. A Poisson potential is a measure of electric potential energy change with distance, ϕ_z . The potential is obtained by calculation of the

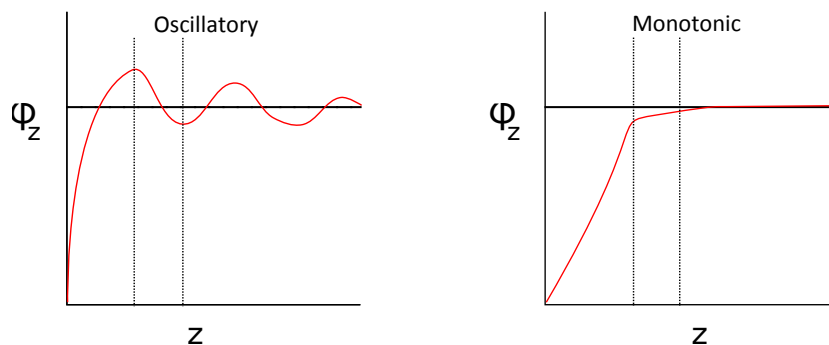


Figure 3.15: A cartoon showing the form of the Poisson potential observed for the overscreening/multilayer regime (left) and the crowded structure (right). The first and second interfacial layers are marked out by means of the dashed perpendicular lines.

distance dependent charge density (in the direction perpendicular to the electrode) from the simulation trajectories. The charge density is then integrated to obtain the electric field in the direction perpendicular to the electrode. The electric field is then further integrated to obtain the Poisson potential⁸.

In a pure ionic liquid the form of the Poisson potential is indicative of whether the reduced surface charge, κ , is greater than or equal to one. For overscreening structures the Poisson potential overshoots the potential of the centre of the cell in the first interfacial layer as shown in Fig. 3.15. However, for the crowded structure the Poisson potential does not reach the potential of the centre of the cell until after the second or even third interfacial layer.

However, the form of the Poisson potential for these mixtures of ionic liquid and propylene carbonate is different. Figure. 3.16 shows the form of the Poisson potential at an electrode with a surface charge of $-10 \mu\text{C}/\text{cm}^2$, $-20 \mu\text{C}/\text{cm}^2$ and $-30 \mu\text{C}/\text{cm}^2$ for each of the studied mole fractions. The black lines on this plot are the potentials at the centre of the simulated box. In the case of $-10 \mu\text{C}/\text{cm}^2$ all solutions have previously been shown to have a multilayer structure in Section 3.6. In all plots we see something along the line of the idealised oscillatory structure for ionic liquids.

⁸As this is a doubly integrated quantity the system must be well sampled to diminish the effect of errors.

This is indicated by progressive oscillations in the Poisson potential either side of the black line (which indicates the potential at the centre of the capacitor). These become increasingly damped with decreasing ionic liquid mole fraction in a similar way to the oscillations in number density observed earlier in the chapter.

It has been previously shown that at $-20 \mu\text{C}/\text{cm}^2$ solutions for which $x_{\text{IL}} = 0.2$ have transitioned from the oscillatory multilayer structure to a monotonic structure, while all the other mole fractions exist in an oscillatory regime. It can be seen that unlike the example of Fig. 3.15 all surface charges have a strong initial peak even for $x_{\text{IL}} = 0.2$ which we know to have a structure characterised by monotonic decay of cations. The anomalous peak at 0.5 nm for $x_{\text{IL}} = 0.2$ will later be shown to be due to the screening of the surface charge by means of the propylene carbonate molecular dipole.

At the surface charge of $-30 \mu\text{C}/\text{cm}^2$ it is possible to compare the three mole fractions, $x_{\text{IL}} = 0.2, 0.4$, and 0.5 , as all three systems exhibit a monotonic structure. Firstly, the first small peak which leads to the anomalous shape of the plot for the $-20 \mu\text{C}/\text{cm}^2$ for a solution of $x_{\text{IL}} = 0.2$, is now a shoulder peak for all three mole fractions for which it is present. Further to this the plots for $x_{\text{IL}} = 0.8$ and 0.6 show zero oscillations after the first trough showing them to be very close to undergoing the transition from an oscillatory to a monotonic structure, and also again indicating the loss of longer range oscillations with increasing dilution.

The Poisson potentials for mixtures with $x_{\text{IL}} = 0.2$ do not appear as conventional ionic liquid, these plots feature additional anomalous peaks at distances between 0.5 nm and 0.8 nm, which would not be expected based on the simplified portrait presented in Fig. 3.15. This peak can be rationalised by considering the effect of the propylene carbonate dipole. Fig. 3.17 shows the cumulative charge density with distance away from the negative electrode (charged to $-20 \mu\text{C}/\text{cm}^2$) for the ions, shown in green, and all components shown in red. From these plots it is possible to

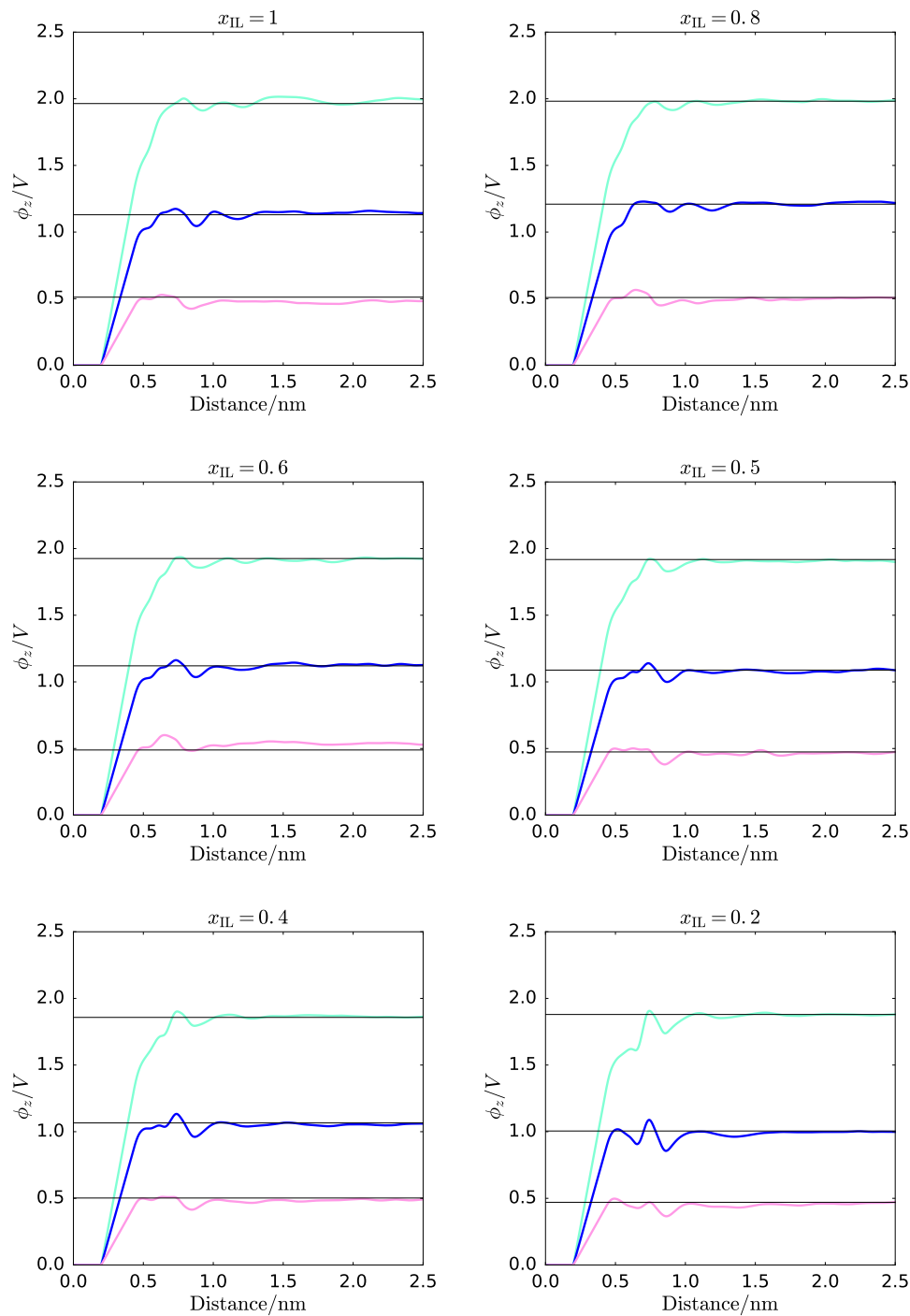


Figure 3.16: The Poisson potentials for each of the mole fractions studied for surface charges of $-10 \mu\text{C}/\text{cm}^2$ (pink), $-20 \mu\text{C}/\text{cm}^2$ (blue), and $-30 \mu\text{C}/\text{cm}^2$ (green). The zero potential is set to be for the negative electrode.

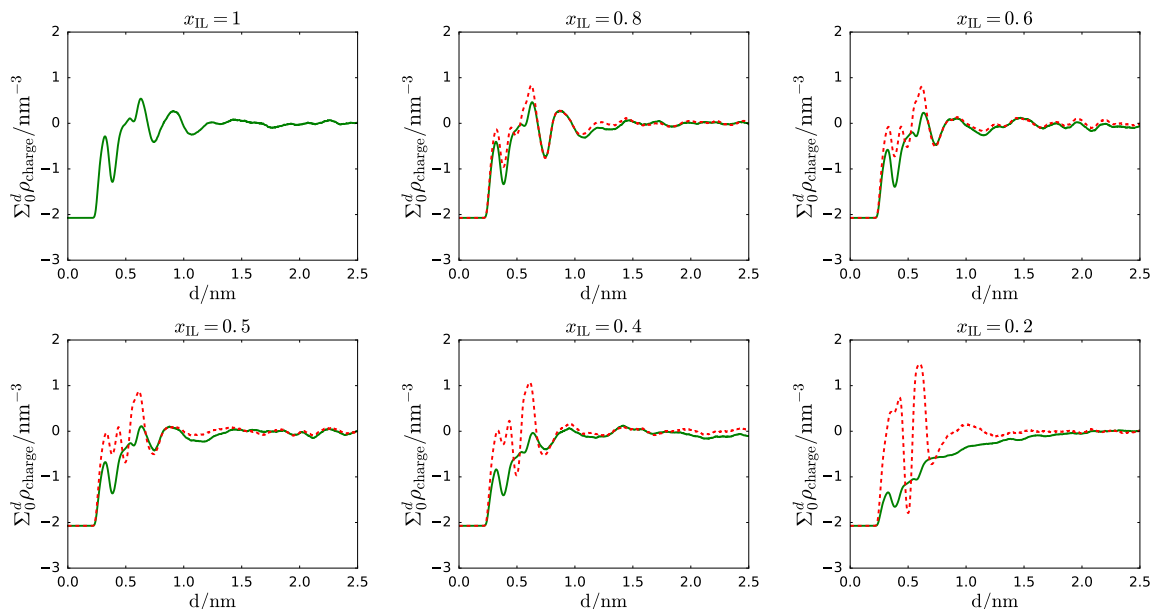


Figure 3.17: Plots of cumulative charge density moving away from a negative electrode, with a charge of $-20 \mu\text{C}/\text{cm}^2$. Total cumulative charge density is plotted as the red dashed line, and the cumulative charge density of ions only is shown as the green dashed line.

see the underlying reason behind the anomalous peaks in the Poisson potentials in Fig. 3.16. At the locations where the anomalous peaks occur the propylene carbonate inclusive cumulative charge density is found to have a large maximum. Smaller maxima are observed for the same reason at lower mole fractions, and these maxima are large enough to have a substantial effect on nanostructure for all mole fractions lower than $x_{\text{IL}} = 0.5$. Study of the cumulative ion charge density for solutions with $x_{\text{IL}} = 0.2$ shows a plot which fits more naturally with the nanostructure observed in Fig. 3.10 than in the previous Poisson plot. The effect of charge screening can be observed for other solutions where the cumulative charge of the ions alone is generally slower in reaching zero than the corresponding Poisson potential. This indicates that interfacial charge screening by the propylene carbonate dipole plays a role in stabilising the crowding like structure.

3.9 The Effect of Cation Identity

Previous sections have explained the anomalous results obtained by Smith *et al.* [131], and some of the underlying behaviours behind those results. However a question arises: if the Ivaništšev model of κ can be extended to this situation there should be a readily explicable change in structure based around the size of the cation.

To these ends simulations were performed for bistriflimide based ionic liquids of two other cations, 1-Ethyl-3-methyl-imidazolium (EMIm) and 1-Butyl-3-methyl-imidazolium (BmIm). These cations are smaller in size than the previously studied BMPyr cation, with EMIm being considerably smaller than BmIm.

The methodology used to perform simulations of the two other ionic liquids is the same as for [BMPyr][TFSI]. The force fields used to study these two liquids are from the same CL&P parameterisation of the OPLS-AA force field, exact parameters of which are listed in Appendix A. As the methodology requires the liquid in the system to be packed to atmospheric density, and these liquids have different densities, the number of ions within each system are listed in Table 3.5.

Table 3.5: Composition of simulation boxes for mixtures of [BmIm][TFSI], and [EMIm][TFSI] and propylene carbonate.

X_{IL}	N_{cations}	N_{anions}	N_{PC}
[BmIm][TFSI]			
0.8	297	297	74
0.5	246	246	246
0.2	147	147	588
[EMIm][TFSI]			
0.8	333	333	83
0.5	271	271	271
0.2	155	155	620

The nanostructures of [BmIm][TFSI], and [EMIm][TFSI] and propylene carbonate, were studied for three mole fractions of ionic liquid 0.2, 0.5, and 0.8. The

interfacial structures are presented in Fig. 3.18 for mixtures of propylene carbonate and [EMIm][TFSI], and in Fig. 3.19 for mixtures of propylene carbonate and [BMIm][TFSI] in the same format as for [BMPyr][TFSI].

Studying the nanostructure for these two new systems it is apparent that the same basic pattern of changing nanostructure with increasing dilution observed for [BMPyr][TFSI] solutions is observed for these other two liquids. Increasing dilution leads to both a decrease in the length and magnitude of oscillations. Further to this a similar pattern of transition from the oscillatory to the monotonic regime occurring at decreasing surface charge with increasing dilution is also observed.

The surface charge at which this transition occurs is far higher for the smaller EMIm cation than for the other two larger ions. For instance for a mole fraction of $x_{IL} = 0.2$ of [EMIm][TFSI] this transition occurs at roughly $-20 \mu\text{C}/\text{cm}^2$, as shown in panel I.I of Fig. 3.18, however for the other two larger ions, shown in panel L.I of Fig. 3.19 and panel F.I of Fig. 3.10 it occurs at roughly $-10 \mu\text{C}/\text{cm}^2$. This is as would be expected from Eq. (3.3),

$$\theta_{ion}^{layer} = \theta_{ion}(\sigma) \cdot (1 - f_{v,PC}), \quad (3.3)$$

and Eq. (3.2)

$$\tilde{\kappa}_{ion} = \left| \frac{\sigma}{\theta_{ion}^{layer}} \right|. \quad (3.2)$$

The smaller EMIm cation should be correlated with an increased value of θ_{ion}^{layer} and thus a decreased value of $\tilde{\kappa}_{ion}$. However the similar values for which the transition occurs in BMIm and BMPyr based ionic liquids do not appear to meet this pattern. In previous work the value of θ_{ion}^{max} calculated for the pure liquids are different with θ_{ion}^{max} being equal to $44.05 \mu\text{C}/\text{cm}^2$ and $36.42 \mu\text{C}/\text{cm}^2$ for BMIm and BMPyr respectively [148]. However for solutions with mole fractions $x_{IL}=0.2$ and $x_{IL}=0.5$ structural transitions occur at approximately the same surface charge.

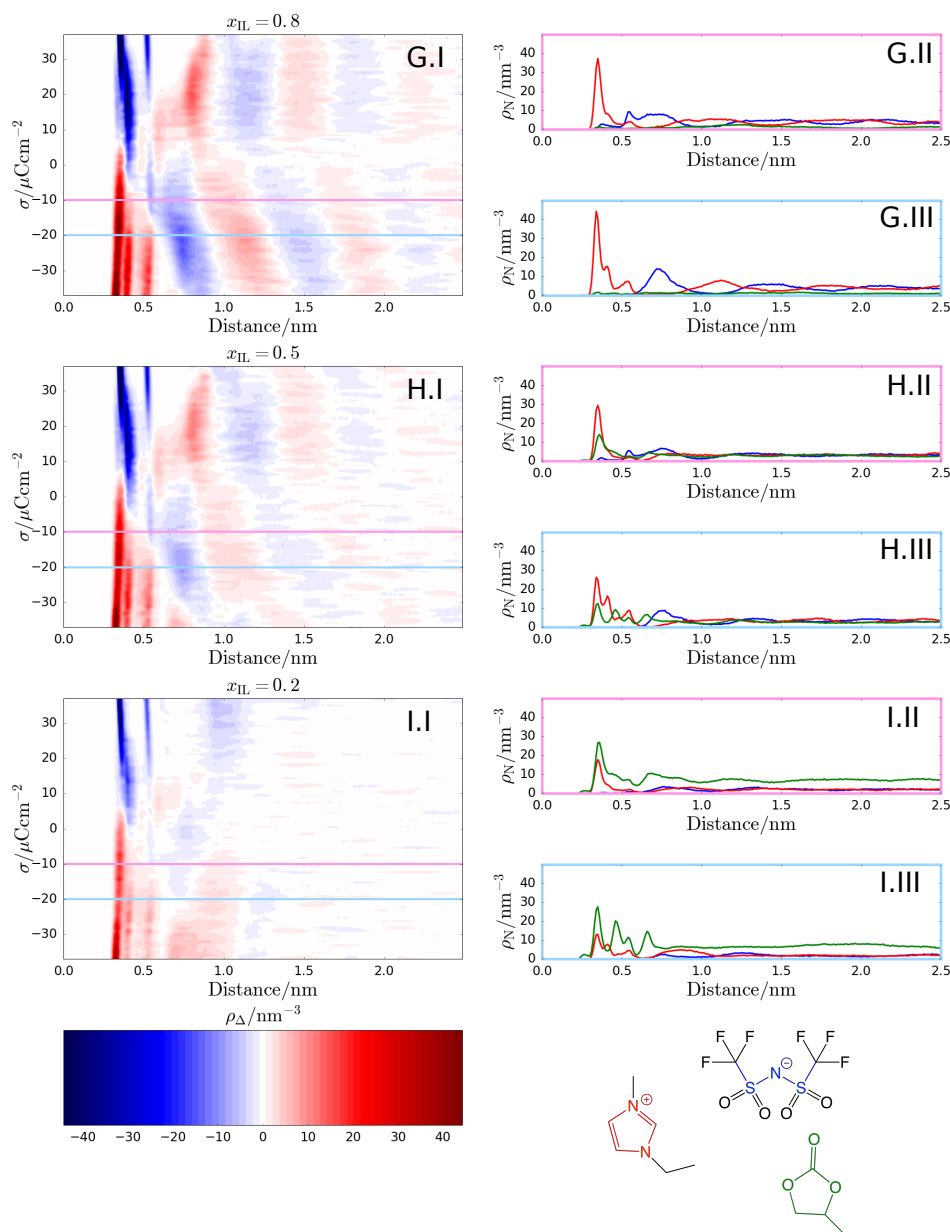


Figure 3.18: Plots demonstrating the interfacial nanostructure of [EMIm][TFSI] propylene carbonate solutions for ionic liquid mole fractions of $x_{IL} = 1$, $x_{IL} = 0.8$, and $x_{IL} = 0.6$. The colourmaps on the left show the variation of $\Delta\rho$ with distance with negative values, (anionic surplus) shown in blue and positive values (cationic surplus) shown in red. On the right hand side exemplar traces of number density of each component with distance are shown. The number density of propylene carbonate is shown in green, cation ring atoms are shown in red and the core of the anion are shown in blue. The exemplar traces are taken for surface charges of $-10 \mu\text{C}/\text{cm}^2$, in the pink box, and $-20 \mu\text{C}/\text{cm}^2$ in the blue box. The graphical legend shows which atoms are used to indicate each component: the cation ring is shown in red, the anion core is shown in blue, and the propylene carbonate is shown in green.

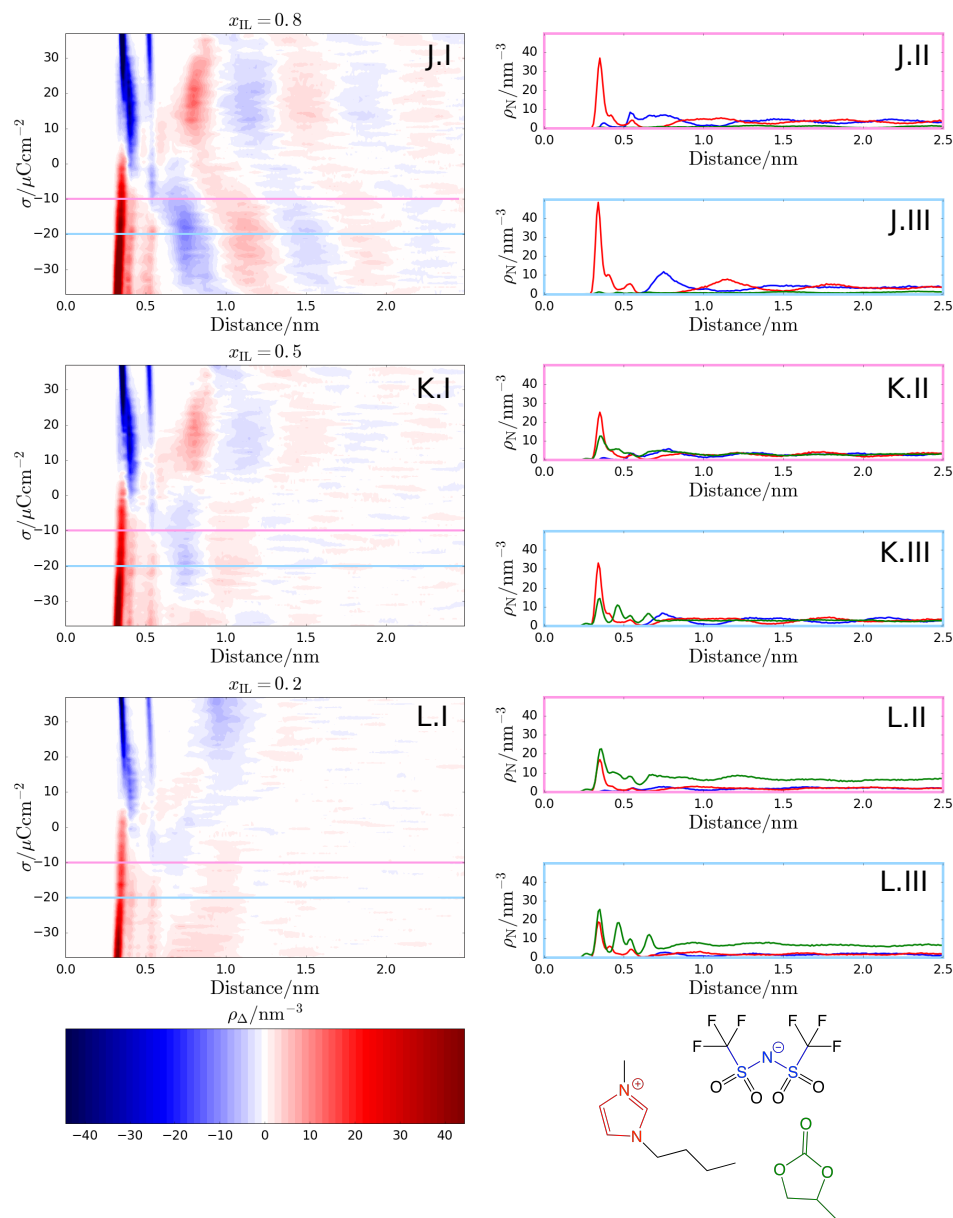


Figure 3.19: Plots demonstrating the interfacial nanostructure of [BMIm][TFSI] propylene carbonate solutions for ionic liquid mole fractions of $x_{IL} = 1$, $x_{IL} = 0.8$, and $x_{IL} = 0.6$. The colourmaps on the left show the variation of $\Delta\rho$ with distance with negative values, (anionic surplus) shown in blue and positive values (cationic surplus) shown in red. On the right hand side exemplar traces of number density of each component with distance are shown. The number density of propylene carbonate is shown in green, cation ring atoms are shown in red and the core of the anion are shown in blue. The exemplar traces are taken for surface charges of $-10 \mu\text{C}/\text{cm}^2$, in the pink box, and $-20 \mu\text{C}/\text{cm}^2$ in the blue box. The graphical legend shows which atoms are used to indicate each component: the cation ring is shown in red, the anion core is shown in blue, and the propylene carbonate is shown in green.

To understand the differences between these three systems it is of interest to look again at the interfacial density of cations and anions, only this time for all three systems. Fig. 3.20 shows the interfacial density of cations and anions in the first interfacial layer.

Looking first at the density of cations it is possible to see some rationalisation for the charge at which the transition from the oscillatory to the monotonic regime occurs for each liquid. For an ionic liquid mole fraction of $x_{\text{IL}}=0.8$ the behaviour appears to resemble the previously reported behaviour for pure ionic liquids. The incorporated number density is highest for EMIm followed by BMIm and then BMPyr. The incorporated densities for each of the cations is clearly distinct and appears to be based largely on the granular size of the ion in question. Allied with this the density of bistriflimide anions in the area closest to the interface is largely constant, which is consistent with the model of pure ionic liquid where the first layer of ionic liquid is comprised solely of anions.

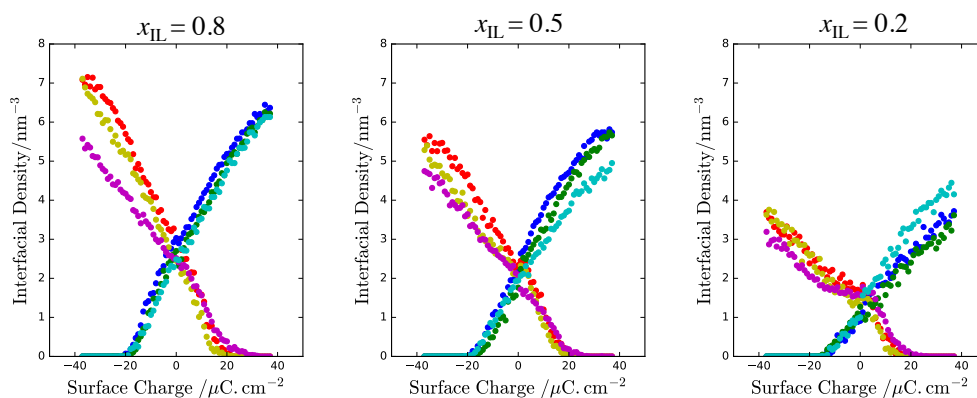


Figure 3.20: The comparative interfacial density, ions within the first 0.7 nm of the electrode, for each of the three studied ionic liquids at mole fractions of $x_{\text{IL}}=0.8$ (left), $x_{\text{IL}}=0.5$ (centre), and $x_{\text{IL}}=0.2$ (right). BMPyr cations are shown in magenta, BMIm are shown in gold, and EMIm are shown in red. Bistriflimide anions in [EMIm][TFSI] are shown in dark blue, Bistriflimide anions in [BMIm][TFSI] are shown in green, and Bistriflimide anions in [BMPyr][TFSI] are shown in cyan.

For an ionic liquid mole fraction of $x_{\text{IL}}=0.5$ there are changes observed for both cations and anions. Firstly the incorporated density of BMIm has become far closer in value to the incorporated density of BMPyr than EMIm explaining the similarity in

the charge at which the transition from oscillatory to monotonic behaviour happens for these liquids. There is also now a growing difference in the incorporated density of bistriflimide. While there are likely a number of effects at play the largest could well be a concentration effect, with the higher ion density in the EMIm and BMIm liquids leading directly to a progressively higher incorporated ion density.

Finally there is the case of ionic liquid mole fractions of $x_{IL}=0.2$. For these systems the charge oscillatory structure is observed for a far wider range of surface charges for [EMIm][TFSI] than for the other two liquids. Fig 3.20 shows there is a slightly higher interfacial density of EMIm cations than for the other two. This can be put down to the small ion size. There is, however, at low charge little difference in the incorporated density of BMPyr and BMIm despite the relatively large difference in θ_{ion}^{max} values previously reported by Ivaništšev *et al.*. In order to understand this similarity it is necessary to look at the specific orientation of cations at the interface.

3.10 Orientation of Cations at the Negative Electrode

In order to get an understanding how the alkyl chains on BMPyr and BMIm cations behave within the first interfacial layer guide atoms on each molecular ion are needed. The last carbon in the butyl tail and the nitrogen atoms in the heterocyclic were chosen to mark the location of the ring and the extreme end of the tail, as shown in Fig. 3.21.

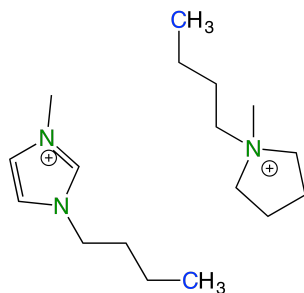


Figure 3.21: A structural diagram showing the designated ring nitrogen atoms, in green, and carbon tail atoms, in blue.

Figs. 3.22 and 3.23 show, for varying x_{IL} and varying σ , the positions of the nitrogen atoms in the ring and terminal carbons as a function of distance from the electrode. The coincidence of these two peaks indicates in-plane orientations whereas displacement of the peaks corresponds to alignment of the alkyl-chain perpendicular to the surface.

Looking first at Fig. 3.22, which describes the behaviour of the BMPyr cations at interfaces, there are a few basic patterns of interest that need to be explained. Firstly, as we would expect based on the decreasing concentration, the number density of all components decreases with decreasing mole fraction.

Secondly, and perhaps far more interestingly, increasing charge leads to a change in orientation. At low charges the larger part of the blue tail peak sits near to the green ring peak. However, with increasingly negative charge this changes. The front most blue peak declines and a new peak emerges further away at approximately 0.8 nm. This is indicative of a realignment of the ion from an orientation where the tail of the cation lies in the plane of the ring at low charge, to one where the tail is more likely to lie normal to the surface of the electrode at high charge. There appears to be no strong correlation between concentration and cation orientation, suggesting that propylene carbonate has a limited role in this effect. This reorientation with increasing surface charge leads to increasing packing efficiency of molecular ions in the first interfacial layer with increasing charge. The alkyl tails are expelled from the first layers, allowing a greater number of cations to be present - as favoured at higher negative surface charge. This in turn leads to the previously discussed term of θ_{ion}^{layer} developing a surface charge dependence.

Moving now to look at the behaviour of BMIm the density of the tail and ring guide atoms is shown in Fig. 3.23. Some of the same pattern still appears to be present with increasingly negative surface charge leading to realignment of the tail from being in the plane of the ring to lying normal to the interface. However in this case the

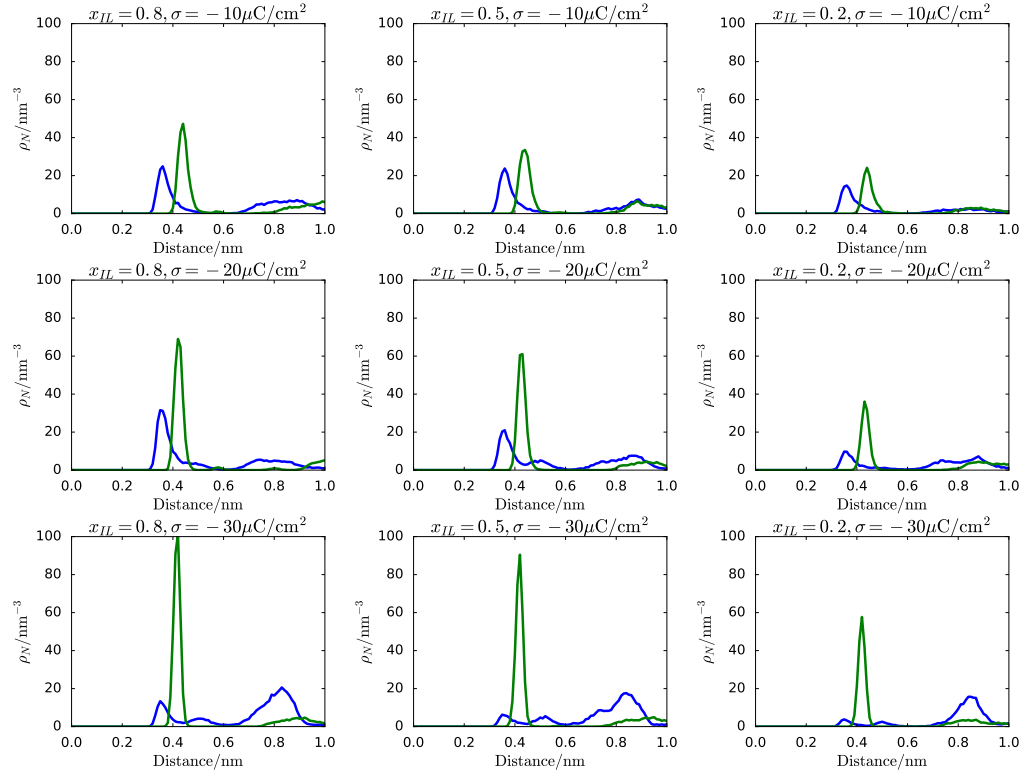


Figure 3.22: Number density of ring nitrogen atoms, in green, and tail carbon atoms, in blue, in [BMPyr][TFSI] at the negative electrode for three surface charges: $-10 \mu\text{C}/\text{cm}^2$, $-20 \mu\text{C}/\text{cm}^2$, and $-30 \mu\text{C}/\text{cm}^2$. And three ionic liquid mole fractions $x_{\text{IL}} = 0.8$, $x_{\text{IL}} = 0.5$, and $x_{\text{IL}} = 0.2$.

realignment appears to be far more complete with near total in-plane alignment in the first incidence and then near total normal alignment for higher charge. This suggests that for this system there is an even greater improvement in packing efficiency with increasing surface charge, leading in turn to an even greater dependence of $\theta_{\text{ion}}^{\text{max}}$ on surface charge.

This reorientation appears to be unable to be induced by the presence of additional solvent and also appears to be independent of the charge screening regime that the system is in for a particular solvent fraction (i.e the orientation appears independent of the oscillatory to monotonic transition). Returning to the portrait presented in

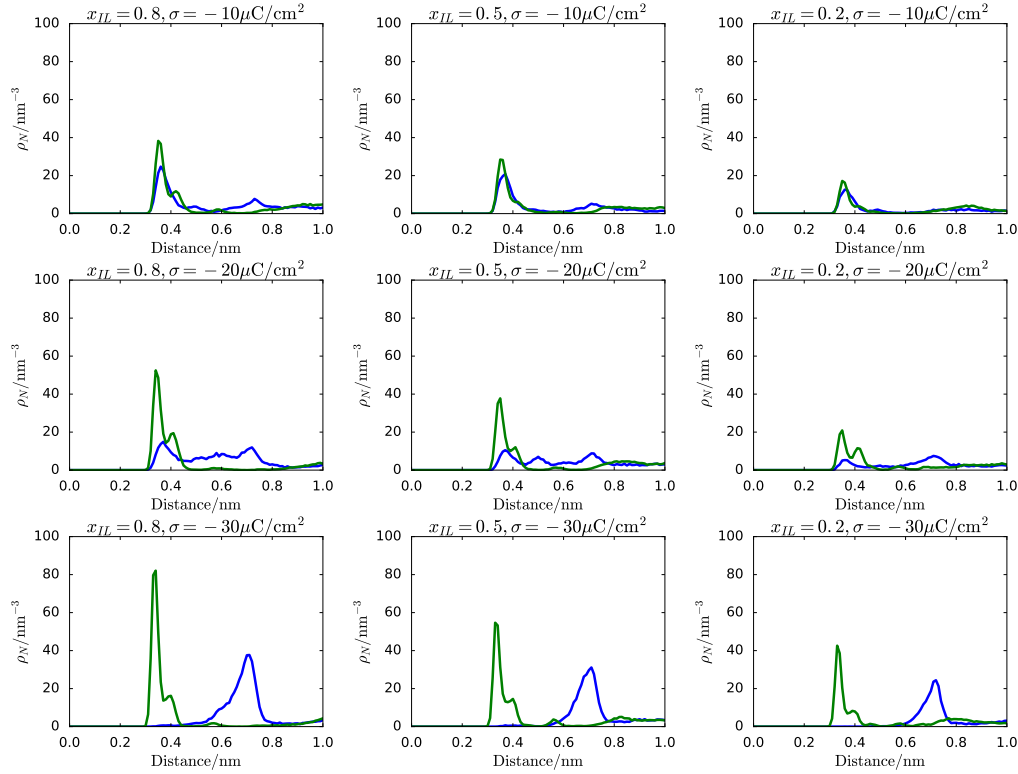


Figure 3.23: Number density of ring nitrogen atoms and tail carbon atoms in [BMIm][TFSI] at the negative electrode for three surface charges: $-10 \mu\text{C}/\text{cm}^2$, $-20 \mu\text{C}/\text{cm}^2$, and $-30 \mu\text{C}/\text{cm}^2$. And three ionic liquid mole fractions $x_{\text{IL}} = 0.8$, $x_{\text{IL}} = 0.5$, and $x_{\text{IL}} = 0.2$.

Section 3.5, the realignment leads to a large dependence of θ_{ion}^{layer} on σ . As shown in Eq.3.3,

$$\theta_{ion}^{layer} = \theta_{ion}(\sigma) \cdot (1 - f_{v,PC}). \quad (3.3)$$

While there will be other reasons for the surface charge dependence of $\theta_{ion}(\sigma)$ the reorientation of ions, and corresponding change in ion packing with surface charge explains the relative trends in κ ,

$$\tilde{\kappa}_{ion} = \left| \frac{\sigma}{\theta_{ion}^{layer}} \right|. \quad (3.2)$$

with increasing surface charge. As the ion packing density of BMIm changes more drastically with increasing surface charge than BMPyr there is a corresponding greater change in κ with propylene carbonate mole fraction. From this it can be predicted that for all cations the addition of propylene carbonate will diminish the surface charge for which $\kappa = 1$. However further to this the form of Eq. (3.2) and Eq. (3.3) may also shed light as to why monotonic decay has rarely been observed in simulations of acetonitrile. Acetonitrile is a smaller molecule with a much lower excluded volume.

3.11 The Positive Electrode

The simulations described in this chapter were designed to explain the experimental observations of Smith *et al.* which were made at a negatively charged surface. As a result the studied ranges of mole fractions and surface charges were chosen to be appropriate for such a system. The structure at the positive electrode is less well captured, and we finish this chapter by considering that now. Fig. 3.24 and Fig. 3.25 show the nanostructure of [BMPyr][TFSI] and propylene carbonate for all six studied mole fractions and for surface charges of $+20 \mu\text{C}/\text{cm}^2$ and $+30 \mu\text{C}/\text{cm}^2$.

Studying Fig. 3.24 for the pure ionic liquid, offset oscillations of cation and anion density can be observed at both the studied surface charges. The oscillations for a surface charge of $+20 \mu\text{C}/\text{cm}^2$ are more extended than for $+30 \mu\text{C}/\text{cm}^2$. With increasing propylene carbonate mole fraction the magnitude of these oscillations decline. This eventually reaches the point where this oscillatory behaviour gives way to the previously discussed monotonic decay.

The structure is shown to break down with increasing mole fraction and surface charge just as at the negative electrode, with the oscillatory structure being observed for all mole fractions at a surface charge of $+20 \mu\text{C}/\text{cm}^2$ except for $x_{\text{IL}} = 0.2$ for where the monolayer structure is observed. For a surface charge of $+30 \mu\text{C}/\text{cm}^2$ a crowded

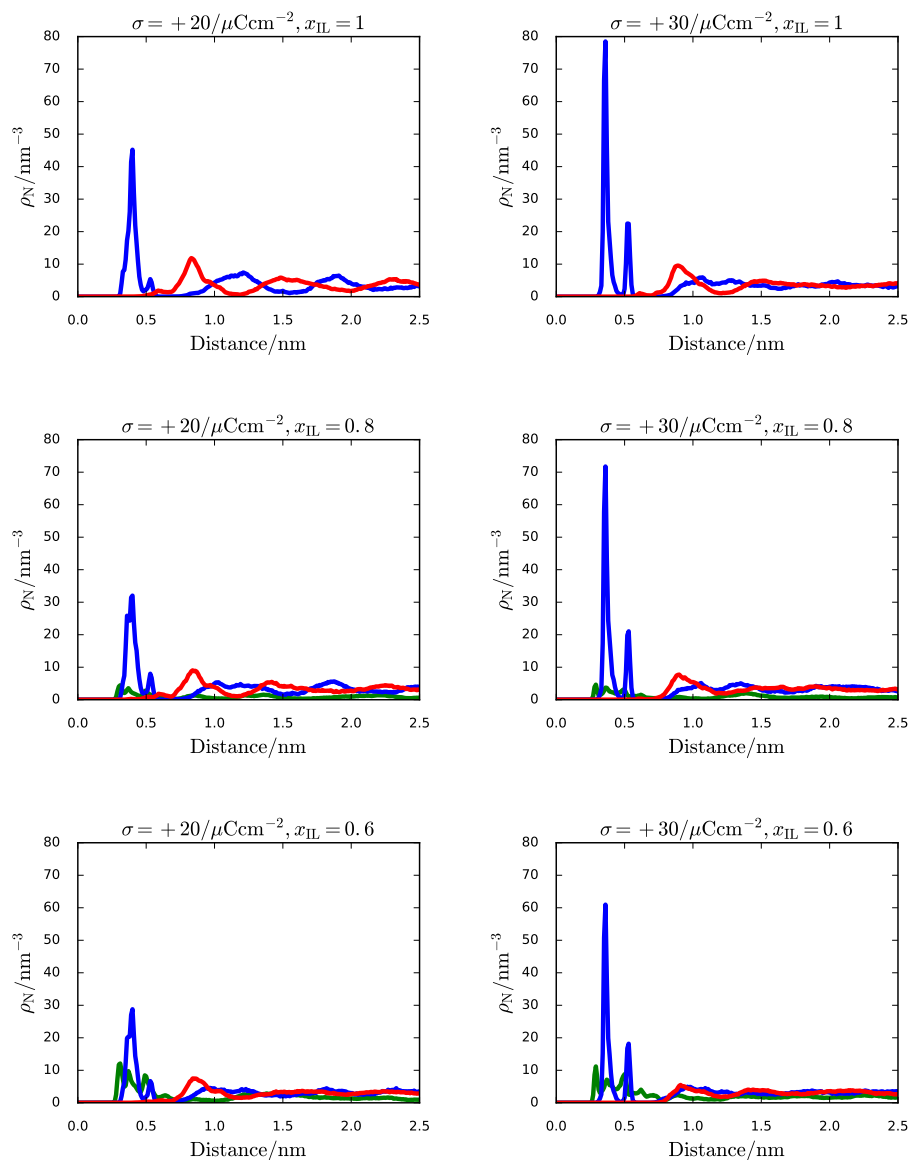


Figure 3.24: Nanostucture of mixtures of [BMPyr][TFSI] and propylene carbonate at the positive electrode for surface charges of: $+20 \mu\text{C}/\text{cm}^2$, and $+30 \mu\text{C}/\text{cm}^2$. And mole fractions of: $x_{\text{IL}} = 1$, $x_{\text{IL}} = 0.8$, $x_{\text{IL}} = 0.6$. The bistriflimide core location is shown in blue, cations rings are shown in red, and propylene carbonate molecules are shown in green.

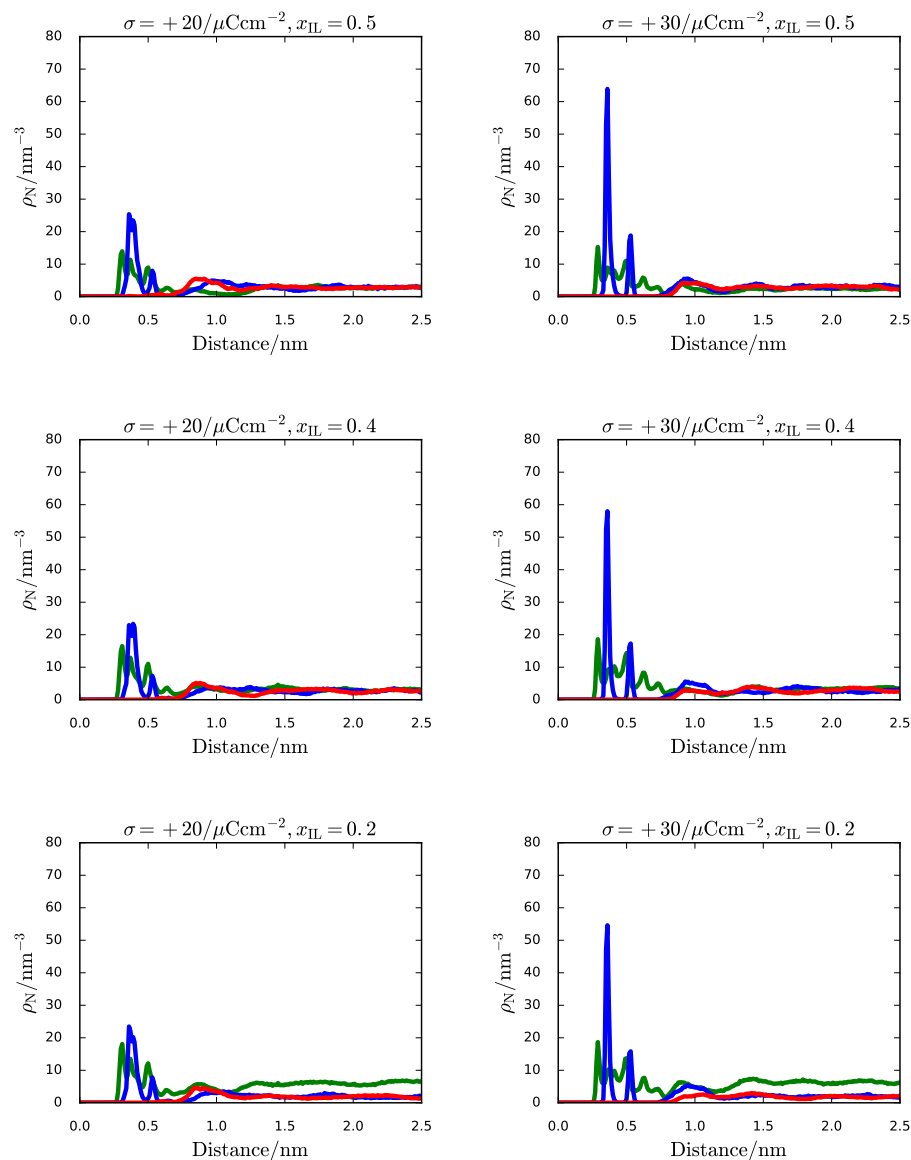


Figure 3.25: Nanostucture of mixtures of [BMPyr][TFSI] and propylene carbonate at the positive electrode for surface charges of: $+20 \mu\text{C}/\text{cm}^2$, and $+30 \mu\text{C}/\text{cm}^2$. And mole fractions of: $x_{\text{IL}} = 0.5$, $x_{\text{IL}} = 0.4$, $x_{\text{IL}} = 0.2$. The bistriflimide core location is shown in blue, cations rings are shown in red, and propylene carbonate molecules are shown in green.

structure is observed for $x_{IL}=0.2$ and $x_{IL}=0.4$. A monolayer structure is observed for mole fractions of $x_{IL}=0.5$ and $x_{IL}=0.6$. The multilayer structure still being observed for $x_{IL}=0.8$ and $x_{IL}=1$. This appears to be somewhat in line with the behaviour observed at the negative electrode, however, it is worth noting that the value of θ_{ion}^{max} is far higher due to the smaller size of the bistriflimide anion meaning this charge corresponds to a far smaller value of $\tilde{\kappa}_{ion}$.

One interesting contributing effect to the difference in nanostructure at the positive electrode is the geometry of the propylene carbonate, which is not symmetrical. It can be tempting to think of dipolar solvents of being like a simple dipolar diatomic like carbon monoxide. However, they are invariably not like this. In nearly every case the positive end of the molecule consists of a relatively uncharged cluster of carbon and hydrogen atoms, whereas the negative end of most dipolar solvents will consist of a highly charged heteroatom. In the particular case of propylene carbonate the carbonyl oxygen carries a large negative charge, while the ethyl and methyl units at the positive end of the molecule are relatively weakly charged. This means there is a stronger interaction between the positive wall and the propylene carbonate molecule than at the negative electrode. The effect of which can be understood through study of the Poisson potentials shown in Fig 3.26 for surface charges of $+30 \mu\text{C}/\text{cm}^2$, $+20 \mu\text{C}/\text{cm}^2$, and $+10 \mu\text{C}/\text{cm}^2$.

The first point of interest from the Poisson potentials is that for all systems the first trough in the Poisson potential always exceeds the potential of the pseudo-bulk region in the centre of the capacitor. This is fundamentally different from the pattern observed for the negative electrode where crowding like behaviour is observed for some mole fractions at the highest charge, even though the nano-structure appears nearly identical, based on study of plots of interfacial number density in Fig 3.25. Study of the cumulative charge plots again helps describe the specific environment observed for this system. Plots of cumulative charge going away from the positive electrode,

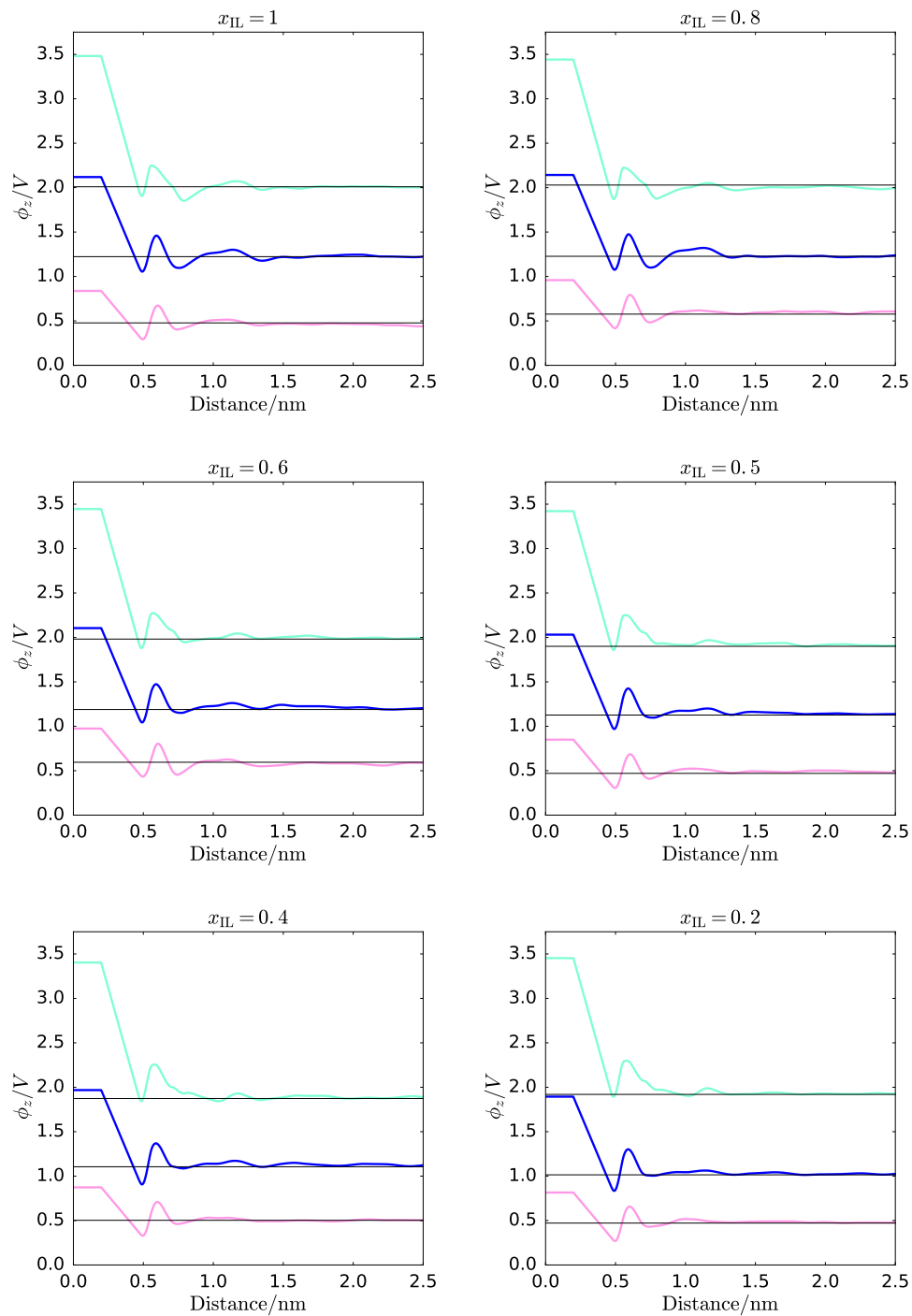


Figure 3.26: The Poisson potentials for each of the mole fractions studied for surface charges of +10 $\mu\text{C}/\text{cm}^2$ (pink), +20 $\mu\text{C}/\text{cm}^2$ (blue), and +30 $\mu\text{C}/\text{cm}^2$ (green). The zero potential is set to be for the negative electrode.

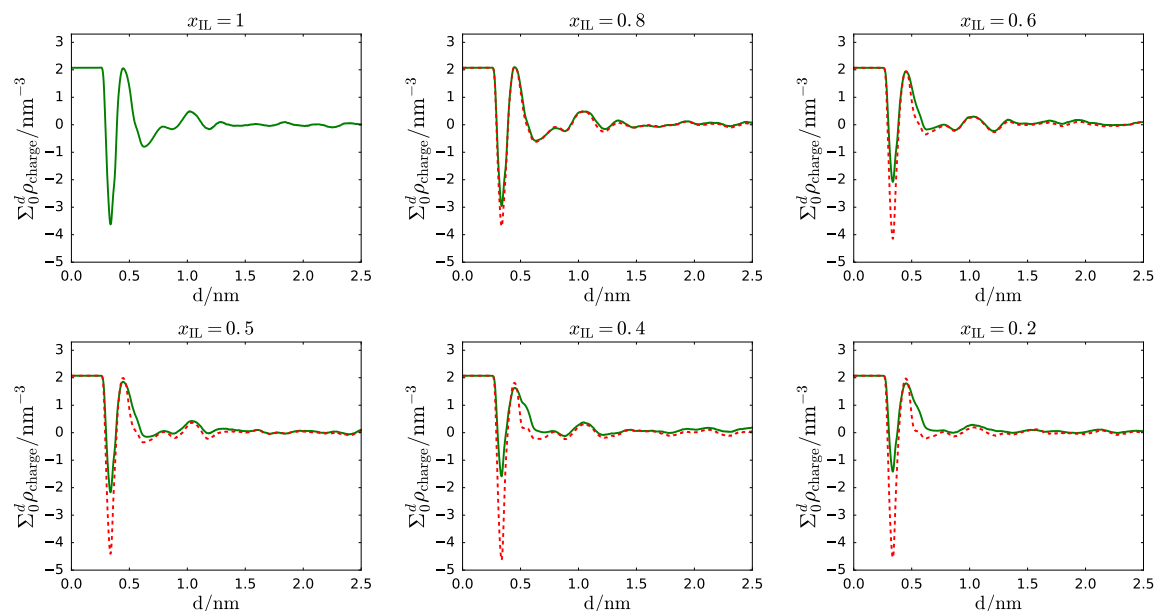


Figure 3.27: Plots of cumulative charge density moving away from a positive electrode, with a charge of $+20 \mu\text{C}/\text{cm}^2$, with total cumulative charge density plotted as the red dashed line, and the cumulative charge density of ions only is shown as the green dashed line.

with a charge of $+20 \mu\text{C}/\text{cm}^2$, both including and excluding propylene carbonate molecules are shown in Fig. 3.27.

The key feature in Fig. 3.27 is the large fore peak, at $d = 0.4$, which is common to all plots. This peak is due to both the anions and the carbonyl oxygen atom in the propylene carbonate molecule. With increasing propylene carbonate mole fraction this peak gets smaller in the cumulative charge due to ions with decreasing x_{IL} (as would be expected), while the same peak in cumulative charge density for all components increases with increasing propylene carbonate mole fraction. This is due to the large attraction between the positively charged electrode and the negatively charge carbonyl oxygen. This effect along with the greater density of bistriflimide anions in the first interfacial layer leads to better screening of electrode charge in the near interfacial region for the same charge and thus a shorter decay length for

cumulative charge for the positive electrode than the negative electrode when given a charge of an equal magnitude.

3.12 Assessing the Applicability of the Model System

The results presented in this chapter were obtained using a simple model system. Both the ionic liquid and electrode were modelled as being unpolarisable bodies. As such the model is not identical to the real liquid. Evidence for the efficacy of the model was described in section 3.7. It was shown that the potential of mean force between a probe particle, and an interface with the same surface charge as muscovite mica submerged in ionic liquid has the same structural periodicity in potential as observed in the force profile obtained in SFB experiments [131].

Futher to this, simulations of related systems (ionic liquids mixed with acetonitrile) have previously shown similar results. Simulations by Vatamanu et al.[94] showed the oscillatory structure giving way to monotonic decay. However, this was only observed for the most dilute solution at the most positive electrode potentials, for the largest anion studied (FAP). This correlates well with the portrait presented in this chapter where: monotonic charge screening is observed at the highest surface charges, and lowest concentrations, and also where the effect of an aprotic solvent is maximised at the anode. This study modelled the system differently with polarisable electrode and electrolyte models employed. The similarity of the results obtained by these two very different methods suggests that the observed effects are due to the underlying physics in the simulated system, and not a quirk of the model. However, while the results are likely to be qualitatively correct it does not mean that the relatively simple electrode model is not having an effect on the dominance and magnitudes of certain effects. The electrode used has some characteristics of mica, and some of graphitic materials. It is possible that the simulations effectively model neither of these interfaces, leading to the structure matching neither interface closely.

While these simulations are effective in detecting an area of monotonic charge decay, it is worth noting that they may be incorrectly calculating the decay length of this feature. Recent studies have suggested that the magnitude of such a region of monotonic decay will be correlated with the Bjerrum length [149]. The Bjerrum length is related to the strength of ion pairing in a liquid, and the dielectric constant of the media, while the simulations were setup with the dielectric constant set to be close the real value, the strength of ion pairing in the liquid is likely to be somewhat incorrect. The unpolarisable ions will not interact as strongly as if a dipole could be induced. And the slight covalency of certain intramolecular interactions cannot be directly represented in the model system. Whilst the force field compensates for these inaccuracies by tweaking other variables, such as the magnitude of ion charges, there is still an inherent inaccuracy in the model. This inaccuracy will lead to inaccuracy in the Bjerrum length, and thus the recorded screening length.

3.13 Conclusion

This chapter has explored the interfacial nanostructure of propylene carbonate ionic liquid solutions. Dissolution of ionic liquids in propylene carbonate appears to decrease the surface charge at which the transition from an oscillatory to a monotonic structure takes place. The level to which this decrease takes place, however, is dependent on both the charge dependence of interfacial ion density and the mole fraction of propylene carbonate in the first interfacial layer. This effect explains the previously explained experimental results achieved by Smith *et al.* [131].

Chapter 4

Molecular Dynamics Simulations of a Solvate Ionic Liquid in the Bulk and at Fixed Charge Electrodes

This chapter presents results examining the nanostructure of solvate ionic liquids at graphitic electrodes, using a simplistic fixed charge electrode model. This section consists of two main parts. The first part details the choice of force field before exploring the behaviours of the chosen force field. The second part focuses on the nanostructure of the solvate ionic liquid lithium tetraglyme bistriflimide ($[\text{Li}(\text{G4})][\text{TFSI}]$). This chapter will end by discussing the limitations of this simulation technique and draw comparison with the previous section discussing conventional ionic liquid mixtures.

4.1 Glyme Based Solvate Ionic Liquids

Solvate ionic liquids are a subclass of ionic liquid formed of an equimolar mixture of a lithium salt, and a coordinating solvent. While the general concept of solvate ionic liquids was introduced in Chapter 1 this section will discuss the specific class of solvate ionic liquids. Specifically it will discuss those based around the chelation of a glyme molecule to a metal cation, which are studied throughout the next two chapters.

A *glyme* is a methoxy-terminated oligoethyleneether. The general structure of a glyme molecule is shown in Fig. 4.1. There are two naming conventions for glymes the short name is written as G_n where n is the number of repeat units in the oligoether, while in the written name the standard prefix for the number of repeat units is applied i.e G_4 is referred to as tetraglyme. It should be noted that each glyme molecule has $n + 1$ oxygen atoms.

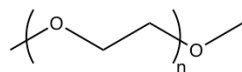


Figure 4.1: Generic structural formula of glyme oligoethers.

Glyme-based solvate ionic liquids occupy an intermediate regime between those complex salt compounds which form solid chelate complexes where complexation is near permanent and the melting point rises to 100°C [150, 151], and concentrated solutions where the properties of the solvent such as the temperature of thermal decomposition are still observed [6]. Nearly all solvate ionic liquids are formed of polydentate solvents such as cryptands, crown ethers, and glymes [6, 151]. The additional entropic driving force of chelation increases the favourability of complexation greatly in comparison to monodentate ligands, such as propylene carbonate [6].

There are two types of solvate ionic liquid: good solvate ionic liquids and poor solvate ionic liquids. In an idealised good solvate ionic liquid, every single solvent molecule is coordinated to a metal ion, and vice versa [6]. The coordination is of such totality and longevity that the liquid appears to be comprised solely of complex cations, and anions. As with all classes of solvate ionic liquids glyme based solvate ionic liquids can be either good or poor dependent on the level of coordination. The degree of solvation is often rooted in relative competitiveness in coordination of the solvent molecule and the anion. Table 4.1 shows the percentage of glyme molecules that are free in solution as calculated by Raman spectroscopy by Ueno *et al.* [7], and this value indicates where a particular mixture sits on the continuum between good, and poor solvate ionic liquids.

The four ions detailed in Table 4.1 are shown on a continuum between good and poor solvate ionic liquids in Fig. 4.2, and careful consideration of their structures can shed light on their location on the continuum. Firstly, comparing BETI and TFSI, which are from the same homologous series, with TFSI being the methyl derivative and BETI the ethyl derivative. The bulkier BETI anion coordinates less favourably

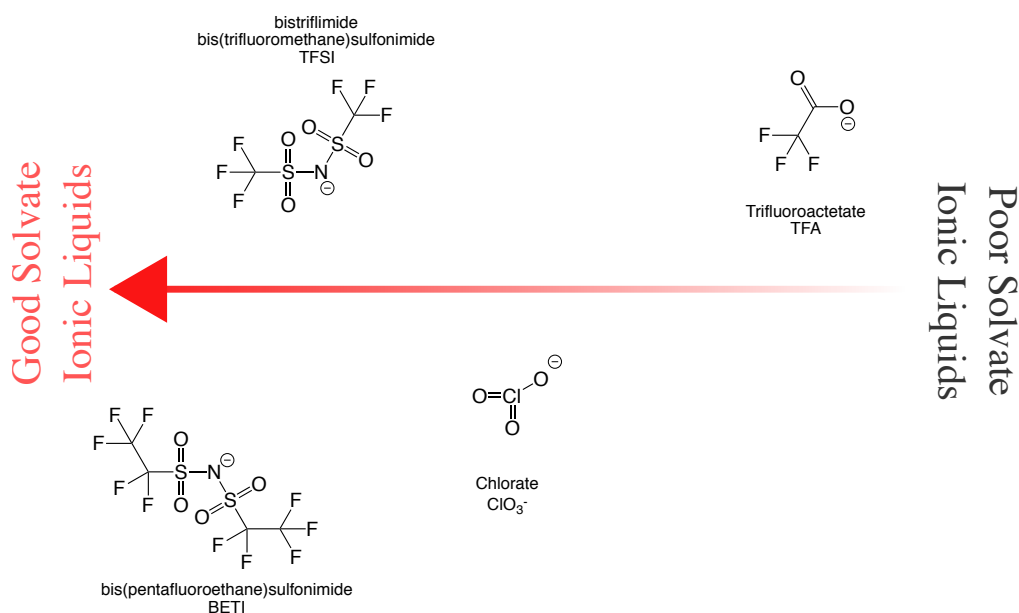


Figure 4.2: Chemical formulae of the anions of four lithium salts commonly employed in solvate ionic liquids. These anions are plotted on a scale bar from good to poor solvate ionic liquids based on the degree of lithium tetraglyme complexation with lithium in the solvate ionic liquids formed of these anions.

Table 4.1: The percentage of free glyme in lithium glyme solvate ionic liquids studied by Ueno *et al.* [7].

Solvate Ionic Liquid	Percentage of Free Glyme
[Li(G4)][TFSA]	2.4
[Li(G4)][BETI]	0.78
[Li(G4)][ClO ₄]	20
[Li(G4)][TFA]	85

than the TFSI anion for steric reasons, leading to a lower proportion of free glyme in the BETI based solvate ionic liquid. However both of these liquids would be classed as good solvate ionic liquids [7] due to their showing of no properties of the pure solvent.

Chlorate coordinates much more successfully with the lithium than the fluoro-sulfonimide based ionic liquids, leading to greater proportion of free glyme. According to Mandai *et al.* this solvate ionic liquid can be classed as a good solvate ionic liquid [6]. However, the thermal decomposition temperature of this mixture,

181°C, is such that it could be considered a borderline case between good and poor solvate ionic liquids.

The fourth anion, trifluoroacetate, is such an effective Lewis base, due to the multiple fluorine substituents, that it coordinates with lithium far more readily than the glyme molecule leading to 85 % of glyme molecules being free in the solution [6]. This system is so dissociated that it may not even be considered a poor solvate ionic liquid, it is instead considered to be a concentrated solution.

While there is yet to be a solvate ionic observed with 0% free glyme, in a good solvate ionic liquid, the liquid exhibits no behaviours that can be ascribed to one of its constituent components [6].

There are a number of ways in which a good or a poor solvate ionic liquid can be distinguished. However perhaps the most illustrative is to consider the diffusion coefficients of the cations and solvent molecules. This is experimentally determined performed using pulsed field NMR. Work performed by Ueno *et al.* [7, 152] showed that for good solvate ionic liquids, the diffusion coefficients of the lithium cation and the glyme molecule are close in value to one and other, while in a poor solvate ionic liquid, there is a greater gulf, with lithium diffusion being more hindered [152]. While previous simulations using classical molecular dynamics have been unable to replicate the transport properties of solvate ionic liquids quantitatively [153], as with conventional ionic liquids [137]. The qualitative aspect of this behaviour can be glimpsed in simulations by either looking at the flux of ions and glyme in an electric field (glyme molecules move in the same direction as lithium ions) [153], or by looking at the discrepancy between lithium diffusion constants, and viscosity trends between good and poor solvate ionic liquids [153].

Secondly, the thermal behaviour of good solvate ionic liquids is fundamentally different from that of poor solvate ionic liquids, or in fact, from concentrated solutions of conventional electrolytes. Thermogravimetric analysis (TGA) shows that glyme

burns off at a much lower temperature for poor solvate ionic liquids than for good solvate ionic liquids [151, 154]. The reason for this is that the free solvent in a poor solvate ionic liquid is able to vapourise while uncoordinated at temperatures above the boiling point of pure glyme. Whereas for a good solvate ionic liquid these solvent molecules are bound to a lithium cation leading to vapourisation only taking place when a particular thermal decomposition temperature is reached. The high thermal stability, and related low vapour pressure provide a clear analogue with properties of conventional ionic liquids. [6]

4.1.1 The Role of the Cation

While the anion in a solvate ionic liquid is predominant in the determination of whether a solvate ionic liquid will act as a good or poor solvate ionic liquid, altering the metal cation has a large effect on the form of the phase diagram of the solvate ionic liquid. This was first observed for solvate ionic liquids comprised of crown ethers and cryptands [151], where, selecting a macrocycle with a cavity radius of roughly $0.1 \text{ \AA}$ greater than the radius of the cation, leads to the greatest minimisation of melting point. The same behaviour can be observed in glyme based solvate ionic liquids, different glymes lead to different eutectic depths with different alkali earth metals [155]. Melting points are minimised for lithium with tetraglyme, and sodium with pentaglyme. In both of these examples, it appears that melting point is minimised by the solvent which decreases cation-anion interactions by screening the electrostatic interactions most effectively [151].

4.2 Bulk Nanostructure of Solvate Ionic Liquids

The bulk nanostructure of solvate ionic liquids has been explored in multiple studies. However a single study by Murphy *et al.* [156] presented different results from the consensus of other studies. Most studies for $[\text{Li}(\text{G4})][\text{TFSI}]$ have shown a lithium

coordination structure in the bulk featuring a single chelate ring coordinating to a single lithium ion with a deficient four coordinate structure [47, 153, 157–159], with lithium to glyme oxygen coordination numbers of 3.8 to 4. This coordination structure has been observed in isotope substitution, Raman spectroscopy and high energy X-ray diffraction experiments (HEXRD); as well as molecular dynamics simulations and second order Møller–Plesset perturbation theory calculations (MP2). However the work of Murphy *et al.* runs contrary to these opinions, this study shows a much lower lithium oxygen coordination number, of 2.32, and a prevalence of double helix type coordination structures, which have previously been reported in studies of the bulk nanostructure of lithium oligoether solutions [160, 161]. Murphy *et al.* asserted that if their conclusions were correct, all previous molecular dynamics force fields were incorrectly parameterised, however due to the substantial evidence to the contrary it is likely this fear is unfounded and whilst considering this work carefully we here work with previous and currently accepted parameters.

4.3 Force Fields for Solvate Ionic Liquids

The uncertainty of coordination environments [156, 157] observed in experiments, and the fundamental difficulty in modeling something with a degree of dative bonding by use of electrostatic and dispersion interactions, has led to a number of different classical force fields for lithium glymes being defined. There are two main sub classes of force fields that have been described; those force fields where the charges on the glyme oxygen atoms are designated from direct calculation of the interaction energies of the three components, and those which are based on well established classical force fields. As yet, there has been no application of polarisable force fields or *ab initio* molecular dynamics to lithium glyme systems.

The first force field devised to study solvate ionic liquids was produced by Tszuki *et al.* based on MP2 calculations of interaction energies, and the bonded parameters

from the standard OPLS-AA force field [158, 159]. However, the resulting liquid coordination structure is not analogous with the structures observed experimentally in solvate ionic liquids. Specifically the chelation of lithium is too complete with coordination numbers well in excess of values observed in HEXRD simulations [153, 157].

There have been three subsequent molecular dynamics studies performed by Eyckens *et al.* [162], Shimizu *et al.* [153] and Saito *et al.* [47]. The force field used by Eyckens *et al.* is largely based on OPLS-AA, and the OPLS-AA derived CL&P ionic liquid force field [100]; the coordination number observed in simulations of [Li(G4)][TFSI] is about 3 and is thus slightly lower than experimentally observed [157].

The final two force fields derived by Saito *et al.* and Shimizu *et al.* produce relatively similar coordination numbers and appear to replicate the bulk nanostructure of solvate ionic liquids in a number of ways. Both force fields obtain an accurate coordination number, as well as showing favorable coordination of interior oxygens over terminal ones. However the mechanism by which this is achieved is somewhat different. While both force fields used CL&P for the anionic components, they used different parameters for lithium, with Saito *et al.* using the force field of Soetens *et al.* [163], and Shimizu *et al.* using the force field developed by Åqvist [114]. In addition to this the partial charges on oxygens in the glyme molecules, and the relative charge on the ions are differently set. Firstly Shimizu *et al.* use the OPLS-AA standard method of setting each oxygen in the glyme molecule to have the same charge [112], while Saito *et al.* use the charges extracted from molecular orbital calculations. The difference in the partial charges on the glyme oxygen atoms is demonstrated in Fig. 4.3. Secondly, Shimizu *et al.* scale the overall charges on the ionic components in the solvate ionic liquids to account for polarisability in a manner similar to that used for conventional ionic liquids [137], while Saito *et al.* do not.

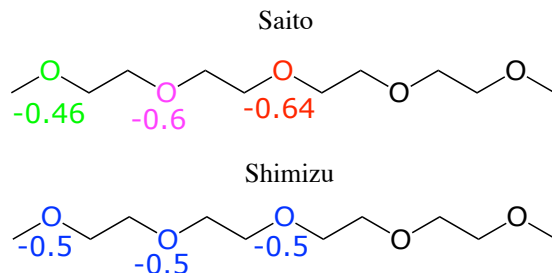


Figure 4.3: Partial charges on each oxygen atom in tetraglyme force fields used by Shimizu *et al.* and Saito *et al.*. The charges used by Shimizu *et al.* have a value of $\epsilon_r = 1.6$, while Saito *et al.* have $\epsilon_r = 1$. In both cases these charges on ions are equal to $1e$, all charge values are stated in values of e .

The work over the next two chapters will use the force field developed by Shimizu *et al.* due to its somewhat better accounting for polarisability. However there are advantages to the Saito forcefield as well.

4.4 Simulations of a $[Li(G4)][TFSI]$ in the Bulk

Prior to interfacial simulation of $[Li(G4)][TFSI]$ bulk simulations of this solvate ionic liquid were performed to confirm the validity of the Shimizu force field, which will be used for interfacial simulations of $[Li(G4)][TFSI]$.

4.4.1 Bulk Simulation Methodology

The bulk liquid was simulated at 350 K and 300 K. The simulations were performed using the Gromacs 5.1.4 [103, 138–143] software. A box containing 100 ions, with initial positions generated using the Packmol algorithm [144] was used for the simulations. Steepest descent energy minimisation was used to generate stable initial conditions after which the system was annealed from the target temperature to 500 K and back again over the course of 2.2 ns. The V-rescale thermostat [126], and the Berendsen barostat [125] were used to maintain temperature and pressure during this stage of the simulations (due to its greater stability in simulations). At the target temperature a 20 ns run is performed with the first nanosecond treated as

equilibration, and a timestep of 1 fs. For this run, the V-rescale thermostat was used again, and the Parinello-Rahman barostat [129, 130] was used. The Coulomb and van der Waals cut-offs were set to 1 nm. Long-range electrostatics were performed using the Particle Mesh Ewald method [124, 145], with a PME order of 4 and a Fourier spacing of 0.12 nm. Throughout the simulations pressure is maintained at 1 bar, and the simulation box is periodic in all directions.

The details of the force field developed by Shimizu et al [153], which was used in these simulations are provided in detail in Appendix B.

4.4.2 Coordination Environment of $[Li(G4)][TFSI]$ in the Bulk Ionic Liquid

The coordination environment of the lithium cations were studied to ensure that the correct proportion of free glyme molecules are coordinated to lithium atoms. Fig. 4.4 shows the radial distribution functions between lithium cations and oxygen atoms from both glyme molecules, and bistriflimide anions.

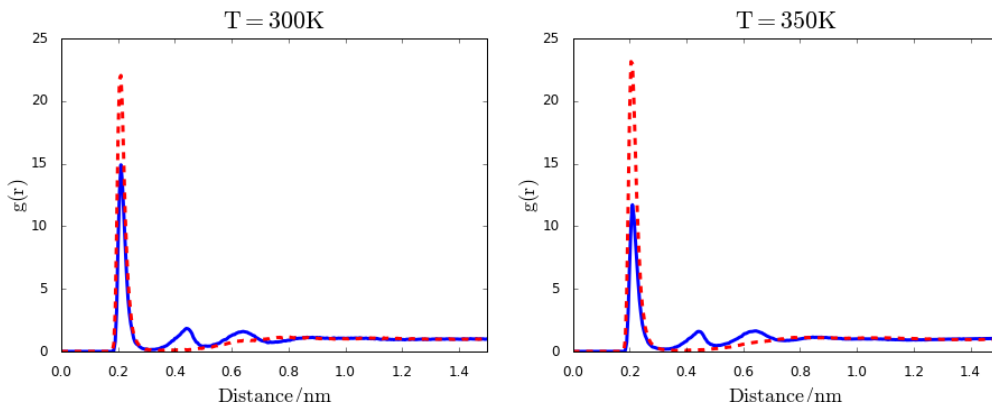


Figure 4.4: Pair correlation functions between lithium cations and oxygen atoms in anions (blue solid lines), and glyme molecules (hashed red lines). Plots are for two temperatures of 300 K, and 350 K.

Studying Fig. 4.4 it is apparent that there is widespread coordination of glyme oxygens to lithium ions, and a smaller amount of coordination to the oxygen atoms

within the bistriflimide anion. However, in order to get a more meaningful understanding of the coordination dynamics it is necessary to look at this interaction in terms of coordination number.

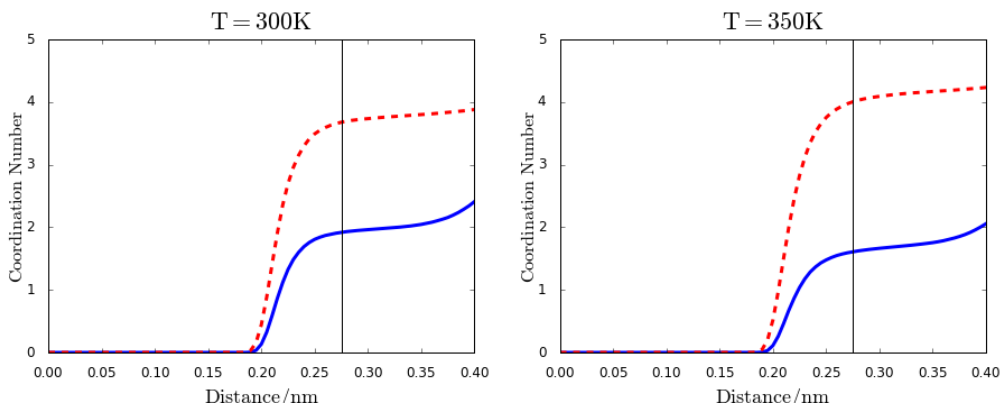


Figure 4.5: Cumulative coordination number of lithium cations to oxygen atoms in anions (blue solid lines), and to glyme molecules (hashed red lines). Plots are for two temperatures of 300 K, and 350 K.

Fig. 4.5 shows the cumulative coordination number of anion and glyme oxygens with distance away from the lithium cation. It is immediately apparent that the exact coordination number is largely dependent on the cutoff applied. The point at which the cumulative number density reaches a plateau could be defined as the value for the coordination number for a particular solvation shell. However, this may include terminal glyme oxygens which are in fact uncoordinated to the lithium cation. Another option is to use the value for σ term in the pair potential between lithium and oxygen calculated from the simulation combination rules, indicated by the black solid line in Fig. 4.5. The coordination numbers achieved at this point are within 0.1 of those previously reported, an acceptable difference in values given the relatively small number of ions. In later calculations a higher cutoff will be used. The difference in coordination number between the two temperatures is relatively small. At 300 K the average lithium glyme oxygen coordination number is approximately 3.8 while

the value for lithium anion oxygen coordination is about 1.4. At 300 K the lithium glyme value is roughly 4 while the lithium anion value is 1.9.

4.4.3 Transport Properties

The transport properties of $[Li(G4)][TFSI]$ provide an important point of comparison with experimental results. Though experimental transport properties are not quantitatively reproduced by use of non-polarisable ionic liquid force fields [137, 153], there is one key feature that must be observed in order for the force field to be considered as correctly mirroring the coordination environment. It is of critical importance that the self diffusion constants of the lithium ion and the glyme molecule are of the same value [6, 153]. If this is not the case then chelation cannot be viewed to have completely taken place. Fig. 4.6 shows self diffusion constants for lithium ions, glyme molecules, and bistriflimide anions at both 350 K, and 300 K. The agreement between values observed for lithium ions and glyme molecules is very close, with even the noise observing the same pattern.

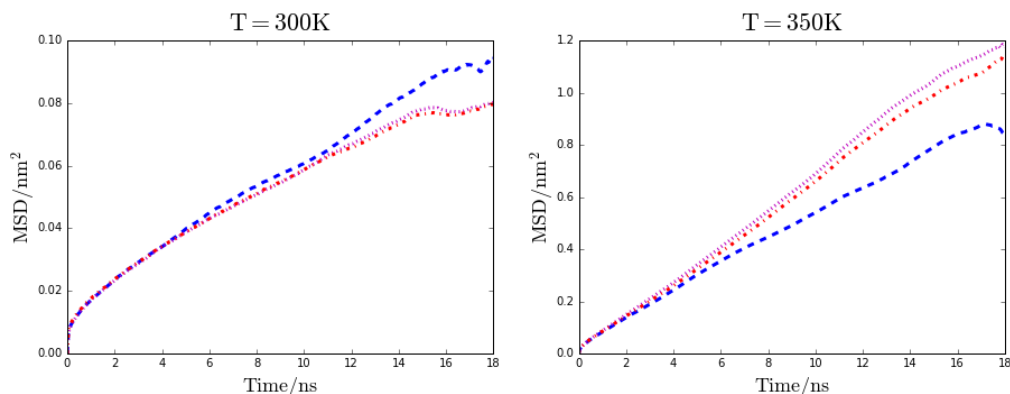


Figure 4.6: Mean square displacement of the three different species at two temperatures, 300K, and 350K. The anion plot is coloured blue, the plot for lithium cations is shown in red, and the glyme molecule is shown in magenta.

There is a second advantage to the results observed here and in the previous section. The fact that temperature increases diffusion, while having little effect on

the relative magnitude of self diffusion constants, or the coordination environment of the lithium cations means that it is possible to run simulations for interfacial properties at a fixed surface charge at a higher temperature. This technique has been used in past studies of conventional ionic liquids [62, 78, 164, 165]. The increase sampling speed decreases computational cost, and in this case due to the lack of change in bulk coordination structure it is possible to assume that this technique can be used.

4.5 Simulations of [Li(G4)][TFSI] at Electrodes with a Fixed Surface Charge

Fixed electrode charge simulations have been used to study conventional ionic liquids at interfaces with a fixed surface charge. Fixed charge simulations have been shown to give greater differences with the experimentally measured capacitance relative to fixed voltage simulations [61, 166] (like those presented in Chapter 5). However they have been effective in providing information regarding the interfacial nanostructure of ionic liquids. Of particular concern for this system, however, is the ability of the electrode to correctly model the dynamics of the dechelation of lithium ions from solvent molecules, in order to coordinate to the electrode. However previous studies have shown however that at low voltages fixed charge electrodes can correctly simulate the interfacial nanostructure of lithium-based electrolytes [167]. The remainder of this chapter will explore the results obtained from simulation of [Li(G4)][TFSI] at electrodes with a fixed charge boundary condition applied.

4.5.1 Methodology

Simulations of electrodes with a fixed surface charge were performed using methods adapted from previous studies by Fedorov, Lynden-Bell, and Ivaništšev [62, 78, 164, 165]. These simulations were performed using the Gromacs 5.0.4 Molecular Dynamics

software [103, 138–143]. The simulated system consists of two 6.8160 nm by 6.8866 nm graphitic slabs, separated by a distance of 12.1 nm. The area between the slabs is filled with ions at atmospheric density using the Packmol algorithm [144]. A vacuum slab, of thickness 6 nm, is placed behind the rightmost electrode to allow for the use of slab PME geometry [124, 145]. While Packmol creates a well distributed arrangement of the three components, due to its relatively coarse nature further equilibration is required to prevent the system from becoming quickly unstable during simulation. Steepest descent energy minimisation is performed four times followed by an initial run of 20,000 steps at a 0.01 fs time step. This somewhat elaborate procedure allows for stable starting conditions for the simulation. At this point the required charge is applied to the electrode, and is spread evenly across all the carbon atoms within the electrode. For this first set of simulations charges of $0 \mu\text{C}/\text{cm}^2$, $-5 \mu\text{C}/\text{cm}^2$, and $-10 \mu\text{C}/\text{cm}^2$ are used.

The first part of the simulation proper is an annealing step; velocities are applied to all atoms within the system in order to create a Boltzman distribution of kinetic energies with an average temperature of 350 K. Over the course of 5 ns, this system is annealed from 350 K, to 800 K, and back. A further equilibration run is performed at 350 K for a time of 0.5 ns. After this has occurred, a further 2 ns production run is performed at 350 K. Three replicas are created through this process, and are shown to converge over this timescale.

From this point, potential of mean force simulations are performed between a selected probe lithium cation and the negative electrode. This procedure is similar to one that has been used for Lennard Jones probe particles used in Chapter 3 and previously for conventional ionic liquids [78], and for alkali metal ions in alkali metal ionic liquid mixtures [168]. However, this system has a key difference from those previous systems. In those systems the coordination between the probe and the other components the liquid was either near non-existent, in the case of the Lennard Jones

probe in conventional ionic liquids, or undergoing far more reversible monodentate coordination in the case of the alkali metal ions. In this system the probe is coordinated to a large molecule, and can be seen to be relatively immobile when near the interface. In previous simulations the standard methodology has been to define a probe at the start of the simulations and move it towards the interface. However, in the case of this simulation system this requires a rather large period of equilibration. To mitigate this problem, a lithium ion, which is particularly close to the electrode at the end of the production run, is selected to be used as a probe particle. This probe is then pulled away from the electrode by means of centre of mass (COM) pulling. Pulling takes place at a constant speed of 0.001 nm/ps over the course of 3.5 ns. During the pulling processing the separation between the electrode and the lithium ion goes from 0.1 nm to 4.8 nm, with snapshots taken every 0.5 nm. Each of these snapshots is used as a starting point for a further 1 ns simulation with the probe held fixed in its starting location. The average force acting on the probe for the last 0.9 ns of each of these runs is taken, and a potential of mean force constructed by integration of forces acting on the probe from each position.

These simulations are performed using the V-rescale thermostat to maintain constant temperature [126], and as with all simulations performed using the Gromacs package in this thesis integration is performed by means of Gromacs's inbuilt leapfrog Verlet integrator. A cut-off of 1 nm is used for both electrostatic and dispersion interactions. While a plain cut-off is used in case of dispersion interactions, long range electrostatic interactions are calculate by means of the Particle Mesh Ewald (PME) method, with an Fourier Spacing of 0.12 nm and a PME order of 4. Finally a slab correction is used to allow for the use of a 3 dimensional PME grid [124, 145]. The bins in the density plots presented in this chapter have a width of 0.01 nm.

4.6 Results and Discussion

These simulations provided four main insights. Firstly, it was found that using electrodes with these boundary conditions, dechelation of lithium cations at the interface does not occur at the studied electrode charges. Further to this the coordination structure of lithium cations at the negative electrode undergoes a novel transition from 1-to-1 glyme to lithium coordination, to 2-to-1 glyme to lithium coordination, with increasingly negative electrode charge. The potentials of mean force provide an illustration of the energetics behind this phenomenon, and finally the nanostructure at the positive electrode appears to be very similar to the structure observed in conventional ionic liquids. Each of these points will be discussed in detail for the remainder of this chapter.

4.6.1 The Interfacial Nanostructure at the Negative Electrode

Fig. 4.7 shows a plot of the number density of lithium cations, the nitrogen atoms within the bistriflide anion, and the central oxygen within the glyme molecule with increasing distance from the electrode¹. Panel a) of Fig. 4.7 is a graphical legend showing the specific atoms for which the density is plotted. Panels b-d Show the number density of each component at surface charges of $0 \mu\text{C}/\text{cm}^2$, $-5 \mu\text{C}/\text{cm}^2$, and $-10 \mu\text{C}/\text{cm}^2$. The oscillations in density of species close to the interface, when compared to the bulk density, show the clear, and expected, presence of a structure that has been induced by the interface.

¹Particular atoms are chosen for the molecular components of the liquid as certain features are lost if a molecular centre of geometry or a molecular centre of mass is used instead of these “guide atoms”. In particular if the glyme center of mass is used instead of the central oxygen atom it is not immediately apparent that the lithium is not the closest body in the system to the negative electrode.

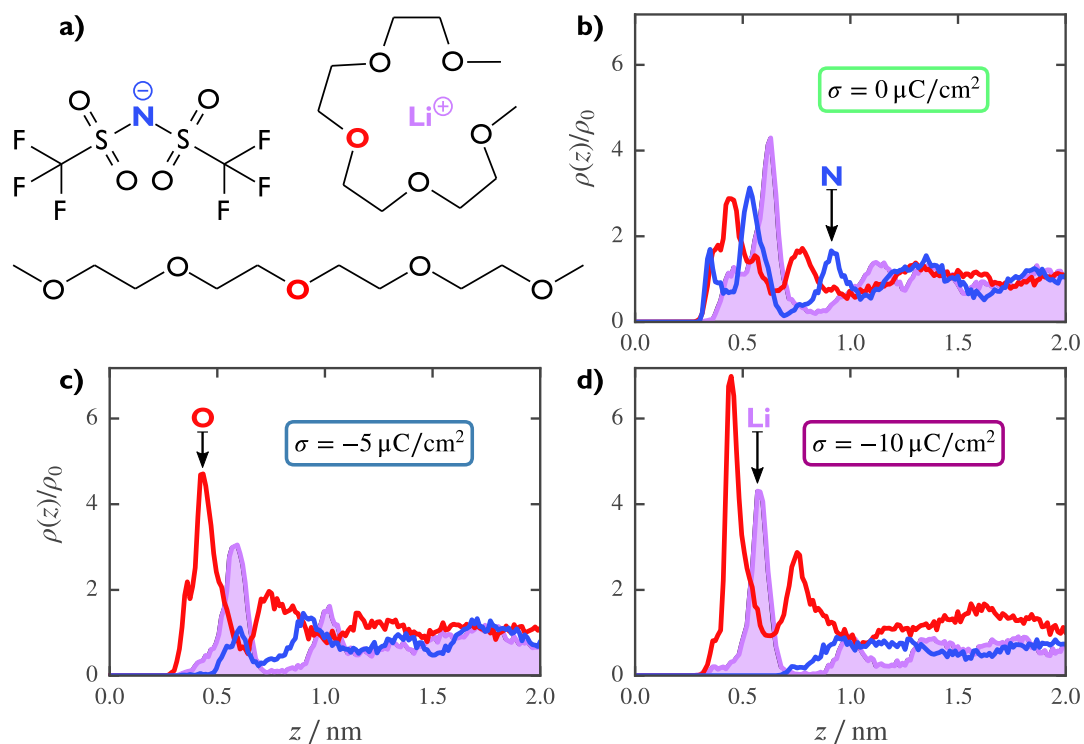


Figure 4.7: Figure explaining the Structural formula of bistriflimide anion, lithium–glyme complex and tetraglyme with colored atoms to indicate the colour code in subsequent panels (a), and relative number density profiles ($\rho(z)/\rho_0$) of bistriflimide nitrogen (blue), Li^+ (purple), and central glyme oxygen (red) (b–d). The model electrode with surface charge values of $0 \mu\text{C}/\text{cm}^2$ (b), $-5 \mu\text{C}/\text{cm}^2$ (c), and $-10 \mu\text{C}/\text{cm}^2$ (d) is situated at $z = 0$ nm.

Consideration of the interfacial nanostructure yields a number of interesting points. Most startlingly, inspection of Fig. 4.7 shows that the lithium ions stay in approximately the same location with ever-increasing charge. This means that there is no surface charge induced lithium dechelation at the electrode at any of the charges studied. In conjunction with this the two peaks for the glyme oxygen atoms either side of central lithium peak also remain in the same locations. Further to this, there is little enhancement in interfacial lithium concentration with increasing surface charge. In fact, interfacial lithium concentration declines on changing surface charge from $0 \mu\text{C}/\text{cm}^2$, to $-5 \mu\text{C}/\text{cm}^2$. However, increasing the magnitude of electrode surface charge still causes this system to react to screen the charge. Charge screening can

take place by either co-ion repulsion, or counter-ion attraction [86, 169]. For this system, screening takes place by the expulsion of bistriflimide anions, with increasing ion expulsion observed with increasingly negative interfacial charge. The space that would have been taken up by these anions is filled with additional glyme molecules, as cation attraction does not take place. In a conventional ionic liquid, the co-ion expulsion, and counter-ion attraction are mutual processes; there can be no expulsion of co-ions without a simultaneous attraction of counter-ions. This is due to them being the only components of the liquid. The simplified portrait of a solvate ionic liquid would seem to only allow for simultaneous attraction, and repulsion in this case as well. However, there are more than two components in solvate ionic liquid, and, in this case, an equimolar concentration of lithium cations and glyme molecules is not observed at the negative electrode.

The nanostructure of solvate ionic liquids at the negative electrodes raises two questions; why does lithium not coordinate directly to the electrode surface? And what effect does the non-equimolar concentration of lithium cations and glyme molecules have on the coordination structure of lithium complexes? The next two sections will discuss the answers to these two questions.

4.6.2 The Interaction Between a Lithium Cation and a Fixed Charge Electrode

The lack of coordination of lithium cations to the negative electrode has a profound effect on the nanostructure observed for this liquid at a fixed charge electrode. This behaviour can be better understood by looking at the potential of mean force for a lithium ion approaching the electrode. Fig. 4.8 shows the potential for each of the studied negatively charged electrodes, as well as for a neutral interface.

The potential of mean force for each of the surface charges shows an increasing favorability for lithium ions to be within the first nanometer from the electrode with

increasingly negative surface charges. This is as would be expected; the electrostatic attraction between the lithium ion and the electrode should lead to an energetic payoff as the lithium ion approaches the electrode.

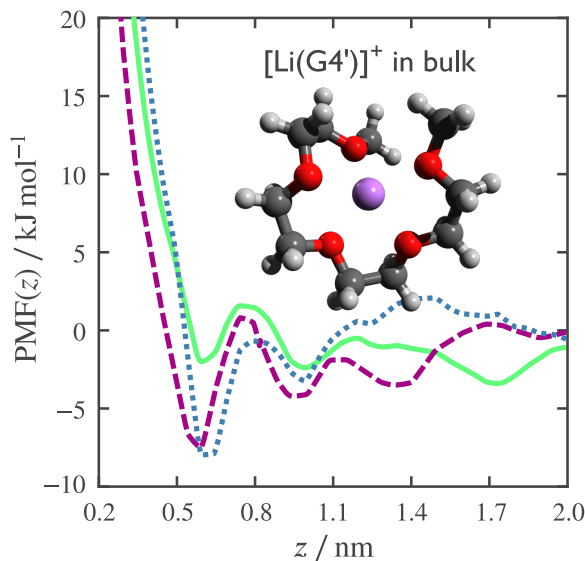


Figure 4.8: Potential of mean force profiles (PMF(z)) for Li^+ approaching the surface with surface charge values of $0 \mu\text{C}/\text{cm}^2$ (light green solid line), $-5 \mu\text{C}/\text{cm}^2$ (blue dotted line) and $-10 \mu\text{C}/\text{cm}^2$ (dark violet dashed line). The inset shows a CPK model of lithium-glyme complex ion with a coordination number of 5 which is typical for bulk $[\text{Li}(\text{G4})][\text{TFSI}]$.

A second, interesting point, to be drawn from the potentials of mean force is that in all cases a hard-wall repulsion is observed at roughly 0.5 nm. This result is, at first perplexing as there are only two potentials acting between the lithium ion and the electrode; the Lennard Jones potential and the electrostatic attraction. In the case of the latter the potential will always be either attractive, or in the case of the neutral electrode, non-existent. While the pauli repulsion is the reason for the eventual hard-wall repulsion, the σ value for the pair potential between the lithium cation and the carbon electrode is roughly 0.3 nm, meaning the Lennard-Jones interaction between the lithium cation and the electrode is still attractive at the point where the hard-wall emerges in Fig.4.8. There must, therefore, be another mechanism by which

this hard-wall is caused beyond the interactions between the lithium cation and the electrode.

The presence of the hard-wall is due to the interactions between coordinating groups and the lithium ion. It is worth noting that even at the highest electrode charges studied the charge on a single electrode atom is not equal in value to the partial charge on the oxygen atoms in both the glyme and the bistriflimide anion. Therefore, it is not energetically favourable for a lithium ion to come into direct coordination with the electrode surface when that leads to the disruption of lithium coordination to oxygen atoms. Due to the bulky size of the glyme ligand, the complex cannot orientate itself in such a way to allow this to happen. This, in turn, causes the lithium cations to be located further away from the electrode, leading to onset of the hard-wall taking place further from the electrode than the van der Waals hard-wall. This effect also explains why the first peak in the lithium number density plot, shown in Fig. 4.7 remains static with increasingly negative surface charge.

A related, and not insubstantial, point is that the hard-wall in Fig. 4.8 for a lithium ion approaching a neutral electrode is of lower gradient than for a negatively charged one. A feature which may be considered counterintuitive, however inspection of panel b) of Fig. 4.7 does provide some explanation. The nanostructure for a neutral electrode is more disordered, with more poorly defined peaks, and a greater number density of lithium ions at distances less than 0.5 nm. This is correlated with a lower relative unfavourability of lithium cations being positioned closer to the neutral electrode. It is not possible from the evidence presented in this thesis the exact reason for this lack of order, however, it is likely that it is rooted in the presence of a greater amount of bistriflimide anions near to the electrode. The presence of these bistriflimide anions disrupts the interfacial structure leading to a structure with less order, and therefore a less well-defined minimum in the potential mean force.

4.7 The Coordination Environment of Interfacial Lithium Cations

Lithium cations in the first interfacial layer, corresponding to the first peaks at approximately 0.5 nm from the interface, shown in Fig. 4.7, exist in a novel coordination environment. As was previously discussed, the charge neutralisation mechanism in this system favours co-ion depletion, over counter-ion enrichment. This process leads to an overall decrease in the interfacial ion density, consequently leading to enrichment in the interfacial glyme density. This is apparent from the increasing relative magnitude of interfacial glyme peaks in Fig. 4.7. Co-ion depletion leads to a non-equimolar concentration of lithium ions relative to glyme molecules in the interfacial layer. This change in concentration leads to the emergence of 2-1 glyme to lithium coordination complexes, a profound change in the coordination structure. The following paragraphs will discuss this transition by looking at the change in lithium coordination environment with increasing surface charge.

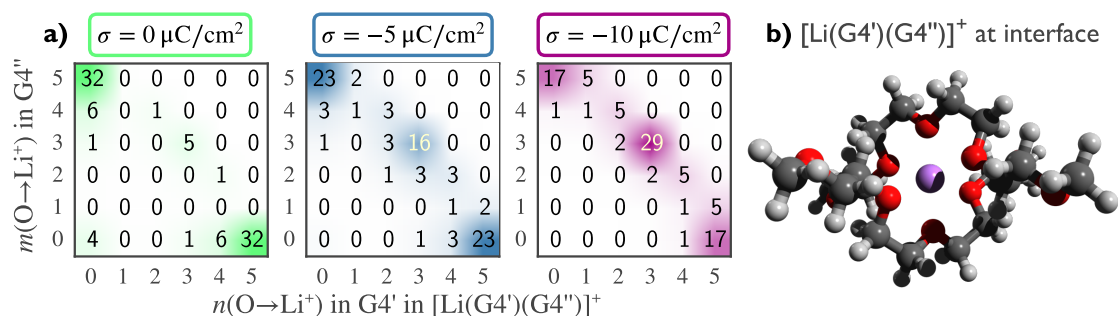


Figure 4.9: Integer percentage of Li^+ coordinated by n oxygens from $\text{G4}'$ and m oxygens from $\text{G4}''$ in the first layer of interface with surface charge values of $0 \mu\text{C}/\text{cm}^2$, $-5 \mu\text{C}/\text{cm}^2$ and $-10 \mu\text{C}/\text{cm}^2$ (a). A CPK model of $[\text{Li}(\text{G4}')(\text{G4}'')]^+$ with $n = 3$ and $m = 3$ found at lower surface charges (b). The sum of integers in each diagram is less than 100 due to rounding down of a large number of elements with small values close to zero.

The coordination structure of interfacial lithium cations, those cations within 0.7 nm of the electrode, is reported in Fig. 4.9 for three different surface charges. The

plots within Fig. 4.9 report the population densities of lithium cation coordination numbers to oxygen atoms from two glyme molecules. The coordination number of one glyme is said to be equal to n , while the coordination number of the second molecule is said to be equal to m . For those lithium cations which are coordinated to a single glyme molecule either m or n is said to be equal to 0. Assignment of glyme molecules to be either m or n is entirely arbitrary, and thus the plot is symmetrical. To reduce noise the cut off for lithium to glyme oxygen coordination number is set to be equal to 0.35 nm, a value where the bulk coordination number, shown in Fig. 4.5, has reached a plateau. As coordination numbers are calculated for each lithium ion for each frame all coordination numbers are integer values.

At a surface charge of $0 \mu\text{C}/\text{cm}^2$, the interfacial lithium cations are shown to be largely coordinated to a single glyme molecule. This can be seen by the fact that the majority of the atoms reported are coordinated to five oxygen atoms in one glyme molecule, and to none in any other glyme molecule. A portion of ions are coordinated to four oxygens due to dynamic coordination, and decoordination of oxygen atoms, an effect which has been described previously for bulk systems [47]. At this surface charge there is a notable fraction of lithium cations, which are coordinated to no glyme molecules. This is again analogous to the bulk coordination structure where a fraction of lithium ions are seen to be solely coordinated to the anions. It is observed that the coordination environment of the interfacial lithium cations at neutral interfaces is relatively similar to the bulk. However, at negatively charged interfaces a very different nanostructure arises.

For a surface charge of $-5 \mu\text{C}/\text{cm}^2$, the number of lithium cations coordinated to no glyme molecules tends to zero. This is due to the decrease in bistriflimide density in the near interfacial region, as discussed in Section 4.6.1. With fewer bistriflimide anions present, lithium cations become even more likely to coordinate to glyme

molecules leading to the disappearance of the (0-0) peak in the plot for $-5 \mu\text{C}/\text{cm}^2$ in Fig. 4.9.

More interestingly, a different coordination mode emerges where lithium cations coordinate to two glyme molecules via three oxygen atoms on each. In order to understand why this happens, it is necessary to consider the coordination number preference of lithium cations. For these force field parameters, lithium cations prefer to coordinate to six oxygen atoms, and for most cations at the neutral, interface this is achieved by coordinating to a single anion, and a single glyme molecule. However, with increasing glyme concentration, and decreasing concentration of anions, the requirement for six coordinating oxygen atoms must be met another way. This can be achieved by coordination to glyme molecules via three oxygens each, allowing lithium to be fully coordinated without need for a coordinating anion. For a surface charge of $-5 \mu\text{C}/\text{cm}^2$, this coordination mode is adopted by approximately 16 % of cations-just under half the number that adopt the conventional (5-0) coordination mode.

An increase in surface charge to $-10 \mu\text{C}/\text{cm}^2$ leads to an even greater percentage of lithium cations adopting this (3-3) coordination mode. This is an expected response to the even greater concentration of glyme molecules, and the concurrent diminishment of bistriflimide anions. For a surface charge of $-10 \mu\text{C}/\text{cm}^2$, more lithium cations adopt (3-3) coordination, than the more conventional (5-0) mode.

There are multiple ways these results could be interpreted. In the past, extended coordination structures have been observed that for non-equimolar solutions of lithium salts in glyme solvent. These structures, such as extended helical chains and helical dimers [160, 161, 170], create solvate complexes with two-to-two lithium to glyme molecule coordination is observed. The data recorded in Fig. 4.9 is not inconsistent with this conclusion. However, further examination of the simulation data shows that under 5 % of interfacial glyme molecules are coordinated to more

than one lithium cation. This means that, in this system a structure based around coordination of two glyme molecules to a single lithium is observed. This appears not to have been previously reported in the literature.

The previous three sections have discussed the novel structure observed at the cathodic interface for solvate ionic liquids. The next section will discuss the interfacial nanostructure at anodic interfaces. This behaviour is far more similar to conventional ionic liquids.

4.8 The Nanostructure of Solvate Ionic Liquids at the Positive Electrode

The nanostructure at the positive electrode is shown in Fig. 4.10. Increasing surface charge leads to enrichment of anions in the interfacial layer. Cations are repelled from the interfacial region. However, unlike in the case of the negative electrode, the glyme molecules and the lithium cations move together as a single species. As observed for conventional ionic liquids counter-ion attraction occurs alongside, and at the same rate as co-ion repulsion [59, 79]. This is as would be expected; the driving force behind the novel structure observed at the negative electrode is the lithium cations' requirement to maintain a full coordination shell. In the case of the positive electrode, these ions are moving away from the interface, and therefore this driving force is not observed. This solvate ionic liquid behaves in the same way as any other bistriflimide ionic liquid. For the charges studied the structure transitions from a mixed monolayer structure to a charged bilayer, as discussed in the introductory chapter. However, this structure is not wholly the same as a conventional ionic liquid. In particular, the behaviour of the lithium cations and glyme molecules in the first interfacial layer is a feature that was not observed for conventional ionic liquids.

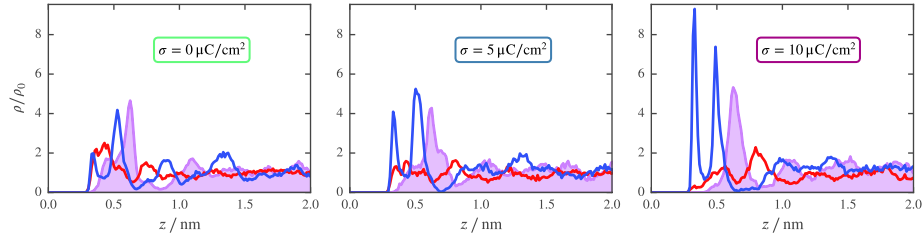


Figure 4.10: Relative number density profiles ($\rho(z)/\rho_0$) of bistriflimide nitrogen (blue), Li^+ (purple), and central glyme oxygen (red). The model electrode with surface charge values of $0 \mu\text{C}/\text{cm}^2$, $+5 \mu\text{C}/\text{cm}^2$, and $-10 \mu\text{C}/\text{cm}^2$ is situated at $z = 0 \text{ nm}$.

4.9 Distribution of Oxygen Atoms Coordinating to Lithium Cations

Given the previously discussed novel coordination environment of lithium cations, it is of interest to consider the geometric arrangement of oxygen atoms around the interfacial lithium cations. In order to explore this, the vector between the lithium cations and the coordinating oxygen atoms from both species is determined, as is the angle between that vector and the vector normal to the interface, as shown in the left panel of Fig. 4.11. This angle, θ , can be used to describe the shape of the coordination shell around the interfacial lithium cation.

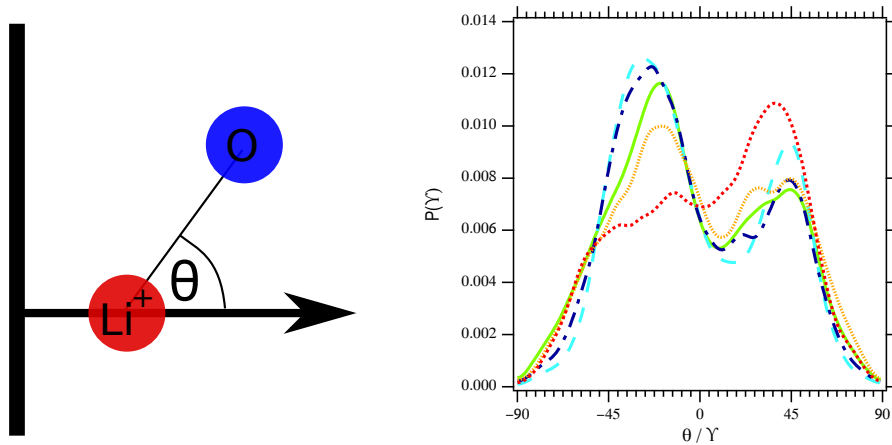


Figure 4.11: The population density of coordination angle θ plotted for the five surface charges $-10 \mu\text{C}/\text{cm}^2$ (dark blue), $-5 \mu\text{C}/\text{cm}^2$ (cyan), $0 \mu\text{C}/\text{cm}^2$ (green), $+5 \mu\text{C}/\text{cm}^2$ (orange), and $+10 \mu\text{C}/\text{cm}^2$ (red).

Fig. 4.11 shows the form of the coordination shell for the five studied surface charges. If coordination were equally probable from any direction the form of the distribution would be expected to follow the equation $P = \sin(\theta - 90^\circ)$, where P is the probability of that value of θ being observed. However, it is clear that none of the distributions studied take the form of a smooth sine curve.

The first point of interest in this plot is that there is a definite form to these distributions. There is a large probability of ions coordinating with any θ angle between -70° and $+70^\circ$. This is indicative of a somewhat disordered structure, with no complex structural arrangement as observed for lithium glyme coordination in other systems [160, 161, 170]. However, there are several significant features that are common across all interfaces. Firstly, for all but the most positively charged interface, the distribution takes a form with two peaks; one at a value $\theta < 0$ and another at a value of $\theta > 0$. These two peaks correspond to two approximate planes of coordination. The formation of these planes is templated by the interface due to steric constraints, and correspond to the peaks in coordinating species seen either side of the first lithium peak in Fig. 4.7.

The relative intensities of the two peaks in Fig. 4.11 are due in large part to the change in nanostructure owing to the change in surface charge. As a general rule, the more negative the surface charge, the greater relative intensity of the front most peak relative to the hind most peak. However, alongside this, the peak at negative values of θ is closer in value to 0 than the peak for a positive value of θ . Both of these effects decline with increasingly positive surface charge. One way to look at this is that, while interfacial lithium cations do not decoordinate from solvents in order to come into contact with the electrodes, there is still an attraction of lithium cations towards the interface. This leads to a warping of the coordination shell, with lithium ions moving closer towards the interface. Secondary evidence for this interpretation can be found in Fig. 4.7 panel (d) where the lithium peak is closer to the front most

oxygen peak (which corresponds to the negative θ peak in Fig. 4.11), than the second oxygen peak (which corresponds to the positive θ peak in Fig. 4.11). The driving force behind the less significant preference observed for some positive charges is probably related to the lower mobility of coordinating substituents of the interface side of the ions. This decreases the ability of these atoms to coordinate and uncoordinate to the lithium cations.

The one anomalous curve for $+10\mu\text{C}/\text{cm}^2$ is largely due to the development of a fully segregated charge bilayer. In this system, the majority of coordination takes place to the glyme oxygens further from the interface, as observed in Fig. 4.10.

4.10 Conclusion

This chapter presented the interfacial nanostructure of solvate ionic liquids at electrodes with fixed charges. The solvate ionic liquid behaves as a conventional ionic liquid at the positive electrode. However, the interfacial nanostructure observed for these systems at the negative electrode is different from the structures observed for conventional ionic liquids. The driving force behind this novel structure is that the electrostatic interaction between the electrode and the lithium cation is far smaller than the interaction between the lithium cation and the oxygen atoms in the glyme molecule. In some ways, this could be anticipated as the electrostatic interaction between a glyme oxygen and a lithium atom in this system must emulate the charge based contribution to dative bonding. However, this fixed charge electrode is non-polarisable, an effect which is un-physical. In next chapter a more complete fixed potential electrode model will be used to study $[\text{Li}(\text{G4})][\text{TFSI}]$ in order to clarify whether this structure is dependent on the electrode model. However, even if this structure is incorrect for a real-world electrode, it may have an applicability for systems where a liquid interacts with an external field, with a particular relevance to possible future studies looking at electrowetting.

Chapter 5

Nanostructure of Solvate Ionic Liquids at Fixed Potential Electrodes

The previous chapter discussed the nanostructure of a lithium glyme solvate ionic liquid at electrified interfaces using fixed charge electrode boundary conditions. However, previous studies of ionic liquids and solutions of lithium salts that there can be substantial differences in the structures observed for those electrodes with a fixed charge boundary condition and fixed potential boundary conditions applied [171].

This chapter uses the methodology developed by Wang *et al.* to simulate the nanostructure of [Li(G4)][TFSI] at electrodes with a fixed surface potential. This chapter starts by introducing the theoretical basis of the method use by Wang *et al.* [167] followed by presenting these new simulations.

5.1 Theoretical Basis of Fixed Potential Simulations

There are a number of methodologies for performing simulations of electrochemical cells with fixed potential electrodes by means of molecular dynamics simulations. This chapter uses the methodology developed by Wang *et al.* [167], which in turn is heavily based on previous work by Gingrich *et al.* [172], Reed *et al.* [173], and Siepmann *et al.* [174]

The core of this method is the linking of the individual potential of every electrode atom to a preset external potential (V),

$$V = \psi_i = \frac{\partial U}{\partial Q_i}, \quad (5.1)$$

where ψ_i is the electric potential on electrode atom i , U is the potential energy of the system, and Q_i is the charge on the electrode atom i . Just as with the calculation of the electrostatic potentials when calculating the forces acting on particles in a conventional molecular dynamics simulation, the electric potential can be split into four terms,

$$\psi_i = \psi_i^{\text{k-space}} + \psi_i^{\text{real}} + \psi_i^{\text{slab}} + \psi_i^{\text{self}}, \quad (5.2)$$

where $\psi_i^{\text{k-space}}$ is the k-space contribution to electric potential, ψ_i^{real} is the real space contribution to electric potential, ψ_i^{self} is the self correction's contribution to electric potential, and ψ_i^{slab} is the slab correction's contribution to electric potential. In order to render the Ewald sum soluble in all circumstances the electrode atoms are modelled as Gaussian charges as opposed to a point charge model. The form of the Gaussian charge is defined as,

$$Q_i(\mathbf{r}) = Q_i \left(\frac{\eta^2}{\pi} \right)^{\frac{3}{2}} e^{-\eta^2(\mathbf{r}-\mathbf{R}_i)^2}, \quad (5.3)$$

where Q_i is the charge on electrode atom i , $Q_i(\mathbf{r})$ is the charge at a location r due to electrode atom i , $\mathbf{R}_i$ is the location of electrode atom i , and η is the characteristic width of the Gaussian charge.

All the potentials are calculated by means of Ewald summation, the real component of the potential is defined as,

$$\psi_i^{\text{real}} = \sum_{l=1}^{n'} \frac{\text{erfc}(r_{li}\alpha) - \text{erfc}(\frac{\eta}{\sqrt{2}}r_{li})}{r_{li}} + \sum_{j=1}^m \frac{\text{erfc}(r_{ji}\alpha) - \text{erfc}(\eta r_{ji})}{r_{ji}}, \quad (5.4)$$

where erfc represents the complementary error function, the left sum represents the interactions between electrode atom i and all other electrode atoms, and the right most sum represents the interactions between atom i and the atoms within the electrolyte. r_{li} is the separation between atom i and the electrode atom l ,

$$r_{li} = |\mathbf{R}_i - \mathbf{R}_l|, \quad (5.5)$$

and r_{ji} is the separation between atom i and electrolyte atom j ,

$$r_{ji} = |\mathbf{R}_i - \mathbf{r}_j|, \quad (5.6)$$

where $\mathbf{r}_j$ is the position of the electrolyte atom j .

The k-space component of the potential is defined as,

$$\psi_i^{\text{k-space}} = \frac{1}{V} \sum_{l=1} \Gamma(\kappa) [e^{-i\mathbf{k} \cdot \mathbf{R}_l} S(\mathbf{k}) + e^{i\mathbf{k} \cdot \mathbf{R}_l} S(-\mathbf{k})], \quad (5.7)$$

where $\mathbf{k}$ is the reciprocal lattice vector, and κ is defined as $|\mathbf{k}|$. The structure factor, $S(\mathbf{k})$, is defined as,

$$S(\mathbf{k}) = \sum_l^n Q_l e^{i\mathbf{k} \cdot \mathbf{R}_l} + \sum_j^m q_j e^{i\mathbf{k} \cdot \mathbf{r}_j} \quad (5.8)$$

and the Fourier coefficient is defined as,

$$\Gamma(\kappa) = \frac{4\pi e^{-\kappa^2/4\alpha^2}}{\kappa^2}, \quad (5.9)$$

where α is the width of the screening Gaussians in the Ewald summation.

In addition to the real space and k-space contributions to electric potential there are two additional corrections. These corrections, which were previously discussed in the Chapter 2, are the self correction,

$$\psi_i^{\text{self}} = \frac{\sqrt{2}\eta - 2\alpha}{\sqrt{\pi}} Q_i, \quad (5.10)$$

which corrects for the interaction of an atom with itself in k-space, and the slab correction, which corrects for the miscalculation of interaction energies due to the usage of a three-dimensional Ewald summation to measure electrostatic interactions within a slab,

$$\psi_i^{\text{slab}} = \frac{4\pi Z_i}{V} \left(\sum_{l=1}^n Q_l Z_l + \sum_{j=1}^m q_j z_j \right), \quad (5.11)$$

where Z_l is the position of electrode atom l in the z direction (the direction perpendicular to the electrode), and z_j is the position of the electrolyte atom j in z direction.

When grouped all of the terms within the calculation of the electric potential energy of an electrode atom can be split into a summation of those terms depending on the positions and charges of electrolyte atoms, and those dependent on the positions and charges of electrode atoms as follows,

$$\psi_i = \sum_l^n a_{li} Q_l + \sum_j^m b_{ji} q_j \quad (5.12)$$

by noting that the electric potential on a single electrode atom is equal to the externally set potential it is possible to rewrite Eq. (5.12) as,

$$\sum_l^n a_{li} Q_l = V - \sum_j^m b_{ji} q_j. \quad (5.13)$$

This can be converted into a set of linear equations,

$$\mathbf{A}\mathbf{Q} = \mathbf{V} - \mathbf{B}, \quad (5.14)$$

where $\mathbf{A}$ is a matrix comprised of a_{li} coefficients, and $\mathbf{B}$ is a matrix comprised of $b_{ji}q_j$ coefficients and V is the external potential. This can be solved for the unknown electrode atom charges, Q . Further to this the term $\mathbf{A}$ only needs to be calculated once for system as the electrode atoms are frozen in place throughout the simulations. The specific Lammmps based methodology implemented by Wang *et al.*, and used in this chapter only uses Ewald summation to calculate the charges on each atom. The actual calculation of the electrostatic component of the forces acting on atoms is performed via a PPPM solver.

Previous studies of conventional ionic liquids have shown a number of differences between simulations performed with a fixed surface charge and those simulations performed with a fixed surface potential [171]. Depending on the property of interest, the differences can be more or less significant. While there is a marked difference in the values obtained for differential capacitance there is little difference in the observed nanostructures, with perhaps one notable difference: it appears for fixed potential simulations the transitions in nanostructural arrangement of ions occur at a higher voltage for fixed charge simulations when compared to fixed voltage simulations [175]. This is not hugely surprising: imposition of a fixed potential boundary condition creates a local polarisability in the electrode which, based on the make up of the electrolyte in the near interfacial region, means that for low applied potentials there will be patches of net positive and net negative charge at the electrode. This stabilises the mixed monolayer structure for higher applied potentials, and leads to increased voltage at which the multilayer structure is first observed [175]. Further to this it leads to a greater integration of co-ions into the first interfacial layer at higher charges. Normally in fixed potential setups the charged multilayer structure features a slightly larger number of ions incorporated into the “wrong layer”. With perhaps the notable exception of recent simulations by Vatamanu *et al.* [94] for ionic liquid acetonitrile mixtures there are far fewer reported cases of crowding or persistent net counter-ion density for more than one interfacial layer for fixed potential simulations than for fixed charge simulations. However results obtained using the two methods are usually qualitatively very similar. Further to this, differences between the two models are not always due to the different electrode boundary conditions. The higher computational cost of fixed potential molecular dynamics simulations leads to most simulations being run with coarse grain electrolyte models [61, 80, 171, 176]. This leads to serious ambiguity about the causality of some effects.

Previous simulations using this exact method to study the interfacial behaviour of solutions of lithium salts in acetonitrile show limited breakdown of the lithium coordination shell at applied potentials below 2 V [167].

5.2 Simulation Methodology

The simulations performed in this chapter use the LAMMPS molecular dynamics package [104] with the fixed potential extension created by Wang *et al.* [167]. The methodology used for these simulations is somewhat different to those used in previous chapters.

Simulation systems are again produced using Packmol [144], however unlike with previous sections the interface consists of three layers of graphene (a thickness used in previous studies with the same method [82]). The dimensions of the electrodes are a little smaller than in the simulations in the prior chapter, with an area of 4.673 nm by 4.331 nm with a separation between each of the three graphenes of 0.335 nm. The two electrodes are separated by 8 nm, with this gap being filled by 346 ion pairs and glyme molecules (an equimolar ratio). Ionic liquids and graphenes are modelled using the CL&P force field and OPLS-AA force field used by Shimizu *et al* [100, 112, 114, 153], which are detailed in Appendix B and were used in the previous chapter.

Initially the charge on the electrode is set to be equal to 0. After preparation steepest descent energy minimisation is performed, followed by a 1 ns run with the temperature increased from 300K to 500K over the course of this run. At this point the fixed potential boundary conditions are applied to the electrode. Over the course of a 1 ns the system is cooled to 300 K, and at this point a 2 ns equilibration run is performed. After this a production run is performed for 6 ns. This process is repeated for four replicas, with potentials of -2 V to 2 V studied in steps of 0.25 V. In all runs timesteps of 1 fs are used, with the potential being updated every 10 timesteps.

While an Ewald summation is used to impose the fixed potential boundary conditions the effect of long range electrostatic interactions is computed using the PPPM solver [119–121] with a maximum error in calculated forces of 1×10^{-6} the size of the relevant force. The system is simulated in a slab geometry with an implicit vacuum slab [124] of twice the system length placed between the periodic boundaries in z direction to prevent the formation of a slab dipole [124]. Cutoffs of 1.2 nm are used for pairwise Lennard Jones and electrostatic interactions for the calculation of forces, but no such parameter is set for the potential fixing Ewald summation. The temperature is maintained using the standard LAMMPS thermostat, which is based on the Nosé-Hoover equations of motion [127, 128]. The Gaussian charge distribution is set so that $\eta^{-1} = 19.79 \text{ nm}^{-1}$ as in previous simulations [167, 173].

5.3 Nanostructure of Solvate Ionic Liquids at Fixed Potential Electrodes

The interfacial nanostructure of solvate ionic liquids at fixed potential electrodes is explored by means of density plots in Figs. 5.1 and 5.2. These plots reveal large differences from those produced from the fixed charge simulations, reported in the previous chapter.

The first major change observed for these new plots is the direct coordination of lithium ions to the electrode over a range of potentials. It was noted in the previous chapter that this does not happen at fixed charge electrodes, a major driving force for the interesting coordination structures observed for those systems. Fixed potential electrodes can be polarised by lithium ions in the near vicinity. This polarisation stabilises lithium ions that move into close contact with the electrode. The stabilisation is so effective that even for low positive potentials there are some lithium ions in near contact with the electrode. The level of stabilisation of lithium ions in direct contact

with the electrode rises with increasing negative electrode voltage, leading to rising intensity of this front most peak.

Further to this, in common with studies of conventional ionic liquids at fixed potential electrodes, a greater level of incorporation of co-ions near to the electrode is observed. In contrast to the observations at fixed charge electrodes, there is no potential at which complete charge segregation takes place. In spite of this however, there is still increasing segregation of counter-ions and co-ions with increasing surface potential. With increasingly positive surface potential there arises a structure with much in common with the multilayer structure observed for conventional ionic liquids. For electrodes with a potential greater than +0.75 V after the first interfacial layer there is an area, at 0.8 nm, with greatly diminished lithium density and a greatly enhanced bistriflimide density; this is followed by an area where there is a slight surplus of lithium ions.

The same appears to be true for increasingly negative surface potential. For electrodes with a potential more negative than -0.75 V, after the first interfacial layer there is a an area with surplus density of lithium cations at 1 nm and an area of net bistriflimide density at 1.4 nm in a manner similar to conventional ionic liquids. This shows a large difference from the results presented for electrodes with a fixed charge in the previous chapter. While these oscillations are small their periodicity is roughly equivalent to the AFM results recorded by Mclean *et al.* [177]. It is likely that this oscillation in density is what lead to the oscillatory force law measured by Mclean *et al.* at electrified graphitic electrodes.

5.4 Lithium Ion Coordination Numbers at the Negative Electrode

The coordination numbers of the interfacial lithium cations, defined as those cations within 0.5 nm of plane of the electrode, are reported for potentials of: 0 V -0.5 V,

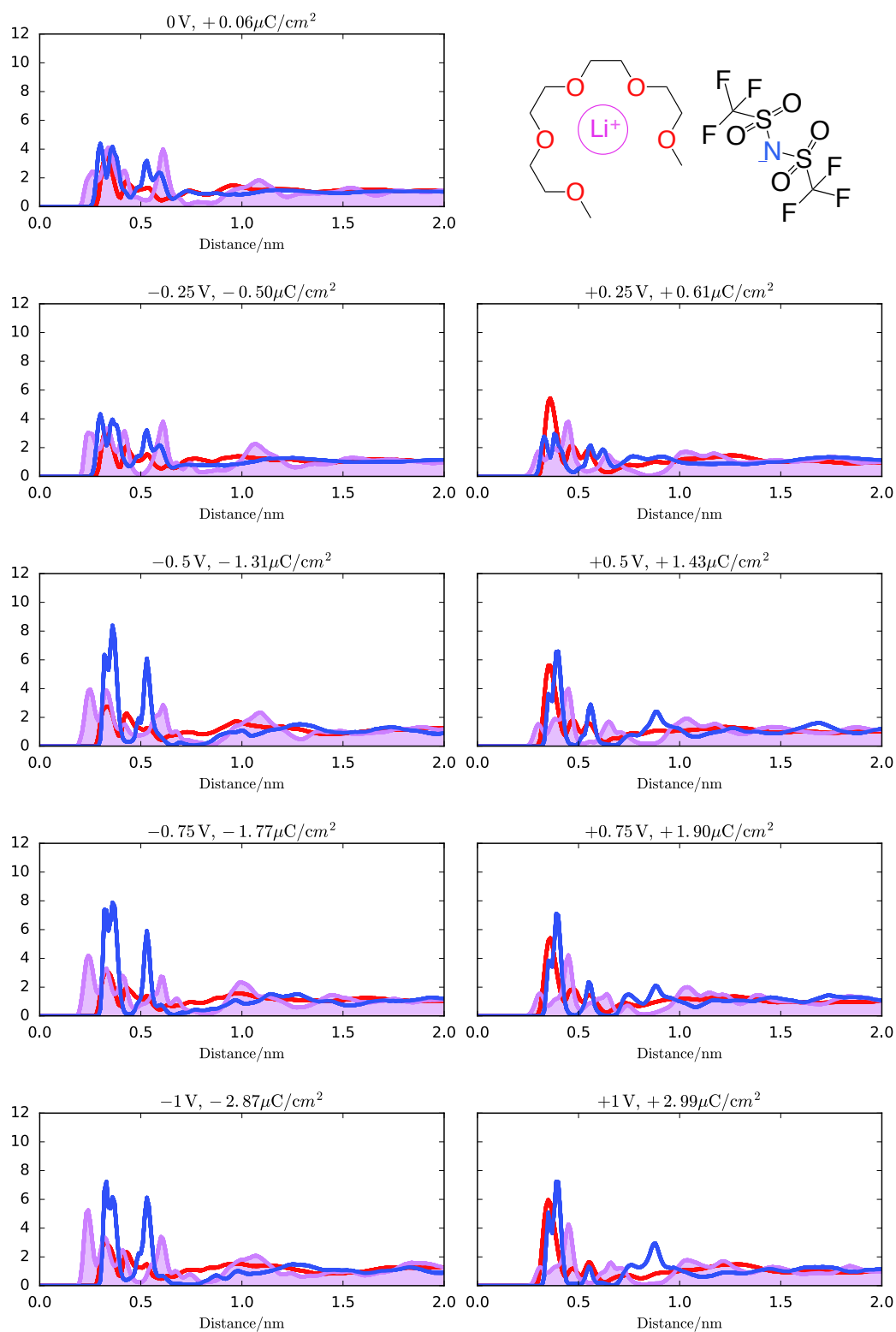


Figure 5.1: Interfacial density plots for $[\text{Li}(\text{G4})][\text{TFSI}]$ at fixed potential electrodes with applied potentials from 0 V to ± 1 V. Lithium cation density is shown in purple, bistriflimide nitrogen atom density is in blue, and central glyme oxygen atom density is shown in red. The average value of surface charge $\langle\sigma\rangle$ is shown for each plot.

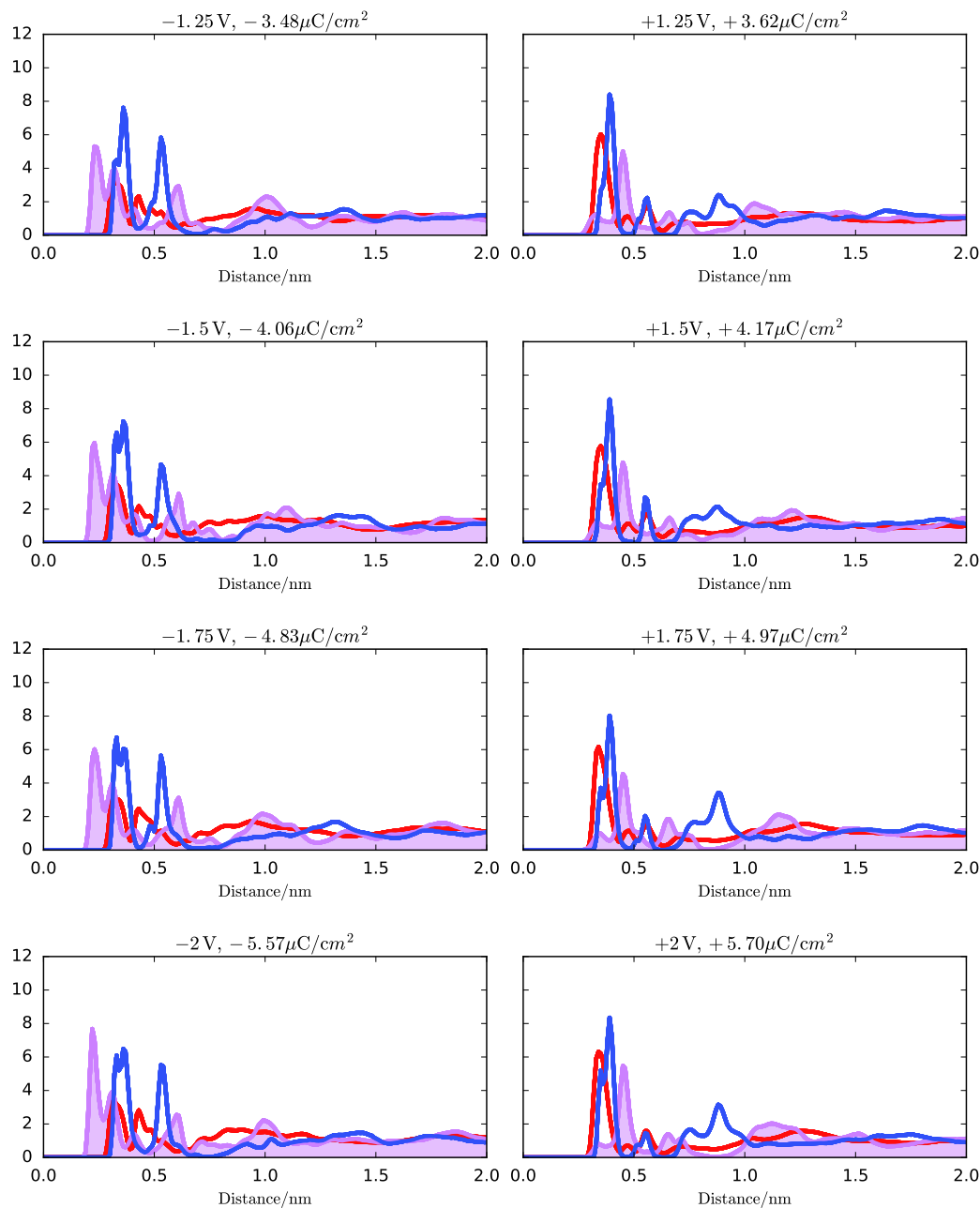


Figure 5.2: Interfacial density plots for [Li(G4)][TFSI] at fixed potential electrodes with applied potentials from ± 1.25 V to ± 2 V. Lithium cation density is shown in purple, bistriflimide nitrogen atom density is in blue, and central glyme oxygen atom density is shown in red. The average value of surface charge $\langle \sigma \rangle$ is shown for each plot.

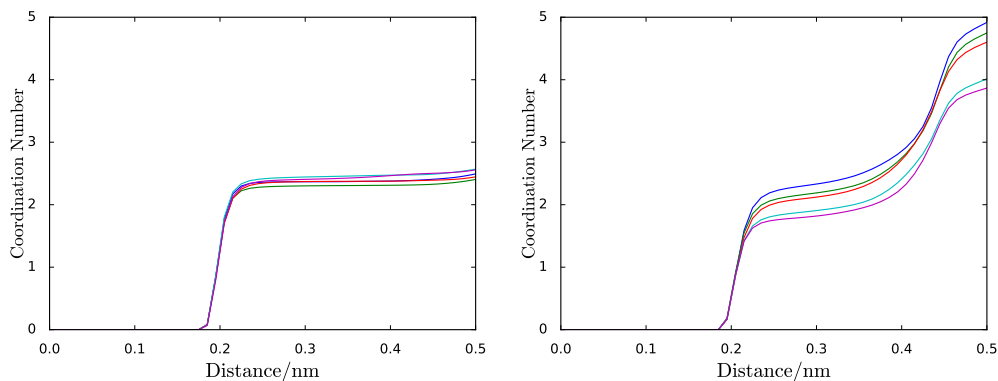


Figure 5.3: Cumulative coordination number with distance for interfacial lithium cations and glyme oxygens (left), and interfacial lithium cations and bistriflimide oxygens (right). Plots are shown for potentials of: 0 V (in blue), 0.5 V (in green), 1 V (in red), 1.5 V (in blue), and 2 V (in pink). Interfacial lithium cations are defined as those lithium cations within 0.6 nm of the electrode.

-1 V, -1.5 V, and -2 V in Fig. 5.3. The coordination numbers of lithium cations to glyme oxygens are all roughly the same regardless of the interfacial voltage, however the coordination numbers are considerably lower than in the bulk where the value is approximately 3.8.

Meanwhile the coordination numbers for lithium cations to bistriflimide oxygen anions decrease with increasing surface potential. This is probably due to the increasing repulsion of bistriflimide anions by an increasingly negative electrode. This in turn leads to a diminished concentration of bistriflimide anions in the first interfacial layer and thus a decreased probability of coordination. For all potentials the coordination number of lithium to anion oxygens is slightly greater than in the bulk liquid, which is a complementary effect to the decreased level of coordination to glyme molecules.

Average coordination numbers as shown in Fig. 5.3 provide an interesting window into changes in coordination number. However, this picture is somewhat incomplete. The lower lithium glyme coordination numbers shown in Fig. 5.3 could be representative of either fewer lithium cations being coordinated by glyme molecules, or the number of contacts between lithium cations and coordinated glyme molecules

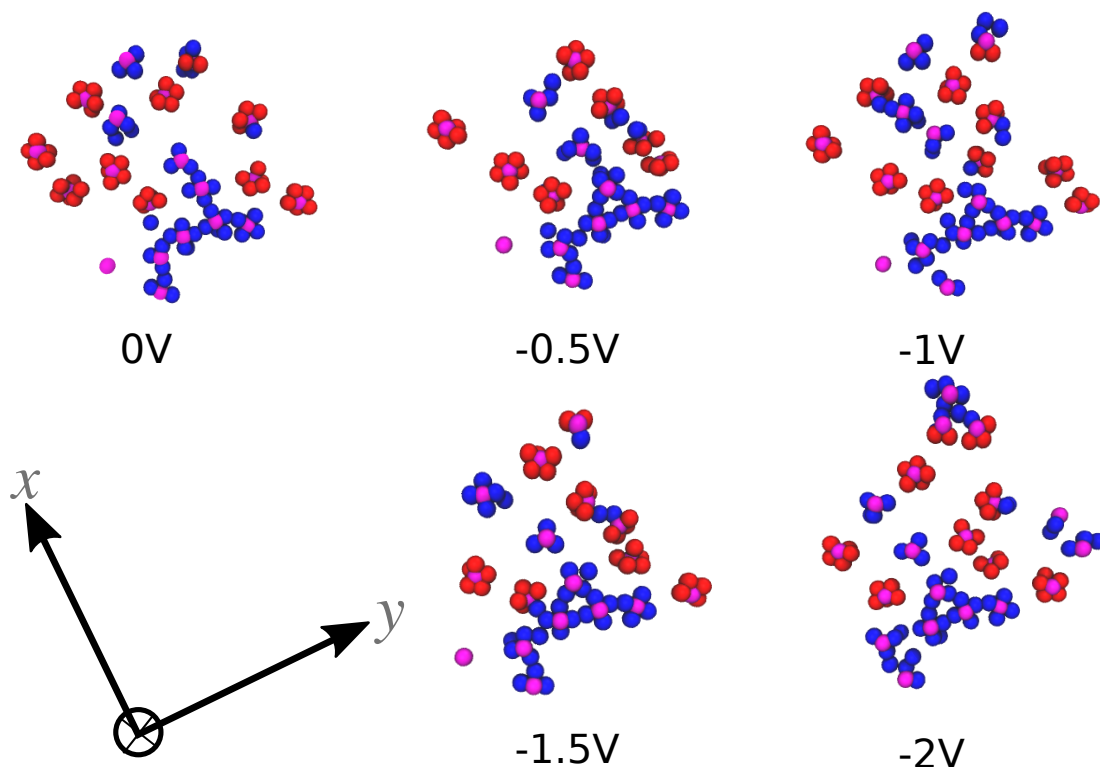


Figure 5.4: Snapshots of the interfacial lithium ions in the plane of electrode, taken from the direction of the electrode. Showing lithium cations within 0.6 nm of the electrode as well of the oxygen atoms coordinating to these lithium cations Snapshots are shown for surface potentials of: 0 V -0.5 V, -1 V, -1.5 V, and -2 V. Lithium cations are shown in pink, bistriflimide oxygens are shown in blue, and glyme oxygens are shown in red. Atoms other than lithium cations and oxygen atoms are excluded in the interest of ease of clarity.

decreasing. Fig. 5.4 shows snapshots of the interfacial lithium cations, and their coordination shells taken from the simulations. The lithium cations are shown in pink, the bistriflimide oxygen anions are shown in blue, and the glyme oxygen atoms are shown in red. On inspection of these snapshots it is clear that there are two distinct types of lithium coordination environment present at the interface. Lithium cations are coordinated primarily to either anions or glymes, some cations are formed of clusters lithium cations and glyme molecules as seen in the bulk structure of solvate ionic liquids. However at the interface clusters of lithium cations and bistriflimide anions

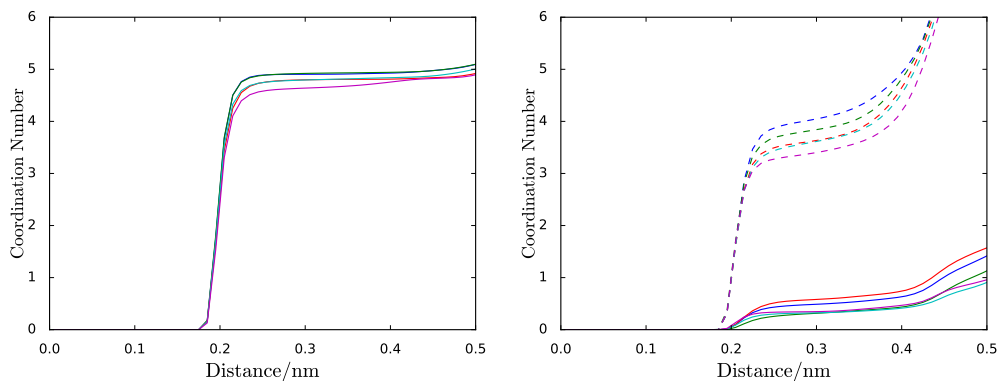


Figure 5.5: Cumulative coordination number with distance for interfacial lithium cations and glyme oxygens (left), and interfacial lithium cations and bistriflimide oxygens (right). Unlike in Fig. 5.3 clusters where lithium is coordinated to glyme and clusters where it is not are plotted separately. The solid lines are plots for those lithium cations coordinated to a glyme oxygen, and the dashed lines are for those coordinated solely to anions. Plots are shown for potentials of: 0 V (in blue), 0.5 V (in green), 1 V (in red), 1.5 V (in blue), and 2 V (in pink). Interfacial lithium cations are defined as those lithium cations within 0.6 nm of the electrode.

are observed. This is corroborated by the plots in Fig. 5.5 of coordination numbers of lithium cations coordinated to glyme molecules and those not coordinated to glyme molecules. These plots show the presence of two widely divergent coordination structures. The solid lines which represent the coordination numbers for lithium cations which are coordinated to at least one glyme oxygen atom show coordination numbers of nearly 5 being observed for these systems, and anion coordination numbers of significantly less than 1¹. The dashed lines show the lithium anion oxygen coordination number for lithium cations which are wholly uncoordinated to glyme molecules. As would be expected these lithium cations exhibit higher lithium-anion coordination numbers with values between 3 and 4. This coordination number appears to decline with increasing surface potential, as previously theorised this is probably due to the potential induced depletion of bistriflimide anions in the first interfacial layer.

¹The dependence on voltage of the coordination number for these systems is difficult due to ascertain due to the poor statistics

The snapshots shown in Fig. 5.4 show the presence of a domainal structure where lithium cations coordinated to bistriflimide anions form extended chains while the glyme complexes concentrate together in regions away from these chains. With increasing surface charge the size and definition of this domain appears to slightly increase, this is likely to have a route in the surface charge polarisability that can be observed for electrodes to which fixed potential boundary conditions have been applied. With net positively charged glyme complexes concentrating at locations of greatest negative charge and the more charge neutral cation anion complexes forming in areas where the electrode surface charge is less intense. A point that is supported by the increasingly defined nature of the domains with increasing surface charge. This structure bears some similarity to the results obtained by Merlet *et al.* [80] for conventional ionic liquids where increasing potential leads to crystallisation of ions in the near interfacial layer.

One last point of interest from the study of coordination environments in Fig. 5.4 is the increasingly geometrically warped nature of the coordination complexes with increasing surface potential. As potential increases the number of lithiums where some of the coordination shell sits between the electrode and the lithium cation decreases markedly. This means that coordination shells of these complexes are increasingly one sided. This complements the observed increase in the size of the front most peak in lithium number density in Figs. 5.1 and 5.2 with increasing surface potential.

5.5 Changes in Electrode Charge Distribution with Increasing Potential

The charges on the electrode in a system with fixed potential boundary conditions can be observed to fluctuate in a manner defined by a Boltzmann distribution. Non-Gaussian distribution of charges in the electrode is indicative of electrode polarisation being caused by another source, an effect which is often observed for systems

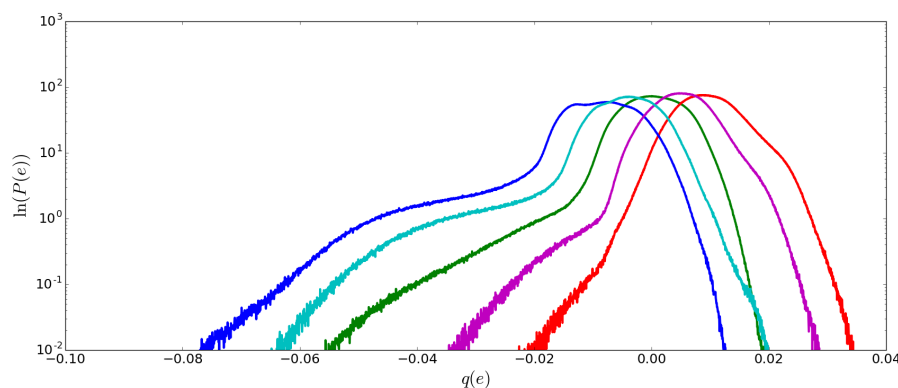


Figure 5.6: Distribution of charge in the inner layer of atoms in each electrode. Plots are shown for applied potentials of: -2 V (blue), -1 V (cyan), 0 V (green), +1 V (magenta), and +2 V (red).

containing lithium. Fig. 5.6 shows the charge distribution within the inner layer of atoms in the electrodes.

These plots are conventionally supposed to have a Gaussian form owing to the standard Boltzmann distribution of energy in the liquids. However all the plots in this system have a bi-Gaussian and even bi-modal quality, with a main peak occurring at a slightly more positive charge and a smaller second peak occurring at a more negative charge. This pattern has previously been observed for similar simulations of lithium solutions [167], and some systems without ions such as water at platinum electrodes [178]. In this case this double peak structure is due to the local polarisation of the electrode by lithium cations within the near surface region. The peak declines with increasingly positive potential due to the depletion of lithium cations in the near surface region. This effect appears to be particularly profound for this system relative to previous studies and is probably due to the exceptionally high concentration of lithium cations. This leads to a far higher density of lithium cations in the near interfacial region.

Further to this, these plots also give reason as to the large difference in nanostructure observed for these liquids at fixed charge and fixed potential electrodes. The ready polarisability of fixed potential electrodes allow for electrode atoms to have

charges closer to the partial charges of the oxygen atoms in the bistriflimide anions and glyme molecules, causing the previously mentioned relative stabilisation of lithium cations.

5.6 Capacitance and Potential of [Li(G4)][TFSI] at Fixed Potential Electrodes

In fixed potential simulations the capacitance, $C(\Delta\Psi)$, of the electrode can be calculated by studying the fluctuations of electrode charge over time using the relationship [82],

$$C(\Delta\Psi) = \frac{\partial Q}{\partial \Delta\Psi} = \beta \langle \delta Q \rangle, \quad (5.15)$$

where Q is the total charge on the electrode, $\beta = 1/k_B T$ (where k_B is the Boltzmann constant) and $\langle \delta Q \rangle$ is the expectation value of δQ over time, where δQ is defined as,

$$\delta Q = Q - \langle Q \rangle. \quad (5.16)$$

Using this method the capacitance curve in Fig. 5.7 was obtained for [Li(G4)][TFSI] at temperatures of 300 K for the three layer graphene slab electrode. The curve exhibits a minimum at a value close to the potential of zero charge, a value which is very close to $\Psi = 0$ V. The capacitance then rises slowly with increasingly negative or positive potential reaching a maximum at a potential of $\Psi = \pm 1$ V at this point the capacitance starts to decline as the potential moves further away from 0 V. The presence of a shoulder peak is somewhat reminiscent of the plot obtained by Merlet *et al.* in previous work [80], which featured the development of a more ordered interfacial structure with increasing potential.

This curve has a form which is reminiscent of both the theoretically predicted capacitance of an ionic liquid using a lattice gas model [84], previous simulations using fixed potential electrodes for ionic liquids [61, 82], and experimentally measured

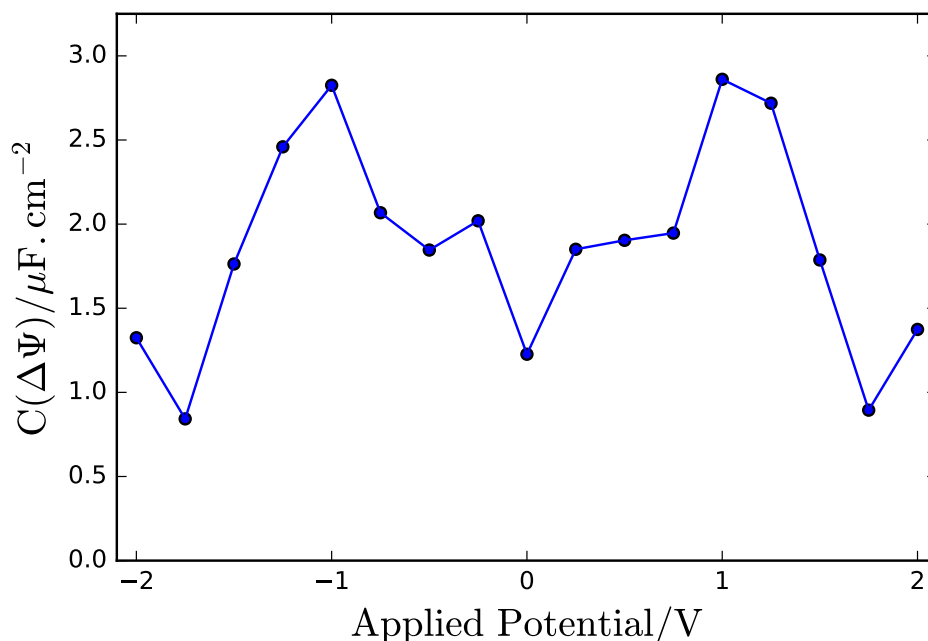


Figure 5.7: A plot showing the calculated capacitance of the system with changing voltage.

capacitances on gold electrodes [83]. When comparing to recent work by Urclan *et al.* [82] it is clear that this curve is reminiscent of an ionic liquid as opposed to a concentrated solution where the secondary minima occur at a far higher capacitance relative to the capacitance minimum located close to the point of zero charge.

The similarity between the simulated capacitance in Fig. 5.7 and previous results for aprotic ionic liquids [61, 82], alongside the multilayer structure observed for $[Li(G4)][TFSI]$ at higher potentials at both positive and negative electrode suggest that, in spite of the interesting coordination environments observed, solvate ionic liquids behave in a manner similar to conventional ionic liquids at fixed potential electrodes.

5.7 Evaluation of the Efficacy of the Two Simulation Models

The model in these simulations provides qualitatively different results from those in the previous chapter where a more simple electrode model was used. The two main points of divergence in the results of the simulations are as follows. Firstly, there is a multilayer structure in the region near to the electrode in the simulations reported in this chapter. Secondly lithium cations are observed in direct contact with the electrode in the newer simulations. It appears that in both cases the results in this chapter are more similar to the results observed in experimental studies. AFM studies of ionic liquid have shown the presence of both a multilayer structure and lithium atoms directly coordinated to the electrode [177]. The presence of lithium at the electrode is corroborated by the experimentally observed intercalation of lithium cations into graphitic electrodes [179].

However, while in a broad sense the simulation appears to mirror the experimental results, there are a few limitations of the model in this simulation, which could cause artefacts and inaccuracies. While the electrode model is polarisable, the electrolyte model is the same that was used in the fixed charge simulations. This force field is limited in that it does not model the effects of polarisability, or the covalency in lithium coordination complexes. It is hard to know whether the energetic and entropic costs of distorting the complex so that it may coordinate to the electrode are correctly modelled. If they are not, the magnitude of the effect in the simulations is likely incorrect.

Further to this, the domainal structure while interesting, is hard to characterise owing to the small box size in the simulations in comparison to the size of the domains.

5.8 Conclusion

This chapter detailed simulation of the interfacial nanostructure of a solvate ionic liquid at electrodes modelled using fixed potential boundary conditions. Unlike for the fixed charge conditions discussed in the previous chapter the interfacial nanostructure is shown to behave in a manner similar to a conventional ionic liquid in both its interfacial nanostructure and the observed capacitance.

One interesting aside, which requires further study, is the coordination structure of lithium cations in the first interfacial layer. While some cations are coordinated to glyme molecules others are coordinated to anions. These two modes of coordination appear to be almost mutually exclusive and further to this these two modes of coordination appear to form domains, possibly templated by the charges on electrode atoms. The presence of the domain structure while heavily implied by these simulations needs to be confirmed for simulations with a significantly larger electrode surface area.

Chapter 6

Conclusions and Future Work

This chapter will summarise the conclusions of the work discussed in this thesis before moving on to discuss the avenues of future work that can follow from the results obtained.

6.1 Conclusions

This thesis looked at the nanostructure of ionic liquid solutions and solvate ionic liquids at electrodes. These systems, have key features in common, one of which is the decoupling of co-ion repulsion and counter-ion attraction mechanisms for charge screening. The third chapter of the thesis showed how dissolution of ionic liquids in propylene carbonate leads to a change in interfacial nanostructure. The fourth chapter explored the behaviour of a solvate ionic liquid when in contact with a simplistic electrode model, while the fifth chapter added another layer of theory to these simulations giving a different result for a surface held at a fixed potential. In all three systems there were key features observed which deviated from the results obtained for simulations of pure aprotic ionic liquids.

In particular the structural transitions in mixtures of ionic and propylene carbonate studied in previous SFB experiments is shown in this work to be connected with a crossover from oscillatory to monotonic nanostructure in the liquid. Further to this a basic relationship between ion size, propylene carbonate mole fraction, and the interfacial orientation of cations was described.

The interfacial nanostructure of a solvate ionic liquid was studied using two different electrode models. When fixed charge boundary conditions were applied to the

electrode a novel nanostructure is observed at the negative electrode. This is caused by the greater level of repulsion of anions relative to the attraction of cations leading to a greater amount of glyme molecules relative to lithium cations. However, this structure is not wholly reflective of the structure observed in AFM experiments of ionic liquid layering at gold and highly orientated pyrolytic graphite [177]. These simulations do suggest that solvate ionic liquids may show particularly interesting behaviours when under an external field.

The employment of electrodes with a fixed potential leads to a different nanostructure. The simulated interfacial nanostructure of these systems is similar to the multilayer structure observed for conventional ionic liquids, and the experimentally obtained nanostructure of this solvate ionic liquid. Further to this these simulations showed the development an increasingly ordered structure in the first interfacial layer, and a capacitance curve that is reminiscent of previous simulations [80, 82].

The fixed charge and fixed potential electrodes show different results but the underlying behaviours are more closely related than they first appear. At the fixed charged electrode the electrostatic interaction between the electrode and lithium atoms is not great enough to lead to decoordination, but the resulting cation repulsion leads to many lithium cations adopting a structure other than the single lithium glyme chelate ring. Meanwhile the polarisability allows for the dechelation of lithium cations, however many of the interfacial lithium cations end up coordinated to bistriflimide anions, again leading to interfacial lithium cations not behaving as they do in the bulk.

6.2 Future Work

Both solvate ionic liquids and ionic liquid solutions require further study. On the side of ionic liquid solutions a further coarse grain study is required to probe further into the underlying physics behind these simulations. It is necessary to look at the wide

array of liquid properties that could not be studied as systematically by means of the atomistic simulations reported in this thesis. In particular the relative sizes of all three components, and their relative dipole moments, the degree to which the solvent molecule is prolate in shape, and the presence of aliphatic tails are all worthy of study. In particular the force field recently developed by the group of Prof. Forsman may be highly applicable to this work [180].

There is further work to be done looking at the nanostructure of solvate ionic liquids at electrodes, in particular it would be of interest to observe the interfacial nanostructure of a poor solvate ionic liquid to see how closely this conformed to the previous study by Mclean *et al.*. Study of the nanostructure of a solvate ionic liquid dissolve in a non competing solvent such as hydroflouroether may also be of interest and tie in with the work in this thesis looking at propylene carbonate [46, 157].

However perhaps the most exciting simulation that could be performed looking at solvate ionic liquids would be one which looked at the intercalation of cations into a nanoporous electrode. Previous studies have performed simulations for ionic liquids and ionic liquid solutions under such conditions [57, 86]. This would have a broad applicability to a wide range of applications, but may not be computationally possible in the next decade as previous simulations of such systems have used very coarse grained electrolyte models [57, 86].

Appendix A

Forcefields For Ionic Liquids and Propylene

Carbonate

This appendix chapter describes the forcefields used in the molecular dynamics simulations described in Chapter 3. Forcefields are based around the OPLS-AA forcefield [112] with additional reparamaterisation having been performed in previous work [100, 134–136]. The first section will start by introducing the forcefields for mixtures of [BMPyr][TFSI] and propylene carbonate. The second introduces the parameters for the BMIm and EMIm cations.

A.1 Force Field for Mixtures of [BMPyr][TFSI] and Propylene Carbonate

The atoms within the forcefield are denoted as shown in Fig. A.1. Additionally to this hydrogen atoms bonded to the ring carbons in the cation are defined as cHr, while the hydrogen atoms bonded to tail atoms are defined as cHt.

A.1.1 Non-bonded Parameters

Table A.1 contains the non-bonded parameters, due to the different value of ϵ_r , the partial charges on propylene carbonate molecule are scaled up relative to the original papers [135, 136]. Simulations are all run with $\epsilon_r = 1.6$ to account for polariseability of ions [137]. Standard OPLS-AA combination rules are used for unlike atoms [112]

For the electrode atoms σ is set as 0.355 nm and ϵ as 0.29288 kJmol⁻¹. Standard OPLS-AA combination rules are used to generate potentials for unlike atoms.

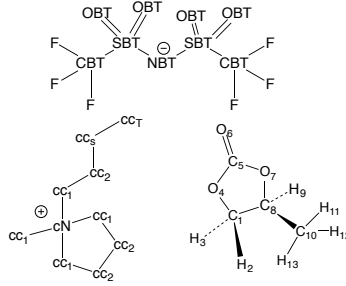


Figure A.1: A cartoon showing the assignment of atom names within the three constituents of the liquid mixtures.

Table A.1: Non-bonded parameters for atoms in [BMPyr][TFSI] and propylene carbonate.

Atom Name	Mass	charge (e)	σ (nm)	ϵ (kJ mol ⁻¹)
NBT	14.000	-0.66	0.325	7.113×10^{-1}
OBT	15.999	-0.53	0.295	8.786×10^{-1}
CBT	12.011	0.35	0.350	2.761×10^{-1}
SBT	32.066	1.02	0.355	1.0462
F	18.998	-0.16	0.295	2.218×10^{-1}
cN	14.000	0.12	0.325	7.113×10^{-1}
cC ₁	12.011	-0.17	0.350	2.761×10^{-1}
cC ₂	12.011	0.13	0.350	2.761×10^{-1}
cC _T	12.011	-0.18	0.350	2.761×10^{-1}
cC _S	12.011	-0.12	0.350	2.761×10^{-1}
cHr	1.008	0.13	0.250	1.255×10^{-1}
cHt	1.008	0.06	0.250	1.255×10^{-1}
C ₁	12.011	0.12	0.355	2.761×10^{-1}
H ₂	1.008	0.09875	0.242	6.276×10^{-2}
H ₃	1.008	0.1	0.242	6.276×10^{-2}
O ₄	15.999	-0.5075	0.300	7.113×10^{-1}
C ₅	12.011	1.060125	0.375	4.393×10^{-1}
O ₆	15.999	-0.69025	0.296	8.786×10^{-1}
O ₇	15.999	-0.50825	0.300	7.113×10^{-1}
C ₈	12.011	0.139875	0.355	2.761×10^{-1}
H ₉	1.008	0.1075	0.242	6.276×10^{-2}
C ₁₀	12.011	-0.138875	0.355	2.761×10^{-1}
H ₁₁	1.008	0.071	0.242	6.276×10^{-2}
H ₁₂	1.008	0.06525	0.242	6.276×10^{-2}
H ₁₃	1.008	0.082375	0.242	6.276×10^{-2}

A.1.2 Bonded Parameters

A large number of atom types have the same bonded parameters, within the cation all carbon atoms are treated as a single type cC, and all hydrogen atoms as cH. While in propylene carbonate molecule all hydrogen atoms are defined as H, all carbon atoms except for the carbonyl, C₅, defined as C_T, and the non carbonyl oxygens defined as OS.

A.1.3 Bonds

Bonds are modelled using a harmonic potential defined below,

$$V_{\text{bond}}(r_{ij}) = \frac{1}{2}k_{ij}^b(r_{ij} - b_{ij})^2, \quad (\text{A.1})$$

where b_{ij} is the equilibrium bond length, k_{ij}^b is the force constant, and r_{ij} is the separation between two atoms. The values of these constants are shown in Table A.2.

Table A.2: Potentials for bonds in [BMPyr][TFSI] and propylene carbonate.

i	j	b_{ij} (nm)	k_{ij}^b (kJ mol ⁻¹ nm ⁻²)
NBT	SBT	0.1570	3.137×10^5
SBT	OBT	0.1437	5.331×10^5
SBT	CBT	0.1818	1.950×10^5
CBT	F	0.1323	3.698×10^5
cN	cC	0.1471	3.071×10^5
cC	cC	0.1529	2.242×10^5
cC	cH	0.1090	2.845×10^5
C _T	C _T	0.1529	2.242×10^5
C _T	OS	0.1410	2.678×10^5
C ₅	O ₆	0.1229	4.769×10^5
C ₅	OS	0.1327	1.791×10^5
C _T	H	0.1090	2.845×10^5

Table A.3: Potentials for angle interactions in [BMPyr][TFSI] and propylene carbonate.

i	j	k	θ_{ijk}^0 (degrees)	k_{ijk}^θ (kJ mol ⁻¹ rad ⁻²)
NBT	SBT	OBT	113.6	789.0
NBT	SBT	CBT	103.5	764.0
SBT	CBT	F	111.7	694.0
SBT	NBT	SBT	125.6	671.0
CBT	SBT	OBT	102.6	870.0
OBT	SBT	OBT	118.5	969.0
F	CBT	F	107.1	781.0
cN	cC	cC	109.5	669.4
cN	cC	cH	109.5	209.2
cC	cN	cC	109.5	418.4
cC	cC	cC	112.7	488.3
cC	cC	cH	110.7	313.8
cH	cC	cH	107.8	276.1
O ₆	C ₅	OS	123.4	694.5
C ₅	OS	C _T	116.9	694.5
OS	C _T	H	109.5	292.9
C _T	C _T	C _T	112.7	488.3
C _T	C _T	H	110.7	313.8
H	C _T	H	107.8	276.1
C _T	C _T	OS	109.5	418.4

A.1.4 Angles

Angles are modelled using a harmonic potential defined as,

$$V_{\text{angle}}(\theta_{ijk}) = \frac{1}{2}k_{ijk}^\theta(\theta_{ijk} - \theta_{ijk}^0)^2, \quad (\text{A.2})$$

where θ_{ijk}^0 is the equilibrium angle, k_{ijk}^θ is the force constant, and k_{ijk}^θ is the separation between two atoms. The values of these constants are shown in Table A.3.

A.1.5 Dihedrals

The dihedral interactions are modelled using the Ryckaert-Bellemans formulation (which is related to the standard OPLS dihedral formulation),

$$V_{\text{dihedral}}(\phi_{ijkl}) = \sum_{n=0}^5 C_n(\cos(\phi_{ijkl}))^n, \quad (\text{A.3})$$

Table A.4: Potentials for dihedral interactions in [BMPyr][TFSI] and propylene carbonate.

i	j	k	l	C_0 (kJ mol ⁻¹)	C_1 (kJ mol ⁻¹)	C_2 (kJ mol ⁻¹)	C_3 (kJmol ⁻¹)
NBT	SBT	CBT	F	0.661	1.983	0.000	-2.644
SBT	NBT	SBT	OBT	-0.008	-0.023	0.000	0.030
SBT	NBT	SBT	CBT	4.369	-21.179	10.420	6.390
OBT	SBT	CBT	F	0.726	2.177	0.000	-2.902
cN	cC	cC	H	-4.0962	-1.552	2.967	-3.958
cN	cC	cC	cC	6.975	0.000	-0.820	-4.602
cC	cN	cC	cC	1.771	3.516	0.536	-5.816
cC	cN	cC	H	1.715	5.088	0.000	-4.686
cC	cC	cC	cC	2.929	-1.464	0.209	-1.674
cH	cC	cC	cH	0.726	2.177	0.000	-2.902
cH	cC	cC	cC	0.726	2.177	0.000	-2.902
H	C _T	C _T	H	0.628	1.883	0.000	-2.510
H	C _T	C _T	C _T	0.628	1.883	0.000	-2.510
O ₆	C ₅	OS	C _T	20.920	0.000	-20.920	0.000
C ₅	OS	C _T	C _T	-2.197	5.201	0.527	-3.531
C ₅	OS	C _T	H	0.414	1.243	0.000	-1.657
OS	C _T	C _T	C _T	2.874	0.582	2.092	-5.548
OS	C _T	C _T	H	0.979	2.937	-3.916	-2.902

Where C_n is the coefficient for term n in the sum. The values of C_n for numbers 0 to 3 are shown in Table A.4. For all dihedral interactions the values of C_4 and C_5 are equal to 0 kJ mol⁻¹.

A.2 Force Fields for the BMIm and EMIm cations

Additional simulations are performed with two additional cations, BMIm and EMIm. These simulations are performed with the same anion and propylene carbonate force fields as for previous simulations. Fig A.2 shows the atom labels used in these two cations. Hydrogen atoms are not shown however can be split into three subgroups those hydrogens bonded to ring carbon atoms cHr , those hydrogens bonded to eC_1 and bC_1 (those carbons bonded directly to the imidazolium ring) cHt_1 , and hydrogens bonded to all other tail carbon atoms $cHt_{e,S,T,2}$.

A.2.1 Non-bonded Parameters

The non bonded parameters are listed in Table A.5 for both cations.

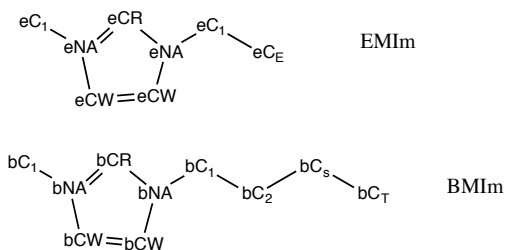


Figure A.2: A cartoon showing the assignment of atom names with the imidazolium atoms.

Table A.5: Non-bonded parameters for atoms in EMIm and BMIm.

Atom Name	Mass	charge (e)	σ (nm)	ϵ (kJ mol ⁻¹)
eCW	12.011	-0.13	0.355	2.929×10^{-1}
eNA	14.000	0.15	0.325	7.113×10^{-1}
eCR	12.011	-0.11	0.355	2.929×10^{-1}
eC ₁	12.011	-0.18	0.350	2.761×10^{-1}
eC _e	12.011	-0.12	0.350	2.761×10^{-1}
bCW	12.011	0.12	0.355	2.929×10^{-1}
bNA	14.000	-0.17	0.325	7.113×10^{-1}
bCR	12.011	0.13	0.355	2.929×10^{-1}
bC ₁	12.011	-0.17	0.350	2.761×10^{-1}
bC ₂	12.011	-0.01	0.350	2.761×10^{-1}
bC _s	12.011	-0.12	0.350	2.761×10^{-1}
bC _T	12.011	-0.18	0.350	2.761×10^{-1}
cHr	1.008	0.21	0.242	1.255×10^{-1}
cHt ₁	1.008	0.13	0.250	1.255×10^{-1}
cHt _{e,S,T,2}	1.008	0.06	0.250	1.255×10^{-1}

A.2.2 Bonds

The bonding coefficients for the two cations are shown in Table A.6. As the bonding coefficients for the corresponding atoms in each of the ions are the same so ions are listed without there e or b suffix. The eC_E atoms values are the same as the listed C_2 value. As each carbon atoms bonds to only one type of hydrogen all hydrogens are listed as H.

Table A.6: Potentials for bonds in EMIm and BMIm.

i	j	b_{ij} (nm)	k_{ij}^b (kJ mol ⁻¹ nm ⁻²)
N_A	C_R	0.1315	3.992×10^5
N_A	C_W	0.1378	3.574×10^5
N_A	C_1	0.1466	2.820×10^5
C_R	H	0.1080	2.845×10^5
C_W	H	0.1080	2.845×10^5
C_1	H	0.1090	2.845×10^5
C_2	H	0.1090	2.845×10^5
C_S	H	0.1090	2.845×10^5
C_T	H	0.1090	2.845×10^5
C_1	C_2	0.1529	2.242×10^5
C_1	C_2	0.1529	2.242×10^5

A.2.3 Angles

The angles coefficients for the two cations are listed in Table A.7.

Table A.7: Potentials for angle interactions in EMIm and BMIm.

i	j	k	θ_{ijk}^0 (degrees)	k_{ijk}^θ (kJ mol ⁻¹ rad ⁻²)
N _A	C _R	N _A	109.8	585.8
N _A	C _R	H	125.1	292.9
N _A	C _W	H	122.0	292.9
N _A	C ₁	H	110.7	313.8
N _A	C _W	C _W	107.1	585.8
N _A	C ₁	C ₂	112.7	488.3
C _W	N _A	C _R	108.0	585.8
C _W	C _W	H	130.9	292.9
C ₁	N _A	C _R	126.4	585.8
C ₁	N _A	C _W	125.6	585.8
H	C ₁	H	107.8	276.1
C ₁	C ₂	H	110.7	313.8
C ₁	C ₂	C _S	112.7	488.3
C ₂	C ₁	H	110.7	313.8
C ₁	C _S	H	110.7	313.8
H	C ₂	H	107.8	276.1
C ₂	C _S	C _T	112.7	488.3
C ₂	C _S	H	110.7	313.8
C _S	C ₂	H	110.7	313.8
C _S	C _T	H	110.7	313.8
H	C _S	H	107.8	276.1
H	C _T	H	107.8	276.1

A.2.4 Dihedrals

The dihedral coefficients for the two cations are listed in Table A.8.

Table A.8: Potentials for dihedral interactions in EMIm and BMIm.

i	j	k	l	C_0 (kJ mol ⁻¹)	C_1 (kJ mol ⁻¹)	C_2 (kJ mol ⁻¹)	C_3 (kJmol ⁻¹)
N _A	C _W	C _W	N _A	44.980	0.000	-44.980	0.000
N _A	C _W	C _W	H	44.980	0.000	-44.980	0.000
N _A	C ₁	C ₂	H	0.184	0.551	0.000	-0.734
N _A	C ₁	C ₂	C _S	-1.177	1.936	-3.164	2.405
C _R	N _A	C _W	H	12.550	0.000	-12.550	0.000
C _R	N _A	C ₁	H	0.000	0.000	0.000	0.000
C _R	N _A	C ₁	C ₂	-2.635	2.635	0.000	0.000
C _R	N _A	C _W	C _W	12.550	0.000	-12.550	0.000
C _W	N _A	C _R	N _A	19.460	0.000	-19.460	0.000
C _W	N _A	C _R	H	19.460	0.000	-19.460	0.000
C _W	N _A	C ₁	H	0.260	0.779	0.000	-1.038
C _W	N _A	C ₁	C ₂	2.927	4.768	-6.106	-1.589
C ₁	N _A	C _R	N _A	19.460	0.000	-19.460	0.000
C ₁	N _A	C _R	H	19.460	0.000	-19.460	0.000
C ₁	N _A	C _W	C _W	12.550	0.000	-12.550	0.000
C ₁	N _A	C _W	H	12.550	0.000	-12.550	0.000
C ₁	C ₂	C _S	C _T	3.567	-1.889	0.657	-2.335
C ₁	C ₂	C _S	H	0.767	2.297	0.000	-3.063
C ₂	C _S	C _T	H	0.767	2.297	0.000	-3.063
H	C _S	C _T	H	0.665	1.996	0.000	-2.661
H	C ₂	C _S	H	0.665	1.996	0.000	-2.661
H	C ₁	C ₂	H	0.665	1.996	0.000	-2.661

Appendix B

Forcefields For Solvate Ionic Liquids

The force field used for simulations of $[\text{Li}(\text{G4})][\text{TFSI}]$ is provided below. It is, as discussed in the main body of the thesis, based on the work of Shimizu *et al.* [153], which is built on the OPLS-AA forcefield [112] and the CL&P reparamaterisation [100].

B.1 Force Field Parameters

B.1.1 Partial Charges

The partial charges of the atoms in the simulations reported are listed below. The experiments are run with value of the relative permittivity (ϵ_r) set to 1.6 to account for polarisability and reproduce experimentally recorded coordination numbers. The names of atoms are assigned in Fig. B.1, all hydrogens in the glyme molecule are given the name H.

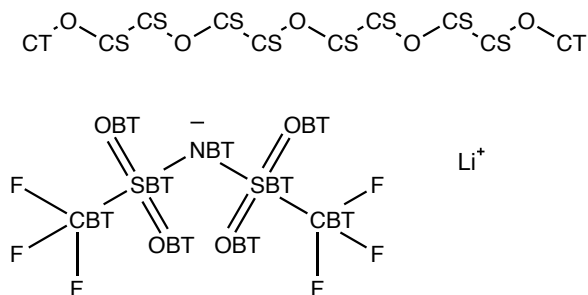


Figure B.1: A cartoon showing the assignment of atom names within the forcefield.

Table B.1: Partial charges for atoms in [Li(G4)][TFSI].

Atom Name	Charge (e)
NBT	-0.6600
OBT	-0.5300
CBT	0.3500
SBT	1.0200
F	-0.1600
OS	0.5000
CT	0.1375
CS	0.1750
H	0.0375
Li ⁺	1.0000

B.1.2 Non-bonded Parameters

Non-bonded parameters are listed in Table B.2. The values for σ and ϵ are listed below, as CT and CS are treated differently only in terms of charge and are hence forth listed as a single entity CG. Standard OPLS-AA combination rules are used for unlike atoms [112].

Table B.2: Non-bonding parameters for atoms in [Li(G4)][TFSI].

Atom Name	Mass	σ (nm)	ϵ (kJ mol ⁻¹)
NBT	14.000	0.325	7.113×10^{-1}
OBT	15.999	0.295	8.786×10^{-1}
CBT	12.011	0.350	2.761×10^{-1}
SBT	32.066	0.355	1.0462
F	18.998	0.295	2.218×10^{-1}
OS	15.999	0.290	5.862×10^{-1}
CG	12.011	0.350	2.762×10^{-1}
H	1.008	0.250	1.255×10^{-1}
Li+	6.941	0.213	7.648×10^{-2}

For the electrode atoms σ is set as 0.355 nm and ϵ as 0.29288 kJmol⁻¹. Standard OPLS-AA combination rules are used to generate potentials for unlike atoms.

B.1.3 Bonds

Bonds are modeled using a harmonic potential defined below,

$$V_{\text{bond}}(r_{ij}) = \frac{1}{2}k_{ij}^b(r_{ij} - b_{ij})^2, \quad (\text{B.1})$$

where b_{ij} is the equilibrium bond length, k_{ij}^b is the force constant, and r_{ij} is the separation between two atoms. The values of these constants are shown in Table B.3.

Table B.3: Bond parameters for bonds in [Li(G4)][TFSI].

i	j	b_{ij} (nm)	k_{ij}^b (kJ mol ⁻¹ nm ⁻²)
NBT	SBT	0.1570	3.137×10^5
SBT	OBT	0.1437	5.331×10^5
SBT	CBT	0.1818	1.950×10^5
CBT	F	0.1323	3.698×10^5
CG	CG	0.1529	7.113×10^5
OS	CG	0.1410	8.786×10^5
CG	H	0.1090	2.761×10^5

B.1.4 Angles

Angles are modeled using a harmonic potential defined below,

$$V_{\text{angle}}(\theta_{ijk}) = \frac{1}{2}k_{ijk}^\theta(\theta_{ijk} - \theta_{ijk}^0)^2, \quad (\text{B.2})$$

where θ_{ijk}^0 is the equilibrium angle, k_{ijk}^θ is the force constant, and θ_{ijk} is the separation between two atoms. The values of these constants are shown in Table B.4.

B.1.5 Dihedrals

The dihedral interactions are modeled using the Ryckaert-Bellemans formulation (which is related to the standard OPLS dihedral formulation),

Table B.4: Partial charges for atoms in [Li(G4)][TFSI].

i	j	k	θ_{ijk} (degrees)	k_{ijk}^θ (kJ mol ⁻¹ rad ⁻²)
NBT	SBT	OBT	113.6	789.0
NBT	SBT	CBT	103.5	764.0
SBT	CBT	F	111.7	694.0
SBT	NBT	SBT	125.6	671.0
CBT	SBT	OBT	102.6	870.0
OBT	SBT	OBT	118.5	969.0
F	CBT	F	107.1	781.0
H	CG	H	107.8	276.1
H	CG	OS	109.5	292.9
CG	OS	CG	109.5	502.4
OS	CG	CG	109.5	418.4
H	CG	CG	110.7	313.8

$$V_{\text{dihedral}}(\phi_{ijkl}) = \sum_{n=0}^5 C_n (\cos(\phi_{ijkl}))^n, \quad (\text{B.3})$$

Where C_n is the coefficient for the n th term of the sum. The dihedral coefficients for the solvate ionic liquids are listed in Table B.5.

Table B.5: Partial charges for atoms in [Li(G4)][TFSI].

i	j	k	l	C_0 (kJ mol ⁻¹)	C_1 (kJ mol ⁻¹)	C_2 (kJ mol ⁻¹)	C_3 (kJmol ⁻¹)
NBT	SBT	CBT	F	0.661	1.983	0.000	-2.644
SBT	NBT	SBT	OBT	-0.008	-0.023	0.000	0.030
SBT	NBT	SBT	CBT	4.369	-21.179	10.420	6.390
OBT	SBT	CBT	F	0.726	2.177	0.000	-2.902
H	CG	CG	H	0.628	1.883	0.000	-2.510
H	CG	CG	OS	0.979	2.937	0.000	-3.916
H	CG	OS	CG	1.590	4.770	0.000	-6.360
CG	CG	OS	CG	1.715	2.845	1.046	-5.607
OS	CG	CG	OS	-1.151	1.151	0.000	0.000

C_4 and C_5 are equal to 0 kJ mol⁻¹ for all interactions.

Appendix C

List of all Software and Programs Used

In the interest of brevity the main body of this thesis has only listed the crucial software used to carry out simulations; and not the smaller scripts, plugins, packages and visualisation software that have been used in this thesis. This next section will list all the software used in the production of this thesis.

C.1 System Preparation and Trajectory Analysis

A number of software packages have been used to generate simulation boxes and analyse simulations trajectories: Packmol [144], fftool by Agillio Padua [181], and Visual Molecular Dynamics [182] including the topol tools [183] and taychon ray tracing plugins [184],

Further to this analysis of trajectories is performed using the mdanalysis [185, 186] and mdtraj [187] python plugins. Graphs are plotted from these scripts using the matplotlib python library [188].

C.2 Molecular Dynamics Software

The work described in this thesis used two molecular dynamics libraries. Gromacs [103, 138–143] was used for the simulations in Chapters 3 and 4. While Lammmps [104] was used with the fixed potential electrodes script developed by Wang *et al.* [167].

Appendix D

Summary of this Thesis for the Non-Scientist

This section will give a brief discussion of the topics described for the non-scientist. The aim of this section is to provide a small description for any friends, or family who wish to get an idea as to what this thesis discussed. This short summary will discuss two main concepts ionic liquids (what this thesis researched) and molecular dynamics(the method by which the research was carried out).

D.1 Ionic Liquids

Ionic liquids are a strange class of matter. While being liquid at room temperature they are comprised solely of charged species, like table salt. This is not what we would expect from basic chemistry, as the interactions between charged particles are normally so strong that they prevent melting at all but the highest temperature.

Ionic liquid ions, however, have a number of features which make them far more likely to melt. Firstly, they are larger, which lessens the attraction between the ions and secondly, they have tails which like to move around unconstrained, which would, if frozen, become very constrained indeed. These features together allow ionic liquids to be liquid at room temperature.

There are a lot of important applications for liquids with lots of ions in, like ionic liquids and more conventional salt solutions, but they are particularly interesting to electrochemical devices. This thesis discusses the use of molecular dynamics simulations to inform the development of devices based on ionic liquids.

D.2 Molecular Dynamics

This thesis mainly used a technique called classical molecular dynamics. Classical molecular dynamics works by stripping away all the complexity of a molecule and replacing it with a set of balls and springs. Provided the balls are the right size and the springs are the right length and strength, a real liquid can be simulated efficiently using a computer.

In order to really simulate a real world liquid the balls and springs are placed in a box. However, the walls of the box are special; they work like the walls in the mobile phone game, ‘Snake 2’. If a molecule hits one side of the box it goes straight through, appearing on the other side of the box. This allows the simulation of liquid without having to worry about the boxes walls causing any trouble.

After the computer has simulated a few nanoseconds of the liquid’s life we can analyse how the particles moved, which will in turn tell us more about the liquid.

In this thesis this technique was used to simulate the behaviour of ionic liquids at the surfaces of electrodes. The aim of this work is to inform the development of batteries and supercapacitors based on these liquids. An example of a simulation box is shown in Fig. D.1

The results presented in this thesis reveal a set of interesting features of solvate ionic liquids, and ionic liquid solutions, which were obtained using molecular dynamics, and which can inform experimental research of electrochemical devices. The second chapter explored the behaviour of mixtures of ionic liquid and propylene carbonate, and produced a framework through which the behaviour of ionic liquid solutions can be understood.

Chapters 4 and 5 looked at the interfacial structure of solvate ionic liquid’s (another class of ionic liquid) and described this liquids exciting interfacial nanostructure, which is somewhat different from that of conventional ionic liquids.

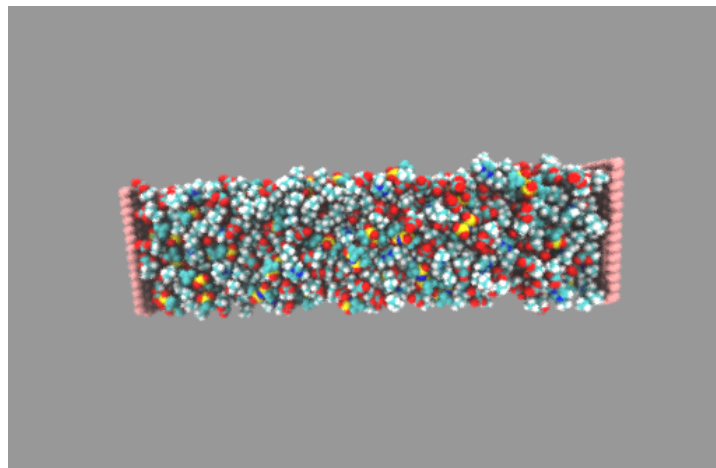


Figure D.1: Snapshot of the simulated system. The snapshot shows a slab of liquid confined between two graphenes, which have a peach colouration in the image.

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