Electrical Double Layer Potential Distribution in Nanoporous Electrodes from Molecular Modeling and Classical Electrodynamics Analysis

Evan Marshall Ney
emn8389@rit.edu

Follow this and additional works at: https://scholarworks.rit.edu/theses

Recommended Citation
Electrical Double Layer Potential Distribution in Nanoporous Electrodes from Molecular Modeling and Classical Electrodynamics Analysis

by

Evan Marshall Ney

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Mechanical Engineering

Supervised by

Assistant Professor Dr. Patricia Taboada-Serrano
Department of Mechanical Engineering
Kate Gleason College of Engineering
Rochester Institute of Technology
Rochester, New York
June 14, 2016

Approved by:

Dr Patricia Taboada-Serrano, Assistant Professor
Thesis Advisor, Department of Chemical Engineering

Dr. Michael Schrlau
Committee Member, Department of Mechanical Engineering

Dr. Kathleen Lamkin-Kennard
Committee Member, Department of Mechanical Engineering

Dr. Agamemnon Crassidis
Department Representative, Department of Mechanical Engineering
Abstract

When a solid surface is immersed in a solution, the surface can become charged in a variety of ways including crystal lattice defects, dissociation of atoms or molecules, ionization of surface groups, and adsorption of external ions or, in the case of an electrode, via the application of an external potential. The excess charge at the surface results in an accumulation of mobile ions in the solution near the surface. Relative to the charge on the surface, ions of opposite charge (counterions) build up near the surface to neutralize the surface charge, and ions of like charge (coions) are depleted in this region due to the effects of entropy and coulomb repulsion. The resulting distribution of charges in the solution creates an excess electric potential at the interface. This potential drops to the Galvani potential in the solution bulk as the distance from the surface increases. The cumulative result is a phenomenon ubiquitous in electrochemistry known as the electrical double layer (EDL). The EDL governs natural phenomena like colloidal stability and electrokinetic phenomena; it also affects the outcome of electrochemical reactions.

Classical Theory describes the EDL via the combination of the Poisson equation for electrical potential and the Boltzmann distribution of charge within an electric field next to a planar charged solid surface. This approach treats ions as non-interacting point charges in the vicinity of a single-charged surface in contact with a bulk solution. However, most current applications where EDL is relevant involve confinement within nanostructures, where the size of the ions is within one or two orders of magnitude of the size of the structure itself. In such cases, Classical Theory fails, and one must turn to either more complicated theories or molecular modeling techniques. This work focuses on Monte Carlo simulation of the EDL.

A method to describe the EDL in confinement that combines Grand Canonical Monte Carlo simulations (GCMC) with electrodynamics concepts to determine not only the EDL structure, but most importantly the distribution of electrical potential within charged slit-type pores is presented. A benefit of the method in this work is that it computes potential with respect to field-free virtual bulk electrolyte solution implicit in the Grand Canonical ensemble; i.e. it does not require a physical bulk to be included in the simulation model. The method was applied to systems for which Classical EDL Theory can be employed (two non-interacting planar surfaces) for comparison purposes, and then extended to increasingly confined spaces. In contrast to Classical EDL Theory, this method accounts for ion-size and ion-ion interactions, and provides insights into the EDL structure within nanostructures.

The GCMC simulations for slit-type pores considered in this work show that entropy effects lead to the exclusion of coions in a counterion layer which packs up against the charged walls of the pore. This, in conjunction with the fact that electrical effects are long range and extend out into space from the location of the source charge, lead to a semi-oscillatory behavior of the potential profiles not predicted by Classical Theory. The oscillatory behavior, comprised of local minima near the walls and a local maximum in the center of the pore, is diminished in smaller pores as the extent of the electrical effects of the coion exclusion regions begin to overlap even when concentration profiles do not overlap, and bulk conditions for concentration are achieved in the center of the pore. The magnitude of the oscillation is directly related to
surface charge, and the local maximum in the pore center becomes a flat, zero-potential region as pore size increases, pointing towards a true bulk region in terms of distribution of ions and electrical potential.
Acknowledgements

I want to extend a special thank you to my adviser, Dr. Patricia Taboada-Serrano, for being a wonderful colleague and dedicating herself to helping me learn the valuable skills I’ve gathered through working on this project. I’d particularly like to thank her for believing in me and helping me to realize my goals to continue into a Ph.D. program in physics.

I would like to thank my committee members, Dr. Ag. Crassidis, Dr. Kathy L-K, Dr. Michael Schrlau, for having the interest in both my work and my success as a student, and dedicating the necessary time to help me achieve my goals.

Others who have guided or encouraged me on this journey include Dr. Joel Shore, for advising me in computational practices and numerical techniques and, through his class, revealing to me my passion for computational physics. I’d also like to thank Dr. Steven Weinstein for helpful discussion regarding the Classical Theory. I’d like to thank my friends and fraternity brothers who supported me. Thank you for making sure I found time for the important thing in life, and for always being available as an extra set of ears for me to brainstorm with. A special thanks to Kris for being not only a valuable resource for programming tips, but also for being a great friend, and to Chloe for helping me through the tough times and always being there for me.

Finally, I’d like to thank my family. Without the love and support you continually provide, I would not be where I am today. It is because of you I have the drive I do which continually pushes me to be my best.
Table of Contents
List of Figures .................................................................................................................. 6
List of Tables ..................................................................................................................... 8
Nomenclature .................................................................................................................... 9
1.0 Problem Introduction and Context ........................................................................... 11
  1.1 Electric Double Layer at the Solid-Liquid Interface and Classical Modeling of EDL .... 12
  1.2 Potential and Surface Charge .................................................................................. 15
  1.3 Electrosorption and Nanopores .............................................................................. 16
  1.4 Molecular Modeling .............................................................................................. 17
  1.5 Conclusions .......................................................................................................... 19
2.0 The Research Question ............................................................................................. 21
  2.1 How can potential profiles be accurately computed from the outputs of existing molecular modeling programs? ................................................................. 21
    2.1.1 How can the method be validated and accuracy quantified? ............................ 21
  2.2 What is the relationship between experimentally dictated parameters and the resulting electrode surface charge and potential profile in slit-type nanopores and can this be established using molecular modeling? ........................................ 21
    2.2.1 What simulation method is most appropriate? .................................................. 22
    2.2.2 What system model is most appropriate? ......................................................... 22
    2.2.3 What parameters affecting EDL structure should be investigated? .................. 22
3.0 Literature Review .................................................................................................... 23
  3.1 Experimental Methods ......................................................................................... 23
  3.2 Classical Theories .................................................................................................. 24
  3.3 System Models ....................................................................................................... 26
    3.3.1 The Primitive Model ....................................................................................... 27
    3.3.2 Non-Primitive Models .................................................................................... 28
  3.4 Electric Double Layer at a Single Planar Interface ................................................ 29
    3.4.1 Early Simulations ............................................................................................. 29
    3.4.2 Ion Valence, Ion Size, and Mixtures of Electrolytes ......................................... 31
  3.5 Electric Double Layer in Pores and Channels ....................................................... 33
    3.5.1 Ion Valence Effects ....................................................................................... 34
    3.5.2 Competitive effects of charge and size asymmetries ....................................... 35
    3.5.3 Explicit Solvent Effects .................................................................................. 36
  3.6 Electric Potential from Monte Carlo Simulation ................................................... 37
4.0 Objectives of the Proposed Work ............................................................................. 39
4.1 Develop a method to convert Monte Carlo simulation concentration profiles to potential profiles .......................................................... 39

5.0 Models of Electrical Double Layer inside Nanoporous Electrodes from Classical Theory ... 41

5.1 The Poisson Equation ........................................................................................................................................................................... 41

5.1.1 The One Dimensional Poisson Equation Between Two Charged Walls ................. 42

5.1.2 The Dimensionless Poisson Equation in One Dimension .................................................. 43

5.2 The Poisson Boltzmann Equation ............................................................................................................................... 44

5.2.1 Single Wall Solution for Single One-One Electrolyte ............................................. 45

5.2.2 Double Wall Solution for Single One-One Electrolyte ........................................ 48

5.2.3 Comparison to Grand Canonical Monte Carlo Concentration Profiles ............... 52

6.0 Models of Electrical Double Layer Potential inside Nanoporous Electrodes from Grand Canonical Monte Carlo Simulations and the Electrostatic Poisson Equation................................. 56

6.1 Work Performed to Date ......................................................................................................................................................... 56

6.2 Potential from Direct Numeric Integration .......................................................................................................................... 57

6.2.1 Obtaining Charge Density and Creating a Continuous Function ....................... 57

6.2.2 Runge-Kutta Half Pore Initial Value Problem ...................................................... 60

6.2.3 Finite Difference Full Pore Boundary Value Problem ........................................ 65

7.0 Models of Electrical Double Layer Potential inside Nanoporous Electrodes from Grand Canonical Monte Carlo Simulations and Fundamental Electrostatic Concepts ................................................................. 68

7.1 Grand Canonical Monte Carlo Energy Calculations ............................................ 68

7.2 The Algorithm ................................................................................................................................................................ ...... 70

7.3 Individual System Results and Discussion ............................................................... 72

7.4 Summary of Results .................................................................................................................. 83

8.0 Conclusions, Recommendations, and Future Work ...................................................... 87

9.0 References ............................................................................................................................................................................. 91

A. Appendix: Excerpts of Grand Canonical Monte Carlo Simulation Code Updated for Potential Profile Calculations ............................................................................................................................ 97
List of Figures

Figure 1: EDL representations according to the Helmholtz (a) Gouy-Chapman (b) and Gouy-Chapman-Stern (c) theories [7] ...............................................................13
Figure 2: Potential Distribution of the GSCG double layer with constant dielectric constants [8] .........................14
Figure 3: Displacement Field Boundary Condition .........................................................................................42
Figure 4: Analytic PB Solution for potential profiles with a single 1:1 electrolyte and a single charged interface .......47
Figure 5: Analytic PB Solution for Concentration Profiles with a single 1:1 electrolyte and a single charged interface ...........................................................................................................48
Figure 6: Analytic PB solution for a single 1:1 electrolyte between two charged interfaces (a) at different surface charges and (b) at different pore widths ........................................................................49
Figure 7: Single-wall and double-wall PB solutions at $\sigma^*=1.191$ for pore widths of (a) 2-nm and (b) 5-nm .........50
Figure 8: Double-wall PB solution for concentration profile of a single 1:1 electrolyte inside a slit-type pore for varying pore sizes. ..........................................................................................51
Figure 9: Double-wall solution for concentration profile of a single 1:1 electrolyte inside a slit-type pore at varying surface charges ........................................................................................................51
Figure 10: Comparison of GCS theory and GCMC simulation concentration profiles for different pore sizes (2-nm (a), 5-nm (b), and 10-nm (c)) at the same surface charge ($\sigma^* \approx 1.191$) ........................................53
Figure 11: Comparison of GCS theory and GCMC simulation concentration profiles for different surface charges ($\sigma^*=0.000$ (a), $\sigma^*=1.166$ (b), $\sigma^*=2.375$ (c), and $\sigma^*=3.802$ (d)) in a 5-nm pore ........................................54
Figure 12: Root mean square error between GCS and GCMC concentration profiles ........................................55
Figure 13: Example of bin division of simulation box in a 3D view (a) and in a 2D view with the charged walls on the left and right sides (b) ........................................................................................................58
Figure 14: Interpolation of the raw GCMC charge density data for a 5-nm pore at $\sigma^*=1.166$ (a) using a cubic spline interpolation (b) and a piecewise constant interpolation (c) ..............................................59
Figure 15: Half pore potential profile from Runge-Kutta solver compared with PB single-wall solution. Plot are for pores at equal surface charge ($\sigma^* \approx 1.191$) with pore widths of 2-nm (a), 5-nm (b), and 10-nm (c) ...............62
Figure 16: Half pore potential profile from Runge-Kutta solver compared with PB single-wall solution. Plot are for pores of equal width (5-nm) with surface charges of $\sigma^*=0.000$ (a), $\sigma^*=1.166$ (b), $\sigma^*=2.375$ (c), and $\sigma^*=3.802$ (d) ....................................................................................................................63
Figure 17: Runge-Kutta solution for half pore potential and derivatives for the left half (a) and right half (b) of the 5-nm pore at $\sigma^*=1.166$ ..................................................................................................................64
Figure 18: Comparison of half pore potential from Runge-Kutta using (a) cubic spline and (b) piecewise constant interpolation of the charge density function ...........................................................................65
Figure 19: Schematic of the main simulation box with charged sheets for long range corrections shown ..............69
Figure 20: Flow chart of method to calculate potential profiles from Monte Carlo simulations .........................71
Figure 21: Example of GCMC simulation box for different pore sizes (2-nm (a), 5-nm (b), and 10-nm (c)) with positive coions (red) and negative counterions (blue) shown to scale for 1M systems at $\sigma^*=0.000$ ..........73
Figure 22: Comparison of concentration profile and potential profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 2-nm pore at $\sigma^*=0.000$ ........................74
Figure 23: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 2-nm pore at $\sigma^*=1.183$ ..............................................................................74
Figure 24: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 2-nm pore at $\sigma^*=2.384$ ..............................................................................75
Figure 25: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 2-nm pore at $\sigma^*=3.815$ ..............................................................................76
Figure 26: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 5-nm pore at $\sigma^*=0.000$ ........................................77
Figure 27: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 5-nm pore at $\sigma^* = 1.166$ ................................................................. 77
Figure 28: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 5-nm pore at $\sigma^* = 2.375$ ................................................................. 78
Figure 29: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 5-nm pore at $\sigma^* = 3.802$ ................................................................. 79
Figure 30: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 10-nm pore at $\sigma^* = 0.000$ ................................................................. 80
Figure 31: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 10-nm pore at $\sigma^* = 1.166$ ................................................................. 80
Figure 32: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 10-nm pore at $\sigma^* = 2.384$ ................................................................. 81
Figure 33: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 10-nm pore at $\sigma^* = 3.815$ ................................................................. 81
Figure 34: Summary plots of potential profiles from GCMC simulations for 2-nm (a), 5-nm (b), and 10-nm (c) pores .................................................................................................................. 84
Figure 35: Average surface potential (a) and potential in the center of the pore (b) in different sized nanopores as a function of surface charge ........................................................................... 85
List of Tables
Table 1: Parameters of systems considered in this work .................................................................46
Table 2: Parameters of systems simulated using GCMC to obtain potential profiles.........................61
Table 3: Estimates of run times for different system sizes and number of iterations ................................82
Nomenclature

CMC = (Canonical Monte Carlo)
CN = Counterion
CO = Coion
c* = Bulk normalized local number concentration
C# = Constant of integration
DFT = (Density functional theory)
D = Electric displacement field (C/m²)
d = Ionic diameter and distance normalization constant (m)
EDL = (Electrical double layer)
E = Electric field (V/m)
e = Elementary charge (C)
GC = (Gouy-Chapman)
GCMC = (Grand canonical Monte Carlo)
GCS = (Gouy-Chapman-Stern)
GCSG = (Gouy-Chapman-Stern-Grahame)
HNC = (Hypernetted chain theory)
IDM = (Ion dipole model)
IHP = (Inner Helmholtz plane)
k = Boltzmann constant (J/K)
k_{RK} = Fourth order Runge-Kutta slope estimate
k# = Slopes to be averaged to get k_{RK}
L = Length of the square wall of the simulation box
N = Number of ions
n = Local number concentration (m⁻³)
n₀ = Bulk number concentration (m⁻³)
̂n = Normal unit vector
MC = (Monte Carlo)
MD = (Molecular dynamics)
MPB = (Modified Poisson-Boltzmann)
MSA = (Mean spherical approximation)
OHP = (Outer Helmholtz plane)
OZ = (Orstein-Zernicke)
PB = (Poisson-Boltzmann)
PM = (Primitive model)
PY = (Percus-Yevik)
Q_{n_{et}}^{bin} = Net charge per bin in the simulation box (C)
Q = Net ionic charge (C)
RPM = (Restricted primitive model)
\( r_{ij} \) = Center to center distance between ions \( i \) and \( j \)

\( \vec{r} \) = Distance vector from a plane (m)

SPC/E = (Simple point charge)

SPM = (Solvent primitive model)

TIP4P = (Four point transferrable intermolecular potential)

\( T \) = Temperature (K)

\( u_{i,\text{sheet}} \) = Interaction potential of ion \( i \) and a charged sheet of specified size centered at the location of ion \( j \)

\( u_{i,\text{wall}} \) = Interaction energy of ion \( i \) and infinite uniformly charged wall

\( V \) = Volume (m³)

\( v_{\text{bin}} \) = Volume of a bin in the simulation box (m³)

\( v_i \) = Interaction energy of ion \( i \) and charged sheet outside simulation box (V)

\( v_{ij} \) = Ion – ion pair potential (V)

\( \bar{E}_i \) = Potential of mean force (V)

\( w^* \) = Normalized pore width

\( x \) = Distance (m)

\( x^* \) = Normalized distance

\( \Delta x \) = Step size of discretized position (m)

\( z_i \) = Valence of ionic species \( i \)

\( \varepsilon \) = Permittivity in a medium (C²/Nm²)

\( \varepsilon_r \) = Dielectric constant/Relative permittivity

\( \varepsilon_0 \) = Permittivity of free space (C²/Nm²)

\( \kappa \) = Debye-Huckle parameter (m⁻¹)

\( \mu \) = Chemical potential (J/kg)

\( \rho \) = Volumetric charge density (C/m³)

\( \rho^* \) = Normalized volumetric charge density

\( \rho_n \) = Normalization constant for volumetric charge density (C/m³)

\( \sigma \) = Surface charge density (C/m²)

\( \sigma_f \) = Free surface charge density (C/m²)

\( \sigma_{ij} \) = Maximum distance of closest approach between ions \( i \) and \( j \) (m)

\( \sigma_n \) = Normalization constant for surface charge density (C/m²)

\( \sigma_0 \) = Surface charge density at charged wall (C/m²)

\( \psi \) = Electric potential (V)

\( \bar{\psi} \) = Transformed \( \psi \) into vector space

\( \bar{\psi}_n \) = Null space of \( \bar{\psi} \)

\( \psi^* \) = Reduced Potential

\( \psi_n \) = Normalization constant for potential (V)

\( \psi_d \) = Potential at the start of the diffuse layer (V)

\( \psi_0 \) = Surface potential at the charged wall (V)
1.0 Problem Introduction and Context

The branch of general chemistry that deals with the influence of electric fields on chemical systems is known as electrochemistry. When systems involving electric charge near an interface are in question, electrochemistry and another subfield called surface chemistry become intimately related. The phenomena which occur under such circumstances is referred to as electric interfacial phenomena and is ubiquitous in nature. One such phenomenon, known as the electrical double layer (EDL), has a strikingly important influence in many physical, chemical, and biological systems. An EDL refers to clouds of ions in solution that are attracted to and become immobilized by an oppositely charged interface.

Electrical double layers play a role in many widely used technologies. For example, using a sacrificial metal in a technique called cathodic protection is a common method to protect pipes and boats from corrosion. The chemical reactions involved are closely tied with EDL formation. Electrical double layers are also prominent in the reactions involved in passivation of metals through anodizing. Anodizing creates a layer of oxide on the surface of the metal that is more resistant to corrosion than the original metal surface. Other systems take advantage of EDL formation between two electrodes. These systems have a wide range of applications in energy storage systems such as batteries, super capacitors, and fuel cells. Such applications are more important than ever in today’s society, which is becoming increasingly dependent on the advancement of electronic capabilities. Another use of EDL formation on the surface of an electrode is in electric field driven separation processes. In nanochannels and porous media, the formation of an EDL effectively traps ions on the surface. Studies indicate that depending on the electrode and ionic properties it may be possible for one ionic species to be trapped over another, a phenomenon known as selectivity [1]. This can be used in potentially low cost and low waste water filtration systems.

To further support the breadth of applications in which EDL play a key role, colloidal suspensions can be discussed. These are mixtures in which the solute particles are significantly larger than those of the solvent, with radii typically on the order of 1-nm to 1-μm [2]. The solute and solvent can be any combination of solid, liquid, or gas, including emulsions, aerosols, foams and sols. Through natural thermodynamic processes, the surfaces of colloidal particles become charged, which then leads to the formation of an EDL. Electric double layers in colloidal systems serve a wide range of purposes, from something as simple as preventing milk from curdling to complex industrial applications in the paper, ink and water treatment industries [3]. Electrical double layers can form in a similar manner in biological systems as well. The formation and structure of an EDL in a biological system can determine the behavior of protein site and membrane processes [4]. With such a wide range of applications in nature and industry, EDL assume an important role that is largely taken for granted.

Ultimately, in any electrochemical processes governed by transfer and transport of charge to surfaces, an EDL will exist. The growing demand for EDL dependent technologies is coupled
with a drive for smaller scale devices. Devices which incorporate nanoscale geometries are being found to possess unique properties that could prove to be invaluable if harnessed properly. For example, electric capacitance can be increased by using an electrode with large specific surface area, such as a nanoporous electrode [5]. When the size of the pores approach the size of a few molecular radii, an anomalous increase in capacitance is observed in electrochemical capacitors [6]. Nanopores can also be beneficial in ion selectivity, where species larger than the size of the pores are not captured in the EDL, but smaller species are able to stick inside the pores. On the nano scale, the size of the pore or channel is on the order of the size of the EDL. Thus, EDL is significantly impactful to the transport of charges in such environments. With this in mind, it is easy to see how a thorough understanding of EDL in nano scale systems is of growing importance. However, it is very difficult to make physical measurements in such systems due to the small length scales involved, so the field relies highly on the use of analytic theories and computer simulations for insight. Unfortunately, a lack of experimental tools makes it difficult to validate theoretical work, and the classical theories developed over a century ago fail to capture newly observed phenomena such as the anomalous increase in capacitance and the mechanisms behind ion selectivity in nanoporous electrodes [6].

1.1 Electric Double Layer at the Solid-Liquid Interface and Classical Modeling of EDL

When a solid surface is immersed in a solution, the surface can become charged in a variety of ways, e.g. crystal lattice defects, dissociation of atoms or molecules, ionization of surface groups, and adsorption of external ions [2]. What happens on the solid side of the interface is not too interesting, as the arrangement of atoms in a solid phase is structured and remains relatively quiescent. However, atoms and molecules on the solution side of the interface are free to move around, which leads to more interesting phenomena. In an electrolyte solution, the solute ionizes when dissolved in the solvent, leaving charged particles (ions) free to move around. In aqueous solution the ions become surrounded by water molecules, or hydrated, due to water’s polar configuration. The excess charge at the solid surface of a certain sign will attract ions of opposite sign (counterions) and repel ions of the same sign (coions) in the solution. A buildup of counterions near the surface creates an excess electric potential in the region close to the surface. This potential drops over some distance, from the value at the surface to some lower Galvani potential in the solution bulk. The resulting structure is known as the EDL, the size of which is characterized by the extent of excess ions and electric potential from the surface.

Helmholtz first proposed the existence of the EDL in the late 1800s, describing the resulting ion distribution as a plane of charge some distance from the surface, equal in magnitude but opposite in sign to that on the solid surface (Fig. 1a) [2]. This is likely where the term double layer originated. In the early 1900s it was found independently by Gouy and Chapman that such a theory was unrealistic, as it was becoming more understood that solutions are comprised of molecules in constant thermal motion. Rather than a solid plane, the Gouy-Chapman (GC) double layer describes the distribution of charge in the solution as being loosely attached to the surface, with a potential that drops off exponentially according to the Boltzmann distribution
The GC theory was further refined by Stern to account for the finite size of ions and adsorption. Stern’s contribution included a stationary, adsorbed layer of finite sized ions between the charged surface and the GC diffuse layer. Stern proposed that, due to the finite size of ions, no charge could exist between the ion’s distance of closest approach (one molecular radius) and the surface. Thus, the so called Stern layer consists of a space devoid of charge extending one molecular radius from the surface, followed by a plane of charge passing through the centers of the adsorbed ions marking the outer edge of the layer [2]. Hence, the Gouy-Chapman-Stern (GCS) theory effectively combines the Helmholtz plane and the GC diffuse layer theories (Fig. 1c).

![Figure 1: EDL representations according to the Helmholtz (a) Gouy-Chapman (b) and Gouy-Chapman-Stern (c) theories [7]](image)

Typically, the potential drop across the Stern layer is assumed linear. The GCS theory effectively accounts for systems in which ions accumulate next to the charged surface without triggering chemical reactions such as dehydration. This type of adsorption is termed electrosorption. The GCS theory of the EDL is exceedingly popular due to its simple analytic nature, despite increased findings of its limited applicability.

Another widely used theory of the EDL, derived from a canonical EDL experiment at a mercury-aqueous solution interface, is a refinement of the GCS theory known as the Gouy-Chapman-Stern-Grahame (GCSG) theory. This theory goes beyond systems involving only electrosorption to account for ions becoming dehydrated and specifically adsorbed to the surface. Figure 2 shows how this theory splits the Stern layer into two planes. The plane closest to the charged surface is known as the inner Helmholtz plane (IHP) and passes through the centers of a layer of specifically adsorbed ions on the surface, in which their hydrating water molecules have been stripped away. Another plane, called the outer Helmholtz plane (OHP), coincides with the
outer edge of the Stern layer, passing through the centers of larger, fully hydrated ions at their plane of closest approach. At distances further into the solution beyond the OHP, the GC diffuse layer takes the structure back to that of the bulk. Expressions of varying complexity can be used for the electric permittivity or dielectric constant in the two spaces into which the Stern layer is divided, but typically the values are assumed constant, although not necessarily equal to the value in the bulk. The OHP is very close to, and often coincides with, a fluid shear plane at which experiments can measure the potential. The potential at this location is an important quantity in colloidal systems known as the zeta potential. Zeta potential is one of the few measurements that can be made to directly characterize potential in EDL.

![Potential Distribution of the GSCG double layer with constant dielectric constants](image.png)

Figure 2: Potential Distribution of the GSCG double layer with constant dielectric constants [8]

To understand the length scales involved in EDL, the mercury-aqueous solution interface experiment can be used to gain insight to a typical system. The extent of the potential distribution across the EDL can range over distances on the order of 100-nm in dilute electrolyte solutions, and contracts to lesser distances with increasing electrolyte concentration. The distance from the solid surface to the inner Helmholtz plane is around the order of one bare ionic radius, roughly 0.1-nm, while that to the outer Helmholtz plane is roughly one hydrated ionic radius, about 0.5-nm [2]. It is easy to see, for example, inside a nanopore with radius of less than 100-nm, the structure of the EDL will become more complex and its influence on ions within the pore will be enhanced.

The EDL is the root phenomenon of a variety of other useful effects known as electrokinetic phenomena. Such effects, including electrophoresis, electro-osmosis, streaming potential and streaming current, are prevalent in many contemporary technologies and are some of the only ways to experimentally measure properties of the EDL. Electro-osmosis refers to the motion of liquid due to an applied electric field and is important to many chemical separation
techniques. Electrophoresis is the motion of charged particles under the influence of an electric field and can be used to characterize particulate materials. Using electrophoresis, one can measure the zeta potential at the shear plane between the adsorbed ions in the Stern layer and the diffuse ions further from the surface of a particle. Zeta potential of porous and flat surfaces can also be measured using streaming potential and streaming current. These electro-kinetic phenomena occur when a pressure difference is applied to a channel or porous body with charged walls. The excess charge near the walls due to EDL formation is moved by the pressure, creating a convective current called streaming current. Charge can then build on one end of the channel, creating a potential difference called streaming potential. Streaming potential is often used in to regulate coagulant levels during wastewater treatment [3]. Electro-kinetic phenomena have many other industrial and technological applications than the few mentioned here. As the underlying phenomenon to so many higher level applications, it is clear to see how a thorough understanding of the EDL is beneficial to many industries. The size of the EDL depends on two factors: the amount of excess charge on the surface, or surface charge density, and the ionic strength, or concentration of ions in solution. The magnitude of the surface charge will determine the amount of charge distributed within the EDL, i.e. the distribution of electric potential.

1.2 Potential and Surface Charge

Two important concepts in understanding the EDL are those of potential and surface charge. Closely related to electric charge, electric potential is a measure of the electric potential energy per unit charge at a location in space [9]. The difference in potential at two locations is equivalent to the work required to bring a unit of charge from one point to the other. In classical electrodynamics, the electric field can be expressed as the negative gradient of the electric potential function. Due to the atomic environment within a material phase, there exists a potential inside the bulk of the phase known as the inner or Galvani potential. When two phases are in electrical contact, the Galvani potential is a theoretical measure of the energy required to bring a test charge from the interior of one phase to the interior of the other. The Galvani potential between two phases cannot be physically measured unless the phases are identical, as it neglects the size of the test charge. An infinitely small charge would be influenced solely by electrical effects, but a real charge of finite size would also interact with the different atomic environments in each phase which cannot be accounted for unambiguously. However, the effect of the Galvani potential can be grouped with the effect of chemical potential, which accounts for the free energy in a system, to form a function which completely characterizes the influences on a particle’s motion within a phase known as electrochemical potential. Electrical, chemical, and electrochemical potentials are important concepts in understanding the EDL, whose structure relies on the motion of charged particles within a phase. Another potential involved with interfacial phenomena is the outer or Volta potential. This is defined as the energy required to bring a positive point charge from infinity to a location very close, but just outside, the surface. This potential difference is easily measured experimentally by placing probes near the surface of the phases and is dependent on the excess charges and dipolar constituents near the surfaces.
Electric potential in particular is a crucial quantity in EDL systems, because other important quantities like electric field, electric force, and electric energy can be calculated from this using electrodynamics [9].

Another important quantity, which is related to electric potential, is surface charge density, or charge per unit area. All materials inherently contain an imbalance of free energy between their surface and the bulk due to the asymmetry of surrounding atoms. When two phases come into contact, charged constituents near the interface (e.g. ions, electrons, and dipolar constituents) arrange themselves to minimize this free surface energy, leading to an effective excess charge on the surface. This surface energy can also lead to phenomena such as crystal lattice defects, dissociation of atoms or molecules, ionization of surface groups, and adsorption of external ions, which comprise a few of the most common processes resulting in a buildup of charge on the surface [2]. From classical electrodynamics it can be shown that surface charge is related to the derivative of electric potential normal to a surface via Gauss’ Law [9]. This leads to an important boundary condition imposed by the laws of classical electrodynamics. Namely, the magnitude of the discontinuity of electric potential across an interface depends on the surface charge and the electric permittivity of the media on either side. Electric permittivity is a measure of how easily an electric field can be formed in a medium. It should be noted that classical electrodynamics is a continuum theory, and thus the surface charge is usually treated as a continuous distribution. This is a simplification of the true nature of charged surfaces, which are comprised of discrete charged sites. This aspect becomes more important when dealing with nano scale geometries, where continuity assumptions become less appropriate. With newer nano manufacturing technologies constantly emerging, the use of nano structures, particularly in electrochemical capacitors, is becoming more commonplace and an increasingly important area of study.

1.3 Electrosorption and Nanopores

Potential induced sorption on a surface in which no chemical reactions take place is known as electrosorption [10]. This is a primary feature in many EDL, and is a key mechanism behind the charge storage capabilities of EDL. In aqueous electrolyte solutions, when the surface charge and potential are within appropriate ranges, mobile charges in the solution effectively stick to the surface via electrosorption without dehydrating. This action plays an important role in EDL capacitors and separation processes. It was briefly discussed how such processes can be enhanced using nanoporous materials. The categorization of nanopores can be slightly inconsistent throughout the literature. Typically, nanoporous materials contain pore sizes in the range of less than 100-nm. More precise terminology is often used to describe materials with pores sizes ranging from less than 2-nm, between 2-nm and 50-nm, and greater than 50-nm as microporous, mesoporous, and macroporous, respectively [11]. A promising candidate for producing highly conductive porous electrodes with well controlled pore sizes is carbide-derived carbon. Metals and metalloids can be removed from the carbide lattice using high temperature chlorination, leaving behind a nanoporous carbon shell. This technique can create nanoporous
carbon with a mean pore size in the range of 0.5-nm to 3-nm, accurate to better than 0.05-nm [12]. Carbon nanotubes are another commonly used conductive material with a highly tunable diameter that can be used for charge storage and ion selectivity.

Electrosorption is the basis for EDL capacitors [13-16]. In its simplest form, the system follows the Helmholtz plane description. The surface charge and the electrosorbed ions assume roles similar to that of the two charged plates in a parallel plate capacitor. Better expressions for the theoretical capacitance value can be obtained from the GC theory and its derivatives, and cyclic voltammetry can be used to experimentally measure the capacitance of EDL systems. Attempts to maximize charge storage in EDL capacitors usually include the use of porous electrode materials, which provide a large specific surface area. Moreover, an anomalous increase in capacitance has been observed in porous electrodes whose pore size is around the size of a few molecular radii [6, 17]. This strange behavior is completely uncaptured by most of the current EDL theories and is largely not understood. Investigation into the mechanisms behind this anomalous behavior of EDL in nanopores is underway and molecular modeling simulations are one of the few methods that may be able to provide detailed insight into the phenomenon.

Another application of electrosorption in nanoporous materials is related to ion selectivity. In systems that contain multiple electrolytes, depending on a few characteristics of the system such as pore size, ion size, and ion valence, it has been shown that under certain conditions one ionic species can become predominantly electrosorbed over another. This is known as ion selectivity and has applications in separation processes for water purification and desalinization [13-16]. The structure of the EDL in nanopores determines selective transport of ions through ionic channels and biological membranes [18-20] and the size of the pore can be used to exclude larger ions. Experimental measurements have shown that a relationship exists between pore size in nanoporous electrodes and dimensions of the ions and can determine the electrosorption behavior [21, 22]. Efforts towards understanding how to tune system parameters in order to selectively remove a desired ionic species from solution through electrosorption in the EDL is a prominent feature in this work.

1.4 Molecular Modeling

Molecular modeling is an alternative theoretical method to study EDL systems that is not as restricted to the many assumptions needed to obtain solutions from classic analytical theories. Molecular modeling uses numerical methods and computers to solve many body problems, such as that of the EDL, which are impossible to solve analytically. Computer simulations were first used to model simple systems was in the late 1950’s, although computational results were not treated without skepticism until years later. Torrie and Valleau are credited as being some of the first to use molecular modeling for EDL systems in the 1980’s [23]. While simulations involving molecular systems are blanketed with the term molecular modeling, there are a variety of different molecular modeling techniques. Most notably, molecular dynamics (MD) and Monte Carlo (MC) simulations are the most common methods [24, 25] incorporated in the
computational study of EDL. Oddly enough, the basic algorithms used in MD and MC simulations have not changed much since the 1950’s.

According to Frenkel and Smit, MD simulations were first applied to a liquid in 1964 [24]. Molecular dynamics simulations have merit in their ability to model the dynamics of a many bodied system. MD simulations use classical mechanics to solve Newton’s equations of motion. The ion-ion interactions are governed by some defined interaction potential, a common example being the Lennard-Jones potential. The interactions are tabulated for all the particles in the system, and Newton’s laws of motion are then numerically integrated to obtain the trajectories of the individual particles. Knowing the positions and velocities and making a few assumptions about the nature of the system then allows the use of statistical mechanics to calculate average macroscopic properties of the system, such as temperature and pressure. A benefit of MD simulations is that they store dynamical information, which allows for the calculation of dynamical quantities like diffusion coefficient. However, the biggest downfall of MD simulations comes with the costly inter-particle force calculation, which usually involves a tabulation of the distance between every possible pair of particles. It is easy to see how this causes the computational cost of MD simulations to be significant and highly dependent on the size of the system. In turn, this usually requires that MD simulations involve either small systems or short simulation times. There are a variety of methods that can be implemented, such as periodic boundary conditions, to allow for meaningful computation in a manageable amount of time, but a common MD simulation typically equates to only a few picoseconds of observation time for a real system.

Another widely used type of simulation for molecular systems is the Monte Carlo (MC) simulation. For identical systems, MC simulations can work quicker than MD simulations because they do not compute details about individual particle trajectories that would be provided by MD simulations. However, the results of MC simulations are used similarly to MD simulations in that statistical averages can be used to compute macroscopic properties. MC simulations do not integrate Newton’s laws of motion to obtain information about the particles. Rather, a statistical ensemble is given a random initial state in the position-momentum phase space, and the state of each particle is changed at random. If the change brings the system to a more stable state by, for example, lowering the total energy, the change is accepted. If the change is not favorable, it is accepted only a specified percentage of the time. This is known as the metropolis algorithm and is ubiquitous in MC simulations. If the simulation is run long enough, the system will eventually reach a stable equilibrium. Hence, MC simulations can only be used for equilibrium studies, not dynamical analysis, but statistical averages of the particle positions and momenta can still give insight into the equilibrium macroscopic properties of the system. In many cases, real systems contain so many particles that information about individual particles is neither desired nor useful. In these scenarios, MC simulations provide a reasonable method for obtaining equilibrium properties of a system by computational means. The results of MC
simulations are, apart from statistical uncertainties, exact for the model to which it is applied, and thus provide a great method of comparison for analytical theories [4].

Both MD and MC simulations have merit in different applications. This work prefers the use of MC simulations, as they are usually more flexibly applied to different systems and models, while MD simulations are more sensitive to these aspects in terms of computational cost. The type of statistical ensemble to which a MC simulation is applied is often tacked onto the name. Typically, canonical MC (CMC) simulations and grand canonical (GCMC) simulations are employed in the study of EDL. Canonical ensembles are isolated systems in thermal equilibrium with a reservoir at constant temperature. Hence, these systems maintain constant particle number (N), volume (V), and temperature (T), but are allowed to exchange energy with the surroundings (reservoir). Grand canonical ensembles are isolated systems that maintain both thermal and chemical equilibrium with a reservoir, and accordingly maintain constant chemical potential (μ), volume, and temperature. Grand canonical ensembles are a more natural choice to apply in pores, as maintaining constant chemical potential with a reservoir allows the number of particles in the system to reach equilibrium with the bulk. This is important because the total number of particles in the pore could have a significant effect on the structure of the EDL in such a confined space.

1.5 Conclusions

As the capabilities of computational technology continue to improve, molecular modeling is becoming an increasingly more useful tool to examine EDL properties. Molecular modeling can be applied to any system, even those in which Classical Theory cannot. While more complicated integral equation theories attempt to capture real effects excluded from the canonical GCS theory such as the discreteness of charge, ion-ion interactions, and finite size effects, molecular modeling can capture the same effects with comparatively little effort. While computer simulations have been shown to predict accurate results for ion concentration profiles in EDL, little emphasis has been placed on tying simulation results to much beyond EDL structure and capacitance in nanoporous systems. Simulations work well to output ion concentration distributions (i.e. number of ions at some distance from the charged surface), but a method to convert these results into the theoretically useful electric potential profile with accuracy has yet to be used with quite an impact. Moreover, using such potential profiles from molecular modeling to relate experimental parameters to theoretically predicted EDL structure could prove valuable in manipulating electrosorption selectivity in real experimental systems.

The objective of this work is to propose a method to accurately convert GCMC simulation results for ion concentration profiles into electric potential profiles. The method will be validated against the classical GCS theory using a benchmark simulation of a simple system in which the theory’s assumptions hold. Once the method has been validated, further simulations will be used to investigate electric potential profiles inside nanopores for various experimental conditions including electrolyte concentrations, electrode surface charges, and pore sizes relevant to real
world applications. Results will be used to develop a relationship between surface potential and surface charge in specific porous EDL systems.

Knowing the electric potential distribution is critical in order to understand EDL systems. Potential at the electrode surface and zeta potential are some of the few quantities that can be physically measured in experiments. In nanopores, measurement becomes even coarser. Only the net charge stored in the double layer can be measured using chronoamperometry. Surface charge at the electrode is a quantity that cannot be measured in experiments, but is intimately related to the structure of the double layer and is therefore important in understanding EDL capacitance and electrosorption selectivity. The nature of this work will allow for a better understanding of the correlation between the experimental parameters, such as surface potential, and the resulting surface charge that will exist in nanoporous EDL. This could open new avenues for experimental design. Conducting experiments is costly both in time and money. Therefore, the ability to use molecular modeling to understand which experimental parameters will provide a desired surface charge and electric potential distribution prior to conducting a physical experiment is invaluable.
2.0 The Research Question

The goal of the present work is to link classical electrodynamic concepts with molecular scale models and simulations in order to fully describe the structure of the electrical double layer (EDL) in terms of ion and potential profiles. If achieved, macroscopically measured parameters on charged interfaces such as applied potential, zeta potential, or total charge accumulated at the interface (EDL capacitance or electrosorption capacity) can be linked to possible molecular scale structures and properties.

2.1 How can potential profiles be accurately computed from the outputs of existing molecular modeling programs?

With the limitations of current experimental techniques, it is not possible to obtain more detail on EDL structure than a few integral quantities such as surface potential or zeta potential from physical measurement of EDL systems [4]. In nanopores, one can only experimentally determine the total charge contained in the EDL. Thus, one must rely on theory or simulation to gain any insight into the full EDL structure and profiles of individual species involved. However, the main output of molecular modeling simulations is ion concentration profiles. Hence, a method to compute electric potential from ion concentration profiles is necessary. Once the potential profile is obtained, it can be integrated to obtain experimental quantities like surface potential, and can also be used to derive the electric field, electrostatic force, and electrostatic energy in a given system. Such quantities play an important role in understanding and predicting how electrical and chemical interactions will ensue in such a system, and some of them can be used to achieve experimental validation.

2.1.1 How can the method be validated and accuracy quantified?

Methods are typically validated by comparing the result in question to other results obtained for the same system. These comparison results can come from other researchers who used the same method, from analytic results obtained from theory, or from experimental data. Regardless of the validation procedure, it is imperative to have confidence in the results obtained from a novel method before the method can be used for any further study. For this work, it is logical to simulate a simplified system for which an analytic solution to the theory is applicable and valid and compare simulation results to this solution.

2.2 What is the relationship between experimentally dictated parameters and the resulting electrode surface charge and potential profile in slit-type nanopores and can this be established using molecular modeling?

Recent findings show an enhanced performance of EDL dependent devices when the EDL is confined within nano scale geometries, such as in nanopores [6, 17]. Despite a lack of experimental methods to perform detailed investigations of EDL in nano scale geometries, still little work has been conducted at this length scale via simulation. Hence, it is important not only
to use established simulation methods to understand the structure associated with EDL in these systems, but also to tie simulation results to experimental quantities like applied potential. If validated, this relationship could allow the efficient development of experimental systems by pre-determining through simulation the experimental parameters needed to achieve a desired EDL structure.

2.2.1 What simulation method is most appropriate?

With a plethora of simulation methods available today, choosing an appropriate method is key. Monte Carlo simulations and MD simulations each have their own benefits and pitfalls, depending on the nature of the system being simulated and the desired results. Specific parameters of the simulation must also be taken into consideration. For example, MC simulations can be used for different statistical ensembles, and operate differently depending on which is used. Commonly, CMC and GCMC simulations are employed for EDL in nanopores. Other aspects of the simulation method, including accounting for long-range interactions and sampling methods must be carefully considered.

2.2.2 What system model is most appropriate?

Many different EDL system models have been studied, each with varying degrees of detail in different aspects of the system. One must choose a model that will provide results with an acceptable accuracy and confidence in validity, but that is simplified enough such that the complexity or computational cost is manageable and practical. This includes deciding system geometry and dimensionality, choosing appropriate boundary conditions, and choosing physical representations to use for the solvent, ions, and solid surface. Furthermore, how one models short range and long range interactions between the solvent, ions, and surface is also significant.

2.2.3 What parameters affecting EDL structure should be investigated?

With a method to extract potential from simulation results developed and validated, it must then be decided how to apply the method to obtain results that will help to answer the second research question. A variety of system parameters are known to affect EDL structure, including how many types electrolytes are involved and their respective concentrations, sizes, and valences. Other properties that affect the double layer include solvent properties, electrode surface charge, and pore size. Obtaining the most meaningful relationships in order to provide a substantial contribution to literature will depend on which parameters are investigated. The specific values used for such parameters should have direct real world applicability.
3.0 Literature Review

To begin investigating the structure of the EDL in nanopores, an overview of the existing theoretical and experimental framework must first be presented. This section starts by briefly describing experimental work on EDL in nanopores to provide a better understanding of the scope of what types of properties can be physically measured and how that is accomplished. Next, this work makes a distinction between theories and models, one that is commonly overlooked. Here, a theory refers to an analytic framework from which a mathematical description of a system can be derived. A model refers to the physical properties with which each component of a system is described. More complex models usually describe a system more realistically, but typically only simplistic models can be applied to a theory to obtain a reasonable solution. Some of the most common and successful theories that have been used to predict EDL structure are discussed. A few widely used models are then covered in their application to theories and in the context of molecular modeling. Finally, an overview of molecular modeling techniques and their use in EDL systems in porous materials is given, including methods that have been used to convert simulation outputs to potential profiles.

3.1 Experimental Methods

Due to the extremely small length scales involved, it is very difficult to experimentally measure properties of the EDL in detail. For obvious reasons, this difficulty is even more prominent in nanoporous electrodes. Some common techniques at a liquid-liquid interface, such as the canonical mercury-electrolyte interface, involve measuring surface tension. Surface tension can be used in conjunction with some thermodynamic relations to calculate estimates of surface charge and capacitance. At the solid-liquid interface, such techniques are not possible. Alternatively, electrokinetic properties can be measured and used to calculate the zeta potential. But, these measurements require particulate or channel systems where the motion of particles under the influence of an electric field can be visually observed. This is also very difficult for nanoporous systems. The few electrochemical measurements that work well for nanoporous systems stem from controlled potential and controlled current techniques [26].

Chronoamperometry is a potential step method and involves measuring current over time. In these experiments, the electrode is connected to a potentiometer, which works to maintain a constant potential. The potentiometer applies a potential to the electrode as a step function. As double layer charge accumulates on the surface of the electrode, the potentiometer provides a current to maintain the surface potential. Once the electrode has reached equilibrium, the total current response can be used to calculate the net charge contained the EDL across the entire electrode. Then, if information is known about the size and density of pores, one can calculate the total EDL charge per unit area of electrode. While this method provides some insight, it is very crude. Only information about the net charge in the EDL is given, which leaves much unknown about the concentration of individual ionic species, not to mention the actual concentration profiles or potential profiles.
Cyclic voltammetry is another technique often employed in the study of EDL. Cyclic voltammetry is a potential sweep method, and is similar to chronoamperometry. It is easy to show from the definition of capacitance that charge is proportional to potential via the capacitive constant. Differentiating with respect to time, one can see that current, the rate of change of charge, is proportional to the rate of change of potential by the same constant. So, one can use an identical setup to that of chronoamperometry, but instead of applying a step function potential, apply a potential sweep that changes at a predetermined rate. Then, by measuring the current response and using the potential sweep rate, the differential capacitance of the electrode can be measured. Another class of methods, known as chronopotentiometry or galvanostatic techniques, measure specific capacitance of an EDL electrode by controlling current rather than potential. These techniques use a galvanostat to provide a constant current source. Then, potential during charging and discharging can be measured and used to calculate electrical capacitance. While the mathematical treatment of controlled current techniques is often simpler than controlled potential techniques, it is more difficult to correct for double layer charging effects (i.e. nonfaradaic current contributions) which are larger and occur throughout the experiment. Moreover, it is more complicated to investigate multi-component systems and step responses using controlled current techniques, and the output curves are often less well-defined than those of potential sweep methods [26].

While experimental techniques are not the focus of this work, it is relevant to understand what EDL properties can be measured with current methods. This provides the reader with the necessary context to understand the need for theoretical methods, and the difficulties in validating such methods. Experimental measurements are only able to provide macroscopic quantities (e.g. capacitance, total potential, and total charge) but reactions are determined by the molecular scale structure. If molecular modeling results for surface charge, ionic concentration profiles, and potential profiles can be directly linked to experimental parameters like applied potential, it will be a good first step in helping to validate results, better understand EDL formation mechanisms, and tune real systems to achieve a desired outcome. More details about experimental electrochemical techniques can be found in “Electrochemical methods: Fundamentals and Applications” by Bard and Faulkner [26].

3.2 Classical Theories

As far as analytic EDL theories go, the Gouy-Chapman (GC) Theory is the canonical example. It is widely used because of its intuitive nature and the simplicity involved in obtaining solutions. The theory is based on the solution of the Poisson-Boltzmann (PB) equation. The equation is derived from a combination of Gauss’ law in electrostatics with a volume charge density described by the Boltzmann distribution governed by a purely electrostatic potential of mean force.

\[ \nabla^2 \psi = -\frac{1}{\varepsilon} \rho \quad \text{where} \quad \varepsilon = \varepsilon_0 \varepsilon_r \]

(1)
Equation (1) is the Poisson equation for electrostatics, where \( \psi \) is the electrostatic potential, \( \varepsilon \) is the electric permittivity in medium, \( \varepsilon_0 \) is the electric permittivity in free space, \( \varepsilon_r \) is the relative permittivity (i.e. dielectric constant), and \( \rho \) is the volumetric charge density. In the PB formulation the charge concentration, and hence the volume charge density, behaves as a Boltzmann distribution, where the work is purely electrostatic. This is shown in Eq. (2), where \( z_i \) represents the valence of ionic species \( i \), \( e \) is the fundamental charge of an electron, \( n^0_i \) is the bulk concentration of ionic species \( i \), \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( E_i \) is the work done in bringing a charge from the bulk to a point in the double layer.

\[
\rho = \sum_i (z_i e) n^0_i \exp \left( -\frac{E_i}{kT} \right) \quad \text{where} \quad E_i = z_i e \psi
\]

Another well-known theory stems of the linearization of the PB equation and is known as the Debye-Hückel theory, which can be used if the electrical energy is small compared to the thermal energy [2]. A constant which comes up in this theory is the Debye-Hückel parameter, which has dimensions of inverse length, and is commonly used as a characteristic length in EDL systems.

The GC theory assumes point charges exist right up to the edge of the interface. Stern modified this theory in an attempt to account for the finite size of ions by including an inner layer that is assumed to have no charge, as ions of finite size cannot get closer to the electrode than their distance of closest approach. Thus, solutions generally yield a linear potential drop across and inner layer, followed by an exponential decay to zero potential difference (relative to the Galvani potential) in an outer, diffuse layer. Despite its appealing analytic nature, significant limitations of the theory for most real systems exist. Torrie and Valleau [27] found the GCS theory does very poorly in predicting results obtained by Monte Carlo (MC) simulations for systems with divalent counter-ions. They found that when the counter-ion is doubly charged, the Classical Theory fails even for low concentrations and surface charge. They also noted that the GCS theory is incapable of predicting oscillatory behavior which was observed in MC simulation results [27]. Using results from a mean spherical approximation method, it was shown that the arbitrary division of the EDL into an inner and outer region on which the GCS theory is based is generally not valid. Furthermore, many of the assumptions necessary for the theory to be applicable are so restrictive that only under unrealistically ideal conditions does it provide useful information that, even then, is only marginally accurate [4]. It has also been shown that in nanopores, when the solvent molecules are explicitly modeled with a four point transferrable intermolecular potential with fluctuating charge, the concentration profiles do not even qualitatively agree with the GCS predictions [28]. Issues with the GC theory and its derivative theories stem from the assumptions made in applying the PB equation. The theory assumes infinitely small point charges and a purely electrostatic potential of mean force. The point charge assumption discounts any steric effects and thus restricts the applicable systems to those in which the ions are very small relative to the system. The Stern layer modification attempts to account for this, but it is not self-consistent as the ion size is only considered for ions adjacent to the
electrode. Furthermore, a purely electrostatic potential of mean force neglects other potential contributions include those of chemical and mechanical natures.

Many alternative theories to the GCS exist. The statistical mechanical Orstein-Zernike (OZ) integral equation can be used in conjunction with secondary equations known as closure equations to obtain ion concentration profiles. The closure equations can account for terms not included in the GC potential of mean force. However, they cannot be related to the OZ equation in closed form. As such, different approximation schemes are used. The most common schemes include the Hypernetted Chain (HNC) approximation, Percus-Yevik (PY) approximation, and the mean spherical approximation (MSA) [2]. HNC results are typically difficult to obtain and must be solved for numerically. MSA is attractive in its ability to obtain exact analytical solutions using certain approximation techniques [29] for a variety of fluid models. It treats the ion diameters self-consistently and, in a general form, has shown to capture effects near the wall that the PY method cannot [30]. However, the MSA is a linearized technique and thus can only be used for low electrode surface charge. Furthermore, all of the OZ approximation schemes inherently give non-unique solutions when statistical mechanical methods are implemented to obtain macroscopic properties due to the nature of the approximation [2].

The modified Poisson Boltzmann (MPB), density functional theory (DFT), and the field-theoretical (FT) approach [31] are a few other methods used to look at fluid structure mathematically. Each theory is with its own benefits and restrictions. MPB is based on the Poisson-Boltzmann equation just as the GCS theory is, but attempts to correct for the GCS theory assumptions one by one [32]. The well-known DFT of Rosenfeld [33] takes into account the neglected terms in the OZ approximation schemes and therefore provides a self-consistent method to calculate density profiles for general fluid mixtures in external fields. Henderson & Boda [4] note that for many GCS alternatives, the small improvements gained are usually outweighed by a drastic increase in complexity or necessary computational effort to obtain a solution. Moreover, even with improvements from more advanced modifications, all PB derived theories still contain inherent assumptions that make them unreliable in many instances (e.g. systems with divalent counterions). Hence, this work turns to computational methods, which are well established for EDL simulations and can be robustly applied to any system model.

3.3 System Models

There are many different models that can be applied to a theory or simulation. Models are representations of a real system, and can range from very simplistic to very detailed depictions. While simplistic models are easy to understand and implement, careful consideration must be taken into the reliability of the results and whether the assumptions of the model are applicable. More detailed models may at first appear to be the best option as they minimize the number and weight of assumptions. However, using a more detailed model generates complexities which often lead to a drastic increase in the effort needed to implement such a model. Furthermore, sometimes the details of how a real system behaves are unknown, and more mathematically
complex models may introduce numerical artifacts into the solutions that do not reflect physical phenomena. Despite the issues inherent in both detailed and simplistic models, it is often surprising how much insight can be obtained through the use of a simple model. As previously stated, when detailed models are applied to analytic theories, the mathematics usually becomes so complex that obtaining a solution in impossible. While the details of such endeavors are beyond the scope of this work, it is important to note that this is also one of the main reasons why computer simulations are so useful in these cases. Molecular modeling methods apply a single computational framework to any given system model and are able to obtain solutions that are exact for that model, aside from some highly quantifiable statistical uncertainties that arise from the use of computational techniques. Moreover, a simple model minimizes complexities and potential numerical artifacts, providing a higher degree of confidence that results are truly due to physics and not unaccounted for numerical artifacts. The following discussion will provide details of commonly used system models in the context of computer simulation.

### 3.3.1 The Primitive Model

A primitive model (PM) is often employed in the study of EDL characteristics. It is one of the simplest models to consider, which is valuable for the relatively low computational effort and complexity required to use it. The PM consists of perfect planar electrode surfaces where surface charge is uniformly distributed precisely at the interface boundary. Ions are represented as hard spheres of a fixed radius with a point charge at their center. The solvent is modeled using a mean field approach in which the molecules are represented as a continuum with uniform electric permittivity. In the PM, the permittivity of the electrode is often considered identical to that of the solvent, which implies polarization of the solid surface does not occur or is neglected. In the case where all ions are taken to have the same diameter, the model may be referred to as the restricted PM (RPM). Some of the first EDL simulations were conducted in the 1980s by Torrie and Valleau [23, 27, 34-37] using a PM and provided new insights into the validity of analytic theories at the time. Henderson et al. [38] are among those who followed up this work, investigating the usefulness of PM simulations over GC theories.

Despite the simplicity of the PM, its use in various studies has been a great tool to better understand many aspects of the structure of the EDL. The PM excludes detailed interactions that might occur due to the electrons or discrete sites at the electrode wall, or detailed interactions of the ion constituent components, and any detail at all about the solvent, including solvent structure and electrons, solvent volume exclusion effects, and solvent polarity. And yet, given the coarse nature of the model, it has been able to predict many features that are non-existent in the PB theories. These include nonmonotonic potential profiles, and overcharging or charge inversion. Charge inversion has important implications in colloid science, biological physics, and electrochemistry and has been observed using the PM [39, 40]. As Henderson and Boda [4] state, over charging is responsible for such effects as the attraction of like-charged particles, DNA condensation, electrophoretic mobility sign inversion, and cement cohesion. From the use of the PM in molecular modeling this phenomenon is better understood. While the PM cannot capture
steric and polar effects of solvent molecules, whose effects may become more significant in smaller geometry EDL systems, the simple model it is still a good starting point for studying EDL structure that is both manageable and insightful, and yields a high degree of confidence in the physics observed.

3.3.2 Non-Primitive Models

Non-primitive models (NPM) go beyond the simple PM in detail and complexity. Evidence has shown that the effect of explicitly modeling solvent molecules in aqueous solutions yields qualitatively different results than those predicted by Classical Theory and PM when pore size is reduced to nano-scale [28, 41]. Hence, there is a desire to further investigate systems in which the solvent molecules are modeled explicitly. Despite this, little work has been done with NPM simulations compared to that with the PM. This is most likely due to a massive increase in computational effort required to implement such methods in simulation and a lingering uncertainty in the validity of different solvent representations. The simplest NPM involves modeling the solvent as a fluid of hard spheres with a background dielectric constant [4]. This is known as the solvent PM (SPM) or molecular solvent model and, although crude, accounts for the finite size of solvent molecules. Zhang et al. [42] investigated the SPM and observed a layering effect that could not be predicted by the PM as well as lowered mean electrostatic potential. Lamperski and Zydor [43] found similar results. The ion-dipole model studied by Boda et al. [44] adds to the SPM by placing point dipoles at the centers of the solvent spheres to take into consideration the polar nature of water. Other, more realistic representations of water that have been used in simulation consist of a rigid structure of point charges with anywhere from 2-6 sites, including the extended simple point charge method (SPC/E) [45], and the four point transferrable intermolecular potential (TIP4P) [46]. Despite the abundance of models, there are still difficulties in developing a model for water which accurately reproduces experimental properties, even for pure water [47]. Hence, there may be apprehension in using a non-primitive solvent model due to uncertainty in how reliable the results really are.

Just as solvent molecules can be modelled in a variety of ways; there also exist different models which are beneficial for modeling electrolytes of varying complexity. All-atom electrolyte models are the most realistic, explicitly taking into account every atom in the electrolyte molecule. However, with more complex electrolytes it may be too computationally expensive to use an all-atom approach, which could exponentially increase the number of particles in a system. To compensate, one can group several atomic groups or sites together using the united-atom or coarse-grained models. The PM treatment of electrolytes can be considered a coarse-grained model, but in simpler systems where the electrolyte is comprised of a single atom (e.g. NaCl) there is no need to consider such grouping techniques, and the PM is implicitly used as an all-atom method. One example that has been used to approximate non-spherical ion shapes in simulation uses a dimer model consisting of two coupled atomic components [48].
Other models of the EDL system that have been used incorporate a more detailed representation of the electrode surface. While the primitive model assumes a uniform charge distribution over the electrode surface, studies have been conducted on the effects of having the surface charge be distributed in discretely charged sites, as would be the case in real systems [49, 50]. Torrie and Valleau [34, 35] investigated the effect of using image charges to represent surface polarization effects, and Alawneh and Henderson [51] have continued looking into similar phenomena, finding that effects are most prominent at low surface charges. The EDL electrode has also been modelled in a way that accounts for the metal’s electrons using a jellium model [52], which was able to account for difference in capacitance seen with different metal electrodes. Non-planar geometries have also been explored in many studies. Patra et al. simulated EDL formation around spherical [53] and cylindrical [54] electrodes using the SPM, while Jamnik and Vlachy studied ion effects within charged cylindrical micropores [55]. EDL structure around DNA molecules in a cylindrical geometry has also been investigated [56, 57].

There is undoubtedly a need to examine the effect of NPMs on EDL formation, and many authors are beginning to delve into such endeavors. However, there is still considerable merit in PM simulations. The PM is simple to implement and requires comparatively little computational effort. Moreover, despite the coarseness of the PM, it has still been very useful in understanding a variety of effects related to charge inversion and steric interactions. The PM includes significant effects that are unaccounted for in the PB theories, predicting qualitatively different results such as nonmonotonic potential profiles and oscillatory behavior. Implementing a NPM in simulation has many implications, including reliability of the representation and computational cost. Extensive computational effort can lead to very long run times that may still only provide a very short observation time, leading to questions about whether equilibrium has been achieved. NPMs also can have an effect on other aspects of the simulation method. For example, it has been shown that some methods for calculating long range electrostatic interactions in a periodic system do not work well in models that include explicit solvent molecules [58]. While many NPMs show prospects of being able simulate more realistic systems with accuracy, there are still many limitations to these approaches at present. Since a main focus of this work is to develop a method to convert concentration profiles generated from MC simulations to electric potential profiles, it is logical to start with simulations using the more simplistic PM to develop the method and validate its use. Then, if desired in future work, the method can be adapted to accommodate NPMs.

3.4 Electric Double Layer at a Single Planar Interface

3.4.1 Early Simulations

The simplest scenario to consider is the EDL at a single planar interface, and accordingly this was the first to be studied using molecular modeling. Both CMC and GCMC simulations have been applied to single planar EDL extensively. Torrie and Valleau set the groundwork in their GCMC simulation for a RPM single 1:1 electrolyte near an unpolarized wall [23]. The
simulation used techniques now ubiquitous in MC simulations of EDL systems. These include the use of a central simulation cell, in this case a rectangular prism, with two parallel impenetrable walls on opposite cell faces. One wall was charged while the other remained neutral, and a neutralizing amount of counterions was included in the system to maintain electro neutrality. Along the other two directions, periodic boundary conditions were used to model an infinite slab of solution between the two walls. To account for long range interactions in the periodic image cells, the authors used an infinite sheet method. This method seems to be one of the best options for including long range interactions as it is efficient and includes all orders in the multipole expansion, as opposed to other methods which only account for the dipole term. The higher order terms become more important when higher fields are involved, thus this method is robust. Moreover, results using the charge sheet method were in agreement with another approximation method involving Ewald sums, a more computationally expensive technique. But, this provides more confidence in the accuracy of the charged sheet method. Boda et al. [44] employed an improved charged sheet method which is now widely used over that of Torrie and Valleau.

In order to use Grand Canonical Monte Carlo (GCMC) methods, the bulk activity coefficients for the ion concentration being simulated must be known independently. Typically, MC simulations of bulk solution are conducted to obtain estimates of these values. This work used results for activity coefficients obtained from previous MC simulations [59], which seems to be the most common method to obtain such information throughout the literature. The MC results were compared to the GCS analytic solution, which are in agreement for concentration profiles, but show consistent discrepancies in potential profiles. The authors show that ion size effects are not the cause of the discrepancies and conclude that it must be due to the purely electrostatic potential of mean force used in the GCS result. Diffuse layer potential is calculated using the MC results as well as MPB and HNC results, and is plotted versus surface charge, but no single method gives results consistent with another. In sum, this work shows that simulation results of concentration profiles agree with GCS predictions only for systems with low concentrations and low surface charge, but significant discrepancies between analytic and simulation potential profiles remain essentially unexplained. An interesting result of this study was a counterion layering effect near the surface at high surface charge. This introduced oscillations which are not predicted by the Classical Theory.

Torrie and Valleau continued this MC study of EDL structure using the same simulation techniques. They looked at the effects of surface polarization using the method of images of electrostatics to represent a polarized planar medium [34]. The effects of surface polarization were studied for the attractive case of a conductor and the repulsive case of an insulator. Using image charges essentially doubles the number of particles in the simulation and requires the simulation to include the long range interactions from the periodic images behind the charged wall as well as those in the periodic images of the central fluid cell. The introduced polarization affected the ion concentration profiles most significantly near the surface, introducing extrema at
low surface charges, but this effect is less pronounced with increasing surface charge. Polarization effects on potential drop across the EDL were minor, and increased (although with a decreasing rate of change) with increasing surface charge. Polarization effects on divalent systems with 2:2 and 2:1 electrolytes were also studied [35]. The fractional change in diffuse layer potential caused by image forces is much larger than in the 1:1 case, and contrary to the 1:1 case decreases with increasing surface charge beyond a certain point. The authors note that for 2:1 electrolytes, the charge asymmetry alone produces a double layer even with zero surface charge. However, it should be noted that this potential at zero charge is so small that it is physically insignificant, but nevertheless still has implications on the resulting EDL structure. Simulation of the divalent system showed limitations in one of the most accurate MPB theories of the time, and is appropriately one of the most stringent tests to which a theory can be subjected.

A further study by Torrie and Valleau provided a lot of insight on the limitations of the GCS theory by looking at the effects of divalent ions [27]. In order to simulate asymmetric ions the authors were forced to place a charge on both walls of the system, but were careful to make sure the walls were far enough apart that the EDL did not interact. Polarization was again neglected in this study. They found that the Classical Theory works comparably well for 2:1 electrolytes when the counterion is singly charged as for 1:1 electrolyte systems, although the Modified-Poisson-Boltzmann (MPB) is slightly more accurate in the symmetric case. However, when the counterions are doubly charged, as in 1:2 and 2:2 electrolyte systems, the Classical Theory fails even for low concentrations and surface charges. They found that oscillations exist in the density profiles at higher surface charges even at concentrations as low as 0.05M, and for almost all negative surface charge values studied for higher concentrations. For systems of doubly charged counterions, the MPB tends to underestimate potential profile but is qualitatively accurate, while the GC theory does not predict oscillations and overestimates potential profiles. The authors also note that for symmetrically charged cases, the strength of ion interactions depends on the ratio of charge (squared) and dielectric constant of the solvent. Thus, failure of the theories for symmetric 2:2 aqueous solutions might also be seen in 1:1 electrolytes in a solvent other than water. They conclude by noting that, while more realistic models of solvent molecules will give more accurate results, even in cases where the PM representation is relatively valid, the theory still does not work well with higher valence ions.

### 3.4.2 Ion Valence, Ion Size, and Mixtures of Electrolytes

Following the early molecular modeling studies of the EDL, published work on the topic dropped off for about 20 years until it picked up again around the late 1990’s. Further studies investigated the effects of multivalent ions, asymmetric ions, and ion size. Recently, studies have focused on mixtures of symmetric and asymmetric multivalent ion systems, as mixtures of multiple electrolytes in solution are a commonly found in nature. Simulations of systems with mixtures of electrolytes have illuminated much about a lack of understanding of the mechanisms behind ion selectivity.
A MC study on the effects of ion size on EDL structure in a single 1:1 electrolyte solution was conducted by Lamperski and Bhuiyan [60]. They found that at relatively high surface charge densities, an ion layering effect occurs near a planar interface. This layer becomes more pronounced as ion size increases. For example, at an ionic diameter of 0.40-nm, two layers were observed, while at a diameter of 0.60-nm a third layer formed. The authors also studied charge asymmetry and found that layering occurred only when the counterion was monovalent. This is probably due to the fact that more monovalent ions are required to screen the surface charge than divalent ions. The observation of layering is an important outcome of simulation studies because it implies an oscillatory behavior of the concentration profiles, which is not predicted by the Classical Theory, and is only moderately captured by more advanced theories.

More studies turned to ion size effects as well, using more realistic values for the ionic diameters. A study by Quesada-Perez et al. [61] used realistic values for hydrated ion sizes, and investigated systems of single multivalent counterions. This work also found ion layering at high surface charges not seen in integral equations for multivalent counterion cases. Furthermore, the existence of overcharging or charge inversion due to ion size correlations was verified. Primitive model CMC simulations were used to investigate charge inversion and ion-ion correlation effects with mixtures of 1:1 and 3:1 electrolytes with realistic hydrated ion diameters [62]. Simulation results are in agreement with experiment when comparing outcomes for increasing monovalent ion concentration in the presence of trivalent ions. This supports that ion size (volume exclusion) plays a key role in determining charge inversion behavior over ion-ion correlation effects in a strongly correlated layer. Another simulation of mixtures of 1:1 and 3:1 electrolytes that used realistic hydrated ion size (0.90-nm for trivalent ions compared to previous studies in which the largest ion diameter simulated was 0.425-nm) [63] found a notable charge inversion while using realistic sizes, while no inversion was observed when all ionic species had the same 0.40-nm diameter. This provides even more evidence that ion size is not a trivial parameter but in fact plays a dominant role in charge inversion.

A competition between ion size and ion charge asymmetries was studied by Valisko et al. [64]. They studied a system of anions with a diameter of 0.425-nm and cations with diameters varying between 0.15-nm and 0.40-nm. For charge asymmetry, 1:1, 2:1, and 3:1 electrolytes were also investigated. It was found that ion size asymmetries cause a positive potential at zero charge, the sign of which is determined by the cations ability to approach the surface more closely. It was also found that charge asymmetry alone is able to produce a potential at zero charge, even if the ion diameters are equal, and is shifted to more negative values. This negative potential shift is more prominent with greater charge asymmetry. The negative influence on potential of the charge asymmetry was shown to be more long range, while the positive influence of size asymmetry is more prominent close to the surface. While these two effects compete, it appears that the charge asymmetry dominates over size asymmetry at larger differences.

Further investigations into the competition between valence and size correlations were conducted. One paper investigated the effect of mixtures of indifferent (fully hydrated) electrolytes, both symmetric and asymmetric, in the presence of a discretely charged surface [49]. Specific focus was given to the effect of ion size, which varies with ion valence. The paper
concludes that size of the ionic species forming the EDL is a key factor in the resulting EDL structure. The thickness of the EDL is determined by the size and associated charge of the ions as well as the ionic concentration. The GC prediction that EDL thickness is proportional to ionic strength is qualitatively correct, but the proportionality factor is influenced by size as well. Solutions with mixtures of electrolytes were shown to reduce the thickness of the EDL as multiple species were able to more effectively screen the surface charge, even if the total ionic strength was the same as for systems of only one electrolyte. An interesting finding was noted about how in mixtures, even though it is energetically favorable for higher valence ions to screen the surface charge, their larger size prevents them from getting close to the surface, while the smaller, lower valence ions are able to get closer to the surface. Hence, smaller valence ions were shown to contribute to most of the screening, as opposed to the expected result of higher valence ions accomplishing this. It was found that this ion exclusion effect was enhanced with higher surface charge. It was noted by the authors that dehydration effects were neglected in this study. They mention that it may be more favorable that higher valence ions tend to dehydrate and adsorb to the surface to accomplish more of the screening than was found during this study. However, they note that based on the results of this work, at higher surface charges the observed ion exclusion effect may hinder higher valence ion’s preference to dehydrate. Another MC simulation of electrolyte mixtures [65] found a similar competitive situation when the monovalent ion was smaller. At low surface charge, the high valence ion is preferentially adsorbed, but at high surface charge, the entropic advantage of the smaller ions win.

The above studies investigated the effects of ion size, ion valence, and mixtures of electrolytes on the structure of the EDL. It was found through the use of MC simulations that monovalent ions form a layered structure not predicted by Classical Theory that is more prominent with larger ion size. This is probably due the need for a higher concentration of ions near the wall to screen the surface charge. It was also found that ion size differences play a key role in charge inversion, an important phenomenon in biological physics. Finally, mixtures of charge and size asymmetric ions were studied. Such mixtures were found to exhibit competitive effects between ion size and ion charge asymmetries. While ion size asymmetry effects dominate close to the charged surface, charge asymmetries effects extend to longer ranges and dominate over size asymmetries at larger differences. It was also found that at low surface charge, larger high valence ions are energetically preferred for screening the surface charge, but at high surface charge, the smaller low valence ions accomplish most of the screening because they are able to get closer to the surface.

3.5 Electric Double Layer in Pores and Channels

Although many studies of the EDL by a charged planar surface have helped provide insight into EDL formation, investigation of EDL structure in nanopores by means of simulation in the literature is limited. A simple way to simulate nanopores stems from the method used for simulations at single planar surfaces. Using the familiar geometry of two charged parallel plates separated by an infinite slab of electrolyte solution, the separation distance between the two plates can be decreased to around the size of a nanopore such that the EDL formed on both plates begin to interact. Such a configuration, more accurately described as a slit-type nanopore, is
often employed. As the separation distance between two charge plates is decreased, steric effects begin to play a more dominant role. An early work that focused on forces between overlapping double layers [66] found that they are often attractive (contrary to the PB prediction that they will always be repulsive\(^1\)) and depend highly on electrolyte concentration, surface charge, and counterion valence.

The distortion of the EDL in micropores where strong overlapping exists contributes to some interesting effects. It was shown that under conditions in which significant EDL overlapping can occur (such as in very small pores with low surface charge), electroosorption does not contribute to the total capacitance in pores smaller than a certain cutoff size because the overlapping effect is so strong [16]. This implies that the pore size distribution is key to EDL capacitance, as it restricts the effective surface area available for electroosorption to a value less than the true surface area of the electrode. It was also shown that this cutoff pore size decreases with increasing concentration, supporting the idea that steric interactions in overlapping double layers are responsible for this effect. Yang et al. [67] observed a minimum in capacitance near the point of zero charge at low concentrations in micropores that was not observed in mesopores. They were able to attribute this expected but previously unobserved effect to EDL overlapping effects in micropores. Hou et al. [5] showed that, while smaller pore size increases total capacitance via an increase in specific surface area, at low concentrations and low surface charge double layer overlapping in micropores can significantly reduce total capacitance. Thus, for efficient electroosorption over a wide range of operating conditions, an optimal balance of surface area ratio between micropores and mesopores in the electrode must be considered. One reason capacitance in these systems is important because it can be a good indication on how well a porous material will perform when used for ion selectivity purposes.

### 3.5.1 Ion Valence Effects

EDL formation in charged cylindrical pores for single electrolytes of varying valence and symmetry was studied using GCMC simulations [55, 68-70]. In a work by Vlachy and Haymet [69], PB theory results for concentration profiles in a cylindrical system were again validated for a single 1:1 electrolyte system with moderate surface charges, but show significant discrepancies when a 2:2 electrolyte is involved, illuminating the important ion-ion correlations that are neglected in the PB theory. An interesting qualitative discrepancy between PB and MC results for the pore size dependence of activity coefficient was observed. While PB predicts larger pore size will cause a decrease in mean activity coefficient, MC results show the opposite behavior. This is due to finite ion size effects neglected by PB theory. The authors note that results for cylindrical pores closely parallel results between two charged planar surfaces, supporting the use of a slit-type model. In other works, a surface charge dependence of ion exclusion in micropores was observed for symmetric [70] and asymmetric [55] monovalent and divalent electrolytes. For both systems, exclusion increases with increasing surface charge up to a maximum, then decreases with further increase in surface charge. This is an important observation because it

\(^1\) The PB predictions that the interaction force is always repulsive is shown to be valid only for low surface charges and concentrations [66].
suggests that not only can micropores can be used to select out specific ions, but also suggests how selectivity might be tuned by controlling surface charge.

Investigation into the effects of mixtures of symmetric and asymmetric electrolytes on EDL formation in nanopores is scarce. One study that used GCMC simulations to investigate mixed electrolytes in cylindrical capillaries found that Classical Theory grossly overestimates exclusion in micropores [71]. The authors found that micropores favor selection of divalent ions. This effect increases with increasing surface charge and is larger for solutions with a smaller fraction of divalent to monovalent ions in the bulk. Boda et al. [72] studied uncharged cylindrical micro channels with polarizable surfaces using MC simulation and found a similar result for divalent ion selectivity. A continuation of this work [73] shows selectivity for divalent ions increases when dielectric constant of the electrode is decreased due to the competition of charge and volume exclusion effects. A significant increase in divalent ion selectivity is also found when pore size is reduced. As pore size decreases, ion density in the pore increases. With limited space in smaller pores, it is more energetically favorable for the divalent ion to neutralize the surface charge because they provide twice the neutralizing charge for the same amount of occupied volume as the monovalent ions. From these works it can be concluded that, in the systems that were investigated, the energetic favorability of higher valence ions to screen surface charge in micropores dominates over any steric or other effects.

Another GCMC simulation in a charged cylindrical capillary with 3:3 electrolyte obtained an interesting result for ion exclusion [74]. Rather than coion exclusion in the pore, as expected, it was found that the concentration of coions in the pore was greater than in the bulk. This was attributed to the very strong ion-ion correlations with such high valence ions. Hence, from the above studies it is reasonable to assume that by carefully considering system properties such as surface charge, permittivity of the electrode, ion valence, and charge symmetry that ion selectivity may be tuned to select ions in a user-specified manner. This has great potential, as it supports the feasibility of a method to separate constituents in aqueous solutions through the use of electrosorption in the EDL, which has many advantages over other separation techniques.

3.5.2 Competitive effects of charge and size asymmetries

The effect of having ions of varying sizes in mixtures of electrolytes in nanopores was also briefly investigated. One study conducted CMC simulations of electrolyte mixtures in nanopores and found further support that characteristics of the ions, including size and valence, play just as important a role in EDL formation as ionic strength or surface charge [75]. Confinement effects on the EDL structure are enhanced with ion size and charge asymmetries. Charge inversion was also observed in this study. It was found to occur most prominently when the size of trivalent counterion is large compared to monovalent ions. This demonstrates that ion size is an important factor in charge storage and ion selectivity, as it helped trap a higher concentration of coions in the pore than in the bulk. This study was limited to CMC simulations however, due to inability to obtain mean activity coefficients in a way that takes account of the
effects of ion size with mixtures of electrolytes. Hence, the systems simulated may not have been at equilibrium with the bulk, but still provide strong qualitative evidence of the impact of ion size to selectivity in pores.

A follow up study incorporated GCMC simulations to specifically investigate electrosorption selectivity in nanopores [10]. Competition between charge and size asymmetries creates an interesting selectivity relationship. With increasing surface charge, the larger, high valence ions are selected over smaller, lower valence ions. This relationship diminishes with increasing surface charge, and eventually the smaller size of the lower valence ions becomes more advantageous and these begin to be selected over the larger ions. It follows that, by tuning surface charge, control of which ions are selected from solution and trapped in the EDL is achievable.

3.5.3 Explicit Solvent Effects

A few studies that ventured beyond the primitive model in nanopores explored the effects of modeling explicit solvent molecules. Feng et al. [28] simulated electrolytes and water molecules in micropores from 0.936-nm to 1.47-nm using MD simulations. They considered ion hydration and water-water interactions and found that these effects are responsible for a deviation from the Classical Theory. The theory predicts that ions accumulate near the walls, and concentration falls off towards the center of the pore, but the MD simulations found that ions accumulated in the center of the pore rather than by the walls for pore sizes between 1.00-nm and 1.47-nm. This study did not include coions, under the assumption that they are essentially rejected entirely from the pores, which may be valid for low valence ions but ion-ion correlations may have a larger impact with higher valence systems. Despite this, the authors used the results to develop a “sandwich” capacitance model which successfully predicts the anomalous increase in capacitance observed experimentally.

Another study [41] combined the use of GCMC and CMC to more efficiently incorporate a TIP4P water molecule with fluctuating charge, proposed by Rick et al. [76, 77]. Simulations were run using a primitive model and GCMC techniques to obtain equilibrium number of ions in the system. This result was then used as an initial condition for CMC which also incorporated the water molecules. Results showed that for high surface charges in a 1-nm pore most of the coions were pushed out of the pores, whereas in the 2-nm pore concentrations were about equal in the center, giving evidence to an ion exclusion effect. The CMC simulation results differed greatly from the Classical Theory. Due to the presence of water molecules, the majority of ions were, just as in the MD simulations of Feng et al. [28], shown to exist in the center of the pore, with concentration values were much greater than predicted by Classical Theory. The high concentration values were attributed to neglecting the occupied volume of water in the primitive model simulation. Thus, the final number of ions obtained was a gross overestimate. The high concentration of counterions in the middle of the pore, as opposed to the walls, suggests that adsorption of water to the charged walls is more favorable, which then pushes the ions to the
center. A difference was also found between whether Na\(^+\) or Cl\(^-\) was the counter ion, due to the differing Lennard Jones potentials of each ion. The sodium atom attracts the water more strongly, and hence has smaller, tighter hydration shell which completely shields the sodium ions from adsorbing to the walls. The chlorine hydration shells are larger and looser, allowing a few chlorine atoms to push through their shells right up to the surface, but the maximum ion concentration was still located at the center of the pore.

While both of these works are making strides to understand the full impact of solvent and ions in electrochemical systems, the studies are highly focused on ion concentration profiles. They make good note of how hydration effects in nanopores cause unexpected behavior in the structure of the double layer that is not predicted by PB theory. This suggests that ion size as well as ion-water interaction plays a role in EDL formation in nanopores, and supports the use of molecular modeling approaches which can more account for such effects more easily than theoretical methods. However, the works do not go beyond the description of the structure of the EDL to discuss other important parameters such as potential profiles, surface potential, surface charge and their relationships in nanopores.

3.6 Electric Potential from Monte Carlo Simulation

While many MC studies report on total potential and even full potential profiles in EDL, there is a lack of focus on the method. Torrie and Valleau [23] calculate electric potential profiles of EDL at a single charged interface (between one charge and one uncharged planar wall) using the relation between concentration profile and potential profile, given by Eq. (3).

\[
\psi(x) = -\frac{\rho e}{\varepsilon} \left( \int_{-\infty}^{x} [n_+(x') - n_-(x')] \times dx' - x \int_{-\infty}^{x} [n_+(x') - n_-(x')] \times dx' \right)
\]

The relationship in Eq. (3) is for a single 1:1 electrolyte with bulk density \(\rho\) and local concentration \(n\), where \(z\) is the distance from the charged surface. Because their system is finite, the location where potential equals zero was defined as one half an ionic diameter from the far, uncharged wall. Imposing these boundary conditions requires that the wall to wall distance used be large enough for the condition to be a valid approximation. Furthermore, rather than directly integrating Eq. (3) the authors tabulated averages of the first integral term (the dipole moment per unit area from charges beyond \(z\)) and the second integral term (\(z\) times the total charge per unit area beyond \(z\)) during the data collection phase of the simulation run. They claim that this method is more accurate than directly integrating Eq. (3). This may be true because there is a restriction how closely spaced the sampling locations can be for concentration profile values due to the finite size of ions. If the spacing is made to be smaller than the size of the ions, the counting of partial ions in a sampling bin will merely introduce non-physical fluctuations in the resulting profile.

A more general form of Eq. (3) can be written for multiple ionic species of any valence, and is shown below.
\[
\psi(x) = \frac{e}{\epsilon} \sum_i z_i \int_x^\infty (x - x') \rho_i(x') dx'
\]  \hspace{1cm} (4)

Other studies calculate EDL potential profiles at a single charged interface by directly integrating the concentration profiles using Eq. (4) \cite{48, 78}. However, details of the method involved and how the large sampling distances are treated in the numerical integration are not discussed. From examination of the figures in the works, it is reasonable to assume that because the potential profile results are located at the same spacing as the MC concentration profile results, the authors merely converted the integral to a summation. Then, using existing concentration data at points located beyond the point in question (as indicated by the integration limits) they computed the value of potential for each location.

While there is significant discussion on EDL potential profiles resulting from MC simulations \cite{43, 79, 80}, and many works calculate the integral diffuse layer potential from simulation results, there is little focus on the method used to convert raw MC outputs to electric potential. Moreover, none of the previously discussed works focus on the potential profile in pores or, more specifically, nanopores. There has been such a focus on the interesting electrosorption, capacitance, and concentration profile behavior in nanopores that calculating the electric potential has fallen to the way side. Hence, there is a need to investigate EDL potential profiles in nanopores. Furthermore, in respect to ion selectivity studies, while selectivity dependence on surface charge has been investigated, there is a need to tie surface charge to potential profiles in nanopores that has not been the focus of prior work. Also, developing a relationship between surface charge and total potential (i.e. the experimental applied potential) for various pore sizes is a necessary step to link macroscopically measurable quantities with potential microscale structure obtain from molecular modeling simulations that is missing from the literature. This work aims to fill that gap, and provide a possible means of experimental validation through the use of molecular modeling.
4.0 Objectives of the Proposed Work

The goal of the present work is to link classical electrodynamic concepts with molecular scale models and simulations in order to fully describe the structure of the EDL in terms of ion and potential profiles. If achieved, macroscopically measured parameters on charged interfaces such as applied potential, zeta potential, or total charge accumulated at the interface (EDL capacitance or electrosorption capacity) can be linked to plausible molecular scale structures and properties.

4.1 Develop a method to convert Monte Carlo simulation concentration profiles to potential profiles

The mathematics to convert a charge concentration profile to electric potential is fairly straightforward. From Gauss’ Law in classical electrodynamics it is easy to show that electric potential arises from the solution of the Poisson equation where volumetric charge density, a quantity directly related to charge concentration, is the forcing function. Thus, converting the concentration profile to volume charge density and integrating twice should yield electric potential. However, a MC simulation output for ionic concentration consists of discrete data points that are coupled with a statistical uncertainty inherited from the MC method. The discreteness requires the results to be integrated using numerical techniques, which can add significant error if not treated properly. The degree of discreteness, coupled with the uncertainty from using MC methods and the error incurred from a using numerical integration technique necessitate that the chosen method be carefully considered and unambiguously validated. Once a method to obtain complete potential profiles is developed and validated, various macroscopic quantities can easily be calculated using the results of MC simulations, allowing experimental and simulated data to be compared.

Action items to accomplish this objective include the following:

1. Conceptualize and develop a method for the calculation of electric potential profiles from MC simulation data with appropriate accuracy.
2. Implement the method using appropriate numerical techniques.
3. Obtain solutions to the PB equation of the GCS theory for a simple system in which the assumptions of the Classical Theory hold.
4. Perform MC simulations for the same system.
5. Use the method to obtain potential profiles and compare the MC results with Classical Theory predictions.
4.2 Apply the method to explore the effects of confinement in the development of EDL within porous electrodes

The structure of EDL in slit-type nanopores will be simulated. Since there is an emphasis on pore size due to the anomalous increase in capacitance observed in a small range of pore sizes, various incremental slit widths will be investigated. Each slit width will be investigated for a 1:1 electrolyte. Parameters to be varied include surface charge and pore size. A relationship between potential profile information within slit-type nanopores from GCMC simulation data will then be obtained. This requires implementing the method developed to convert MC concentration profiles to potential profiles on simulation data obtained for the various nanopore systems. Once completed, the results can be used to describe the molecular structure and electrical properties within porous electrodes that could be potentially linked to macroscopic electrical properties measured by electrochemical experiments like chronoamperometry, chronocoulometry and cyclic voltammetry (wide-spread electrode-characterization methods). This naturally leads to experimental validation of simulation models, a topic for future work.

Activities for this objective include:

1. Use GCMC to simulate systems with different parameters of pore size and surface charge densities to obtain concentration profiles from molecular modeling.
2. Use the method developed in this work to obtain potential profiles from molecular modeling for these systems.
3. Use molecular modeling results to characterize EDL micro structure in terms of level of confinement and electrical properties.
4. Draw conclusions about the relationships observed.
5.0 Models of Electrical Double Layer inside Nanoporous Electrodes from Classical Theory

One of the most widely used theories to predict electrical double layer (EDL) structure is the Gouy-Chapman-Stern (GCS) theory. It combines a charge free Stern layer with a Gouy-Chapman (GC) diffuse layer, and is based around the Poisson-Boltzmann (PB) equation, as explained in Chapter 1, section 1.1. It is largely accepted due to its simple derivation and implementation. Despite the increasing evidence of its limited applicability it has still been useful for gaining insight into EDL structure. Moreover, this simple equation generates predictions for both concentration profiles and potential profiles, and can therefore be used as a reference to validate any molecular modeling results for these quantities, given the systems under consideration are appropriate in that the underlying assumptions in the PB equation are valid.

Solutions to the PB equation have been used to obtain expressions for EDL capacitance for simple, planar electrodes. This quantity can also be experimentally measured, and therefore compared to theoretical predictions. However, these expressions are restricted to simple, planar electrodes [26]. While capacitance is a useful quantity that provides insight into some of the mechanisms of EDL systems, it does not fully characterize electrochemical behavior. Knowledge of the true micro-scale structure of the EDL would be more ideal in this regard. However, there is no experimental method to directly probe EDL structure in terms of concentration profiles or electrical potential profiles [26].

5.1 The Poisson Equation

The PB equation is the canonical equation to describe EDL. It comes from a combination of classical electrodynamics concepts and Boltzmann statistics. To develop the PB equation we can start with the electrostatic Poisson equation, which is derived from Gauss' Law,

\[ \nabla \cdot \vec{D} = \rho \]  

(5)

Here \( \vec{D} \) is the electric displacement field and \( \rho \) is the free charge density in a system. Applying some assumptions about the system at hand (i.e. the primitive model), it can be assumed that the continuous medium representing the solvent is linear and isotropic, allowing the displacement field to be written in terms of the electric field and a constant electric permittivity. Making this substitution we get,

\[ \nabla \cdot (\varepsilon \vec{E}) = \rho \quad \text{where} \quad \varepsilon = \varepsilon_0 \varepsilon_r \]  

(6)

Since we are considering electrostatics, Maxwell’s equations dictate that the electric field is irrotational (i.e. the curl of the field is zero). Hence, by Helmholtz’s theorem the field can be expressed in terms of the negative gradient of a scalar field \( \psi \). Substituting this into Eq. (6) yields,
\[ \nabla \cdot [\varepsilon(-\nabla \psi)] = \rho \]

The above expression can be written more simply as,

\[ \nabla^2 \psi = -\frac{1}{\varepsilon} \rho \] (7)

This second order partial differential equation is known as the Poisson equation and is ubiquitous in physics [2]. This derivation can be found in any introductory electrodynamics text, including that by Griffiths [9].

5.1.1 The One Dimensional Poisson Equation Between Two Charged Walls

Our molecular modeling systems include fluid between to infinite, parallel charged walls, and are periodic in directions parallel to the walls. When the ions are counted up to create concentration profiles, the system is reduced to one dimension since the profile extending out normal from the walls is all that is considered. Aligning the Poisson equation with such a system reduces it to a one dimensional boundary value problem in which the direction is normal to the walls and the boundary are the walls themselves. The one dimensional Poisson equation is written as,

\[ \frac{d^2 \psi}{dx^2} = -\frac{1}{\varepsilon} \rho(x) \] (8)

Since the surface charge on the walls is a dictated parameter in the MC simulations, we can use this value to define imposed boundary conditions for solving Eq. (8) From Maxwell’s equations it can be shown that the boundary condition of the displacement field across an interface like the one in Figure 3 (identified as 1 – 2) is given as [9],

\[ \mathbf{D}_2 \cdot \hat{n}_{1,2} - \mathbf{D}_1 \cdot \hat{n}_{1,2} = \sigma_f \] (9)

Figure 3: Displacement Field Boundary Condition

Again, making the assumptions that we have a linear, isotropic medium, the displacement field can be written in terms of the electric field and a constant permittivity.

\[ \varepsilon_2 \mathbf{E}_2 \cdot \hat{n}_{1,2} - \varepsilon_1 \mathbf{E}_1 \cdot \hat{n}_{1,2} = \sigma_f \]
And if we assume the solid and the solution have the same dielectric constant, and again represent the electric field by the negative gradient of the potential,

\[ \varepsilon_2 = \varepsilon_1 = \varepsilon \quad \text{and} \quad \vec{E} = -\nabla \psi \]

The boundary condition simplifies to,

\[ -\frac{d\psi_2}{d\hat{n}} + \frac{d\psi_1}{d\hat{n}} = \frac{\sigma_f}{\varepsilon} \quad \text{(10)} \]

Since the solid in this system is a conductor, the potential across it is constant, so the derivative of \( \psi_1 \) is zero and we can eliminate this term. Examining the opposite wall as depicted in Figure 3, the direction of \( \hat{n}_{1,2} \) switches. This changes the signs of the results of the dot products in Eq. (8) resulting in the negation of Eq. (10). Hence, we have derived two Neumann boundary conditions for the potential between the two walls that depends on surface charge and permittivity. If we continue to use the same convention that the direction normal to the walls is \( x \), the boundary conditions can be written as,

\[ \left. \frac{d\psi}{dx} \right|_0 = -\frac{\sigma_f}{\varepsilon} \quad \text{and} \quad \left. \frac{d\psi}{dx} \right|_w = \frac{\sigma_f}{\varepsilon} \quad \text{(11)} \]

where \( w \) is the total distance between the walls. In sum, we have Eq. (8) and Eq. (11) to fully describe the potential distribution between two charged walls in one dimension due to some volumetric charge density \( \rho \). However, it can be shown that in general, the solution to the Neumann problem for the Poisson equation is non-unique up to an additive constant. This makes sense physically, because the absolute value of potential by definition is arbitrary; it is only the change in potential that has physical significance. A detailed mathematical proof of the lack of a unique solution is discussed in section 6.2.3.

### 5.1.2 The Dimensionless Poisson Equation in One Dimension

Since the parameters in the above derivation will be used throughout this work, it is convenient to define non-dimensional parameters for simple, system independent comparisons. If we choose constants relative to our EDL system, we can consider a normalization constant for the distance from the charged wall to be the ionic diameter, \( d \), and for potential we can use the quantity \( \psi_n \) as defined in Eq. (12). These can be used to obtain the non-dimensional quantities,

\[ x^* = \frac{x}{d} \quad \text{and} \quad \psi^* = \frac{\psi}{\psi_n} \quad \text{where} \quad \psi_n = \frac{kT}{ze} \quad \text{(12)} \]

According to Hunter, the quantity \( \psi^* \) is known as the reduced potential [2]. Inserting the non-dimensional parameters in Eq. (12) into Eq. (8) gives rise to the dimensionless equation,

\[ \frac{d^2\psi^*}{dx^{*2}} = \left( \frac{ze^2}{kT\varepsilon} \right) \rho(x) \]
which reveals the form of the non-dimensional charge density,

$$\rho^* = \frac{\rho}{\rho_n} \quad \text{where} \quad \rho_n = \frac{kT\varepsilon}{zed^2}$$

and the now fully defined non-dimensional Poisson equation in one dimension becomes,

$$\frac{d^2\psi^*}{dx^*^2} = -\rho^*(x)$$

The boundary conditions can also be converted to a non-dimensional form. This gives rise to a dimensionless parameter for surface charge. Substituting the parameters in Eq. (12) into Eq. (11) yields,

$$\left| \frac{d\psi^*}{dx^*} \right| = \left| \left( \frac{zed}{kT\varepsilon} \right) \sigma_f \right|$$

This shows that the non-dimensional surface charge is given as,

$$\sigma^* = \frac{\sigma_f}{\sigma_n} \quad \text{where} \quad \sigma_n = \frac{kT\varepsilon}{zed}$$

We will use the non-dimensional values in Eq. (12), (13), and (15) throughout this work to normalize all results for easy comparison of different systems.

5.2 The Poisson Boltzmann Equation

Now, to apply Eq. (7) to EDL it is necessary to predict what the charge distribution actually looks like. Maxwell Boltzmann described the ions in EDL as point particles which obey Boltzmann statistics, and therefore the distribution of charges looks exponential [2] as,

$$n_i = n_i^0 \exp \left( -\frac{E_i}{kT} \right)$$

where \(n_i\) is the total number of ions per unit volume for species \(i\), and \(n_i^0\) is the number of ions per unit volume in the bulk for species \(i\). And if only electrostatic forces are considered, then the energy \(E_i\) is comprised only of the electrostatic potential energy, which is,

$$E_i = z_i e\psi$$

Finally, the charge distribution of each species can be converted to charge density straightforwardly by multiplying by the electronic charge and the valence of the species. Then the cumulative charge density can be computing by summing the results.

$$\rho = \sum_i (z_i e) n_i$$

Substituting this in to the Poisson equation (Eq. (7)) we recover the PB equation for EDL.

$$\nabla^2 \psi = -\frac{1}{\varepsilon} \sum_i (z_i e) n_i^0 \exp \left( -\frac{z_i e\psi}{kT} \right)$$
Just as the Poisson equation was considered in one dimension, the analogous one dimensional form of Eq. (19) will also be used in this work.

Through this derivation one can identify some of the restrictions inherent in PB-based EDL descriptions. For example, PB-based theories only account for electric interactions of the ions with the electric field stemming from the charged surface, and they neglect the finite size of ions by assuming point charges. As such, this description only yields reasonable predictions for systems in which those assumptions are mostly valid. These include large systems relative to the size of the ions, and systems of moderate to low surface charge and low ionic strength. As discussed in the introduction, increasing evidence is being compiled on the failure of PB based solutions to accurately predict structure in common systems [2, 4, 27, 28].

Nevertheless, the PB equation predicts both charge distribution and potential profiles. So, as long as the system under consideration adequately upholds the PB assumptions, it can be used as a method of validation for molecular modeling results for both potential and concentration profiles. An important note about the PB equation is that its solution for potential is unique. It implicitly assumes a zero potential in the bulk of the solution by the way the Boltzmann distribution is defined, hence the potential profile it calculates is relative to this zero point.

5.2.1 Single Wall Solution for Single One-One Electrolyte

For simplicity, this work considered a single one-one electrolyte only, which means that there are only two species and their valences are $z^+ = -z^- = 1$. The concentration profiles in the Monte Carlo simulations were counted in bins divided normal to the charged surfaces, thus reducing the system to one dimension. So, we will consider a one dimensional problem with the PB equation to align with this. The PB equation under such conditions simplifies to the following nonlinear, ordinary, second order differential equation,

$$\frac{d^2 \psi}{dx^2} = -\frac{2e n^0}{\varepsilon} \sinh \left( \frac{e \psi}{kT} \right)$$  \hspace{1cm} (20)

For a single wall, the potential in the bulk infinitely far away from the surface and its derivative are assumed zero. After some manipulation and applying these boundary conditions, one can integrate from a point in the bulk to the plane at the start of the diffuse layer where the potential is some value $\psi_d$. This yields a closed form analytic solution for the diffuse layer potential, and is shown in Eq. (21). The expression for the concentration in the diffuse layer is then calculated by substituting the potential profile from Eq. (21) into Eq. (16) and (17). This is typically normalized such that the bulk concentration is one, which is expressed in Eq. (22) below.

$$\psi(x) = \frac{4kT}{e} \text{atanh} \left( tanh \left( \frac{e \psi_d}{4kT} \right) \exp(-\kappa(x - d)) \right)$$  \hspace{1cm} (21)

$$c^* = \exp \left( -\frac{ze\psi(x)}{kT} \right) \hspace{1cm} \text{where} \hspace{1cm} \frac{c^*}{n_0} = \frac{n}{n_0}$$  \hspace{1cm} (22)
Equations (21) and (22) include the potential at the surface, $\psi_0$, and the Debye-Hückel parameter, $\kappa$. These terms can be calculated from the expressions in Eq. (23) as a function of known parameters including surface charge density and concentration. In Eq. (21)-(23) a subscript $d$ represents the value at the outer Helmholtz plane (i.e. the start of the diffuse layer), and a subscript $o$ denotes the value at the charged surface, i.e. the solid-liquid interface of the electrode.

\[
\sigma_0 = -\sigma_d \quad \text{and} \quad \psi_0 = \left(\frac{2kT}{ze}\right) \text{asinh} \left(\frac{-\sigma_d}{\sqrt{8\varepsilon n_0 kT}}\right) \quad \text{and} \quad \kappa = \sqrt{\frac{2e^2 z^2 n_0}{ekT}} \quad (23)
\]

This result is incorporated into the full Gouy-Chapman-Stern (GCS) theory result by also considering a charge free Stern layer between the diffuse layer (which the above analysis describes) and the charged surface. A charge free Stern layer implies electrosorption is occurring. So, the ions can be modeled like hard spheres of finite radius with point charges at their centers, resulting in the region less than an ionic radius from the charged interface with zero free charge. The Poisson equation in this region simplifies to,

\[
\frac{d^2\psi}{dx^2} = 0
\]

which yields a linear solution for the potential across the Stern layer,

\[
\psi(x) = \left(\frac{\psi_d - \psi_0}{d}\right) x + \psi_0 \quad (24)
\]

The above derivation is outlined in many elementary electrochemistry texts, including Hunter [2].

A MATLAB script was implemented to calculate the single wall 1:1 electrolyte PB solution for a given surface charge and ionic concentration, according to Eq. (21)-(24). Multiple systems were considered here with the PB equation, and throughout this work. Parameters whose values were maintained constant across each system include temperature, relative permittivity of the solvent medium, ionic diameter for both species, and molar concentration of the electrolyte. The parameters considered for generating PB solutions are shown below in Table 1.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Relative Permittivity of Solvent ($\varepsilon_r$)</th>
<th>Ionic Diameter (nm)</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>78.5</td>
<td>0.425</td>
<td>1.003</td>
</tr>
<tr>
<td>Pore Size (nm)</td>
<td>Pore Size ($z^*$)</td>
<td>Surface Charge (C/m$^2$)</td>
<td>Surface Charge ($\sigma^*$)</td>
</tr>
<tr>
<td>2</td>
<td>4.706</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>5</td>
<td>11.77</td>
<td>0.050</td>
<td>1.191</td>
</tr>
<tr>
<td>10</td>
<td>23.53</td>
<td>0.100</td>
<td>2.231</td>
</tr>
<tr>
<td>15</td>
<td>35.29</td>
<td>0.160</td>
<td>3.810</td>
</tr>
</tbody>
</table>

Table 1: Parameters of systems considered in this work
Example PB solutions for these 1M systems at a single charged interface can be seen in Figure 4 and Figure 5 for potential profiles and concentration profiles, respectively. The surface charges used in the GCMC simulations differ slightly from those listed in Table 1 due to the quantization of the ion charges and the necessity for exact electroneutrality.

Figure 4: Analytic PB Solution for potential profiles with a single 1:1 electrolyte and a single charged interface
As expected, Figure 4 shows that as surface charge increases, the surface potential increases. The profiles contain a linear drop from the charged surface to the beginning of the diffuse double layer exactly half of an ionic diameter from the wall, after which an exponential decay behavior takes the potential to a value of zero in the bulk. The extent of the double layer in these cases is roughly 5 ionic diameters, or just over 2-nm. The concentration profiles indicate an excess of counterions (CN) and a depletion of coions (CO) relative to the bulk in the region near the wall. Counterions (CN) are ions that bear charge of opposite sign to the one on the surface, and coions (CO) are ions that bear charge of the same sign as the surface. The Stern layer region can be seen to contain zero charge up to one ionic radius from the charged surface.

### 5.2.2 Double Wall Solution for Single One-One Electrolyte

Obtaining a solution to the PB equation between two walls is not as straightforward as the single wall solution. Analytic methods lead to integral equations which are difficult to solve and must be done so numerically. Instead, this work obtained a solution using traditional numerical integration techniques on the second-order differential equation directly. Specifically, a finite difference method was implemented in a Gauss-Seidel algorithm with successive over-relaxation.

To begin, Eq. (20) must now be solved with different boundary conditions than in the single wall case. These boundary conditions must be implemented differently than in the single wall solution because there is no longer an integration from infinity (i.e. the bulk) where the potential can be set to zero in order to simplify the result. However, we can take advantage of the
known surface charge on the walls, and use the boundary conditions from Eq. (11). Again it should be emphasized that although the solution generated from solving this boundary value problem with the most general form of the Poisson equation yields a non-unique solution, the same problem with the PB equation does yield a unique solution where the potential is with respect to that in the bulk solution. So, we should expect to achieve bulk concentration of ions and an electrical potential of zero in the center of the pore, for large pores where EDL overlap does not occur.

To solve this problem (i.e. Eq. (20) with Eq. (11)) numerically, a Gauss-Seidel algorithm was implemented with successive over-relaxation. This method discretizes the differential equation and the boundary conditions, begins with an initial guess of the solution, and iterates using finite differences until the solution converges within a desired error. Relaxation methods are useful for solving non-linear boundary value problems like the one dimensional PB equation. The details of this type of method are outlined nicely in a lecture by Dr. Robert E. Hunt [81], but can also be found in most introductory numerical methods texts. The over-relaxation parameter used was 1.9, and the convergence criterion was set such that when the maximum percent change from one iteration to the next was less than 0.01% the system was considered converged. Representative solutions for the 5-nm pore and various surface charges and for a variety of pore widths at a surface charge of $\sigma^* = 1.191$ are shown in Figure 6 below.

![Figure 6: Analytic PB solution for a single 1:1 electrolyte between two charged interfaces (a) at different surface charges and (b) at different pore widths.](image)

The potential profiles for one half of the 5-nm pore exactly match those from the single wall solutions in Figure 4. A discrepancy can be seen between the single wall and double wall solutions as the distance between the two walls decreases, i.e., for smaller pore sizes. This is to be expected, because when the walls become close enough the double layers on each wall begin to overlap, and bulk in the middle of the pore is not reached. Hence the single wall solution
which extends to bulk cannot capture this phenomenon. Figure 7 demonstrates this effect graphically by comparing the two solutions over half the pore for a 2-nm pore and a 5-nm pore at equal surface charges.

Figure 7: Single-wall and double-wall PB solutions at $\sigma^* = 1.191$ for pore widths of (a) 2-nm and (b) 5-nm

The concentration profiles for counterions and coions can be obtained via the numerical solution as well. They demonstrate all the appropriate characteristics, and have identical trends to the concentration profiles generated from the single wall solutions. Plots of local concentrations of ions with respect to the bulk concentration for varying surface charges and pore widths can be seen in Figure 8 and Figure 9 below.
Figure 8: Double-wall PB solution for concentration profile of a single 1:1 electrolyte inside a slit-type pore for varying pore sizes.

Figure 9: Double-wall solution for concentration profile of a single 1:1 electrolyte inside a slit-type pore at varying surface charges.

In sum, we have the ability to generate solutions to the PB equation in a pseudo-one dimensional nanopore or slit-type nanopore (i.e. it is identical in all directions other than normal to the charged surfaces), both analytically for the single-wall solution and numerically for the double-wall solution. These can be used to compare results from molecular modeling methods. However, the double-wall numerical solution can more accurately capture the physics of EDL formation within a pore when the single-wall solution cannot. The double-wall method seems then more suitable for comparison of molecular simulation results with Classical Theory.
5.2.3 Comparison to Grand Canonical Monte Carlo Concentration Profiles

The Fortran 90/95 code used in prior work [10] for Grand Canonical Monte Carlo (GCMC) simulation of ions in a slit-type pore was used to simulate the same single 1:1 electrolyte systems considered above, with the exception of the 15-nm pore due to high computational cost. The simulations were run on a Dell Precision T5610 workstation with an Intel® Xeon® Processor E5-2650 v2 (Eight Core HT, 2.6 GHz Turbo, 20 MB Cache). The specific features of the code are described in detail in Dr. Taboada-Serrano’s dissertation “Colloidal interactions in aquatic environments: Effects of charge heterogeneity and charge asymmetry” [82]. The activity coefficient needed to simulate a Grand Canonical ensemble for a 1.003M system was obtained in prior work to be 0.8803 in confinement. Concentration profiles were compared between the GCMC results and the GCS predictions. Figures 10a-10c show the relative ion concentration profile comparisons for different pore sizes at the same surface charge, while Figures 11a-11d show different surface charges in the same pore.

Figures 10a-10c show a progression with decreasing pore size, i.e. the double layers on each wall approach each other. At 2-nm the double layers begin to overlap and interact. At 5-nm, the double layers are significantly separated, with a region in the middle of the pore where bulk concentration is reached. The separation increases with larger pores, as expected. The relative counterion concentration next to the walls remains relatively constant at about 2.25, with a slight increase in the 2-nm pore that is not predicted by the GCS result. In larger pores where the extent of the double layer is clearer, it reaches out from the wall roughly 4 to 5 ionic diameters, with relatively good agreement between GCS and GCMC results. There is a slight discrepancy in the shape of the coion profile close the walls, most likely due to the finite size of the ions in the GCMC simulation creating a coion exclusion effect. This explains the slight concave up region which deviates from the Classical Theory prediction in Monte Carlo coion concentration values near the wall.
Figure 10: Comparison of GCS theory and GCMC simulation concentration profiles for different pore sizes (2-nm (a), 5-nm (b), and 10-nm (c)) at the same surface charge ($\sigma^* \approx 1.191$).

As for the effect of surface charge (Figures 11a-11d), we can see that concentrations in the pore with no surface charge are entirely that of the bulk. As surface charge increases, the relative concentration near the wall increases significantly. The GCS result appears to overestimate the surface concentration more as surface charge increases. This is expected because the PB assumptions become less valid for higher surface charge. The steric effects that are unseen in the GCS result become more of a factor with higher surface charge, preventing the GCMC concentration near the wall from increasing as drastically as the point charges in the GCS result. Again, the extent of the double layers are all roughly 2-nm from the walls. The coion exclusion effect near the wall is again seen, and becomes clearer with increasing surface charge.
Figure 11: Comparison of GCS theory and GCMC simulation concentration profiles for different surface charges ($\sigma^* = 0.000$ (a), $\sigma^* = 1.166$ (b), $\sigma^* = 2.375$ (c), and $\sigma^* = 3.802$ (d)) in a 5-nm pore.

Qualitatively the results agree well for larger pore sizes and moderate surface charges. A quantitative comparison of the data was made for all systems simulated using a root mean square error between GCMC data points and the corresponding values given from the Classical Theory (GCS). Results of this comparison are plotted in Figure 12. It is clear that the Classical Theory fits the MC data better for larger pores, and for lower surface charges, both of which are expected from the restrictions of PB based theories.
Figure 12: Root mean square error between GCS and GCMC concentration profiles

Overall, the 1M systems simulated match relatively well with the Classical Theory predictions for concentration profiles. Pores with moderate surface charges agree the best, as expected. The pore size appears to not have a significant impact on the root mean square error, and is very close for all pores at various surface charges. While a trend between the 2-nm and 5-nm pore data is difficult to see, the 10-nm pore error is on average about the same as or lower than the two smaller pores. The counterion (CN) profiles differ from PB predictions much more than the coion (CO) profiles, but errors for both increase with increasing surface charge. At the highest surface charge, error in the 5-nm pore data exceeded that of the 2-nm pore data. All errors were under 0.9 normalized number density units ($c^*$), with the lower surface charges differing by an error of under 0.25 normalized number density units. These findings support the choice to use a 1M system with larger pore size and moderate surface charge as a benchmark system for validating potential profiles calculated using the method to be developed in this work, as such systems are relatively well predicted by the Classical Theory.
6.0 Models of Electrical Double Layer Potential inside Nanoporous Electrodes from Grand Canonical Monte Carlo Simulations and the Electrostatic Poisson Equation

Almost all potential profiles that have been calculated from molecular modeling are based on Eq. (7). The trick to all EDL modeling is to find out what the charge density function looks like. The output of Monte Carlo simulations gives the equilibrium charge distribution, or the number of charges as a function of position, which can be straightforwardly converted to charge density in a primitive model. So, the charge density function is essentially computed from molecular modeling and can be used in the Poisson equation to solve for the potential. This problem is fundamentally different from the PB equation in a subtle way. The charge density function from molecular modeling is a function of position, but the Boltzmann distribution uses the energy to describe the distribution which causes the charge density to be a function of the potential itself. So, in the case of the PB description, Eq. (7) is a non-linear second order differential equation. However, if the density function from molecular modeling is used, Eq. (7) becomes linear. The solution to the linear case can be obtained in a number of ways.

6.1 Work Performed to Date

The canonical convolution integral solution to the Poisson equation in one dimension (Eq. (8)) is used in a number of works to obtain the solution for electric potential [48, 78].

\[ \psi(z) = \frac{e}{\varepsilon} \sum_l z_l \int_{z}^{\infty} (z - z') \rho_l(z') \, dz' \]  
(25)

This is derived from Eq. (8) accounting for multiple ionic species contributing to the charge density. A simplified form of this equation for a single 1:1 electrolyte can be written as follows:

\[ \psi(z) = -\frac{\rho_e}{\varepsilon} \left( \int_{z}^{\infty} [n_+(z') - n_-(z')] \, dz' - z \int_{z}^{\infty} [n_+(z') - n_-(z')] \, dz' \right) \]  
(26)

The solutions to Eq. (25) and Eq. (26) can be computed using a variety of methods. For example, Torrie and Valleau use sums within the Monte Carlo code itself [23]. They calculate averages of the two integral terms in Eq. (26). They calculate the first integral term, which physically is the dipole moment per unit area from charges beyond z, and the second integral term, which is z times the total charge per unit area beyond z, during the data collection phase of the simulation. They claim that this method is more accurate than directly integrating Eq. (26) by using the resulting concentration profile from simulation. However, the implications of using this method to compute potential are unclear, and the accuracy is not clearly quantified. Other works did solve Eq. (26) by direct integration using the resulting concentration profiles [48, 78]. This requires numeric integration via Riemann sums, however, which are not ideal due to their limited accuracy, and which compounds on the error in the density profiles themselves incurred from the nature of the Monte Carlo method. Furthermore, the general case solution (Eq. (25)) inherently contains a few restrictions in validity. The boundaries and corresponding boundary conditions are taken at the charged wall and in the bulk infinitely far away. As such, it is not practical for obtaining solutions confined between two finitely spaced walls, unless the walls are far enough
apart for the conditions in the middle of the pore to approximate those of a bulk solution contained within the walls infinitely far away. Since this work in particular is concerned with nanopores where the walls may be so close that double layers tend to overlap, this approach to obtaining the potential profile is especially impractical.

Integral expressions that are better suited for confined systems have also been explored [83]. By directly integrating Eq. (8) twice, it is easy to obtain Eq. (27).

\[
\psi(x) = -\frac{1}{\varepsilon} \int_{-\infty}^{x} \left[ \int_{-\infty}^{x'} \rho(x'') dx'' \right] dx' + C_1 x + C_2
\]  

(27)

The integration constant \(C_1\) is obtained from a boundary condition on the derivative of the potential, i.e. the electric field. Therefore, one can see how this method also contains drawbacks because it requires the system to include a point where the electric field is known; the most logical point would be a value of zero in the bulk. Moreover, even if this condition were known somewhere, the solution is still not unique since \(C_2\) is arbitrary. One approach to obtain a unique solution is to use the Galvani potential of the fluid as a reference, and therefore set \(C_2\) such that the value of the potential in the bulk of the fluid is zero. The solution must still be obtained through Riemann sums, which maintain the same restrictions in accuracy as discussed above, including requiring extremely small step sizes or more complicated implementations. It is a crucial factor that the bulk must be physically included in the simulation system in order to obtain a unique solution to Eq. (27) because this requires modification and complication of the molecular modeling code from traditional methods for slit-type pores.

6.2 Potential from Direct Numeric Integration

This work explored more straightforward numerical techniques to obtain a solution to the Poisson equation. Rather than working from pre-existing integral solutions to Eq. (8) and using some form of discrete sums, this work explored direct numeric integration techniques. Methods considered include a fixed step fourth-order Runge-Kutta method and a finite difference Gauss-Seidel method with successive over-relaxation. Because these numerical techniques are dependent on step size, it was necessary to connect the discrete data points resulting from Monte Carlo simulations with a finer function of position. Two different methods to accomplish this will be discussed.

6.2.1 Obtaining Charge Density and Creating a Continuous Function

First, the concentration profiles obtained from Monte Carlo simulations need to be converted into a volumetric charge density function that will be used with the Poisson equation. The raw output from the Monte Carlo simulation is obtained as follows: the simulation box is divided into bins in the direction normal to the charged surfaces. Then the simulation is run until equilibrium is reached, at which point the number of ions (for each ionic species) in each bin is averaged for the remainder of the simulation. The final counts for number of ions are arbitrarily assigned to the location of the right edge of the bin to which the number applies. A representative
The figure of the bins is displayed in Figure 13. The bin spacing in this figure is exaggerated for visual effect. In the actual systems simulated in this work, the simulation box was divided into 100 bins. Also note that an in-built algorithm tracks the position of the centers of the ions, so if an ion is partially in two bins, it is the center point of the ion that will dictate the bin in which this ion is counted.

![3D Example of Simulation Box Bins](a)

![2D Example of Simulation Box Bins](b)

**Figure 13**: Example of bin division of simulation box in a 3D view (a) and in a 2D view with the charged walls on the left and right sides (b)

In order to convert the number of ions in each bin to volumetric charge density, one can first convert the ion counts in each bin to net charge in each bin. This is done by multiplying the charge count for each species by its respective valence and the electronic charge, and then adding the results for all the species in the same bin. This is exactly what was done in Eq. (18) for the PB equation, only now \( n_i \) is a result from Monte Carlo simulations. Then, in order to get volumetric charge density, one can divide the resulting net charge in each bin by the volume of each bin. This conversion process is summarized in Eq. (28) below.

\[
\rho_{\text{bin}} = \frac{\sum_i (z_i e)n_i}{v_{\text{bin}}} = \frac{Q_{\text{net/bin}}}{v_{\text{bin}}}
\]  

(28)

This process combines the multiple GCMC data sets for each ionic species into a single volumetric charge density function.

Next, a cubic spline interpolation was considered merely as a simple, robust method to create a continuous charge density function from the discrete GCMC data set. A cubic spline interpolation assumes that the charge density smoothly increases or decreases across each bin in which the charges are counted during the Monte Carlo simulation. However, the Monte Carlo
outputs are actually average values that represent an average number of ions throughout the entire bin obtained over thousands of probable ion configurations with an acceptable potential energy distribution. So, using the most physically direct interpretation of the data in order to create a continuous function would result in a piecewise function of constants, where the Monte Carlo data point values are smoothed out across the full length of the bins. Both of these options were considered in this work and are shown in Figure 14. They were also corrected by forcing the interpolations to zero at points closer than one ionic radius from the walls. The GCMC code arbitrarily assigns the ion count in each bin to the right side edge of that bin. Without this correction it is possible to get data points located in the forbidden region if, for example, a bin partially extends into the region less than the closest approach of an ion.

![raw volumetric charge density from GCMC](a)

![cubic spline interpolation](b)

![piecewise constant interpolation](c)

Figure 14: Interpolation of the raw GCMC charge density data for a 5-nm pore at $\sigma^* = 1.166$ (a) using a cubic spline interpolation (b) and a piecewise constant interpolation (c)

Smoothing the data using a moving average technique was also considered in the creation of a continuous charge density function from GCMC data. However, smoothing was discounted
based on two factors. First, the moving average treats the values closest to the surface as outliers, since they are so drastically different from the roughly constant values in the middle of the pore. As such, this would require more complex techniques to ensure that true physics (i.e. the accumulations of charge close to the surface) captured by the data is not lost. Moreover, even accepting that the smoothing may impact the values next to the surface, results using the smoothed data versus using the non-smoothed data were found to exhibit negligible differences at the center of the pore, thus they are not discussed further in this work.

6.2.2 Runge-Kutta Half Pore Initial Value Problem

A fourth order Runge-Kutta solver was implemented with the cubic spline interpolation of the Monte Carlo charge density function to solve Eq. (8). This method is used for solving initial value problems, so the integration was carried out from the middle of the pore to the wall for both halves of the pore. This allows us to define the initial values for the Runge-Kutta solver using the assumptions that the value of the potential and its derivative are zero in the middle of the pore. This is expected to be the case for pores that achieve bulk in the center. The results of this method for each half of the pore were then averaged together, and then compared with the analytic single wall solution of the PB equation (Eq. (21)-(24)).

A fixed step fourth order Runge-Kutta algorithm is one of the most widely used methods to perform integration numerically. Runge-Kutta methods are based on the fact that any order ordinary differential equation can be written in terms of a set of first order differential equations, and first order differential equations contain information about the slope of the desired function. For example, the non-dimensional Poisson equation can be written as,

\[
\frac{d\psi^*}{dx^*} = -\rho^*(x)
\]

\[
\frac{d\psi^*}{dx^*} = \psi^{**}
\]

(29)

The variables \(\psi^*\) and \(\psi^{**}\) can be approximated using linear interpolations between consecutive points of the function. These interpolations can cumulatively give a good approximation of the true function if the distance between consecutive points, or the step size, is small enough. For this specific problem, if \(\psi^*\) and \(\psi^{**}\) are discretized into \(n\) points with a step size \(\Delta x\) between them and the initial conditions for both \(\psi^*\) and \(\psi^{**}\) are known, the slopes from Eq. (29) can be used to estimate the change in the functions across \(\Delta x\). This process can be used find an approximate solution for both the variables, and is summarized in Eq. (30) below.

\[
\psi_{i+1}^{**} = \psi_i^{**} + (\Delta \psi_i^{**})\Delta x \ (i = 1,2, ..., n)
\]

\[
\psi_{i+1}^{*} = \psi_i^{*} + (\Delta \psi_i^{*})\Delta x \ (i = 1,2, ..., n)
\]

(30)
The Euler method uses exactly Eq. (29) to estimate the $\Delta \psi_i'$ and $\Delta \psi_i^*$. However, this method is only accurate to first order, and so the error in the approximate solution is directly proportional to step size. This requires larger computational cost and machine precision errors associated with very small step sizes. Runge-Kutta is an adaptation of this process that results in a higher order method with better accuracy and a reduced dependence on step size. Fourth order Runge-Kutta uses Eq. (29) to first get the slope $k_1$ at point $x_i$, then uses this slope in Eq. (30) to predict the function value at the midpoint of the step, $x_i + \frac{1}{2} \Delta x$ and the slope here, $k_2$, is found. The slope $k_2$ is then used to get a better estimate of the function value at $x_i + \frac{1}{2} \Delta x$, and slope $k_3$ is obtained at this new point. Finally, slope $k_3$ is used to get an estimate of the function at $x_i + \Delta x$, and the slope $k_4$ is found at this final point. All four slopes are then combined using a weighted average to ultimately get more accurate values of $\Delta \psi_i'$ and $\Delta \psi_i^*$ to use in Eq. (30). This averaging scheme is shown below.

$$k_{RK} = \frac{1}{6} (k_1 + 2k_2 + 2k_3 + k_4)$$  \hspace{1cm} (31)$$

Here, $k_{RK}$ may represent $\Delta \psi_i'$ or $\Delta \psi_i^*$. The process is repeated over all points, $i$, to obtain a fourth order accurate estimate of the function over interval $x_i$ to $x_n$.

This approach is useful for validation as long as the pore is large enough to reach bulk conditions in the middle. It should be noted that this method is not robust because it requires the potential in the middle of the pore to be zero; this condition may not be true in nanopores that are small enough to have overlapping double layers.

The method described above was implemented in a MATLAB script for the same GCMC results obtained for comparisons in section 5.2.3. Table 2 outlines the parameters used for GCMC simulations.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Relative Permittivity of Solvent ($\varepsilon_r$)</th>
<th>Ionic Diameter (nm)</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>78.5</td>
<td>0.425</td>
<td>1.003</td>
</tr>
<tr>
<td>Pore Size (nm)</td>
<td>Pore Size ($z^*$)</td>
<td>Surface Charge (C/m²)</td>
<td>Surface Charge ($\sigma^*$)</td>
</tr>
<tr>
<td>2</td>
<td>4.706</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>5</td>
<td>11.77</td>
<td>0.050</td>
<td>1.191</td>
</tr>
<tr>
<td>10</td>
<td>23.53</td>
<td>0.100</td>
<td>2.231</td>
</tr>
</tbody>
</table>

Table 2: Parameters of systems simulated using GCMC to obtain potential profiles

Figure 15 below shows representative results for the 5-nm pore at $\sigma^* = 1.166$. It is clear that results from this method do a poor job at matching PB predictions. The potential profiles from the interpolation of GCMC results and integration of the Poisson equation clearly exhibit a non-
exponential behavior with minima roughly 1.5 ionic diameters from the walls. This was unexpected, because the concentration profiles appear to match rather well with PB predictions.

Figure 15: Half pore potential profile from Runge-Kutta solver compared with PB single-wall solution. Plot are for pores at equal surface charge ($\sigma^* \approx 1.191$) with pore widths of 2-nm (a), 5-nm (b), and 10-nm (c)
Figure 16: Half pore potential profile from Runge-Kutta solver compared with PB single-wall solution. Plot are for pores of equal width (5-nm) with surface charges of $\sigma^* = 0.000$ (a), $\sigma^* = 1.166$ (b), $\sigma^* = 2.375$ (c), and $\sigma^* = 3.802$ (d).

On closer examination, a very small positive bias in the charge density in the middle of all pores with nonzero surface charge was observed. This bias caused the solution for potential to be pulled in the negative direction as the integration was carried out towards the wall, due to the calculated negative concavity and slope. Figure 17 demonstrates this effect by displaying the values of the potential and its first and second derivatives calculated from Runge-Kutta.
Figure 17: Runge-Kutta solution for half pore potential and derivatives for the left half (a) and right half (b) of the 5-nm pore at $\sigma^* = 1.166$

Figure 17 suggests that the unexpected shape of the potential might be due to a numerical artifact of the integration method, compounding on the method of interpolation of the charge density function. In larger pores the surface potential is very small, and so this effect gave results where the predicted surface potential was negative in these systems. This also caused the shape of the distribution to deviate from the classically expected monotonic exponential.

The bias believed to be responsible for this deviation was very small, so it was posited that the reason could be due to a slightly inaccurate representation of the true charge density by the interpolation method, i.e. failure to accurately represent the physics of the problem. In an attempt to counteract this, the piecewise constant interpolation was considered, with the expectation that it might be a slightly better representation of the true physical nature of the charge density and correct for this small bias. Figure 18 shows that making this adjustment improved the resulting profiles, but only slightly. The potential profiles generated for the left half of the pore and the right half of the pore were shifted by a small amount for all systems, but the average half pore potential remained relatively unchanged. The minimum of the average half pore potential for the 5-nm pore in Figure 18 increased only slightly, so ultimately the resulting potential profiles were almost identical for both methods of interpolation of the charge density function.
These results raised the questions that either the assumption of a zero potential in the center of the pore may not be valid, or that there may be some numerical artifact due to the small bias in the concentration profile that was compounding on itself as the numerical integration was carried out. Therefore, the accuracy of a Runge-Kutta initial value problem to obtain the potential was placed into question.

### 6.2.3 Finite Difference Full Pore Boundary Value Problem

An alternative method was considered to further investigate this unexpected shape in the potential profiles. The boundary value problem where the surface charge on the walls is used to dictate Neumann boundary conditions on the potential profile (explained in section 5.1.1) could be used in conjunction with the resulting charge density function to solve for the potential. We already had the means of getting the solution for the PB potential using the Gauss-Seidel method with successive over relaxation (from section 5.2.2). So, all that was needed was to implant the continuous charge density function created from the Monte Carlo data into Eq. (8) as the forcing function. However, solutions obtained were orders of magnitude off from PB predictions, and varied grossly from the half pore Runge-Kutta potential.

In order to understand the discrepancy between the proposed method and the solutions from the PB equation, the mathematical nature of the problem was examined more closely. The boundary value problem, considered in its non-dimensional form for ease of calculation, is restated below.

\[
\frac{d^2\psi^*}{dx^*^2} = -\rho^*(x) \quad \text{with} \quad \frac{d\psi^*}{dx^*}|_{w^*} = -\sigma^* \quad \text{and} \quad \frac{d\psi^*}{dx^*}|_{w^*} = \sigma^* \quad (32)
\]
Here $x^*$ is taken as zero in the center of the pore, so the boundaries are at $-\frac{w^*}{2}$ and $\frac{w^*}{2}$, where $w^*$ is the non-dimensional width of the pore. From this point forward in the section, the star superscripts will be dropped for clarity of the equations, but all variables referred to in the equations will be dimensionless. To analyze the existence and uniqueness of the solution to Eq. (32) we must first homogenize the boundary conditions so the solution lies in a vector space and can be analyzed using linear algebra techniques. To do this we can assume the solution takes the form,

$$\psi(x) = \bar{\psi}(x) + \left(\frac{\sigma}{w}x^2\right)$$

(33)

In this form, the boundary conditions for $\bar{\psi}(x)$ are now homogeneous and thus the solutions lie in a vector space. This allows us to examine $\bar{\psi}(x)$, and then transform the result back to $\psi(x)$ in the last steps. Substituting Eq. (33) into Eq. (32), the problem for $\bar{\psi}(x)$ now becomes,

$$\frac{d^2\bar{\psi}}{dx^2} = -\rho(x) - \frac{2\sigma}{w} \quad \text{with} \quad \frac{d\bar{\psi}}{dx}\bigg|_{-\frac{w}{2}} = 0 \quad \text{and} \quad \frac{d\bar{\psi}}{dx}\bigg|_{\frac{w}{2}} = 0$$

(34)

To test for uniqueness of the solution, the null space of $\bar{\psi}(x)$ can be examined. The problem to obtain the null space is as follows,

$$\frac{d^2\bar{\psi}_n}{dx^2} = 0 \quad \text{with} \quad \frac{d\bar{\psi}_n}{dx}\bigg|_{-\frac{w}{2}} = 0 \quad \text{and} \quad \frac{d\bar{\psi}_n}{dx}\bigg|_{\frac{w}{2}} = 0$$

(35)

The solution can be obtained straightforwardly by direct integration to obtain a linear function with two constants of integration. Applying the boundary conditions, the solution for the null space is given as,

$$\bar{\psi}_n = C_2 \quad \text{so} \quad \dim(\psi_n) = 1$$

(36)

where $C_2$ is a constant of integration. Since the dimension of the null space is not zero, by the fundamental theorem of linear algebra the solution for $\bar{\psi}(x)$ is not unique; it directly follows that the solution for $\psi(x)$ is also not unique.

So, while the method of using finite difference techniques to solve Eq. (32) in order to obtain potential profiles from GCMC outputs is attractive because it is not restricted to systems where the potential in the middle of the pore is zero, any solution obtained by this method will not be unique up to an additive constant, as deduced from the null space solution.

One way to get around the lack of a unique solution is to physically include the bulk in the simulation box during the molecular simulations. Then the additive constant can be chosen such that the potential at the bulk is zero, and the result would be unique and with respect to the bulk potential. However, the Grand Canonical ensemble has been adopted in this work, which translates into the bulk being a virtual reservoir that is not physically included in the system.
Therefore, the non-unique solution coupled with the fact that the bulk is virtual, leaves no way to set a reference value for the potential calculated using this method. An absolute value of the potential relative to some reference is necessary if results are to be used to relate the information learned from molecular modeling to real systems. With all this taken into consideration, this work did not find it feasible to put in the efforts to create and use a more reliable finite difference solver for this particular problem (i.e. solving Eq. (32) with the Monte Carlo charge density functions).

In sum, the Runge-Kutta method is simple to implement, but results were not as expected. Moreover, this method is not robust enough to obtain solutions for very small pores because it relies on knowledge of initial values for the potential and its derivative at some location inside the pore. The finite difference method makes up for this by relying only on the surface charge as boundary conditions but fails to give a unique solution. This last method may be useful for understanding trends in the shape of potential profiles in slit-type pores. The fact that the finite difference solution is not unique renders this method invalid for obtaining an absolute value of potential relative to a known reference, which is needed in order for the potential profile to be useful in experimental comparison. Hence, this work did not pursue obtaining solutions through this method. However, the non-unique solution to the boundary value problem can be remedied by including a physical bulk in the simulation box, as was done by Kovács et al. [83], which implies using a Canonical Ensemble (closed system) to simulate the pore and its surroundings. This approach will involve modifying the main Monte Carlo simulation code we have been using, which consists of an open system allowed to establish thermodynamic equilibrium with its surrounding (Grand Canonical Ensemble). The rationale behind choosing a Grand Canonical Ensemble is to mimic common electrochemical experiments where porous electrodes are submerged in large quantities of bulk solution and allowed to reach thermodynamic equilibrium during charging-discharging cycles.
Models of Electrical Double Layer Potential inside Nanoporous Electrodes from Grand Canonical Monte Carlo Simulations and Fundamental Electrostatic Concepts

Because of the difficulties in obtaining both a robust and unique solution for potential profiles from solutions to the Poisson equation, a different approach was considered which involves even more basic principles from electrostatics. Considering the operations occurring within the Monte Carlo simulation, the exact equilibrium configurations of the ions are already accessible, including the positions and the energies of every ion in the system. Electric potential in its most fundamental form is the electrostatic potential energy a unitary point charge would experience at a specified location in space. The value itself depends on a reference value used for the energy calculation, typically a value of zero at infinite distance from the source charge. Hence, it was proposed that if one considers a single ion, the electrostatic potential energy of that ion in its current configuration can be calculated using the same energy calculations needed for the Monte Carlo simulation, and then divided by the charge of the ion. The result would represent a value for the potential at the location of the ion with respect to the same reference used for the energy calculation. This reasoning was then used as a basis for a new method to calculate potential that not only bypasses the need to numerically solve the Poisson equation but also results in a unique solution. Moreover, the fact that the energies of the ions are already computed by the Monte Carlo simulation makes this method computationally efficient.

7.1 Grand Canonical Monte Carlo Energy Calculations

In the GCMC simulation there are four different types of energies associated with any given ion. The energies stem from the Coulombic ion-ion pair interaction, a correction for long range interactions of the ion with periodic ions outside the main simulation box, and the interaction between the ion and the charged walls. The ions are modeled as charged hard spheres, so the complete pair interaction is defined as,

$$
\nu_{ij} = \begin{cases} 
+\infty & r_{ij} < \sigma_{ij} \\
\frac{Q_i Q_j}{4\pi \varepsilon r_{ij}} & r_{ij} \geq \sigma_{ij}
\end{cases}
$$

Here $\nu_{ij}$ is the ion-ion pair potential, where subscript $i$ represents one ion and $j$ represents a different ion. $Q_i$ and $Q_j$ are the charges of the respective ions, and $r_{ij}$ is the center to center distance between the ions. $\sigma_{ij}$ is the maximum distance of closest approach between the two ions, which is defined as the square root of the sum radius of each ion squared [82]. In practice, the infinity term, which accounts for the hard sphere interaction, ultimately means that any moves in the Monte Carlo simulation that results in a center to center distance of any ion pair being less than $\sigma_{ij}$ is always immediately rejected. Thus, for the purposes of calculating the electric potential, only the Coulombic term needs to be considered.
There are many ways to account for long range interaction of ions with periodic ions that are outside the main simulation box. A popular method developed by Boda et al. [44] uses infinite charged sheets associated with each ion that are outside the simulation box, parallel to the charged walls, and centered at the location of the corresponding ion. The total charge on each sheet is equal to the charge of the respective ion at its center, and represents the image ions in repetitive fluid boxes outside the main simulation box. As explained in Chapter 3.0, Monte Carlo simulations are run for a central simulation box that has periodic boundary conditions[44]. A schematic of these sheets is shown below.

![Figure 19: Schematic of the main simulation box with charged sheets for long range corrections shown](image)

The interaction energy of an ion \(i\) with the charged sheet of another ion \(j\) can be calculated by first finding the interaction energy of ion \(i\) with an infinite sheet located at ion \(j\), then subtracting out the interaction energy of ion \(i\) with a finite charged sheet of dimensions \(L \times L\) at the same location. Mathematically this is expressed as,

\[
v_i = u_{i,j,\text{sheet}}(x_i, x_j, \infty) - u_{i,j,\text{sheet}}(x_i, x_j, L)
\]

(38)

Where \(x_j\) and \(x_j\) are the normal distances of the ion or sheet from the charged wall at the end of the simulation box. The explicit form of the interaction energy for the finite sheet is given as,

\[
u_{i,j,\text{sheet}}(x_i, x_j, L) = \frac{Q_i Q_j}{L^2} \int \frac{L}{2} \int \frac{L}{2} dydz \quad \text{where} \quad \mathbf{r} = (x_i - x_j, y, z)
\]

(39)
And finally, the form of the interaction energy of an ion with one of the uniformly charged impenetrable walls (as shown in Figure 19) is given as,

\[ u_{i,\text{wall}}(x_i, \infty) = \frac{Q_i \sigma |x_i - x_{\text{wall}}|}{2\varepsilon} \]

Details of the derivations of the exact energy terms can be found in other works [44].

7.2 The Algorithm

All of these energy terms are already being calculated within the Monte Carlo simulation so that the simulation can minimize the configurational energy of the system as a whole to eventually reach the equilibrium configuration. Thus no extra effort is needed to obtain the energy of an individual ion in order to implement this new method for calculating the electric potential. Now, in order to use this information to obtain potential profiles, augmenting the existing histogram function in the Monte Carlo code that is responsible for accumulating ion counts and averaging them to obtain the final concentration profiles with an algorithm to accumulate and average the ion potentials is needed. The histogram function identifies which ions are in which bin (see Figure 13), and counts them. When the program identifies which ions are in which bin, it can now also calculate the potential of each ion but summing its energy and dividing by the charge of the ion. Since this represents the potential at the location of the ion due to the current configuration, we can average the potential values for all ions in each bin. This will result in an average bin potential for each bin, and result in a potential profile similar to the concentration profile that is obtained. Now, in order to increase accuracy in the result, we can repeat this process over many configurations after the system has reached thermodynamic equilibrium and average the configurational potential profiles. This is precisely how the concentration profiles are averaged, so we expect accuracy in the potential to be proportional to that of the concentration profiles. The process just described is outlined graphically in the flow chart shown in Figure 20.
It should be noted that this algorithm must contain a check to see if there are zero charges in a bin, in which case the average bin potential must be forced to zero. This will leave the total equilibrium average unaffected by this bin, since it has no information to contribute, and will also avoid a division by zero in the calculation. Furthermore, the region less than one ionic radius from the charged walls will result in potential values of zero based on this approach. So, in this charge free region a linear increase should be appended to the calculated profile that extends from one ionic radius from the wall to the wall itself. The increase is proportional to the surface charge in accordance with Eq. (11).

In order to analyze the meaning of this potential more precisely, consider the case in which the impenetrable walls have zero surface charge. In such a scenario, there is no external field from the charged walls. So, the energy of an ion is determined solely by ion-ion interactions, whether that be short range (Eq. (37)) or long range (Eq. (38)). This situation corresponds to that of an ion in an infinite, charge neutral bulk solution. In other words, this scenario is identical to that of the virtual reservoir bulk in the Grand Canonical Ensemble. Due to electroneutrality, we expect an even and random distribution of both positive and negative ions in the bulk. Thus, the positive and negative contributions to the potential energy (and therefore the potential) are expected to balance out to zero. So, a potential of zero using this method is expected to represent that of a field free bulk solution identical to that in the virtual bulk.
reservoir in the Grand Canonical Ensemble. In effect, the proposed method can account for the bulk solution within the electrical potential calculation without the need to physically include it in the simulation box. In other words, any potential within the pore will be effectively expressed with respect to a potential in the bulk solution with which the solution inside the pore is in thermodynamic equilibrium.

A desirable aspect of this approach is its simplicity. Monte Carlo code can be straightforwardly adapted to compute the necessary values, and because the approach uses such fundamental concepts, there is a high level of confidence that the results are a true representation of the physics. Moreover, it is robust in that it requires no numerical integration techniques, can be used for both single and double wall systems, and will always result in a unique solution. Using this method, the resulting potential in the presence of an external field will be a clear indication of the relative number of positive to negative ions at a location in the simulation box, based on the sign of the potential. Moreover, an absolute value of the potential (in particular, the surface potential) can be unequivocally identified because the computed values are with respect to the virtual bulk solution, as explained above. This is very attractive because the virtual bulk is a representation of the liquid phase outside of the pore in an experimental system. The potential in the bulk of the liquid phase outside the pore is the Galvani potential, which is a viable option for a reference potential. So, results obtained from using this method should be able to be correlated to absolute values of potential in experimental systems by using the Galvani potential of the fluid phase.

7.3 Individual System Results and Discussion

The method described in section 7.2 was implemented for the systems listed in Table 2. The results will be discussed system by system to thoroughly analyze and accurately interpret the observed physics. To begin, a three dimensional view of the simulation box for the different sized pore systems is shown in Figure 21. These are representative plots of snapshots of possible configurations of ions taken during the last cycle of the MC simulation for the various pores with zero surface charge on the walls at $x=0$ and $x=w^*$. They represent equilibrium configurations of the systems, and the box and ion diameters are to scale in normalized coordinates. One can get a sense of the different sizes of the simulation boxes in order to get a feel for the physics of the systems. The simulation box for smaller pores has larger wall sizes so that the box is large enough to be able to contain the bulk number of ions. As pore size increases, the wall size is decreased to limit the computational cost of the simulations by keeping the number of ions needed in the simulation box close to the minimum number of ions required for the results to be independent of system size.
Figure 21: Example of GCMC simulation box for different pore sizes (2-nm (a), 5-nm (b), and 10-nm (c)) with positive coions (red) and negative counterions (blue) shown to scale for 1M systems at $\sigma^* = 0.000$

A random distribution of blue anions (counterions) and red cations (coions) can be seen, affirming that the systems have qualitatively achieved bulk conditions in the pores. The calculated concentration and potential profiles divide this three dimensional simulation box into bins and count the average number of ions and average potential in each bin, thus grouping the results in a way that reduces the system effectively to one dimension. The three dimensional view of the simulation box can be viewed in a two dimensional orientation to align it with the calculated profiles to get a better sense of the meaning behind the profiles and aid with interpretation of the physics.

Considering the 2-nm pore first, the concentration profiles are plotted alongside the potential profiles for comparison. The two dimensional view of the final configuration of the ions is also shown with the potential profile overlaid (using an arbitrary scale).
Figure 22: Comparison of concentration profile and potential profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 2-nm pore at $\sigma^* = 0.000$

In the case of zero surface charge, it is evident that bulk conditions are reached for both the potential and concentration profile. The zoomed in scale shows the potential in the pore oscillates tightly around zero, while the concentration of both the coions and counterions are that of the bulk. The two dimensional view of the final configuration shows a relatively even and random distribution of both coions (red) and counterions (blue), and the relatively constant potential across the pore.

Figure 23: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 2-nm pore at $\sigma^* = 1.183$
With a moderate surface charge of $\sigma^* = 1.183$ applied to the walls, one can see that the surface potential increases to a value greater than zero at the walls, but also dips to a value of less than zero in the middle of the pore. The potential minimum occurs exactly in the center of the pore. It appears that the increased number of counterions near the walls is excluding the positively charged coions in the double layer region due to steric or entropy effects (i.e. packing of the finite-sized spheres). This coion exclusion zone extends roughly 2.35 ionic diameters from the walls. In this region, the negative potential due to the counterions dominates, causing the potential in the pore to continue to drop lower than that in the field free bulk across almost the entire pore. The small region where bulk concentration is reached in the middle of the pore may have the same number of ionic species as that in the bulk, but electrically it varies from bulk conditions due to the far reaching electrical effects of the negatively charged double layer region.

Figure 24: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 2-nm pore at $\sigma^* = 2.384$

With a larger surface charge of $\sigma^* = 2.384$ applied to the walls, the coion exclusion near the walls increases, as more counterions are required to screen the charge. The potential at the distance of closest approach of an ion to the wall is almost exactly zero, displaying how the negative ions in the double layer completely screen the positive surface charge. Again, the negative potential due to this layer extends farther than half the pore width, causing the overlap of the potential profile extending from each wall contribute to an even more negative potential in the center than in the $\sigma^* = 1.183$ system. Because the pore is so small, the potential due to the positive coions is not able to overcome dominant negative potential in the double layer.
Figure 25: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 2-nm pore at $\sigma^* = 3.815$

At an even larger surface charge of $\sigma^* = 3.815$, the effect is further enhanced. The coion exclusion region is clearly visible as the screening ions are packed against the wall, and the potential drops dramatically towards the center of the pore to a value well below that in the bulk. It can also be noted that the surface potential for the 2-nm pore systems increases with increasing surface charge, as expected.

Examining the 5-nm pore systems, similar effects are observed as in the 2-nm pores, but with a few clear differences in the systems with higher surface charges.
Figure 26: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 5-nm pore at $\sigma^* = 0.000$

The 5-nm pore at zero surface charge system looks just like that of the 2-nm pore. Bulk conditions are reached for the ionic concentrations and also electrically, as evidenced by the mean value of zero for the potential across the pore.

Figure 27: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 5-nm pore at $\sigma^* = 1.166$

When a surface charge of $\sigma^* = 1.166$ is applied to the pore walls, an interesting behavior in the potential is observed. The potential reaches local minima at the locations where the concentration
profiles first achieve bulk, and a local maximum in the middle of the pore. This behavior grossly disagrees with PB predictions, which are only capable of producing monotonically decreasing profiles. The ideas discussed with the 2-nm pore again apply here. Due to packing effects near the wall, a coion exclusion region is produced. This region full of negative charges dominates electrically. It fully screens the surface charge by a distance of just under one ionic diameter from the walls. Moreover, because the negative field created by this charge layer extends farther in space than the layer itself, the effects are seen all the way to the middle of the pore. The combination of this effect from both walls meeting in the pore center leaves a net negative potential here. The coion exclusion region in the 5-nm pore extends roughly 2.35 ionic diameters, similar to the 2-nm pore. However, the 5-nm pore has more space beyond this region than the 2-nm pore, so the coions do better at attempting to neutralize the negative effects of the double layer towards the center of the pore. This explains why the minima occur right where the coion exclusion region ends, and why the maximum is seen in the middle of the pore.

![Figure 28: Comparison of concentration profile and potential profile and final configuration with arbitrarily scaled potential overlay for 5-nm pore at $\sigma^*=2.375$](image)

At $\sigma^*=2.375$ in the 5-nm pore, the packed ions in the double layer become more evident. The extent of the coion exclusion region remains the same as with $\sigma^*=1.166$, but since there are more negative charges in this region, the potential drops to an even lower value than the case with lower surface charge. In turn, the coions in the center of the pore are not able to neutralize the negative potential as much, resulting in an even lower potential in the pore center than in the $\sigma^*=1.166$ case.
At high surface charge \( \sigma^* = 3.802 \), the region near the walls is very tightly packed with counterions. The potential drop is even more significant here. The extent to which the coions can neutralize the negative potential appears to remain roughly the same in all cases of surface charge, hence the potential in the pore center becomes increasingly negative as surface charge increases. Also, the surface potential appears to increase with increasing surface charge in these systems, which agrees with expectations.

Continuing to examine large pore sizes, the 10-nm pore is considered next. Again, the same physics is observed as in the smaller pores with respect to effects of surface charge on the potential profiles. However, unlike the 2-nm and 5-nm pores, the 10-nm pore is large enough to just barely allow the coions to completely neutralize the negative potential from the double layer. A small region of truly bulk conditions, both in ionic concentration and electrically, is observed in the center of the pore, for all cases of surface charge as evidenced from Figures 31 to 33.
Figure 30: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 10-nm pore at $\sigma^*=0.000$

The zero surface charge case again reaches bulk conditions and looks similar to the smaller pores also at zero surface charge.

Figure 31: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 10-nm pore at $\sigma^*=1.166$

At $\sigma^*=1.166$, the 10-nm pore has even more pronounced minima at the locations where bulk concentration is first reached. The location of these minima is the same as in the 5-nm pore, roughly 2.35 ionic diameters from the walls. A maximum is again observed in the middle of the pore, only now the value reaches zero in the pore center. This indicates that the 10-nm pore is just large enough for the coions in the center to neutralize the negative potential due to the coion exclusion region near the walls. Since bulk potential is just barely reached in the center of the
pore, this is a good indication that the extent of the electrical effects of the double layer are roughly 11.7 ionic diameters (i.e. half the width of the 10-nm pore).

Figure 32: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 10-nm pore at $\sigma^* = 2.384$.

Figure 33: Comparison of concentration profile (a) and potential profile (b) and final configuration with arbitrarily scaled potential overlay (c) for 10-nm pore at $\sigma^* = 3.815$.

The two higher surface charges, $\sigma^* = 2.384$ and $\sigma^* = 3.815$, follow the expected trend. The closer packing of counterions with higher surface charge causes a more dramatic drop in the potential across this region. The minima occur at the same distance from the walls for all cases of surface charge, and the coions are able to bring the potential back up to zero in the center of the pore for all surface charges.
An even larger pore size can be simulated to confirm the expected pattern in the behavior of the potential based on observations of the 2-nm, 5-nm and 10-nm pores. The profiles are expected to look qualitatively similar to those in the 10-nm pore. However, since there is even more space in the larger pore, a larger region of zero potential is expected in the middle of the pore. The extent of the electrical effects of the double layer appears to be invariant with pore size and surface charge, so local minima are expected around 2 ionic diameters from the walls, while zero potential is expected to be reached around 11.7 ionic diameters from the walls. Due to the extreme computational cost necessary to run a GCMC simulation of a large pore and achieve equilibrium conditions, this work was not able to include results for such a system within the required timeframe.

Multiple simulations of different system sizes were timed to get forecasts of total run times on our workstation. The time per Monte Carlo iteration was plotted against the number of ions needed to achieve the desired 1M concentration in the simulation box. Since run time is directly related to the number of ions per pair, which is proportional to the square of the number of ions, a quadratic curve was fit to the data. This curve was then extrapolated to predict the run time per iteration for larger systems. The results were then used to estimate total run times for a given number of iterations, as shown in Table 3. For example, a 20-nm pore with a simulation box of 10-nm x 10-nm x 20-nm requires about 1200 ions. With a surface charge of $\sigma^*=3.815$ the simulation could require up to 8 million iterations to reach equilibrium, which is estimated to take almost 67 days to complete with the processing power of our workstation.

<table>
<thead>
<tr>
<th>Number of Ions</th>
<th>Seconds per Iteration</th>
<th>Run time in days for given number of iterations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8 million Iterations</td>
<td>7 million Iterations</td>
</tr>
<tr>
<td>100</td>
<td>0.0038</td>
<td>0.4</td>
</tr>
<tr>
<td>200</td>
<td>0.0179</td>
<td>1.7</td>
</tr>
<tr>
<td>300</td>
<td>0.0422</td>
<td>3.9</td>
</tr>
<tr>
<td>400</td>
<td>0.0767</td>
<td>7.1</td>
</tr>
<tr>
<td>500</td>
<td>0.1215</td>
<td>11.2</td>
</tr>
<tr>
<td>600</td>
<td>0.1764</td>
<td>16.3</td>
</tr>
<tr>
<td>700</td>
<td>0.2417</td>
<td>22.4</td>
</tr>
<tr>
<td>800</td>
<td>0.3171</td>
<td>29.4</td>
</tr>
<tr>
<td>900</td>
<td>0.4028</td>
<td>37.3</td>
</tr>
<tr>
<td>1000</td>
<td>0.4988</td>
<td>46.2</td>
</tr>
<tr>
<td>1100</td>
<td>0.6050</td>
<td>56.0</td>
</tr>
<tr>
<td>1200</td>
<td>0.7214</td>
<td>66.8</td>
</tr>
</tbody>
</table>

Table 3: Estimates of run times for different system sizes and number of iterations
7.4 Summary of Results

Section 7.3 presented results for potential profiles calculated using averages of the potential at the location of ions in equilibrium configurations. Unexpected shapes of the potential profiles not predicted by PB theory from section 6.2 were observed in all cases except in the 2-nm pore. These unexpected shapes included local minima near the walls. However, we now are able to have confidence that the shape is not due to any artifacts of numeric integration, but rather a reflection of the physics of EDL formation within pores. Moreover, unlike the Runge-Kutta solutions in section 6.2.2, the potential in the center of the pore is not arbitrarily assigned to be zero but is allowed to depict a true value with respect to the potential of the bulk. So, we can learn more about the physics of the system from these results. The results from the method for calculating potential discussed in section 7.2 are so different from PB predictions that the PB solutions are evidently not useful for validation of the potential profiles computed from molecular modeling. However, the concentration profiles do agree well between PB and simulation, so with careful examination of both the method itself and the physics of the system, we can have confidence in the results for potential profiles.

Since the potential calculated in this work is relative to a field free bulk with evenly and randomly distributed positive and negative charges, the value of the potential here is an indication of the relative number of positive to negative ions within the pore. The positively charged walls create a positive potential right at the surface. A layer of negative counterions forms next to the wall, which not only completely screens the potential due to the surface charge, but drastically drops the potential negative relative to the charge neutral bulk farther from the walls. Here, steric or entropy effects result in coion exclusion in this region near the wall; counterions pack closely to the surface to most efficiently screen the surface charge (i.e. an energy-driven effect), and do not allow coions to coexist in this region. It is clear that the extent of the field created by this coion exclusion region dominates for about 2.35 ionic diameters (1-nm) from the wall. The presence of positive coions in regions greater than 2.35 ionic diameters from the wall then begin to have a more dominant effect on the potential to bring it back up to that of the charge neutral bulk, provided there is enough pore space to allow the on-set of electroneutrality from the electrical potential perspective. So, even though the concentration profiles show that bulk number of ions is achieved around 1-nm to 1.5-nm for all pores, the electrical effects of the ions in the double layer extend further than this, as evidenced by the negative regions (with respect to the bulk) of the potential profiles. This makes sense, since electric effects drop off smoothly and are proportional to the distance to the source charge. The extent of the electrical effects of the negative ion layer near the walls is roughly 11.7 ionic diameters, or 5-nm, as evidenced by its clear influence on the profiles in section 7.3. Summary plots of the potential profiles for different surface charges applied to each pore are shown below.
Figure 34: Summary plots of potential profiles from GCMC simulations for 2-nm (a), 5-nm (b), and 10-nm (c) pores

While all pore sizes simulated appear to achieve bulk ionic concentration in the center of the pore (as shown in section 7.3), the case is not true for electrical conditions in the pore. Because the electrical influence of the highly negative coion exclusion region extends over a longer range than the layer itself, the electrical conditions are only able to be achieved in larger pores. The 10-nm pore just barely reaches bulk in the middle of the pore. For the smaller pores, the extent of the electrical effects of the double layers on either wall overlap, preventing the pore from ever achieving the conditions of bulk from the electrical potential perspective. The 5-nm pore clearly shows how this effect increases with surface charge, as the coion exclusion region is bolstered with more negative screening charges. One can also note that the maximum at the center of the pores becomes sharper with increasing surface charge. This effect is particularly clear in the 10-nm pore profiles where zero potential in the center is reached. The, $\sigma^+ = 3.815$ profile just barely touches a value of zero at the pore center, while the profile for $\sigma^+ = 1.166$
maintains a value of zero for an extended region about the pore center. This is because at lower surface charge, the potential drop is less dramatic, so the coions in the middle of the pore are more easily able to neutralize the negative potential from the double layer ions.

The disappearance of the multiple extrema in the 2-nm pore profiles is due to the fact that the extent of the dominant electrical influence of the coion exclusion region is larger than the distance to the center of the pore, so there is no opportunity for the coions to raise the potential like in the 5-nm pore. Works that used Eq. (27) to solve for potential [83] may not have noticed these effects in this way, since the pore sizes used in those works were even smaller relative to the ion size (a pore size to ion diameter ratio of 3.33, versus 4.71 in our 2-nm pore). The profiles look deceptively agreeable with the PB-predicted exponential behavior of electrical potential profiles in these works. Other works that obtained potential profiles for a single charged wall did not explore as high of surface charge as this work [23], or used a more complex system model whose results are not easily comparable to this work [48]. However, the work that used a dimer model did obtain a minimum in the potential near a single charged interface [48], which qualitatively aligns with results presented here.

Figure 35: Average surface potential (a) and potential in the center of the pore (b) in different sized nanopores as a function of surface charge

An analysis of the resulting surface potential and potential in the pore center was conducted by examining the plots in Figure 35. A surface potential was calculated by averaging the values of the potential at the left wall and at the right wall for each system. This quantity shows a clear trend with increasing surface charge. The magnitude of the average surface potential is about the same for all pore sizes across all surface charges, except the larger 10-nm pore which drops off slightly lower than the smaller pores at higher surface charge. As surface charge increases, the average surface potential also increases, but at a decreasing rate. These results agree with expectations, as surface charge should be the only parameter to affect surface
potential, thus it should be unaffected by pore size. The lower values in the 10-nm pore at high surface charges might indicate an overcharging effect, where there are more counterions near the wall than needed to completely screen the surface charge, thus lowering the potential at the surface.

As for the potential in the center of the pore, we can see that the larger 10-nm pore reaches a value of zero within uncertainty for all surface charges. As for the smaller pores, the 5-nm pore center potential drops almost linearly with increasing surface charge. The 2-nm pore center potentials also appear to drop linearly, but at a steeper rate than the 5-nm pore. This further exemplifies the extent of the electrical effects of the coion exclusion zone in the double layers. It shows how the effects from both walls overlap and compound on each other in smaller pores to give an extremely negative potential in the center of the pore relative to the bulk that becomes more prominent with increasing surface charge. The effect is enhanced in smaller pores because there is more overlap that occurs, but goes unseen in larger pores because the pore is large enough to attain the electrical conditions of the bulk in the pore center.
Conclusions, Recommendations, and Future Work

This work has discussed a very broad range of topics related to electrical double layers (EDL) and their properties. This includes the abundance of applications in which EDL plays a role, and how their impact on electrochemical systems in confined spaces (on the molecular length scale) is becoming increasingly relevant in the literature. It was discussed how EDL properties can be experimentally measured, and the issues in carrying out measurements in nanopores. Thus, the best way to learn about EDL structure and properties is by theory and computer simulation. Molecular modeling can provide the means of unambiguously validating analytic theories, since all of the assumptions involved in the model under consideration will be well understood. Moreover, since many analytic theories are difficult to use to obtain solutions for EDL properties and many still have issues predicting empirical phenomena, molecular modeling is one of the most attractive and reliable means of learning about EDL. The Poisson-Boltzmann (PB) equation is an attractive theoretical model of EDL structure since it is one of the simplest to implement, but PB involves assumptions that become completely obsolete in nanopore systems (e.g., non-interacting ions treated as point charges). Monte Carlo (MC) methods are the main focus of this work, specifically in the Grand Canonical Ensemble. The Grand Canonical Ensemble lends itself nicely to porous systems, since it allows flux of both ions and energy in and out of the pore in order to reach thermodynamic equilibrium with a bulk reservoir. This scenario most closely represents actual experimental setups in which porous electrodes are submerged in large quantities of bulk solution and allowed to reach thermodynamic equilibrium during charging-discharging cycles.

Grand Canonical Monte Carlo (GCMC) simulations have been used extensively to obtain concentration profiles for EDL next to a single charged interface, between two charged interfaces (i.e. a slit-type pore), and in other geometries. The focus on systems at the nanoscale is more recent and appears less thoroughly represented in the literature than larger systems. The work that has been done with GCMC simulations of EDL in nanopores focuses largely on EDL structure, and the effects of ion size, ion valence, and mixtures of electrolytes on the resulting ionic concentration profiles for different pores and different electrode surface charges. However, the focus on using GCMC simulations to obtain the electric potential profiles, an important quantity for understanding the performance of electrochemical systems, is lacking. The works that do look into EDL potential profiles do not focus on the method used to obtain these profiles, leaving ambiguity in the results. Moreover, most works that investigate EDL potential do so for larger pores or single charged interfaces, not in nanopores. Therefore, there is a need for a well-defined method that predicts the electric potential distribution of EDL in nanopores in a way that accurately represents the physics of the system.

The first approach in developing a method to obtain EDL potential profiles from GCMC concentration profile outputs was based off prior work in that it involved solving the electrostatic Poisson equation. The GCMC concentration data was converted into a continuous volumetric charge density function that could then be used in the Poisson equation and directly integrated.
using numerical techniques. The first technique explored in this work used a fixed step fourth-order Runge-Kutta solver to obtain the potential from the center of the pore to the charged wall, assuming the potential and its derivative were zero at the pore center. These assumptions proved to be incorrect, as the results differed greatly from PB predicted profiles and did not seem to capture the physics of the problem correctly. A finite difference boundary value problem solver was considered next, because it was not restricted to pores with zero potential at the center. However, upon further investigation it was found that the solution to such a problem is non-unique, which would not be beneficial for the purposes of this work, i.e. to eventually use molecular modeling results to guide experimental work. This feat requires knowledge of the absolute value of EDL potential with respect to some useful reference. So, it was concluded that the issues discussed demonstrate that direct numerical integration of the Poisson equation using GCMC concentration profile outputs is not an appropriate technique to obtain EDL potential profiles. A different approach had to be considered.

It was decided that a more rudimentary approach, grounded in basic electrostatics concepts, could be used to calculate the potential rather than attempting to use GCMC outputs to solve the Poisson equation. The new method makes use of the ion energies which are already being calculated within the GCMC simulation. Ion energies could be used to extract average electrostatic potentials across the pores. Moreover, this in effect gives results for potential with respect to the virtual bulk associated with the Grand Canonical Ensemble without physically including it in the system. Because of the simplicity of the method and the large amount of known information about the steps involved, it was expected that this method’s results will yield a physically accurate representation of the electrical environment in the EDL system. This also allows the results of this method to be meticulously analyzed and interpreted, and easily tied to molecular-level structure predicted by the simulations. It was found that the true potential profiles in the nanopores from the GCMC simulations considered in this work differ from PB predictions. While the number of ions at each location in space (i.e. concentration profiles) agrees with PB, the potential profiles do not. The finite size of ions in the GCMC simulations introduces steric effects in terms of “capability to pack ions within a confined space” that can be thermodynamically understood as entropic effects. Thus, we have an energy-driven process via the imposition of an electric field in antagonism with an entropic effect caused by the finite size of the system (ions and pores). This leads to entropy dominating in the ion layer that screens the surface charge at the charged walls. The finite ion size excludes coions from occupying this layer, and therefore leads to a sharp drop in potential to values lower than in the bulk. This effect is not seen in PB solutions because the ions are considered non-interacting point charges. Furthermore, local minima in the potential profiles were observed near the walls, while a local maximum was observed in the center of the pore. This was attributed to the coions in the center of the pore attempting to neutralize the negative potential in the coion exclusion layer next to the charged walls. In small pores, the extent of the electrical effect of the coion exclusion region is larger than half the pore, and so the coions cannot completely bring the potential back to bulk conditions. In larger pores there is enough room for electrical bulk conditions to be achieved,
however. The important points are that the GCMC simulations considered in this work show that entropy effects exclude coions in the ion layer packs up against the charged walls. This, in conjunction with the fact that electrical effects are long range and extend out into space from the location of the source charge, lead to the semi-oscillatory behavior of the potential profiles observed here. The oscillatory behavior is diminished in smaller pores as the extent of the electrical effects of the coion exclusion regions begin to overlap.

Recommendations from this work are geared towards implementation of the method to calculate potential from section 7.2 into GCMC code. The method involves including extra energy calculations within the GCMC simulation. The energy calculation is the most computationally expensive operation carried out in the code, so it is desirable to have the code optimized to avoid extensive run times. One way this can be accomplished is by tabulating and maintaining an array with the energy associated with each ion throughout the entire simulation. This will speed up the code by avoiding the pairwise energy calculation when the potentials are being calculated and averaged, reducing it to simple operations on elements of an existing array. Since the code essentially computes the potential at the location in space of each ion in equilibrium configuration, it seems desirable to have a large number of potential values stored in memory to average together for a better result, i.e., a large system in terms of ions in the central simulation box. However, the computational cost increases significantly with number of ions in the system, so an optimized system size should be considered. Another thought to improve the result would be to use smaller bin sizes. However, smaller bin sizes reduce the number of ions in each bin, and therefore lower the accuracy of the average bin potentials that will be computed. This would lead to increased noise in the result, rather than more accurate values in the profile, so optimal bin size should be another consideration. However, longer run times might reduce this effect, so investigation into the effect of bin size on the result might be a factor to consider.

Future work includes more extensive application of this code to a variety of systems. Systems of varying ionic concentration are one example. Simulating systems of 0.1M, and 4M would provide results that can be compared to real world applications, such as EDL in water deionization systems and supercapacitors. However, in order to use GCMC simulations, activity coefficients must first be computed using a Canonical Ensemble simulation and thermodynamic principles. Other possible work would be to explore the effects like ion size, ion valence, mixtures of electrolytes, and surface polarization on EDL potential profiles in nanopores. Exploring simulations that incorporate non-primitive models is another opportunity for future work. On top of using this work for further simulation of EDL systems, results for potential from the method developed in this work can also be used as a link to experimental validation. The potential predicted from this method is with respect to the Galvani potential in the field free fluid bulk, so the values of potential across the profile (e.g. the surface potential) can be directly related to experimental setups. The GCMC calculated surface potential for a given surface charge can be used to understand what surface charge in experiment would result from a given
applied electrode potential. Hence, using this method as a means to link experimental parameters and predicted EDL structure is a topic for future work as well.


9.0 References


Carlo Computations," Journal of Chemical Physics, 72(11), pp. 5935-5941.

[60] Lamperski, S., and Bhuiyan, L. B., 2003, "Counterion Layering at High Surface Charge in an 
Electric Double Layer. Effect of Local Concentration Approximation," Journal of Electroanalytical 
Chemistry, 540, pp. 79-87.

8618-8626.

Double Layers Undergoing Charge Inversion: Mixtures of Mono- and Multivalent Ions," Langmuir, 
21(20), pp. 9231-9237.

Electrolyte Mixtures: Integral Equations Theories and Simulations," Journal of Physical Chemistry B, 
110(3), pp. 1326-1331.

in Ion Diameters and Charges in an Electrical Double Layer Studied by Monte Carlo Simulations and 


Carbon Aerogel Obtained by Cyclic Voltammetry," Journal of Electroanalytical Chemistry, 540, pp. 159-
167.

Cylindrical Capillary as Seen by the Modified Poisson-Boltzmann Theory and Monte Carlo Simulations," 

American Chemical Society, 111(2), pp. 477-481.


[71] Jamnik, B., and Vlachy, V., 1995, "Ion Partitioning between Charged Micropores and Bulk 
Electrolyte Solution - Mixtures of Monovalent and Divalent Counterions and Monovalent Co-Ions," 
Journal of the American Chemical Society, 117(30), pp. 8010-8016.


A. Appendix: Excerpts of Grand Canonical Monte Carlo Simulation Code Updated for Potential Profile Calculations

! Monte Carlo Simulation of Electrical Double Layer inside Nanopores
! Two uniformly charged surfaces in a simulation box
! Grand Canonical Ensemble (GCMC)
! Patricia Taboada-Serrano (2004)
! Chiahung Hou (2006)
! Patricia Taboada-Serrano (2013)
! Evan Ney (2016)
! FORTRAN 90/95 COMPILE
! Version for single 1:1 electrolyte
! Calculation of electrosorption capacity

MODULE Poreedl
IMPLICIT NONE
SAVE

integer,parameter::nstep=5000000,nw=2
double precision,parameter::conc=1.003 !bulk electrolyte concentration
integer::np=475,nn=510 !initial # of ions - THIS WILL CHANGE ACCORDING TO CONCENTRATION AND PORE SIZE
double precision,parameter::nw4wcharge=35.0
integer::nump,numn !add/delete ions per step
integer::N !total number of ion
double precision,parameter::nhist=100!number of intervals for conc. profiles
double precision,parameter::deltaz=1.5000 !Z coordinate evaluation [A] - THIS WILL CHANGE ACCORDING TO PORE SIZE
double precision,parameter::epso=8.8541E-22,elec=1.60219E-19
double precision,parameter::kb=1.38062E-23
double precision,parameter::eps=78.5
double precision,parameter::pi=3.1415297
double precision,parameter::temp=298
double precision,parameter::const=4.1142476E-21 !Kb*Temp

double precision,parameter::L=75.00,W=150.00 !simulation box - THIS WILL CHANGE IN EACH CASE

double precision,parameter::wcharge=nw4wcharge*elec/(2.0*L*L) !exactly neutral surface charge [C/A^2]

!Characteristic of ionic species involved in EDL
double precision,parameter::dp=4.25,dn=4.25,dw=3.0
double precision,parameter::qp=1.0,qn=-1.0,qw=1.0
double precision::rminp,rminn,rminp,rminn,rminp,rminn

double precision,dimension(2000)::xp,yp,zp,vionp
double precision,dimension(2000)::xn,yn,zn,vionn
double precision,dimension(nhist)::zw

double precision,dimension(nhist)::zcoord
double precision::countc

!Calculate average conc. and # of ions after equilibrium
double precision,dimension(nhist)::cpav,nav
double precision,dimension(nhist)::vbinav

!Electrosorption capacity
!double precision, dimension(2000)::nadsp,nadsn !number of electrosorbed ions
!double precision::elcapp,elcapn
!double precision::NAV=6.023E17 !number of ions per micromole - Avogadro's number
!double precision::Areafactor=1E16 !Amstrong2 in 1 cm2

97
double precision, parameter :: acoff = 0.8803 ! 1.003 M activity coefficient

END MODULE Poreedl

! Procedure to save intermediate configurations
! if (mod (step, isave) == 0) then
! call writcn (step)
! end if

if (step > limit) then
  if (mod (step, ihisto) == 0) then
    call histogram (step) ! Procedure to calculate conc. profiles
    countc = countc + 1.0
  end if
end if

END DO ! End of cycles

WRITE (*, *) "The end of Grand Canonical Monte Carlo simulation"

! Average concentration profiles

do j = 1, nhist
  cpav(j) = cpav(j) / countc
  cnav(j) = cnav(j) / countc
  vbinav(j) = vbinav(j) / countc
end do

subroutine histogram (printnum)
  USE Poreedl
  IMPLICIT NONE

  integer :: j, k
  integer, intent (in) :: printnum
  integer :: aux
  double precision, dimension (np) :: indexp
  double precision, dimension (nn) :: indexn
  double precision, dimension (nhist) :: concp, cconcn
  double precision, dimension (nhist) :: vbinp, vbinn
  double precision :: xj, yj, zj, vcur, ovrdummy

  ! Opening a file
  open (unit = 10, file = "histo.dat")

  ! Initializing variables

do j = 1, nhist
  concp(j) = 0.0
concn(j)=0.0
vbinp(j)=0.0
vbinn(j)=0.0
end do

! zero count-index, vionp, and vionn for the current configuration
do j=1,np
  indexp(j)=0.0
  vionp(j)=0.0
end do

do j=1,nn
  indexn(j)=0.0
  vionn(j)=0.0
end do

ovrdummy=0.0

! Calculate the energy associated with each individual ion
do j=1,np !positive ion energies
  xj=xp(j)
yj=yp(j)
  zj=zp(j)
  vcur=vionp(j)
call energyp(xj,yj,zj,j,vcur,ovrdummy)
  vionp(j)=vcur*const/elec !Potential at each ion location in volts
end do

do j=1,nn !negative ion energies
  xj=xn(j)
yj=yn(j)
  zj=zn(j)
  vcur=vionn(j)
call energyneg(xj,yj,zj,j,vcur,ovrdummy)
  vionn(j)=vcur*const/(-elec) !Potential at each ion location in volts
end do

! Count up ions and average potential in each bin
! Z coordinate

do k=1,nhist
  ! Positive ions
  do j=1,np
    if(indexp(j)==0.0) then
      aux=aint(zp(j)/deltaz)
      if(aux<k) then
        indexp(j)=real(k)
        concp(k)=concp(k)+1.0
        vbinp(k)=vbinp(k)+vionp(j)
      end if
    end if
  end do

  ! Negative ions
  do j=1,nn
    if(indexn(j)==0.0) then
      aux=aint(zn(j)/deltaz)
      if(aux<k) then
        indexn(j)=real(k)
        concn(k)=concn(k)+1.0
        vbinn(k)=vbinn(k)+vionn(j)
      end if
    end if
  end do
end do

! Accumulating average concentrations
do k=1,nhist
    cpav(k)=cpav(k)+concp(k)
    cnav(k)=cnav(k)+concn(k)
    !if there are ions in the bin, update the potential counter
    if(concp(k)/=0.0 .or. concn(k)/=0.0) then
        vbinav(k)=vbinav(k)+(vbinp(k)+vbinn(k))/(concp(k)+concn(k))
    end if
    !otherwise both are zero, vbin=0, leave vbinav(k) unchanged
end do

! Saving the data
if(mod(printnum,1000)==0) then
    write(unit=10,fmt=810)printnum
    do j=1,nhist
        write(unit=10,fmt=820)zcoord(j),concp(j),concn(j),     &
        & vbinp(j),vbinn(j)
    end do
end if

810 format(1x,I8)
820 format(1x,E14.6,3x,E14.6,3x,E14.6,3x,E14.6,3x,E14.6)

if(printnum==nstep) then
    end file (unit=10)
    close (unit=10)
end if

return

end subroutine histogram