UNDERSTANDING ELECTROCHEMISTRY AT THE MOLECULAR SCALE: MOLECULAR DYNAMICS METHODS AND APPLICATIONS

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Understanding Electrochemistry at the Molecular Scale:
Molecular Dynamics Methods and Applications

by

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Abstract

The relatively new field of nano-electrochemistry stands to enable more efficient energy storage and electrochemical techniques. However, traditional mean-field models which generally average over macroscopic detail may be inappropriate for understanding electrochemistry at the nanoscale. We propose a combination of methods for the molecular dynamics simulation of constant potential, electrochemically active devices and use these methods to reveal the importance of molecular character on nanoscale device behavior. For example, a macroscopic relationship between transference number and battery performance is shown not to hold up in nanoscale cells due to the nanoscale cell’s ability to support significant deviations from electroneutrality. This result demonstrates the necessity of carefully reconsidering macroscopic phenomenology when designing nanoscale systems.

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Chapter 1

Introduction

The past twenty years has ushered in a renewed interest in the field of electrochemistry. The interconversion of chemical and electrical energy is central to the development of numerous emerging energy capture and storage technologies including solar-to-electrical energy conversion, as well as energy storage in batteries, capacitors, and fuel cells. The development of these energy technologies has become an international priority and new technologies increasingly leverage advancements in the field of nanomaterials and nanoscience.[1] However, traditional mean-field electrochemical theories, while greatly successful in describing many electrochemical behaviors with minimal complexity, are ill-equipped for understanding electrochemistry on the nanoscale. Over nanometer length scales, the discrete molecular nature of the charge-carrying species leads to fluctuations in the instantaneous energy landscape. Over large time and lengthscales, these fluctuations average out and a mean-field approach is appropriate, but nanoscale theories will need to explicitly account for these fluctuations. This thesis introduces methodology for the molecular dynamics simulation of constant-potential electrochemical cells including nonequilibrium charge transfer. These models are then used to understand the fundamental behavior of nanoscale electrochemical devices.
The reactions that drive most electrochemical systems take place at the electrode-electrolyte interface. The unique properties of this interface are primarily due to the physical characteristics of the electrode and its influence on the adjacent electrolyte. The electrode serves as a physical barrier that can support a tunable buildup of surface charge. This barrier breaks the translational symmetry of the electrolyte, promoting the emergence of anisotropic and possibly highly correlated interfacial molecular structure. The presence of surface charge provides an electrochemical potential gradient, and an associated potential drop, that ultimately leads to the formation of the electrical double-layer. In reactive systems, the electrode provides a source or sink of electrons, thereby facilitating (and sometimes catalyzing) the redox reactions that drive the flow of charge (and sometimes mass) in driven electrochemical applications such as batteries. Capturing these interfacial properties in a single model framework is challenging because their interactions span a wide range of characteristic time and length scales.

A common solution to this challenge is to model the electrolyte as continuum that interacts empirically with the electrode.[2–4] Continuum modeling approaches have been widely used in the analysis and interpretation of electrochemical measurements because they are highly efficient and are easily extended to experimentally relevant time and length scales. However, because these models are highly parameterized and contain very few specific molecular details, they are not reliable as a predictive framework and therefore of limited use as a basis for molecular insight and design.

Another common approach to modeling electrode-electrolyte interfaces is to utilize simulation methods based on first-principles electronic structure calculations. *Ab initio* molecular dynamics (AIMD), usually based on density functional theory (DFT), provides the ability to explicitly describe the electronic rearrangements involved in electrochemical reactions.[5] First-principles electronic structure and AIMD have been extensively used to compute reaction mechanisms [6, 7] and energy barriers [8, 9], as well as to describe molecular structure and dynamics at the electrode-solvent interface.
Despite having generated an enormous amount of valuable physical insight, these approaches are generally limited in scope to very small systems (typically 100s of atoms over 10s of ps) due to the inherent computational expense of electronic structure calculation. Connecting the results of these first-principles studies to experimentally relevant systems therefore often requires assumptions about the role of fluctuations, disorder, and molecular correlations in the extended system.

Classical molecular dynamics (MD) simulation can effectively bridge the system size gap between continuum and first-principles modeling approaches. However, traditional force fields lack the functionality to model constant potential electrodes or to simulate chemical reactivity. Over the past 20 years, numerous methodological advances have targeted this lack of functionality. This includes the development of methods for simulating constant potential electrodes [11, 12], reactive force fields for simulating bond making/breaking [13, 14], and stochastic approaches to modeling interfacial electron transfer events. [15] This thesis describes our contribution to this field, an MD-based model that combines both tunable constant potential electrodes and the capability for interfacial electron transfer which is sensitive to fluctuations in the electrolyte system. This model is then used to investigate how discreteness and molecular fluctuations affect the results of traditional mean-field models of electrochemical systems.

1.2 Traditional models of the electrochemical interface structure

The equilibrium properties of an electrochemical interface are determined in large part by the electric field created by charge buildup at the electrode and the response of the electrolyte. Our fundamental understanding of this response derives primarily from theoretical models that treat the electrolyte as a simple, polarizable continuum. This includes the mean field models upon which Debye-Huckel theory [16] and Onsagers theory of solvation [17] are based, as well as their extensions to electrochemical
systems as pioneered by Gouy, Chapman, Stern, and Grahaem.[18–21] These continuum models make it possible to predict how changes in electrolyte properties or an applied electrode potential will affect the interfacial fields that drive electrochemical reactivity. This capability is essential to enabling the interpretation of a wide range of electrochemical measurements.

The phenomenon that contributes most to shaping the electric fields at the electrochemical interface is the formation of a double-layer. The double-layer describes a space-charge region of the electrolyte that is responsible for screening the charge of the electrode. The theoretical basis for describing the structure of this space-charge region originates from the theoretical developments of Gouy, Chapman, Stern, and Grahame. The electrochemical double-layer is generally assumed to contain one layer of strongly polarized solvent, possibly containing elevated concentrations of one ionic species, that is in direct contact with the electrode surface, and a second more diffuse layer of electrolyte solution with a non-neutral ionic concentration that decays to neutral away from the electrode surface into the bulk electrolyte. The plane that separates these two layers, known as the inner-Helmholtz plane, is roughly set by the diameter of the molecules that make up the first layer and the width of the second, more diffuse layer is determined by the composition of the electrolyte solution. Figure 1-1 shows an example of both a molecular scale snapshot from a molecular dynamics simulation as well as an example of a Gouy-Chapman-Stern-like potential decay. The linear decay close to the electrode is due to the strongly-polarized region of solvent at the interface and the exponential decay is due to the diffuse screening layer. The inner-Helmholtz plane is indicated by the grey dashed line. However, this figure also shows that at an instantaneous, nanometer scale, the delineation between the Stern layer and diffuse layer is not easy to pinpoint and may resemble a varying landscape more than a plane due to the discrete nature of the charge-carrying ions.

Nevertheless, continuum models provide a convenient formalism for predicting the interfacial profile and how it depends on system properties such as the electrolyte composition and applied electrode potential. The statistical mechanical framework upon which the modern concept of an electrochemical double-layer is based includes
several implicit physical assumptions.

One of the primary assumptions in the formulation of the double-layer is that the electrolyte is rapidly relaxing over experimental timescales. Under this condition, the electrolyte structure and composition can be taken to be isotropic in all directions parallel to the planar electrode surface. It thus follows that the double-layer can be expressed as a function of a single spatial coordinate perpendicular to the electrode surface.

A second assumption in the formulation of the double-layer is that the electrolyte is dilute. In concentrated electrolyte solutions, ion-pairing effects can lead to the emergence of long range oscillatory structure in ion pair correlation functions.[22] At an interface, where translational symmetry is broken, this oscillatory structure can manifest in the interfacial charge density profile. In the dilute limit, ion correlations are trivial and their contribution to double-layer structure is simple and easy to predict.

A third assumption in the formulation of the double-layer is that constituents of the electrolyte solution do not interact with the electrode through strong specific adsorption interactions. That is, electrolyte-electrolyte interactions only include relatively weak non-bonded chemical interactions. The interactions that govern specific adsorption are much stronger than those of charged particles interacting with interfacial fields. The statistical mechanical consequence of these strong interactions is that they promote the formation of an adlayer, whereby the surface of the electrode is coated by a tightly bound monolayer of a specific electrolyte species. An adlayer has two primary influences on the electrostatic profile of the electrochemical interface. First, the adlayer excludes volume from the electrolyte and can thus effectively shift the position of the electrolyte double-layer away from the electrode surface. Second, the adlayer contributes to reducing the effective electrode potential through partial screening. The adlayer dielectric properties that govern this screening generally differ from that of the bulk electrolyte due to reduced molecular mobility and narrowed chemical composition.

However, when the above assumptions are valid (i.e., for systems with rapidly
relaxing dilute electrolyte solutions that are non-electrode adsorbing), the spatial profile of the electrochemical interface can be described as a simple one-dimensional function that decays in the direction perpendicular to the plane of the electrode surface. The parameters of this function depend on the properties of the electrolyte, such as its ionic strength and dielectric constant, and on the value of the applied electrode potential.

These theories have been successful in describing a large range of electrochemical trends and behaviors, in large part due to their simplicity. The development of more complex one-dimensional continuum theories of the double layer structure are additionally able to account for deviations from assumptions two and three.[22, 23] However, deviations from assumption one, that the electrolyte relaxes quickly, requires the consideration of the discreteness of the individual charge carriers and the possibility of electrostatic fields parallel to the electrode. In this thesis, we take the approach of using molecular dynamics simulations to investigate electrochemical systems with an ultimate goal of understanding when and how the assumption of a quickly-relaxing electrolyte breaks down.
1.3 Electron transfer at the electrochemical interface

In addition to the electrostatic environment, electrochemical devices are also characterized by the transfer of electrons to and from the electrode. The behavior of electron transfer at the electrochemical interface differs from electron transfer in solution in several important ways. First, the reaction is limited to the space adjacent to the electrode surface. Depending on the specific reaction, this may mean a reactive species is chemically absorbed to the electrode surface before an electron transfer takes place, known as an inner sphere electron transfer. Alternatively, a reactive species may be completely solvated by the electrolyte, but near enough to the electrode for an electron to tunnel, known as an outer sphere electron transfer. Another difference between electrochemical reactions and solution reactions is the electrode’s role as an electron donor/acceptor. Unlike a solvated molecule, the electrode has a continuum of accessible electronic levels, so there is no inverted regime like there is in the case of an electron transfer between two molecular species. Finally, the chemical potential of the electrode is tunable. The applied potential shifts the Fermi level of a metal electrode as well as changes the charge buildup on the electrode, possibly inducing changes in the width and composition of the double layer.

1.3.1 Electron transfer using molecular dynamics simulations

One key insight of the Marcus theory of electron transfer is that the energy barrier for outer sphere electron transfer is almost entirely due to the rearrangement of solvent polarization. [24–28] In this diabatic picture, it is convenient to use the vertical energy gap between diabatic energy surfaces as the reaction coordinate. In contrast to some direct, ground-state measure of degree of solvent polarization, the use of the vertical energy gap, or vertical excitation energy as the reaction coordinate leads to many simplifications when dealing with free energy perturbation methods. Warshel was then the first to use this idea in the simulation of electron transfer reactions and the relationship between the vertical excitation energy and free energy perturbation methods allowed Warshel and coworkers to develop methods for calculating
1. Two systems which differ by a diabatic electron transfer. In system A, the electron is on the neutral molecule. In system B, the electron has transferred to the electrode leaving behind a positively charged ion. The potential on the electrode is maintained through the use of image charges. Importantly, all nuclear degrees of freedom are identical between system A and B.

2. Free energy profiles for systems A and B as the nuclear coordinates evolve. Vertical excitation energies are marked by the arrows. $\delta E'$ represents the transition from state B to state A.

3. By propagating molecular dynamics simulations and sampling the vertical excitation energy at various points along the nuclear trajectory, statistics of the magnitude of the energy gap can be built up.

4. Using the relationship between $\delta E$ and $\Delta E$ and taking the negative log of the probability distributions, Marcus curves for the reaction free energy are constructed. $A_A$ and $A_B$ are free energy surfaces. By construction they must cross at $\Delta E = 0$. $\Delta A$ is the free energy difference between the equilibrium reactant ($x_A$) and equilibrium product ($x_B$) states. $\lambda_A$ and $\lambda_B$ are the reorganization free energies.

activation free energies informed by the microscopic details of molecular simulation.

[29–31] The simplifications resulting from adopting the vertical energy gap as the reaction coordinate are again emphasized by Bloomberger and Sprik in a review of \textit{ab initio} molecular dynamics methods for calculating redox free energies. [32] Figure 1-2 emphasises the difference between the diabatic potential energy surfaces along which molecular dynamics are propagated and the \textit{free energy surfaces} relative to which quantities like reorganization free energy ($\lambda$) and the reaction free energy are defined.

Constructing Marcus curves from molecular dynamics simulation trajectories is fairly straightforward and has been successfully applied to classical molecular dy-
dynamics simulations with various implementations of constant potential electrodes. [12, 33] At various points along the trajectory, a vertical excitation is performed computationally. This means that an electron is moved, and electronic degrees of freedom are relaxed, but nuclear degrees of freedom are not relaxed (fig. 1-2-1). The energy difference between the system before and after the excitation ($\delta E$) are recorded, the simulation is reset to the configuration before the excitation, and the simulation continues. Over several trajectories that sample the energetic environment, distributions of the frequencies of $\delta E$ can be calculated (fig. 1-2-3). If the environmental fluctuations are in the linear response regime, these distributions will be Gaussian. For molecular simulations run in the NVT ensemble, the well-sampled statistics of the a system at equilibrium should be related by the negative log to the Helmholtz free energy of the underlying energy surface. A couple of details are required to ensure the relationship between $\delta E$, the sampled excitation energy and $\Delta E$, the Marcus theory reaction coordinate:

$$\Delta E_{A \rightarrow B} = \delta E + I + \delta qW$$ (1.1)

where $I$ is the ionization potential of the species that lost an electron to the electrode and $\delta qW$ is the energy associated with moving a charged electron through any electrostatic fields between the species and the electrode. For the reduction reaction,

$$\Delta E_{B \rightarrow A} = -\delta E + A_E + \delta qW$$ (1.2)

where $A_E$ is the electron affinity of the oxidized species. The free energy for the initial and final surfaces are then given by

$$A_A(\Delta E) = -k_B T \ln P(\Delta E_{A \rightarrow B}) + \tilde{A}_A$$ (1.3)

$$A_B(\Delta E) = -k_B T \ln P(\Delta E_{B \rightarrow A}) + \tilde{A}_B$$ (1.4)

where $\tilde{A}_A$ and $\tilde{A}_B$ correspond to the free energy at the minimum of the $A$ and $B$ curves respectively.
Chapter 2

Constant Potential, Reactive Boundary Simulations

In this chapter, we present the model for electrochemically active and electrostatically consistent electrodes held under constant potential conditions that is fully compatible with standard classical molecular dynamics. Specifically, this model (i) treats the constant potential boundaries in a computationally efficient manner, (ii) allows for outer-sphere oxidation and reduction at both electrodes, and (iii) can include the effect of ion intercalation into the electrode, so that both the total charge and number of redox-active particles in the electrolyte can fluctuate throughout the course of the simulation. We demonstrate the application of this model by simulating a nanoscale Li-ion-type battery system, such as illustrated in Fig. 2-1. The physical processes that determine the performance of this type of battery system, namely interfacial electron transfer and the transport of ions across the interface and through the electrolyte, cannot be simulated with standard classical MD. The functionality provided by our model enables a computationally efficient simulation of the microscopic dynamics of the electrolyte-electrolyte interface under operating conditions.

One of the primary challenges in modeling an electrochemical cell is efficiently handling the electrostatic interactions between the electrodes and the electrolyte. To capture the correct electrostatic behavior, proper treatment of the simulation cell boundary conditions and electrode polarizability are essential. Because of the
Figure 2-1: A diagram of a model battery system. Two electrodes are held at a constant potential difference, $\Delta V$. $V_0$ and $V_1$ set the chemical potential of electrons in the electrodes, $\mu_{\text{anode}}$ and $\mu_{\text{cathode}}$, respectively. Current is driven by the preference for oxidative formation of cations at the anode (1a at the left-hand electrode) and reductive elimination of cations at the cathode (1b at the right-hand electrode), and mediated by the diffusion of cations across the electrolyte (2). Thus, the overall performance is dominated by ion migration through the electrolyte and redox reactions at the electrodes.

The long-range nature of Coulomb interactions, distance-based cutoff methods give the incorrect asymptotic behavior [34] and the periodicity of the system needs to be considered carefully. Here we focus specifically on simulation cells with parallel planar electrodes positioned at the boundaries of the $z$ directions and periodically replicated in the other $x$ and $y$ directions. Figure 2-2 shows the difference in long range symmetry between a bulk system periodically replicated in all directions and a two-dimensional slab system appropriate for modeling an interfacial system. Summation techniques for the calculation of electrostatic forces and energies in a two-dimensional slab system exist, but are more computationally expensive and less numerically robust than a standard three-dimensional calculation [35].

Another challenge in modeling electrochemical systems is describing the surface charge of the electrode. A straightforward approach is to treat the electrode as a constant and uniformly charged surface. However, despite being easy to implement and computationally efficient, this approach lacks important physical effects, such as the ability to polarize in response to local charge fluctuations, that can qualitatively alter the static and dynamic properties of the electrode-electrolyte interface. [36] Under
Figure 2-2: A schematic comparison of I. a fully three-dimensional periodic system and II. a slab system with finite width in the z direction. Both systems are illustrated in two-dimensions for convenience.

constant potential conditions, surface charge distribution polarizes in response to nearby charge density. A variational procedure, introduced by Siepmann and Sprik [37] and applied to electrochemical cells by Madden and co-workers [11, 33], enforces the constant potential condition by allowing the charge on individual electrode atoms to fluctuate based on the surrounding environment. While computationally expensive, this method has the distinct advantage of being able to enforce a constant potential condition in systems with non-planar electrodes. In systems with planar electrodes held at zero potential, it has long been understood that the electrostatic potential in the system can be obtained through the use of image charges [38–40]. Perram and Ratner have shown that the periodic repetition in the image charge solution can be included in an MD simulation using full periodic boundary conditions and a double cell.[41] More recently, Voth and coworkers have developed a computationally efficient procedure for enforcing constant potential boundary conditions based on use of explicit first order image charges and a uniform correction term.[12] Here, we build upon these efforts by reformulating the image charge approach for describing constant potential electrodes so that the forces and energies can be computed using the more efficient, full three dimensional Ewald summation.

Methods for including redox reactions in classical molecular dynamics necessarily neglect most electronic detail. In this paper, we limit our scope to simple Marcus-type outer sphere electron transfer, where the active species is not electronically coupled to the electrode. The standard method for calculating electron transfer rates using
classical MD simulation are based on the generation of free energy surfaces for the reactant and product states by sampling the equilibrium fluctuations in the vertical energy gap \((i.e., \text{the canonical Marcus theory reaction coordinate})\). With this method, the average kinetics of the electron transfer can be inferred from Marcus free energy curves and the average Marcus rate can be applied to treat the interconversion of products and reactants at an electrode boundary in nonequilibrium simulations. [12] To account for the effects of spatial and temporal variability in electron transfer rate, Subotnik and coworkers have developed a surface hopping method where the probability of electron transfer for a given redox active species is related to the instantaneous value of its vertical energy gap. This method inherently encodes the concentration dependence of the rate and allows for the study of correlations between electron transfer events. We build upon this method to include the mass transfer associated with the exchange of electrochemically active ions between the electrolyte and the electrode material.

The structure of this chapter is as follows: First, in section 2.1 we describe a computationally efficient method for enforcing the constant potential boundary conditions and compare the results and complexity to existing methods. We then describe the model for electron and mass transfer. The details of the implementation of the two methods are briefly described in section 2.1.3.

### 2.1 Methods

#### 2.1.1 Enforcing Constant Potential Boundary Conditions

The distribution of charge within a constant potential electrode can fluctuate in response to the dynamics of charged species within the electrolyte. The ability to properly describe these fluctuations is essential for understanding the equilibrium and nonequilibrium properties of the electrode-electrolyte interface. Here, we consider model systems that are bounded by two parallel, planar, polarizable electrodes, each with an independently assigned voltage. Each electrode imposes a boundary con-
dition where the value of the electrostatic potential is equal to the assigned electrode voltage at all points along the electrode surface.

We define our coordinate system so that the electrode boundaries lie along the $z$-axis, with one electrode at position $z = 0$ and the other at position $z = d$, as illustrated in Figs. 2-2 and 2-3. We decompose the constant potential conditions into two components. One component that describes the polarization fluctuations that are native to neutral constant potential electrodes and one component that describes the uniform electric fields that result from charging the electrodes. This decomposition is possible due to the additive nature of electrostatic interactions.

We enforce the neutral component of the constant potential condition at each boundary using the method of image charges reflected across the two planes at $z = 0$ and $z = d$. Reflecting all charges, including images generated by previous reflections, across both electrode planes leads to a periodic system consisting of the active system of interest, a reflected system, and infinite periodic replicas as illustrated in Fig. 2-3. The active and reflected system together compose an electrostatically neutral repeat unit, extending from $z = -d$ to $z = d$, which is periodic in all three dimensions. Perram and Ratner showed using a Green’s function formalism that the total electrostatic energy in such a system is exactly twice that of a slab system sandwiched between two ideal metal boundaries. [41] This configuration ensures that the potential at $z = 0$ and $z = d$ are zero, while also transforming the system to a fully three-dimensional periodic system (see Fig. 2-2I) where electrostatic interactions can be calculated using the more computationally efficient and robust family of fully three dimensional k-space summation techniques (e.g. pppm [42]). Further computational speedup can be gained by exploiting the symmetry of the unit cell. [41]

To enforce the electrostatic effect of a potential drop $\Delta V$ across the cell, we introduce a uniform field of magnitude $\Delta V/d$ between $z = 0$ and $z = d$ along the $z$-axis which preserves a constant potential along each image plane. Notably, in an isolated system the absolute value of the reference potential is irrelevant and so we pin it to the $z = 0$ electrode. As such, this system setup corresponds to an electrostatic potential of $\Psi = 0$ at $z = 0$ and $\Psi = \Delta V$ at $z = d$, as shown in more detail in
Appendix A.

In theory, the field generated by the potential drop has magnitude $-\Delta V/d$ in the region $z = -d$ to $z = 0$ giving a repeat unit with a net field of zero. In practice, only the forces in the active system need to be calculated to propagate molecular dynamics since the configuration of the reflected system is completely determined by the configuration of the active system.

**Active System Energy**

The method of image charges ensures that the electrostatic potential is correct within the active system (*i.e.* the volume confined between the electrodes), but interactions between particles in the reflected system are not physically meaningful. The energy of the active system therefore includes all active-active and active-image coulomb interactions, but excludes all contributions from image-image interactions. The forces on the active particle are derived from this energy. Since force calculation can be restricted to atoms within the active system, propagating the dynamics of the active system using molecular dynamics is straightforward.

Including short range, nonbonded energy terms and the electrostatic potential energy described above, the total active system potential energy $U_{\text{act}}$ is given by,

$$U_{\text{act}}(\{r\}, \Delta V) = U_{\text{SR}}(\{r\}) + U_{\text{Coul}}(\{r\}) + U_F(\{r\}, \Delta V),$$  

(2.1)
where \( \{ \mathbf{r} \} \) denotes the nuclear configuration of all members of the active system, \( U_{\text{SR}} \) is the potential energy of the system due to short range (e.g., Lennard-Jones-type interactions) within the active system (and its periodic replicas), \( U_{\text{Coul}} \) is the electrostatic energy of the active system (including its interactions with image charges), and \( U_F \) is energetic contribution of the potential drop on the active system. The short-range contribution is typically given by,

\[
U_{\text{SR}}(\{ \mathbf{r} \}) = \sum_{(ij)} w_{\text{SR}}(\mathbf{r}_i, \mathbf{r}_j) + \sum_i w_{\text{wall}}(\mathbf{r}_i),
\]

(2.2)

where the summation denotes a sum over all unique pairs of particles, \( w_{\text{SR}} \) is the pair-wise shortwave interaction potential between particles, and \( w_{\text{wall}} \) describes the interaction between particles and the electrode surface. The Coulomb contribution can be expressed as,

\[
U_{\text{Coul}}(\{ \mathbf{r} \}) = \sum_i q_i \Phi(\mathbf{r}_i),
\]

(2.3)

where \( q_i \) is the charge on species \( i \) and \( \Phi(\mathbf{r}) \) is the electrostatic potential (due to active species, inactive species, and their periodic images) evaluated at position \( \mathbf{r} \).

the contribution from the potential drop is given by,

\[
U_F(\{ \mathbf{r} \}, \Delta V) = \sum_i \Delta V q_i z_i / d,
\]

(2.4)

where \( z_i \) is the position of species \( i \) along the \( z \)-axis.

From a practical standpoint, we want to implement the system in such a way that the total active system energy can be calculated using existing standard molecular dynamics (MD) routines. For the Coulomb interactions, the active system energy is exactly half the total energy of the repeat unit which can be calculated using an Ewald summation or faster particle-mesh techniques. [41, 43] For short-range interactions, treating the reflected system atoms as point charges with no short-range interactions means that the calculated total short-range energy can be used as-is. For the contribution to the potential due interactions with the constant field, only charges
in the active system should be included.

**Comparison to existing methods**

As discussed in the introduction, there are several existing methods for including electrode boundary conditions in MD simulations of electrochemical systems. Table 2.1 shows a summary of the highlights and limitations of each method. The first two columns indicate whether a method correctly reproduces the phenomena of conducting electrodes at zero applied voltage and when the boundaries are held at an applied potential. The third column indicates whether the method can be applied to systems without planar electrodes. The last column uses the number of charged particles in a system as a proxy for the computational cost of the method. $N$ is the number of charged particles in the active system and this column gives the total number of charged particles required in the total system. Since calculating electrostatic interactions scales roughly as $M^3$, where $M$ is the number of charged particles, it is often the most computationally expensive step of MD simulation.

Although conceptually simple and computationally efficient, constant distribution of charge on the electrode surfaces fails to reproduce the results of experimentally relevant conducting, or constant potential, boundary conditions. By adding an explicit term for the applied potential to the method developed by Perram and Ratner [41], we are able to leverage the computational benefits of fewer charged particles and a fully three dimensional periodicity in a system with a potential bias.

In order to verify the equivalency of this method to previous methods, we compare the energy contributions of a test charge in a simulation held at constant potential. We have recreated a version of the validation system, System I, used by Voth and coworkers where the image planes reside at $z = 0$ and $z = 51.1$ Å. [12] The cell is 50 Å in the $x$ and $y$ dimensions. A single charge of $q = -e$ was placed at the center of the $x$ and $y$ directions and energy was measured as a function of $z$ position. For comparison to the energies obtained by Voth and coworkers, an arbitrary energy constant was added to the results from these simulations since there are no explicit electrode atoms in this simulation and an addition of a constant energy term does not
Table 2.1: Comparison of methods for including electrode boundary conditions

<table>
<thead>
<tr>
<th></th>
<th>Const. Potential at $\Delta V = 0$</th>
<th>Const. Potential at $\Delta V \neq 0$</th>
<th>Non-planar Electrodes</th>
<th>System Size</th>
<th>System Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>constant charge</td>
<td>x</td>
<td>x</td>
<td>✓</td>
<td>N</td>
<td>2D-slab</td>
</tr>
<tr>
<td>Ratner [41]</td>
<td>✓</td>
<td>–</td>
<td>✓</td>
<td>2N</td>
<td>3D</td>
</tr>
<tr>
<td>Voth [12]</td>
<td>✓</td>
<td>✓</td>
<td>x</td>
<td>3N</td>
<td>2D-slab</td>
</tr>
<tr>
<td>This paper</td>
<td>✓</td>
<td>✓</td>
<td>x</td>
<td>2N</td>
<td>3D</td>
</tr>
</tbody>
</table>

This method adjusts the charges on the electrode atoms in the simulation through an iterative procedure. Each step of this iteration requires a full electrostatic calculation so the computational cost also includes a factor of the number of iterations required.

a This method affects the magnitude of the calculated forces used to propagate dynamics in section 3.1. Figure 2-4 shows that the total system energy for System I as a function of the test charge position. In agreement with previous methods, the total energy of a charged particle between biased electrodes includes a nonlinear term due to image charge effects and a linear term whose slope is determined by the applied potential.

2.1.2 Electrochemical boundary conditions

We model charge transfer as a stochastic process with a rate that fluctuates in response to the dynamics of the electrolyte. In this manuscript, we consider the most simplified case of coupled ion-electron transfer, analogous to the intercalation or deintercalation processes that drive the performance of Li-ion batteries. We model this process in the limit where adiabatic effects are fast compared to the simulation time step and thus are only described empirically. Specifically, we express the probability per unit time for creating a new ion or removing an existing ion (i.e., deintercalation or intercalation, respectively) as a function of the energy change to create a neutral particle at the interface and then pass a charge to it (or vice versa). The procedure we describe can be easily simplified to model the case where only charge (and not mass) is transferred.

As an example of our procedure, consider the deintercalation of a cation, as illus-
Figure 2-4: Energy of a test charge as it is moved across an empty cell with constant potential boundary conditions. A single charge of $q = -e$ was placed at the center of the cell and total energy was computed as a function of $z$ position. Orange (open) shapes are the results from the iterative method by Siepmann and Sprik. [37] Black (closed) shapes are the energies obtained by Petersen et al.[12] and Blue lines are the result of the method described in this paper. Squares and the solid line represent the total energy of the active system. This energy is decomposed into two terms, long-dashed and circles mark the contribution to the total energy due to all image charge interactions and the short-dashed lines and triangles mark the contribution due to the applied potential.

trated in Fig. 2-5. We model this concerted process as the product of two sequential steps. We first insert a neutral dummy particle into the electrolyte at the electrode interface and then we pass an electron from the particle to the electrode to create a cation. We express the total probability for this event as a product of probabilities to perform each step independently. More formally, we express the probability for adding a new cation to the system as,

$$P_{ox} = P_{ox}^{(1)} P_{ox}^{(2)},$$  \hspace{1cm} (2.5)

where $P_{ox}^{(1)}$ is the probability to insert a neutral particle at a specific position in the system and $P_{ox}^{(2)}$ is the probability for outer-sphere electron transfer from the neutral particle to the electrode.

The probability for the first step is given by a standard grand canonical Monte
Figure 2-5: The leftmost panel shows the system where a site (shown as a dotted circle) might be the site of a new cation. The middle panel shows the change in nuclear positions associated with the insertion of a neutral test particle. The final panel shows the electronic rearrangement necessary to result in a positively charged ion in the simulation box. $\Delta U_{\text{ox}}^{(1)}$ and $\Delta U_{\text{red}}^{(1)}$ involve a change in nuclear configuration and thus are compared against a Boltzmann distribution to determine a probability of success. $\Delta U_{\text{ox}}^{(2)}$ and $\Delta U_{\text{red}}^{(2)}$ involve a change in electronic configuration and are compared to the density of electronic states in the electrode.

Carlo acceptance criteria,

$$P_{\text{ox}}^{(1)} = \min \left[ 1, \exp \left( -\beta \Delta U_{\text{ox}}^{(1)} \right) \right],$$

where $1/\beta = k_B T$ – the Boltzmann constant times temperature – and $\Delta U_{\text{ox}}^{(1)}$ is the energy change associated with the addition of the neutral particle [44]. This expression does not include a term for the chemical potential or fractional volume element of the neutral test particle since the neutral particle is replaced with a positively charged ion if the oxidation is successful.

The probability for the second step is taken from the method of Subotnik and coworkers [15], where the energy to remove an electron from the simulation is compared to the distribution of unoccupied electronic states in a metal. Specifically,

$$P_{\text{ox}}^{(2)} = \frac{\Gamma(z)}{1 + \exp \left( V_{\text{electrode}} - \beta \Delta U_{\text{ox}}^{(2)} \right)},$$

where $\Gamma(z)$ is the distance dependent electronic coupling between the particle and electrode, $V_{\text{electrode}}$ specifies the Fermi level of the electrode, and $\Delta U_{\text{ox}}^{(2)}$ is the energy
change associated with the charge transfer, which includes contributions from all induced image charges. We use $\Gamma(z) = \Gamma_0 \exp(-\Delta z/\lambda)$, where $\Gamma_0$ is the normalized maximum coupling strength, $\Delta z$ is the closest distance between the particle and the electrode surface, and $\lambda$ is a decay parameter.

We define the probability for the reverse process, \textit{i.e.}, cation reduction and intercalation, analogously to Eq. 2.5. Specifically, we define,

$$
P_{\text{red}} = P_{\text{red}}^{(1)} P_{\text{red}}^{(2)} = \left( \frac{\Gamma(z)}{1 + \exp\left(\beta \Delta U_{\text{red}}^{(1)} - V_{\text{electrode}}\right)} \right) \min\left[1, \exp\left(-\beta \Delta U_{\text{red}}^{(2)}\right)\right], \quad (2.8)
$$

where $\Delta U_{\text{red}}^{(1)}$ and $\Delta U_{\text{red}}^{(2)}$ correspond to the change in system energy associated with electron transfer from the electrode to the cation and the removal of the remaining neutral dummy particles, respectively.

This method describes a process where the change in charge state is accompanied by an intercalation of the species into the electrode, removing it from the electrolyte. In a system where an electrochemically active species acts as a redox couple (\textit{i.e.} both charge states are solvated species) the particle insertion/removal steps are no longer required and this method reduces to the model presented by Subotnik and coworkers. [15]

Notably, this idealized model neglects several important details. In particular, the solid-electrolyte interphase (SEI), which can be hundreds of nanometers thick, is absent. Since this phase can have its own energy barrier for intercalation [45, 46] and even support part of the double layer formation [47], its inclusion will be important in future models.

2.1.3 Implementation Details

Separate fixes were developed to handle the image charge placement and the electrochemical boundaries. For the image charges, the fix ensures that every charged atom in the active system has a corresponding oppositely charged particle reflected across the image plane. The fix also keeps track when charged particles are added or re-
moved from the system and adjusts the image system accordingly which is necessary for the correct computation of the change in energy due to the addition of a charge (e.g. \( \Delta U_{\text{ox}}^{(2)} \) and \( \Delta U_{\text{red}}^{(1)} \)).

For the electrochemical reactions, the routine is summarized below:

1. Attempt frequency: an appropriate frequency must be chosen to control how often a redox event is attempted. Since each trial requires a full system energy calculation, we choose a frequency that allows for a well-sampled system while avoiding computational waste due to unnecessary attempts. This frequency can be adjusted to model the dynamics of specific chemical systems.

2. Type selection: it is first decided whether a redox attempt will be an oxidation or a reduction through a random selection. The probability of a reduction attempt is \( f_{\text{reduction}} \) and oxidation is \( 1 - f_{\text{reduction}} \).

3. Site selection: The trial redox event is attempted at a randomly selected site. For computational efficiency, the statistics of \( \Gamma(z) \) are used to weight the site selection such that it is exponentially more likely that a site closer to the electrode is selected for evaluation. For oxidation, the selected site becomes the center of mass for the insertion of the test particle. For reduction of an existing particle, the selected site serves as the center of a sphere with radius \( r_{\text{search}} \), within which any active cation may be reduced. The exact relationship between \( f_{\text{reduction}} \), \( r_{\text{search}} \), and the volume concentration of active and inactive species is not considered in this work. Simulations in this work use \( f_{\text{reduction}} = 0.9 \) and \( r_{\text{search}} = 2.8 \) Å.

4. Acceptance criteria: equations 2.5 and 2.8 are used to calculate the probability of acceptance based on the energy differences. Note that the \( \Gamma(z) \) term is included in the site selection statistics and is thus not included explicitly in the evaluation of equations 2.5 and 2.8. This probability is then compared to a pseudo-random number and on a successful attempt the number of particles in the active system changes by one. On a failed attempt, the system is reset to the previous configuration.
2.2 Electrostatic potential at the boundary: details of result used in section 2.1.1

For simplicity, and without loss of generality, we can consider the metal boundaries to be at \( z = 0 \) and \( z = d \). For each particle in the active system at position \( \mathbf{r}_{\text{act}} = (x_i, y_i, z_i) \) and charge \( q_i \), the reflected particle is at position \( \mathbf{r}_{\text{ref}} = (x_i, y_i, -z_i) \) and has charge \(-q_i\).

The electrostatic potential \( \Psi \) in the active system in this system is given by eq 2.9.

\[
\Psi(x, y, z) = zF + \sum_{l=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} \sum_{i=0}^{N} \frac{q_i}{\sqrt{A + (z - (z_i + 2dn))^2}} + \frac{-q_i}{\sqrt{A + (z - (-z_i + 2dn))^2}}
\]  

(2.9)

Note that the definition of \( A \) is given by equation 2.10 and involves the \( x \) and \( y \) contributions to the distance which are the same for active charges and image charges.

\[
A = (x - (x_i + lx_0))^2 + (y - (y_i + my_0))^2
\]  

(2.10)

The sums over \( l, m \) and \( n \) account for periodic images in the \( x, y \), and \( z \) dimensions respectively and \( N \) is the total number of atoms in the active system. \( x_0 \) and \( y_0 \) are the length of the periodic cell in the \( x \) and \( y \) directions respectively.

The first term accounts for the applied potential while the first term comes from including the reflection of each particle. By breaking the summation over \( n \) into a sum from 1 to infinity, we can rewrite the expression as shown in equation 2.11, where the \( n = 0 \) term is accounted for by \( \psi_{n=0} = \sum_{l=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \sum_{i=0}^{N} \frac{q_i}{\sqrt{A+(z-z_i)^2}} + \frac{-q_i}{\sqrt{A+(z-(-z_i))^2}}. \)
Note that $\psi_{n=0} = 0$ when $z = 0$

\[
\Psi(x, y, z) = zF + \psi_{n=0} + \sum_{l=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \sum_{n=1}^{N} \sum_{i=0}^{N} \frac{q_i}{\sqrt{A + (z - (2d) + 2dn))^{2}}} 
+ \frac{q_i}{\sqrt{A + (z - (z_i - 2dn))^{2}}} 
+ \frac{-q_i}{\sqrt{A + (z - (z_i + 2dn))^{2}}} 
+ \frac{-q_i}{\sqrt{A + (z - (-z_i - 2dn))^{2}}} 
\]

(2.11)

At the $z = 0$ plane, the first and fourth terms inside the the summation will cancel as will the second and third terms. Thus $\Psi = 0$ at $z = 0$ as desired. Since the system is infinitely periodic, we can rewrite equation 2.9 in terms of a repeat unit spanning $z = 0$ to $z = 2d$. In this case, a repeat unit will include a particle at position $z_i$ and reflection $-z_i + 2d$. Again splitting the sum over $n$ into two parts gives equation 2.12. With the shifted frame, the $n = 0$ term is now $\psi_{n=0} = \sum_{l=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \sum_{n=1}^{N} \sum_{i=0}^{N} \frac{qi}{\sqrt{A + (z - (2d - z_i))^{2}}} + \frac{-qi}{\sqrt{A + (z - (2d - z_i))^{2}}}$. Note that here $\psi_{n=0} = 0$ when $z = d$.

\[
\Psi(x, y, z) = zF + \psi_{n=0} + \sum_{l=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \sum_{n=1}^{N} \sum_{i=0}^{N} \frac{q_i}{\sqrt{A + (z - (2d - z_i))^{2}}} 
+ \frac{q_i}{\sqrt{A + (z - (z_i - 2dn))^{2}}} 
+ \frac{-q_i}{\sqrt{A + (z - (z_i + 2dn))^{2}}} 
+ \frac{-q_i}{\sqrt{A + (z - (-z_i - 2dn))^{2}}} 
\]

(2.12)

Evaluated at $z = d$, the first and fourth terms inside the summation add to zero as do the middle two terms. This gives a total potential of $\Psi = dF = \Delta V$ everywhere along the $z = d$ plane as desired.
2.3 Electroneutrality

2.3.1 Choice of absolute $V_{\text{electrode}}$

Because the two electrodes are coupled to separate, infinite reservoirs at potentials $V_0$ and $V_0 + \Delta V$ instead of to each other, the net system charge can be driven away from zero. Phrased another way, the potential of zero charge for each electrode is not necessarily zero, and a poor choice of $V_0$ can lead to excess charge flooding or leaving the system. Depending on the absolute value of $V_0$, the steady-state concentration of electrochemically active ions will vary. Thus, baseline offset required to maintain a net neutral system will depend on the total ion concentration. The top panel of figure 6-3 shows the average steady-state charge in the active system as a function of the left electrode’s voltage relative to an arbitrary ground, $V_0$. All simulations were done at $\Delta V = 350\text{mV}$.

The lower panel shows the average charge density as a function of inter-electrode distance for the extreme values of $V_0 = -0.31\text{mV}$ and $V_0 = -0.21\text{mV}$. In order to more clearly see the localization of excess charge, these calibration simulations were run with $F = 0$ to avoid Gouy-Chapman double layer formation. The total charge imbalance comes from excess charge at the interface where it is stabilized by image charge interactions. Once the interface is saturated, the total cell charge remains the same as $V_0$ is varied.

Although the idea of removing charge from a battery-like system is unintuitive, it is the expected behavior for this system setup since there is no feedback between the two electrodes. The next section proposes a scheme for electronic coupling between the two electrodes.

2.3.2 Electronic coupling between electrodes

In the October 2019 update to the electrodeboundaries fix\textsuperscript{1}, electronic coupling between the electrodes was added. This implementation keeps track of the net number

\textsuperscript{1}https://github.com/kdwelle/lammps-fixes/commit/04cc216a815859b34271cd522af698963e4a1f
Figure 2-6: Behavior of the system as $V_0$ is changed. Because the two electrodes independently enforce a voltage relative to some external reference instead of a voltage difference, the total amount of charge in the system is a function of $V_0$. Upper: each circle is the average net cell charge over the last 2 ns of a 2.8 ns run. The dark line is a fitted logistic function. Lower: average charge density profiles for simulations driven far from charge neutrality. The dotted line is for $V_0 = -0.31$ mV. The solid line is the average over the $V_0 = -0.21$ mV simulations. The asymmetry in the solid line is due to the voltage difference between the left and right electrodes which directly impacts cation concentration.
of electrons donated/accepted by each electrode and increments \( V_0 \) to produce a negative feedback loop. \( v0\text{Increment} \) is a tunable parameter that determines how much \( v_0 \), and thus the fermi level of both electrodes is changed by with each electron transfer. Higher values of \( v0\text{Increment} \) lead to a system which is punished more severely for deviations from total system neutrality.
Chapter 3

Concentration Profiles in Nanoscale Cells

Nanoscale batteries and battery architectures are one avenue for developing new energy storage technologies. [1] However, many mean-field models are inappropriate for nanoscale applications because they assume that the charge carrying ions act as a continuous electrostatic field. At the molecular scale however, ions are discrete molecules and subject to thermal (and other) fluctuations. As a proof of concept of our method, we investigate whether it can reproduce the correct equilibrium picture and how the nonequilibrium picture changes on a nanoscale.

At the nanoscale, two phenomena begin to approach the same lengthscale. At a molecular scale, we know the interface is dominated by the interactions of the electrolyte with the electrode. The formation of a double layer screens this effect in the bulk, but in small enough scales, the double layer may be a large fraction of the cell, certainly large enough to affect overall transport. Additionally, there is a macroscopic phenomena caused by the difference in chemical potential at the two electrodes. This difference drives a concentration gradient from one end of the cell to the other. The slope of this gradient depends, among other things, on the length of the physical cell. In nanoscale systems, these two profile-modifying phenomena are no longer separated by many orders of magnitude in length scales. The methods developed in the previous chapter are well-suited to investigate the complex problem
of understanding concentration profiles in nonequilibrium, nanoscale battery systems.

### 3.0.1 Simulation Details

All simulations were run using the open-source molecular dynamics software LAMMPS. Simulations included two oppositely charged ionic species with the same mass and radius. The simulation box was 70 Å by 70 Å in the x and y directions with a 140 Å electrode separation giving a total periodic z distance of 280 Å including the explicit image charges. The initial concentration of each species was 1.2 mol/L. Solvent interactions were treated implicitly using a Langevin thermostat with a damping time of 30 fs and temperature of 302 K. Ion-ion interactions were treated using a Lenard Jones 12-6 potential and Coulomb interactions were calculated using the pppm method. The ion-electrode short range interaction was included using a wall interaction derived by integrating over a three-dimensional half-lattice of Lennard Jones 12-6 particles. Simulations were run with a timestep of 5 fs.

Figure 3-1 shows a rendering of the active system (i.e. not including reflected system) for scale.
3.1 Results and Discussion

3.1.1 Emergent Double Layer Formation

One important benchmark is that the model is efficient enough to reach equilibrium conditions under an applied field. For an electrochemical cell, this field arises from the differential charge buildup on the electrode surfaces when held at a potential. Migration of the ions to screen the field through the formation of a double layer structure can take times ranging from microseconds to minutes (or longer) depending on the total concentration of mobile charge carriers, viscosity of the electrolyte, and distance between electrodes since ions may need to diffuse nearly the entire length of the cell.

Gouy-Chapman theory proposes that the distribution of these screening ions can be understood by taking into account the electrostatic interactions between charged ions and the surface as well as the entropic contribution of ion position. [50] The resulting interfacial potential can be solved using the Poisson-Boltzmann equation, and results in a diffuse layer over which the interfacial field is screened. More sophisticated models include the effects of finite-volume charge carriers and short-range interactions on the double layer structure. [51, 52] For simplicity, we will compare the results of our simulations to the linearized Poisson-Boltzmann solution even though we expect the lack of excluded volume interactions to lead to a more compact predicted double layer.

Figure 3-2 shows the average equilibrium distribution of ions for simulations with an applied field ranging from 300 to 2700 MV/cm. Densities are normalized to the bulk concentration at equilibrium and the net charge density is computed by subtracting the negative charge density from the positive charge density. As expected, the Gouy-Chapman solution, shown for the highest field as a dashed black line, predicts a more compact double layer structure since charge can build up at the interface to an arbitrary density whereas real systems, and this model, are limited by the finite volume of charge-carrying ions.
Figure 3-2: The equilibrium distribution of ions as a function of distance from the left electrode. Upper and middle panels show the density of positive and negative ions normalized by the average density with no applied field respectively. Field strength increases as the color changes from teal to dark blue. The dashed black lines show the linearized Poisson-Boltzmann solution for the highest applied field in the region near the left electrode. Lower: The net charge density obtained by subtracting the negative ion density from the positive ion density.
3.1.2 Current-Voltage Response

One strength of this model in comparison to those that use a fixed reaction rate is the ability to better understand the non equilibrium behavior before a steady state is reached. In order to verify that this microscopically defined model correctly reproduces the expected macroscopic response, we computed an ensemble of trajectories where the system was first equilibrated for 140 ns with $\Delta V = 0$ mV and at time $t = 0$ the potential was instantaneously increased to $\Delta V = 350$ mV.

The current density is computed by keeping track of the number of successful oxidations and reductions at both the left and right boundary. The total average flux
through the system is then given per time interval by

\[
\text{flux} = \frac{1}{2} \text{abs} (\#e_{\text{in, left}}^- + \#e_{\text{out, right}}^-) = \frac{1}{2} \text{abs} ([n_{\text{red, left}} - n_{\text{ox, left}}] + [n_{\text{ox, right}} - n_{\text{red, right}}])
\]  

(3.1)

\(n_{\text{ox}}\) and \(n_{\text{red}}\) are the number of successful reductions or oxidations at the given boundary. It should be noted that while this count of electron transfer events gives the Faradaic current through the system, this definition does not include the capacitive current generated by the movement of charge within the cell. At steady-state, however, the total current in an electrochemical cell has no contribution from non-faradaic, or capacitive, current. A future model which includes explicit enforcement of a voltage differential as discussed in the previous section should address these issues.

Figure 3-3 shows the current density as a function of time averaged over 1000 independent trajectories. At \(t < 0\), fluctuations around zero are an indication that even at equilibrium, there is still electrochemical activity with deviations from zero driven by thermal fluctuations. At \(t = 0\), the spike initial current in driven by the large difference between the initial electrochemically active ion concentration at the interface and the concentration at steady state. The decay to steady-state is fit well by an exponential decay plus an offset equal to the steady-state current density, shown in the figure by the orange dashed line. Typically, current decay due to a diffusion-limited depletion of active concentration at the interface is characterized by a \(t^{-1/2}\) dependence[50], however we observe an exponential decay which is characteristic of bulk depletion of a reactant due to a first order reaction. This is most likely an indication that the chosen set of parameters favors a charge transfer limited current instead of a diffusion limited current at early times. The current density for the simulation is notably much higher than existing electrochemical cells. Factors contributing to this include the inherently smoother dynamics of the implicit solvent and the large surface area to volume ratio of the nanoscale cell. Incorporation of more chemical detail into the solvent dynamics will lead to slower reaction rates. The rate can also be tuned by varying the electronic coupling decay parameter \(\lambda\) or the trial frequency for charge transfer events. Additionally, the current model describes a system with
zero overpotential, but its inclusion would also provide another physically relevant parameter for obtaining more realistic current densities.

The response of the system to the potential jump can also be understood through the response of the ion concentration profiles. Figure 3-4 shows the ion densities as a function of time over the first 1400 ps after the application of the voltage difference. The cation density at the left interface decays and the density at the right interface increases, setting up a concentration gradient across the cell. The initial spike and decay in observed current is due to the large charge transfer rate at the beginning when the chemical potential of the system at the interface is far away from the chemical potential enforced by the electrode boundary conditions. Additionally, at the left

Figure 3-4: The early-time concentration density as a function of time. Upper: The normalized concentration profiles of the electrochemically active cations. At $t = 0$ (lightest) the voltage in stepped from zero to 350mV. The concentration then decays at the left electrode and increases at the right electrode, driving the change in current density seen in figure 3-3. The darkest line is the density averaged over the $t = 1.1$ns to $t = 1.4$ns after the application of the potential difference. Lower: The normalized density profiles of the electrochemically inactive counterion (anion).
interface, the larger initial concentration of positive ions at the interface leads to an increase in the probability of any one ion being reduced. As the concentration at the interfaces approaches the steady state concentration, the reaction rate at the interface decays to the steady state rate. The anion density changes much less dramatically than the cation density since any changes are second order effects due to the Coulombic interactions with the density profile. The small increase in ion concentration at the interface is due to image charge stabilization, the same interactions which lead to the decay in free energy near the interface for an isolated ion shown in figure 2-4.
Chapter 4

Transference Number at the Nanoscale

The performance of a lithium-ion (Li-ion) battery depends significantly on the properties of the electrolyte, which mediates the flow of ions from one electrode to the other. Along with chemical stability and conductivity, the transference number, $t_+$, has been considered an important property to optimize in order to develop high performing battery systems. [53, 54] In electrolytes for Li-ion batteries, $t_+$ defines the fraction of overall ionic conductivity that comes from Li$^+$. [55] Electrolytes with high transference numbers (i.e., $t_+ \approx 1$) are understood to experience very little concentration polarization, an effect where the intercalation/deintercalation of Li$^+$ at the electrodes leads to spatial gradients in the net ionic concentration of the electrolyte. [56–58] In this work, we use atomistic simulations to investigate the influence of $t_+$ on the performance of batteries with nanoscale architectures. We find that over length scales of $\sim 10$nm, the tendency for concentration polarization gives rise to local deviations from charge neutrality that serve to mitigate the predicted performance improvement at high $t_+$. By analyzing the results of many simulations, we demonstrate that the transference number is not predictive of model device performance and that in cases where concentration polarization is reduced, very immobile anions can slow cation dynamics and lead to poor overall performance even at high transference numbers. This result demonstrates the necessity of carefully reconsidering
macroscopic phenomenology when designing nanoscale systems.

Transference number is difficult to measure experimentally, because it requires a deconvolution of a collective property (conductivity) into its microscopic components. Most popular methods, such as the Bruce & Vincent method,[59] or diffusion NMR techniques,[60] rely on assumptions of a dilute solution of noninteracting ions. The commonly cited expression for the transference number is similarly valid only under dilute conditions,

\[ t_{NMR}^{+} = \frac{D^{+}}{D^{-} + D^{+}} \]  

(4.1)

where \( D^{+} \) and \( D^{-} \) are the diffusion coefficients for cations and anions, respectively.

More sophisticated corrections [61, 62] require the measurement of additional properties like the salt activity coefficient or the electrophoretic mobilities. In reality, most reported transference numbers are inaccurate due to non-idealities introduced by concentrated solutions, which may contain transient or long-lived ionic clusters. [54, 63] Ionic clustering has been shown to affect the relationship between \( t_{+} \) and power density in ionic liquids, with high concentrations showing transference numbers nearing unity, along with lowered overall conductivity. [64, 65] Additionally, the effect of ion clustering has been shown to lead to negative transference numbers in both ionic liquids and traditional electrolytes. [66–68]

Due to the difficulty of accurately measuring and systematically controlling \( t_{+} \), most insight about its impact on device performance has been derived from theoretical or simulation-based studies. Newman and coworkers published a one-dimensional continuum model of a battery system like the one shown in the top panel of Fig. 4-1, and demonstrated that over macroscopic length-scales, concentration polarization can be limited or even eliminated with high transference number systems ( \( t_{+} > .99 \)). [53] The elimination of concentration polarization is due to the interplay of two physical effects: first, when \( t_{+} \approx 1 \) the anion density profile is uniform across the device and essentially static on the timescale of cation motion and battery discharge; and second, the constraint of local electroneutrality constrains the cation density to match the flat anion density profile. There is reason to suspect that the details of this interplay differ
over microscopic length scales, where the discrete molecular nature of the electrolyte is apparent. As interest in nanometer scale batteries increases, it is important to understand how macroscopic theories translate to nanoscale systems.

Ion-conducting polymers have notoriously sluggish cation mobility at room temperature due to the intimate relationship between polymer segmental motion and lithium ion transport. [69] A well-explored strategy for improving battery performance is to decrease the separator thickness, leading to less resistance and theoretically better battery performance. Although separator thicknesses below 10 micrometers currently poses safety risks [70], battery-like systems have been synthesized using nano-wires and a 10nm thick polymer coating. [71] Over nanometer length scales, charge neutrality can be broken, especially near the interface where charge buildup can be stabilized by image charge interactions. [72] While this electrified interface is very small on the scale of macroscopic systems, it may span a large fraction of the electrolyte in ultra-thin systems where unscreened electric fields have already been shown to lead to enhanced transport under certain conditions. [73] While the magnitude and direction of these fields depend on the exact concentration and strength of the active and supporting electrolyte, the field enhancement of transport suggests that the properties that determine the performance of ultra-thin electrolytes may be fundamentally different than those in macroscopic systems.

We use electrochemically-active molecular dynamics [74] to simulate a variety of cation and anion mobilities in an active electrochemical cell. Building off the work of Newman and coworkers [53, 75], we simulate a battery cell with a lithium foil anode, polymer electrolyte separator, and composite cathode composed of cathode particles surrounded by electrolyte matrix. Our simulations find that for ultrathin cells (14nm), charge polarization and thus power density are relatively unaffected by transference number. In fact, there is evidence that battery performance can be hindered at very high transference number due to the current-carrying cations’ attractive interactions with relatively immobile anions.

The details of our simulation methods are described in the following section. Then, in the Results and Discussion section, we discuss the results of our simulations and
their physical implications.

Figure 4-1: Diagram of the system under consideration. Top: a battery cell with a lithium foil anode, polymer electrolyte separator, and composite cathode composed of cathode particles surrounded by electrolyte matrix. Bottom: the two reactions that determine the electrochemical reactivity of the model. At the anode, an equilibrium between elemental Li in the anode and Li+ ion in the electrolyte. In the composite cathode, an equilibrium between Li+ ion in the electrolyte and occupied Li site in the porous cathode. Importantly, both reactions can react in the forward and reverse directions depending on the energetics of the instantaneous configuration.

4.1 Methods

4.1.1 Dynamics

The battery model is an extension of the electrochemically active molecular dynamics methodology described in chapter 2. [74] The cations and anions are explicitly simulated as Lenard-Jones particles with $\sigma = 1.9$ Å and $\epsilon = 0.4$ kcal/mol, mass of 7 g/mol, and concentration of 0.2 Molar. Cations and anions were given point charges of +1 and -1 elementary charge respectively. The electrolyte is simulated implicitly by the use of Langevin dynamics to propagate the ion dynamics. All particle mobilities are tuned separately by changing the damping of the Langevin thermostat. As was done in the continuum model by Newman and coworkers, the dynamics in the porous...
cathode ($\delta_s < x < \delta_c$) are simulated via an effective diffusivity,

$$D_{\text{eff}} = D\epsilon^{0.5}$$ (4.2)

where $D$ is the diffusivity in the electrolyte region, and $\epsilon$ is the porosity of the cathode, taken to be 0.3 in this work. Thus, the strength of the damping on each particle is a function of its location in the simulation box. The simulation box was 7nm by 7nm by 140nm with the porous cathode region beginning at 42 nm.

Simulations are run using a constant voltage procedure where there is initially no lithium in the cathode, and a constant voltage is applied across the cell to drive the oxidation of lithium from the foil anode, across the electrolyte separator, and into the composite cathode where it can be reduced. Although the total power capacity of a real battery is determined by the amount of lithium which can be intercalated into the cathode before the voltage at constant current drops below some threshold, the work of Newman and coworkers showed that the increased capacity of high transference number batteries is due to changes in concentration polarization which can be evaluated during steady-state discharge. We consider the power output of our model battery under pseudo-steady-state conditions, where current is constant under an applied voltage, and favorable changes in the concentration profile, and thus overall power density, manifest as higher current under the same applied voltage.

### 4.1.2 Simulating Reactivity

The cations and anions share the same physical parameters, but only the cations can carry faradaic current by electrochemical reaction at the electrodes. The active electrochemistry is described by two equilibria, one at the anode and the other in the porous cathode, as shown in figure 4-1. At the foil anode, the equilibrium is given by

$$\text{Li(intercalated) + } \Theta_e \rightleftharpoons \text{Li}^+ \Theta_e + e^-$$ (4.3)
where $\Theta_e$ is a site in the electrolyte (e.g. a coordinating site in an ion conducting polymer) and $\text{Li}^+ - \Theta_e$ is a site occupied by a lithium ion. This corresponds to an equilibrium between unoccupied and occupied electrolyte sites. The dynamics of the $\text{Li}^+$ in solution are simulated explicitly, while the electron and the intercalated $\text{Li}^0$ are only included through the effects of the applied voltage on the equilibrium. In the composite cathode, the intercalation process is described by

$$\text{Li}^+ - \Theta_e + \Theta_e + e^- \rightleftharpoons \text{Li}^- \Theta_e + \Theta_e$$

(4.4)

where $\Theta_c$ is an unoccupied cathode intercalation site, and $\text{Li}^- \Theta_c$ is an occupied site. This describes an equilibrium between the occupied electrolyte site and the occupied cathode site. Cathode intercalation sites are uniformly distributed on a cubic lattice with a lattice spacing of 2.1 Angstroms between sites. Filled or unfilled, sites do not diffuse or migrate, so the unrealistically close packing mimics the extra space that would be available for reduced ions if filled sites were to migrate toward the back of the cathode where no reactions could take place.

For computational efficiency, simulations were carried out with a chemical potential difference between the two electrodes of 3.5V. Notably, these boundary conditions produce electrochemical driving forces ($\sim 0.25 \text{ V/nm}$) that are large relative to those generated in typical devices. Simulating conditions with more realistic, low driving forces is computationally difficult in nanoscale cells because the net average ionic current is small relative to that arising from ordinary thermal fluctuations. Simulating systems with large currents significantly reduces required computational time while still providing physical insight that can be generalized to systems with smaller currents. So, although our results only apply quantitatively to systems with unphysically large driving forces, we expect the qualitative conclusions to apply more generally.

Additionally, this model excludes the effects of the solid electrolyte interphase (SEI) and cathode electrolyte interphase (CEI). At the nanoscale, the effects of these layers may be very large due to their thickness relative to the overall cell length. However, due to the difficulty of correctly modeling the mechanism and phenomenology
of the SEI and CEI, this study focuses on the effects of the ion mobilities and ion-ion interactions in the electrolyte, phenomena that should not be greatly affected by the absence of and SEI and CEI.

4.1.3 Defining transference number

The transference number, \( t_+ \), is defined as the fraction of current carried by a given species in a system with no concentration gradients [55, 76]. Since Ohm’s law relates current and conductivity, \( i = \sigma E \), where \( i \) is current, \( \sigma \) is conductivity, and \( E \) is the electric field), we can write \( t_+ \) as

\[
t_+ = \frac{\sigma_+}{\sum \sigma_i}
\]  (4.5)

where the sum is over all species in the system. For simplicity, we will only consider binary salt systems with no supporting electrolyte so \( \sum \sigma_i = (\sigma_+ + \sigma_-) = \sigma \). In our simulations we tune the electrophoretic mobility, \( \mu_i \), which determines how susceptible a species is to motion under an electric field \( (v_i = \mu_i E \) where \( v_i \) is the velocity). The relationship between conductivity, \( \sigma \), and mobility, \( \mu \) is given by

\[
\sigma = F \sum_i z_i \mu_i c_i
\]  (4.6)

where \( F \) is Faraday’s constant, \( z_i \) is the charge on species \( i \) and \( c_i \) is the concentration of species \( i \). The transference number can then be written as

\[
t^\text{ideal}_+ = \frac{\sigma_+}{\sigma} = \frac{z_+ \mu_+ c_+}{\sum_i z_i \mu_i c_i} = \frac{\mu_+}{\mu_+ + \mu_-}
\]  (4.7)

where the last equality is for a monovalent, binary electrolyte under the assumption of electroneutrality \( (\sum z_i c_i = 0) \). Thus, by tuning the mobility of the anions and cations separately (via changing the damping of the Langevin thermostat), we can directly control the expected transference number of the simulations and measure the power output as a function of transference number.
4.2 Results and Discussion

By running simulations over a range of cation and anion mobilities, we have modeled systems with electrolyte properties spanning from $t_+ = 0.008$ to $t_+ = 0.9992$, including a 14-fold difference in output current density.

We first examine the influence of transference number, as given by Eq. 4.7, on the flux of cations and anions within the electrolyte separator. Specifically, we have calculated the forward and reverse flux separately for cations and anions through a plane 30 Å from the left electrode (i.e. in the center of the separator region). We compare the ratios of these fluxes to their ideal value computed using Eq. 4.7 and equilibrium mobilities. The results of these calculations are plotted in Fig. 4-2.

Figure 4-2A contains a plot of the relative fraction of total ionic flux for left- (in the direction of the composite cathode) or right- (in the direction of the foil anode) diffusing cations or anions at various values of the transference number but at constant $\mu_+ = 21.5$. We define the fractional flux of a population of ions in terms of,

$$f_{d,c} = \frac{j_{d,c}}{j_{l,+} + j_{r,+} + j_{l,-} + j_{r,-}}$$

(4.8)

where $j$ indicates the number of ions crossing the plane per unit time, and the subscripts $d$ and $c$ denote the direction (i.e., “l” for left and “r” for right) and charge (i.e., + for cations and - for anions) of the associated population. For a given value of $t_+$, these four fractional fluxes sum to unity (by construction), and their relative values reveal how much of the overall flux is carried by each population.

The overall device current is carried by cations flowing left-to-right and as expected we observe an imbalance between left-flowing cation flux and right-flowing cation flux, with $f_{r,+} > f_{l,+}$. Unexpectedly, however, the anion flux remains roughly constant over the range of $0.5 < t_+ < 0.75$, despite a significant decrease in anion mobility over that range. This indicates that effective anion mobility is increased through correlations with the cations in the system, for example due to the joint diffusion of ion pairs or clusters, as proposed in previous studies. [65, 67, 68] For $t_+ > 0.75$ we observe the expected behavior that the overall flux becomes dominated by cations.
Figure 4-2: Breakdown of ion motion through the center of the electrolyte. (A) fraction of flux through a plane a distance 30 Å from the left electrode as a function of $t_+$ at constant $\mu_+ = 21.5$. Lines show the fraction of flux due to cations traveling right (dot-dashed), cations traveling left (dashed), anions traveling right (solid), and anions traveling right (dotted). The value of anion mobility at the top axis are given in $\mu m^2 V^{-1} s^{-1}$. (B) comparison of $t_+$ and $f_+$, the fraction of ion flux through the plane due to positive ionic motion. Blue circles each represent the average of 23 simulations with the same $\mu_-$ and $\mu_+$ and the red line plots the $y = x$ line of perfect correspondence.

Additionally, we calculate the ratio of total flux due to Li$^+$ motion, given by $f_+ = (f_{l,+} + f_{r,+})$. This ratio is plotted in Fig. 4-2B along with the idealized expectation based on the assumption of that anion/cation mobilities are uncorrelated. We observe that for roughly 90% of the range of $t_+$, approximately half the total ion flux through the electrolyte is due to cation motion. This observation further supports the idea that for moderate transference numbers, the coupling between anion and cation dynamics cannot be reliably neglected. Additionally, these results show that our model effectively captures the correlated ion dynamics present in real systems and is therefore a useful candidate for understanding the effect of transference number on overall battery performance.

Figure 4-3 contains the results of steady-state currents computed for systems with a variety of different cation and anion mobilities, and plotted as a function of transference number. Dashed lines connect simulations at a constant $\mu_-$, which generally
Figure 4-3: Average current as a function of transference number. Black circles are the result of a simulation and lines connect the means of each parameter set. Solid orange lines connect points at a constant $\mu_+$ with darker lines having a higher value of $\mu_+$. Blue dashed lines connect simulations at a constant $\mu_-$ with darker lines having a higher value of $\mu_-$. Values of $\mu_+$ are sampled at values of 0.17 (lightest orange), 1.7, 6.6, 11.5, 16.5, and 21.5 (darkest orange) $\mu$m$^2$V$^{-1}$s$^{-1}$ and values of $\mu_-$ are sampled at values of 0.02 (lightest blue), 0.17, 1.7, 6.6, 11.5, 16.5, and 21.5 (darkest blue) $\mu$m$^2$V$^{-1}$s$^{-1}$.

increase with $t_+$, suggesting that the systematic improvement in average current with increased transference number is the result of higher cation mobility. This positive correlation is expected since it is obvious that better battery performance is correlated with a more mobile active species. Solid lines connect simulations at a constant $\mu_+$, i.e. where higher transference number is the result of slowing the anionic species. In these simulations, we see no evidence of power enhancement, even at extreme transference numbers. In fact, nearly immobile anions seem to be correlated with slower cation dynamics.

Because transference number involves a combination of two transport properties, the cation and anion mobilities, we have also shown the same data as a function of
Figure 4-4: Average current as a function of ion mobilities. Left: orange lines show the current as a function of anion mobility. Darker lines correspond to a higher cation mobility. Specific line colors correspond to those in Fig. 4-3. Right: blue lines show the current as a function of cation mobility. Darker lines correspond to a higher anion mobility.

The data plotted with solid orange lines demonstrate that extremely slow anion populations (below values of $5 \mu m V^{-1} s^{-1}$) actually decrease the battery performance, presumably due to cation-anion attractive interactions. Because of the attractive Coulomb interactions, cations may experience a type of Coulombic friction at very slow anion mobilities. This simulation data is consistent with many experimental measurements where limiting the counterion mobility leads to a decrease in overall conductivity. [77]

The right-hand panel of Fig. 4-4 shows a monotonic increase in battery performance as cation mobility is increased. The trend levels off at higher cation mobilities because the system transitions from a diffusion-limited current where an increase in cation mobility leads to a large change in the output current, to a charge-transfer-limited current regime which is relatively insensitive to changes in the cation mobility. Figure 4-4 suggests that the trends in battery performance are relatively consistent as a function of mobility, and the change in curvature in the anion isosurfaces (blue dashed lines) in Fig. 4-3 is the result of the form of Eq. 4.7 rather than a change in physical behavior of the system in different regimes.

We also analyze the concentration polarization in our simulated systems for a
variety of transference numbers by plotting the average concentration as a function of distance between the electrodes for systems with a fixed transference number of $t_+ = 0.5$, but varying cation mobilities. As shown in Fig. 4-5, systems with a higher cation mobility have lower concentration polarization and generate better battery performance. Figure 4-5 contains plots of the concentration profiles and the power densities and maximum cation densities (a proxy for concentration polarization). The right-hand panel of Fig. 4-5 shows that lower cation polarization correlates well with higher current at a fixed voltage, as expected. In a model where charge neutrality were maintained across the electrochemical cell, this improvement to power output could also be recovered by limiting the anion mobility, and thus overall cation polarization.

However, in an ultra-thin cell, reducing anion mobility does not appear to flatten cation concentration profiles. Figure 4-6 looks at a fixed cation mobility over a range of transference numbers by plotting the concentration profiles at a constant $\mu_+ = 21.5 \mu \text{m}^2\text{V}^{-1}\text{s}^{-1}$, (i.e. the darkest orange line in Fig. 4-4) as well as the current at a fixed applied potential and maximum cation density in the same style as in Fig. 4-5. Despite the transference number spanning from 0.5 to 0.999, the concentration profiles
Figure 4-6: Left: Cation concentration profiles as a function of distance from the left foil anode over a range of transference numbers at fixed cation mobility. The grey dashed line indicates the boundary between the electrolyte and composite cathode regions. Right: Current at a fixed voltage (blue circles) and polarization (orange diamonds) as a function of transference number for the same systems plotted to the left. Polarization is plotted as the maximum normalized cation density observed near the foil anode.

remain relatively constant in comparison to the scale of changes seen by varying the cation mobility. For very high transference numbers (> 0.99), the cation density could be interpreted as less polarized, consistent with predictions from macroscopic models [53]. However, the steady-state current is much lower than for moderate numbers (right panel), supporting the idea that the otherwise mobile cations are being slowed by their attractive interactions with the very slow anions, and breaking the expected trend between transference number, polarization, and battery performance.

These simulations suggest that in nanoscale electrode systems, the relationship between transference number and battery performance is complex, and that the same degree of battery performance can be found in systems with a range of transference numbers. We attribute this deviation from the macroscopic theory to the breakdown of electroneutrality at small scales due to the discrete nature of charge carrying ions. These simulations suggest that for ultrathin electrolyte systems, there is no clear benefit to optimizing the transference number in order to improve concentration polarization. Instead, concentration polarization is a function of the relative rates of reaction at the interface, and cation mobility. At very high transference number, the attractive interactions between ions may indeed contribute to reduced performance
observed in macroscopic single ion conductor systems.[77].

4.3 Future work: Calculating the transference number as a function of effective diffusivity

In this chapter we have used the equilibrium determination of mobility to define the transference number. However, these trajectories can also be used to elucidate the relationship between NMR-determined transference numbers and the equilibrium values used in this work. Since NMR-determined transference numbers compare the effective diffusivities of the relevant species, including their interactions with one-another, the effective mobilities of each species could be recalculated from this trajectory data. This would provide a mapping between $t_{+}^{\text{ideal}}$ and $t_{+}^{\text{NMR}}$ for a variety of mobilities in a nonequilibrium system. The difference between these measurements in the active, nonequilibrium system and an equilibrium simulation should also be considered. Finally, the simulations should be repeated at a variety of dielectric constants since the effective diffusivity will depend on the strength of the attractive interactions between the cations and anions.
Chapter 5

Statistics of the Electrochemical Interface

5.1 Introduction

The 21st century has seen a renewed interest in the field of electrochemistry. Electrochemical processes play a key role in vital technologies for energy conversion and storage which are expected to play a large role as global energy supply transitions away from fossil fuels. Additionally, the application of electrochemical technologies has led to advances in the fields of biochemistry, materials science, and analytical chemistry. Electrochemistry is an inherently interfacial process, and thus is it vital to understand the structure and behavior of the interfacial regime in order to better understand and design electrochemical technologies. Mean field theories, like Gouy-Chapman-Stern, have found enormous success in explaining and predicting the behavior of fundamental electroanalytical techniques like cyclic voltametry. [18–21] These theories treat the charge and concentration gradients set up by ionic species as continuous and uniform in the electrode plane. However, on a molecular scale, due to the discrete nature of charge-carrying species and water-electrode interactions, the energetic landscape is both temporally and spatially heterogeneous. [78, 79] Over large, planar electrodes, these deviations are averaged out by sampling over a large area and traditional mean-field models effectively capture the observed phenomenology.
Nevertheless, solutions to modern analytic, catalytic, and energy storage challenges may require the development of nanoscale or nanoarchitected electrochemical cells. [1] For the design of these cells it is crucial to understand how the electrolyte fluctuates on the time and lengthscales of individual molecular reactants. In this chapter, we aim to understand the heterogeneity of the equilibrium double layer. We begin by suggesting that equilibrium simulations of nanoscale cells require the application of large fields in order to accurately simulate the potential drop across the double layer. We then use a series of constant potential molecular dynamics simulations to investigate the fluctuations in local concentration and the Madelung potential of the double layer.

5.2 Methods

This chapter focuses on two reference points for understanding electrochemical reaction at an interface. The first, more common frame of reference is the local concentration or potential field with respect to the electrode. In this laboratory, or electrode, point of view, there are short-time fluctuations in local concentration as individual ions drift past the electrode, but there are also oscillations in the long-time averaged concentration profiles perpendicular to the electrode due to the effects of molecular layering and the emergence of the double layer to screen an applied potential. This is the point of view of double layer theories like Guoy-Chapman-Stern. [18–21]

In contrast, we can focus on the point of view of the individual ionic species. This is the electrostatic frame of reference most relevant to understanding outer sphere electron transfer involving the species. [33, 80] This is the frame of reference that gives rise to theories like Debye-Huckel which take into account how the correlations between ionic species are a phenomena which depends on an ion’s interactions with all other species in the system. [16] An important quantity here is the Madelung potential on an individual particle $i$, $\phi_i$.

$$\phi_i = \sum_{j \neq i} \frac{k_e q_j}{r_{ij}}$$ (5.1)
The sum is over all other particles \( j, k \), \( k_e \) is Coulomb’s constant or the electrostatic constant, and \( r_{ij} \) is the distance between the particles. This is a convenient quantity because it encodes all of the electrostatic information about the surrounding environment relevant to the vertical energy gap \( \Delta E \), a convenient quantity for the reaction coordinate of an outer sphere electron transfer. [81] Put another way, the fluctuations in \( \Delta E \) are almost directly proportional to the fluctuations in \( \phi_i \) where \( i \) is an ion donating to or receiving an electron from the electrode.

5.2.1 Simulations

Molecular dynamics simulations are run using the LAMMPS simulation software. Constant potential boundary conditions were enforced using the image charge method developed by Dwelle and Willard. [74] The active simulation cell contains 1000 TIP3P water molecules and 60 NaCl ion pairs (3-M concentration). [82, 83] After NPT equilibration, the active simulation cell measures 34.6 Å by 31.5 Å by 31.5 Å with Lennard-Jones 9-3 walls at either end of the longer dimension to simulate the electrode surface. The platinum-like walls used parameters \( \sigma = 2.535 \) Å and \( \epsilon = 7.80 \) kcal/mol. [84] Notably, this homogeneous wall potential does not replicate the orientational dependence of the metal-electrolyte interaction, but is significantly faster than simulation of individual metal ions and we are interested more in the phenomenology of interfacial electrolyte systems in general rather than replicating the exact chemical details of a particular interface. Lorentz-Berthelot combining rules were used between all species. Simulations were run for 250ps after equilibration with the last 200ps used for data analysis.
5.3 Results and Discussion

5.3.1 Appropriate fields for nanoscale simulations of the electrochemical double layer

Before we can use simulation to understand the structure of the double layer and how its equilibrium fluctuations change on the application of a potential, we have to understand how to properly simulate the double layer structure present in macroscopic experimental systems ($\sim$ cm) which are far too large to be simulated explicitly by molecular dynamics. However, if the goal is to understand the equilibrium structure of the double layer using nanometer-scale simulations, it is necessary to apply unphysically large fields. This is because regardless of the size of an electrochemical cell $^{1}$, the total potential difference between the two electrodes is screened by the formation of the double layers, and increasing the cell size only increases the length of the screened regime.

5.3.2 Averaged Double Layer Structure

It is well-understood that the average charge profile near the interface oscillates in space due to the effects of molecular layering induced by interactions with the electrode. Additionally, under an applied potential, electrode charge is screened at by the buildup of charged ions, leading to different charge profiles at the left and right electrodes. Figure 5-1 shows the average charge density as a function of distance from the left electrode. These density profiles are averaged over 50 simulations of 250ps each. When the water partial charges are included in the overall charge densities, water dipole orientation at the interface dominates the charge profile (panels A and B of figure 5-1). However, the partial charge on the water molecules is inherently part of a dipole system and cannot screen the applied potential. Thus we also look at the charge density profiles solely due to the ionic species in the electrolyte (panels C and D of figure 5-1). As expected, there is some structure due to the molecular layering.

$^{1}$the exception of course is a cell which is too small to support the formation of a double layer, or a field which is too high to be screened by the complete separation of the electrolyte
of the ionic species at the interface, even at zero applied potential and additionally
the formation of a double layer structure as a response to the application of a potential. However, these profiles are all the result of averaging over 10s of nanoseconds
of trajectories. We would like to understand how robust this layering structure is at
the sub-nanosecond timescale.

5.3.3 Charge Fluctuations

We can divide the total simulation cell into voxels of $3.1 \, \text{Å} \times 3.1 \, \text{Å} \times 3.1 \, \text{Å}$. Every 500fs,
we can count the total net charge in each voxel. Figure 5-2 shows the heterogeneity
of the charge in the voxels at a distance of $2.1 \, \text{Å}$ from the left electrode. If the charge
were distributed evenly, each voxel would have a uniform net charge of $-0.0018$, or
net charge concentration of $25 \, \text{M}$ negatively charged particles. However, by breaking
the electrode into smaller spacial volumes, we can see that the distribution of charge
is heterogeneous. The top panel of figure 5-2 shows that there is a great deal of
instantaneous heterogeneity is quickly averaged over in the first few picoseconds.
However, after about 80ps, the width of the distribution remains relatively constant.
The spacial distribution of the net charge after averaging over 200ps is plotted in the
bottom panel of figure 5-2. Although this plane is net-negatively charged overall, there
are still many voxels which are positively charged, even after hundreds of picoseconds.

In the case of a homogeneous electrode, this heterogeneity is averaged over and not
apparent in electrochemical measurement. However, if an electrode were patterned
with reactive ligands, this translational heterogeneity would result in a lowered effective reaction rate.

5.3.4 Madelung Potential

In contrast to the profiles in figure 5-1, the Madelung potential reports on the electro-
static environment relevant to the a specific ion. Importantly, the Madelung potential
is dependent on the chemical identity of the species. This is because each ion’s electro-
static environment is affected by its own charge. E.g. a positive ion’s nearby
Figure 5-1: Charge density as a function of distance across the cell with and without an applied potential. After ~ 7 Å from the interface the charge density is bulk-like and electroneutral for both ions and water. Charge density due to the partial charge on water oxygens is plotted as a solid orange line, charge density due to the partial charge on water hydrogens is plotted as a dashed grey line. Charge density due to the anions and cations are plotted at solid teal and dashed navy respectively. The solid black lines show the total net charge density at a given distance from the interface.

A) Charge density at zero potential of all charges including those from water. The bottom panel shows the net charge density. B) Charge density of water and ions at a potential of 1V across the cell. C) Charge density of the ions only at zero potential across the cell. D) Charge density of the ions only at a potential of 1V across the cell.
Figure 5-2: Fluctuations of charge 2.1 Å from the electrode. Top: Average net charge per voxel plotted as a function of time. The red line plots the running average of all voxels. Bottom: average charge in each voxel over 250ps as a function of voxel location. The average charge concentration over the 250ps is -25 M.
environment will likely be more negatively charge due to favorable electrostatic interactions. Figure 5-3 shows none of the molecular layering which dominates the charge (and by extension Poisson potential) profile in the vicinity of the electrode. Instead, the Madelung potential is smooth and bends toward zero in the vicinity of the electrode. This feature is due to the image interactions of the ion with the polarizable electrode. [33] Interestingly, the change in the overall Madelung potential after the double layer has been established is very similar to the zero-potential profile. There is a slight shift of the potential of the ions nearest to the electrode due to the influence of the charged electrodes. However, the change is small, especially when compared to the fluctuations in the potential.

The very large variations in the Madelung potential are much larger than would be expected from thermal fluctuations. Additionally, the distributions of individual ions’ Madelung potentials does not differ significantly from the overall distribution. Figure 5-4 shows that the distribution of Madelung potentials sampled by a single anion over 200 ps does not differ much from the distribution sampled by the whole population of anions over 200 ps. Furthermore, looking at the time series of individual ions, the large fluctuations are on the order of picoseconds. Taken together, this suggests that the Madelung potential is subject to some kind of correlated motion, possibly water rotation, that greatly influences its electrostatic environment. Unfortunately, changes in the Madelung potential can provide important chemical information about a system and its electrochemical environment. [85] Thus it is necessary to develop tools for averaging over these large fluctuations to extract the relevant information without losing the dependence of the Madelung potential on the configurational variables of interest (e.g. quantifying the response to an electrochemical perturbation).

We can still use the Madelung potential distributions from our simulations to illuminate an interesting energetic difference between implicit and explicitly solvated systems. We can separate out the role of water on an ion’s electrostatic environment by calculating the Madelung potential for the ions in the system both including and excluding the partial charges on the water molecules.

As a dipolar molecule, water can screen small fields on a timescale on the order
Figure 5-3: Madelung potential of anions ($\phi > 0$) and cations ($\phi < 0$) as a function of inter-electrode distance. Grey circles plot the instantaneous Madelung potential and the black line is the average over all the grey points binned into 1 Å bins. The navy dashed line in the lower panel is the $\Delta V = 0$ average plotted on the same axes for comparison.
Figure 5-4: Variation in individual ions’ Madelung potentials. Top: Madelung potential probability distribution of the entire population (heavy black line), and two individual ions (orange and green lines). Bottom: Time series of individual ions’ Madelung potential plotted in the top panel. Colors correspond to the same ion as in the top panel.
Figure 5-5: Comparison of the electrostatic potential energy felt by ions at 4.7 Å from the zero-potential electrode. Solid lines indicate the potential felt by anions while the dashed lines indicate potentials felt by cations. Filled histograms show the distributions of Madelung potentials calculated using all atoms in the simulation (other ions, water, and image charges) over 400ps with snapshots every 500fs. Lines plot the distribution of Madelung potentials felt by ions excluding water (i.e. other ions and image charges due to ions) over 4ns with snapshots every 500fs.

of molecular rotation. In contrast, point charges alone can fully screen an applied potential through arrangement into a double layer as shown in figure 5-1-D. Figure 5-5 shows the distribution of the Madelung potential including all ions and water interactions, as well as without the water dipoles. As expected, the mean of the Madelung potential shifts toward zero when the water dipoles are excluded for both cations and anions. This shift reflects the fact that the water dipoles are preferentially oriented toward/away the ions to screen the ion charge. However, the shape of the distribution also changes when the water dipoles are excluded. Charge screening due to water molecules appears to mask some amount of ion-ion correlation. Since ionic diffusion is much slower than water rotation, these correlations may be transiently revealed due to thermal fluctuation and transient rotation of water dipoles. More obviously, this discrepancy between the ion-ion Madelung potential distribution calculated with an explicit solvent and the Gaussian distribution observed when dynamics are propagated in a uniform dielectric suggests that a uniform dielectric solvents may be even more inappropriate than previously realized for understanding
the dynamics of electrolyte systems.

Taken together, these results suggest that the electrochemical interface, even of an ideal, featureless electrode, is temporally and spatially heterogeneous. However, the exact type of heterogeneity depends on the quantity measured.
Chapter 6

Ultra-Coarse-Grain Simulations

Although we have shown in the previous chapters that it is possible to simulate small cells with explicit solvent or larger cells with an implicit solvent, there is still a need for simulation methods that can accommodate larger cells while still maintaining the discreteness of the charge carriers and physics-based electron transfer methodology. This chapter is dedicated to preliminary results focused on three methods for running less detailed (ultra-coarse-grain) simulations: 1. The use of a lattice framework on which ions and polymer sites migrate; 2. The development of new methods for predicting a window of probable vertical excitation energies that might be sampled between large timesteps; and 3. The use of stochastic methods (specifically Monte Carlo) for sampling nonequilibrium dynamics. The development of each of these methods and recommendations for further refinement will be discussed in the following sections.

Both the lattice models and coarse-grain electron transfer (CGET) methods have promise, but the use of stochastic methods where trial moves are evaluated using energy changes is strongly not recommended for electrostatic systems. Due to the long-range nature of electrostatic interactions, calculation of energy changes scale with the system size (in contrast to e.g. spin systems where only nearest-neighbor interactions are included). Therefore each trial move requires a large energy calculation and only results in a probability of a single particle’s movement. In contrast, molecular dynamics simulations can propagate every particles’ motion forward in time with
each force calculation.

6.1 Lattice models

The use of lattice models has a long history in the field of statistical mechanics and in particular the field of polymer dynamics. Lattice models have been used to estimate critical exponents as well as simulate the behavior of ion conducting polymers. [86–89] In a lattice model, an array of sites is used to restrict the available positions of the ionic species, usually arranged as a three-dimensional cubic lattice. The polymer can be represented as a series of adjacent sites where no site can be occupied by multiple polymer units (self-avoiding walk). [90] These models can be made to have more chemical detail by assigning chemically-informed interaction potentials or using a more chemically-relevant lattice structure. [91, 92]

6.1.1 Explicit polymer dynamics

After laying down a polymer onto the lattice, it is desirable to propagate some dynamics to mimic the physical reality that ion conducting polymers move more slowly than the ions themselves, but are not a static field. One way to add these dynamics to stochastic models is to introduce a set of polymer conformational moves. [93] Here we will consider four of them, end move, slither snake, crankshaft, and kink jump. Examples of each of these are shown in figure 6-1. An example of a simple Monte Carlo model for an explicit polymer on a lattice developed in this work can be found on the author’s github.  

6.1.2 Dynamic percolation theory

A more coarse-grained approach is to mimic only the effect of the polymer without explicitly mapping blocked sites to polymer repeat units. The simplest models, with randomly distributed blocked sites (percolation models) are successful for may ma-
Figure 6-1: Examples of four trial moves to sample polymer configurational space. Diamonds represent occupied lattice sites and lines connect adjacent sites. Purple shows the state of the polymer before the move and blue shows the state of the polymer after the move.

Materials science problems, but are inappropriate for polymer dynamics. To address this, Druger, Nitzan and Ratner developed a dynamic percolation model. [94–99] In this approach, the slow moving polymer dynamics are mimicked by the migration of blocked lattice sites. The migration of the sites is much slower than the migration of the ion movement, but still relevant on the timescale of the total simulation. Importantly, in this scheme there is no percolation limit where at a certain percentage of blocked sites an ion is unable to make it from one end of a cell to another. At higher blocked site density, the overall effective movement of ions is determined by the slower, polymer migration rate. This mimics the mechanism of ion transport by poly-ethylene oxide (PEO), a well-studied candidate for a solid-polymer electrolyte. Molecular dynamics simulations have shown that the mechanisms of ion transport in PEO are hopping events facilitated by polymer segmental motion or co-diffusion of ion and polymer together. [100, 101] Both of these mechanisms rely on polymer motion for ion conductivity. Thus the ability of dynamic percolation theory to include both of these timescales without the computational complexity of an explicit polymer model makes it an attractive candidate for understanding fundamental poly-
mer ion conductivity behavior. A chemically-specific, off-lattice version of the theory was developed by Miller and coworkers. [102] This allowed for the investigation of ion conductivity in timescales which are unreachable with full molecular dynamics simulation while retaining some chemical specificity.

We propose an alternate model for introducing the different ion-polymer interactions for cations and anions. In this scheme, the polymer is still represented as a density of blocked sites on a lattice that migrate with some time constant much larger than ion migration. However, the cations and anions interact with different versions of these blocked sites. This allows for properties like the transference number to be tuned. Figure 6-8 shows an example of this kind of scheme on a two-dimensional lattice. A description and results from off-lattice implementation of a related scheme using Lennard-Jones particles instead of blocked lattice sites can be found in the Bachelor’s thesis of Chen, mentored by this thesis’ author. [103]

6.2 Coarse-grain electron transfer

The slowly-relaxing nature of solid polymer electrolytes necessitates long simulations that remove as much detail as possible. However, the nature of diabatic electron transfer means that the rate of electron transfer in these heterogeneous, ill-sampled electrolytes should be highly dependent on the instantaneous electrolyte configuration. Thus it might be inappropriate to simply calculate a mean electron transfer rate and implement it as a constant through the course of a nonequilibrium simulation. Thus it is desirable to include some kind of configuration-dependent coarse-grain electron transfer (CGET).

6.2.1 The problem of finite timestep

A key concept in Marcus theory is that electron transfer is fast relative to nuclear motion and thus excess energy from an electron transfer cannot be dissipated as heat (nuclear degrees of freedom). Thus for two species to have a chance to exchange an electron, the total energy of the electron removal, transfer, and affinity with the
Figure 6-2: Capturing electron transfer with a large timestep. **Top:** Two continuous nuclear potential energy functions as a function of time, $E_1$ and $E_2$. For an electron transfer to occur, $E_1 = E_2$. The functions are evaluated at $t_1$ and $t_2$, at which times the functions are not equal. However, between $t_1$ and $t_2$, the functions crossed at time $t_\ast$. Instead of sampling time in fine enough increments to capture this event at $t_\ast$, a more coarse-grained approach is proposed. **Bottom:** The fluctuations in $E_1$ and $E_2$ have been characterized, and the instantaneous evaluations of $E_1$ and $E_2$ are used as the mean. The probability of attempting an electron transfer at $t_n$ is now the overlap between the two Gaussians. At $t_1$ there is a larger probability than at $t_2$ where there is virtually no overlap.
accepting species must sum to zero. In the simplest case, there must be a match between the energy of the occupied donating electron energy ($E_1$) and the acceptor’s lowest unoccupied electron energy ($E_2$), both of which depend on the electrostatic and energetic landscape mediated by the surrounding environment. For example, figure 6-2-top, shows the continuous energy of the two states as a function of time with energy evaluation at $t_1$ and $t_2$. In any given instantaneous evaluation of the electronic levels will lead to a comparison between two discrete energy values which are almost guaranteed to be unequal assuming some degree of numerical precision. However, in reality, time is not discrete and potential energy is continuous as a function of time. Thus while two discrete energy levels will almost never instantaneously match when checked infrequently, there will likely be moments of crossing that are not captured by the infrequent checkpoints (e.g. $t_*$ in fig 6-2-top). A more coarse-grained method of checking for electron transfer events is to characterize each energy as a distribution of energies centered at the observed values. Then the probability to attempt an electron transfer is given by the overlap of the two probability distributions instead of an equality of two discrete numbers. Obviously, in the limit of very large timesteps, this method, correctly parameterized, should reduce to the same dynamics given by the use of an average rate. However, for situations like the case of a solid polymer electrolyte where the electrostatic environment relaxes slowly, there may be long periods of time where the functions $E_1$ and $E_2$ fluctuate around very different means. In this case, some information about the characteristic short-time fluctuations of the energy functions can be used to estimate configuration-dependent electron transfer probabilities.

### 6.2.2 A simple electrode example

When dealing with electron transfer to and from an ideal metal electrode, the problem is a little different. Since an ideal metal conductor is a *continuum* of electronic states instead of a series of finite energy levels like an isolated molecule, the probability of an electronic transition to any arbitrary energy level is proportional to an evaluation of the Fermi function for that metal at that energy. In work by Subotnik and coworkers
they simply multiplied the probability by the timestep to account for time between
timesteps (equation 10). [15] However, we can also apply the same method of treating
the fluctuations as Gaussian around some mean determined by the instantaneous
energy evaluation. This example is described below.

Assume that an ion near the interface samples a Gaussian width around its in-
stantaneous chemical potential in the time between samples. Additionally, we can
assume that the distribution of electronic states in the electrode can be described by
the Fermi equation:

$$f(\mu) = \frac{1}{1 + e^{\beta(\mu - \mu_0)}}$$ (6.1)

where $\mu_0$ is determined by the chemical potential of the electrode and $\beta = 1/kT$. If
an adjacent ion is observed to have an electrochemical potential at $\phi$, we make the
assumption that the probability distribution function of the states sampled is given
by a Gaussian:

$$g(\mu|\phi, \sigma) = \frac{1}{\sigma\sqrt{2\pi}} e^{\left(-\frac{(\mu - \phi)^2}{2\sigma^2}\right)}$$ (6.2)

where $\phi$ is the mean of the distribution, assumed to be the instantaneous value of
the chemical potential. $\sigma$, the width of the distribution, is related to the size of
the timestep as the width of the distribution of energies sampled by fast degrees of
freedom.

In order for an electron transfer to take place, $\Delta E = 0$ where

$$\Delta E = e_A + \delta qW + \delta q\Psi^-.$$ (6.3)

e_A is the electron affinity of the ion, $W$ is the work function of the metal, and $\delta q\Psi^-$
is the electrical work done by transferring the charge from the cathode to the ion. This
ensures the conservation of energy during the transfer since the electronic transfer
is assumed to be much faster than the nuclear degrees of freedom and excess energy
cannot be dissipated as heat. Thus it is required that the electronic state of the
metal where the electron originates and the LUMO of the ion where the electron is
transferred should differ in energy by exactly the work required to move the electron.
If we assume that the states sampled by the electrode and the ion are statistically independent, the probability that $E_{\text{occ}} = \mu = E_{\text{LUMO}} + \delta q \Psi^-$ is given by

$$\text{pdf}(\mu) = f(\mu) g(\mu - \delta q \Psi^-|\phi)$$ (6.4)

Integrating this expression over all $\mu$ gives the total probability that $E_{\text{occ}} = E_{\text{LUMO}} + \delta q \Psi^-$ at any $\mu$, the condition for a charge transfer. Thus the probability of energy levels aligning in the next timestep given that the ion is at potential $\phi$ is

$$P(\phi) = \int_{-\infty}^{\infty} f(\mu) g(\mu - \delta q \Psi^-|\phi) d\mu$$ (6.5)

Since the broadening of the states is not dependent on the Madelung potential of the ion and $g$ has mirror symmetry the transition probability can be computed \textit{a-priori} by convolution of $f$ and $g$ as shown in figure 6.2.2.

Since convolution with a Gaussian simply “blurs” edges, this gives a distribution similar to a higher temperature Fermi distribution, but with a slightly different functional form. The larger $\sigma$, the more gentle the slope of the transition area of $P(\phi)$. This means that the instantaneous energetic environment has less of an impact on whether an electron is transferred since the assumption is that similar environments would be sampled by the system, just not seen explicitly in any given measurement. In this exact example, the difference in dynamics may not be noticably different than the use of other, less computationally intense methods (a constant reaction rate for example), but with a more complicated energy landscape it’s worth considering a method that can take into account some information about the energy landscape as well as allow for large timesteps.

### 6.2.3 Energy surfaces far from equilibrium

In some cases it may be worth considering a greater upfront cost to obtain slightly more accurate electron transfer probabilities while maintaining a large timestep. In addition to using the instantaneous energy as the mean of the probability distribu-
Figure 6-3: Convolution of a Fermi distribution with a Gaussian. Top: the dark black line is the original Fermi distribution of electrons in the electrode. Three Gaussian distributions are shown centered at -2, 0, 1 to represent the ensemble of LUMO energies sampled by an acceptor molecule between timesteps. The total probability of transfer at the center of each Gaussian would then be proportional to the product of the two distributions, shown as the blue-grey shading inside each Gaussian. Lower: The black line is the original Fermi distribution. The bold pink line is the result of the convolution, \( P(\phi) \). \( P(\phi) \) resembles a higher temperature Fermi distribution.
tion, there is information in the rest of the average free energy surface about where
the energy is likely to be in the next timestep. For example figure 6-4 the free en-
ergy curves determined by sampling over many vertical excitations as described in
section 1.3.1 are the solid parabolas. We then look at a subset of the distribution by
marginalizing over particles with a vertical energy gap of $\Delta E_0$ and looking at their
distribution of energies one timestep later (shown and grey and blue shaded distribu-
tion in figure 6-4. The simplest approximation would be to assume that the fraction
of the population which passed through a $E=0$ crossing event in time $\Delta t$ is the
fraction which is now at a value of $\Delta E < 0$.

By discretizing the space of $\Delta E$ we can calculate the probability of crossing $\Delta E = 0$ in the next timestep given starting at a value of $\Delta E_0$. This gives the results shown
in figure 6-5. Since the underlying free energy surfaces were parabolic, it makes sense
that the overall crossing probabilities fit well to a switching function like a fermi
function (shown in orange in figure 6-5). As expected, the probability of crossing
increases to a maximum at $\Delta E = 0$. However, it may be surprising at first that there
is asymmetry to the left and right of the $\Delta E = 0$ point. However, the magnitude of
this asymmetry is related to the reorganization energy, $\lambda$. Since the thermodynamic
minimum of the free energy surface is not at $\Delta E = 0$, there is a slope on the free
ergy surface at $\Delta E = 0$. Thus is it more likely to see a $\Delta E = 0$ crossing when
starting "uphill" of the crossing than "downhill". This asymmetry is not captured
by the method described in the earlier section of simply incorporating information
about the mean into the crossing probability. The results here fit well to a simple
shifted fermi function, but this technique of marginalizing over $\Delta E$ to predict crossing
probabilities could potentially give more useful results when used with systems which
are not well-characterized by a linear response regime.

6.3 Monte Carlo simulation methodology

Stochastic methods for sampling equilibrium configurations of a system also have a
long history of usefulness in the fields of statistical mechanics and materials science.[44]
Figure 6-4: Simulation data showing the broadening of vertical excitation energies $\Delta E$ over a timestep $\Delta t$. The blue and grey parabola are the free energy surfaces near the electrode determined from sampling $\Delta E$ over many simulations. The vertical grey line shows a population of ions with $\Delta E = \Delta E_0$ at timestep $t$. That same population of ions was sampled again at timestep $t + \Delta t$, plotted as the blue and grey distribution. Ions with a value of $\Delta E < 0$ were assumed to have crossed $\Delta E = 0$ since $\Delta E$ is a continuous function. This fraction can be tabulated at every point along the surface and a probability of crossing $\Delta E = 0$ in the next $\Delta t$ given an ion starts at $\Delta E_0$ can be used for simulations with a large timestep $\Delta t$.

Figure 6-5: Probability of crossing the $\Delta E = 0$ point in one timestep given an initial starting probability of $\Delta E_0$. Black dots are statistics from many simulations. Orange lines are a fit to a fermi function, $f (\Delta E_0 < 0)$ or $1 - f (\Delta E_0 > 0)$.
In comparison to deterministic simulations, stochastic sampling can be a computationally more effective way to sample from a desired distribution since a deterministic simulation may become kinetically trapped or require many re-initializations to adequately sample the desired ensemble. Additionally, for the lattice models discussed in section 6.1, configurations are best sampled with a stochastic scheme due to the severity of rounding errors that would occur when propagating deterministic dynamics on a lattice. Monte Carlo sampling has been used to understand ion transport in polymers, [91] as well as understand the properties of large macromolecules in general [87, 93, 104–106].

Though there has been much work on improving sampling schemes, optimizing displacement parameters, and minimizing the number of rejected moves, this work focuses only on the most basic iteration, described in algorithm 1.

Algorithm 1: A simple Monte Carlo sampling protocol for the grand canonical ensemble

```
get total system energy $E_i$
// initialization
while running do
    make a trial move
    evaluate energy of new system $E_f$
    $\Delta E = E_f - E_i$
    calculate the Boltzmann weighted probability of the move $P = ae^{-\beta \Delta E}$
    generate a random number on [0:1], $\alpha$
    if $\Delta E < 0$ OR $P > \alpha$ then
        // accept trial move
        update $E_i = E_f$;
    else
        // reject trial move
        reset system to before trial move;
    end
end
```

6.3.1 Total system energy

Unlike molecular dynamics simulations which require knowledge of the forces in a system, Monte Carlo simulations require calculation of the system energy or changes
in system energy due to particle movement.

We can define the electrostatic potential felt by any given ion $i$ in a system of point charges by its Madelung potential $\phi$:

$$\phi_i = \sum_j^N \frac{q_j}{r_{ij}}$$  \hspace{1cm} (6.6)

where we sum over all $N$ ions in the system, $q_j$ is the charge on ion $j$ and $r_{ij}$ is the distance between ions $i$ and $j$. The energy to bring the ion of interest into the system is then $q_i\phi_i$ and the total system energy can be written as a sum over Madelung potentials:

$$\Psi_{sys} = \frac{1}{2} \sum_i^N q_i \phi_i$$  \hspace{1cm} (6.7)

Where $\Psi_{sys}$ is the electrostatic potential of the system and the factor of $\frac{1}{2}$ is introduced due to the double counting of the double sum.

### 6.3.2 Energy of a system including image charges

**One image plane**

Because of the corollary of the first uniqueness theorem for Poisson’s equation, we can solve for the local potential of a system with a charge near a perfectly polarizable, grounded, conducting surface. Although it is straightforward to calculate the forces on the system from the local potential in the area of interest, the total energy of the system is slightly more complicated since the system energy includes only the contribution to bring in the explicit system charges into the field of all charges (both explicit and image).

In a system with only a single conducting plane, the system energy can simply be calculated as half the total energy of the system including the image charges:

$$\Psi_{sys} = \frac{1}{2} \sum_{i}^{N-1} \sum_{i<j}^N \frac{q_i q_j}{r_{ij}}$$  \hspace{1cm} (6.8)
where $\Psi_{\text{sys}}$ is the electrostatic energy of the system, $i$ and $j$ are indexes over $N$ total charges (including image charges), $q_i$ is the charge of ion $i$ and $r_{ij}$ is the distance between ions $i$ and $j$.

Example

For the system in figure 6.3.2 we can explicitly write out the energetic contributions:

$$
\Psi_{\text{sys+img}} = \frac{1}{2} \left( \frac{q_1q_2}{r_{12}} + \frac{q_1q'_1}{r_{11'}} + \frac{q_1q'_2}{r_{12'}} + \frac{q_2q_1}{r_{21}} + \frac{q_2q'_1}{r_{21'}} + \frac{q_2q'_2}{r_{22'}} + \frac{q'_1q_2}{r_{1'2}} + \frac{q'_1q'_1}{r_{1'1'}} + \frac{q'_1q'_2}{r_{1'2'}} + \frac{q'_2q_1}{r_{2'1}} + \frac{q'_2q'_1}{r_{2'1'}} + \frac{q'_2q'_2}{r_{2'2'}} \right) 
$$

(6.9)  
(6.10)  
(6.11)  
(6.12)  
(6.13)
Condensing terms gives:

\[
\Psi_{\text{sys+img}} = \frac{q_1 q_2}{r_{12}} + \frac{q_1 q'_1}{r_{11'}} + \frac{q_1 q'_2}{r_{12'}} + \frac{q_2 q'_1}{r_{21'}} + \frac{q_2 q'_2}{r_{22'}} + \frac{q_1 q'_1}{r_{11'}}
\]

(6.14)

Because of the symmetry of the system, \( \frac{q_1 q_2}{r_{12}} = \frac{q'_1 q'_2}{r_{12'}} \) and \( \frac{q_1 q'_1}{r_{11'}} = \frac{q_2 q'_2}{r_{12'}} \) so we can rewrite as:

\[
\Psi_{\text{sys+img}} = \frac{q_1 q_2}{r_{12}} + \frac{q_1 q'_1}{r_{11'}} + \frac{q_1 q'_2}{r_{12'}} + \frac{q_2 q'_1}{r_{21'}} + \frac{q_2 q'_2}{r_{22'}} + \frac{q_1 q'_1}{r_{11'}} = q_1 \phi_1 + q_2 \phi_2 = 2 * \Psi_{\text{sys}}
\]

(6.15)

Two parallel image planes

However, in the case of two parallel conducting planes with a system of interest sandwiched between them, a complete equivalent image charge system would be infinitely periodic. If we truncate image charges at any finite order, the system no longer has the symmetry of a single-plane system. For example in figure 6.3.2, we can see that there are two image charges for each charge in the active system. This is the type of system used by Voth and co-workers in their implementation of a constant potential system. [12]. In this case, we can still calculate the total energy of the active system by considering the potential energy of each active ion in the field of all other ions (image and active). However, like in the case of the single image plane, each active-image interaction only has the energy of half of an interaction between point charges (see Griffiths section 3.2). [40] Thus the total energy is given by summing over all active-image interactions as well as all active-active interactions leading to

\[
\Psi_{\text{sys}} = \frac{1}{2} \sum_{i \in \text{sys}} q_i \phi_i
\]

(6.16)

where \( \phi_i = \sum_{j \in \text{sys+img}} q_j / r_{ij} \). In the case of active-active interactions, the factor of one-half comes from double counting.

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6.3.3 Energy to remove or change a charge

A convenient feature of the Madelung potential is that when dealing with simulations of charge transfer, calculation of vertical excitation energies (i.e. the energy change to excite an electron without relaxing any nuclear degrees of freedom) can be calculated from the Madelung potential of the species in question. The energy of the vertical excitation is simply the difference in energies between the system with the electron on the donating species and the electron on the accepting species. For simplicity we will say that an electron is transferred from ion $k$ to the electrode (i.e. out of the system).

$$
\Psi_{\Delta E} = \Psi_{\text{final}} - \Psi_{\text{initial}}
$$

$$
= q_{k,\text{final}} \sum_{i \neq k} \frac{q_i}{r_{ik}} + \frac{1}{2} \sum_{i \neq k} \sum_{j \neq i, k} \frac{q_i q_j}{r_{ij}} - q_{k,\text{initial}} \sum_{i \neq k} \frac{q_i}{r_{ik}} + \frac{1}{2} \sum_{i \neq k} \sum_{j \neq i, k} \frac{q_i q_j}{r_{ij}}
$$

$$
= (q_{k,\text{final}} - q_{k,\text{initial}}) \phi_k
$$

Since the only interactions in the system that change are those involving ion $k$, the excitation energy can be calculated from the Madelung potential of $k$, which is about an order of magnitude less computationally intensive than calculating the total system energy.

However, when there are image charges involved, the excitation energy is not quite as simple to calculate due to the fact that the images also change charge. In this case, the vertical excitation energy can still be calculated, but a few more terms...
Here the sum over images is over the number of explicit image planes so in figure 6.3.2, there would be terms for the interactions of \( q_i^0 \) with \( q_{i2} \) and \( q_i^0 \) with \( q_2 \). The factor of one-half in the image interaction term again comes from the fact that the energy of each image-system interaction is only half that of a two-charge system. Note that the image interactions exclude the interaction of the ion \( k \) with its induced image charges as it is already accounted for in \( \phi_k \).

The same logic can be extended to changes in ion position. In this way, the total change in energy due to a trail move of a single ion can be calculated without the redundant work of calculating a total system energy. However, this calculation still scales proportionally with the size of the system and needs to be repeated at every trial move, resulting in much computation which does not lead to new system configurations.

6.4 Results from a nonequilibrium lattice model

Although the procedure described in algorithm 1 cannot be generally used for dynamics, by only including microscopically reversible trial moves with physically realistic displacements and averaging over many many trajectories.

6.4.1 Model

The model consists of three main components, constant potential boundary conditions, active electrochemistry at the interface, and ion transport within an implicit polymer electrolyte. These components are summarized in figure 6-8. The procedure for electron transfer is the same as described in section 2.1.2 with the exception of
Figure 6-8: A schematic description of the nonequilibrium lattice model. 1. Ions can move to neighboring sites as long as the site is not blocked to that type of ion. 2. Cations, the electrochemically active species can be created and destroyed when they are within one site of the electrode. Cations are represented by blue circles, anions by yellow circles. Blue sites are blocked to cations, yellow sites are blocked to anions, and green sites are blocked to both.

The simulation cell is 20x20x20 sites with insulating boundaries in two dimensions and either insulating or conducting boundaries in the electrode dimensions. Results in the following sections was averaged over between 10 and 500 randomly initialized simulations.

Like the molecular dynamics model in section 3, the lattice model produces the excepted nonequilibrium behavior when averaged over a sufficient number of sim-
Figure 6-9: Nonequilibrium lattice response to a step-voltage input. A) step voltage input and current response B) Steady state ion distribution as a function of distance from the electrode C) Cation (electrochemically active ion) density profiles as a function of distance and time. Lighter blue lines are from earlier time points. $t_0$ and $t_1$ correspond to the times labeled in panel A.

Simulations. Figure 6-9 shows that the current response to a step-voltage input gives the expected spike followed by an exponential decay. The initial spike is due to the large difference between the initial (flat) concentration profile and the concentration required to match the chemical potential of the electrodes. As the concentration polarization builds up, the current falls to its steady-state value. At steady-state, the cation density and anion density are both polarized across the cell although there are still some regions which are not electroneutral.
6.4.2 Current enhancement at high transference numbers

Under some conditions, in nanoscale cells, breaking electroneutrality can lead to a current enhancement. This is distinct from the effect predicted by Newman and described in section 4. [53] This type of enhancement relies on the development of large electric fields due to concentration differences between cations and anions across the cell, and thus is limited to systems with nanoscale lengthscales. This enhancement effect relies on the shift from an electroneutral, but polarized cell at low ion confinement to a charge-polarized cell at large anion confinement. Figure 6-10 shows an example of the electric field enhanced concentration profiles.

Effect of temperature

Because electroneutrality is not guaranteed at nanometer lengthscales, it is possible that no current enhancement will be observed with anion confinement. This is the case at sufficiently high temperatures where the entropic gain of a flat profile out-competes the enthalpic gain of an electroneutral system. Figure 6-11 shows an example of this transition in a system with no anion or cation confinement. As the temperature becomes higher, the anion profile flattens completely.

As anion constraints are added and the transference number is increased, only the lowest temperature system shows any current increase at high anion confinement. This is expected because the high temperature systems have profiles that remain largely unchanged with the addition of a constrained anion population. Figure 6-12 shows that the low temperature system, anion confinement corresponds with an increase in steady-state current. The concentration profiles at zero and 90 percent anion confinement show the flattened anion profile an associated buildup of electrolyte with a net charge. This leads to an induced electric field enhancement of current as described earlier.
Figure 6-10: Comparison of the effect of a high transference number on a macroscopic cell compared to a nanoscale cell. a) For both cells, when anions and cations can diffuse freely, cations polarize across the cell due to the difference in chemical potentials at the left and right electrodes. Anion concentration matches the cation concentration due to attractive anion-cation interactions, leading to electroneutrality on a macroscopic scale. b) In a macroscopic cell at $t_+ = 1.0$, the anions are immobile and thus do not polarize across the cell. Because of the electroneutrality constraint, the cations match this flat profile. c) In a nanometer-scale cell at $t_+ = 1.0$, the anion density is still restricted to a flat profile. However, electroneutrality can be broken over microscopic lengthscales. Thus the cation concentration profile is not restricted to match the anion one. In this case, the excess of cations on the left and depletion on the right sets up an electric field which helps propel cations, the electrochemically active species, in the correct direction.
Figure 6-11: Steady-state concentration profiles as a function of distance from the electrode. System has no anion or cation confinement and insulating boundary conditions. Orange lines plot cation density and blue lines plot anion density. Higher temperatures are plotted by darker colors.

Figure 6-12: Current enhancement with anion confinement. **Left:** ion concentration profiles with no confinement and 90 percent anion confinement. Cations are plotted in orange and anions are plotted in blue. Solid lines are from simulations with no confinement and dashed lines are from simulations with 90 percent anion confinement. **Right:** Relative current at steady-state as a function of anion confinement. All currents are normalized to the average current at no confinement. Blue dots each represent a single simulation and the trend line if the average of the ensemble at each fraction of blocked sites.
Figure 6-13: Steady-state concentration profiles as a function of distance from the electrode. System has no anion or cation confinement and \textit{conducting} boundary conditions. Orange lines plot cation density and blue lines plot anion density. Higher temperatures are plotted by darker colors.

**Effect of constant potential**

In systems small enough to support large deviations from electroneutrality, boundary effects, like that of a constant potential boundary also play a large role. A constant potential boundary stabilizes free charge near the interface by inducing an image charge effect. Simulations of cells at the same temperatures as those in the previous section show qualitatively different behavior. Figure 6-13 shows that the anion profiles are flat at all temperatures. This is likely due to the effect of image charge interactions screening the large positive field of ions at the left interface. Interestingly, even at the lowest temperatures, the system seems to favor a cation profile which is closer to the electrode (more screened) over a polarized anion profile.

The lack of anion polarization in the systems with conducting boundary conditions manifests in the loss of current enhancement with anion confinement. Figure 6-14 shows that the concentration profile of the anions and cations remain relatively unchanged with 90 percent anion confinement. Additionally, with the introduction of one image reflection for each electrode, the trend of higher current with anion confinement is reduced. For truly conducting parallel plate electrodes, an infinite number of image reflections are needed (see chapter 2). In simulations of systems with conducting boundary conditions there is no longer any trend between anion
Figure 6-14: ion concentration profiles with no confinement and 90 percent anion confinement. Cations are plotted in orange and anions are plotted in blue. Solid lines are from simulations with no confinement and dashed lines are from simulations with 90 percent anion confinement. Right: Relative current at steady-state as a function of anion confinement. All currents are normalized to the average current at no confinement. The dotted line shows the trend for systems with insulating boundaries. The solid line shows the trend for systems with a single image charge interaction at each electrode. Triangles show the average current of systems with full constant potential, parallel electrodes (e.g. infinite image charge interactions).

confinement and current enhancement.

**Effect of concentration**

Finally, even with a sufficiently small cell, low enough temperature, and insulating boundary conditions, too low of a total ion concentration can also eliminate the electrostatically-boosted current. Figure 6-15 shows the relationship between steady-state current and the fraction of sites blocked to anions. There is little to no improvement to steady-state current for the systems with a concentration of 0.005 ions per lattice site. At a concentration of 0.01 ions per lattice site, there is a much more pronounced increase in current at higher anion confinements.

These nonequilibrium lattice simulations suggest that the idea of current enhancement driven by the confinement of the electrochemically inactive species is improbable except under a narrow set of circumstances. In addition to a device small enough to support deviations from charge neutrality, the enhancement also requires a sufficiently strong driving force to polarize the inactive ion in cases of moderate transference number. When these conditions are not met, confinement of the anion population has
Figure 6-15: Comparison of the effect of concentration on current enhancement. **Left:** Relative current at steady-state as a function of anion confinement at a concentration of 0.005 ions per lattice site. All currents are normalized to the average current at no confinement. Blue dots each represent a single simulation and the trend line is the average of the ensemble at each fraction of blocked sites. **Right:** Relative current at steady-state as a function of anion confinement at a concentration of 0.01 ions per lattice site. All currents are normalized to the average current at no confinement. Blue dots each represent a single simulation and the trend line is the average of the ensemble at each fraction of blocked sites.

Little effect on the overall performance because in many cases, the anion population was already entropically driven to a flat profile even without confinement. These simulations also neglect the effects of the solid electrolyte interphase which can be many nanometers thick, very large in comparison to these cells.

### 6.4.3 Drawbacks of a stochastic sampling method

Although we were able to obtain some interesting results with our lattice model, the stochastic sampling scheme severely limited the overall utility of the model. Because the energetic effects of ion migration are long-ranged, each energy calculation is relatively expensive, and scales with the size of the system. Additionally, the use of a stochastic sampling scheme means that many energetic calculations resulted in rejected moves. While this is the nature of the method, problems that are well-suited to a Monte Carlo simulation have a function which is fast to evaluate. For example, spin models include only nearest-neighbor interactions and thus energetic evaluations take a fixed amount of time, even for very large systems. Compounding this, the nature of
ion migration across a cell means that larger cells will take longer for concentration profiles to reach steady-state. Since we were also interested in investigating screening behavior in electrochemical cells, we needed the ability to run simulations which were large enough to support double layer formation at each interface and a bulk region in the middle. Unfortunately, setting up a double layer requires the migration of ions across the length of the cell. In these longer cells, it was not computationally feasible to run simulations long enough to observe double layer formation and the decision was made to move to a molecular dynamics method.
Chapter 7
Conclusions

The promise of nanoscale or nanoarchitectured electrochemical devices has driven a renewed interest in the fundamental science of electrochemical phenomena. This thesis has outlined the development of a new combination of tools for running molecular dynamics simulations of active electrochemical simulations.

Chapter 2 describes these methods for constant potential boundary conditions and the incorporation of stochastic electron transfer. The combination of correct electrostatic treatment of the boundary conditions and electron transfer based on the local electrostatic environment provide a flexible toolset for evaluating nanoscale electrochemical phenomena. Chapter 3 shows one example of unexpected behavior due to the unique properties of nanoscale battery-like cells. Because the double-layer regime extends a large fraction into the cell, the overall "bulk" concentration profile can be affected by the charge buildup at the double layer. This interplay is size dependent and needs to be investigated further in order to be fully quantified, but gives an example where traditional mean-field theories do not hold up in nanoscale systems.

Chapter 4 describes another example where macroscopic theory does not translate to nanoscale cells. Due to the same effect of interfacial phenomena extending dominating a large fraction of the cell, local electroneutrality cannot be assumed in nanoscale cells. This leads to an unexpected breaking of traditionally understood relationships between transference number and battery performance. Chapter 5 takes a step back from the complicated nonequilibrium behavior and uses constant potential equilib-
rium simulations to understand the robustness of the double layer over molecular
time and lengthscales. Surprisingly, the charge in mean Madelung potential due to
the application of a 1V potential drop is very small in comparison to the fluctuations
inherent in the potential. Finally, chapter 6 summarizes some earlier work on models
which are more coarse-grain than atomistic molecular dynamics. The idea of using
information about the mean free energy surface when deciding to make an on-the-
fly electronic transition is interesting and could be developed further in future work,
but the use of stochastic models should be avoided when dealing with electrostatic
systems.

Understanding the fundamentals of electrochemical phenomena in nanoscale de-
vices is crucial to engineering and optimizing new technologies. This thesis shows
an example of the fundamental differences that can emerge from nanoscale phenom-
ena. Molecular fluctuation, averaged over in traditional mean-field theories can lead
to unexpected behavior when devices approach the scale of molecular detail. Addi-
tionally, electrochemistry is inherently a nonequilibrium process, only complicating
the molecular picture. Hopefully this thesis provides one example of incorporating
nonequilibrium physics into classical simulation and also showcases the need to con-
sider molecular phenomena explicitly when designing for nanoscale devices.
Bibliography


