Understanding the Mechanism of Permeation through Graphene-Based Membranes Using Molecular Dynamics Simulations

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List of Abbreviations

RO – Reverse Osmosis	Page	25
PA – Polyamide	Page	26
GO – Graphene Oxide	Page	27
GNP – Graphene nano-pore	Page	27
RDF – Radial Distribution Function	Page	29
MD – Molecular Dynamics	Page	32
PME – Particle-mesh Ewald	Page	51
MSD – Mean-squared displacement	Page	54
WHAM – Weighted Histogram Analysis Method	Page	56
PMF – Potential of Mean-Force	Page	83
DFT – Density Functional Theory	Page	85
Ow – Water oxygen atom	Page	99
EDLC – Electric double layer capacitors	Page 2	108

Abstract

The UN predicts that by 2050 there will water shortages throughout the globe. Current sources for safe, clean drinking water are being over mined and exhausted. Seawater provides an alternative water source, but a high salt content makes it unsuitable for the majority of applications. However, reverse osmosis lowers the salt content producing water that is safe for human consumption. Reverse osmosis uses a semi-permeable membrane to prevent the transport of salt but allows for the transport of water. Currently these membranes are susceptible to fouling and contamination, which reduces their efficiency.

Graphene-oxide membranes offer a new material for reserves osmosis membranes. Sheets of graphene-oxide are stacked in a layered structure. The separation between the sheets can be controlled using physical confinement, resulting in limited ion permeation of abundant cations in seawater, like Na⁺ and K⁺. This is believed to be due to the separation of 0.76 nm between the graphene sheets, forcing the ions to lose its surrounding water molecules, making it unfavourable for the ion to travel through the membrane.

Molecular dynamics simulations can give an atomic level insight into the molecular processes within GO membranes. Recent simulations have shown that charged species are attracted to graphene surfaces due to polarisation of the pi-electron system. This work has managed to incorporate these ion-pi interactions into molecular dynamics simulations. Including ion-pi interactions caused some ions, like Na⁺ and K⁺, to prefer to lose water molecules and reside at a graphene surface. This work observed the same phenomena when ions were confined to graphene channel ranging from 1.3 nm – 0.7 nm. This observation could have a large impact on whether dehydration is limiting the permeation of these two ions, or if there are additional processes that limit their molecular transport.

Declaration

The author, J. Dix, declares that no portion of the work referred to in this thesis has been submitted in support of another application for another degree or qualification of this or any other university or any other learning institute of learning.

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About the Author

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K. S. Vasu, *et al.*, "Van der Waals pressure and its effect on trapped interlayer molecules", *Nature Communications*, 7:12168 (2016)

C. D. Williams, *et al.*, "Effective Polarization in Pairwise Potentials at the Graphene– Electrolyte Interface", *J. Phys. Chem. Lett.*, **8** (2017) 703

V. Satarifard, *et al.*, "Reversible structural transition in nanoconfined ice", *Phys. Rev. B*, **95(6)** (2017) 064105

J. Abrahams, *et al.*, "Tuneable Sieving of Ions Using Graphene Oxide Membranes", *Nat. Nanotechnol.* **12**, 546 (2017)

In addition he has been part of two recently submitted publications:

A. Hardy, J. Dix, C. D. Williams, F. R. Siperstien, P. Carbone, H. Bock, "Design rules for graphene solvents and dispersants derived using the Corresponding Distances Method", *Submitted*.

J. Dix, L. Lue, P. Carbone, "Systematic Comparision of Water Models Under Nanoconfinement by Graphene Sheets", *Submitted*.

Chapter 1 Introduction

Demand for water will increase by 55% over the next 30 years due to economic development, and agriculture and human consumption¹⁷. Currently, clean water is primarily obtained from ground water sources¹⁷. Ground waters are areas of water that are found underground or near to the ground surface¹⁸; however, they are being over mined¹⁹. To fulfil increasing demand it is important to use other sources of water. Desalination removes salt from high salinity sources, like sea water, turning it into clean, safe drinking water. This requires a lot of energy compared to mining ground water sources²⁰. Graphene²¹ is being developed for application in membranes and nanomaterials^{22,23} to help satisfy the future demand for water.

1.1 Desalination

Seawater has an ionic species concentration of $43.4 - 10.1 \text{ g L}^{-124-26}$. Safe and clean drinking water has a concentration of $\approx 1 \text{ g L}^{-127}$. To produce clean water, desalination needs to reduce ionic species in seawater by 97.7 - 90.1%. Some common desalination methods are:

- pervaporation²⁸ (Figure 1-1a),
- reverse osmosis (RO)²⁹ (Figure 1-1b)
- forward osmosis³⁰ (Figure 1-1c).

All of these methods require using a semipermeable membrane that allows water transport through but limits ionic transport^{28–30}. Pervaporation (schematically shown in Figure 1-1a) puts a hot salt feed in contact with a semipermeable membrane²⁸. The membrane allows the water vapour evaporating off the salt feed to pass through. The water vapour is condensed and collected at a cold plate away from the membrane (Figure 1-1a). RO (schematically shown in Figure 1-1b) uses a pressure gradient across a semipermeable membrane to force water from a high-salinity feed through, while preventing the transport of ionic species²⁹. Forward

osmosis (schematically shown in Figure 1-1c) uses an osmotic pressure gradient across the semipermeable membrane to draw water from the high salinity sea water feed into a permeate feed³⁰. The permeate solution, commonly called a draw solution, has an easy to remove additive that increases the osmotic pressure compared to the feed solution³⁰. RO is the most common desalination method with 53% of the world's plants using it³¹.





Current commercial RO membranes have a composite structure with a thin-film of polyamide (PA) or cellulose triacetate making up the active layer^{32–35}. PA is preferred over cellulose triacetate as it has a larger working pH range for the feed solution^{35,36}. Commercial PA membranes are incorporated into pipes where the feed solution has a large contact area with the thin-film layer. When in contact with the thin-film layer water molecules will pass through the membrane in a permeate stream. RO membranes are typically built into a spiral wound configuration because they have an easy operation, can control fouling and have a good permeation rate³⁷. Spiral wound cylinders wrap a combination of the composite membrane and a feed spacer from the centre to the edge of the cylinder³⁷. PA membranes prevent the transport of 99.85–99.25% of the ionic species^{33,34}. This is called the ion rejection ratio (R_1) and is calculated from³⁸:

$$R_{I} = \frac{c_{feed} - c_{perm}}{c_{feed}} \times 100$$
(1.1)

Where c_{feed} and c_{perm} are the feed and permeate ionic concentrations. Unfortunately PA membranes suffer from fouling^{39,40}, which reduces their selectivity and productivity⁴¹. Graphene-based membranes offer a new set of materials that could be less susceptible to fouling²²; have low thermal degradation⁴² allowing them to operate at higher temperatures than PA membranes^{43,44}; show rejection of organic materials in a high pH environment⁴⁴ and using graphene as the base structure provides strong mechanical properties⁴⁵ for membrane operation at high pressures⁴⁶.

1.2 Graphene Membranes

Graphene is a single layer of graphite that has very strong mechanical properties⁴⁵ and very fast electronic properties²¹. It can be produced by mechanically exfoliating a single sheet from graphite²¹, through chemical vapour deposition⁴⁷ or through electrochemical exfoliation⁴⁸.

Graphene has been used in separation applications^{49–51} because it can be functionalised⁵², is one atomic layer thick²¹ and can form composite materials⁵¹. Ion rejection in graphene-based membranes needs to be comparable to commercial membranes if they are to replace commercial membranes. Primarily, they must limit NaCl transport, as it is the most abundant ionic species in sea water²⁵. Graphene-oxide (GO) membranes have been previously shown to reduce the transport of Na⁺ by two orders of magnitude²². However, this work did not report any ion rejection rate to compare directly with commercial membranes.

Graphene nano-pores (GNPs) have been previously prepared by bombarding Ga⁺ at a graphene sheet⁵³. This method produced pores with a diameter of 0.05 - 0.5 nm ²³. GNPs showed selectivity between Na⁺ and K⁺ but did not show rejection of Na⁺²³. Neither GO nor GNP membranes show the ion rejection needed for desalination. However, these current results do show promise at their capability in the future. GO membranes can use cheap fabrication methods by using spin or spray coating of a GO suspension onto a desired substrate^{54,55}. Using Ga⁺ drilling is an expensive method and creates a broad distribution of pore diameters^{23,53}. This makes GO membranes more commercially viable than GNP membranes⁴¹.

1.2.1 Graphene-Oxide Membranes

Graphite-oxide is thermally⁵² or mechanically⁵⁶ separated into GO sheets. Graphiteoxide is formed from graphite using Hummer's method⁵⁷. Hummer's method uses strong oxidising agents⁵⁷ to add hydroxyl and epoxy groups on to the basal carbon plane and carboxyl group around the edge of a graphite layer^{58–63}. Mechanical separation, like sonication, can readily disperse GO sheets in water due to the additional hydrophilic groups^{56,64}. GO suspensions can be spin or spray coated onto a substrate creating membranes with thicknesses ranging from $0.1-100 \,\mu m^{22,49,54}$.

Nanoscale stacking of GO sheets will determine the molecular transport through a GO membrane. Cross sections of GO membranes show that the sheets stack in a laminar structure^{54,55}. In a laminar structure molecules will travel through channels made between GO sheets. Around 40-60% of the basal plane carbons have additional oxygen functionality^{22,62,65}. As a result, at the surface of a channel there will be a mixture of oxidised and unoxidised regions. Ions are believed to travel through the unoxidised regions as they cannot displace water bound to the hydroxyl and epoxy functionalities⁵⁴. However, this has yet to be confirmed through experiments. Carbon planes in GO membranes swell to a separation of 1.3-1.4 nm when submersed in water^{22,49,54,66}, depending on the oxygen content of the GO sheets. Swelling is due to the intercalation of three layers of water⁶⁷.

1.3 Ion Rejection Mechanism

The ion rejection mechanism of polyamide thin-films needs to be understood to further develop GO membranes. Small network pores were detected in PA thin films, using Positron Annihilation Spectroscopy, that had an effective radius of 0.1-0.3 nm⁶⁸. Diffusion of organic solutes through PA thin films showed a Stokes radius cut-off of 0.225 nm⁶⁹. A crosslinked bicontinuous polymer liquid crystal

assembly that consisted of an organic network separated by a continuous network of water pores, achieved an NaCl ion rejection ratio of 95% with an effective pore radius of 0.375 nm^{70} . These three results suggest that for effective ion rejection there needs to be small pores throughout the membrane to limit ion transport. To compete with PA membranes these pores need to have an effective pore radius of 0.1-0.3 nm. To limit ion transport through these pores there must be a large freeenergy barrier for an ion to enter or travel through a pore.

Water forms concentric shells around an ion due to the strong Coulomb interactions^{2,3,71–76}. The concentric shells are called hydration shells, with the shell closest to the ion being the primary or 1st hydration shell and subsequent shells being the second, third etc.. Water molecules will orientate to maximise the favourable interactions with the ion⁷⁶. There is a large negative free energy when taking an ion from a vacuum and fully hydrating it in water⁷⁷. This free energy change is called the hydration free energy and it is proportional to the strength of interaction between an ion and the water molecules⁷⁸. When water molecules are removed from the hydration shells there is a positive free energy change^{22,79,80}. The free energy change is largest for water molecules in the primary hydration shell⁷⁹.

A simulated radial distribution function (RDF) between Na⁺ and water O atoms is shown in Figure 1-2. It shows the common structure for water around a cation. The position of peaks shows the radial distance of the hydration shells around the ion. Vertical lines have been added to show the position of first maximum and minimum in the Na⁺-O RDF. These two points are for the first hydration shell, and occur at a position of 0.234 nm^{76} and 0.33 nm^{5} . For Na⁺ to travel through a pore and still possess all of the first hydration shell the effective pore radius must be $\geq 0.33 \text{ nm}$. Lower than this and Na⁺ will have to remove some of the water molecules in the first hydration shell. Apart from Li⁺, Na⁺ has the smallest first hydration shell for group 1 cations³. If a pore can prevent Na⁺ transport then it will prevent the transport of the larger group 1 cations³. This dehydration argument is a strong reason why PA membranes are effective for desalination. The small network pores of 0.1-0.3 nm force ions to have to remove surrounding water molecules in their

first hydration shells. This stops ions from entering or traveling through PA membranes.



Figure 1-2. Simulated radial distribution function for Na⁺ and water O atoms ($g(r_{Na-O})$) against Na⁺-water O radial distance (r_{Na-O}) at 298.15 K and 1 bar for an unconfined Na⁺ cation at infinite dilution. Vertical lines correspond to position of first hydration shell maximum (solid) and minimum (dashed).

1.3.1 Pore Geometry

Effective desalination membranes need an effective pore radius of 0.1-0.3 nm. GNPs show some ion rejection with effective pore radii of 0.3-0.5 nm⁸¹. However, they have been shown to stop water transport when the effective pore radii was less than 0.135 nm²³. GNP membranes have circular pores (Figure 1-3a), whereas GO membranes have a slit pore configuration (Figure 1-3b). Experimental measurement of the channel width in GO membranes uses X-ray diffraction to determine the spacing between carbon-carbon planes (d_{chan} in Figure 1-3b)⁵⁴. Some of the channel volume is occupied by the carbon atoms, meaning the effective channel width that an ion would experience (d_{eff}) will be smaller than the measured channel width. Typically for GO membranes the thickness of the carbon atoms ($\sigma = 0.34$ nm) is subtracted from d_{chan} to obtain d_{eff} (Figure 1-3)⁴⁹. An effective pore radius for a circular pore (r_{eff}) is half of d_{eff} for the circular pore (Figure 1-3a). In a sit pore r_{eff} is approximately half of d_{eff} . A circular pore with the same value of r_{eff} will remove more water than a slit pore with r_{eff} . This is due to the smaller accessible area at a circular pore.

In a fully hydrated GO membrane $d_{chan} = 1.3 \text{ nm}$, with $d_{eff} = 0.96 \text{ nm}$. This would produce $r_{eff} = 0.48 \text{ nm}$. To mimic a PA membrane $r_{eff} = 0.1 - 0.3 \text{ nm}$, this corresponds to $d_{chan} = 0.54 - 0.94 \text{ nm}$. This shows that for effective desalination in a GO membrane the separation between graphene sheets needs to be controlled to be smaller than in a fully hydrated state.





1.3.2 Controlling Graphene-Oxide Membrane Separation

There are currently three methods for controlling the separation between GO sheets in a membrane:

- 1. UV reduction of epoxy group⁸²
- 2. Thermal reduction of epoxy and hydroxyl groups^{42,83}
- 3. Physical confinement²²

Only physical confinement has been used to make a GO membrane for desalination. Physically confined GO membranes are formed by vacuum filtering the solvent from a GO suspension. The GO sheets are stacked in a laminate structure and still have some water intercalated between the sheets. The membranes are dried to remove the intercalated water. Dry membranes are then placed in a constant relative humidity environment. The separation between the GO sheets varies depending on the relative humidity^{22,54}. Relative humidity is a measure of the amount of water vapour in the air.

When the sheet-sheet separation has become constant the membranes were encased in an epoxy resin²². This is to stop the GO sheets from swelling again once they are submersed in water. This method managed to create GO membranes with sheet-sheet separations of 0.98 - 0.64 nm²². These membranes showed limited transport for monovalent and divalent cations²². The greatest reduction in Na⁺ permeation was observed with a sheet-sheet separation of 0.76 nm^{22} . This is within the range of separation a GO membrane would be expected to show ion rejection based on a polyamide membrane. At $0.64 \mathrm{nm}$ there was no permeation of ions or water through the membrane²². This limits the range for the separation between the GO sheets to provide effective ion rejection while retaining water permeation of $0.64~{\rm nm}\,{<}\,d_{{\rm chan}}\,{<}\,0.76{\rm nm}$. GO membranes potentially have more control over the rejection of ions compared to PA membranes. The structure of pores in PA membranes are limited by the molecular shape and size of PA molecules^{68,84}. Whereas the channel width in GO membranes can be controlled through a combination of chemical functionality^{42,82,83} and mechanical confinement²². This will give GO membranes the flexibility to tailor the channel width to precisely control the ion rejection and water permeation.

1.4 Modelling Graphene-Oxide Membranes

Experiments are difficult and time consuming to perform on GO membranes. Computational methods can be used to understand and guide the design of these systems. Macroscopic flow equations, like the Hagen-Poiseuille equation, breaksdown for nano-sized channels²². Atomistic molecular dynamics (MD) simulations can be used to build up an atomic level insight into the ionic transport through GO channels.

MD uses averaged pairwise potentials between two atoms to describe molecular interactions⁸⁵. Newton's Equations of Motion can then be used to follow the position of atoms moving through space (see Chapter 2)⁸⁵. This approach has

already been used to investigate several phenomena: Ion permeation in carbon nanotubes^{80,86}, ion permeation in GO membranes²² and ion permeation in GNPs^{87,88}. Modelling makes it possible to trial different conditions and structures to understand the key features for a GO membrane.

Ion transport through a GO membrane is thought to occur through the unoxidised regions^{49,54}. Hence, most GO models in MD simulations use unoxidised slit pore configurations^{22,49,79}. Models of GO with oxygen functionalities have been developed^{89–91}, however most of these models only investigate water transport. One study has investigated the transport of NaCl through an oxidised GO model⁹². This study showed no ion permeation at 0.95 nm with 100 MPaof applied pressure across the membrane. This is contrary to what is observed experimentally²². The difference between the experiments and simulations are most likely due to the parameters for the interaction of Na⁺ and Cl⁻ with water. These interaction parameters do not reproduce the hydration free energy for these ions.

Different simulation set-ups can be used to look at ion permeation in GO. The most straight forward method is to put a carbon slit pore channel in contact with a salt solution⁹³. Salt transport across the channel can then be measured. This can be adjusted to be more realistic by having a concentration gradient across the channel, from this the flux across the channel can be measured⁴⁹. Typical desalination processes occur with an applied pressure around 1 MPa^{29} . If this pressure isn't included in a MD simulation then it will underestimate ion transport rates, and overestimate the ion rejection rate. The extra force from the applied pressure can force ions across the channel. Simulations have applied pressure gradients across the channel^{49,92,94,95}. However, this method still lacks an accurate description of the energy barrier for an ion to enter a channel. Umbrella sampling can be used to calculate the energy barrier for an ion to enter the channel^{22,79,96}. This provides a quantitative measure for the ease of ion entry into a channel. Although very effective, umbrella sampling is computationally time consuming⁹⁷. Small simulations can be run of an ion at infinite dilution between two graphene sheets. Disruption to the hydration shells around the ion will give an idea of the free energy penalty for

entering the channel. This method can be very convenient compared to umbrella sampling as it requires fewer simulations and has no external reservoirs.

Umbrella sampling has been used to calculate the energy barrier for water⁹⁸, monovalent ions^{22,79} and divalent ions^{22,79} to pass through a graphene slit pore. The free energy barrier for entry of the cations and most of the anions studied was positive^{22,79}. This is similar to the positive free energy observed for the entry of Na⁺ and Cl⁻ in carbon nanotubes^{80,86}. The positive free energy was associated with the loss of surrounding water molecules^{22,79,80}. Anionic TcO₄⁻ has shown to have a negative free energy for entering a carbon slit pore⁷⁹. This is due to favourable interactions between the graphene walls and TcO₄⁻, as well as an increase in the number of water-water interactions compensate for a loss of water surrounding TcO₄⁻⁷⁹.

1.4.1 Cation-Pi Interactions

Interactions between two atoms in MD simulations are based on the average interactions between the atoms. These interactions are optimised to reproduce experimental properties like hydration free energy^{78,99,100}, ion-oxygen distances^{78,99,100} and water-carbon contact angles¹³. There are reliable interaction parameters that describe the ion-water and water-carbon interactions. However, interactions between graphene and ions have an increased attraction due to the ion polarising the pi-electrons^{1,101}. The averaged interactions do not include any polarisation of the atoms. This shows a need to optimise new parameters that include the polarisation effects.

The polarisation effects have so far only been observed through simulations¹. However, to completely verify them it is important to obtain reliable experimental data. Recent experiments have made unoxidised graphene channels where the separation is mechanically controlled¹⁰². These channels show an unexpected trend in the water permeation rate, where smaller channel widths showed faster water permeation¹⁰². They also could be used to investigate ion permeation through unoxidised graphene slit pores to provide more information about hydrated ion – graphene interactions.

1.5 Graphene Enclosures

Two graphene sheets can be brought together and confine any molecules between them under a very high pressure^{103,104}. The confined molecules are "encapsulated" by the graphene. These systems are called graphene enclosures. Using Raman spectra of pressure sensitive molecules showed that the confined molecules experience a pressure of 1.2 ± 0.3 GPa¹⁰³.

MgCl₂, and other common salts, undergo a hydrolysis reaction at room temperature when confined in graphene enclosures¹⁰³. However at atmospheric pressure this reaction occurs at $250^{\circ}C^{105}$. These enclosures have also shown the formation of square ice at room temperature¹⁰⁴. This form of ice has not been observed in unconfined conditions. The square formation has been questioned in the literature, an alternative theory says that the transmission electron micrographs of square ice are due to salt contamination¹⁰⁶. This highlights the difficulty in conducting experiments on a nanoscale.

MD simulations could be used to help understand these systems and verify the experiments. However, simulations of this system disagree depending on what model of water is used^{104,107}. This shows a need to understand how the water models affect the structure of confined water, so that MD simulations can aid this system. A more detailed understanding of graphene enclosures could make it possible to use them as nano-reactor systems.

1.6 Fouling

A large issue for RO membranes is their ability to resist fouling. Fouling of a membrane can reduce the water flux and ion rejection through the membrane^{39,40}. The main source of fouling is a build-up of organic matter at the membrane surface⁴⁰. Organic fouling is a combination of both the adsorption of organic molecules^{40,108} and the development of a biofilm^{40,109}.

GO membranes have the potential to be developed and used for desalination applications but there is no knowledge about their resistance to fouling. Graphitic materials are known to absorb hydrocarbons from the air. This can affect the water contact angle^{110–112}. Unoxidised regions of the GO membranes may absorb hydrocarbons, resulting in a build-up of organic matter. GO films have been shown to have both anti-bacterial¹¹³ and bacteria enhancing^{114,115} properties. It is not currently known whether GO membranes develop a surface biofilm.

Inorganic fouling is also an important type of fouling for RO membranes. This typically involves the build of $CaSO_4$ and $Ca_3(PO_4)_2$ at the membrane surface⁴⁰. Reasonably strong absorption has been predicted between ions and the unoxidised region of the GO surface¹. It is not clear whether GO membranes will reduce the degree of fouling they experience compared to PA membranes. This is an area that needs further work to determine the capability of GO membranes for RO.

1.7 Structure of Thesis

The subsequent chapters of this thesis will discuss the following:

- Chapter 2 Will discuss the theoretical and computational background behind using molecular dynamics simulations. The subsequent chapters after this will discuss work that has been conducted using molecular dynamics simulations.
- Chapter 3 Will discuss the structure and dynamics of ions confined in graphitic slit pores with a 1.3 nm separation. These pores are much larger than those needed for desalination, but provide a good basis to understand how ions and water molecules structure and orient themselves when under some confinement.
- Chapter 4 Will discuss work that is based on the publication C. D. Williams,
 J. Dix, A. Torisi, P. Carbone, J. Phys. Chem. Lett. 8, 703 (2017) "Effective
 Polarisation in Pairwise Potentials at the Graphene-Electrolyte Interface".
 This work concerns the fitting of new interaction parameters that include
 the cation-pi interaction between ions and a graphene surface. It will then
 be extended to see how the new parameters change the structure and
 transport properties of ions at a graphene surface.
- Chapter 5 Will discuss how the inclusion of graphene-ion interactions alters the dynamics and structure of hydrated ions in the unoxidised graphene channels.
- Chapter 6 Will discuss the structure of different water models confined by graphene sheets to investigate the aforementioned square ice observation. This work is based on a publication by J. Dix, L. Lue and P. Carbone titled "Systematic Comparison of Water Models under Nanoconfinement by Graphene Sheets" that has been submitted to the Journal of Chemical Physics for review.
- Chapter 7 Will draw all of these papers together to conclude about the understanding of GO membranes that has been brought about by this work and where future developments in this field could stem from based on this work.

Chapter 2 Theory and Methodology

Computer simulations help supplement experimental results, and can reduce the need to conduct an experiment. This can save time when trying to develop new materials or processes. To build up the understanding of ionic transport through graphene oxide (GO) membranes it is necessary to use an atomic level model. This is because macroscopic equations do not hold for the nanoscale systems that are of interest²².

This chapter will start off discussing how atomic properties can be used to build up the macroscopic systems used in experiments (Section 2.1). This is the basis of statistical mechanics, which is needed as groundwork to discuss atomic simulations. These arguments will be extended to show how statistical mechanics feeds into dynamic systems (Section 2.2). Once the theoretical framework has been discussed it will move onto how atomistic molecular dynamics (MD) simulations operate and model molecular systems (Section 2.3). Further discussions will mention some common analysis techniques (Section 2.4). The last chapter will focus on discussing the advanced MD technique of umbrella sampling (Section 2.5).

2.1 Statistical Mechanics

A macroscopic system is made up of $\approx 10^{23}$ atoms. Each atom (*a*) will have seven degrees of freedom: three position degrees of freedom (\mathbf{q}_a), three momentum degrees of freedom (\mathbf{p}_a) and a kinetic energy degree of freedom (E_a). If there are a total of *N* atoms there will be 7*N* degrees of freedom of an atomic system. Using all of the atomic information to describe the macroscopic system will need the storage and use of $\approx 10^{24}$ pieces of information. For a time dependent process, the information would have to be stored every step through time. This level of data storage is impossible for modern computers. The macroscopic system can be thought of being made up of a lot of smaller systems, called cells. Each cell will be a manageable size for a computer, but each cell will have enough particles that it accurately resembles the macroscopic system. The cells can be built back up to make the macroscopic system. An averaged property over all of the cells ($\langle A \rangle$) corresponds to the measured property for the macroscopic system (A_{exp}):

$$A_{\rm exp} = \langle A \rangle \qquad (2.1)$$

The collection of cells is called an ensemble; because only be measuring and using all of cells together is it possible to obtain the full macroscopic picture. The angular brackets ($\langle ... \rangle$) denote the ensemble average over all of the cells for the property inside of the bracket.

Figure 2-1 shows a schematic representation of how a macroscopic system can be spilt up into nine microscopic cells. Each cell has the same volume (V) and number of particles (N) and can exchange energy with the other cells. This means that the energy within each cell can be different. From quantum mechanics, there are a discrete number of possible energy levels (L) that a cell can occupy^{116,117}. In the schematic in Figure 2-1, each cell can occupy an energy level with a value between 0 and 9. The energy value for the cell j is given the notation E_j . This means that the total energy for the macroscopic system (E) is given by the sum of the energies over all of the cells:

$$E = \sum_{j=0}^{J} E_j \qquad (2.2)$$

a) 3 4 0 8 5 0 7 1 2 1 2 3 4 5 6 7 8 9 1 2 3 4 5 6 7 8 9 1 2 3 4 5 6 7 8 9 2 0 3 8 5 0 1 4 7 1 2 3 4 5 6 7 8 9	b) 8 1 4 0 3 3 6 0 5 1 2 3 4 5 6 7 8 9 5 3 8 6 0 1 3 0 4 1 2 3 4 5 6 7 8 9 0 3 0 8 1 4 3 5 6 1 2 3 4 5 6 7 8 9	1 0 5 9 7 0 8 0 1 2 3 4 5 6 7 8 9 1 2 3 4 5 6 7 8 9 1 2 3 4 5 6 7 8 9 1 2 3 4 5 6 7 8 9 1 2 3 4 5 6 7 8 9 1 2 3 4 5 6 7 8 9
$n_0 = 2$	$n_0 = 2$	$n_0 = 4$
$n_1 = 1$	$n_1 = 1$	$n_1 = 1$
$n_2 = 1$	$n_2 = 0$	$n_2 = 0$
$n_3 = 1$	$n_{3} = 2$	$n_{3} = 0$
$n_4 = 1$	$n_4 = 1$	$n_4 = 0$
$n_{5} = 1$	$n_{5} = 1$	$n_{5} = 1$
$n_{6} = 0$	$n_{6} = 1$	$n_{6} = 0$
$n_7 = 1$	$n_7 = 0$	$n_7 = 1$
$n_8 = 1$	$n_8 = 1$	$n_8 = 1$
$n_9 = 0$	$n_9 = 0$	$n_9 = 1$
$n_{\rm T} = \sum_{k=0}^9 n_k k = 30$	$n_{\rm T} = \sum_{k=0}^{9} n_k k = 30$	$n_{\rm T} = \sum_{k=0}^{9} n_k k = 30$

Figure 2-1. Schematic representation of three distributions of ten energy levels distributed over nine microscopic cells. The three replicas spread vertically show how the same distribution of energy levels can be arranged differently amongst the cells. The sum over all of the cells in one row reaches 30.

The macroscopic energy is a constant, but allows energy to be exchanged between the cells as long as the total energy remains the same. There are then several different ways of distributing the possible energy levels over all of the cells. In the case of Figure 2-1, the three distributions are given the same constraint that the sum of values over all of the cells is 30. The number of cells that have $E_j = E_l$ is called the occupancy for that energy level (n_l) and will change for each of the distributions. The set of occupancies for each distribution is called n, such that the occupancy of an energy level is dependent on the distribution it was taken from $n_l(n)$. For example, in the schematic in Figure 2-1 for the three distributions, a, b and c, the occupancy of the l = 0 energy level is $n_0 = 2$, $n_0 = 2$ and $n_0 = 4$ respectively. In each distribution of the occupancies other energy levels also change. The probability of then picking one of the cells at random with $E_j = E_l$ for the distribution n is:

$$P(E_{l},n) = \frac{n_{l}(n)}{\sum_{l=1}^{L} n_{l}(n)} = \frac{n_{l}(n)}{J}$$
(2.3)

Figure 2-1 shows that for a specific distribution of the occupancy for each energy level, there are several ways that the energies can be distributed over the cells. The total number of ways the energy level occupancies can be distributed over the cells $(\Omega_{tot}(n))$ is given by the ratio of the total number of cell combinations over the product of the energy level occupancies for each of the energy levels^{116,117}:

$$\Omega_{\text{tot}}(n) = \frac{(n_1 + n_2 + \dots + n_L)!}{n_1! n_2! \dots n_L!} = \frac{J!}{\prod_{l=1}^L n_l!}$$
(2.4)

The probability of picking a cell at random with $E_j = E_l$ over all possible distributions can now be written as the average number of cells with $E_j = E_l$ over all of the distributions, divided by the total number of configurations of all of the distributions¹¹⁶:

$$P(E_l) = \frac{\overline{n}_l}{J} = \frac{1}{J} \frac{\sum_{n} \Omega_{\text{tot}}(n) n_l(n)}{\sum_{n} \Omega_{\text{tot}}(n)}$$
(2.5)

Equation (2.5) can be rearranged and expressed as a series of logarithms:

$$P(E_{l}) = \exp(\ln(P(E_{l})))$$
$$= \exp\left(\ln\left(\sum_{n} \Omega_{tot}(n)n_{l}(n)\right) - \ln(J) - \ln\left(\sum_{n} \Omega_{tot}(n)\right)\right)$$
(2.6)

For equations (2.5) and (2.6) the largest contribution to $P(E_l)$ will come from the distribution of energies that has the largest number of configurations of the energy levels. This distribution (n^*) will occur for $\Omega_{tot}(n^*) = \max[\Omega_{tot}(n)]$. The distribution n^* has to satisfy the conditions that the total number of cells and energy are conserved:

$$\sum_{l=0}^{L} n_l = J \tag{2.7}$$

$$\sum_{l=0}^{L} n_l E_l = E \qquad (2.8)$$

Maximising $\ln(\Omega_{tot}(n^*))$ is preferable to maximising $\Omega_{tot}(n^*)$, as it makes it possible to use the rules of logarithms to separate the contributions of all of the individual levels from the total number of levels. Information theory uses an alternative derivation where the logarithmic form occurs during the derivation¹¹⁸. This shows that it is sufficient to maximise $\ln(\Omega_{tot}(n^*))$. It is necessary to use Stirling's approximation of¹¹⁹:

$$\ln(N!) \approx N \ln N - N, N \to \infty \tag{2.9}$$

(2.11)

 $\therefore n_l^* = e^{-\alpha - \beta E_l}$

To determine the distribution of energy levels that satisfies equations (2.7) and (2.8) it is common to use the Lagrange method of undetermined multipliers¹¹⁹. This method maximises the logarithm of equation (2.6) while under the constraints of equations (2.7) and (2.8):

$$\Lambda(n_{1}^{*}, n_{2}^{*}, \dots, n_{L}^{*}, \alpha, \beta) = J \ln J - J - \sum_{l} n_{l}^{*} \ln(n_{l}^{*}) + \sum_{l} n_{l}^{*} + \alpha \left[J - \sum_{l} n_{l}^{*} \right] + \beta \left[E - \sum_{l} n_{l}^{*} E_{l} \right]$$
(2.10)
$$\frac{\partial \Lambda}{\partial n_{l}^{*}} = -\ln n_{l}^{*} - 1 + 1 - \alpha - \beta E_{l} = 0$$

The distribution of the levels n_l^* when $\Omega_{tot}(n^*) = \max[\Omega_{tot}(n)]$ must obey equation (2.11). Equation (2.11) has two unknowns, α and β . Equation (2.11) can be substituted into equation (2.5) to get the probability for cell j having $E_j = E_l$ over all of the possible distributions:

$$P(E_l) = \frac{1}{J} \frac{\Omega_{\text{tot}}(n^*)n_l^*}{\Omega_{\text{tot}}(n^*)} = \frac{n_l^*}{J} = \frac{e^{-\alpha}e^{-\beta E_l}}{e^{-\alpha}\sum_l e^{-\beta E_l}} = \frac{e^{-\beta E_l}}{\sum_l e^{-\beta E_l}}$$
(2.12)

In equation (2.12) the sum over all the distributions disappears. This is because as $J \rightarrow \infty$, only n^* contributes to $P(E_l)^{116}$. α is cancelled out of the calculation for

 $P(E_l)$, leaving only the need to determine β . Using the kinetic theory of gases and the Maxwell-Boltzmann distribution β can be related to the temperature by¹¹⁹:

$$\beta = \frac{1}{k_{\rm B}T} = \frac{3}{2} \frac{E}{N}$$
(2.13)

In equation (2.13): $k_{\rm B}$ is Boltzmann's Constant and T is temperature of the macroscopic system. Equation (2.13) provides a link between the total macroscopic energy and the temperature. As the macroscopic energy is constant, equation (2.2), and the cells have the same number of particles and volume, the distribution of cell energies comes from the constant- *NVT* ensemble. From equations (2.12) and (2.13) the probability of finding cell j with $E_j = E_l$ in the constant- *NVT* ensemble is:

$$P(E_{l}) = \frac{e^{\frac{-E_{l}}{k_{\rm B}T}}}{\sum_{j=0}^{J} e^{\frac{-E_{l}}{k_{\rm B}T}}}$$
(2.14)

Similar equations to (2.14) exist for the constant-NpT ensemble. p is the macroscopic pressure exerted on the system. This is also called the isothermal-isobaric ensemble.

Using the probabilities from equation (2.14), the ensemble average for A can be written as a sum over all of the energy states, where the value of A in each state is A_i :

$$\langle A \rangle = \sum_{l} A_{l} P(E_{l})$$
 (2.15)

Equations (2.1) and (2.15) provide a link between observed properties of a system and the probability of finding a microscopic cell in a specific energy state. It is now important to understand how a simulation could generate the microscopic cells and build up probabilities or ensemble averaged properties for the macroscopic system.

2.2 Generating Configurations – Molecular Dynamics

Simulations need to be able to generate atomic configurations that are the same as the microscopic cells in section 2.1. Creating these cells will make it possible to

determine the probabilities that are needed in equation (2.15). The denominator in equation (2.14) is called the partition function. The partition function is the sum of the contribution of all possible energy states. This can be used to relate to a lot of different aspects of statistical thermodynamics. The partition function needs to be calculated to determine the probability distribution of energy states in equation (2.14). It can be difficult to generate all possible energy states to determine the partition function exactly. However in equation (2.14) high energy states will occur with a low, almost vanishing, probability. It is difficult to generate atomic configurations for high energy states, so it is permissible to only sample the lowenergy configurations.

Section 2.1 relied on discrete energy levels that a cell could occupy. As the size of the macroscopic system increases, energy differences between states become thermally negligible. This allows energy to be thought of as being a continuous variable that is dependent on all of positions (**p**) and momenta (**q**) of the atoms. These systems obey Newton's classical equations of motion. The probability of being in a specific energy range is determined by the Hamiltonian of the system ($H(\mathbf{p},\mathbf{q})$). In a time independent system $H(\mathbf{p},\mathbf{q}) = E^{120}$. The possible range of values that **p** and **q** can be, is called the phase space. The partition function in equation (2.14) can be written as a double integral over the position and momenta of all the particles:

$$Q_{\rm NVT} = \frac{1}{N!} \frac{1}{h^{3N}} \iint d\mathbf{q} d\mathbf{p} \exp(-H(\mathbf{q}, \mathbf{p})/k_{\rm B}T)$$
(2.16)

In equation (2.16): *h* is Planck's constant and appears due to the indistinguishability of identical particles in quantum mechanics¹²⁰. It is assumed that there are no momentum dependent forces, such as frictional forces. The Hamiltonian can then be split into a kinetic part ($K(\mathbf{p})$), depending only on \mathbf{p} , and a potential part ($\Psi(\mathbf{q})$), depending only on \mathbf{p} . The partition function in equation (2.16) can then be split into an ideal gas integral and an excess integral⁸⁵:

$$Q_{\rm NVT} = \frac{1}{N!} \frac{1}{h^{3N}} \int d\mathbf{p} \exp(-K(\mathbf{p})/k_{\rm B}T) \int d\mathbf{q} \exp(-\Psi(\mathbf{q})/k_{\rm B}T)$$
(2.17)
$$Q_{\rm NVT} = Q_{\rm NVT}^{\rm id} Q_{\rm NVT}^{\rm ex}$$

The ideal gas integral can be solved analytically⁸⁵:

$$Q_{\rm NVT}^{\rm id} = \frac{V^N}{N!\Lambda^{3N}} \qquad (2.18)$$
$$\Lambda = \left(h^2/2\pi m k_{\rm B}T\right)^{\frac{1}{2}}$$

The excess integral needs to be calculated or estimated to determine the full partition function. The position dependence in the excess integral is called the configuration integral (Z_{NVT}):

$$Q_{\rm NVT}^{\rm ex} = V^{-N} \int d\mathbf{q} \exp(-\Psi(\mathbf{q})/k_{\rm B}T) = V^{-N} Z_{\rm NVT}$$
(2.19)

The partition function for the *NVT* ensemble can be related to the NpT ensemble:

$$Q_{\rm NpT} = \sum_{V} \exp(-pV/k_{\rm B}T)Q_{\rm NVT} \qquad (2.20)$$

Equations (2.17) – (2.20) make it possible to create a model with separate kinetic and potential energy components. Equations (2.17) and (2.18) means that the kinetic component can be treated like an ideal gas system. The potential component is only position dependent. This provides the basic structure for a model.

Liouville's theorem states that the density of states of an ensemble (ρ_{ens}) is independent of time⁸⁵:

$$\frac{\partial \rho_{\rm ens}}{\partial t} = 0 \qquad (2.21)$$

This means that when a system is in equilibrium there is no change in the probability of an energy state as a function of time. Atomic positions can be propagated through time to generate different atomic configurations to build-up an ensemble average. If the atomic positions were propagated through N_t steps with an atomic configuration being used for the average at every τ step then the ensemble average would be⁸⁵:

$$\langle A \rangle = \frac{\tau}{N_{\rm t}} \sum_{i=0}^{N_{\rm t}/\tau} A_i$$
 (2.22)

Equation (2.22) does not contain any probabilities, unlike equation (2.15). This means that there is no need to fully calculate the partition function. Equation (2.22) is equivalent to equation (2.15) because the probability of a configuration occurring with a property A_i when propagated through time will be the same as picking a cell at random. The initial factor in equation (2.22) was to normalise for the number of configurations that have been averaged. Molecular dynamics can build up ensemble averages by creating different atomic configurations by propagating the atomic positions through time.

2.3 Molecular Dynamics Simulations

It is possible to build up an equilibrium model for atomic and molecular movement through time. This is the basis for molecular dynamics. If a sufficient number of equilibrium configurations are generated then it is possible to produce ensemble averages that can be compared to experimental values.

The kinetic component for the model can be modelled as an ideal gas. There are several different models that can be used to describe the potential interaction. Explicit electron models solve Schrödinger's equations to determine the electron distribution over molecules^{121–123}. These models can then see how the nuclear positions change based on these distributions¹²⁴. Although accurate, these models are computationally time-consuming and are limited to ~ 100 ps. Most chemical phenomena occur on a longer time scale, making this too short to investigate ion permeation in graphene channels. Implicit electron models, like MD, use simple interaction potentials that are fitted to recreate the electron-electron, electron-nuclei and nuclei-nuclei interactions. Implicit electron models have a loss of accuracy but with the benefit of a reduced computational cost. With simulations there is always the trade-off between accuracy and length/time-scale the simulation can probe¹²⁵.

For the molecular dynamics simulations investigated here, an implicit electron model is used. To mimic the electron interactions the interaction potentials are split into non-bonding and bonding interaction potentials.

2.3.1 Non-Bonded Interaction Potentials

Non-bonded interactions are split up into two interaction potentials: electrostatic interactions between partial charges on each atom; electron-electron interactions from spontaneous dipole-spontaneous dipole interactions and electron-electron overlap. It is assumed that the interactions only occur between pairs of atoms. The interactions are said to be "pairwise". Three-body interactions¹²⁶ and local polarizability¹²⁷ can be added into the model to account for local variations in the chemical environment. However, these methods are more computationally intensive and reduce the size and length scales that are accessible.

Electrostatic interactions (V_{Coul}) are modelled with Coulomb's potential:

$$V_{\text{Coul}}(r_{ij}) = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}^2}$$
(2.23)

In equation (2.23): ε_0 is the permittivity of free space; q_i and q_j are the partial charges on atom *i* and *j* respectively; r_{ij} is the distance between atoms *i* and *j*.

Other electron-electron interactions are typically modelled using the Lennard-Jones potential ($V_{\rm LJ}$). Convention has the attractive interaction varying as r^{-6} and repulsive interaction varying as r^{-12} . This form is called the Lennard-Jones 12-6 equation:

$$V_{\rm LJ}(r_{ij}) = 4\varepsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right)$$
(2.24)

In equation (2.24): ε_{ij} is the attractive well depth between atoms *i* and *j*; σ_{ij} is the distance between *i* and *j* where the potential reaches zero. The potential well in equation (2.24) occurs when $r_{ij} = \sqrt[6]{2}\sigma_{ij}$. Values for ε_{ij} and σ_{ij} are determined from the individual atom parameters using either the Lorentz-Berthelot or geometric mixing rules:

Lorentz-Berthelot:
$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}; \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$$
 (2.25)

Geometric: $\sigma_{ij} = \sqrt{\sigma_i \sigma_j}; \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$ (2.26)

In equations (2.25) and (2.26): σ_i , σ_j and ε_i , ε_j are the values used in equation (2.24) for σ_{ij} and ε_{ij} when atom *i* and *j* are the same atom type. Values for σ_i and ε_i are determined by fitting simulated results to experimental data.

2.3.2 Bonded Interaction Potentials

Bonding interactions are used to give a molecule a realistic shape, vibration and flexibility. There are three main bonding interactions: bond stretching, angle stretching and dihedral rotations.

Bond stretches occur between two atoms that are bonded together. They aim to get the right vibration between the two bonded atoms. This stretch is modelled by a harmonic interaction potential (V_{bond}) between the two atoms:

$$V_{\text{bond}}(r_{ij}) = \frac{k_{\text{bond}}}{2} (r_{ij} - r_{\text{e}})^2$$
 (2.27)

In equation (2.27): k_{bond} is the force constant for the harmonic potential, it changes between pairs of atoms; r_{ij} is the distance between atoms *i* and *j*; r_{e} is the equilibrium bond distance. Some simulations constrain the bond length of fast moving atoms, like hydrogen atoms. This allows for larger steps in time, making it possible to cover longer time-scales.

Angle stretches are applied between two sets of bonded atoms where one of the atoms is the same in each set. The angle between the two sets (θ_{ijk}) is the dot product between the vectors of the atoms in the first set (\mathbf{r}_{ij}) and the second set (\mathbf{r}_{ik}). This interaction (V_{angle}) typically also uses a harmonic potential:

$$V_{\text{angle}}(\theta_{ijk}) = \frac{k_{\text{angle}}}{2} \left(\theta_{ijk} - \theta_{\text{e}}\right)^2$$
(2.28)

In equation (2.28): k_{angle} is the force constant for the angle stretch; θ_e is the equilibrium bond angle between the sets of atoms [i, j] and [j, k].

The dihedral interaction (V_{dih}) is not used in most of this work, but it is still an important interaction in MD simulations. This interaction occurs between four atoms. Either the four atoms are made up of three sets of adjacent bonds (proper dihedral) or are four atoms that are no necessarily bonded together (improper dihedral). Improper dihedral interactions are useful for keeping a plane of atoms rigid, like the nitrogen centre in triphenylamine¹⁰³. Both dihedrals work in a similar way, there is an interaction potential that is based on the angle between two planes of atoms. The main focus here is proper dihedrals. There are three sets of bonded atoms [i, j], [j, k] and [k, l]. Two planes can be made up of the atoms [i, j, k] and [j, k, l]. The angle between these two planes is the dihedral angle (ϕ_{ijkl}). The most typical form for V_{dih} is based around the Ryckaert-Bellmans form¹²⁸, of using a Fourier series to obtain a periodic function:

$$V_{\text{dih}}(\phi_{ijkl}) = \sum_{n=0}^{5} C_n (\cos(\psi))^n \qquad (2.29)$$
$$\psi = \phi_{iikl} - 180^o$$

In equation (2.29): C_n are fitting coefficients for the interaction to get the correct strength and periodicity. The force for this potential is only applied to the atoms i and l, as the forces on the other atoms cancel.

2.3.3 Periodic Boundary Conditions

The number of atoms in modern MD simulations can range from 10,000-1,000,000. The atoms are typically placed randomly in a cubic or rectilinear box. If the walls were real, then the atoms would order at the wall surface¹²⁹. Unhindered properties for the system will then only be obtained in the centre of the box where ordering at the wall has no affect. This would waste the information and computational time on the atoms around the edge of the box. This is avoided by using the "periodic boundary conditions"⁸⁵, where the walls of the box are "transparent". The atoms can travel through a wall and will reappear through the opposite wall. None of the atoms are created or destroyed, but they can feel the interactions and forces with other atoms through the periodic boundary. This makes it possible to use all of the atoms in the simulation. This method can introduce some error in the simulations due to the finite size of the original box. These finite size effects can be quite noticeable when calculating 3D diffusion coefficients^{130,131}.

2.3.4 Cut-Offs

Non-bonded interactions are pairwise, so there will be N(N-1) total interactions to calculate for every time step for N atoms. To reduce the computational cost, energy or distance cut-offs are used to limit the number of interactions that are calculated. Both work on the principle that when the interaction energy is small enough then the interactions can be ignored. An energy cut-off ignores all interactions that are less than the cut-off. A distance cut-off says that any interactions outside of a spherical radius around an atom are ignored. The spherical radius should be chosen carefully to ensure all of the ignored interactions are small enough so that there are no artefacts brought about by the introduction of the cut-off. There are three main cut-off schemes for the spherical radius^{85,132}:

- Direct cut-off
- Shifted potential cut-off
- Switching potential cut-off

A direct cut-off sharply reduces the interaction energy to zero beyond a cut-off distance (r_c). As the force is calculated from the gradient of the potential energy, this causes a sharp increase in the forces experienced around the cut-off. The shifted potential compensates for this by shifting the whole potential energy curve, so that the interaction energy is zero at r_c . Alternatively, a switching potential can be used to ensure that both the interaction energy and the gradient of the energy are zero at r_c , which prevents large anomalies in the forces on the atoms. This is done by having two cut-off regions, the first cut-off (r_1) is where the switching function is initially applied to the interaction potential. By the second cut-off, r_c , both the interaction potential and the gradient are zero.

To calculate the overall pressure and energy in a simulation, all of the interactions need to be taken into account. A lot of small ignored interactions can lead to a big discrepancy in the energy or pressure of a system. For the Lennard-Jones 12-6 interaction an analytical correction can be applied to the energy and pressure to correct for the loss of long-range interactions^{85,132}.

Electrostatic interactions are split up into a short-range real space sum, a long-range reciprocal space sum and a self-interaction contribution. The real space sum is calculated using equation (2.21). The reciprocal space sum is calculated using an Ewald summation over several periodic images. A Gaussian function is used in the Ewald sum to cancel out the charge distribution over the simulation box⁸⁵. The cancelling distribution is Fourier transformed and summed in reciprocal space. The real space, reciprocal space and self-interaction contributions are combined to get the total electrostatic interactions. Current MD simulations use a particle-mesh Ewald (PME) summation. The computational cost for the PME summation varies as $N \log N^{133,134}$. This increases slower as a function of N compared to N(N-1) as $N \rightarrow \infty$. This resulted in a lower computational cost to calculate the PME summation compared to the calculation of all of the pairwise electrostatic interactions interactions can also be taken into account in non-neutral systems, by using the Ewald summation with an additional neutralising background charge density across the whole simulation box¹³⁵⁻¹³⁷.

2.3.5 Time Integration

At the start of a simulation the atoms are placed randomly within a box. Velocities are randomly assigned to the atoms based on the Maxwell-Boltzmann velocity distribution for an ideal gas¹³². This is allowed based on the separation of the Hamiltonian in equation (2.17).

From the initial positions and velocities the atoms are propagated through time using the forces from neighbouring atoms that alter the trajectory of each atom. The force on each atom provides the acceleration from Newton's $\mathbf{F}_i = m_i \mathbf{a}_i$ equation. Subscript *i* is used to show the force and acceleration that are experienced by atom *i*. The interaction potentials can then be used to obtain \mathbf{a}_i^{85} :

$$\mathbf{a}_{i} = \frac{\mathbf{F}_{i}}{m_{i}} = -\frac{1}{m_{i}} \nabla V_{\text{tot}}(\mathbf{r}_{i}) = -\frac{1}{m_{i}} \left(\frac{\partial V_{\text{tot}}(\mathbf{r}_{i})}{\partial x} \hat{\mathbf{i}} + \frac{\partial V_{\text{tot}}(\mathbf{r}_{i})}{\partial y} \hat{\mathbf{j}} + \frac{\partial V_{\text{tot}}(\mathbf{r}_{i})}{\partial z} \hat{\mathbf{k}} \right)$$
(2.30)

In equation (2.30): $V_{tot}(\mathbf{r}_i)$ is the total interaction, which is the sum of the potential energies in equations (2.23), (2.24), (2.27)-(2.29); \mathbf{r}_i is the position of atom *i* in the simulation box; $\hat{\mathbf{i}}$, $\hat{\mathbf{j}}$ and $\hat{\mathbf{k}}$ are the unit vectors for the x, y and z axes, respectively.

The aim of MD is to create a trajectory of the atoms moving through space within a simulation box as a function of time. This is done by sequentially solving the equation of motion for all of the atoms based on the atomic positions, velocities and accelerations between small time steps (∂). The size of ∂ must be small enough such that the trajectory captures all of the collisions and vibrations of the atoms. Otherwise energy is not conserved in the simulation, which could lead to unphysical trajectories. Atomic movement is calculated using the Leapfrog integration algorithm. The Leapfrog algorithm provides good energy conservation and a quick computation for the integration^{85,138}.

In the Leapfrog algorithm the positions ($\mathbf{r}_i(t)$), velocities ($\mathbf{v}_i(t)$) and accelerations ($\mathbf{a}_i(t)$) are all offset by half a time step. At $t = t_0$, the values of $\mathbf{r}_i(t_0)$, $\mathbf{v}_i(t_0 - \delta t/2)$ and $\mathbf{a}_i(t_0 - \delta t)$ will be stored. They are used to calculate the position at the subsequent time step ($\mathbf{r}_i(t_0 + \delta t)$). The Leapfrog algorithm uses the following scheme to propagate the atomic positions through time:

At start: $t = t_0$

Step 1: Calculate $\mathbf{a}_i(t_0)$ from equation (2.30)

Step 2: Advance velocities by δt using $-\mathbf{v}_i(t_0 + \delta t/2) = \mathbf{v}_i(t_0 - \delta t/2) + \delta t \mathbf{a}_i(t_0)$

Step 3: Advance positions by δt using - $\mathbf{r}_i(t_0 + \delta t) = \mathbf{r}_i(t_0) + \delta t \mathbf{v}_i(t_0 + \delta t/2)$

Update: $t = t_0 + \delta t$

In a modern MD simulation programs, like GROMACS^{132,139–141}, there are many additional steps within the above scheme. Calculating \mathbf{a}_i in step 1 is the largest computational demand. Hence a lot of effort has gone into optimising this step. Additional steps can include, but are not limited to: recalculating atoms within cut-off criteria; passing information between parallel processors; writing data; calculating pressure, temperature and energies. Positions are not stored at each time step to reduce the amount of data storage that is needed. This also helps to avoid sampling a lot of configurations from the same region of phase space, which can result in skewed ensemble averages.

2.3.6 Temperature and Pressure Control

Pressure and temperature need to be controlled in a simulation to ensure that all of the configurations are in the same ensemble. A common method of controlling the pressure and temperature is Berendsen's method of rescaling the velocities and positions of the atoms based on¹⁴:

$$\frac{dA'}{dt} = \frac{A - A'}{\tau_A} \tag{2.31}$$

In equation (2.31): A is the desired value for the property; A' is the instantaneous value of A; τ_A is the time constant used to determine the strength of the restoring force. Equation (2.31) ensures that A' is pulled back towards the desired value of A. Although this method can reproduce some properties of the constant *NVT* - ensemble¹⁴², it does not rigorously sample the *NVT* -ensemble^{85,143}.

Nosé and Hoover have derived a thermostat that can rigorously control the temperature in the *NVT* -ensemble^{15,16}. Their method involves scaling the velocities based on the interaction with an external thermal reservoir^{15,85}. Andersen developed a method of scaling the atomic positions to obtain a constant pressure¹⁴⁴. This method was originally only used for isotropic systems, until Parrinello and Rahman extended this method further to allow the simulation box to change shape and size in an anisotropic manner^{145–147}.

2.4 Analysis

After all of the configurations have been generated through a MD simulation, they need to be analysed to draw conclusions about the system. The exact analysis used depends on the system and properties of interest. For example: molecular structures can be understood by looking at order parameters, density profiles and radial distribution functions (RDFs). Dynamics properties would be understood by using the mean-squared displacement (MSD) and by calculating diffusion coefficients.

Two main analysis techniques will be discussed here: Radial distribution functions and diffusion coefficients. These two methods are heavily used in subsequent chapters. Other analysis methods will be discussed where necessary.

2.4.1 Radial Distribution Function

Pair distribution functions are called radial distribution functions. They measure the distribution of atoms at a distance r_2 away from a central atom r_1 . The formal definition is⁸⁵:

$$g(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{\rho^2 Z_{\text{NVT}}} \int d\mathbf{r}_3 d\mathbf{r}_4 \dots d\mathbf{r}_N \exp(-\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)/k_{\text{B}}T)$$
(2.32)

In equation (2.32): *N* is the total number of atoms; ρ is the number density of the atoms; Z_{NVT} is the configuration integral from equation (2.19); $\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$ is the potential energy as a function of all the atomic positions.

In equation (2.32) the indices can be exchanged on the atoms if they are the same type of atom. This allows equation (2.32) to be compressed into the ensemble average of distances between the pair of atoms⁸⁵:

$$g(\mathbf{r}) = \rho^{-2} \left\langle \sum_{i} \sum_{j \neq i} \delta(\mathbf{r}_{i}) \delta(\mathbf{r}_{j} - \mathbf{r}) \right\rangle = \frac{V}{N^{2}} \left\langle \sum_{i} \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle$$
(2.33)

In equation (2.33): δ is the delta function; g(r) is the radial distribution function; V is the volume of the system.

The RDF can be calculated from a simulation by using the ratio of the histogram of atoms around a central atom compared to an ideal gas⁸⁵. The histogram is built up by counting the number of atoms that are a distance between r and $r + \delta r$ away from the central atom. The bin width of the histogram is δr . The histogram is averaged over all of the possible atoms to obtain the ensemble average. This also improves the statistical accuracy. The RDF can now be written as a histogram:

$$g(r) = \frac{n(b)}{n^{\rm id}(b)} = \frac{3}{8\pi\rho\delta rr^2} \sum_{n=0}^{\tau_{\rm b}} \sum_{i\neq j} H(n\delta r - r) - H((n+1)\delta r - r)$$
(2.34)
$$H(x) = \begin{cases} 1 & x > 0\\ 0 & x \le 0 \end{cases}$$

In equation (2.34): H(x) is the Heaviside function. Equation (2.34) makes it possible to understand the structure and arrangement of atoms in a system.

2.4.2 Diffusion Coefficient

The diffusion coefficient (D) measures how quickly molecules move through a system. It can be calculated from the gradient of a linear plot of MSD against time using the Einstein relation⁸⁵:

$$2nD = \lim_{t_i \to \infty} \frac{1}{t_i} \left\langle \left(\mathbf{r}_i(t_0) - \mathbf{r}_i(t_i) \right)^2 \right\rangle$$
(2.35)
$$MSD(t_i) = \left\langle \left(\mathbf{r}_i(t_0) - \mathbf{r}_i(t_i) \right)^2 \right\rangle$$

In equation (2.35): $r_i(t_i)$ is the position of particle *i* at time t_i ; $MSD(t_i)$ is the ensemble averaged mean squared displacement for a set of particles between time t_0 and t_i ; *n* is the dimensionality of the system¹⁴⁸, n = 2 for 2D transport^{149,150} and n = 3 for 3D transport¹⁴⁸. To improve statistical accuracy for the MSD there are several starting points, t_0 , that are used throughout the simulation trajectory. The values for $MSD(t_i)$ are averaged together over all of the different starting points.

2.5 Umbrella Sampling

Often in chemical systems it is useful to know the free energy between two points. This can be achieved by using the Weighted Histogram Analysis Method (WHAM)^{96,151–153}, which is often called umbrella sampling. Figure 2-2 shows a schematic representation of using the WHAM in a MD simulation. The ion is pinned to regions along a reaction pathway, in the case of Figure 2-2 this is shown by the dashed black arrow. Ultimately, in this example only the points 1 and 4 at the end of the reaction pathway are of interest (Figure 2-2). The free energy difference of these points will show the free energy difference for moving an ion from an unconfined system into a confined channel. This will make it possible to know whether it is energetically favourable for an ion to enter the channel or not.



Figure 2-2. Schematic representation to show how molecular dynamics simulations are used to sample along a reaction pathway (dashed black arrow) for an ion moving from an unconfined system into a confined system. This is done by using harmonic potentials in separate simulations to restrict the atom to a region of the reaction pathway. Each colour shows a separate simulation.

However, to calculate the relative free energy of end two points, the WHAM requires a continuous sampling of all of the points along the reaction pathway. In an unbiased simulation an ion will not sufficiently sample all of the points along the reaction pathway. This is particularly true if there is a large free energy barrier for an ion to sample part of the reaction pathway, like for an ion to enter a channel. This is circumvented by applying harmonic potentials to a series of simulations along the reaction pathway. Each simulation provides a "window" into a specific point along the reaction pathway to ensure sufficient sampling along the whole reaction pathway. The harmonic potential is typically given the form of^{96,153}:

$$V_{\text{bias}}^{i}(\xi) = K_{i}(\xi - \xi_{i})^{2} \qquad (2.36)$$

In equation (2.36): V_{bias}^i is the bias potential of the *i* th window along the reaction coordinate; K_i is the force constant at the *i* th window; ξ_i is the reference position for the *i* th window; ξ is the position of the system along the reaction coordinate. The simulation is allowed to vary away from the reference point, but the biasing potential always pulls it back towards the reference position on the reaction coordinate. K_i determines how broad or narrow the distribution of ξ is during a simulation.

For the reaction coordinate described in Figure 2-2, the reference position for window *i* would be a position on the x-axis, $\xi_i = r_x^i$. The position along the reaction coordinate would simply be the x position of the ion, $\xi = r_x$.

By minimising the error on the density-of-states for each window it is possible to derive two simultaneous equations^{151,152}:

$$P(\xi) = \frac{\sum_{i=1}^{N_{w}} g_{i}^{-1} h_{i}(\xi)}{\sum_{j=1}^{N_{w}} n_{j} g_{j}^{-1} \exp[-\beta (V_{\text{bias}}^{j}(\xi) - f_{j})]}$$
(2.37)

$$\exp(-\beta f_i) = \int d\xi \exp[-\beta V_{\text{bias}}^j(\xi)] P(\xi)$$
(2.38)

In equations (2.37) and (2.38): N_w is the number of windows along the reaction coordinate; n_j is the number of data points within the histogram h_i ; V_{bias}^j is the statistical weight based on equation (2.36); β is the inverse temperature of $1/k_BT$; f_i are undetermined free-energy constants; $P(\xi)$ is the unbiased probability distribution. g_i is the statistical inefficiency of the simulation data and is given by $g_i = 1 + 2\tau_i$, where τ_i is the integrated autocorrelation time for the window i^{96} .

The unbiased potential of mean-force ($W(\xi)$) can be obtained from $P(\xi)$ using the relation⁹⁶:

$$W(\xi) = -\beta \log \left(\frac{P(\xi)}{P(\xi_0)}\right)$$
(2.39)

In equation (2.39): $P(\xi_0)$ is the unbiased probability for the reference point ξ_0 . From equation (2.39), at $\xi = \xi_0$, $W(\xi_0) = 0$. Both $P(\xi)$ and f_i in equations (2.37) and (2.38) are unknown. They both need to be solved iteratively to obtain $P(\xi)$. Once $P(\xi)$ is determined the potential of mean force can be calculated along the whole reaction coordinate using equation (2.39).

Chapter 3 Confined Ion Structure

Ion rejection in graphene-oxide (GO) membranes requires a sheet-sheet separation of 0.98 - 0.64 nm. This is needed as it greatly distorts the hydration structure around an ion, which means there will be a large free energy barrier against the ion entering a GO pore. The overall aim of this work is to be able to understand, and potentially quantify the degree of distortion or dehydration of the water structure around an ion.

To be able to quantify these changes, it is important to understand how water both structures and behaves around unconfined ions. For sheet-sheet separations of 1.3 nm GO membranes do not show any rejection of small ions, like Na⁺ and K^{+ 22,49}. Confining ions to this separation should not show much alteration in the hydration structure between the confined and unconfined ions. Changes in the structure or dynamics will show how the hydrated ions interact with the graphene walls.

This chapter focuses on the structure and dynamics of unconfined and confined alkali metal cations where the channel width is larger than that needed for desalination applications. This is to act as a study and investigation into the general behaviour of hydrated ions that can be linked with a direct comparison to their confined counterparts. There has been several works that have discussed and suggested that there is an enhanced interaction between ions and a graphene surface^{1,101,154–156}. This will be discussed in more detail in Chapter 4 and is not the focus of this chapter. The results and analysis of the confined ions in this chapter will provide a good groundwork to be built upon in subsequent chapters with the inclusion of ion-pi interactions (Chapter 4 and Chapter 5) and use of smaller channel widths (Chapter 5).

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and analysed by the author (J. Dix). The author (J. Dix), C. D. Williams and P. Carbone all contributed to the preparation of the original manuscript; however the author (J. Dix) took the lead on writing the manuscript and implemented changes suggested by other contributors.

This chapter is split into six sections:

Section 3.1 Introduction into the technical aspects and underlying reasons behind investigating the confinement of ions.

Section 3.2 Discussion of the simulation set-up and how the simulations were run.

Section 3.3.1 Analysis of the hydration structure for the alkali metal cations Li^{+} , Na^{+} , K^{+} and Cs^{+} .

Section 3.3.2 Analysis of the ion interaction with graphene surfaces.

Section 3.3.3 Analysis of the diffusive properties of the cations in a confined pore.

Section 3.4 Conclusions about the results and how they fit into the overarching structure of research.

3.1 Introduction

Scarcity of clean water is becoming a global problem¹⁵⁷. The demand for more water is increasing due to the industrialisation of developing nations and the global population increase. Water demand is likely to be further exacerbated due to contamination of current water sources and the uncertain future of the global climate¹⁵⁷. The UN predicts that by 2050, 40% of the global population will face a water shortage²⁰.

Seawater and brackish water are both available in large quantities on earth. However, they both contain large amount of dissolved salt. The typical total dissolved salt for seawater is around $43.4 - 10.1 \text{ g L}^{-124-26}$ and a concentration fit for human consumptions is $< 1 \text{ g L}^{-127}$. Reverse osmosis (RO) is the most widespread

desalination method to reduce the amount of dissolved salt in seawater^{31,38,157}. RO uses a semi-permeable membrane to separate a high salinity feed solution from a low salinity product solution²⁹. The high salinity seawater is pressurised against the membrane, forcing water through the membrane but preventing the transport of ionic species. The technical limitations for RO membranes are due to poor fouling resistance, slow water permeation and large pore size distributions¹⁵⁸.

Carbon-based nanomaterials have a range of different porous structures with good mechanical properties for desalination^{159,160}. These structures can be easily fabricated¹⁶⁰. Molecular simulations have shown that both carbon nanotube bundles^{161–163} and graphene nanopores (GNP)^{87,88} exhibit fast water permeation and ion rejection capabilities. These results are promising but it is unclear how easy it will be manufacture these membranes on a commercial scale. For carbon nanotubes and GNP there are a lot of technical difficulties in preparing these membranes with consistent size and distribution of pores^{23,53,160,164,165}. For a carbon nanotube membrane it is difficult to ensure all of the nanotubes are uniformly aligned¹⁶⁵. GO membranes present a breakthrough in this field because they show limited ion permeation²² while using low-cost fabrication methods^{54,55,57,166}. The GO structure consists of a layered structure of graphene sheets with oxygen functionalities^{54,55,167}. Oxygen groups prevent the aggregation of the graphene sheets creating channels through a GO membrane. These 2D nanopores provide a channel for fast water permeation⁵⁴. When submersed in the water these membrane swell to a graphene sheet – graphene sheet separation of 1.3 nm^{49} . Various studies have investigated ion permeation through GO membranes and have shown a size-selectivity for the ion^{49,94,168–170}. Latter studies have shown that this size-selectivity is closely related to the dehydration of water shells around an ion²².

This study focused on the structure and dynamic properties of the group 1 cations Li⁺, Na⁺, K⁺ and Cs⁺ when confined between two graphene sheets. The "slit-pore" configuration had a graphene-graphene separation of 1.3 nm . Experimental results have suggested that molecular transport occurs through unoxidised regions of the GO capillary. Na⁺ and K⁺ were chosen because they are two of largest cationic contributions for dissolved salt in seawater²⁵. Li⁺ and Cs⁺ were chosen because they

will make it possible to build up the trends for the group 1 cations. Hydrated properties for unconfined ions, like diffusion coefficients, hydration shell structure and ionic size may be important to understand ion permeation. These results and comparisons will be important for using desalination applications in GO membranes.

These simulations were performed using molecular dynamics (MD). Links with experimental data has helped validate the intermolecular potential for ions in solution⁷⁸. Concentration effects were ignored in this work by focusing on the case infinite dilution. In each simulation there was only one ion and counter ions were neglected. The effects of periodic boundary conditions on diffusive properties were also considered. Since dehydration²², and historically size exclusion⁴⁹, are the expected ion rejection mechanisms attention was paid to the definition of the size of a hydrated ion.

3.2 Methodology

3.2.1 Intermolecular Potential

In MD, finite difference approaches are used to the evolve the positions and momenta of atoms in time with Newton's equations of motion⁸⁵. Forces acting between particles are calculated using an intermolecular potential (Ψ). Reliable simulation results are obtained when the intermolecular potential captures the true nature of the interactions in the system. In this work Ψ was evaluated as the sum of the short-range Lennard-Jones and longer range Coulombic interactions:

$$\Psi(r_{ij}) = 4\varepsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right) + \frac{q_i q_j}{4\pi\varepsilon_0}$$
(3.1)

In equation (3.1): r_{ij} is the distance between atoms *i* and *j*; q_i and q_j are the partial atomic charges on atoms *i* and *j* respectively; ε_0 is the permittivity of free space and ε_{ij} and σ_{ij} are the Lennard-Jones cross parameters. The cross parameters were obtained from individual atomic parameters using the Lorentz-Berthelot combining rules:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \qquad (3.2)$$
$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \qquad (3.3)$$

In equations (3.2) and (3.3): ε_i, σ_i and ε_j, σ_j are the Lennard-Jones interaction parameters for atom *i* and *j* respectively interacting with the same type of atom. For the ions, the individual Lennard-Jones parameters were: $\varepsilon_I = 6.1 \times 10^{-4}$ kJ mol⁻¹ and $\sigma_I = 0.287$ nm, 0.381 nm, 0.453 nm, 0.517 nm for Li⁺, Na⁺, K⁺ and Cs⁺ respectively⁷⁸. These ion parameters were chosen because they reproduce the experimental hydration free energy and hydrated radii⁷⁸. The hydration free energy is a measure of the strength of the interaction between an ion and surrounding water molecules. Ion entry into narrow pores requires removing water molecules surrounding the ion^{162,171}. This dehydration mechanism has been proposed as the main process for ion rejection²².

The membrane model used here consists of two unoxidised parallel graphene sheets. This model recreates regions of a channel in a GO membrane where there are no oxygen functionalities. Carbon atoms in the graphene sheets were treated as neutral Lennard-Jones spheres using the interaction parameters:

 $\varepsilon_{\rm C} = 0.4899 \, \rm kJ \, mol^{-1} \, and \, \sigma_{\rm C} = 0.3214 \, \rm nm$. These parameters recreate a contact angle of 50.7° on a graphite surface¹³. This is similar to the water contact angle on an uncontaminated graphene sheet¹¹⁰.

All of these parameters were derived with the SPC/E water model⁶. This model was used for all of the simulations and performs reasonably well at reproducing the properties of unconfined bulk water compared to similar models^{172–174}. SPC/E is a three site water model with a charge of -0.848 e on the O atom and charges of +0.424 e on the two H atoms, where e is the charge of the electron. There is a single Lennard-Jones site on the O atom with Lennard-Jones parameters of: $\varepsilon_{\rm O} = 0.650 \,\rm kJ \, mol^{-1}$ and $\sigma_{\rm O} = 0.317 \,\rm nm$. The geometry is fixed with $d_{\rm OH} = 0.1 \,\rm nm$ and $\theta_{\rm HOH} = 109.47^{\circ}$.

3.2.2 Initial Configurations

Initial configurations for unconfined simulations were generated by placing a single ion in a cubic simulation box with a box length (L) of 3.5 nm full of SPC/E water molecules. These configurations were equilibrated for 1 ns in the *NVT* -ensemble. They were subsequently run for 100 ns for the production run in the *NpT* ensemble. To account for finite size effects when calculating the ionic diffusion coefficient the values for the box length ranged from 3.0 nm - 10.0 nm.

Graphene capillaries were prepared by fixing two graphene sheets with the dimensions of $L_x = 3.68$ nm and $L_y = 3.83$ nm with a separation of 1.3 nm (Figure 3-1). The separation was defined as the distance between the carbon planes of the graphene sheets. The sheets were periodic in the x and y dimensions. The simulation cell was 3.0 nm in the z dimension, perpendicular to the graphene sheets (Figure 3-1). This was to ensure that the molecules do not interact with their periodic images. Water molecules were added to obtain a density of 1029.9 kg m⁻³ within the channel. A single water was then replaced by an ion. A production run for the systems lasted 100 ns in the NVT -ensemble. To understand finite size effects on ion diffusion coefficients several other sheet sizes were investigated maintaining roughly square sheets. $L_{\rm x}$ ranged from $3.2\,{\rm nm}-20.1\,{\rm nm}$. $L_{\rm y}$ ranged from $3.4\,\mathrm{nm}-20.4\,\mathrm{nm}$. A simulation was run with large graphene sheets of $L_{\mathrm{x}}=12\,\mathrm{nm}$ and $L_{\rm v}=10\,{\rm nm}$ in contact with water reservoirs, which resulted in a final density of 1029.9 kg m^{-3} in the channel. This simulation was performed for 5 ns in the NpT ensemble followed by 10 ns in the NVT -ensemble to ensure that the final density was fully equilibrated. Only one ion was added to each simulation box, which resulted in a net +1.00e charge in the simulation box. This was compensated in the long-range electrostatic interactions by uniformly distributing a -1.00 e charge across the simulation $box^{137,140}$. This approach can introduce some errors in the potential of mean force across an inhomogeneous interface¹³⁷. Alternatively, a counter ion could be added resulting in a neutral simulation box. Parameters for halide anions have been derived using a similar procedure as the cation-water interaction parameters⁷⁸, however it is unclear how well these parameters

reproduce the activity coefficient for a dilute system with the cations. To avoid issues with incorrect ion-ion interactions, it was decided to maintain a net positive charge instead of having a neutral simulation box. Having only one cation made it possible to see how the cation influences the structure of water around the ion without the influence of any other ionic species.



Figure 3-1. Snapshot of the confined system in the *x-z* plane, where $L_x = 3.2 - 20.2 \text{ nm}$. Solid blue lines mark the edge of the simulation cell. O – red, H - white, C – cyan and Li – blue.

3.2.3 Simulation Protocol

All the simulations were run using GROMACS 4.5.4¹³². The equations of motion were integrated using the Leapfrog algorithm^{138,175} with a 2 fs timestep. Lennard-Jones interaction used a switching function between 1.0 nm and 1.2 nm ensuring that the potential goes to zero at 1.2 nm. Coulombic interactions used a short-range cut-off of 1.2 nm and long-range interactions were taken into account using the particlemesh Ewald (PME) summation^{133,134}. For unconfined simulations a three dimensional PME summation was used. For confined simulations a two dimensional PME summation was used as implemented in GROMACS 4.5.4¹³². This was used to prevent interaction were periodic images in the z-dimension in the confined systems. A Nosé-Hoover thermostat^{15,16} was used to maintain an average temperature of 298.15 K with a coupling constant of 5 ps. For the constant pressure simulations the Parrinello-Rahman barostat^{145–147} was used to maintain a pressure of 1 bar with a 1 ps coupling constant with a water compressibility of 4.5×10^{-5} bar⁻¹.

Periodic boundary conditions were used in three dimensions for all of the simulations. Configurations were saved every 1 ps for analysis.

3.3 Results and Discussion

3.3.1 Hydrated Structure

The radial distribution function (g(r)) was calculated to understand the structure of water around an ion. The structure of g(r) is similar for the unconfined and confined systems (Figure 3-2). The radial distribution functions show a succession of decreasing peaks separated by troughs that eventually tend to 1 (Figure 3-2). The first peak and trough are called the first maximum and first minimum respectively and have the postions of $r_{1,max}$ and $r_{1,min}$ respectively. The first peak corresponds to water molecules in the first hydration shell. Each subsequent peak is due to water molecules in a hydration shell further away from the ion. The number of water molecules around an ion can be calculated from the integral of $g(r)^{176}$ and is called the coordination number (n(r)) (Figure 3-2). Both g(r) and n(r) were calculated using a 0.5 pm radial bin width with a spherical normalisation factor. The values for the peak intensities, maxima and minima positions and coordination numbers are summarised in Table 3-1. In many cases it was only possible to give the position of the maxima and minima to one decimal place.





Figure 3-2 and Table 3-1 show that the intensity of $g(r_{1,\max})$ and $g(r_{2,\max})$ are larger in the confined systems. Both radial distribution functions were calculated using a spherical normalisation constant. In the confined systems the two-dimensional nature of the channel means that density used for normalisation in equation (2.33) is under estimated. This normalisation factor is cancelled out when integrating g(r). The values of n(r) are similar in the unconfined and confined systems. This shows that the differences in the peak intensity is just an artefact of the normalisation method. The position of the first maximum in both systems moves to larger radial distances as the ions are further down the group (Figure 3-2). This shift is also seen for the second maximum (Figure 3-2). The position of the first and second maxima are the same in the unconfined and confined systems for K⁺ and Cs⁺. The first and second maxima for Li⁺ and the second maxima for Na⁺ are shifted to shorter distances when they are confined. The hydrated radius from herein will be refferring to as the position of the first maximum, $r_{1,max}$, as this is a common definition^{80,177}.

The coordination number of the first (n_1) and second (n_2) hydration shells were definied as: $n_1 = n(r_{1,\min})$ - the value of n(r) at the first minimum; and $n_2 = n(r_{2,\min}) - n_1$ - the difference between the coordination number at the second and first minima. The value of n_1 increases from 4 for Li⁺ to 7 for Cs⁺ (Table 3-1). The position of the second minimum is less clearly definied compared to the first minimum (Figure 3-2). This makes it more diffiuct to accurately determine the number of water molecules in the second hydration shell (Figure 3-2). The range for the number of water molecules in the second hydration shell overlaps between the unconfined and confined systems (Table 3-1). This suggests that the second hydration shell is similar in both the confined and unconfined cases. Most of the simulated studies already in the literature (Table 3-1). The most notable exception is for Cs⁺ where the number of water molecules in the first molecules in the first hydration shell is underestimated compared to neutron scattering results¹⁷⁸, MD simulations⁵ and quantum mechanics/molecular mechanics calculations¹⁷⁹.

Table 3-1. Positions, intensities and coordination numbers for the first and second maxima and minima from unconfined and confined simulations in this work and unconfined literature values for Li⁺, Na⁺, K⁺ and Cs⁺. The superscripts denote the reference for the literature data: a^{2-4} , b^{5} , c^{2-5} and $d^{2,5}$. Data from ^{2,3} are from experiment results whereas ^{4,5} are from simulations. Subscripts on the ions denote where the values are obtained from: unconf – unconfined system, conf – confined system, sim – simulated in this work and lit – obtained from literature.

lon	$r_{1,\max}^{a}$	$g(r_{1,\max})^{b}$	$r_{1,\min}^{b}$	$g(r_{1,\min})^{b}$	n_1^{c}	$r_{2,\max}^{d}$	$g(r_{2,\max})^{b}$	$r_{2,\min}^{b}$	$g(r_{2,\min})^b$	n_2^{d}
Li ⁺ uncon,sim	0.20	14.6	0.25 - 0.28	0.0	4.0	0.43	1.7	0.51 - 0.54	0.9	14.9 - 18.6
${\sf Li}^+_{\sf uncon,lit}$	0.19 - 0.23	14.0	0.27	0.0	3.9 - 4.2	0.40 - 0.45	1.7	0.53	0.9	14.2 - 16.1
Li ⁺ con,sim	0.19	46.2	0.24 - 0.27	0.0	4.0	0.41 - 0.42	4.9	0.52 - 0.53	1.9	14.1 - 15.4
$Na^{+}_{uncon,sim}$	0.23	8.3	0.30 - 0.33	0.1	5.4 - 5.6	0.47	1.5	0.52 - 0.60	0.9	15.4 - 25.2
$Na^{+}_{uncon,lit}$	0.23 - 0.25	7.2	0.33	0.2	5.3 - 5.9	0.44 - 0.48	1.4	0.54	0.8	12.4 - 17.5
$Na^+_{con,sim}$	0.23	25.0	0.31	0.4	5.5	0.43 - 0.44	4.3	0.54	2.2	16.2 - 17.1
K ⁺ uncon,sim	0.26	6.0	0.33 - 0.35	0.3	5.9 - 6.2	0.46 - 0.47	1.3	0.54 - 0.60	0.9	16.6 - 24.8
$K^+_{uncon,lit}$	0.26 - 0.30	4.6	0.37	0.5	6.0 - 8.3	0.46 - 0.53	1.2	0.58	0.9	17.4 - 21.2
$K^+_{con,sim}$	0.25 - 0.26	17.0	0.33 - 0.34	1.0	6.1 - 6.4	0.45 - 0.46	3.9	0.55 - 0.59	2.3	17.4 - 21.9
Cs ⁺ uncon,sim	0.28	4.2	0.35 - 0.37	0.5	6.5 - 7.1	0.47 - 0.51	1.2	0.57 - 0.60	0.9	18.3 - 25.0
Cs^+ uncon,lit	0.30 - 0.32	3.2	0.39	0.7	8.0 - 9.6	0.49 - 0.54	1.1	0.63	0.9	21.3
Cs ⁺ con,sim	0.28	12.2	0.36	1.8	7.1 - 7.4	0.47 - 0.48	3.6	0.57 - 0.61	2.4	18.7 - 23.7

From the values of n_1 the structure of the first shell of water around the ions can be described by basic ion-ligand structures, like tetrahedral and octahedral. The structure of the first hydration shell can change how an ion interacts with a graphene surface. This is particularly true when the channel width is a similar size to the first hydration shell. The structure of the first hydration shell was assessed by examining the O-X⁺-O angles (θ) for all of cations with water molecules in the first hydration shell (Figure 3-3). Moving down the group causes the values $\cos(\theta)$ to move towards +1. This means that the angles between water molecules become smaller by moving down the group. Li⁺ shows a main peak in the angle distribution at an angle of 108° (Figure 3-3). The value of n_1 is 4.0 (Table 3-1). These two facts suggest that the water forms a tetrahedral structure. This has been seen in previous ab-initio work¹⁷⁶.

The other three ions have two main peaks in their angle distributions (Figure 3-3): one peak corresponds to when $\theta = 180^{\circ}$, and the other corresponds to peaks at 88°, 83° and 79.6° for Na⁺, K⁺ and Cs⁺ respectively. For Na⁺ and K⁺, these angles and the value of n_1 suggest that the waters are arranged into an octahedral structure. For Cs⁺ there is an additional low-angle shoulder around 56°. As $n_1 > 6$, this could suggest that the first hydration shell is more complex than an octahedral structure.

When confined, Li⁺ and Na⁺ show very similar hydration structures compared to their unconfined structures (Table 3-1 and Figure 3-3). The main angle peak for Cs⁺ decreases to 76.1° upon confinement (Figure 3-3). The low angle shoulder also increases in intensity for Cs⁺ (Figure 3-3). There is a slight shift in the main peak in K⁺ towards smaller angles when confined (Figure 3-3). The rest of the K⁺ angle distribution remains similar to the unconfined system (Figure 3-3). The smaller cations of Li⁺ and Na⁺ show no change. The larger cations of K⁺ and Cs⁺ show a decrease in the angle between water molecules in the first hydration shell upon confinement. This suggests that the hydration structure of K⁺ and Cs⁺ is affected by the graphene surface.



Figure 3-3. Probability distribution for the O-X⁺-O angle (θ) for water molecules in the first hydration shell where X⁺ is Li⁺ (blue), Na⁺ (red), K⁺ (green) and Cs⁺ (orange). Unconfined simulations are shown with filled symbols and confined simulations with unfilled symbols. Inset shows the definition for θ .

Orientation of water molecules around the ion was measured by calculating the angle (ϕ) between the ion – water oxygen vector (\mathbf{r}_{I-O}) and the water dipole moment vector (\mathbf{r}_{u}):

$$\cos(\phi) = \frac{\mathbf{r}_{\text{I-O}} \cdot \mathbf{r}_{\mu}}{|\mathbf{r}_{\text{I-O}}||\mathbf{r}_{\mu}|}$$
(3.4)

The distribution for ϕ was calculated for water molecules in different hydration shells around the ion (Figure 3-4). Water molecules in the first hydration shell were chosen when $r_0 < r_{1,\min}$, when the oxygen atom was between the ion and the first minimum in the radial distribution function. Water molecules in second hydration shell were chosen when $r_{1,\min} \leq r_0 < r_{2,\min}$, when the oxygen atom is between the first and second minima in the radial distribution functions. Further spherical shells were obtained by selecting successive concentric shells with a thickness of 0.25 nm. The first hydration shell for all of the ions orients the water O atom towards the ion $(\cos(\phi) = 1, \phi = 0)$ (Figure 3-4a). This effect is most prominent for Li⁺ and decreases down the group towards Cs⁺ (Figure 3-4a). The orientational ordering decreases for Na⁺, K⁺ and Cs⁺ when they are confined. The decrease in order is most likely due to water molecules ordering because they are in contact with a graphene surface^{67,180}. The amount of relaxation of the ordering increases going down the group.



Figure 3-4. Orientation angle for water molecules around Li⁺ (blue), Na⁺ (red), K⁺ (green) and Cs⁺ (orange) when unconfined (solid lines) and confined (dashed lines) (a). Inset in (a) shows expanded region of $\cos(\phi) = 0.75 - 1.0$. Water orientation angle for five concentric shells around Li⁺ for unconfined (top) and confined (bottom) systems (b).

There is orientational ordering of water molecules around Li⁺ up to a fifth concentric shell around the ion (Figure 3-4b). The fifth concentric shell was between 1.04 nm - 1.29 nm and 1.03 nm - 1.28 nm for the confined and unconfined systems respectively. There may be ordering of water molecules at larger distance from the
ions, however the size of the simulation cell prevents further investigation of this. The amount of orientational ordering decreases as the concentric shells move further away from the ion (Figure 3-4b). The decrease in the orientational ordering is expected because the main cause for orientational order is Coulomb interactions. These interactions decay as 1/r, and the fifth concentric shell was partly within the direct cut-off for the Coulomb interaction, so still experiences Coulomb interaction from the ion. For the first and second hydration shells there is no difference between the confined and unconfined orientation (Figure 3-4b). This is most likely due to the first two hydration shells around Li⁺ to be small enough to be unaffected by the presence of graphene sheets.

3.3.2 Position of the lons in the Capillary

The water oxygen density forms 3.5 layers between the graphene sheets at 1.3 nm (Figure 3-5). There is a clear layer of water oxygen atoms at both of the graphene surfaces (Figure 3-5). There is a doublet water oxygen peak density in the centre of the channel (Figure 3-5). All of the ions show a smooth and continuous density between the graphene sheets (Figure 3-5). The ion density peaks are in two positions: they are at the graphene surface and slightly offset from the centre of the channel (Figure 3-5). None of the ions prefer to stay directly in the centre of the channel. As the hydrated radius increases for the ions, their density at the graphene surface decreases. The larger cations prefer to reside towards the centre of the channel.

When confined, ions will try to maximise the number of water molecules in the first hydration shell. The energy penalty for losing water molecules from a hydration shell increases as the shell is closer to the ion. Larger ions like K⁺ and Cs⁺ prefer stay towards the centre of the channel. This allows them to maintain a full first hydration shell. When in the centre of the channel Na⁺ has a full octahedral first hydration shell (Figure 3-6a). However, when Na⁺ is at the graphene surface the first hydration shell is too large so it loses a water molecule from the octahedral structure (Figure 3-6b). K⁺ and Cs⁺ have a larger first hydration shell than Na⁺, so they would experience more dehydration than Na⁺ if they move towards the

surface. Hence they stay towards the centre of the channel. Li⁺ forms a tetrahedral first hydration shell. This structure makes it possible to orientate the water molecules in the first hydration shell so that Li⁺ can sit at the graphene surface (Figure 3-6c). In the centre of the channel an ion can maximise the number of water-ion interactions. The entropy of hydration for Li⁺ is negative³, this means that Li⁺ may be forced to the graphene surface to increase the entropy of the water molecules by reducing the number of Li⁺-water interactions. The loss in enthalpy can then be compensated by ion-graphene interactions.







Figure 3-6. Snapshots of confined simulations for Na⁺ near the centre of the channel (a), Na⁺ at the edge of the channel (b) and Li⁺ at the edge of the channel (c). Water molecules in the first hydration shell have been highlighted for clarity.

3.3.3 Diffusion

Calculating the diffusion coefficient (D_i) of a species is an easy way of understanding the molecular transport in a system. Diffusion coefficients are obtained from the gradient of the linear regime of mean-squared displacement (MSD) against time (t). This is linked by the Einstein relation⁸⁵:

$$\left\langle \left| \mathbf{r}_{i}(t+t_{0}) - \mathbf{r}_{i}(t_{0}) \right|^{2} \right\rangle = 2nD_{i}t$$
 (3.5)

In equation (3.5): $\mathbf{r}_i(t_0)$ is the displacement vector for *i* at a time t_0 ;

 $\langle |\mathbf{r}_i(t+t_0) - \mathbf{r}_i(t_0)|^2 \rangle$ is the mean-squared displacement for $i; t_0$ is the time origin used to calculate the MSD; t is the time from the time origin $t_0; n$ is the dimensionality for the system with n = 2 for 2D transport^{181,182} and n = 3 for 3D transport¹⁴⁸. For the unconfined ions the MSD was taken over all three dimensions using n = 3 in equation (3.5). For the confined ions the MSD was taken as the displacement parallel to the graphene sheets using n = 2 in equation (3.5). Plots of MSD against time for both confined and unconfined ions showed a linear region between 5 psand 25 ps (Figure 3-7). This region was used to calculate the diffusion coefficient in equation (3.5). Time origins were chosen every 25 ps to avoid sampling the same displacements¹⁴⁸. All of these different time origins were averaged together to get the MSD.

Diffusion coefficients in unconfined systems with periodic boundary conditions are very sensitive to finite-size effects^{130,131,183–185}. These finite size effects are mainly due to long-range hydrodynamic interactions that decay as $1/r^{130,131,186}$. Orientational ordering of water molecules extends to the edge of a 3.5 nm simulation box. Ordering of water molecules may then effect the transport of water molecules in the "neighbouring" simulation cell due to periodic boundary conditions. The finite size effects of MD simulations must be removed to be able to compared between experimental infinite dilution diffusion coefficients and simulated values.



Figure 3-7. Mean-squared displacement (MSD) against time for Li⁺ (blue), Na⁺ (red), K⁺ (green) and Cs⁺ (orange) in unconfined (solid lines) and confined (dashed lines) systems. For unconfined systems MSD is for all three dimensions, for confined systems MSD is only for transport parallel to the graphene sheets.

Finite size effects are removed by calculated the diffusion coefficient for several different simulation box sizes with periodic boundary conditions ($D_i^{\rm PBC}$). Periodic boundary diffusion coefficients can then be plotted against 1/L to obtain a linear fit^{130,131}. This fit can then be extrapolated to obtain the diffusion coefficient where 1/L = 0 (D_i^0) (Figure 3-8). This corresponds to when the simulation box is an infinite size. Diffusion coefficients for confined systems with periodic boundary conditions were plotted against $1/A^{0.5}$, where A is the cross sectional area of a graphene sheet. These plots were compared with the unconfined systems (Figure 3-8). $1/A^{0.5}$ was used instead of 1/L because the graphene sheets are slightly rectangular rather than square, $L_x \neq L_y$. Confined systems do not show the same linear scaling as unconfined systems (Figure 3-8). This is because the periodic transport is only in two dimensions for the confined systems. It suggests that the diffusion in the confined systems follows a different relationship to the unconfined systems. Values for D_i^{PBC} are systematically lower than for unconfined systems. This is most likely due to limited diffusion perpendicular to the graphene sheets (Figure 3-9).



Figure 3-8. Ionic diffusion coefficients (D_i^{PBC}) against the reciprocal simulation box length (1/L) for unconfined (square) and confined (crosses) systems for Li⁺ (blue), Na⁺ (red), K⁺ (green) and Cs⁺ (orange). Dashed lines show extrapolated linear fits used to calculate the infinite dilution diffusion coefficient for the unconfined systems.

For K⁺ and Cs⁺ the diffusion perpendicular to the graphene sheets is very limited during the simulations (Figure 3-9). Li⁺ shows a periodic oscillation in the MSD perpendicular to the graphene sheets with a period of approximately 7.2 ns (Figure 3-9). There is also a small fluctuation in the perpendicular MSD for Na⁺ (Figure 3-9). Only the density profiles for Na⁺ and Li⁺ show peaks at the graphene surface (Figure 3-5). This suggests that the presence of peaks at the graphene surface result in the observation of some hopping in the perpendicular MSD. The density profile for ${\rm Li}^{+}$ shows that it prefers to reside at the graphene surfaces, whereas Na⁺ prefers to reside towards the centre of the channel (Figure 3-5). The peaks for Na⁺ towards the centre of the channel are in a similar position to K^{+} (Figure 3-5), however K^{+} does not show much fluctuation in the perpendicular MSD (Figure 3-9). This suggests that the fluctuation observed by Na^+ occurs when the ion transitions between the graphene surface peaks and the central channel peaks. The transition will not occur between the two surface peaks for Na⁺ as the ion would get trapped at the central peaks during the transition (Figure 3-5). This also explains the different magnitude in the fluctuation, with Li⁺ having a much larger fluctuation than Na⁺. Li⁺ will predominantly transition between the two graphene surface peaks as they have much

higher densities than the central peak (Figure 3-5). The graphene surface peaks for Li⁺ have a much larger distance separation (0.52 nm) than the Na⁺ transition between the surface and central peaks (0.14 nm). Hence Li⁺ exhibits the largest "hops" in the perpendicular MSD between the two graphene surfaces.





There is a good agreement between the unconfined simulated diffusion coefficients and the experimental values (Table 3-2). Both sets of the diffusion coefficients show an increase as the hydrated and ionic radii increases. They also show that the hydration free-energy decreases^{78,187,188} as the diffusion coefficient increases. This suggests that diffusion of ions is related to how strongly bound the surrounding water molecules are. Diffusion coefficients were not part of the original parameterisation scheme for the ion-water interaction parameters⁷⁸, however hydration free energies were. This is likely the reason why these parameters are able to reasonably reproduce the infinite dilution diffusion coefficients. Diffusion coefficients are sensitive to the separation between the graphene sheets^{22,189,190}. This means that the trend in diffusion coefficients presented here will change for the different graphene-graphene separations. At smaller separations there will be a lower number of water molecules surrounding the ion. This will mean that it is even more important to ensure that the ion-carbon interaction parameters are correct at small separations.

lon	$D_i^0 / 10^{-9} \text{ m}^2 \text{ s}^{-1}$			
1011	Unconfined	Experiment ¹⁸⁷		
Li ⁺	1.269	1.029		
Na^+	1.362	1.334		
K^{+}	1.766	1.957		
Cs⁺	2.060	2.056		

Table 3-2. Infinite dilution diffusion coefficients for unconfined simulations for Li⁺, Na⁺, K⁺ and Cs⁺.

Stokes' radius (r_s) of an ion is typically used as the hydrated radius in membrane permeation studies^{191,192}. Stokes' radius can be calculated from the infinite dilution diffusion coefficient by¹⁹³:

$$r_{\rm s} = \frac{k_{\rm B}T}{6\pi\eta D_i^0} \tag{3.6}$$

In equation (3.6): $k_{\rm B}$ is Boltzmann's constant; *T* is the temperature and η is the viscosity of water, which is 0.729 mPa s for SPC/E at 298 K ¹⁷³. Stokes' radii obtained from simulated infinite dilution diffusion coefficients agree well with the experimental values (Table 3-3). Stokes' radius is inversely proportional to the ionic radius¹⁹¹ and the hydration radius (Table 3-1). Increasing diffusion coefficients as particles get larger is contrary to Stokes' law for diffusion of a spherical particle¹⁹³. For charged ions where there are strong interactions between the ion and surrounding water molecules Stokes' law does not hold.

Confining an ion between graphene sheets causes dehydration of the hydration shells around an ion⁸⁰. The hydrated radius used here based on g(r) is a direct measure of the distance between an ion and surrounding water molecules. This will give a measure of how many water molecules will be removed for an ion to enter a specific pore width. Stokes' radius is based on the hydrodynamic radius from the diffusion of a spherical particle. This measure of size breaks down for particles where there is a strong association between the ion and the solvent. It would

generally be more appropriate to use the hydrated radius when discussing size for ionic confinement^{177,193}.

lon	r _s / nm		
юп	Unconfined	Experiment ¹⁹¹	
Li ⁺	0.237	0.238	
Na^+	0.221	0.184	
K ⁺	0.171	0.125	
Cs^+	0.146	0.119	

Table 3-3. Unconfined simulated and experimental Stokes' radii for Li^+ , Na^+ , K^+ and Cs^+ under infinite dilution conditions.

3.4 Conclusions

As q_1 and ε_1 were the same for all of the ions it means that infinite dilution diffusion coefficients for group 1 cations can be controlled solely by the values of σ_1 . For Na⁺, K⁺ and Cs⁺ the first hydration shell showed evidence of being an octahedral or more complicated structure. Li⁺ showed evidence of a tetrahedral structure. When confined Li⁺ preferred to reside at the graphene surface, whereas the other three cations preferred to reside towards the centre of the channel. Li⁺ has shown a "hopping" mechanism between the graphene sheets with a period of 7.2 ns . Simulations of unconfined infinite dilution diffusion coefficients followed the trend of Li⁺ < Na⁺ < K⁺ < Cs⁺. This showed that ions with a larger hydrated radius diffused faster. A similar trend was observed for when these ions were confined between two graphene sheets.

A significant change in the hydrated structure of confined ions would suggest they experience a large free energy barrier for entering the channel. This is because a loss or removal of water molecules around an ion comes with a large positive free energy change⁸⁰. With a 1.3 nm channel width the hydrated structure of the confined ions is very similar to the hydrated structure of the unconfined ions. This suggests that there will be only very slight ion rejection for a GO membrane with

this channel width. This has been shown to be the case experimentally^{22,49}. Smaller separations where ions are forced to remove their first hydration shell can prevent ion transport²². It is important to investigate smaller channel widths to observe changes in the hydrated structure and ionic dynamics. Combining these simulations with the direct calculations of the free energy barrier for entering the channel^{22,79,98} would provide valuable information to be able to understand the ion rejection mechanism of GO membranes for future desalination applications.

Appendices

The work of the "Supplementary Information" for this paper has been included in Appendix A. Within Appendix A there is: Table for all of non-bonding parameters used in this section (Table A-1); Details for the unconfined (Table A-2a) and confined (Table A-2b) simulation sizes; Plots for the orientational order of water models in five concentric shell around Na⁺, K⁺ and Cs⁺ (Figure A-1); Diffusion coefficients for unconfined (Table A-3a) and confined (Table A-3b) simulations set-ups.

Chapter 4 Cation-π Interactions

To accurately model graphene-oxide (GO) membranes it is important to have the correct carbon, ion and water interactions. GO membranes have shown ion adsorption of transition metal ions¹⁹⁴ and group 2 cations¹⁶⁹. Molecular dynamics simulations tend to struggle to reproduce this trend⁹². There is a disagreement between the experimental and simulated energy barriers for K⁺ entry into a GO membrane²². There are a few factors that could contribute to this; it could be due to using a too simplistic model of a GO channel, by modelling it as rigid parallel graphene sheets; or it could be due to inaccuracies in the interaction parameters. This work has focused on trying to tackle and improve the latter issue. This is because there are three main interactions that are required to simulate a GO membrane. An inaccurate description of any of these interactions can cause discrepancies between experimental and simulated results^{22,92}.. The three main interactions are:

- 1. Ion water
- 2. Water-graphene
- 3. Ion-graphene

These interactions need to be able to reproduce the dehydration energy barrier for ion entry in a GO membrane. The ion-water interaction needs to be able to reproduce the ion hydration free energy. If the ion-water interaction doesn't reproduce the ion hydration free energy, then water molecules are either too strongly or weakly bound around the ion, which results in too large or too small free energy barriers for entry respectively. Several studies have derived water-ion interaction parameters based on reproducing the hydration free-energy with the SPC/E water model for group 1 cations^{78,100}, group 2 cations⁹⁹ and halide anions^{78,100}. Graphene-water interactions are controlled by the carbon-water interaction parameters. The carbon-water interactions can change a channel from being hydrophilic to hydrophobic¹³. Studies have obtained carbon-water interaction parameters that reproduce the water contact angle for a graphene surface¹³.

Adsorption of group 2 cations was suggested to occur through cation-pi interactions¹⁶⁹. Simulations have shown that there are strong carbon-ion interactions for delocalised pi electron systems in graphene^{1,101,154–156} and carbon nanotubes^{195,196}. Experiments have also shown favourable adsorption for ions at graphene surfaces^{197,198}. In molecular dynamics (MD) simulations standard pairwise interaction parameters are typically non-polarisable and therefore cannot capture electronic effects such as polarisation.Hence, they do not include ion-pi interactions.

This chapter describes the development of new carbon-ion interaction parameters for MD simulations based on the publication C. D. Williams, *et al.*, J. Phys. Chem. Lett. **8**, 703 (2017)¹. Data for the potentials of mean-force (PMF) and density profiles were taken from this publication¹ and were originally obtained by the author (J. Dix). The text and the figures have been produced independently from this publication by the author (J. Dix). Discussions with C. D. Williams have helped formulate the structure and content of this chapter.

This chapter is split into five sections:

Section 4.1 Scientific introduction into how cation-pi interactions are added to MD simulations.

Section 4.2 How the MD simulations were run, set-up and analysed to investigate the ion-pi interactions.

Section 4.3.1 Results for PMF calculation with original and modified interaction parameters.

Section 4.3.2 Structure of concentrated cholride salt solutions at a graphene surface with original and modified interaction parameters.

Section 4.4 Conclusions about the impact of the modified interaction parameters.

4.1 Introduction

In contrast to the work of Abraham *et al.*²² that suggested ion permeation was limited by dehydration, other researchers have suggested that their ion permeation rates were the result of cation-pi interactions limiting diffusive transport through membrane¹⁶⁹. Work of Abraham *et al.* shows that for K⁺ the diffusion is only slightly affected by the change in channel width²². Additionally, the MD energy barriers for diffusion of K⁺ are less than the experiment energy barriers for K⁺ permeation²². MD dehydration energy barriers achieved a closer agreement with experiments, suggesting that ion dehydration is the main limitation for ion permeation²². These energy barriers were still lower than the experimental values. Although cation-pi interactions are not the main limitation for ion permeation in GO membranes, they are still important in achieving experimental and simulated agreement. First-principles MD¹⁹⁵ and polarisable models^{180,196,199} have been used to account for cation-pi interactions. However, these simulations are time consuming to run. Ion-pi interaction can be introduced into quicker classical MD simulations by modifying interaction parameters¹.

Interactions between atoms are modelled using Lennard-Jones 12-6 (V_{LJ}) and Coulomb (V_{Coul}) interaction potentials:

$$V_{\rm LJ}(r_{ij}) = 4\varepsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right)$$
(4.1)

$$V_{\text{Coul}}(r_{ij}) = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}}$$
(4.2)

In equation (4.1): σ_{ij} is the distance when V_{LJ} reaches zero; ε_{ij} is the well depth for V_{LJ} . In equation (4.2): ε_0 is the permittivity of free space; q_i and q_j are the charges on atom *i* and *j* respectively. In equations (4.1) and (4.2): r_{ij} is the separation between atoms *i* and *j*.

Ion-pi interactions mainly occur through charge-qaudrupole interactions between the ion and the electron density of the graphene surface. Benzene^{200,201}, polyaromatic molecules^{200,201} and graphite²⁰¹ all exhibit a permeant quadrupole moment. Graphene is also expected to exhibit a permeant quadrupole moment²⁰². The quadrupole moment comes from the π -electron density occupying the space above and below the carbon ring²⁰³. This results in an effective positive charge density on the carbon nuclei in the plane of the ring. The charge distribution is then similar to that observed for CO₂, which also exhibit a permanent quadrupole moment²⁰³.

Coulomb interactions are based on the charges on both atoms. To model Ion-pi interactions charges could be added around the carbon atoms of the graphene to recreate the guadrupole moment²⁰². This would discriminate between differently charged species within the same simulation, which may not appropriate for modelling mixtures. It would also modify the interaction between water and graphene because the Coulomb interaction acts indiscriminately between pairs of atoms. To use this approach would require reparametrizing both the ion-graphene and water-graphene interactions. Instead, it is possible to only modify the Lennard-Jones 12-6 interaction potential in equation (4.1) between ions and the graphene. This also would not increase the number of charge sites in the simulation. Chargequadrupole interactions have the same distance dependence as the dipole-induced dipole interactions of $r^{-6\ 204,205}$. Dipole-induced dipole and London dispersion interactions are both taken into account in molecular simulations using the attractive part of equation (4.1), which varies as r^{-6} . Density Functional Theory (DFT) calculations have already shown that as the size of a graphene flake increases the attractive component of the Lennard-Jones interaction increases, tending towards the value for an infinite graphene sheet²⁰⁶. The attractive component of equation (4.1) can be modified by changing \mathcal{E}_{ij} or σ_{ij} between carbon atoms and the ion. Typically these parameters are determined using the Lorentz-Berthelot (LB) mixing rules:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}; \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$$
 (4.3)

In equation 4.3: ε_i and σ_i are the interaction parameters for atom *i* when it interacts with the same type of atom. Instead of using the mixing rules in equation (4.3) it is possible to directly specify the values for ε_{ii} and σ_{ii} . DFT calculations have calculated the adsorption energy for some common ions onto a 54C graphene flake in a water solvent¹. These calculations used a conductor-like continuum model^{207,208} to create an implicit water environment around the ion instead of using explicit water molecules. Including explicit water molecules increases the computation time for the simulations. Previous simulations by Shi et al. used up to nine explicit water molecules to hydrate Na⁺ on a graphene flake¹⁵⁴. This work showed that the adsorption energy becomes less negative as the number of water molecules around the ion increases. At nine water molecules the adsorption energy still had not reached a plateau¹⁵⁴. To recreate the full hydration shell around an ion to accurately describe ion adsorption would require approximately 30 water molecules, which is beyond the capability of most computational resources. Using an implicit water model made it possible to calculate the free energy of adsorption for the ion in an aqueous medium. MD simulations can determine the adsorption free energy from a calculation of the PMF. The use of an implicit water model means that the DFT calculations do not reproduce the correct structure of a water hydration shell around the ion. Therefore, they may not determine the correct distance for the energy minimum of an ion from the graphene flake. To model the cation-pi interactions, the value of σ_{ii} was determined from the LB mixing rules (equation 4.3) and ε_{ii} was modified to reproduce the DFT adsorption energies. The strength of the Lennard-Jones 12-6 interaction is determined by ε_{ij} . A larger value of ε_{ij} results in a stronger interaction between atoms *i* and *j*.

DFT calculations show that cation adsorption on a 54 C graphene flake is in the range of $-10 \text{ kJ mol}^{-1} \text{ to} - 16 \text{ kJ mol}^{-1}$. In a concentrated solution this will have a large effect on the ordering and density of ions at a graphene surface. This paper focuses on the PMF for LB and modified interaction parameters that include ion-pi interactions. The modified interaction parameters will then be used to investigate how ion-pi interactions effect ordering at a graphene surface. These results will be important in understanding how ions interact with a GO membrane.

4.2 Simulation Methods

Two simulation set-ups were used in this chapter. The first set-up, discussed in section 4.2.1, involves a single finite graphene flake surrounded by solvent with one ion above the flake surface. This set-up was used to pull the ion towards the graphene flake to calculate the adsorption energy and PMF for the ion towards the surface. The second set-up, discussed in section 4.2.3, was concerned with the structure of a concentrated solution of ions at an infinite graphene surface. This was used to see the effect that including graphene-ion polarisation had on a concentrated solution in contact with a graphene surface.

4.2.1 Umbrella Sampling Simulations

Umbrella sampling simulations used a cubic box with 3.5 nm box lengths (Figure 4-1). A 54 C graphene flake terminated by H atoms was placed in the centre of xyplane. The flake was 0.875 nm above the bottom of the simulation box in the zdirection. The ion was initially 1.4 nm above the graphene flake. 3D periodic boundary conditions were used throughout. Simulations were initially run for a 500 psequilibration run in the NpT -ensemble. The ion was fixed in place for the equilibration run. After this, there was a 10 ns production run with only the last 9 ns being used for analysis. The production run was also run in the NpT -ensemble therefore the reported free energies are Gibbs adsorption energies.





Figure 4-1. Starting configuration in the zx-plane (a) and xy-plane (b) for umbrella sampling simulations. Solid blue line shows the edge of the simulation box. Colours used: Ion – red, C – cyan, O – blue, H – white.

Three umbrella potentials were applied to the ion at the start of the production run. All of the umbrella potentials (V_{bias}) were modelled using a harmonic potential^{96,153}:

$$V_{bias}(r) = k_i (r - r_i)^2$$
(4.4)

In equation 4.4: k_i is the force constant for the *i* th umbrella potential; *r* is the position of the ion in simulation box and r_i is the reference position for the *i* th umbrella potential. Two umbrella potentials used force constants of 1000 kJ mol⁻¹ to keep the ion in the centre of the xy-plane. The third potential changed both strength and reference position to move the ion closer to the graphene flake. There was between 18 and 19 separate simulations with reference positions for the third umbrella potential ranging from 1.4 nm to 0.2 nm above the graphene surface in the z-direction. The force constants for each window ranged from 1000 kJ mol⁻¹ to $75000 \text{ kJ mol}^{-1}$ and were maintained the same for all of the PMFs. For the divalent cations additional windows were placed at the first energy maximum to ensure sufficient sampling. The reference positions and force constants were chosen so that the distance between the ion and graphene flake (r_{Gra-I}) was continuously sampled from the graphene surface to 1.4 nm above the flake (Figure 4-2). Each separate simulation creates a distribution of values for $r_{\text{Gra-I}}$. To be able to calculate the full PMF the distributions must overlap to sample the whole set of separations. The PMFs were set to equal zero at 1.4nm, as this was far away from the graphene flake. The PMF was calculated from the simulations using the GROMACS Weighted Histogram Analysis Method^{96,141}.

GROMACS calculates an error for the PMF based on a bootstrapping method; however this underestimates the error on the values of the PMF. A more accurate error was calculated by running replicas of the same simulation and averaging over the adsorption energy of these simulations. The PMF for Na⁺ at a graphene flake was run 10 times with a random distribution of the velocities being assigned at the start of each simulation. Figure 4-3 shows that there is a distribution for PMF values across the simulations. The first minimum was taken as the adsorption energy for an ion onto the graphene flake. The standard deviation in the adsorption energy over the replicas was 0.62 kJ mol^{-1} . With a normally distributed adsorption energy, 89.2% of simulations will have an adsorption energy that falls within two standard deviations of the average value. Therefore, two standard deviations were used as

the accuracy for the adsorption energy. The error on the adsorption energies was 1.24 kJ mol^{-1} . This error captures all of the adsorption energies for the replica simulations (Figure 4-3).



Figure 4-2. Set of distributions along the graphene-ion distance reaction coordinate for Na⁺ on a graphene flake. Each colour and histogram represents a separate window and simulation.



Figure 4-3. Potential of mean force ($W(r_{\text{Gra-I}})$) against vertical distance above a graphene flake ($r_{\text{Gra-I}}$) for 10 replica simulations with Na⁺. Inset shows a close-up of the global minimum. In inset: solid horizontal line shows average adsorption energy, dotted horizontal lines show maximum and minimum range for adsorption energy within two standard deviations.

The simulations were performed using GROMACS 5.0.4¹³² with the leapfrog integrator^{85,138} with timesteps of 1 fs and 2 fs , for the equilibration and production runs, respectively. A target temperature of 298.15 K was used with the Nosé-Hoover thermostat^{15,16}. A target pressure of 1 bar was used with the Berendsen¹⁴ and Parrinello-Rahman^{145–147} barostats for the equilibration and production runs respectively. The barostats used isotropic scaling with the water compressibility of 4.5×10^{-5} bar⁻¹. A switching function was used between 1.0 nm and 1.2 nm , so that the Lennard-Jones 12-6 interaction smoothly went to zero at 1.2 nm . Coulomb interactions used a direct cut-off at 1.2 nm with a particle-mesh Ewald summation^{133,134} for long-range electrostatics interactions.

4.2.2 Interaction Parameters

The SPC/E water model⁶ was used for the water solvent, because it is compatible with the water-carbon and water-ion interactions used in this study^{13,78,99,100}. Joung and Cheatham have derived interaction parameters for the monovalent ions of Li⁺, Na^+ , K^+ and Cl^{-100} . Mamatkulov *et al.* have derived interaction parameters for the divalent cations Mg^{2+} and Ca^{2+99} . Using a similar fitting procedure Horinek *et al.*⁷⁸ have derived a Cl⁻ model to work with the divalent cations⁹⁹. All of these interaction parameters have been derived to reproduce the hydration free energy and ionwater separation^{78,99,100}. The Joung and Cheatham interaction parameters have been chosen for monovalent cations because these parameters reproduce the activity coefficient for salt solutions²⁰⁹. Mamatkulov *et al.* has developed modified mixing rules based on LB mixing rules to produce the activity derivate for divalent salt solutions⁹⁹. There were two separate Cl⁻ models, one to work with the monovalent cations and the other to work with divalent cations. For the monovalent cations the Cl⁻ model was from the work of Joung and Cheatham¹⁰⁰and will be called Cl⁻_{IC}. For the divalent cations the Cl⁻ model was from the work of Horinek *et al.*⁷⁸ and will be called Cl_{H} . Both of these chloride models reproduce the hydration free energy^{78,100}, but they use different parameters to achieve this. Both σ_{ii} and ε_{ii} in equation 4.1 can be varied to ensure an ion recreates the hydration free energy. This results in a range of suitable values for σ_{ii} and ε_{ii} . The values for

 $\sigma_{\rm CI-C}$ are 0.40 nm and 0.38 nm for Cl⁻_{JC} and Cl⁻_H respectively. Lennard-Jones 12-6 water-carbon interaction parameters were: $\sigma_{ij} = 0.319$ nm and $\varepsilon_{ij} = 0.564$ kJ mol⁻¹. These values produce a contact angle of water on three layers of graphite of 50.7° ¹³, which is in the range of the experimental values of $45^{\circ} - 65^{\circ}$ ¹¹⁰.

Interaction parameters between ions and carbon atoms of graphene were derived to reproduce the aqueous ion adsorption energy from DFT results¹. DFT is an electronic structure method, so can produce very accurate values for energies. Parameters derived by LB mixing rules do not include any polarisation interactions. Initially the ion adsorption energies were calculated for the LB parameters. The Lennard-Jones epsilon cross term between the carbon and the ion (ε_{C-1}) was modified until the adsorption energy was within 1.24 kJ mol⁻¹ of the DFT adsorption energy. The final results for this process are shown in Table 4-1. Adding the charge-quadrupole interactions into the value of ε_{C-1} in equation (4.1) results in much larger values for ε_{C-1} compared to the Lorentz-Berthelot mixing rules. This resulted in an increase in ε_{C-1} ranging from 370% – 2650% . These substantial increases could be evidence that the strength of the interactions are too large to be taken into account solely by modifying the Lennard-Jones potential.

4.2.3 Single Sheet Simulations

Modified interaction parameters were compared to LB parameters by investigating the ion structure for a 1 mol dm^{-3} chloride salt solution in contact with a graphene surface. The configuration for these simulations is shown in Figure 4-4. A $5.10 \text{ nm} \times 5.16 \text{ nm}$ graphene sheet was placed at the bottom of a simulation box. The graphene sheet covered the whole of the simulation box. A salt solution with 5 nm height and an area the same size as the graphene sheet was placed above the graphene sheet. There was a 5 nm vacuum gap from the water-vacuum interface and the other surface of the graphene sheet. The vacuum gap was used to stop aggregation of ions on the other side of the graphene sheet affecting the structure of the ions. 75 stoichiometric sets of cation-chloride ions were placed randomly within the water. Simulations were run for 20 ns in the *NVT* -ensemble with the first 10 ns being discarded for equilibration time. Configurations were saved every

1 ps. All other simulation parameters were the same as the umbrella sampling simulations.

Table 4-1. Reference density functional theory adsorption energies (E_{ads}^{DFT}) in kJ mol⁻¹; carbon-ion Lennard-Jones 12-6 interaction parameters (ε_{C-I}) in kJ mol⁻¹ for both Lorentz-Berthelot mixing rules and modified interaction parameters; Adsorption energy determined from potential of mean-force calculations in molecular dynamics simulations (E_{ads}^{MD}) in kJ mol⁻¹ and the position of the first minimum in the potential of mean force (r_{min}) in nm for Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺ and both Cl⁻ models.

lon	$E_{\it ads}^{\it DFT}$ a		\mathcal{E}_{C-I}	E^{MD}_{ads}	r _{min}
Li ⁺	-10.4	LB	0.8308	-4.48	0.386
		Mod	4.0000	-10.76	0.367
Na⁺	-13.8	LB	0.8502	1.72	0.356
		Mod	3.0000	-14.52	0.294
K ⁺	-12.6	LB	0.9385	2.92	0.338
		Mod	2.2000	-12.26	0.307
Mg ²⁺	-16.5	LB	0.5376	-2.86	0.463
		Mod	14.250	-16.36	0.431
Ca ²⁺	-15.7	LB	0.6786	-3.89	0.449
		Mod	5.0000	-16.31	0.429
СГ _Н	-6.98	LB	0.4536	N/A	N/A
		Mod	1.3000	-7.36	0.387
Cl_ ^{JC}	-6.98	LB	0.1619	N/A	N/A
		Mod	0.6000	-7.00	0.491

^{*a*} is taken from C. D. Williams *et al.*¹



Figure 4-4. Initial configuration for single sheet simulations in the yz-plane. Colours: Ion – red, Cl^2 - black, C – cyan, O – blue, H – white.

4.2.4 Residence Time

Ion residence time at the graphene surface was compared between the two parameters sets to see how the different parameters change ion dynamics at the surface. An ion was defined as being at the surface when the position of the ion ($r_z^{\rm I}$) is closer to the graphene surface then the first minimum in the ion density profile with the modified interaction parameters ($r_{\min}^{1 \text{ st}}$), so $r_z^{I} < r_{\min}^{1 \text{ st}}$. The modified ions have a larger ion density at the graphene surface. The larger density means that their maxima and minima are more clearly defined than with the LB parameters. Hence, the first minimum from the modified interaction parameter density profile was used for the definition of r_{\min}^{1st} . The number of timesteps between an ion entering the surface layer and leaving was called the residence time ($t_{\rm res}$). A histogram was built up for the number ions ($N_{\rm I}$) that had left the surface layer at each possible residence time. The minimum resolution for the residence time was determined by the frequency that configurations were saved (1 ps). Previous experimental work fitted the distribution of Rb⁺ residence times at a mica surface to a triple exponential decay model²¹⁰. A triple exponential model was not used here because any long time decays (> 50 ps) that would need a third exponential to be

fitted were not sufficiently sampled in the simulations to achieve a reasonable fit. A single exponential has been used to fit the decay in residence time for water molecules in the hydration shell of monovalent cations²¹¹. However, a single exponential decay does not accurately describe the residence times from 5 ps - 50 ps. Instead a double exponential model was used:

$$N_{\rm I}(t_{\rm res}) = T_1 e^{-t_{\rm res}/\tau_1} + T_2 e^{-t_{\rm res}/\tau_2}$$
(4.5)

In equation (4.5): T_1 and T_2 are the magnitude of the decay process; τ_1 and τ_2 are the decay constants for the first and second decay processes. Equation 4.5 was fit to the residence time distribution using scipy's curve_fit function in python²¹².

4.2.5 Coordination Number

Coordination number of water molecules around an ion (n_w) was calculated from the radial distribution function (RDF) using¹⁷⁶:

$$n_{\rm W}(r_{\rm I-O}) = 4\pi\rho \int_{0}^{r_{\rm I-O}} g(r)r^2.dr \qquad (4.6)$$

In equation (4.6): r_{I-O} is the ion-water O distance; ρ is the density of ion and water O pairs; g(r) is the radial distribution function between an ion and water O atoms. The water coordination number for the first hydration shell (n_1) was taken as the coordination from equation (4.6) at the first minimum in the water-ion RDF. The water coordination number for the second hydration shell (n_2) was taken as the difference in n_w between the second and first minima in the RDF,

 $n_2 = n_W (r_{I-O}^{2ndmin}) - n_1$ where r_{I-O}^{2ndmin} is the position of the second minimum in the water-ion RDF. n_1 and n_2 are the number of water molecules in the first and second hydration shells around the ion respectively. All of the coordination numbers presented in subsequent figures are for simulations with the modified interaction parameters. This was because there were minimal differences between the coordination numbers for the LB and modified interaction parameters.

4.3 Results

4.3.1. PMFs

Increasing the favourable interactions between the ion and the graphene surface by including the polarisation interactions pulls the ions towards to surface. This is not observed for LB mixing rules.

Positions of the peaks and troughs in the Li⁺ PMF do not change between the modified and LB interaction parameters (Figure 4-5a). The global minima for both LB and modified interaction parameters are both the wells closest to the graphene flake. At the global minimum there is a decrease in the value of n_2 compared to 1.4 nm (Figure 4-5a). n_1 stays the same at global minimum compared to 1.4 nm (Figure 4-5a). Water molecules that are displaced in the second hydration shell are compensated by the graphene-ion interactions. The incorporation of polarisation into graphene-ion interactions is insufficient to displace water molecules in the first hydration shell.

The global minimum for Na⁺ and K⁺ with the modified interaction parameters occurs at shorter graphene-ion separations than Li⁺ (Figure 4-5b and Figure 4-5c). Unlike Li⁺, there is a decrease in the number of water molecules in the first hydration shell for both of the ions. With the modified interaction parameters the graphene-ion interaction is strong enough to compensate for the loss of water molecules in the first hydration shell. With LB interaction parameters, the global minimum observed for the modified interaction parameters was energetically unfavourable (Figure 4-5b and Figure 4-5c). For LB parameters Na⁺ has both the first and second hydration shells intact, whereas K⁺ only has the first hydration shell intact.



Figure 4-5. Potential of mean-force ($W(r_{\text{Gra}-1})$), and the first (n_1 - circles) and second (n_2 -square) coordination numbers against the graphene-ion separation ($r_{\text{Gra}-1}$) for Li⁺ (a – blue), Na⁺ (b – red), K⁺ (c – green) and Cl⁻_{JC} (d – black). Dotted lines are for Lorentz-Berthelot interaction parameters and solid lines are for the modified interaction parameters.

Cl⁻_{JC} shows no energy minimum at the graphene surface with LB parameters (Figure 4-5d). With the modified parameters the global energy minimum occurs with a decrease in the second coordination shell (Figure 4-5d). At the global minimum the first hydration shell is intact (Figure 4-5d).

The number of water molecules in the hydration shells slightly increases before it continually decreases for all of the ions (Figure 4-5).

The global minimum with the modified parameters for Mg²⁺ and Ca²⁺ is the energy well that is closest to the graphene flake (Figure 4-6a and Figure4-6b). This well occurs with a decrease in the second coordination shell. The first coordination shell stays intact for the two ions. This was observed for the global minimum for Li⁺ (Figure 4-5a). With LB interaction parameters Ca²⁺ has the same global minimum as the modified interaction parameters (Figure 4-6b). However, the well depth is

smaller for the LB interaction parameters. For LB interaction parameters with Mg²⁺ the global minimum is further away from the graphene flake than with the modified interaction parameters. At this minimum Mg²⁺ retains both the first and second hydration shells.



Figure 4-6. Potential of mean-force ($W(r_{\text{Gra}-I})$), and the first (n_1 - circles) and second (n_2 -square) coordination numbers against the graphene-ion separation ($r_{\text{Gra}-I}$) for Mg²⁺ (a – magenta), Ca²⁺ (b – orange) and Cl⁻_H (e – black). Dotted lines are for Lorentz-Berthelot interaction parameters and solid lines are for the modified interaction parameters.

The PMF for Cl⁻_H is similar to Cl⁻_{JC} for LB parameters – there is no energy minimum closer than 1.4 nm (Figure 4-5d and Figure 4-6c). The PMF for both Cl⁻_H and Cl⁻_{JC} increases as the ion gets closer to the graphene flake. Each step is due to the successive loss of water molecules from surrounding hydration shells. The global minimum for the modified interaction parameters and Cl⁻_H keeps the first hydration shell intact. However, there is a decrease in the number of water molecules in the second hydration shell. The second well in the Cl⁻_H PMF is better defined than the Cl⁻_{JC} PMF. The larger value of σ_{Cl-C} for Cl⁻_{JC} is why the global minimum occurs at a larger graphene-ion separation.

PMFs show two different types of ion at the global minimum for the modified parameters:

Type 1 ions keep their first hydration shells intact at the graphene surface – Li^+ , Mg^{2+} , Ca^{2+} , Cl_{JC}^- , Cl_{H}^- .

Type 2 ions lose water molecules from their first hydration shell – Na^+ , K^+ .

In type 1 ions the water-ion interaction in first hydration shell is too strong for dehydration to be compensated by the graphene-ion interactions. In type 2 ions the water molecules are more weakly bound to the ion so dehydration can be easily compensated by the graphene-ion interactions. For type 2 ions there are no energy minima in the PMF at that position when using LB parameters. This shows that ionpi interactions are important to obtain the correct ion structure at a graphene surface.

4.3.2 Single Sheet Simulations

4.3.2.1 Ion Density Profiles

Intensity of cation density peaks at the graphene surface for the modified parameters has the trend (Figure 4-7): $Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+}$. The trend does not follow the adsorption energy for the monovalent cations (Table 4-1). Based solely on adsorption energies Na⁺ would be expected to have a larger ion density than K⁺ at the graphene surface.



Figure 4-7. Ion (ρ_N) and water oxygen (ρ_{OW}) number density profiles against the vertical distance (z) from the graphene sheet for LiCl_{JC} (a), NaCl_{JC} (b), KCl_{JC} (c), MgCl_{H 2} (d) and CaCl_{H 2} (e). Solid lines are for ions with the modified interaction parameters, dotted lines are for ions with the Lorentz-Berthelot interaction parameters and the dashed lines are for the water oxygen atom density. Line colours: Li⁺ - red, Na⁺ - blue, Na⁺ - green, Mg²⁺ - magenta, Ca²⁺ - orange, Cl⁻_{JC} and Cl⁻_H – black.

The first density peak for Na^+ and K^+ with the modified interaction parameters from the graphene surface occurs at the same position as the first layer of water oxygen atoms (Ow) at the graphene surface (Figure 4-7b and Figure 4-7c). With modified interaction parameters these two ions occupy the same positions at the graphene surface as surface water atoms. The first density maximum for the other three cations and two Cl⁻ models occur at a larger distance from the graphene flake beyond the Ow peak (Figure 4-7). The global minimum in the PMF for these five ions was where the first hydration shell was intact (Figure 4-5 and Figure 4-6). The first hydration shell for these ions is from water molecules at the graphene surface, but these ions are not in direct contact with the graphene surface.

For LB interaction parameters there is depletion in the ion density at the graphene surface compared to the bulk ion density (Figure 4-7). With the modified interaction parameters the ion density at the surface is greatly increased. The ion density at the graphene surface is much greater than the bulk ion density.

The main Cl⁻ peak is closer to the graphene surface for divalent cations than monovalent cations (Figure 4-7). This is due to the different Cl⁻ models used for the divalent and monovalent cations. The Cl⁻_H model has a shorter ion-graphene separation for the global minimum in the PMF (Figure 4-6) compared to the Cl⁻_{JC} model used for monovalent cations (Figure 4-5). This could explain the difference in the Cl⁻ position.

4.3.2.2 Ion Residence Times

The residence time histogram decreases very sharply at short residence times around 1-2 ps (Figure 4-8). There is a secondary and more gradual decay that occurs over 10-300 ps. Ions are most likely to leave the graphene surface within the first ps. Configurations were only saved every ps, making it hard to accurately understand the first decay process. In equation (4.5) there are two terms. Each term corresponds to the fit for either the first or second decay process. The logarithm of each term in equation (4.5) results in a straight line with the gradients $1/\tau_1$ and $1/\tau_2$ for the first and second decay process respectively. Plotting $\ln(N_1(t_{\rm res}))$ against $t_{\rm res}$ makes it possible to compare the simulated distributions with the fitted models (Figure 4-8). The fitted models follow the time decay of ions being at the graphene surface. For some of the ions (Cl⁻_H in MgCl_{H 2} and CaCl_{H 2}) the fitted models do not agree with the simulated data beyond 25 ps. It is unclear whether this is due to the need for a third exponential term or if the simulations do not sample this time

range sufficiently enough. Either way would need more data to verify what the issue is. This could be done with larger or longer simulations.

From the fitted models (Table 4-2) and the histogram decays (Figure 4-8) there are five different behaviours seen for the ions between the LB and modified interaction parameters:

- 1. First and second decay time constants increase. Second decay constant greatly increases. This is seen for Na⁺, K⁺ and Cl_{JC}^{-} when in a salt solution with Na⁺ and K⁺.
- Time constant for second decay process increases for the modified parameters. This is seen for Cl⁻_{JC} in an LiCl solution.
- The time decay for the second process decreases with the modified interaction parameters. This is seen for Mg²⁺ and Cl⁻_H.
- The second decay process disappears completely for the modified interaction parameter. This is seen for Ca²⁺.
- There is no change in the time constants between the LB and modified interaction parameters. This is seen for Li⁺.

For an individual ion an increase in the adsorption energy at a surface will increase the ion residence time at the surface. The time decay constant will increase for the ion leaving the surface. However, other ions in the solution and the relative position to the graphene sheet can have additional effects on the residence time. An ion is assumed to be at the surface when it is between the first density minimum for the ion and the graphene surface. Based on the PMFs (Figure 4-5) and the density profiles (Figure 4-7) Na⁺ and K⁺ are in direct contact with the graphene surface, with no other molecules between them and the surface. The other ions have a first hydration shell between themselves and the graphene surface.



Figure 4-8. Natural logarithm of the histogram of the number of ions leaving the graphene surface ($\ln(N_{\rm I}(t_{\rm res}))$) against the residence time ($t_{\rm res}$) at the surface for the Lorentz-Berthelot (empty symbols and dotted lines) and the modified (filled symbols and solid lines) interaction parameters. The figures are for the salt solutions LiCl_{JC} (a) , NaCl_{JC} (b), KCl_{JC} (c), MgCl_{H 2} (d) and CaCl_{H 2} (e). Straight lines show the gradient for the two fitted decay processes. The inset focuses on shorter timescales than the main figure. Colours are: Li⁺ - blue, Na⁺ - red, K⁺ - green, Mg²⁺ - magenta, Ca²⁺ - orange, Cl⁻_{JC} and Cl⁻_H - black.

The second decay process is influenced by the strength of the graphene-ion interaction. Modified parameters for Na⁺ and K⁺ showed a much slower decay with the modified parameters compared to the LB parameters. The modified parameters had larger values for ε_{I-C} compared to the LB parameters for all of the ions. As Na⁺

and K⁺ are closest to the graphene surface this will have the largest effect on the dynamics for these ions. Cl⁻_{JC} also showed a much slower second decay time constant with the modified parameters. With LB parameters there was no energy minimum in the PMF for Cl⁻_{JC} (Figure 4-5d). With the modified parameters there was an energy minimum at the surface. These dramatic changes in the energy profile for these three ions results in the slower second decay process from the surface. As the main difference for all of these ions is an increase in \mathcal{E}_{I-C} , it is likely that stronger graphene-ion interactions slow the process where these ions migrate away from the graphene surface.

Table 4-2. Characteristic decay times for two processes for an ion leaving the graphene surface with the Lorentz-Berthelot and modified interaction parameters and position of the first minimum from the modified ion density profiles. For the $LiCl_{JC}$, $NaCl_{JC}$, KCl_{JC} , $MgCl_{H 2}$ and $CaCl_{H 2}$ salt solutions.

Solution	lon	L	В	Mod	lified	
		$ au_1$ / ps	$ au_2$ / ps	$ au_1$ / ps	$ au_2$ / ps	$r_{\rm min}/\rm nm$
LiCl _{JC}	Li⁺	0.64	3.02	0.65	3.23	0.57
	٦L	0.84	5.28	0.90	17.21	0.55
NaCl _{JC}	Na^+	0.65	7.75	0.79	108.58	0.43
	٦L	0.70	4.21	0.93	18.77	0.55
KCl _{JC}	K ⁺	0.61	4.57	0.74	61.56	0.45
	٦L	0.75	4.40	0.83	18.08	0.55
MgCl _{H 2}	Mg ²⁺	0.55	3.07	0.72	3.96	0.59
	СГ _Н	0.79	6.79	0.65	3.43	0.55
CaCl _{H 2}	Ca ²⁺	0.39	2.61	1.51	-	0.63
	СГ _Н	0.68	6.13	0.78	4.21	0.55

Based on this Mg^{2+} and Ca^{2+} would be expected to show the same trend as Na^+ and K^+ for the modified parameter because of their increased attractive interaction with the graphene surface (Table 4-1). However, Mg^{2+} shows a faster second decay process. With Ca^{2+} the second decay process has completely disappeared. Cl^-_H also shows a faster second decay with the modified parameters. With the monovalent cations Cl^-_{JC} showed a faster second decay with the modified parameters. Because both the divalent cations and Cl^-_H show a faster decay it is likely that there is a cooperative effect between the cations and Cl^-_H . Potentially, the presence of a

larger number of ions at the graphene surface is shielding various electrostatic interactions with other ions and water molecules. Changing the interaction the ions experience could make it easier for the ions to leave the graphene surface.

There is only a very small change for the decay processes for Li⁺. This is because there are only small differences in the PMF for Li⁺ between the LB and modified interaction parameters.

4.4 Conclusions

Based on recent DFT calculations it has been possible to develop MD interaction parameters that incorporate ion-pi interactions. This was achieved by fitting adsorption energies from PMF calculations with DFT calculated energies. The PMFs showed that there was an increased attraction between the ions and the graphene surface when the ion-pi interactions are included. In some cases this changed the adsorption process to the graphene surface from being energetically unfavourable to energetically favourable. The ion density at a graphene surface in a concentrated salt solution increased when using parameters with ion-pi interactions. The cations followed the density trend of: $Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+}$. Residence times for the ions at the graphene surface. The first process decays between 2.1 ps - 5.5 ps. The second process decayed between 10.1 ps - 24.2 ps for the LB interaction parameters. The second process showed a more noticeable dependence on the strength of the carbon-ion interaction.

These results have helped to understand how ions behave at a graphene surface. This approach to developing new parameters will be useful for electrolyteconducting surface interactions. They will particularly be useful for electrolytegraphene applications, where it is clear that ion-pi interactions need to be taken into account to be able to model these systems. Recent experiments have shown that the adsorption of SCN⁻ to a graphene surface is -8.5 ± 1.1 kJ mol^{-1 197}. This favourable adsorption is in agreement with the trends that were observed from the

DFT calculations for ionic species on a graphene flake¹, backing up the use of these DFT calculations.

These results show that there is only a modest change in the dynamics of the ions at the graphene surface. This is unlikely to cause the drastic change in transport properties to confirm that cation-pi interactions are limiting the ion transport in GO membranes. Instead, it is more likely that the dehydration process is still limiting ion transport. However, the inclusion of polarisation interactions does show that some ions can dehydrate at a graphene surface and be compensated by graphene-ion interactions. This may alter the rejection mechanism for ions like Na⁺ and K⁺ that showed that they favoured losing water molecules to reside at the graphene surface.

Chapter 5 Confined Ion Transport

It is believed that ion transport through graphene-oxide (GO) channels occurs in unoxidised regions^{49,54}. Strong graphene-ion interactions in these regions have tried to explain the experimental ion permeation rates of group 2 cations in GO membranes¹⁶⁹. Subsequent experiments have suggested that the ion permeation rates in GO membranes are due to a dehydration entry barrier for the ions²². With a complex and only partially aromatic structure for the GO sheets⁶², it is unlikely that the graphene-ion interaction is limiting the ion permeation in GO membranes, but it could still have an impact on the desalination process. Additionally, experiments have fabricated unoxidised graphene channels with a sub-nanometre control of the sheet-sheet separation to investigate water permeation¹⁰². This set-up has the potential to be used to investigate the transport of ions through unoxidised graphene channels. Moreover, it can be easily modelled using the unoxidised slitpore configuration presented in Chapter 3. This model can also be improved by including the graphene-ion interactions presented in Chapter 4.

This chapter aims to merge two investigations into ion transport through unoxidised graphene pores, by considering both the effects of different channel widths and graphene-ion interactions. The channel widths ranged from 1.3 nm - 0.7 nm and used the graphene-ion interaction parameters discussed in Chapter 4. Like with Chapter 3, the structure of water around the ion will be important to understand the implication that these unoxidised channels could have on desalination. However, with the inclusion of graphene-ion interactions, more importance will need to be placed on the preference of where an ion resides within the channel. This will highlight how graphene-ion interactions can compensate and compete with water-ion interactions. To provide a comparison for experimental permeations rates, a lot of the focus of this chapter has been put into understanding the diffusion of ions through the graphene channels. Especially, how ionic diffusion is affected by the graphene-ion interactions.

This chapter is an unpublished manuscript written in 2017 by the author (J. Dix). The results, analysis and text have all been produced by the author (J. Dix) with helpful discussions from C. D. Williams, J. Boni and P. Carbone.

This chapter is split into six sections:

Section 5.1 Provides a scientific and technical introduction into the work completed in the paper.

Section 5.2 Discussion of the simulation set-up and the analysis for ion diffusion.

Section 5.3.1 Results and analysis for ion dynamics through graphene channels with different channel widths.

Section 5.3.2 Results, analysis and discussion for the ion density profiles and ion hydration structures.

Section 5.4 Discussion linking some aspects of the dynamics with structural properties.

Section 5.5 Conclusions about the results and analysis shown in the previous three sections and how these fit into the larger body of research.

5.1 Introduction

GO membranes can prevent ion transport through graphene channels by forcing the ion to remove water molecules from its first hydration shell to enter the channel²². This occurs for graphene sheet-sheet separation of $0.64 \text{ nm} - 0.98 \text{ nm}^{22}$. These separations in a GO membrane are only achievable by physical confinement²², UV-reduction⁸² or thermal reduction^{42,83}. Only physical confinement has been used for desalination applications²². When GO membranes are fully submersed in water they tend to swell to 1.3 nm^{49} . At this separation there is no ion rejection for small cations like Na⁺, K⁺ and Mg^{2+ 49}.

The structure of water is changed depending on the separation between graphene sheets^{67,107,190}. This means that the ion hydration structure can also be altered

depending on the separation between the graphene sheets. A large reduction or change in the hydration structure compared to a bulk ion would show a large free energy barrier for entering a channel^{22,79,80,163}. This is particularly important for water molecules closer to the ion in the first hydration shell⁷⁹.

Measuring the dynamics of ions in graphene channels, with different channel widths means that it is possible to develop trends for the simulated data. These can then be used to compare with experimental results to help validate the inclusion of graphene-ion polarisation interactions¹ in MD simulations. Ion transport is believed to occur in unoxidised regions of GO channels^{49,54}. This makes it possible to use a "slit-pore" simulation configuration consisting of frozen graphene sheets for the channel walls⁶⁷. Hydrated structures of the group 1 and group 2 cations in carbon slit-pores has been of interest for their application in electric double-layer capacitors (EDLC)^{93,213–220}. A lot of these studies have focused on the ion density within the slit pore with differing charge densities on the graphene sheets^{93,213–220}. Work of Wander *et al.*²¹⁷ showed that the bulk diffusion of Na⁺ is only slightly faster than the diffusion of Na⁺ confined to a channel width of 1.0 nm. This suggests that at this channel width the confinement does not affect the ionic transport. Sala et al.²²¹ showed that Na⁺ diffusion parallel to a graphene surface is enhanced compared to the bulk diffusion. This shows that it is possible that the orientation of water molecules at a surface enhance ionic diffusion. There will be a trade-off between the amount of confinement an ion experiences and ease of transport through the channels along the graphene-water interface.

Experiments have fabricated nanoscale graphene channels with a sub nanometre separation between the graphene sheets¹⁰². This system was used to investigate the transport of water¹⁰². However, it could be extended to investigate the transport of ionic species through the graphene channel. Several studies have suggested that there is an enhanced adsorption of ions to a graphene flake or graphene surface^{1,101,154–156}. This is due to the ion polarising the pi-electron system of the graphene surface. Work by Williams *et al.* derived interaction parameters for MD simulations that include this polarisation interaction¹. There have been experimental results using second harmonic generation spectroscopy that show
favourable adsorption of ions at a graphene surface^{197,198}. It is important to compare between standard Lorentz-Berthelot mixing rule parameters (LB) and the parameters by Williams *et al.* (W)¹ to understand the effects that graphene-ion polarisation have on confined ions. The parameters of Williams *et al.* increase the attraction between ions and a graphene surface¹. As a result, they may show different trends for diffusive properties compared to standard LB parameters. This will allow experiments to determine whether the approach of Williams *et al.* is a more accurate description of the graphene-ion interactions in MD simulations.

This work uses classical MD simulations to investigate the structure and dynamics of hydrated Li⁺, Na⁺, K⁺, Mg²⁺ and Ca²⁺ in graphene slit-pores. Channel widths were varied from 1.3 nm - 0.7 nm as this is within the range of experimentally achievable channel widths for GO membranes^{22,49}. These results will aim to show how increased attraction between graphene and ions alters the structure and dynamics of ions in graphene slit-pores. These results will also provide a good repository of simulated results to allow for easy comparisons with experimental data.

5.2 Methodology

5.2.1 Interaction Parameters

Interactions between two atoms are calculated from averaged pairwise interaction parameters. The interaction potential (Ψ) between two atoms is made up of the sum of Lennard-Jones 12-6 and Coulomb interaction potentials:

$$\Psi(r_{ij}) = 4\varepsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right) + \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}}$$
(5.1)

In equation (5.1): r_{ij} is the distance between atom *i* and *j*; q_i and q_j are the partial electron charges on atoms *i* and *j* respectively; ε_0 is the permittivity of free space; σ_{ij} and ε_{ij} are the Lennard-Jones cross parameters for when *i* and *j* are different

atom types. Cross parameters for the Lennard-Jones interaction are obtained from the individual atom parameters using the Lorentz-Berthelot mixing rules:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \qquad (5.2)$$
$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \qquad (5.3)$$

In equations (5.2) and (5.3): σ_i, ε_i and σ_j, ε_j are the individual atom interaction parameters for the Lennard-Jones interaction between atoms of the same type.

It is important to have interaction parameters that accurately reproduce the physical system of interest. Ion-water interactions for Li⁺, Na⁺ and K⁺ were modelled using the parameters from the work of Joung and Cheatham¹⁰⁰. For Mg^{2+} and Ca^{2+} the parameters were obtained from the work of Mamatkulov *et al.*⁹⁹. These parameter sets reproduce the experimental hydration free energy and hydrated radius for the ions^{99,100}. The Lennard-Jones parameters for the cations are shown in Table 5-1. The partial charge is +1.00 e and +2.00 e for the monovalent and divalent cations respectively where *e* is the charge of an electron. These interaction parameters were also the basis of the new parameters derived by Williams et al. (W) to account for graphene-ion polarisation¹. The W parameters only increase the epsilon value for the Lennard-Jones interaction (Table 5-1). The carbon-ion sigma ($\sigma_{\rm I-C}$) value for the Lennard-Jones interaction in equation (5.1) was the same for both the LB and W parameter sets and was obtained from the individual atom parameters using equation (5.3). For Lorentz-Berthelot (LB) interaction parameters the carbon-ion epsilon ($\varepsilon_{\rm I-C}$) was obtained from the individual atom parameters using equation (5.2). Both parameter sets are shown in Table 5-1. All of these interaction parameters were obtained using the rigid SPC/E water model⁶. Descriptions of the SPC/E water model can be found in the work by Vega *et al.*²²². This model has been shown to reasonably reproduce the properties of unconfined water^{172,173}.

Carbon-water interaction parameters were taken from the work of Werder *et al.*¹³. This work used the SPC/E model with neutral carbon atoms and carbon Lennard-Jones parameters of $\varepsilon_{\rm C} = 0.4899 \,\text{kJ mol}^{-1}$ and $\sigma_{\rm C} = 0.3214 \,\text{nm}$ to reproduce the

water contact angle of 50.7° on a graphene surface¹³. This is in the range of experimental water contact angles on an uncontaminated graphene sheet¹¹⁰

Table 5-1. Lennard-Jones 12-6 sigma (σ_{I-O}) and epsilon (ε_{I-O}) cross terms for the water-ion interaction in units of nm and kJ mol⁻¹ respectively; Lennard-Jones 12-6 sigma (σ_{I-C}) and epsilon (ε_{I-C}) cross terms for ion-carbon interaction in units of nm and kJ mol⁻¹ respectively for Lorentz-Berthelot (LB) and Williams *et al.*¹ (W) interaction parameters.

lon	$\sigma_{ ext{I-O}}$	${\cal E}_{\rm I-O}$	$\sigma_{ ext{\tiny I-C}}$		${\cal E}_{\rm I-C}$
Li⁺	0.229	0.957	0.231	LB	0.831
				W	4.000
Na⁺	0.266	0.979	0.269	LB	0.850
				W	3.000
K⁺	0.300	1.081	0.302	LB	0.939
				W	2.200
Mg ²⁺	0.240	0.619	0.242	LB	0.538
				W	14.250
Ca ²⁺	0.279	0.782	0.281	LB	0.679
				W	5.00

5.2.2 Simulation Set-Up

Confined simulation set-ups were made up of two parallel frozen graphene sheets with sheet- sheet separations (d) of 1.3 nm , 1.1 nm , 1.0 nm , 0.9 nm , 0.8 nm and 0.7 nm . The graphene sheets had the dimensions of 3.68 nm × 3.83 nm . They formed infinite sheets due to periodic boundary conditions. The simulation box in the z-dimension, perpendicular to the graphene sheets, was 5.0 nm . This was used to prevent interaction between periodic images in the z-dimension. Water density in carbon slit-pores oscillates as a function of channel width^{223,224}. The target water density for the slit-pore was taken from simulations with several "open" channels^{22,79}. These channels were in contact with unconfined water reservoirs and

allowed water within the channel to leave to go into the unconfined reservoirs and vice versa. The average water density over these channels provided the densities for the slit-pore configurations (Table 5-2). The water structure obtained for different channel widths are shown in Figure 5-1. When a channel was filled to the appropriate water density (Table 5-2) one of the water molecules was replaced by an ion.

A net charge of +1.00 e or +2.00 e was maintained in all of the simulation cells for the monovalent and the divalent cations respectively. This is compensated in the long-range electrostatic interaction by using a uniformly distributed screening charge over the whole simulation cell^{137,140}. No counter anions were added because the monovalent and divalent interaction parameters come from different parameter sets^{99,100}. Both parameter sets have different parameters for the Cl⁻ model, which is the only anion that has interaction parameters that include graphene-ion interactions¹. The two different sets of interaction parameters for Cl⁻ produce different potentials of mean force at the graphene surface with the Williams *et al.* interaction parameters (Chapter 4)¹. To avoid any inconsistencies between the monovalent and the divalent cations only the structure and dynamics of an individual cation were considered.



Figure 5-1. Snapshots of water structures confined between two graphene sheets for separations of 1.3 nm (a), 1.1 nm (b), 1.0 nm (c), 0.9 nm (d), 0.8 nm (e) and 0.7 nm (f). Colours: C – cyan, O – red, H – white.

This simulation set-up was then evolved through time by solving Newton's equation of motion using the GROMACS 5.0.4 software package¹⁴¹. Confined simulations were run for 100 ns in the *NVT* -ensemble. The first 10 ns were discarded to ensure the system was in equilibrium. Atomic configurations were saved every 1 ps. Simulations used the Leapfrog algorithm¹³⁸ with a 2 fs timestep to evolve the system through time. The Lennard-Jones interaction used a switching function between 1.0 nm and 1.2 nm to ensure the Lennard-Jones interactions go to zero at 1.2 nm. Short range Coulomb interactions were cut-off at 1.2 nm. Long-range Coulomb interaction were taken into account using the particle-mesh Ewald summation^{133,134}. Temperature was maintained at 298.15 K using the Nosé-Hoover thermostat^{15,16} with a time coupling constant of 5 ps. Simulations were run at 11 different temperatures between 278.15 K and 308.15 K to obtain the activation energy for the diffusion process. Apart from the diffusion and activation energy results shown in Figure 5-2 and Figure 5-3, the rest of the results were run at a temperature of $298.15 \,\mathrm{K}$.

Simulations were also run for a 5 nm cubic box filled with water and one ion. These results were used to compare between the confined and unconfined systems. Unconfined systems were run in the NpT -ensemble where the pressure was maintained at 1 bar by using the Parrinello-Rahman barostat^{145–147}. The pressure coupling time constant was 0.4 ps and the compressibility was 4.5×10^{-5} bar⁻¹. Simulations were run for 10 ns with the last 9 ns being used for analysis. All of the other simulation parameters were the same as the unconfined systems.

Table 5-2. Channel water density (ρ_{sol}) in kg m⁻³ and number of water molecules added to the channel (N_{sol}) for channel widths (d) of 1.3 nm, 1.1 nm, 1.0 nm, 0.9 nm, 0.8 nm and 0.7 nm.

<i>d /</i> nm	$ ho_{ m sol}/ m kgm^{-3}$	$N_{ m sol}$
1.3	955.1	441
1.1	985.3	362
1.0	1018.0	326
0.9	1113.3	304
0.8	832.2	188
0.7	1029.4	184

5.2.3 Diffusion

The process of molecular transport through a system can be understood by calculating the diffusion coefficient (D). The diffusion coefficient can be calculated from the gradient of the linear regime of the mean-squared displacement (MSD) against time. These two properties are linked through the Einstein relation⁸⁵:

$$\left\langle \left| \mathbf{r}_{i}(t'+t_{0}) - \mathbf{r}_{i}(t_{0}) \right|^{2} \right\rangle = 2nDt'$$
 (5.4)

In equation (5.4): *n* is the dimensionality of the system, for a 2D system $n = 2^{181,182}$, for a 3D system $n = 3^{148}$; $\langle |\mathbf{r}_i(t'+t_0) - \mathbf{r}_i(t_0)|^2 \rangle$ is the mean-squared displacement between $t = t_0$ and $t = t_0 + t'$, where t is the time in the simulation; t_0 is the time origin for a set of MSD calculations; t' is the time from t_0 . Time origins were taken every $25 \,\mathrm{ps}$. The range of times used to determine the gradient for D in equation (5.4) was between 5 ps and 25 ps. For unconfined systems the diffusion coefficient was calculated based on the MSD in all three dimensions. For the confined systems the diffusion coefficient was calculated based only on the diffusion parallel to the graphene sheets. This is because there is only limited diffusion perpendicular to the graphene sheets. Hence, if all three dimensions are used to calculate the diffusion coefficient, the diffusion will be slower than the unconfined systems. This would make it difficult to compare between the two systems. It is also possible to calculate the activation energy for a diffusion process by running several simulations at different temperatures. In this case the temperatures ranged from 278.15 K - 308.15 K. The diffusion coefficients can then be modelled as a Arrhenius process^{181,225,226}:

$$D(T) = D_0 \exp\left(\frac{-E_a}{RT}\right)$$
(5.5)

$$\ln(D(T)) = \ln(D_0) - \frac{E_a}{RT}$$
 (5.6)

In equations (5.5) and (5.6): E_a is the activation energy for the diffusive process; D_0 is a diffusive constant; R is the gas constant; T is the temperature. Equation (5.6) makes it possible to calculate the diffusive activation energy from the gradient of a plot of $\ln(D(T))$ against 1/T.

5.3 Results

5.3.1 Dynamics

Diffusion of the cations is fastest with a channel width of 0.8 nm (Figure 5-2). The diffusion at 0.8 nm is faster than the bulk diffusion for all of the ions except for K⁺

(Figure 5-2c). The density of the bulk diffusion simulations is around 996 kg m^{-3} . The diffusion at $0.8 \,\mathrm{nm}$ is faster than the other systems because the water density is lowest for this channel width (Table 5-2). The diffusion of K⁺ is fastest of the monovalent cations (Figure 5-2a, b and c), which is observed for unconfined systems². It is difficult to distinguish between the diffusion of Li⁺ and Na⁺ from Figure 5-2a and Figure 5-2b. However, it seems that Na⁺ is faster than Li⁺ with the original parameters, but slower with the modified parameters (Figure 5-2a and Figure 5-2b). Li⁺ is relatively unaffected by the two parameter sets. Ca^{2+} and Mg^{2+} have similar diffusive properties for the different channel widths. The only exceptions are at 0.8 nm where Mg²⁺ is clearly faster than Ca²⁺ (Figure 5-2d and Figure 5-2e) and at 1.0 nm where the reverse is true (Figure 5-2d and Figure 5-2e). The diffusion of divalent cations is relatively unaffected by changes between the two parameter sets (Figure 5-2d and Figure 5-2e). The channel width of $0.9\,\mathrm{nm}\,\mathrm{has}$ the lowest diffusion coefficient (Figure 5-2). As the channel width increases from 0.9 nm to 1.3 nm the diffusion coefficients increase, tending towards the unconfined values (Figure 5-2). Na⁺ and K⁺ show much slower diffusion for the W parameter set compared to the LB parameter set (Figure 5-2b and Figure 5-2c). This shows that for these two ions the increased attraction with the graphene surface decreases the diffusion through the channel (Figure 5-2b and Figure 5-2c). Arrhenius fits from equation (5.6) fit nicely within the simulated diffusion data (Figure 5-2). The straight lines were fit to the diffusive data using linear regression. The lowest value of R^2 for the fits was 0.88, however most of the fits had values around 0.95. A value of $R^2 = 1$ corresponds to a perfect fit. Based on the accuracy of the fits the Arrhenius process in equations (5.5) and (5.6) were applied to the diffusive data to calculate the diffusion activation energy.

Fits to the diffusive data at 0.7 nm were very poor. This was due to the diffusion coefficients for this channel width being 10 times slower than the other channel widths. To obtain reasonable calculations for the diffusive activation energy for this channel width the simulation would need to be run for roughly 10 times longer. This was not feasible during this work, so has not been achieved.



Figure 5-2. Natural logarithm of the ionic diffusion coefficient $(\ln(D))$ against the reciprocal temperature (T^{-1}) for cations Li⁺ (a), Na⁺ (b), K⁺ (c), Mg²⁺ (d) and Ca²⁺ (e). This is shown for the Lorentz-Berthelot (unfilled symbols) and Williams *et al.*¹ (filled symbols) interaction parameters for sheet-sheet separations of 0.8 nm (orange, leftwards triangles), 0.9 nm (green, upwards triangles), 1.0 nm (red, diamonds), 1.1 nm (blue, squares), 1.3 nm (black, circles) and unconfined systems (turquoise, downwards triangles). Straight lines show the Arrhenius fits for Lorentz-Berthelot (dashed) and Williams *et al.*¹ (solid) interaction parameters.

The simulated diffusive activation energy for unconfined Li^+ and Na^+ is $\approx 1 \text{ kJ mol}^{-1}$ lower than the experimental activation energies²²⁷. Ion transport through water will be due to both the ion and the surrounding water molecules. The diffusion activation energy for the SPC/E water model is $\approx 3 \text{ kJ mol}^{-1}$ lower than the experimental value for water¹⁷³. This could be part of the reason why the unconfined diffusive activation energy is lower than the experimental value. Currently there are no experimental diffusion activation energies for ions through graphene channels. However, based on the unconfined diffusion activation energies, it is likely that the values reported here slightly underestimate the diffusion activation energy.

Li⁺, K⁺ and Ca²⁺ for both parameters sets and Na⁺ with the LB parameters show a maximum confined diffusive activation energy at 0.9 nm (Figure 5-3a, b, c and e). These ions then show a drop in the activation energy going to a smaller channel width of 0.8 nm. This trend in the activation energy is similar to the trend in channel densities (Table 5-2). It suggests that as the density of water in the channel increases the activation energy for diffusion becomes higher. This is most likely because at a higher densities there are more molecules that will have to be displaced for an ion move through the channel. Mg²⁺ does not show much variation in the diffusive activation energy against channel width within the error bars for the activation energies (Figure 5-3d). There are not a lot of differences between the activation energies of the two parameter sets (Figure 5-3).The most obvious difference is for Na⁺ at 0.9 nm where the W parameter set has a much lower activation energy than the LB parameter set (Figure 5-3b).

Some ions exhibit a hopping transition between the graphene surfaces (Figure 5-4). This is observed by jumps in the MSD perpendicular to the graphene sheets for the ions (Figure 5-4). If an ion stays in one position in the channel then the perpendicular MSD will fluctuate around an average value (Figure 5-4). The number of jumps indicates how often the ion transfers between the two surfaces. The magnitude of the jumps shows how far an ion is travelling to transfer between the surfaces. For channel widths of 0.7 nm and 0.8 nm there is no hopping between the graphene surfaces. Na⁺ and K⁺ with the LB parameters show no hopping between the surfaces (Figure 5-4a, c, e and g). With the LB parameters Li⁺ shows hopping between the graphene surfaces (Figure 5-4a, c, e and g).

1.0 nm (Figure 5-4a, c and e). At 1.0 nm, Li⁺ with the LB parameters exhibits poorly defined jumps between the two graphene surfaces (Figure 5-4e). Mg²⁺ and Ca²⁺ with the LB parameters only show hopping with a channel width of 1.3 nm (Figure 5-4a). These two ions with the LB parameters show no hopping for channels width smaller than 1.3 nm (Figure 5-4c, e and g).

Na⁺ with the W parameters shows hopping for the channel widths 1.3 nm, 1.1 nm, 1.0 nm and 0.9 nm (Figure 5-4b, d, f and h). The frequency of hops decreases for Na⁺ as the channel width decreases (Figure 5-4b, d, f and h). K⁺ with the W parameters shows some slight hopping for the channel widths of 1.3 nm and 1.1 nm (Figure 5-4b and Figure 5-4d). The hopping is suppressed for K⁺ with the W parameters at a channel width of 1.0 nm (Figure 5-4f). However, the hopping occurs again at 0.9 nm for K⁺ with the W parameters (Figure 5-4h). The frequency and magnitude of hopping is similar for both Na⁺ and K⁺ with the W parameters at 0.9 nm (Figure 5-4h). The similarity suggests that the two ions interact in the same way with the graphene surface.

For Li⁺ and the W parameters the hops between the graphene surfaces are slower for the channel widths 1.3 nm , 1.1 nm and 1.0 nm compared to the LB parameters (Figure 5-4a, b, c, d, e and f). The magnitude of the hops for Li⁺ at 1.3 nm is larger with the W parameters compared to the LB parameters (Figure 5-4a and Figure 5-4b). Li⁺ shows no hopping at 0.9 nm with either the W or LB parameters (Figure 5-4g and Figure 5-4h). Ca²⁺ shows very slow hopping at 1.3 nm with the W parameters (Figure 5-4b). It also shows small and fast hops at 1.1 nm with the W parameters (Figure 5-4d). Ca²⁺ with the W parameters shows no hopping for channel widths smaller than 1.1 nm (Figure 5-4f and Figure 5-4h). Mg²⁺ with the W parameters shows some hopping at 1.3 nm and 1.1 nm but not for any of the smaller channel widths (Figure 5-4b, d, f and h). Mg²⁺ with the W parameters at 1.3 nm shows a flat section in the MSD between 7.5 ns and 12.5 ns (Figure 5-4b). This suggests that the Mg²⁺ cation stays strongly adsorbed to the graphene surface for this period of time with only very small movement perpendicular to the graphene sheets.



Figure 5-3. Diffusion activation energy (E_a) against channel width (d) for Li⁺ (a), Na⁺ (b), K⁺ (c), Mg²⁺ (d) and Ca²⁺ (e) for Lorentz-Berthelot (unfilled) and Williams *et al.*¹ (filled) interaction parameters. Solid and dashed horizontal lines show the average unconfined activation energy and the range of possible unconfined activation energy and the average respectively.



Figure 5-4. Perpendicular mean-squared displacement (MSD) against time for Li⁺ (red), Na⁺ (blue), K⁺ (green), Mg²⁺ (magenta) and Ca²⁺ (orange) with the Lorentz-Berthelot (a, c, e and g) and Williams *et al.* (b, d, f and h) interaction parameters. The channel widths shown are 1.3 nm (a, b), 1.1 nm (c, d), 1.0 nm (e, f) and 0.9 nm (g, h).

There are a lot of interesting results from the diffusive data shown in Figure 5-2, Figure 5-3 and Figure 5-4. The lack of a drastic change between the LB and W parameters for Li⁺, Mg²⁺ and Ca²⁺ shows that the graphene-ion interaction does not alter their diffusion through the graphene channel. However there are still some questions about the diffusive data that will be answered by the structural data in the following section:

- Why is the diffusion slower for Na⁺ and K⁺ with the W parameters compared to the LB parameters (Figure 5-2b and Figure 5-2c)?
- 2. Why is the diffusion activation energy for Na⁺ with a 0.9 nm channel width lower for the W parameters than the LB parameters (Figure 5-3b)?
- 3. Why are some ions capable of hopping between the graphene surfaces, but only at specific channel widths (Figure 5-4)?

5.3.2 Structure

Density profiles perpendicular to the graphene sheets show the positions of atoms within the channel. Profiles for the water oxygen atoms at 1.3 nm show that there is a main water density peak at both of the graphene surfaces (Figure 5-6a). There is a split peaks about the centre of the channel (Figure 5-6a). Although there are four peaks, they are not four individual peaks as the central split peaks overlap. This means that there are 3.5 layers of water for this channel width. As the channel width decreases down to 0.9 nm there are only two peaks for the oxygen density (Figure 5-6g). This shows that there is a bilayer of water for this channel width. Ions tend to reside in between peaks in the water oxygen density. This allows them to maximise the number of ion-water interactions by interacting with water molecules in different water layers. There are three different positions that the ions can occupy:

 The graphene surface (S). When the ion density peak is closer to the graphene surface than the interfacial water density peak then the ion is at the graphene surface. Example – Na⁺ at 1.3 nm with the W parameters (Figure 5-5b).

- 2. Centre of the channel (C). When the ion sits directly in the middle of the channel. Example $Ca^{2+} at 0.9 nm$ with the LB parameters (Figure 5-5g)
- Off-centre of the channel (OC). When the ion sits between the centre of the channel and the interfacial water density peak. Example – Li⁺ at 1.1 nm with the LB parameters (Figure 5-5c).

All of the peak positions for the density profiles shown in Figure 5-5 and Figure 5-6 have been summarised in Table 5-3.

For channel widths of 1.3 nm , 1.1 nm , 1.0 nm and 0.9 nm Li⁺ prefers to reside in the OC position for both parameter sets (Figure 5-5). Both sets of parameters have the same position for the energy minimum for Li⁺ at the graphene surface¹. In this instance the hydration structure for the energy minimum also doesn't change for the two parameter sets¹. There is a layer of water molecules between Li⁺ and the graphene surface (Figure 5-5). This suggests that Li⁺ maintains its first hydration shell in the OC position.

Na⁺ with the LB parameters has two OC positions for a 1.3 nm channel width (Figure 5-5a). One position is near the interfacial water layer and the other is near the central water layers (Figure 5-5a). The more central OC position is favourable over being near the interfacial water layer. As the channel width decreases to 1.1 nm, 1.0 nm and 0.9 nm the favourable position for Na⁺ with the LB parameters moves to the C position (Figure 5-5c, e and g). There are still peaks in the OC position near the interfacial water layers, but they have a lower density than the central position (Figure 5-5c, e and g). For W parameters the favourable position for Na⁺ is moved towards the S position. The larger graphene-ion attraction pulls the ion towards the graphene surface. The potential of mean force (PMF) for the W parameters has an energy minimum closer to the graphene surface than the LB parameters¹. For the W parameters this minimum forced Na⁺ to lose water molecules from the first hydration shell¹. This change in the ion-graphene energetics is most likely the cause for the different density profiles between the W and LB parameters.

For K^+ with the LB parameters at 1.3 nm, similar to Na^+ , K^+ has two OC peak positions (Figure 5-5a). One is near the interfacial water layer and the other is near

the central water layer (Figure 5-5a). When the channel width decreases to 1.1 nm and 1.0 nm the ion moves towards the centre of the channel (Figure 5-5c and Figure 5-5e). At 0.9 nm with the LB parameters K⁺ moves from favouring the centre of the channel to favouring an OC position near the interfacial water layers (Figure 5-5g). For the W parameters K⁺ prefers to reside at the graphene surface for channel widths of 1.3 nm , 1.1 nm , 1.0 nm and 0.9 nm (Figure 5-5b, d, f and h). At 1.0 nm with the W parameters there is an additional central peak alongside the surface peak (Figure 5-5f). The difference between the two sets of interaction parameters is again due to the energy minimum being closer to the graphene surface for the W parameters¹.

Mg²⁺ and Ca²⁺ have a main peak in the OC position for both parameter sets for the channel widths 1.3 nm and 1.1 nm (Figure 5-5a, b, c and d). Mg²⁺ has an additional peak in the centre of the channel for the LB parameters at 1.3 nm (Figure 5-5a). At 1.0 nm The water density is reduced from a trilayer into a broad bilayer structure (Figure 5-5c and Figure 5-5e). This causes Mg²⁺ and Ca²⁺ to stay in the centre of the channel with the LB parameters at 1.0 nm (Figure 5-5e). Mg²⁺ and Ca²⁺ at 1.0 nm with the W parameters prefer to reside in an OC position, close to the centre of the channel (Figure 5-5f). The W parameters cause the density of Mg²⁺ and Ca²⁺ to be split away from the centre of the channel at 1.0 nm because of the increased attraction between the cations and the graphene surfaces¹. At 0.9 nm both parameter sets for Mg²⁺ and Ca²⁺ have only a central peak (Figure 5-5g and Figure 5-5g).



Figure 5-5. Ion density profiles (ρ_{I}) and water oxygen density profiles (ρ_{OW} , black dashed lines) perpendicular to the graphene sheets against the z-position in the simulation cell for Li⁺ (blue), Na⁺ (red), K⁺ (green), Mg²⁺ (magenta) and Ca²⁺ (orange). The centre of the channel is z = 2.5 nm. These profiles are shown for the channel widths 1.3 nm (a, b), 1.1 nm (c, d), 1.0 nm (e, f) and 0.9 nm (g, h) for the Lorentz-Berthelot (a, c, e and g) and Williams *et al.*¹ (b, d, f, and h) parameters.

At 0.8 nm there are 1.5 water layers between the graphene sheets (Figure 5-6a). When the channel width is reduced down to 0.7 nm there is only a monolayer of water (Figure 5-6c). For the LB parameters all of the cations sit in the centre of the channel for channel widths of 0.8 nm and 0.7 nm (Figure 5-6a and Figure 5-6c). K⁺ has the broadest density of the cations at 0.8 nm (Figure 5-6a). For the W parameters Li⁺ and Ca²⁺ stay in the centre of the channel for both 0.8 nm and 0.7 nm channel widths (Figure 5-6b and Figure 5-6d). For the W parameters Mg²⁺ resides in the centre of the channel at 0.8 nm (Figure 5-6b). However, Mg²⁺ resides at the graphene surface at 0.7 nm (Figure 5-6d). The density at the graphene surfaces for Mg²⁺ at 0.7 nm with the W parameters is asymmetric. This means that the Mg²⁺ cation rarely transfers between the two graphene surfaces. Both Na⁺ and K⁺ reside at the graphene surface with the W parameters at 0.8 nm (Figure 5-6b). Na⁺ also resides at the graphene surface with the W parameters at 0.7 nm (Figure 5-6d). K⁺ is moved into a central position at 0.7 nm with the W parameters at 0.7 nm (Figure 5-6d). K⁺ is moved into a central

The position of the ions within the channel is a trade-off between the water-water, water-ion and ion-graphene interactions. There are water-graphene interactions, however this only occur through the Lennard-Jones interaction that are weaker than the other three interactions. The PMF of a ion being pulled towards a graphene flake shows how the ion-graphene interaction changes as a function of separation¹. With the W parameters there is a much larger attraction between the ion and the graphene surface¹. This means that the stronger attraction was capable of pulling the ions from the centre of the channel towards the graphene surface (Figure 5-5, Figure 5-6 and Table 5-3). This will most likely occur at the cost of losing water-ion interactions. The ions all exhibit different behaviours, which is most likely due to their different water-ion interactions.



Figure 5-6. Ion density profiles (ρ_{I}) and water oxygen density profiles (ρ_{OW} , black dashed line) perpendicular to the graphene sheets against the z-position in the simulation cell for Li⁺ (blue), Na⁺ (red), K⁺ (green), Mg²⁺ (magenta) and Ca²⁺ (orange). The centre of the channel is z = 2.5 nm. These profiles are shown for the channel widths 1.3 nm (a, b), 1.1 nm (c, d), 1.0 nm (e, f) and 0.9 nm (g, h) for the Lorentz-Berthelot (a, c, e and g) and Williams *et al.*¹ (b, d, f, and h) parameters.

Typically ions try to optimize the number of water molecules in the hydration shells surrounding the ion. The number of water molecules in a hydration shell can be calculated by integrating the radial distribution function between an ion and water oxygen atoms^{1,176}. The integral of the radial distribution function is called the coordination number. The coordination number at the position of the first minimum in the radial distribution function (n_1) gives the number of water molecules in the first hydration shell. The difference in the coordination number between the first and second minima (n_2) is the number of water molecules in the second hydration shell. The number of water molecules in the second hydration shell. The number of water molecules in the second hydration shell. The number of water molecules in the second hydration shell. The number of water molecules in the second hydration shell. The number of water molecules in the second hydration shell. The number of water molecules in the second hydration shell. The number of water molecules in the second hydration shell. The number of water molecules in the second hydration shell tends to decreases for all of the ions and both parameter sets as the channel width decreases (Figure 5-7). This decrease is most obvious when going from channel widths of 0.9 nm down to 0.8 nm. This is also associated with the transition

from a bilayer to a monolayer water structure (Figure 5-1, Figure 5-5g and Figure 5-6a). Removing the space for a second layer of water makes it difficult for water molecules to orientate around an ion to form a second hydration shell. There are no obvious different trends between the LB and W parameters (Figure 5-7).

Table 5-3. Positions of the peaks in the perpendicular density profiles for Li⁺, Na⁺, K^+ , Mg²⁺ and Ca²⁺ with the Lorentz Berthelot (LB) and Williams *et al.*¹ (W) interaction parameters with channel widths of 1.3 nm , 1.1 nm , 1.0 nm , 0.9 nm , 0.8 nm and 0.7 nm . The ions can occupy three positions: the graphene surface (S), the centre of the channel (C) or off-centre of the channel (OC). Numbers in brackets indicate the number of peaks in that position if there are more than one. Two peak positions are separation "/". The first peak position written has the largest density.

<i>d</i> / nm	L	i ⁺	Na) ⁺	K	F	M	²⁺	Ca	a ²⁺
	LB	W	LB	W	LB	W	LB	W	LB	W
1.3	OC	OC	OC(2)	S	OC(2)	S	OC/C	OC	OC	OC
1.1	OC	OC	C/OC	S	C	S/C	OC	OC	OC	OC
1.0	OC	OC	C/OC	S/C	C	S	С	OC	С	OC
0.9	OC	OC	C/OC	S	OC	S	С	С	С	С
0.8	С	С	C	S	C/OC	S	C	С	С	С
0.7	С	С	C	S	C	С	C	S	С	С

Li⁺ preserves its first hydration shell for all of the channel widths and both parameters sets (Figure 5-7a). For Li⁺ in both the unconfined and confined systems $n_1 = 4$ (Figure 5-7a). Na⁺ and K⁺ with the LB parameters show a decrease in the first hydration shell for channel widths of 0.7 nm and 0.8 nm, compared to the other channel widths and the unconfined ion coordination numbers (Figure 5-7b and Figure 5-7c). Values for n_1 are lower with the W parameters for channel widths ranging from 1.3 nm – 0.9 nm for Na⁺ and K⁺ compared to the LB parameters. With the W parameters these two ions sit at the graphene surface (Figure 5-5b, d, f and h). When they do this there is no water oxygen density between the ions and the graphene surface. This means that these two ions have to lose water molecules in the first hydration shell to sit at the graphene surface.

For Mg^{2+} the value of n_1 only decreases for a channel width of 0.7 nm for both parameter sets (Figure 5-7d). For the unconfined system and channel widths larger than $0.7 \text{ nm } n_1 = 6$. The water molecules arrange themselves around Mg^{2+} into an octahedral structure. When the channel width decreases to 0.7 nm , $n_1 = 4$ and $n_1 = 5$ for the LB and W parameters respectively. For the LB parameters with a channel width of 0.7 nm Mg^{2+} sits in the centre of the channel (Figure 5-6c). This is achieved by Mg²⁺ losing two water molecules in the axial positions of the octahedral structure, leaving only four water molecules in the equatorial positions. With the W parameters the ion moves closer to the graphene surface (Figure 5-6d). This gives the water molecules around the ion enough space to fit five water molecules in the first hydration shell (Figure 5-7d). This is why there is such a sharp density for Mg^{2+} at the graphene surface in Figure 5-6d. For Ca^{2+} there is only a slight difference between the LB and W parameters at $0.8 \,\mathrm{nm}$ (Figure 5-7e). At other separations the number of water molecules in the first hydration shell is the same between the two parameter sets for Ca^{2+} (Figure 5-7e). There is also an increase in the value of n_1 for Ca^{2+} at 0.8 nm for both parameter sets compared to the larger channel widths (Figure 5-7e). The value of n_1 then decreases for a channel width of 0.7 nm (Figure 5-7e).



Figure 5-7. First (n_1 , circles) and second (n_2 , diamonds) hydration shell coordination numbers against channel width (d) for Li⁺ (a), Na⁺ (b), K⁺ (c), Mg²⁺ (d) and Ca²⁺ (e) with the Lorentz-Berthelot (unfilled) and Williams *et al.* (filled) parameters. Error bars on n_2 show the range of possible values for n_2 . Horizontal dashed and dotted lines show the range for the unconfined values of n_1 and n_2 respectively.

5.4 Discussion

At the end of section 5.3.1 there were three questions about the diffusive results that could be answered by the structural properties of confined ions. From the results in section 5.3.2 it is now possible to address and answer these questions more thoroughly:

1. Diffusion of Na⁺ and K⁺ is slower with the W parameters than the LB parameters because Na⁺ and K⁺ reside at the graphene surface for the W parameter set (Figure 5-5). By moving towards the graphene surface the ions have removed water molecules from their first hydration shells (Figure 5-7b and Figure 5-7c). Apart from Na⁺ at 0.9 nm there is no discernible change in the activation energies between the two parameter sets (Figure 5-3b and Figure 5-3c). As the diffusion activation energy barrier is the same, this rules out a different diffusive process, i.e. the molecules hopping between hollow positions at the graphene surface. This means that the surrounding water molecules are still limiting the ionic transport through the channel. The slow diffusion is then due to the ions being in contact with the frozen graphene surface. As the graphene surface does not move, this reduces the number of molecules that the ions can push through to diffuse through the channel. Hence the diffusion coefficients are lowered for this parameter set.

2. The diffusion activation energy barrier for the W parameter set with Na⁺ at a channel width of 0.9 nm is lower than for the LB parameters (Figure 5-3b). This is because the ion has moved from occupying the centre of the channel to the graphene surface (Figure 5-5g and Figure 5-5h). At 0.9 nm there are two layers of water molecules in the channel (Figure 5-1d and Figure 5-5g). This separation makes it possible for the water molecules to form hydrogen bonds between the two layers²²⁸ (Figure 5-1d). For the LB parameters the main ion density is in the centre of the channel. To diffuse through the centre of the channel requires that the ion breaks up hydrogen bonds between the two layers. For the W parameters, Na⁺ sits at the graphene surface (Figure 5-5h). When Na⁺ travels parallel to the graphene sheets at the surface it does not have to disrupt hydrogen bonding between the two water layers. This reduces the activation energy for the ion to travel through the channel.

3. Hopping between graphene surfaces occurs for all of the ions; however it occurs at a variety of different channel widths for the two parameters sets (Figure 5-4). Changing from the LB to the W parameters for Na⁺ shows the most notable change in the hopping dynamics (Figure 5-4). For the W parameters the ion shows hopping for channel widths of 1.3 nm , 1.1 nm , 1.0 nm and 0.9 nm (Figure 5-4b, d, f

and h). For LB parameters Na⁺ shows no hopping for any of the channel widths (Figure5-4a, c, e and g). The density profiles for Na⁺ shows that it moves towards the graphene surface for the W parameters (Figure 5-5). When it is at the graphene surface, Na⁺ only shows two density peaks across the whole channel (Figure 5-6b, d, f and h). These peaks are only at the graphene surface and there is a very low ion density in between them (Figure 5-6b, d, f and h). This means that for Na⁺ with the W parameters, it only occupies a position at either graphene surface. This means that it will hop between the two surfaces. This can be extended to the other ions, when they only show two density peaks with very little density in between then the ions will show a hopping motion between the peaks.

5.5 Conclusions

MD simulations have investigated the diffusive and structural properties of Li⁺, Na⁺, K^{+} , Mg^{2+} and Ca^{2+} for different channel widths and temperatures. All of the ions showed that the fastest diffusion occurs with a channel width of $0.8\,\mathrm{nm}$. The slowest diffusion was observed for channel widths of 0.9 nm. The difference in diffusion against channel width was attributed to the changes in the water density in the channel. For Li^+ , Mg^{2+} and Ca^{2+} a stronger attraction to the graphene sheets did not significantly alter their dynamics through the graphene channels. Na $^{+}$ and K $^{+}$ showed slower diffusion with a stronger attraction between the ion and the graphene channel. The stronger attractions were added to recreate the effects of graphene-ion polarisation. This attraction alters the dynamics of Na⁺ and K⁺ by pulling the ions towards the graphene surface. Being at the frozen graphene surface meant that the two ions had less area that they could use to diffuse through the channel. Hence they showed slower diffusivities. Ions that exhibited a preference for staying at the graphene surface showed a hopping mechanism between the surfaces. This hopping could be induced by adding stronger attraction between the ions and the graphene surface.

Including the graphene-ion interactions makes it difficult to use alteration to the hydration structure as a guide for ion entry barriers. This is because the loss of water molecules in the hydration shells can be compensated for by favourable graphene-ion interactions. To see what impact graphene-ion interaction have on

the potential for desalination it is necessary to directly calculate the entry barrier from the potential of mean force^{22,79}.

These results have shown that the inclusion of graphene-ion interactions does not alter the diffusive transport for Li⁺, Mg²⁺ and Ca²⁺. However, it does have an effect on the transport of Na⁺ and K⁺. The relative diffusion between Li⁺ and Na⁺ changes if the graphene-ion interactions are included. This could be a useful feature to compare with experimental results. The array of channel widths and temperatures studied here make it possible to compare the diffusion for Na⁺ and K⁺ in unoxidised graphene channels to experimental results. Comparisons with experimental data would back-up the inclusion of graphene-ion interactions in MD simulations and gauge the accuracy for the parameters derived by Williams *et al.*¹.

Chapter 6 Confined Water Structure

Strong interactions between two layers of graphene mean that it is possible to confine molecules to within a sub-nanometre dimension at high pressure¹⁰³. These high pressure enclosures can promote hydrolysis reactions for some common salts¹⁰³. These environments could be an interesting method for controlling and promoting specific reactions. However, these environments are difficult to create reliable and reproducible experiments^{104,106}. This would be a prime environment for simulations to provide information that experiments lack or find difficult to determine. Unfortunately, there are discrepancies between different simulated results, particularly around what structure of ice is formed in these confined channels^{104,107}.

This chapter aims to make a systematic comparison between the confined water structures produced by different water models at high pressure. This is done by first using the 2D bond orientational order parameter^{229,230} to determine the nature of the different structures. Once different structures have been characterised, it is possible to compare the energetics for the different structures to highlight the reasons why the water models produce specific structures. The formation of different structures seems to be driven by the strength of hydrogen bonds for the different water models. Hence, a lot of the focus towards the end of this chapter is concerned with the energetics and hydrogen bonding within the structures.

This chapter is the manuscript for a paper that has been submitted to the Journal of Chemical Physics on 16th July 2017 titled "Why different water models predict different structures under 2D confinement". The author (J. Dix) ran all of the simulations and produced all of the analysis, expect for results related to hydrogen bonding. L. Leo produced the hydrogen bonding analysis for the confined structures. The author (J. Dix), L. Leo and P. Carbone all contributed to the preparation of the manuscript; however the author (J. Dix) took the lead on writing the manuscript and implemented changes suggested from the other contributors.

This chapter is split into five main sections:

Section 6.1 An introduction into more of the background behind the difficulties of simulating confined water.

Section 6.2 Computational methodology describing how the simulations were run and some of the analysis techniques used.

Section 6.3.1 Discussion of the structural characteristics of the confined phase of water with different water models.

Section 6.3.2 Analysis of the hydrogen bonding structure and the energetics of the confined structure to understand what components of the water models contribute to the different confined phases.

Section 6.4 Conclusions about the simulated results and how they fit into broader scientific interests.

6.1 Introduction

Graphene enclosures with a separation of around 1.0 nm have been shown to promote chemical reactions¹⁰³ and liquid-solid phase transitions¹⁰⁴ that are unexpected in unconfined systems. Due to favourable graphene-graphene interactions within the enclosure, the confined molecules experience high pressures of ≈ 1.2 GPa¹⁰³. The combination of both the high pressure and restricted movement in one dimension makes graphene enclosures a distinctive physical environment.

To be able to exploit graphene enclosures for uses like chemical reactors, it is important to understand the structure and dynamics of confined molecules under high pressure. These properties can be difficult to obtain from experiments, particularly for water which exhibits a large array of anomalous behaviour²³¹. The recent experiments of Algara-Siller *et al*.¹⁰⁴ showed that in an enclosure with \approx 1.0 nm height, which can accommodate three layers of water, water molecules can

form a square ice structure with an AA-stacking conformation. AA-stacking involves having the water oxygen atoms in each layer lying on top of each other. However, this observation has been debated in the literature¹⁰⁶ highlighting the difficulty of conducting these experiments.

Computer simulation techniques, like Molecular Dynamics (MD), can aide in the understanding of confined systems that are hard to investigate experimentally. MD has already been shown to be useful in understanding confined systems^{49,54,103}; however, accurately modelling the phase behaviour of unconfined water through MD simulations has proved to be difficult due to its complex phase diagram^{232,233}. The combination of movement limited to two dimensions and water/surface interactions add an extra challenge as they can both influence the properties of confined water. Limited experimental data makes it hard to validate the confined models of water and the water/surface interactions.

Despite these difficulties, many studies have used MD simulations to investigate confined water. Previous studies have recreated the high pressure environment by either applying pressure to external reservoirs to increase the water density in the channel^{107,234,235}, or by placing a fixed number of water molecules between two infinite parallel sheets to impose a specific density^{236–239}. These studies have used different water models, including SPC/E²³⁹, TIP4P/2005^{107,234,235} and TIP5P²³⁷; interactions between the water molecules and the carbon walls^{11,67,236,240,241}; as well as various sheet-sheet separations, ranging from 0.6 – 2.0 nm^{67,107}. This variety in simulation set ups can predict different confined water structures and values of transition pressure^{104,107}, which makes it difficult to compare between different studies.

Therefore, there is a clear need to test how different water models behave under the same confined environment to understand what properties of the water model control their behaviour. In this work we have aimed at understanding this variation by systematically comparing three common water models (SPC/E, TIP4P/2005 and TIP5P). This was done for a two dimensional channel comprised of rigid graphene sheets with a separation of 0.9 nm between the sheets both with and without contact to an external reservoir of water. Although there is limited experimental

data, we have seen that TIP4P/2005 and TIP5P water models can reproduce an AAstacked hexagonal structure observed in Quantum Monte Carlo calculations²⁴².

6.2 Computational details

6.2.1 Water and graphene models.

In this work we have analysed three common water models which have been used extensively in simulations under confinement^{11,49,67,107,234,235,237,240,241}: SPC/E⁶, TIP4P/2005⁷ and TIP5P⁸. All of these models have a Lennard-Jones 12-6 interaction site at the position of the oxygen, O, atom and positive partial charges on the hydrogen, H, atoms. To counterbalance the partial charges on the hydrogen atoms in SPC/E a partial negative charge is placed on the O atom, in the TIP4P/2005 model it is shifted towards the H atoms (point M in Figure 6-1a) and in the TIP5P model it is split between the two lone pair sites of the oxygen atom (points L in Figure 6-1a). All of the water models are rigid and non-polarizable, see B.1 for all of the used parameters. Comparative studies between water models for unconfined water have shown that TIP4P/2005 is the best of these water models at producing the unconfined ice phase diagram and ice densities^{172,173,232}.



Figure 6-1. Schematic structures of SPC/E, TIP4P/2005 and TIP5P water models (a), images of the starting configuration and equilibrated structures for a reservoir simulation (b) and the corresponding parallel plate simulation (c).

The water/graphene interaction was modelled by using a Lennard-Jones 12-6 potential for all of the carbon, C, atoms⁶⁷ rather than the 9-3 Lennard Jones "featureless walls" potential²⁴³. This was because the "featureless wall" approach is expected to break down for inter-wall separations below 1.6 nm⁶⁷. Additionally, to capture the structure of water on a surface it is important to use explicit surface atoms as their lattice spacing alters the structure of surface water²⁴⁴. The parameters for the graphene/water interactions are based on work by W. A. Steele *et al.* ^{9,10} as they have been used previously to study water confined by graphene sheets or in graphitic slit pores^{67,104,245-247}. The C-O cross parameters are shown in Table 6-1 and are derived from the single atom parameters using the geometric mixing rules (See B.1)

Table 6-1. Carbon-oxygen (CO) Lennard-Jones 12-6 cross term parameters for theSPC/E, the TIP4P/2005 and the TIP5P water models.

	$\sigma_{ m CO}({ m nm})$	$\varepsilon_{\rm CO}$ (kJ mol ⁻¹)
SPC/E	0.328	0.388
TIP4P/2005	0.328	0.424
TIP5P	0.326	0.394

6.2.2 Simulation Set-Up.

The simulations were performed in two steps: initially a 2D channel with a 0.9 nm height and a 7 nm length, (See B.2) was connected at either end to an external reservoir, both containing 2000 water molecules (Figure 6-1b). This channel height was enough to accommodate two layers of water²⁴⁷. Pressures were applied along the direction of channel (z-axis), P_{ZZ} , and ranged from 1 bar to 5.0 GPa, but the x and y-axis dimensions were kept constant meaning that these simulations were run using the $NP_{ZZ}A_{XY}T$ -ensemble. These simulations took between 10 and 45 ns to reach equilibrium (See B.4). The channel density that was reached after the equilibration time was then used to fill another channel between two infinite

parallel plates (Figure 6-1c) (See B.3). Due to periodic boundary conditions this acted as an infinite channel and allowed us to remove any influence that the reservoirs and channel entrance had on the water structure. The parallel plate setup was further run in the NVT ensemble and reached equilibrium within 10 ns – 80 ns (See B.4). The short-range Lennard-Jones, short-range Coulomb and long-range Coulomb interaction energies were monitored to ensure that our systems had reached equilibrium (See B.5). Comparison between the structure in parallel-plate and reservoir simulation set-ups showed that there was no difference between the confined water structures in the two methods (See B.6). Results were obtained from both set-ups to help understand the confined structures. Reservoir simulations were used to obtain the bond orientational order parameter and channel densities, whereas the parallel plate set-up was used to obtain 2D radial distribution functions, the number of hydrogen bonds and interaction energies.

All simulations were run using GROMACS 4.5.4^{132,139,140}. Both simulation set-ups had used the Berendsen thermostat¹⁴ with a coupling constant of 0.2 ps at 300 K with a 0.5 fs time step with the Leapfrog integrator¹⁷⁵. The Berendsen thermostat¹⁴ showed minimal difference in the confined water structure compared to the Nosé-Hoover thermostat^{15,16} for the parallel plate simulation set-up (See B.7). The short range cut-offs were 1.1 nm for both the electrostatic and van der Waals interactions. Long-range electrostatic interactions were taken into account using the Particle-Mesh Ewald Summation^{133,134} in 3D and 2D for the reservoir and parallel plate simulations respectively. The graphene sheets were treated as being neutral and periodic boundary conditions were applied in all three dimensions. Pressure coupling was controlled using the Berendsen barostat¹⁴ with a 4.0 ps coupling constant using a semiisotropic scaling scheme. See B.2 and B.3 for any further details for the simulation set-ups.

6.2.3 Analysis

To quantify the ordering of water molecules between the two confining walls the 2D bond orientational order parameter^{229,230} (ψ_n) was calculated. This order parameter produced values between 1 and 0, with 1 relating to a highly ordered

structure and 0 to a disordered structure. The value of *n* was changed between 4 and 6, and allowed us to distinguish between the degree of square (or rhombic) and hexagonal ordering respectively, within each layer of confined water. This order parameter was used to analyse the local ordering of water oxygen atoms in each layer separately. Initially a Voronoi tessellation was used to determine all the nearest neighbour oxygen atoms (*n_i*) for a selected oxygen atom, *i*. For each pair the angle (θ_{ij}) between the x-axis, parallel to the sheet, and the vector formed between atom *i* and its nearest neighbour *j* was subsequently calculated. These angles were then used in the following equation to calculate $\psi_n^{229,230}$:

$$\psi_n = \frac{1}{N} \left| \sum_{i=1}^{N} \frac{1}{n_i} \sum_{j=1}^{n_i} \exp(in\theta_{ij}) \right|$$
 (6.1)

In equation (6.1): *N* is the total number of water O atoms in the channel. These values were calculated using an in-house code that made use of the MDAnalysis python $package^{248,249}$.

The alignment of the two water layers relative to each other was determined from a 2D radial distribution function $(RDF)^{237,250}$. The 2D RDF projects the position of all of the water atoms onto the plane of a graphene sheet. Once the transverse position in the channel for all the atoms are removed, one can identify what the relative conformation of atoms between the two layers are. The 2D RDF is given by²⁵⁰:

$$g_{\parallel}(r_{xy}) = \frac{1}{2\pi\rho z r_{xy} \delta r} \sum_{n=0}^{b} \sum_{i \neq j} (H(n\delta r - r_{xy}) - H((n+1)\delta r - r_{xy}))$$
(6.2)
$$H(x) = \begin{cases} 1 & x > 0 \\ 0 & x \le 0 \end{cases}$$

In equation (6.2): ρ is the density of water oxygen atoms, r_{xy} is the distance in the xy-plane of the graphene sheet between atoms *i* and *j*, H is the Heaviside function, b is the number of bins used for the distribution function and z is the size of the simulation box in the direction perpendicular to the graphene sheets.

6.3 Results

6.3.1 Confined Water Structure

The bond orientational order parameter is a useful tool to follow the changes in the structure of water upon changing the channel pressure and is an effective way to highlight the differences between the water models. We observe that for both TIP4P/2005 and TIP5P, as the applied pressure increases the hexagonal component (n = 6) of the bond orientational order parameter, ψ_6 , also increases (Figure 6-2a). The emergence of hexagonal symmetry occurs at different pressures for the two models. TIP5P shows hexagonal symmetry at 1 GPa while TIP4P/2005 needs to reach 2 GPa. Neither model showed any presence of square symmetry associated to the value of ψ_4 . SPC/E requires a higher pressure of 3 GPa to achieve an ordered structure (Figure 6-2a) which shows, contrary to the other two models, a square or rhombic symmetry ($\psi_4 \approx 0.25$) and not a hexagonal symmetry ($\psi_6 \approx 0.05$). Here it is important to notice that a value of $\psi_4 \approx 0.25$ is too low for a perfect square structure and is more indicative of a rhombic structure.

The pressure values at which the order parameters ψ_4 and ψ_6 change are marked on Figure 6-2a by dashed vertical lines. These lines coincide with the position of discontinuities in the water channel density, ρ_{chan} (Figure 6-2b). At 1 bar pressure SPC/E is the model that predicts the lowest channel density of 860 kg m⁻³, which is substantially smaller than the bulk density value of 996.5 kg m⁻³ at 1 bar and 300 K²⁵¹. The other two water models studied predict a density more similar to that of bulk water of 960 kg m⁻³ and 930 kg m⁻³ for TIP4P/2005 and TIP5P respectively (Figure 6-2b). As the pressure increases these initial differences in density between the water models fade away.



Figure 6-2. Order parameters, ψ_6 and ψ_4 (a) and channel density, ρ_{chan} (b) plotted against the applied pressure, P_{ZZ} , for SPC/E (green), TIP4P/2005 (red) and TIP5P (blue). Snapshots of confined water in the zx and zy-planes (c) for TIP5P at 1.0 GPa, TIP4P/2005 at 2.0 GPa and SPC/E at 3.0 GPa. Vertical dashed lines in (a) and (b) correspond to transition points in the order parameter for the water models. See B.8 for raw data for (a) and (b).

A top-down view through the graphene sheets (Figure 6-2c) show that TIP4P/2005 and TIP5P form a hexagonal structure where the oxygen atoms in the two layers sit on-top of each other. The hexagonal structure gives rise to large values of ψ_6 in Figure 6-2a. A snapshot for SPC/E (Figure 6-2c) highlights its rhombic structure and that the oxygen atoms in each layer are offset. Side-on snapshots of the water models in the graphene channel shows that TIP4P/2005 and TIP5P have hydrogen atoms pointing between the two layers of water, whereas SPC/E has no hydrogen atoms between the two layers. A more quantitative analysis of the stacking geometry between the two layers of water can be achieved by looking at the 2D RDF. The 2D RDF looks at the projection of the positions of the atoms onto a graphene sheet. This means that the vertical distance between atoms is ignored, which allows for peaks at separations less than the first peak in a 3D O-O RDF⁶. In this case any peak below the O-O separation of 0.28 nm^{6,7} is due to the two atoms being in different layers. For the ordered TIP4P/2005 structure the position of the first peak in the oxygen-oxygen RDF, calculated at 2.0 GPa, lies close to $r_{ij} = 0$ (Figure 6-3). This indicates that the oxygen atoms in the two layers sit directly on top of each other , in what is called an AA-stacking configuration¹⁰⁴, which agrees with the snapshot in Figure 6-2c. On the contrary, the ordered SPC/E structure presents a first peak of the RDF around 0.176 nm, which indicates that the oxygen atoms in the two layers configuration.



Figure 6-3. 2D oxygen-oxygen radial distribution function $(g_{\parallel}(r_{ij}))$ for SPC/E calculated at 2.75 GPa (green, dotted) and 3.0 GPa (green, solid), TIP4P/2005 at 1.75 GPa (red, dotted) and 2.0 GPa (red, solid), and 2D oxygen-hydrogen radial distribution function for SPC/E at 3.0 GPa (green, dashed) and TIP4P/2005 at 2.0 GPa (red, dashed).

Additionally, the oxygen-hydrogen 2D RDF for the ordered SPC/E structure presents a peak in a similar position to the oxygen-oxygen 2D RDF. This indicates that in this case the hydrogen atoms sit above the oxygen O atoms in the layer below (Figure 6-3). It is interesting to notice that TIP4P/2005 already shows evidence of AA-stacking before it undergoes the ordering transition as there is the presence of a peak around $r_{ij} = 0$ in the 2D RDF at 1.75 GPa (Figure 6-3). However the SPC/E model does not show any ordering until it forms a completely ordered structure.

From Figure 6-2a it is clear that TIP4P/2005 and TIP5P form hexagonal structures at different pressures. When ψ_6 is plotted against ρ_{chan} (Figure 6-4), it shows that both of these models form a hexagonal structure in a similar density range of 1272 – 1305 kg m⁻³ for TIP4P/2005 and 1202 – 1313 kg m⁻³ for TIP5P. SPC/E requires a higher density range of 1356 – 1431 kg m⁻³ to form an ordered rhombic structure (Figure 6-4).



Figure 6-4. Orientational bond order parameters, ψ_6 and ψ_4 , plotted against the channel water density, ρ_{chan} , for SPC/E (green), TIP4P/2005 (red) and TIP5P (blue). Dashed vertical lines correspond to the transition points in the order parameter for the water models. See B.8 for raw data.

For all three water models the oxygen atoms form two layers and show a similar position in channel both before (Figure 6-5a) and after (Figure 6-5b) the ordering transition takes place. After going through the ordering transition the two layers of oxygen atoms are slightly closer to each other by 0.01 nm for SPC/E and TIP4P/2005 and 0.005 nm for TIP5P. Hydrogen atoms arrange into two positions: in between
the two planes of oxygen atoms or in the same plane as the oxygen atoms. The peaks around 0 nm shows that the hydrogen atoms are between the planes of oxygen atoms (Figure 6-5). Before ordering, all three water models have hydrogen atom peaks in both positions. After ordering, TIP4P/2005 and TIP5P still show peaks in both positions, while for SPC/E the hydrogen atoms are mainly in the same planes as the oxygen atoms (Figure 6-5b). This suggests that there are very few hydrogen bonds between the two planes of water for SPC/E, which agrees with the snapshots in Figure 6-2c.





Previous simulation work has observed the AB-stacked rhombic SPC/E structure¹⁰⁴. The AA-stacked hexagonal structure has been observed for TIP4P/2005¹⁰⁷, as well as for TIP5P confined between featureless graphene walls²³⁷ and silica sheets²⁵². The latter finding suggests that the structure of confined water is not very sensitive to the graphene/water interaction potential. To test this further we have investigated different commonly used carbon-oxygen interaction parameters with the Lennard-Jones 12-6 potential. We observed a slight variation in the transition density and pressure but no noticeable effects on the confined water structure (see B.9 and B.10). These results lead us to conclude that the water model has the most dominant role in determining the ordered structure of confined water. Of particular importance is a water model's capability to form hydrogen bonds. If the electrostatic interactions, and by proxy hydrogen bonding, are turned off the resulting structure shows an AB-stacked hexagonal symmetry (See B.11), which is not observed for any of the water models. This suggests that the structure and strength of hydrogen bonds control the differences in the structures for the three water models.

6.3.2 Hydrogen bonds

To understand the underlying reason behind the formation of the different structures, we calculated the average number of hydrogen bonds per water molecule ($n_{\rm hb}$). Several different methods have been used to define a hydrogen bond, based typically on either energetic or geometric criteria²⁵³. We have opted for geometric criteria. The schematic in Figure 6-6 shows the definition we used to identify a hydrogen bond which involves the O-H---O angle ($\theta_{\rm OH-O}$) formed between the oxygen and hydrogen atoms of the donor water molecule and the oxygen atom of the acceptor water molecule, and the distance between the hydrogen atom of the donor molecule and the oxygen atom of the acceptor molecule ($d_{\rm H-O}$). In our analysis we identified a hydrogen bond exists when $\theta_{\rm OH-O} > 130^{\circ}$ and

 $d_{\rm H-O} < 0.24 \, nm$. These criteria are similar to those used in other simulations with water^{254–256} and were verified using 2D contour plots (see B.12), which is a common method to determine the geometric criteria for dilute²⁵⁷ and condensed²⁵⁸ polymer systems. As there are two layers of water within the channel, an additional criterion was used to differentiate between hydrogen bonds that are within a layer (intralayer) and between the layers (interlayer). When the difference in the z-coordinate between the donor and acceptor atoms is greater than half the length of the hydrogen bond then it is classed as being between the two layers.



Figure 6-6. Average number of hydrogen bonds per water molecule, $n_{\rm hb}$, against the applied pressure, $P_{\rm ZZ}$, calculated for SPC/E (green), TIP4P/2005 (red) and TIP5P (blue). Total number of hydrogen bonds - solid lines, hydrogen bonds within the plane - dashed lines, hydrogen bonds between water layers - dotted lines. Dashed vertical lines correspond to the transition pressure for the water models. The scheme shows the definition of $\theta_{\rm OH-O}$ and $d_{\rm H-O}$ used to determine the presence of a hydrogen bond.

The analysis shows that when in the disordered state, TIP4P/2005 and SPC/E possess a higher number of hydrogen bonds per molecule compared to TIP5P (Figure 6-6). Additionally both TIP4P/2005 and TIP5P prefer to form interlayer hydrogen bonds, whereas SPC/E mainly forms intralayer hydrogen bonds (Figure 6-6). Once SPC/E goes through the ordering transition the number of interlayer hydrogen bonds reduces dramatically, mainly leaving intralayer hydrogen bonds in the ordered structure. This was contrary to what is observed for TIP4P/2005 and TIP5P where interlayer hydrogen bonds still dominate over intralayer ones.

Analysis of the energetics of forming a hydrogen bond can help to clarify the cause of the different confined structure for the water models. The main energetic trade off to form a hydrogen bond is between the increasingly attractive electrostatic energy against the increasingly repulsive energy of the Lennard-Jones potential. As the Lennard-Jones energy varies as r^{-12} whereas the Coulomb energy varies as r^{-1} , at small separations the Lennard-Jones energetic term will dominate over the electrostatic one. At larger separations the reverse is true, meaning that there are energy minima at short separations between the water molecules where hydrogen bonds are formed. These minima can be easily identified as the global minima for all three water models reported in Figure 6-7.



Figure 6-7. Sum of the short range Lennard-Jones, $E_{\rm LJ}$, and Coulomb, $E_{\rm Coul}$, interaction energies for pairs of water molecules against the distance between the hydrogen and the oxygen atoms forming a hydrogen bond, $d_{\rm H-O}$, calculated for SPC/E (green) at 1 bar (dashed) and 3.0 GPa (solid), TIP4P/2005 (red) at 0.25 GPa (dashed) and 2.0 GPa (solid), TIP5P (blue) at 1bar (dashed) and 1.0 GPa (solid).

SPC/E has both the strongest and shortest hydrogen bonds of all the three water models (Figure 6-7). TIP4P/2005 and TIP5P present similar hydrogen bond strengths and lengths, which suggests that they would show similar interactions and form similar structures, which we have observed.

Further analysis of the solvent-solvent interaction energies shows that as the pressure increases the Coulomb interaction energy becomes more negative (Figure 6-8a), whereas the Lennard-Jones interaction becomes more positive (Figure 6-8b). The Coulomb interaction energy is roughly 4-5 larger in magnitude that the Lennard-Jones interaction energy. SPC/E and TIP4P/2005 have similar electrostatic and Lennard-Jones interaction energies. This agrees with their similar water channel densities (Figure 6-2b) and number of hydrogen bonds (Figure 6-6). TIP5P has a smaller magnitude for the Coulomb and Lennard-Jones interaction energies compared to the other two water modes (Figure 6-8a & 6-8b). TIP4P/2005 has the

most attractive solvent-graphene interaction energy whereas SPC/E has the least (Figure 6-8c). This follows the same trend as the values for the Lennard-Jones cross term ε_{CO} for the two water models (Table 6-1).

When there are no electrostatic interactions the oxygen atoms form an AB-stacked hexagonal structure (see B.11). This is the lowest energy structure for the Lennard-Jones fluid confined at 0.9 nm, so will have reduced the Lennard-Jones interaction energy. TIP4P/2005 and TIP5P both form an AA-stacked hexagonal structure (Figure 6-2a). Despite the increase in pressure, when they order there is a decrease in the Lennard-Jones solvent-solvent interaction energy (Figure 6-8c). This also results in a decrease in the total number of hydrogen bonds in their ordered structures (Figure 6-6). To reduce the Lennard-Jones interaction they both form a hexagonal structure of the oxygen atoms within each layer. The hexagonal structure makes it hard to only form intralayer hydrogen bonds, so there is a combination of both inter and intralayer hydrogen bonds. The hydrogen bonding between the layers can overcome some of the Lennard-Jones repulsion causing both TIP4P/2005 and TIP5P to form an ordered AA-stacked structure.

When SPC/E orders there is a slight increase in the Lennard-Jones solvent-solvent interaction energy (Figure 6-8b), but the Coulomb interaction energy becomes more negative (Figure 6-8a). As the Lennard-Jones solvent-solvent interaction energy increases, the ordered structure does not try to reduce the Lennard-Jones repulsion in the same way that the TIP4P/2005 and the TIP5P water models do. However, there is a large increase in the number of hydrogen bonds in the ordered SPC/E structure compared to its' disordered structure. This most likely explains the decrease in the Coulomb energy. To form the largest number of hydrogen bonds, SPC/E has to form a rhombic structure within each layer where it can easily donate and accept two hydrogen bonds. As there are no hydrogen bonds between the layers the oxygen atoms minimise the Lennard-Jones repulsion by forming an AB-stacked structure.



Figure 6-8. Short-range Coulomb interaction energy, $E_{\rm Coul}$ (a), solvent-solvent Lennard-Jones interaction energy, $E_{\rm LJ,s-s}$ (b), solvent-graphene Lennard-Jones interaction energy, $E_{\rm LJ,s-g}$ (c) all per water molecule against applied pressure, $P_{\rm ZZ}$, for SPC/E (green), TIP4P/2005 (red) and TIP5P (blue). Dashed vertical lines show transition pressure.

These different structures occur because SPC/E can form stronger hydrogen bonds than TIP4P/2005 and TIP5P. The stronger hydrogen bonds are more capable of overcoming repulsive Lennard-Jones interactions resulting in different structures.

6.4 Conclusions

This work aimed to do a systematic comparison of the structure of water confined within a 0.9 nm graphene channel when using the common classical molecular dynamics water models of SPC/E, TIP4P/2005 and TIP5P. Unfortunately, all of these models formed ordered structures at different pressures. However TIP4P/2005 and TIP5P have similar behaviours by both forming an AA-stacked hexagonal structure within a similar density range. SPC/E instead forms an AB-stacked rhombic structure. Through analysis of the number and energetics of hydrogen bonding in the different models it was clear that hydrogen bonding determined what ordered structure is formed. SPC/E forms stronger hydrogen bonds than TIP4P/2005 and TIP5P. The increased hydrogen bond strength meant that SPC/E was more capable of overcoming repulsive Lennard-Jones interactions to form a rhombic structure. Our results have showed that the confined structure of water is dominated by the choice of water model, not by the water/surface interactions.

Due to the current lack of robust experimental data, it is difficult to determine which model is the best suited for simulations under confinement. Therefore, care should be taken when analysing the results of confined simulations. Recent density functional theory calculations at 0 K have suggested that for the interlayer distance of 0.9 nm, investigated here, and for pressures above 0.5 GPa, a hexagonally close packed structure is the most stable structure²⁴². Although this work did not include the investigation of AB-stacked structures, it could suggest that the TIP4P/2005 and the TIP5P models are more accurate than the SPC/E model. As the experimental techniques to investigate nanoconfined systems are constantly improving, future experiments like Raman or dielectric spectroscopy, could help to verify which model is the most accurate at reproducing the confined structure of water.

Appendices

The work of the "Supplementary Information" for this paper has been included in Appendix B. Within Appendix B there is: the interaction parameters (B.1), reservoir simulation set-up (B.2), parallel plate simulation set-up (B.3), simulation equilibration times (B.4), analysis for simulations reaching equilibrium (B.5), comparison between parallel plate and reservoir simulation set-up (B.6), discussion on the role of thermostat in the confined structure (B.7), raw data for bond orientational order parameters and channel densities (B.8), channel density for different interaction parameters (B.9), confined water structure for different interaction parameters (B.10), simulation results when electrostatic interaction are removed (B.11) and 2D contour plots for θ_{OH-O} against d_{H-O} (B.12).

Chapter 7

Conclusions and Future Perspectives

7.1 Conclusions

lons confined in a nanometre sized channel are very complicated systems because there is a competition between the water-ion, water-water and graphene-ion interactions. Each ion had a specific structure of water around the ion. This alters how the ion interacts with the graphene surface. It can dictate whether it is energetically favourable for an ion to enter a graphene channel. When there are no graphene-ion interactions there is only a slight disruption of the ion hydration shells for channel widths of 1.3 nm - 0.9 nm (Chapter 3 and Chapter 5). Below this separation there is no longer a bilayer of water (Chapter 5). This reduces the number of water molecules that can orientate around an ion, which could prevent ion transport into a graphene channel. Graphene oxide (GO) membranes can be produced with control over the separation between graphene sheets²². However, there is around a 0.1 nm fluctuation in the graphene sheet separation in the experimental GO membranes²². To precisely control the ion rejection and dehydration there needs to less variation in the graphene separations, as a change from 0.8 nm to 0.9 nm could allow a cation like Na⁺ to travel through the membrane.

Delocalised pi-electron systems show a strong attraction with ionic species. These polarisation effects were incorporated into molecular dynamics (MD) simulations within this work (Chapter 4). Without these effects it is easy to draw conclusions on whether an ion will permeate through a membrane based on changes in the hydration structure. Including polarisation effects makes it much more difficult, as dehydration of an ion will only prevent ion entry into the channel if it is not

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compensated by graphene-ion interactions. Potentials of mean-force (PMFs) for an ion being pulled towards a graphene flake showed that Li^+ , Mg^{2+} and Ca^{2+} did not lose water molecules from their first hydration shell at the energy minimum at the surface when graphene-ion interactions were included (Chapter 4). However, Na⁺ and K⁺ did lose water molecules from their first hydration shell at the graphene surface when graphene-ion interactions were included (Chapter 4). They also showed that they preferred to reside at the graphene surface when confined at the cost of water molecules in the first hydration shell (Chapter 5). Na⁺ has a more negative hydration free energy than K^{+188} , so it will experience a larger energy penalty to remove water molecules from the hydration shells. But Na⁺ will then be compensated more because it has a higher charge density so can more effectively polarise the graphene surface¹. Ions that do not dehydrate at the graphene surface when graphene-ion interactions are included are likely to be prevented from entering into a channel through dehydration if the channel width is small enough to remove water molecules from the first hydration shell. Ions that do dehydrate at the graphene surface when graphene-ion interactions are included will need to be prevented from travelling through the membrane by a different means. Any dehydration of the ion will be compensated by favourable graphene-ion interactions. Unfortunately, Na⁺ is one of these, which is a key ion to reject for desalination. This means it will be important to assess other mechanisms for preventing the transport of Na⁺ through a GO membrane.

Graphene channels and enclosures can force ions into confined regions while under a very high pressure. These regions can force salt solutions to undergo a hydrolysis reaction, forming an oxide compound in this environment¹⁰³. This could provide a method of using graphene to precipitate salt out of a high salinity feed. To be able to exploit and model these systems it is important to understand how water interacts in this environment. Water is a very common solvent for group 1 and group 2 salts. This means that it is a good starting point for understanding these systems. Different water models show different confined water structures while in this environment (Chapter 6). This is mainly due to the different strengths of hydrogen bonding for the water models (Chapter 6). However, this does pose a problem of how to accurately model these systems.

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There are a lot of interesting results for confined graphene systems. These results show that ion rejection could be achieved for some ions, even if graphene-ion interactions are important for these systems. It is clear that there also needs to be further development in the understanding of the interaction of Na⁺ and K⁺ in GO channel to optimise these membranes for desalination. Further studies into modelling high pressure, confined water will help to develop and utilise graphene enclosures.

7.2 Future Perspectives

There are many interesting aspects of this work that could be extended, both to help further the development of GO membranes and to extend the understanding of confined phenomena. The main focus of this work has been to tackle the use of GO membranes for desalination. A few potential aspects for further research are:

- Calculating the free energy barriers for ions entering graphene slit-pore with and without graphene-ion polarisation interactions. PMFs can be used to calculate the energy barrier for an ion to enter a graphene channel^{22,79}. This provides a direct measure for the trade-off between dehydration and graphene-ion interactions.
- 2. More detailed structures for the pore and channel widths of a GO membrane. Throughout this work, it has been assumed that transport through a GO membrane occurs through unoxidised regions of the membrane. This made it possible to use unoxidised graphene slit-pore as the GO membrane model. It is unlikely that GO sheets will stack perfectly to form a constant separation. In fact, experimentally there is a range for the channel widths within a membrane rather than one specific channel width²². This suggests that there is a more complex structure for GO channel and there may be additional effects brought about by oxygen functionalities on the surface.
- Understand how counter ions affect the structure of Na⁺ and K⁺. Both of these cations dehydrate water molecules to sit at a graphene surface.
 However in the presence of counter anions, the ion pair may interact differently with the graphene and surface and within the channel. Through a 155

combination of PMF calculations and confined parallel plate simulations it would be possible to see how an anion affects the interaction of Na^+ and K^+ with graphene surfaces.

- 4. Observe how Na⁺ and water behave for smaller channel widths. The best ion rejection is a trade-off between getting the largest ion free-energy barrier for entry against the ease of water permeation. If the sheet-sheet separations are reduced further than those studied in this work then it may be possible to make the graphene-ion interactions unfavourable, or the cost of dehydration too high for Na⁺ to enter to channel. However, this only works if water molecules can still easily permeate through the channel. Using a combination of PMF calculations and confined parallel plate simulations would give an insight into Na⁺ rejection against water permeation.
- 5. Calculate more experimental properties for confined systems. One of the main difficulties for simulating nano-confined systems is the sparsity of experimental data. To try and bridge the gap between the experiments and simulations it would be useful to calculate more spectroscopic information to compare simulations with experiments. For example, calculating the structural decay time for hydrogen bonding around a confined ion²⁵⁹. Alternatively, for confined water it could be possible to compare the dielectric response of a confined water phase with experimental observations.
- 6. Extended the phase diagram of confined water models. To make comparisons between experimental and simulated confined water structures easier. The phase diagram for confined water could be extended to investigate the effects that temperature and channel width have on the different water models. This will help to determine the most accurate water model for investigating confined systems.

It is likely that some of the ideas will be carried forward with the aid of new experimental results. The combination of both experimental and simulation investigations will provide a good understanding for the behaviour of molecules in confined systems.

Appendix A

Supplementary Information for Chapter 3

i	σ_i (nm)	$arepsilon_i$ (kJ mol ⁻¹)	<i>qi</i> (<i>e</i>)
С	0.3214	0.48990	0.0000
Li	0.2870	0.00061	1.0000
Na	0.3810	0.00061	1.0000
К	0.4530	0.00061	1.0000
Cs	0.5170	0.00061	1.0000
0	0.3166	0.65000	-0.8476
Н	-	-	0.4238

Table A-1. Non-bonded parameters used in Chapter 3.

$\left\langle L ight angle$ (nm)	$N_{ m sol}$	$ ho_{ m sol}$ (kg m $^{-3}$)
2.996	894	995.3
3.486	1410	995.2
4.031	2179	995.2
4.489	3008	995.1
4.993	4141	995.1
7.463	13823	995.1
9.978	33045	995.1

Table A-2a. Details of the unconfined system simulation cells. $N_{\rm sol}$ is the number of water molecules and $ho_{\rm sol}$ is the density

 Table A-2b. Details of the confined system simulation cells.

$L_{ m X}$ (nm)	$L_{ m _Y}$ (nm)	$N_{ m sol}$	$ ho_{ m sol}$ (kg m ⁻³)
3.193	3.403	366	1029.0
3.684	3.829	476	1030.9
4.667	4.680	736	1029.5
5.158	5.158	888	1030.3
6.140	6.140	1321	1030.0
7.614	7.657	1965	1029.6
10.070	10.210	3466	1029.9
20.134	20.419	13864	1029.9





Table A-3a. Diffusion coefficients $(10^{-9} \text{ m}^2 \text{ s}^{-1})$ obtained from the unconfined simulations.

I (nm)		lon		
$\langle L angle$ (nm)	Li ⁺	Na⁺	K⁺	Cs^+
2.996	0.960	1.120	1.462	1.802
3.486	1.019	1.150	1.480	1.847
4.031	1.051	1.173	1.519	1.811
4.489	1.056	1.222	1.542	1.865
4.993	1.105	1.228	1.551	1.906
7.463	1.153	1.236	1.607	1.945
9.978	1.170	1.305	1.709	1.998

Table A-3b. Diffusion coefficients $(10^{-9} \text{ m}^2 \text{ s}^{-1})$ obtained from the confined simulations.

.05		Ion		
A ^{0.3} (nm)	Li⁺	Na⁺	K ⁺	Cs^+
3.296	0.779	0.888	1.259	1.375
3.756	0.745	0.876	1.239	1.361
4.215	0.819	0.875	1.278	1.364
4.673	0.802	0.903	1.250	1.374
6.259	0.840	0.916	1.256	1.462
7.635	0.850	0.993	1.348	1.468
10.140	0.917	1.008	1.378	1.537
20.279	0.984	1.126	1.448	1.625

Appendix B

Supplementary Information for Chapter 6

B.1 Interaction Parameters

We used the Lennard-Jones 12-6 potential to describe dispersion interactions and the Coulomb potential to describe electrostatic interactions between atoms in these simulations. They are respectively described by the following equations:

$$V(r_{ij}) = 4\varepsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right)$$
(B.1)

$$V(r_{ij}) = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}}$$
(B.2)

In equation (B.1): r_{ij} is the separation between atoms *i* and *j*; ε_{ij} is the interaction energy strength between the atom type of atom *i* and atom type of atom *j*; σ_{ij} is the value for r_{ij} where the potential in equation (B.1) reaches zero. ε_{ij} and σ_{ij} are made up from the individual atom interaction parameters using the geometric mixing rules of $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}, \sigma_{ij} = \sqrt{\sigma_i \sigma_j}$.

In equation (B.2): q_i and q_j are the charges on atom *i* and *j* respectively and ε_0 is the permittivity of free space.

Table B-1. The interaction parameters and physical properties for the SPC/E^6 , TIP4P/2005⁷ and TIP5P⁸ water models.

	$\sigma_{ m o}$	\mathcal{E}_{0}	q_{0}	q_{M}	$q_{\scriptscriptstyle m L}$	$q_{ m H}$	r _{OH}	r _{om}	r _{ol}	θ_{HOH}
	/nm	/kJ mol ⁻¹	/e	/e	/e	/e	/nm	/nm	/nm	/deg
SPC/E	0.317	0.650	0.848	-	-	0.424	0.100	-	-	109.47
TIP4P/2005	0.316	0.778	0.000	-1.113	-	0.556	0.096	0.015	-	104.52
TIP5P	0.312	0.669	0.000	-	-0.241	0.241	0.096	-	0.07	104.52

Table B-2. Interaction parameters for the three different sets of C atom force fields Steele $(S)^{9,10}$, CHARMM $(C)^{11,12}$ and Werder $(W)^{13}$.

	$\sigma_{ m c}$ / nm	$\varepsilon_{\rm C}$ / kJ mol ⁻¹
S	0.340	0.231
С	0.355	0.293
W	0.321	0.490

B.2 Reservoir Simulation Set-up

The reservoir simulations used 8 graphene sheets to separate two water reservoirs with one 0.9 nm high channel travelling between the reservoirs; there was a 0.335 nm separation between each graphene sheet resulting in a box dimension of 3.25 nm (y-axis). The sheets were 5.15 nm wide (x-axis) and around 7 nm long (z-axis). Energy and pressure long-range dispersion corrections were used⁸⁵. The x and y box dimensions were kept constant and the graphene sheets were rigid in the x and y-dimensions, so that the compressibility and flexibility of the graphene sheets didn't affect the water channel density. The graphene sheets were restrained in the z-dimension using a position restraint of 1000 kJ mol⁻¹ nm⁻² to allow for pressure scaling in the z-dimension. This was to make sure that the simulation box could fluctuate in the z-axis. Using position restraints at these high pressures did mean that the z-axis length of the graphene sheet varied from 7.09 – 6.99 nm.

B.3 Parallel Sheet Simulation Set-up

Parallel plate simulations were made up of two frozen graphene sheets with the dimensions 5.16 nm x 5.10 nm in the x and y axes. In the z-axis the simulation box was 5.0 nm, which was used to ensure there was no interaction between periodic images. The simulation cell was frozen throughout with the dimensions 5.16 nm x 5.10 nm x 5.0 nm. The channel was filled be using the coordinates of all of the water molecules at the end of a reservoir simulation where the O atom was in the channel, but 1.0 nm away from the channel edge. This was to ensure that we removed any affects that the edges of the sheets may have on the confined water density. The pressure dispersion correction was used⁸⁵.

B.4 Simulation Times

Table B-3. Total simulation time for SPC/E with external reservoirs at different applied pressures and the time that the simulation reached equilibrium with the **S** C-O interaction parameters.

P_{zz} / GPa	Total Simulation Time / ns	Equilibration Time / ns
5	55	40
4	25	15
3	30	20
2.75	35	25
2.5	25	10
2.25	35	15
2	25	15
1.5	25	15
1	25	10
0.5	30	10
0.0001	45	25

Table B-4. Total simulation time for TIP4P/2005 with external reservoirs at differentapplied pressures and the time that the simulation reached equilibrium with the SC-O interaction parameters.

P_{zz} / GPa	Total Simulation Time / ns	Equilibration Time / ns
5	35	20
4	20	10
3	20	10
2.75	25	10
2.5	25	20
2.25	30	15
2	30	10
1.75	25	15
1.5	25	10
1.25	45	15

1	20	10
0.75	60	10
0.5	40	10
0.25	30	20
0.0001	60	25

Table B-5. Total simulation time for TIP5P with external reservoirs at differentapplied pressures and the time that the simulation reached equilibrium with the SC-O interaction parameters.

P_{zz} / GPa	Total Simulation Time / ns	Equilibration Time / ns
2.5	35	30
2	50	20
1.5	45	35
1	65	45
0.75	30	20
0.5	40	30
0.0001	55	20

Table B-6. Total simulation time for SPC/E for parallel plate simulations at differentapplied pressures and the time that the simulation reached equilibrium with the SC-O interaction parameters.

P_{zz} / GPa	Total Simulation Time / ns	Equilibration Time / ns
5	50	30
4	80	40
3	50	20
2.75	20	10
2.5	20	10
2.25	20	10
2	20	10
1.5	20	10
1	20	10

0.5	20	10
0.0001	20	10

Table B-7. Total simulation time for TIP4P/2005 for parallel plate simulations at different applied pressures and the time that the simulation reached equilibrium with the **S** C-O interaction parameters.

P_{zz} / GPa	Total Simulation Time / ns	Equilibration Time / ns
5	80	10
4	20	10
3	50	20
2.75	50	40
2.5	50	20
2.25	110	60
2	20	10
1.75	20	10
1.5	20	10
1.25	20	10
1	20	10
0.75	20	10
0.5	20	10
0.25	20	10
0.0001	110	10

Table B-8. Total simulation time for TIP5P for parallel plate simulations at differentapplied pressures and the time that the simulation reached equilibrium with the SC-O interaction parameters.

P_{zz} / GPa	Total Simulation Time / ns	Equilibration Time / ns
2.5	80	20
2	20	10
1.5	80	20
1	110	80

0.75	50	10
0.5	50	10
0.0001	20	10

B.5 Equilibrium













To ensure that the simulations had reached equilibrium we continued to run the simulations until the short-range Lennard-Jones, short-range Coulomb and reciprocal Coulomb interaction energies had reached a plateau. From Figures B-1 – B-3, it can be seen that there is a clear plateau in all of the interaction energies after the vertical lines. This allows us to use simulation times greater than the equilibrium time to average over the desired properties of a simulation.





Despite not being used to determine whether the simulation has reached equilibrium, the z-box length had also reached a plateau in the region that the interaction energies had reached a plateau (Figure B-4). This suggests that our decision of using these three energy components to decide whether a system is in equilibrium means that other properties in the system have also reached equilibrium.

B.6 Comparison Between the Water Structure in Both the Parallel Plate and Reservoir Simulation Set-Up



Figure B-5. Shows ψ_4 and ψ_6 against ρ_{chan} for SPC/E for the reservoir (empty symbols) and parallel plate (filled symbols) simulation set-ups. The vertical dashed and solid lines correspond to the midpoint densities for the reservoir and parallel plate simulation set-up respectively. The **S** C-O interaction parameters were used for these simulations.



Figure B-6. Shows ψ_4 and ψ_6 against ρ_{chan} for TIP4P/2005 for the reservoir (empty symbols) and parallel plate (filled symbols) simulation set-ups. The vertical dashed and solid lines correspond to the midpoint densities for the reservoir and parallel plate simulation set-up respectively. The **S** C-O interaction parameters were used for these simulations.



Figure B-7. Shows ψ_4 and ψ_6 against ρ_{chan} for TIP5P for the reservoir (empty symbols) and parallel plate (filled symbols) simulation set-ups. The vertical dashed and solid lines correspond to the midpoint densities for the reservoir and parallel plate simulation set-up respectively. The **S** C-O interaction parameters were used for these simulations.

It was important to ensure that the reservoir and parallel plate simulation set-ups produced similar results, as this allowed us to use results obtained from the two simulation set-ups cooperatively to understand the differences in the structure of the water models. Our first test to check this was to observe how the bond orientational order parameter differed as a function of channel density for the two systems. We used the channel density rather than pressure, as the channel density seems to be a better marker for whether a confined system will form an ordered structure or not. From Figure S5 – S7 it was seen that the parallel plate and reservoir simulations have very similar plots for the bond orientational order parameter as a function of the water channel density. The vertical lines in the Figures S5 – S7 show the mid-point water channel density before and after the ordering transition had occurred. There was a shift between the position of the vertical lines from the reservoir and parallel plate simulations, which was most likely due to the discrete nature of the density that was sampled. It would be expected that as more of the density axis is sampled, these points will move closer together and converge for all of the water models.



Figure B-8. ρ_{chan} against P_{ZZ} (solid lines) and P_{\parallel} (dashed lines) for the reservoir and parallel plate simulations respectively, for SPC/E (a), TIP4P/2005 (b) and TIP5P (c). The **S** C-O interaction parameters were used for all of the simulations.

We also tested how the applied pressure (P_{ZZ}) in the reservoir simulations agrees with the measured in-plane pressure (P_{\parallel}) from the parallel plate simulations. Values of P_{\parallel} were calculated using:

$$P_{\parallel} = \left(\frac{L_{\rm Z}}{d - \sigma_{\rm CO}}\right) \left(\frac{P_{\rm XX} + P_{\rm YY}}{2}\right) \tag{B.3}$$

In equation (B.3): $L_{\rm Z}$ is the z box length; *d* is the graphene-graphene sheet separation and $\sigma_{\rm CO}$ is the C-O Lennard-Jones 12-6 interaction parameter; $P_{\rm XX}$ and $P_{\rm YY}$ are the XX and YY components of the pressure tensor from the NVT parallel plate simulations. The first bracket in (B.3) is to account for both the vacuum space in the z-direction of the simulation cell, which was originally included to prevent interaction between periodic images, and the actual occupied volume by water molecules within the channel. We estimated that this was is the channel width between the two graphene sheets minus the carbon thickness, which we took at $\sigma_{\rm CO}$. It was seen that P_{\parallel} and $P_{\rm ZZ}$ were similar as a function of $\rho_{\rm chan}$ for the parallel plate and reservoir simulation set-ups respectively (Figure B-8). This showed that both simulation set-ups produce similar physical properties making it possible to

allow for a direct comparison between the two simulation set-ups. There is a noticeable discrepancy for TIP5P at low pressure, it was not clear where this discrepancy came from, however, from the bond orientational order parameter (Figure B-7) this does not seem have a noticeable impact on the ordered structure that forms.

B.7 Effect of Thermostat

It is known that the Berendsen thermostat¹⁴ can produce artefacts in simulated results due to violating the equipartition theorem²⁶⁰. To ensure that the confined water structures produced by the Berendsen thermostat in this work are reasonable they have been compared to structures formed with the more reliable Nosé-Hoover thermostat^{15,16}. This was done by using the parallel plate set-up for all three water models with the Berendsen thermostat using simulations ranging from 20 ns - 110 ns depending on the water model. These simulations were continued for a further 20 ns using the Nosé-Hoover thermostat^{15,16} with the last10 ns being used for analysis (Table B-9). The largest discrepancy in the bond orientational order parameters between the two thermostats is 0.01 (Table B-9). This corresponds to a shift of 1.8% - 12.5% (Table B-3). This is less than the difference in the bond orientational order parameter brought about by the different simulation set-ups (Section B.7). For these simulations the choice of thermostat has a nominal effect on the structure of confined water.

Table B-9. Values for the four-fold (Ψ_4) and six-fold (Ψ_6) bond orientational order parameter for a simulation of the SPC/E water model at 3.0 GPa, TIP4P/2005 water model at 2.0 GPa and TIP5P water model at 1.0 GPa for the Berendsen¹⁴ and Nosé-Hoover thermostats^{15,16}.

	Berer	ndsen	Nosé-Hoover		
	Ψ_4 Ψ_6		${\Psi}_4$	${\Psi}_{_6}$	
SPC/E	0.22	0.09	0.23	0.08	
TIP4P/2005	0.03	0.17	0.03	0.17	
TIP5P	0.15	0.56	0.15	0.57	

B.8 Values for the Bond Order Parameters

The following tables contain the raw data used in Figure 6-2a and 6-2b.

Table B-10. Shows the data for the channel density (ρ_{chan}), at different applied pressures (P_{ZZ}), and the values of ψ_4 and ψ_6 for SPC/E for the reservoir simulation set-up with the **S** C-O interaction parameters. This data was used in Figures 6-2a and 6-2b in the main text.

P_{ZZ} /GPa	$ ho_{ m chan}$ /kg m ⁻³	ψ_4	${\psi}_6$	
5	1480(4)	0.2186(5)	0.207(2)	
4	1451(4)	0.2394(7)	0.050(1)	
3	1431(4)	0.2421(7)	0.041(1)	
2.75	1356(5)	0.0246(7)	0.073(2)	
2.5	1341(7)	0.0251(5)	0.067(1)	
2.25	1327(7)	0.0255(5)	0.064(1)	
2	1310(7)	0.0245(6)	0.057(2)	
1.5	1271(8)	0.0255(7)	0.051(1)	
1	1222(8)	0.0270(6)	0.048(1)	
0.5	1145(9)	0.0302(5)	0.0444(8)	
0.0001	880(20)	0.0378(8)	0.0472(9)	

Table B-11. Shows the data for the channel density (ρ_{chan}), at different applied pressures (P_{ZZ}), and the values of ψ_4 and ψ_6 for TIP4P/2005 for the reservoir simulation set-up with the **S** C-O interaction parameters. This data was used in Figures 6-2a and 6-2b in the main text.

P_{ZZ} /GPa	$ ho_{ m chan}$ /kg m ⁻³	ψ_4	ψ_6		
5	1430(5)	0.0170(4)	0.8233(5)		
4	4 1408(5) 0.0228(5)		0.7935(7)		
3	1373(5)	0.0179(5)	0.736(1)		
2.75	1358(6)	0.0255(5)	0.699(1)		
2.5	1348(6)	0.0210(8)	0.674(2)		
2.25	1333(7)	0.0214(5)	0.631(2)		

2	1310(10)	0.0237(4)	0.458(6)	
1.75	1272(7)	0.0271(7)	0.123(4)	
1.5	1251(8)	0.0280(6)	0.078(2)	
1.25	1228(8)	0.0287(4)	0.067(1)	
1	1201(7)	0.0304(8)	0.055(2)	
0.75	1170(8)	0.0300(3)	0.0509(6)	
0.5	1131(9)	0.0325(5)	0.0467(7)	
0.25	1080(10)	0.036(1)	0.046(1)	
0.0001	960(20)	0.03400(6)	0.0490(7)	

Table B-12. Shows the data for the channel density (ρ_{chan}), at different applied pressures (P_{ZZ}), and the values of ψ_4 and ψ_6 for TIP5P for the reservoir simulation set-up with the **S** C-O interaction parameters. This data was used in Figures 6-2a and 6-2b in the main text.

P _{ZZ} /GPa	$ ho_{ m chan}$ /kg m ⁻³	ψ_4	${\psi}_6$	
2.5	1385(5)	0.0383(8)	0.6803(9)	
2	1376(2)	0.1080(4)	0.6969(4)	
1.5	1340(6)	0.0581(7)	0.637(1)	
1	1313(7)	0.0993(5)	0.6444(6)	
0.75	1202(8)	0.0267(7)	0.065(2)	
0.5	1162(9)	0.0281(8)	0.051(1)	
0.0001	950(20)	0.0382(6)	0.0492(7)	

B.9 Channel Density as a Function of Applied Pressure



Figure B-9. ρ_{chan} against P_{ZZ} for SPC/E (green), TIP4P/2005 (red) and TIP5P (blue) for the reservoir simulation set-up, using the **C** C-O interaction parameters.



Figure B-10. ρ_{chan} against P_{ZZ} for SPC/E (green), TIP4P/2005 (red) and TIP5P (blue) for the reservoir simulation set-up, using the **W** C-O interaction parameters.

To understand the affect that the carbon-water interactions had on the confined structure these simulations were run with different force-fields. The water channel density against the applied pressure for both the **C** (Figure B-9) and **W** (Figure B-10) interaction parameter sets showed that they have a very similar structure to those

of the Steele parameters (Figure 6-2b). This shows that the water channel density is not largely affected by the water-carbon interactions. There are no clear trends for what specific C-O parameter set produces a consistently lower or higher density that the other sets.



B.10 Force Field Parameters on Confined Water Structure

Figure B-11. ψ_6 and ψ_4 against ρ_{chan} for SPC/E with the **S** (solid line), **C** (dotted line) and **W** (dashed line) C-O interaction parameters for the reservoir simulation set-up.



Figure B-12. ψ_6 and ψ_4 against ρ_{chan} for TIP4P/2005 with the **S** (solid line), **C** (dotted line) and **W** (dashed line) C-O interaction parameters for the reservoir simulation set-up.



Figure B-13. ψ_6 and ψ_4 against ρ_{chan} for TIP4P/2005 with the **S** (solid line), **C** (dotted line) and **W** (dashed line) C-O interaction parameters for the reservoir simulation set-up.

To account for the thickness of carbon atoms in our simulations we have used an effective channel width ($d_{\rm eff}$) given by: $d_{\rm eff} = d - \sigma_{\rm CO}$, where $\sigma_{\rm CO}$ is the Lennard-Jones C-O interaction parameter, and determines the distance from a carbon atom that the C-O Lennard-Jones interaction is zero. This allows us to compare between different force fields and water models where the value of $\sigma_{\rm CO}$ is different. As a result the channel density was calculated by:

$$\rho_{\rm chan} = \frac{N_{\rm chan} M_{\rm H_2O}}{N_{\rm A} (A_{\rm chan} \times d_{\rm eff})}$$
(B.4)

In equation (B.4): N_{chan} is the number of water molecules in the area A_{chan} in the channel; N_A is Avogadro's number; $M_{H,O}$ is the molar mass of water.

It is difficult to directly deduce the impact that different parameter sets will have on the transition pressure of the different water models, because they typically have different values for both σ_{co} and ε_{co} . As both of these parameters can dictate the position of a phase transition^{107,129,261} it is important to determine the impact they have on our simulations. We saw that the three different sets of force field parameters produced a similar ordering to the O position in the confined structures (Figure B11-B13). This suggested that these C-O interactions do not change the nature of the ordered structure that is formed.

Our main phase transition of interest is the first phase transition, which we have defined as the first discontinuous increase in the value of ψ_n for either n = 4 or n = 6. To make the force field comparison easier, we have tabulated the position of the transition for both the channel density and the applied pressure (Table B-13). The range for the transition densities are lowest for the **W** set for all of the water model, but this is most prominent for TIP4P/2005 where this range is on the edges of the density range for the **C** parameter set. This is most probably due to the **W** parameter set having a smaller σ_{co} than the other two sets.

Table B-13. Shows the applied pressure (P_{ZZ}) and water channel density (ρ_{chan}) before and after the SPC/E, TIP4P/2005 and TIP5P had undergone the transition into an ordered structure and the values for ψ_4 and ψ_6 after the water had formed

Water Model	SPC/E		TIP4P/2005			TIP5P			
Forcefield	С	S	W	С	S	W	С	S	W
Min $P_{\rm ZZ}$ (GPa)	2.5	2.75	2.5	1.75	1.75	1.5	0.5	0.75	0.5
Max $P_{\rm ZZ}$ (GPa)	2.75	3.0	2.75	2	2	1.75	1	1	1
Min $ ho_{ m chan}$ (kg m ⁻³)	1354.0	1355.6	1336.8	1287.4	1272.2	1255.5	1185.0	1202.1	1179.6
Max $ ho_{ m chan}$ (kg m ⁻³)	1436.6	1431.0	1405.6	1326.0	1305.2	1291.7	1332.7	1312.7	1299.4
${arPsi_4}$ at max $P_{ m ZZ}$	0.247	0.242	0.234	0.022	0.024	0.024	0.102	0.099	0.055
${\Psi}_{_6}$ at max $P_{_{ m ZZ}}$	0.052	0.041	0.049	0.500	0.458	0.507	0.643	0.644	0.606

an ordered structure. These value are all for the reservoir simulation set-up.

B.11 Removing Electrostatics



Figure B-14. Snapshots of the position of water O atoms when the electrostatics are removed for SPC/E at 3.0 GPa (a), TIP4P/2005 at 2.0 GPa (b) and TIP5P at 1.0 GPa (c) in the xy-plane. The associated values for Ψ_4 and Ψ_6 are shown below the images. Red and blue sphere are used to separate the water O atoms into the two different layers.

It was important to understand the affect that both the electrostatic and Lennard-Jones interactions had on the formation of the different ordered water structures. This was done by running simulations with the parallel plate simulation set-up where the electrostatic interactions were removed, leaving only the Lennard-Jones interactions. They were run with the **S** C-O interaction parameters. These simulations were run for 20 ns using only the last 10 ns for analysis. From snapshots of the simulations (Figure B-14) it was seen that the structure for all of the water models was very similar, and consisted of a hexagonal structure with an AB-stacking conformation. Analysis of the bond orientational order parameter for each of the water models showed that there is a high ψ_6 with a low ψ_4 (Figure B-14) agreeing with the hexagonal structure seen in the snapshots. It was clear from this that the electrostatic interactions are fundamental in controlling the ordered structure that is formed.


B.12 Choice for H-Bonding Criteria

Figure B-15. Contour plots of $d_{\rm H-O}$ against $\theta_{\rm OH-O}$ for parallel plate simulations of SPC/E at 1bar (a), SPC/E at 3.0 GPa (d), TIP4P/2005 at 1bar (b), TIP4P/2005 at 2.0 GPa (e), TIP5P at 1bar (c) and TIP5P at 1.0 GPa (f). The **S** C-O interaction parameters were used. The blue rectangle shows the region that encloses the geometric criteria for a hydrogen bond.

Contour plots of $\theta_{\rm OH-O}$ against $d_{\rm H-O}$ exhibit a region in the top left corner of the plot that is due to hydrogen bonding water molecules (Figure B-15). The geometric criteria of $\theta_{\rm OH-O} > 130^{\circ}$ and $d_{\rm H-O} < 2.4$ Å, can be seen to encompass all of this region (Figure B-15).

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