ATOMISTIC MODELING OF AN
ELECTROCHEMICAL INTERFACE

A Thesis in
Chemical Engineering

by

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ABSTRACT

Electrochemical interfaces are present in a variety of applications. Despite their prevalence, the electrode/electrolyte interface is not well understood from a molecular standpoint. Variations in the electrolyte structure near an electrode surface give rise to fluctuations in the electric field which can affect surface reaction kinetics. One device affected by such phenomena is the proton exchange membrane fuel cell (PEMFC). The cathode half of a PEMFC, at which the oxygen reduction reaction takes place, accounts for nearly 70% of the total performance losses during typical operation. Characterizing the interfacial structure at a PEMFC cathode can give insight into what causes these performance losses. In this study, we develop a new method to analyze an electrochemical system. Molecular dynamics simulations can be used to describe systems with atomistic detail, and explain macroscopic phenomena. Using the Central Force Model to describe liquid water, and Electrode Charge Dynamics to account for electronic polarizability in a platinum electrode, we will simulate the electrochemical interface in a manner that can produce a more accurate characterization of the interfacial structure. We use sulfuric acid in the electrolyte to approximate the behavior of the Nafion ® membrane used in PEM fuel cells. We describe sulfuric acid in a reactive manner by incorporating the acid into the Central Force Model.
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Chapter 1

Background and Motivation

Electrochemical systems are prevalent in a great number of applications, such as fuel cells, batteries, solar cells, and electrocatalysis. Despite the diversity of systems involving electrochemical interfaces, or a charged electrode at which chemical reactions take place, there has been little research in the way of computationally describing the solid/solution interface in a manner that both provides atomistic detail to the metal electrode and can model reactions in solution [1-5]. Changes in the interfacial structure, or the structure created in solution at an electrode/electrolyte interface, lead to changes in the local electric field. Electrochemical reactions are strongly dependent on the local electric field due to the kinetic dependence on electrode potential [6,7]. Because the electric field is dependent on the local structure and distribution of charges around an electrode surface, atomistic characterization of this region can give insight to the interplay between the interfacial structure and the achievable reaction kinetics under defined electrochemical conditions.

Classical electrochemistry describes the interface on a macroscopic scale using different models such as the Helmholtz double layer or Gouy-Chapman models [6]. These models differ on the level of detail considered, but the phenomenological consideration is similar. The electrode is considered to be a flat layer of charge with no atomistic distinction. Counterions specifically adsorb to the electrode surface in a uniform fashion, creating a well defined electric field normal to the electrode surface. As distance increases from the electrode surface, the descriptions vary. However, all models essentially describe a region of high counterion concentration outside the adsorbed layer which slowly approaches bulk solution values. The important notes are the well-defined electric field normal to the electrode surface and a lack of atomistic distinction. Because of model limitations, double layer theory cannot describe time and spatial variations in surface...
potentials, ion distribution near the surface, or dynamic interfacial structure; all of which lead to an inaccurate description of the electric field [8]. The electric field plays an important role in surface phenomena, which cannot be predicted through classical means. It is unclear how the double layer prediction changes in systems with different species or surface potential, and the model cannot easily differentiate between ions that may be present. Though these models may be able to describe some macroscopic phenomena, an atomistically precise picture of the electrochemical interface is not obtained. Figures 1-1.a,b show the approximation of the surface given by classical considerations [9]. A more realistic surface would describe surfaces with atomistic variations in charges and an electric field that reflects the ordering of species near the electrode surface [3].

Figure 1-1: Comparison of classical electrochemical interface to a more accurate description attainable from simulations. (a) Idealized electrochemical interface with specifically adsorbed counterions [9]. (b) Stern layer description gives well defined electric field in all regions. The vertical lines represent the inner (left) and outer (right) Helmholtz planes, and horizontal line define the potential at the Helmholtz planes. (c) MD simulation snapshot showing distinct atomistic charges on metal [3]. (d) Z-direction variation in electric potential due to an applied cell voltage in an MD study [3].
A Quantum Mechanics (QM) study using the Vienna Ab Initio Simulation (VASP) package has shown the strong influence of cell potential on the reaction kinetics in the reduction of molecular oxygen to water [7]. Yeh et al also showed that the inclusion of water in these models to solvate the surface using a variety of solvation techniques leads to a favorable initial step in the reaction mechanism for the reduction of oxygen at all relevant potentials. Figure 1-2 shows how potential strongly affects surface phenomena, in this case the surface replacement of water with oxygen.

Figure 1-2: The Gibb’s energy of reaction (eV) for an oxygen molecule replacing a water molecular at a Pt(111) surface shows strong dependence on potential (V), water density, and water layer thickness ((a) has 36H₂O and (b) 24H₂O) [7].

Despite its importance in surface kinetics calculations, the description of water using QM methods is not representative of that expected experimentally. Many studies have shown QM to produce a more ice-like structure for water rather than what is known for the liquid structure because water-water interactions are not properly represented [70-73]. Additionally, there is disagreement on the structure of water near an electrode surface in a charged system. As Figure 1-2 shows, there are significant differences in the reaction energies depending on the local water structure. It is important to maintain an accurate electronic description of the system for reaction energy purposes, but a broader description including dispersive forces is necessary to describe the liquid phase behavior of water.
Atomistic modeling techniques

QM is not able to describe the dynamic fluctuations and average structures that define an electrochemical interface. Because this method is typically used to minimize the electronic energy of a system to find the lowest energy structure, there is no description of time, or how the structure of a system may change with time. To consider system fluctuations at an atomistic level, a higher scale model such as Molecular Dynamics (MD) is required.

Figure 1-3: Description of simulation scales from QM to continuum. The highlighted point is the longer time and length scales achievable through MD compared to QM (electronic structure) [10].

Figure 1-3 shows that MD can reach time and length scales upwards of 4-5 orders of magnitude greater than QM, and thus simulation sizes can be significantly larger [10]. The larger dimensions are important for describing electrochemical interfaces. QM techniques are limited by approximately 100-200 atoms. To ensure that a reasonable explanation is attained, it is necessary to have large enough simulations to realize sufficient bulk solution away from the electrode. The length scales required for our problem are on to 10-100 Å scale with a 100 ps scale needed to
reach diffusive solution behavior [1]. However, surface reactions cannot be accurately described using MD, so some combination of QM and MD is required.

In MD simulations, forces acting on atoms calculated from interatomic potentials, or a force field, are used to determine the acceleration of each particle in the system using Newton’s second law [12]. Forces are calculated from defined intermolecular potentials using Equation 1-1, which say that the force acting on the particles is equal and opposite to the slope of the interaction potential curve at a given separation distance. Then, Newton’s second law is solved to determine the acceleration in each direction on each particle using Equation 1-2.

\[ F_x(r) = -\frac{\delta U(r)}{\delta x} \quad \text{Equation 1-1} \]

\[ F(r) = m * a(r) \quad \text{Equation 1-2} \]

It is possible, through the use of MD, to reach considerably higher length scales than QM methods due to the decrease in complexity of the calculations that are used, as well as to resolve these systems in time. Because MD simulations require the iterative solution to all interatomic pair force calculations, more complex expressions lead to longer simulation times. Thus, there is an inherent balance of complexity and computational expense that must be considered in MD. Force fields can be as complex or simple as the user desires, and in many cases more simple force fields can be used when certain features of the system do not need to be considered. Therefore, it must be decided \textit{a priori} which features of the system are required in the simulation, and the force field can be designed to yield those features.
Description of research plan

Our method will look to capture the physical phenomena occurring at electrochemical surfaces and, specifically, how the interfacial structure varies with simulation conditions and its subsequent effect on reaction kinetics. Because neither QM nor MD is capable of describing the system of interest independently, a multi-scale simulation technique will be developed. Our goal is to build a MD force field capable of accurately describing the interaction of solution species with electrode surfaces to produce images of the electrolyte structure present at the electrode interface. With this force-field in place, simulations will be performed on an electrochemical system of interest to characterize the interfacial structure. Results from this work can be used to study the effect of our simulated interfacial structure on reaction kinetics using QM methods.

Selecting a model system

As stated, electrochemical interfaces are present in many applications. To begin our force field development, we chose a specific electrochemical system to analyze. We have chosen the proton exchange membrane fuel cell (PEMFC) as our first system of study due to its high profile and potential use in transportation applications.

Petroleum based fuels and other nonrenewable sources have powered a great deal of the daily lives of people for the majority of the last century. However, the large scale use of these fuels has led to a diminishing long-term supply and negative effects on the climate. Primarily due to these reasons, there has been a surge in the amount of research conducted on alternative devices for fuel conversion.
Figure 1-4: A proton exchange membrane fuel cell uses hydrogen fuel at the anode and oxygen at the cathode and converts the chemical energy to electrical energy with a maximum potential of 1.23 V [13].

One of the most heavily researched of these devices is the PEMFC depicted in Figure 1-4 [13]. In general, a fuel cell is a device capable of converting energy released from chemical reactions into electrical energy for use in some external device. A PEMFC uses the production of water from hydrogen fuel and oxygen. The device is split into two half cells, each of which is responsible for a half reaction. Hydrogen fuel enters the anode where H₂ molecules are oxidized at the electrode surface into two protons and electrons as in Equation 1-3. The protons are transported to the cathode side of the cell through a proton exchange membrane, which is generally a polyfluorosulfonic membrane such as Nafion®. Electrons travel through an external circuit, powering a device connected to the cell, and to the cathode. At the cathode, oxygen is reduced by the free protons and electrons producing water and some residual heat as byproducts, shown in Equation 1-4. The maximum cell voltage is 1.23 V, based on the total reaction energy for Equation 1-5 [14].
The PEMFC has gained a lot of popularity due to its clean byproducts, its ability to
operate at low temperatures, and its high energy density. However, there are a number of
problems preventing fuel cells from becoming economically feasible [15]. Dr. Steven Chu, the
United States Secretary of Energy, has pointed out that there are four main problems preventing
the use of PEMFC’s, or a hydrogen based economy, from being realized. He points to a lack of an
adequate source of hydrogen gas, difficulties in storing large amounts of hydrogen, the inability
to effectively distribute gas from manufacturers to customers on the scale required, and
inadequacies in the fuel cells themselves [16]. Of the fuel cell inefficiencies, cathodic losses make
up approximately 70% of the total overpotential at typical operating conditions [17].

Due to our interest in building a simulation technique capable of describing
electrochemical interfaces and the level of interest PEM fuel cells, we choose the cathode half of
the PEMFC as our first system of interest.

Because MD simulations rely on user specified force fields, before designing a force field
to describe a system it is important to consider the phenomena associated with that system that
must be described accurately. Atomistic simulation cannot consider all phenomena associated
with a system with reasonable computational expense, so it is necessary to sacrifice the
description of certain aspects of the system to describe those that are truly important.

As described previously, cell potential and electric field have been shown to strongly
affect reaction kinetics for the surface reaction that take place in fuel cells, and the local electric
field is determined by the ordering of charges near the electrode surface. We therefore wish to
build a model that can accurately describe the region near a metal surface in electrochemical
systems. Because of the importance of local structure on the electric field, we require a model that is capable of mimicking the structure of species present near the surface. We will use a method capable of matching the bulk dynamics of water to allow for reasonable simulation times and proper structural rearrangement. Methods which cannot reproduce accurate dynamic behavior may hinder the diffusion of simulation species towards electrode surfaces. Additionally, as we are most interested in structural behavior in the region near the electrode surface, short range interactions between species in solution and electrode atoms must be properly accounted for.

Many MD simulations have been performed using plane-of-charge, image-charge or other methods to describe the electrode surface, which over predict the short range interactions [5]. We will describe the metal atoms in a manner which allows for atomistic resolution and accurately captures short-range phenomena and structure.

Because designing a simulation of a full cathode is an intensive process, we will make approximations on the system. We first choose to let water represent the bulk solution. Water is the main product of the PEMFC reaction, as it is produced via the oxygen reduction reaction, and is required in the cell during normal operation to aid both the transport of species to the electrode surface and the transfer of protons through the membrane.

![Figure 1-5: Proton transport through water is assisted by Grotthus hopping. Solid lines denote full bonds and dotted line denote hydrogen bonds. The charged species moves from the “first oxygen” to the “third oxygen” with no molecular rearrangement. (White-H, Red-O)](image)

The description of water must include the ability to break and form bonds. Hydrogen diffusion through aqueous solutions relies on a process known as the Grotthus mechanism by
which free protons can bond to a water molecule forming a hydronium ion [18]. A different hydrogen atom can then dissociate from the ion and form a bond with another water molecule, thereby moving the positive charge with minimal atomic rearrangement. The Grotthus mechanism is shown in Figure 1-5, in which the hydronium ion starts on the first water molecule and moves to the third by rearranging the O-H bonds from direct to hydrogen bonds.

![Diagram of the Grotthus mechanism](image)

Figure 1-6: Nafion is a polyfluorosulfonic structure with an active sulfate group on its side chain [19].

Secondly, we need to describe the proton exchange membrane by some representative structure. Nafion is a popular electrolyte because of its ability to allow rapid proton diffusion through the cell at low temperatures and not to break down during operation. Side groups on the Nafion structure include active sulfate groups, which may prevent the diffusion of reactants to the surface in some cases, or even adsorb and block active sites from catalyzing the reaction. The Nafion ® structure is approximated by adding sulfuric acid to the simulation box. Nafion ®, as a polyfluorosulfonic membrane, has very active sulfate groups, as shown in Figure 1-6 and Nafion ® has similar properties to sulfuric acid in solution [19,20]. These groups have the ability to dissociate protons via the O-H bond on the sulfate group, and serve as sites for “proton hopping” through solution. An accurate description of aqueous sulfuric acid over an electrode surface can give insight on the behavior of the membrane layer and the importance of the interplay between the electrode and electrolyte, including the effect that it may have upon interfacial structure, and therefore upon the reaction kinetics.
Our goal is to build a molecular dynamics force field to describe aqueous sulfuric acid over a platinum (111) electrode surface, because it is the most common electrode in a PEMFC [21-25]. The force field will be reactive on all O-H bonds to mimic the Grotthus mechanism by which protons are conducted through aqueous solutions. Additionally, the force field will accommodate fluctuating charges on metal atoms to allow them to react to local environments, as well as produce atomistically distinct charges on electrode atoms and accurately describe short range interactions. The MD simulations will be carried out on a time scale of hundreds of picoseconds, due to the computational expense involved with accurately describing electrode surfaces, and the short time steps needed to accommodate the reactive O-H bonds. From these simulations, we will analyze the effect of various simulations parameters on the local structure that is obtained near the electrode surface, and determine the variation in electric field to see how this deviates from classical double layer models of electrochemical surfaces. Upon completion, we will have the ability to analyze the structure of aqueous sulfuric acid in electrochemical systems, and infer as to the impact that electrolyte membranes have on structuring and transport at these interfaces.

The following chapters will describe computational methods that will be used for the project. Force field development for MD work is described in detail, as results are strongly dependent on the form of the force field used. We validate our choice to describe liquid water, which is the bulk component in our simulations. Then, we describe the addition of sulfuric acid to water to approximate the activity of the electrolyte in an electrochemical cell. Finally, the whole system is simulated through the addition of a platinum electrode, and we discuss the findings from our full scale electrochemical simulations.
Chapter 2

Molecular Dynamics Force Field Selection

For the atomistic simulation of an electrochemical system, a force field must be selected to represent attraction among system components. Our system will be described in this section, along with the force fields that will be used to describe the majority components. Some modifications to literature force fields are required for our work, and they will be discussed in subsequent chapters.

Selection of a force field for liquid water

Water is the most abundant resource on the planet, so it is unsurprising that water is also one of the most heavily researched compounds in simulation work. Because of the important role that water plays as a solvent in many systems, there have been water force fields developed for various applications. In many cases, describing water as nonreactive and nonpolarizable is enough to describe the phenomena of interest in a problem. Much of the work carried out in molecular dynamics has described water in this manner. MD simulations have had a profound effect on the understanding of processes taking place at the atomistic scale over picosecond time periods.

In many biological applications, or other studies in which water is viewed as a bulk solvent, use of a water model as simple as TIP3P is sufficient [26]. The Amber Force Field provides users with the ability to solvate any simulation box using TIP3P water [27]. The TIP3P model describes water using a $104.52^\circ$ fixed molecular angle with $0.95 \text{ Å}$ O-H bond length and three fixed point charges of $0.417 \text{ e}$ and $-0.834 \text{ e}$ for H and O, respectively [27].
Figure 2-1: Various TIPnP models describe the water molecule using a different number of charge centers for different levels of accuracy with dipole moments and intermolecular interactions [28].

Other similar models try to make improvements to these approximations by changing the charge distributions or using additional local charges to more accurately represent the charge distribution around the water molecule and include more interaction sites for the molecule. These geometries are summarized in Figure 2-1. The common theme amongst these models, however, is that they all view water as a rigid molecule with fixed charges that cannot be changed based upon the other charges in the system [28].

A brief review of available models for liquid water

A full comparison of all available water models would be an exhaustive undertaking. Countless water models have been suggested by research groups, independent models have been developed for specific simulations, and many models simply do not perform well under any desired range of conditions. A good review of common classical and polarizable water models is undertaken by Baranyai and Kiss. In this paper the common TIP4P, TIP5P and SPC classical models, as well as various modifications to those models are examined for geometric analysis, dynamic behavior and other important simulation qualities [28]. The authors also test a select few
polarizable models, including the BSV, DC, SWM4, and GCP force fields. Improvements to early water models have been made and bulk solution descriptions of water have become more accurate. However, most models cannot accurately describe liquid water entirely, due to their inability to describe water’s self-ionization and its ability to assist in proton transport. A schematic of water in common TIPnP water force fields is shown in Figure 2-1, including molecular geometries, charge distributions and van der Waals radii.

Newer models have looked to improve the performance and transferability of polarized water models [29-32]. The goal of these models has been to create a model capable of accurately describing both small water clusters with similar accuracy to quantum mechanics calculations, and to describe bulk water. Recently, Baranyai has developed a new charge-on-spring water model with the goal of making calculations less expensive [29]. This model uses fixed molecular geometries from experimental values. Like many of the current models, positive charges of 0.557e are placed on the hydrogen atoms with the corresponding negative charge of 1.114e placed on the axis of rotation, a distance of 0.24 Å from the oxygen atom toward the positively charged hydrogen atoms, thus adding a fourth point to the water molecule. The important feature of this work is the inclusion of the charge-on-spring. Similar models have been constructed, but the idea is to allow the negative charge in the center of the molecule to fluctuate in space [26]. The charge is considered a massless entity, and after each molecular movement time step, the position of this spring is equilibrated with respect to other charges in the system. Equilibration of this spring essentially allows for lengthening and shortening of the dipole on water with respect to surrounding molecules. Considerations are made to maintain the dipole of each molecule near its experimental value of 1.855 D, but the position of the dipole can change and its value can fluctuate slightly. An important point reached in Baranyai’s conclusions is the necessity for a minimum of four points in all water models to accurately describe the geometries of the molecules and allow for charge polarization.
Despite using fixed geometry, nonreactive water in biological applications allows for accurate representation of the phenomena of interest in certain systems. Many areas, however, require water to take on a flexible geometry, or have the ability to break and form bonds. As computer speeds have increased and molecular simulation has become a more powerful tool, its range of applications has increased dramatically. With the availability of computational resources and the speed with which computers can process information constantly increasing, the complexity of simulations can increase, as evidenced in Figure 2-2 [33]. The ability to describe liquid water in a more accurate way is important in some non-biological systems, including water at electrochemical interfaces. We will next survey current reactive force fields for liquid water.

**Modeling water using reactive bonds**

Though they are less frequently used, many models exist to describe water in a reactive nature [34-38]. Reactive molecular dynamics allows for bonds to break and reform between atoms, leading to molecular dissociation and the formation of ionic species. In liquid water, bond
reactivity is especially important because proton mobility in solutions is dependent upon it.

Protons diffuse readily through solution via the Grotthuss mechanism by which protons bond to water molecules and can transfer positive charge through a cluster of water molecules by the movement of bonds rather than atoms [39]. For the purposes of describing electrochemical systems and, in particular, a proton exchange membrane fuel cell, various reactive models of liquid water were considered.

Mathematically, the difference between a reactive and nonreactive force field lies within the two-body potential between atoms [12]. In a nonreactive simulation, two-body interactions for bonded atoms are described using a harmonic potential which is typically symmetric about the equilibrium bond distance. Because the force acting between particles is equal to the slope of this potential, atoms are always forced to their equilibrium bond lengths. Atoms that are too close together cause a repulsive interaction and atoms that are too far apart are attracted to one another so that the actual bond length oscillates about the equilibrium distance.

$$U = \frac{1}{2} k(r - r_0)^2 \quad \text{Equation 2-1}$$

$$U = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \quad \text{Equation 2-2}$$

In reactive simulations, the attractive portion of the potential, or long range interaction, is altered. Rather than mirroring the repulsive force, the attractive force typically tapers off to zero, and the magnitude of the slope decreases with increasing distance. Eventually, the attractive force becomes weak enough that the atoms are no longer bonded to one another, and these atoms can form bonds with different atoms in the simulation box. General forms for the two types are given in Equations 2-1,2 and the difference between these methods, shown with a Lennard-Jones potential for the reactive force, is graphed in Figure 2-3. In Equation 2-1, k is a force constant, adjustable for the flexibility of the bond, r is the interatomic distance and r_0 is the equilibrium
bond distance. In Equation 2-2, $\epsilon$ serves a similar role to $k$ as a force constant which controls the well depth, and $\sigma$ is a bond distance parameter which controls the location of the well.

![Graph](image.png)

Figure 2-3: Comparison of reactive and non-reactive potentials used in MD simulations

The first reactive water model was developed by Frank Stillinger in 1975 and subsequently revised in 1977 [34-36]. This model, known as the central force model (CFM), relies solely on pair potentials between oxygen and hydrogen atoms to describe liquid water, unlike most nonreactive models which contain an additional three-body term to account for the bending angle of water. The three pair interactions each have a unique form. The bonded term for O-H, as alluded to previously, is a non-harmonic potential with an attractive well at the equilibrium bond distance and eventually tapers off to equal the electrostatic interaction. The O-O interaction is purely repulsive at all distances and deviates only slightly from the electrostatic repulsion. The H-H interaction is quite unique. To account for the appropriate bending angle in H$_2$O, there is a small well in the interaction at the H-H distance typical of water molecules. This well is followed by a short attractive region meant to hold the proper molecular geometry, and
gradually reaches the pure electrostatic repulsion. The potentials, including electrostatic interactions, are given in Equations 2-3 (O-O), 2-4 (H-H), and 2-5 (O-H), and are plotted in Figure 2-4.

\[
U_{OH} = -\frac{72.269}{r} + \frac{6.23403}{r^{0.19912}} - \frac{10}{1 + \exp[40(r - 1.05)]} - \frac{4}{1 + \exp[5.49305(r - 2.2)]}
\]

Equation 2-3

\[
U_{HH} = \frac{36.1345}{r} + \frac{18}{1 + \exp[40(r - 2.05)]} - 17\exp[-7.62177(r - 1.45251)^2]
\]

Equation 2-4

\[
U_{OO} = \frac{144.538}{r} + \frac{26758.2}{r^{0.8591}} - 0.25\exp[-4(r - 3.4)^2] - 0.25\exp[-1.5(r - 4.5)^2]
\]

Equation 2-5

Figure 2-4: Pair potentials used to describe liquid water in the revised central force model

The same group went on to develop a more complex model known as the polarization model (PM) for liquid water in 1978 [37]. As an extension of the CFM, the PM contains many of
the same terms. The PM consists of two different sets of potential forms. The first term, \( \Phi_1 \), is the summation of pair-wise additive terms, which is the foundation of the CFM. However, PM alters the first term in each equation to model the atoms using full atomic charges and also includes a second term, \( \Phi_2 \), which is an electrostatic term that accounts for polarizability of particles. Within the electrostatic polarization description is a screening function which softens the short range interactions. Partial charges are used in most water models because full charges over-predict the value of the dipole moment of water molecules. The PM very accurately represents many features which cannot be described well by CFM such as bond stretching frequencies, bond energies, and movement of charges. The model also is the only reactive water model to our knowledge that can accurately reproduce reaction energies of forming water’s bonds. However, the PM struggles with structural information on large scales because it was designed for small water clusters, and thus cannot be used to simulate the system sizes in which we are interested. Water’s diffusion coefficient is also greatly under predicted, and the PM leads to essentially stagnant behavior as demonstrated by Erin Boland within our research group [40], and has not been used for bulk water simulations to our knowledge.

The recent model from D’Aguanno et al. was created using recursive fitting [38]. This group used experimental radial distribution functions for water at three different sets of experimental conditions; A – 268 K and 27 MPa, B – 298 K and 0.1 MPa, and C – 423 K and 10 MPa. The model maintains the central force description via the use of only pair-wise additive potentials between atomic species to describe water. Hofmann demonstrated the existence of proton transfer events predicted by the model for liquid water over a non-reactive, DREIDING description of Nafion ® [41-42]. The DREIDING force field is a generic non-reactive force field developed by Goddard III et al. for molecular simulations. Its details are not relevant to this thesis, and can be found in reference 42. The reactive water model of D’Aguanno et al. showed
good behavior in terms of structure at different temperatures, but was otherwise similar to the CFM from which it was derived.

Another reactive molecular dynamics model is ReaxFF, designed by Goddard III et al [43]. This model was originally designed as a reactive model for hydrocarbons, and has been recently used to describe metals, mixed oxide surfaces and some biological applications [44–48]. ReaxFF is a variable bond order model parameterized from QM calculations. The force field is very complex, and includes terms to describe bonding interactions for stretching, bending and torsion; bond under and over-coordination terms to ensure proper bond distances for given bond orders and overall bond order conservation; valence terms, conjugation energy terms, Coulombic and van der Waals interactions, as well as energy penalty terms [43]. Though this force field is precisely parameterized, it has not been shown to accurately depict liquid water, and the level of parameterization required to add new species to the simulation system is very time consuming and cannot be done without the force field creators.

Ab initio molecular dynamics

Another interesting method that has been used to describe water and aqueous solutions is ab initio MD (AIMD). The field of ab initio MD began in 1985 through the work of Car and Parrinello with the motivation to create a unified method of performing MD simulations without the need to parameterize force fields [49]. AIMD is particularly useful for simulations involving many different atom types or simulations in which the electronic structure of atoms is expected to change drastically [50].

The basic principles of AIMD are relatively straightforward. In classical MD, all particles are considered classically and force-fields are input to the simulations between these particles. In ab initio calculations, all particles are considered with QM algorithms [50]. That is, the electronic
wave function is minimized for the system through the solution of the Schrödinger wave equation. AIMD bridges the gap between the two. Nuclei in the system are considered classically, whereas the forces between atoms are calculated based upon the electronic wave functions. This method requires a separation of the nuclear and electronic terms in the time-dependent Schrödinger equation. The Born-Oppenheimer approximation is therefore made, assuming that electron distribution occurs on a much faster time scale than molecular or nuclear rearrangement.

Though AIMD is considered to be more accurate than MD in determining the forces between atoms, it is very computationally expensive and parameters cannot be adjusted to describe phenomena which are not accurately captured by the specific \textit{ab initio} methods applied. Because large length scales are required to generate an accurate picture of an electrochemical interface due to the need to simulate large enough systems to reach bulk solution behavior away from the electrode, AIMD is considered too expensive for these systems [1]. An additional concern is the structure of water predicted by these methods. QM techniques struggle with describing liquid water, and produce a more ice-like structure for water. Because AIMD relies upon QM calculations for electronic structure, the bulk water structure may be misrepresented, as shown by Galli et al [71,72]. A recent AIMD study of aqueous sulfuric acid found the diffusion coefficient of water to be $0.05 \times 10^{-5}$ cm$^2$/s, which is significantly below that of the experimental value of $2.3 \times 10^{-5}$ cm$^2$/s [51]. The diffusion coefficients of various water models from each class of MD simulations are shown in Table 2-1 [52]. Non-reactive MD is able to reproduce liquid dynamics quite accurately, but does not meet our requirements. Of the reactive models considered, CFM most accurately predicts the liquid water self-diffusion coefficient. For comparison, experimental values of the diffusion coefficient are given for each study. Differences in these values from one study to the next are due to different simulation temperatures, for which the diffusion coefficient is observed to change experimentally.
Table 2-1: Comparison of the diffusion coefficient for various water models [52]

<table>
<thead>
<tr>
<th>Force Field</th>
<th>Class</th>
<th>Diffusion Coefficient (Experimental Value) (x10^5 cm^2/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPC</td>
<td>Non-reactive MD</td>
<td>4.2 (2.3)</td>
</tr>
<tr>
<td>SPC/E</td>
<td>Non-reactive MD</td>
<td>2.7 (2.3)</td>
</tr>
<tr>
<td>TIP3P</td>
<td>Non-reactive MD</td>
<td>5.4 (2.3)</td>
</tr>
<tr>
<td>Central Force Model (1)</td>
<td>Reactive MD</td>
<td>0.73 (2.1)</td>
</tr>
<tr>
<td>Central Force Model (2)</td>
<td>Reactive MD</td>
<td>1.12 (2.4)</td>
</tr>
<tr>
<td>Polarization Model</td>
<td>Reactive, polarizable MD</td>
<td>~0 (2.3)</td>
</tr>
<tr>
<td>Ikeshoji et al AIMD</td>
<td>ab initio MD</td>
<td>0.05 (2.3)</td>
</tr>
</tbody>
</table>

Going forward, we choose the revised central force model of liquid water, developed by Stillinger and Rahman, to describe water in our simulations [36]. We base this choice on the ability of this method to describe bond breaking and forming events, which is a key feature in systems in which proton transfer occurs, as well as its ability to accurately describe liquid water’s structure and diffusion coefficient. Because we are developing a method to describe the dynamic structure near an electrical interface, we feel that structural and dynamic accuracy are requisite to any model used in our simulations. The task of incorporating sulfuric acid into CFM is described in Chapter 3.

Describing an electrode surface with atomistic resolution

With CFM being used to describe water, which will be the most prevalent species in our electrochemical simulations, we next choose a method of describing the electrode surface. Because the region of interest is that close to the electrode surface, the description must accurately capture short range phenomena. For this reason, typical electrode simulations that view the metal surface as a slab of charge or use image-charge techniques cannot be used. We require a
method capable of describing a metal surface with atomistic distinction, and with the ability to influence the charges on atoms in response to local environment so that short range interactions are not over predicted.

**Early simulations of electrochemical systems**

Some of the earliest use of molecular dynamics for the use of electrochemical systems was performed by Spohr [53] and Philpott and Glosli [54]. At the time, computational power was not great enough to provide atomistically distinct electrode surfaces in the manner in which we wish to consider them; that is with polarizable electron clouds that can react to local environments.

Spohr studied a 2.2 molal solution of NaCl in water over a metallic surface. The water in this model is described using the SPC/E rigid water model [55]. In his study, an image-charge consideration was adopted for the metal surface, and the identity of the metal was insignificant. The image charge method allows the metal to interact differently with solution species at different distances from the metal. Figure 2-4 shows how the method is implemented. If a charge approaches a metal surface, a charge of equal but opposite magnitude is envisioned as an image to the solution charge beneath the metal surface. The separation distance of these charges is twice that of the separation distance between the real charge and the metal surface. This method can reproduce long range interactions between a metal surface and a solution charge, but because the interaction energy is inversely proportional to the square of the distance between charges, at short ranges this method can severely over predict interaction energies. There is no means by which to screen this interaction at short distances. However, Spohr was able to show that the classical electrochemical models suffer from a lack of atomic description and cannot properly predict the
charge distribution near a surface due to atomic layering that cannot be described macroscopically.

Figure 2-4: The image-charge representation of interactions between charged species and electrode surfaces

Philpott used a plane of charge method for his electrode surface description. In this method, NaCl salt is added to a SPC/E water box over a metal surface. To charge the simulation, excess positive charges are added to the box, and the metal surface takes on an excess negative charge to maintain a neutral solution. The model has similarities to the image-charge method, but does not provide the same level of atomistic distinction. Rather than image charges being envisioned for solution charges, an image plane of charge is placed at the center of the metal nuclei to interact with solution charges. Forces between the charges and metal surface are then calculated using both a dispersive interaction term, similar to that of a Lennard-Jones interaction,
and an electrostatic terms between the charge and metal plane of charge. This model also suffers from inaccurate predictions of short range interactions. Despite lacking the precise description of the metal surface we desire, both of these studies motivate the need to describe electrode surfaces using methods that allow for atomistic resolution of the electrode/electrolyte interface. We wish to use a method that provides for a more careful consideration of short range interactions to obtain a more accurate description of the electric field at this interface.

**Electrode charge dynamics**

Electrode charge dynamics (ECD) is a method developed by Wheeler et al. which allows for electronic polarizability of all metal atoms to mimic the charge fluctuation response these atoms have to changes in local environments. Whereas previous simulations consider a flat plane of charge, this method gives atomistic distinction to electrode atoms.

There are two main drawbacks to previous methods. First, these methods cannot give atomistic distinction. Any point on the surface is considered equal with an image charge located as a certain distance beneath the entire surface to respond to local charges. Second, because the underlying equation is Poisson’s equation, forces between the charge and image charge scale with $d^{-2}$, where $d$ represents the distance between them (or twice the distance between the charge and metal surface). At short separation distances, this force becomes exaggerated and the description of a local structure near an electrode surface can be dramatically affected by inaccuracies in the short range interactions.

To correct these shortcomings, Wheeler’s method is capable of essentially reproducing the image-charge description at long ranges, and obtaining an accurate short range description with atomistic resolution of the metal surface. The surface atoms are described in two parts. Each
metal atom has a positive, fixed charged center to represent the nucleus and core electrons as point charges. The valence electrons are then described as a Gaussian distribution of negative charge about the center. This Gaussian region of valence electrons can change its overall charge in response to charges near the surface. If one envisions the surface of the electrode, the nucleus and core electrons are within the surface at a fixed position with an overall positive charge. In a neutral environment, the valence electrons can be spread evenly about a given center. Figure 2-5 shows what this description might look like in 2-D for a single surface atom.

Figure 2-5: ECD description of electrode atoms as a positive core surrounded by a Gaussian distribution of negative charge representing the valence electrons. In this image, the horizontal line can be thought of as the electrode surface. Nuclei are beneath the surface and valence electrons extend away from the surface in a Gaussian distribution [5].

**Incorporating ECD into a molecular dynamics simulation**

The two mathematical requirements of the method, given in Equations 2-6, are that the valence electron charge on each metal atom, \( q_i^v \), cannot be greater than zero and that the sum of all valence electron and core charges, \( q_i^c \), must equal the fixed total charge of the metal slab, \( Q_{\text{total}} \). That is, a metal atom may essentially give up all valence electrons but cannot lose any core electrons. Equation 2-6.b ensures that no electron density can be exchanged with the electrolyte. This model does not have the ability to describe redox reactions at the electrode surface. The
actual valence charge on a metal atom at any point in time determines the size of the “electron cloud.” This cloud is defined by a distribution function given in Equation 2-7, where $\rho$ is the probability density of electrons at a point in space, $r$, near a metal atom, $i$. The parameter $\gamma$ is defined as an inverse-width parameter related to the Fermi wave vector.

$$q_i^v \leq 0$$  \hspace{1cm} \text{Equation 2-6.a}

$$\sum_{i=1}^{n} (q_i^v + q_i^c) = Q_{total}$$  \hspace{1cm} \text{Equation 2-6.b}

$$\rho_i(r) = q_i^v \gamma_i^v \pi^{-1.5}(-\gamma_i^2 r^2)$$  \hspace{1cm} \text{Equation 2-7}

$$L = U - \lambda \left[ \sum_{i=1}^{n} (q_i^v + q_i^c) - Q_{total} \right] - \sum_{i=1}^{n} \mu_i q_i^v$$  \hspace{1cm} \text{Equation 2-8}

$$U = \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} q_i^v q_j^v C_{ij} + \sum_{i=1}^{n} \sum_{j=1}^{n} q_i^c q_j^c C_{ij}^* + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1, j \neq i}^{n} q_i^c q_j^c \frac{1}{r_{ij}} + \sum_{i=1}^{n} q_i^v \Phi_i^{set} + U_{ext}$$  \hspace{1cm} \text{Equation 2-9}

$$C_{ij} = \frac{\text{erf}(y_{ij} r_{ij})}{r_{ij}} \hspace{1cm} C_{ij}^* = \frac{\text{erf}(y_{ij} r_{ij})}{r_{ij}}$$  \hspace{1cm} \text{Equation 2-10}

During the simulation, ECD solves for the valence electron charge on each metal atom at every time step to minimize the Coulombic potential energy of the metal. Because this charge varies in response to local charges, the energy associated with all diffuse charge interaction is minimized to determine the favored electronic configuration. This minimization is performed using the Lagrangian shown in Equation 2-8, and $\mu$ and $\lambda$ are solved to minimize the function. The function $U$, given in Equation 2-9, defines the total system energy. The terms $C_{ij}$ and $C_{ij}^*$ are error functions designed to describe the overlap of their respective integrals (Equation 2-10), $\Phi_i^{set}$ is a term that allows a user specified charge difference over the electrode, and $U_{ext}$ consists of the interaction of the electrode with non-electrode charges, such as those of the electrolyte. At any
given time, all values in the energy terms are fixed but for the value of the diffuse charge. This charge is optimized for each atom in the system, and repeated as the local structure changes.

To incorporate ECD with the CFM description of water, force-field parameterization based on QM calculations was performed in collaboration with Kuan-Yu Yeh. A small platinum cluster arranged in a (111) surface geometry was used to represent the electrode. A water molecule was placed above the surface in different orientations (with the hydrogen atoms toward the surface, the plane of the molecule parallel to the surface, and the hydrogen atoms away from the surface). For each orientation, QM energies were obtained at various distances from the electrode. Then, using a genetic algorithm to minimize the error for a selected functional form, parameters were fit to a MD function to match the energy vs. distance QM data. The functional forms used were those reported by Wheeler et al. for the interaction of water with a Cu(111) cluster. This potential is given in Equation 2-10.

\[ U(r) = -\varepsilon [1 - (1 - \exp(-A(r - r_0)))^2] \]  

Equation 2-10

Parameterization of our system, consisting of aqueous sulfuric acid over a platinum (111) electrode surface with ECD, will be discussed in the final chapter of this work. We will next describe the parameterization of CFM to include sulfuric acid to produce a novel description of aqueous sulfuric acid including the ability to break and form bonds to simulate deprotonating acid groups. After designing a model capable of describing aqueous sulfuric acid, we will be able to move on to simulate that model in an electrochemical environment to approximate the behavior of the electrode/electrolyte interface of a PEMFC cathode.
Chapter 3

Molecular Dynamics Simulation of Aqueous Sulfuric Acid

In proton exchange membrane fuel cells (PEMFC), the proton conducting polymer often used is Nafion ®. Nafion is a polyfluorosulfonic membrane with high proton conductivity at low temperatures. PEMFCs typically operate at or above room temperature, with maximum operating temperatures near 80 °C [15]. At temperatures higher than this, water produced by the oxygen reduction reaction (ORR) may begin to vaporize and the fuel cell no longer operates correctly. Nafion ® will also begin to degrade around 90 °C, but it remains thermally stable at temperature of interest to the system [56].

Approximating the behavior of Nafion with sulfuric acid

Because molecular dynamics (MD) simulations require parameterization for all atomic pairs, it is a very long process to directly build a full simulation of a PEMFC cathode including reacting species, water byproduct, metal slab and proton exchange membrane. For this thesis, we approximate the behavior of Nafion ® through the simulation of aqueous sulfuric acid. The acidic group on the end of the side chain on Nafion ® is SO₃H, seen in Figure 1-6. This acid group contains free oxygen atoms that can act as proton hopping sites to assist in the transport of protons through the membrane. In addition to mimicking the proton exchange behavior, both sulfuric acid and Nafion ® are acidic in nature and will donate protons to solution [20].

Finally, sulfur and sulfuric acid are known to be strong adsorbates in surface studies. Markovic et al showed the activity of the ORR in rotating disk electrode experiments over a platinum surface in sulfuric acid to be structure dependent [57]. The activity over a Pt(111) surface was very low due to the adsorption of bisulfate anions deactivating the catalyst surface.
Though other surfaces may not be as active for bisulfate adsorption, the (111) surface cut is the lowest energy surface and most likely to be exposed. Ishikawa et al. used QM calculations to show that at potentials of interest, sulfuric acid is a strong adsorbate over the Pt(111) surface [58]. Adsorption begins at ~+0.40 V(NHE) and gets stronger with increased potential (the typical PEMFC operating potential is ~+0.8 V). The bulk of the membrane, if it gets too near the electrode surface, may also prohibit the diffusion of gaseous oxygen to the surface. Through the simulation of aqueous sulfuric acid in an electrochemical environment, we hope to shed light on the activity of a proton exchange membrane in a similar electrochemical environment. The results from this work will provide a unique electrochemical description of aqueous sulfuric acid.

**Structural characterization of the sulfuric acid molecule**

To include sulfuric acid in our CFM description of water, our first consideration is the structure of the $\text{H}_2\text{SO}_4$ molecule. There is little very structural information available on experimental studies of sulfuric acid. In studies that have provided structural data, the data given are of vibrational information. Thus, to determine the proper structure of the $\text{H}_2\text{SO}_4$ molecule, quantum mechanical (QM) calculations were used to find the lowest energy electronic configuration. All QM calculations were performed using the Vienna *ab-initio* simulation package (VASP), developed at the Institute for Material Physics at the University of Vienna [59-61]. For the study of a single $\text{H}_2\text{SO}_4$ molecule, the projected augmented wave method was used for electron/ion interaction. A 400 eV cutoff for the plane-wave basis set was used and the Brilloiun zone sampling was performed using the gamma point only [62]. The structure was considered optimized when the forces acting on all atoms was less than 0.05 eV/Å.
There are two distinct bond distances for the S-O bonds in sulfuric acid. Those oxygen atoms which bond protons have a weaker interaction with the central sulfur atom, and thus a longer bond. This bond, denoted S-O_H has a distance of 1.61 Å. The oxygen to which there is no proton bonded has a shorter equilibrium bond distance with the sulfur atom and a formal double bond. The bond distance for the “free” oxygen, denoted S-O_F was calculated to be 1.43 Å. The equilibrium bond distance for the H-O_H bond is 0.979 Å.

The SO_4 group does not have a tetrahedral geometry because the protons have an interaction that attracts a second neighbor oxygen atom. The O_F-S-O_F angle is 124.3°, and that for the O_H-S-O_H group is 101.8°. The two other types of angles seen are those for O_F-S-O_H for which the hydrogen is angled toward the free oxygen and that for which the hydrogen is angled away from the free oxygen. The former case has an angle of ~107.8°, while the latter has a slightly smaller angle of ~106.3°.

Incorporating H_2SO_4 into the MD force field to run aqueous sulfuric acid is necessary before the solution was simulated over platinum. The CFM description of atoms, in terms of partial atomic charges and the description of liquid water, is maintained because water is the primary component of our system. Partial charges are assigned to each atom to ensure proper prediction of the dipole moment and correct water dynamics. The charge on the hydrogen atom,
q_H is assigned a value of 0.32983 e, and all other atoms in the system are scaled naturally from the hydrogen charge [36].

Table 3-1: Atomic charges for reactive MD simulations

<table>
<thead>
<tr>
<th>Atom</th>
<th>Charge, q_i (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.32983</td>
</tr>
<tr>
<td>O_w</td>
<td>-0.65966</td>
</tr>
<tr>
<td>O_s</td>
<td>-0.65966</td>
</tr>
<tr>
<td>S</td>
<td>1.97898</td>
</tr>
</tbody>
</table>

Developing a molecular dynamics description of sulfuric acid

To parameterize H_2SO_4 with water, certain decisions had to be made a priori. First, because there is no experimental data available, a structural basis for comparison was needed. There have been several studies to consider aqueous sulfuric acid from an classical MD simulation standpoint [63-65]. Most of these studies have used classical molecular dynamics with fixed molecular geometries, and they do not allow for proton dissociation or other proton transfer events to occur. Others look only at simulating small acidic clusters in water and use force fields which are not computationally efficient for large scales. From the literature on aqueous H_2SO_4 simulation, only two papers were found to be relevant to the present study.

Laaksonen et al use the only example to our knowledge of classical MD simulations in which oxygen atoms in sulfuric acid are differentiated (O_H and O_F are considered different atoms) [63]. Differentiating between the two types of oxygen atoms allows for proper matching of angular data for the sulfate cluster. This study was performed using non-reactive MD parameterized from ab initio data. The bonds for the different oxygen atoms, S-O_H and S-O_F can be fit explicitly to match the calculated equilibrium distances. A unique feature of the model of Lasksonen et al. is the use of only pair potentials. That is, interactions between oxygen atoms
within a sulfate group are controlled using a bond-like potential rather than through the use of an angular term on the O-S-O plane. Similar considerations are taken for all atomic interactions.

Laaksonen uses simulations of bisulfate (HSO$_4^-$) and hydronium (H$_3$O$^+$) in water as well as sulfuric acid (H$_2$SO$_4$) in water to show that the bisulfate anion is favored in solution when the hydration in the system is large enough.

![Molecules used in the MD simulation of H$_2$SO$_4$/H$_2$O system with bisulfate anions and hydronium cations using different potentials for sulfuric acid oxygen atoms for the presence/absence of protons performed by Laaksonen et al.](image)

Figure 3-2: Molecules used in the MD simulation of H$_2$SO$_4$/H$_2$O system with bisulfate anions and hydronium cations using different potentials for sulfuric acid oxygen atoms for the presence/absence of protons performed by Laaksonen et al.

Ikeshoji used *ab initio* molecular dynamics (AIMD) to study small H$_2$SO$_4$/H$_2$O systems [51]. The benefit of this method is the ability to study proton transfer events, and the electronic structure calculations allow simulations to be run without the need for parameterization of all interactions in the system. Ikeshoji, like Laaksonen, found that the bisulfate anion was most stable in low concentration systems. This work went on to include electric field effects on the structure of acid and solution dynamics through the application of a homogeneous electric field of 1.03 V/nm in one direction. These results showed that, under the influence of an external electric field, sulfuric acid tends to dissociate more readily for low concentration systems. In a 0.84 molar
H$_2$SO$_4$ solution in water, 100% of the structures existed as HSO$_4^-$ without electric field, whereas application of the electric field caused 11% of the bisulfate anions to further dissociate to SO$_4^{2-}$.

Figure 3-3: Radial distribution function of sulfuric acid oxygen atoms with water hydrogen atoms provided by an AIMD study for two acid concentrations [51].

Because AIMD cannot be used for the time and length scales that we would like to consider in the construction of a MD model for electrochemical interfaces, a separate MD force field description of the acid/water system is required. The RDFs for sulfuric acid in water from Ikeshoji et al were used to add water to our sulfuric acid molecule because they are considered to be the most reliable structural information available for the aqueous system. The main basis of comparison for our parameterization, the RDF for sulfuric acid oxygen atoms with hydrogen atoms, is shown in Figure 3-3 for two concentrations. Some deviation from these results is expected because our method relies only on Newton’s equations of motion and can more accurately capture dynamics of aqueous systems. Ikeshoji et al. do not give information on the structural information of water in their simulations, and it is unknown whether a more ice-like configuration is reached. The dynamics associated with AIMD are also greatly under predicted.
Diffusion coefficients for water and sulfuric acid are two orders of magnitude lower than their respective experimental values [66].

**Design of the intermolecular potentials**

To develop our description of the acid/water system it is necessary to parameterize interactions for all new atom types. Firstly, the force-field is optimized to describe the sulfuric acid group by itself. Because our force field will allow the breaking and forming of bonds involving protons, we cannot provide atomistic distinction between $O_H$ and $O_F$. If all oxygen atoms in the acid cluster are treated equally, it will be equally likely for a free proton to bond to or dissociate from any oxygen atom. To avoid confusion between oxygen in water molecules and oxygen in sulfuric acid, the latter will henceforth be termed $O_S$. Having decided that all $O_S$ atoms will be treated equally, a compromise must be made on the equilibrium bond distance for $S-O_S$, as well as the geometric angle at which the $S-O_S$ bonds exist with one another.

As stated previously, the $S-O_S$ bond distances are longer for oxygen to which a proton is bonded (1.613 Å compared to 1.434 Å). For all $S-O_S$, an equilibrium distance of 1.51 Å was selected. This distance was selected as a weighted average of QM bond lengths. Because research has shown the bisulfate anion to be favored, the bond distance was selected to be closer to that of the $S-O_F$ bond in $H_2SO_4$. Finally, because each $O_S$ will be considered identical, the equilibrium molecular geometry is a tetrahedral orientation. Because all $S-O_S$ bond lengths are 1.51 Å, the equilibrium $O_S-S-O_S$ bond angle is 109.5°.
molecular dissociation of the SO\textsubscript{4} group is not an event that would be expected under reasonable conditions. Formation or breakup of the SO\textsubscript{4} will not be included in our model, so these bonds will not be considered reactive. Figure 3-4 shows the interaction potentials used for the SO\textsubscript{4} group in these simulations. Harmonic potentials will be used for all S-O\textsubscript{5} bonds with an equilibrium distance of 1.51 Å. To maintain the two-body force field description characteristic of the central force model for water, the method of Laaksonen is implemented to maintain molecular geometry in the sulfate group [63,64]. Rather than describing O\textsubscript{5}-S-O\textsubscript{5} angles via a three body angular term, identical two body interactions are used to O\textsubscript{5}-O\textsubscript{5} bonds. The atomic distance between to O\textsubscript{5} atoms corresponding to a 109.5° O\textsubscript{5}-S-O\textsubscript{5} angle, with a S-O\textsubscript{5} bond distance of 1.51 Å, is 2.466 Å. To maintain the desired geometry, a harmonic potential with an equilibrium bond distance of 2.466 Å is used for O\textsubscript{5}-O\textsubscript{5} pairs within a sulfate group. For S-O\textsubscript{5} pairs and O\textsubscript{5}-O\textsubscript{5} pairs interacting between different sulfuric acid molecules, different potentials are used and will be discussed. Harmonic potentials can be controlled via a force constant. These potentials are analogous to Hooke’s law in describing springs. A force constant controls the magnitude of the
force acting on particles to return them to the equilibrium position. Both sets of atomic pairs are described with the same equation, Equation 2-1, and the constants are given in Table 3-2. Bond flexibility can be controlled through the value of the force constant.

Table 3-2: Interaction parameters for harmonic sulfate bonds, functional form U(r)=0.5k(r-r_0)^2

<table>
<thead>
<tr>
<th>Bond Pair</th>
<th>Force Constant, k (kcal mol^{-1} Å^{-2})</th>
<th>Equilibrium Distance, r_0 (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-O_S</td>
<td>1000</td>
<td>1.51</td>
</tr>
<tr>
<td>O_S-O_S</td>
<td>600</td>
<td>2.466</td>
</tr>
</tbody>
</table>

For all O_S non-bonded interactions, O_S is considered identical to O_W. The non-bonded O_S-O_S or O_S-O_W is identical to that of the O_W-O_W interaction. Sulfur atoms on different sulfate groups are limited in their approach by molecular sterics. Because each sulfur atom has four oxygen atoms bound to it at a distance of 1.51 Å and the oxygen atoms themselves have a natural tendency to repel one another, sulfur atoms cannot approach each other to a distance closer than c.a. 4.5 Å at any time. Because this distance is well outside of that expected to have any strong electronic effect, the S-S interaction is described in a purely repulsive electrostatic manner with no additional force terms, given in Equation 3-1.

\[ U_{SS}(r) = \frac{q_5^2}{r} \times 332.1669 \]  \hspace{1cm} \text{Equation 3-1}

Similarly, the approach between sulfur and oxygen atoms to which it is not bonded, both O_S atoms on other sulfate groups and O_W, will not be very close. The closest expected approach between these atomic pairs is outside of 3 Å. Because these pairs will always exist at distances outside the primary influence of electrostatics, there will be only a weak attractive force between the atoms due to their opposite charges. A simple Lennard-Jones interaction, given in Equation 3-2, is used for these pairs and is identical for both non-bonded S-O_S pairs and all S-O_W pairs. The
weakness of this interaction leaves a force dominated by electrostatics, with a small region of repulsive behavior at close distances, though these distances are closer than the atoms are expected to approach during a simulation. Figure 3-5 shows how this interaction deviates only slightly from, and is dominated by, the electrostatic potential. To give this fit, weak interactions are required so as not to overpower the electrostatics. For the given function, \( \sigma \) is given as 12 Å and \( \varepsilon \) is \( 1 \times 10^{-7} \) kcal/mol.

\[
U_{SOw,S_{NB}}(r) = \frac{332.1669q_s q_0}{r} + 4 \times \varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]
\]

Equation 3-2

Figure 3-5: Non-bonded interaction potential for S-O\(_5\) and S-O\(_w\)

The parameterization of the O\(_5\)-H bond requires a balance of a bonding interaction and the ability to dissociate protons. Because it has been shown that the bisulfate anion, HSO\(_4^-\) is the most prevalent species at low acid concentrations in solution, a bond force must be designed so that it is strong enough to hold a proton on the sulfate group, but weak enough to allow a proton
to dissociate. There are three interactions which play a role in the dissociation of protons from a sulfate group. The most obvious interaction is the $O_S$-$H$ pair. The $S$-$H$ and $O_W$-$H$ potentials also affect a protons’ tendency to dissociate. Because hydrogen atoms from water and sulfuric acid are not considered different in our simulations, the $O_W$-$H$ bond potential does not change from that described in CFM. Intuitively, the $O_S$-$H$ potential must then be designed to provide a force that is weaker than that of the CFM O-H description, but not so weak so as to completely dissociate both protons from sulfuric acid, yielding an average solution structure of $\text{HSO}_4^-$.

Meanwhile, there must be an attractive force between the sulfur atom and protons in an acid molecule. Though this attraction may be counter-intuitive because both atoms have positive charges, it is required in a simulation to attain the bending of the $S$-$O_S$-$H$ group. Without some attractive force between the proton and molecular center, a $180^\circ$ bend angle would be expected for this group rather than the $\sim 107.5^\circ$ angle predicted by QM calculations, as shown in Figure 3-1. The potential chosen for $S$-$H$ follows a common form. As in the CFM description of $H$-$H$ pair interactions, our $S$-$H$ interaction has a small attractive well at a distance corresponding to typical $S$-$H$ distance in $\text{H}_2\text{SO}_4$ of approximately 2.1 Å. This interaction potential is shown in Figure 3-6 and described in Equation 3-3. Using this potential, the average $H$-$O_S$-$S$ angle calculated is $121^\circ$. It is important to note that the average angle for a fully bonded $S$-$O_S$-$H$ group may be slightly different. Because our force-field is reactive the calculation method cannot differentiate protons that are in the act of dissociating from those bonded to a $O_S$, which may lead to an inaccurate angle calculation.
Figure 3-6: Pair interaction potential for S-H in reactive sulfuric acid simulations

$$U_{SH}(r) = \frac{332.1699}{r} q_s q_h + \frac{-40}{1 + \exp(4(r - 2.4))} + 500\exp(-15(r - 1.1))$$  \text{Equation 3-3}

Because every atomic pair interaction in the system affects the structures that are obtained, the potential for O$_5$-H was the last to be parameterized in an attempt to simulate aqueous sulfuric acid and produce bisulfate anions as the predominant sulfate form. To balance the selective dissociation of protons from the H$_2$SO$_4$ group, a parametric design process was performed to fit a potential for O$_5$-H. Three different potential forms were studied. The first, termed CFM-1 (Equation 3-4), is based on the potential form used by Stillinger and Rahman for O-H in the original version of the CFM[34,35]. The second, termed CFM-2 (Equation 3-5), is the same potential form used by Stillinger and Rahman for O-H in the CFM, which is the original version of the force field used for liquid water [34,35]. The third, termed CFM-OO (Equation 3-6), attempted to describe the O$_5$-H interaction using a potential form used for O-O in the revised CFM, but altered to produce an attractive interaction rather than a repulsive one [36]. The functional forms are given, without electrostatic terms, in Equation 3-4, 5, 6.
All tests for sulfuric acid parameterization were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) Molecular Dynamics Simulator [67]. These tests were designed to parameterize force parameters to produce our desired solution structure of HSO$_4^-$ and our desired RDF. LAMMPS is a classical molecular dynamics code typically used for polymer, metal, biological or semiconductor systems capable of handling both all-atom or coarse-grained simulations. Our simulations were done on all atoms. Force fields were user specified in a tabular format, with 1000 equidistant bins for distances between 0 – 10 Å for atom pairs with potential forms not included in the package. Harmonic bonds were specified for O=S-S and O=S-O=S pairs within a sulfate group and Lennard-Jones forms were specified for all non-bonded sulfur-oxygen interactions with a cutoff of 9.0 Å. Charges were defined for all atoms to be those previously specified per the CFM partial charges. The Verlet algorithm was used for integration of Newton’s equations and periodic boundary conditions were applied in all directions to remove end effects. The simulation temperature was 300 K.

The simulation box was 19.403 X 19.204 X 23.36 Å$^3$ consisting of 897 atoms. The solution consists of six sulfuric acid molecules and 285 water molecules, corresponding to a sulfuric acid concentration of 1.14 M and a solution density of 1.09 g/cm$^3$, matching the experimental value of density for the given concentration. The box size was chosen to facilitate later simulations including the platinum surface and will be described in the next section. For pre-screening runs to differentiate between functions, simulations were run for 2x10$^6$ steps with a
time step of 0.25 fs for a total of 500 ps. Short time steps are required due to the reactive nature of the O-H bonds. Coordinates were output every 1000 steps, so the RDF plots were generated from a sample of 2001 coordinate files (including the initial structure). Subsequent runs used to decide on a final version of the force field used identical parameters and set up, but were run for $16 \times 10^6$ steps, or 4000 ps (4 ns).

For all potentials tested, the results were analyzed against two criteria, both of which were based upon radial distribution function (RDF) plots. A RDF plots, as a function of distance, the likelihood of finding an atom at a given position in space relative to another atom. Areas on the chart in which the value of the RDF is greater than 1 denote a region in which atoms are more likely to be found, and vice versa. All plots will reach a value of 1 at a distance far enough away from the reference point, indicating that coordination is no longer a function of distance.

Of the two criteria, the first was the average coordination for $\text{O}_5$-$\text{H}$ in the first peak. Because the bisulfate anion is favored in our simulation, information from the first peak can be used to determine the average structure. The first peak in the $\text{O}_5$-$\text{H}$ RDF occurs near 1 Å in all of the tests. Because there are four $\text{O}_5$ atoms on each sulfate group, and one proton is desired on the sulfate group, a correct structure would provide a numerical integration of the first peak equal to 0.25, or 0.25 hydrogen atoms for every $\text{O}_5$. The second criterion is a comparison to the only available \textit{ab initio} MD structural data for aqueous sulfuric acid [51]. All RDF plots were compared to that provided by Ikeshoji et al, shown in Figure 3-3.

The three potential forms were differentiated primarily through the shape of the RDF after the first peak. The first peak height and location can be tuned through the adjustment of the first term parameters in the force equation ($A/r^B$), so it was not considered as strongly in the prescreening. However, for all values tested for the equations, a poor RDF was obtained. In the case of CFM-1, there was no well defined second peak. Each fitting produced a continuous increase in the value of the RDF until a maximum value at a distance of approximately 3.4 Å.
Instead, we expect a well defined second peak near 1.7 – 1.9 Å, followed by an obvious well and a final peak feature at approximately 3.3 Å. The oscillations in peaks produced by CFM-1 were reproducible for all runs and steered us away from the use of the CFM-1 description for a O₅-H potential.

![RDF for both CFM](image)

Figure 3-7: RDF for the S-H distance for CFM-1 and CFM-OO (right image is zoomed in to show the second peak information used to eliminate these potentials from consideration)

Results from CFM-OO also failed based on the shape of the second peak. In all tests performed there was a strong region of vacuum-like space outside the first peak. This trend showed that dissociated protons, or hydrogen atoms on water molecules, have a large region of repulsive behavior outside of the equilibrium O₅-H bond distance. In other words, if a proton dissociates, it spends very little time near the atoms from which it dissociated. This feature is not echoed in the AIMD studies. After this extended region of zero coordination, there is a slow rise to a second peak which is not well defined, before reaching a well defined third peak similar to the trend seen in CFM-1 studies. The CFM-OO potential form was also discarded based upon the long range features in the O₅-H RDF generated from the prescreening tests. Figure 3-7 shows the RDF for both CFM-1 and CFM-OO used to decide against these potentials for our study.

CFM-2 potentials produced a much better fit against available data. Though trends in the first peak were not indicative of our simulation producing an average bisulfate structure indicated
by very high O$_3$-H coordination, the location of key features matches well with those presented by Ikeshoji et al. CFM-2 was selected as the best potential form based on its ability to accurately capture the location of key features on the RDF. The strong second peak, compared to the lack of a second peak in the CFM-OO potential is depicted in Figure 3-8.

![Figure 3-8: CFM-2 prescreening S-H RDF, shown against CFM-OO S-H RDF to highlight the presence of the second peak at ~1.9 Å.](image)

### Finalizing the O$_3$-H potential for sulfuric acid

A further parametric design was used to screen for the best combination of parameters in the CFM-2 potential description of this interaction. From trends observed in the potential selection previously described, it was noticed increased ‘A’ values caused lowering of the first peak and slight shifting to the right. For a given ‘A’ value, increasing the value of ‘B’ would shift the peak right and change the peak height (some peak heights increased with B while other
decreased). The desired first peak has a distance of approximately 0.97 Å and integrates to 0.25 to a certain cutoff distance.

The parameterization on CFM-2 optimized each of the 5 parameters through a parametric design process. That is, a range of values was selected for each parameter, and all permutations of those values were simulated. After a range of values was tested, recommendations were made for narrowing the range of values and the process was repeated. All prescreening runs were performed for 500 ps. Of these runs the eight best, based on the appearance of all RDF features, were selected for further simulation. The extended runs were carried out for 4 ns, and the optimal parameters were chosen.

**Comparison of final screening tests for force field fitting**

To select the best parameter fit, RDF plots were created for the final 2 ns of each 4 ns simulation. Analyzing only the final 2 ns would remove any initial configuration bias from the plots and give an equilibrium indication of the features predicted by the force field. The RDF was numerically integrated to a cutoff value to determine the average hydrogen coordination about each sulfate group. Two cutoff distances were chosen for selecting the best fit. The first was the “full-width at half-max” method. This method cut off the integration at the point at which the value of the RDF reached the halfway point between the first maximum and the next minimum. The second method was to cutoff the integration at a distance corresponding to 10% greater than the equilibrium bond distance. For both of these tests, the “Fit 2” produced the best integration, with both values being within 2% of the desired 0.25. Thus, “Fit 2” was chosen as the optimal potential to describe the interaction between O₅ atoms and H atoms.
Table 3-3: Integration analysis of various O₅-H potentials for average sulfate molecular configuration

<table>
<thead>
<tr>
<th>Fit</th>
<th>First Max (Å)</th>
<th>RDF at first max</th>
<th>Integrating to Max +10%</th>
<th>Integrating to “half max” from 1ˢᵗ max to 1ˢᵗ min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.045</td>
<td>1.539</td>
<td>0.281</td>
<td>0.274</td>
</tr>
<tr>
<td>2</td>
<td>1.075</td>
<td>1.356</td>
<td>0.245</td>
<td>0.252</td>
</tr>
<tr>
<td>3</td>
<td>1.075</td>
<td>1.112</td>
<td>0.206</td>
<td>0.206</td>
</tr>
<tr>
<td>4</td>
<td>1.075</td>
<td>1.047</td>
<td>0.204</td>
<td>0.197</td>
</tr>
<tr>
<td>5</td>
<td>1.075</td>
<td>1.606</td>
<td>0.307</td>
<td>0.316</td>
</tr>
<tr>
<td>6</td>
<td>1.025</td>
<td>1.314</td>
<td>0.230</td>
<td>0.261</td>
</tr>
<tr>
<td>7</td>
<td>1.055</td>
<td>0.955</td>
<td>0.174</td>
<td>0.184</td>
</tr>
<tr>
<td>8</td>
<td>1.035</td>
<td>1.936</td>
<td>0.344</td>
<td>0.344</td>
</tr>
</tbody>
</table>

The final potential is one that is similar to the CFM description of O-H because it shares the same functional form with differences in parameters. The O₅-H fit potential has a minimum at a similar distance, because the equilibrium bond distance is almost equal to that in water. However, the well in the fit potential is not as weak, and the approach to equal the electrostatic interaction is much more gradual. This decrease in steepness of the well in the attractive region facilitates proton dissociation, as the force attracting the atoms back to their equilibrium bond length is lessened. The final functional form is presented in Equation 3-7 and is compared to the original CFM description of the O-H bond in Equation 3-8 and Figure 3-9, including electrostatic interactions.

\[ U_{OH}(r) = -\frac{332.1669q_o q_H}{r} + \frac{16}{r^4} - \frac{1}{1 + \exp[5(r - 2.2)]} \]  

Equation 3-7

\[ U_{OH}(r) = -\frac{72.269}{r} + \frac{2.6677}{r^{14.97}} - \frac{6}{1 + \exp[5.493(r - 2.2)]} \]  

Equation 3-8
Figure 3-9: Final form of O$_3$-H potential compared to that of CFM potential for OH

Figure 3-10: Overlay of my O$_3$-H RDF with that of Ikeshoji et al. Ikeshoji removes the bonded proton from consideration in RDF calculation, which is why there is no peak at ~1 Å

In the final chapter, aqueous sulfuric acid will be parameterized with platinum, which serves as the electrode in our study, to run a full simulation. We will describe the parameterization of sulfuric acid with platinum, and the simulation of the full electrochemical
system. Results from these simulations will be discussed for various potentials and future recommendations for continuing this work will be given.
Chapter 4

Simulating Aqueous Sulfuric Acid between Platinum Electrodes

We have developed a molecular dynamics (MD) force field capable of describing aqueous sulfuric acid in a reactive manner. The force field has been parameterized to allow for selective proton dissociation to obtain an average solution structure of HSO$_4^-$, which is the most abundant species in aqueous sulfuric acid at low concentrations. Sulfuric acid was chosen to represent the activity of a Nafion proton exchange membrane in solution. This chapter will discuss the incorporation of electrode charge dynamics (ECD) into our force field to provide atomistic distinction to platinum metal atoms of an electrode surface and the running of our full scale electrochemical system, with preliminary data analysis.

Parameterization of Pt (111) surface with aqueous sulfuric acid

To accurately describe average structure at the electrode/electrolyte interface in electrochemical systems, short range interactions must be represented correctly. Because image-charge methods cannot mimic the interaction expected near an electrode surface, ECD is used in its place [5]. Forces defined between metal atoms and atoms in the electrolyte/solution region are parameterized from *ab initio* calculations in which single point calculations are performed to determine the energy for a system as a function of adsorbate distance away from a metal surface. In our calculations, water molecules and bisulfate anions were separately considered over a Pt (111) metal cluster consisting of 25 metal atoms in four layers. The (111) surface of platinum is used because it is the most energetically favorable surface cut, and is the most active for the ORR. For description of the platinum metal, parameters from Equations 2-6, 2-7 are needed. The core charges, $q_i^c$, are assigned a value of 1 e, leading to an initial value of -1 e for all diffuse charges, $q_i^d$, to yield a neutral surface. During simulation, the diffuse charges change from their
Parameterization of the Pt (111) surface with water

The first interaction considered in developing a force field to include a platinum electrode was that of the Pt (111) surface with water. To obtain data for this interaction, \textit{ab initio} calculations were run using VASP to give an energy landscape for a water molecule above a Pt (111) surface. Three different water molecule orientations were considered: one with the dipole pointing into the surface (0°), one with the dipole parallel to the surface (90°), and one with the dipole pointing out of the surface (180°). For each orientation single point calculations were performed for a range of 10 H$_2$O-Pt distances, including the equilibrium distance. Fitting to \textit{ab initio} data was then performed using a genetic algorithm relying on a global minimization to system energy from MD compared to QM [69]. The function fitting is described by Erin Boland, with the results of the fitting of O-Pt and H-Pt being described by Equation 4-1, with parameters given in Table 4-1 [40].

\[
U(r) = -\epsilon \left[1 - \left(1 - \exp(-A(r - r_e))\right)^2\right] + \frac{A_2 \exp(-A_3 r)}{r} + \frac{B}{r^c} \quad \text{Equation 4-1}
\]
Table 4-1: Parameters for the initial force field interaction between water and Pt (111)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Hydrogen</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$ (kcal/mol)</td>
<td>0.0140742</td>
<td>39.3183</td>
</tr>
<tr>
<td>$A$ (Å$^{-1}$)</td>
<td>1.4712</td>
<td>1.00555</td>
</tr>
<tr>
<td>$r_e$ (Å)</td>
<td>0.26348</td>
<td>0.556786</td>
</tr>
<tr>
<td>$A_2$ (kcal Å/mol)</td>
<td>39095.6</td>
<td>19502.4</td>
</tr>
<tr>
<td>$A_3$ (Å$^{-1}$)</td>
<td>825.29</td>
<td>608.289</td>
</tr>
<tr>
<td>$B$ (Å$^3$)</td>
<td>109379</td>
<td>8604.8</td>
</tr>
<tr>
<td>$C$</td>
<td>18.7382</td>
<td>7.11049</td>
</tr>
</tbody>
</table>

Face centered cubic (FCC) metals with a (111) surface exposed have 4 primary adsorption sites because they arrange in a 3 layer repeating structure (ABCABC): atop, FCC hollow, HCP hollow, and bridge. With atop adsorption, an atom adsorbs directly above a metal atom on the top layer. The bridging adsorption occurs when an atom bridges between two metal atoms and interacts directly with both. Hollow sites are created between 3 atoms on the top layer, where a “gap” is seen in the layer and the adsorption interacts with all 3 metal atoms. HCP (hexagonal closed packed) hollow sites have an atom in the second layer directly below the “gap” and are so named because all hollow sites exist with this feature in HCP metals. FCC hollow sites exist with no atom from the second layer beneath the hollow site, but have an atom from the third metal layer below the adsorption site. These sites are so named because they are specific to metal with a FCC structure.
Figure 4-1: Comparison of initial water/Pt(111) fitting to expected surface adsorption sites. (a) Equilibrated surface structure from initial MD runs with adsorption to FCC hollow site (H removed). (b) Non-reactive MD simulation of water over a platinum surface adsorbing to the atop site [3].

After using this potential, we noted that the interaction yielded an unfavorable organization of water molecules on the metal surface. Though the interfacial structure is not well known, and has not been structurally characterized, it can be shown through QM calculations that the preferred adsorption site of water is in an atop site. Our first water/Pt interaction yielded a surface structure in which water molecules adsorbed to FCC hollow sites. Figure 4-1 compares the adsorption events we saw in our simulations to those that would be expected of a surface organization of water on Pt (111) [3]. For clarity in Figure 4-1a, the hydrogen atoms have been removed from the water molecules, and the top two metal layers are shown to demonstrate adsorption over the FCC hollow site.

To correct this, we had to alter our force field between water and platinum. Due to the lack of clarity as to the arrangement of water at an electrode surface, two different potentials were used, both of which follow the same modified Morse potential described in Equation 2-10. The first fitting, termed the “weak potential,” was taken from a computational study performed by Cummings et al on ssDNA electrophoresis which included a model for non-reactive TIP3P water over a Pt (111) surface [68]. The second fitting, termed the “strong potential,” used the same
length parameters with a greater strength of interaction, obtained through doubling the energy parameter. The two fittings were used to determine the effect of interaction potential on the interfacial structure. Table 4-2 gives the parameters for the two force fields used.

Table 4-2: Interaction parameters for the new water/Pt(111) interaction using Equation 2-10

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Weak – O</th>
<th>Weak – H</th>
<th>Strong – O</th>
<th>Strong -H</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$ (kcal/mol)</td>
<td>0.19880</td>
<td>0.38779</td>
<td>0.39761</td>
<td>0.7756</td>
</tr>
<tr>
<td>$A$ (Å$^3$)</td>
<td>2.00</td>
<td>2.320</td>
<td>2.00</td>
<td>2.320</td>
</tr>
<tr>
<td>$r_o$ (Å)</td>
<td>3.073</td>
<td>2.768</td>
<td>3.073</td>
<td>2.768</td>
</tr>
</tbody>
</table>

The newly fit interaction provides a more mobile surface structure without the strong affinity to stay locked in hollow sites. Figure 4-2 shows a time resolved surface structure. This image, creating using Visual Molecular Dynamics, shows how the oxygen atoms in the first layer move over a 25 ps time period. The color of the dot denotes the position of the atom relative to its starting position, with red being used for the initial positions and changing to blue over the time period. The figure shows that water molecules can escape hollow sites and are mobile on the surface.

Figure 4-2: VMD image of the movement of water molecules (shown as oxygen atoms) on a Pt(111) surface during an MD simulation using updated water/Pt force field
Parameterization of the Pt(111) surface with sulfuric acid

With a force field developed for the simulation of reactive water over a platinum electrode using central force model water with electrode charge dynamics, we move on to complete our force field description for our electrochemical system. Sulfuric acid is used to approximate the activity of Nafion in solution. Chapter 3 described our incorporation of sulfuric acid into the central force water description to provide a reactive description of the acid. In this section we will discuss parameterizing sulfuric acid with Pt (111).

Because the most prevalent species in solution at the concentration of sulfuric acid that we are studying is the bisulfate anion, we developed our force field based upon the interaction of the bisulfate anion with a Pt (111) cluster. We have shown that the energetically favorable configuration of \( \text{HSO}_4^- \) on a Pt (111) surface is with 3 O atoms directed downward over Pt atop sites, and the O atom with the bound H pointing away from the surface. This surface orientation is depicted in Figure 4-3.

![Figure 4-3: View of the preferred bisulfate ion orientation on a Pt (111) surface. (a) Side view (b) Top view](image)

Given the surface configuration and the data obtained for a description of the change in energy with distance from the surface, a force field was parameterized using the same genetic algorithm which was used for water/Pt interaction fitting. Only the Pt-S interaction was fit, as the
Pt-Os interaction was initially decided to be the same as that of the Pt-Ow to simplify the force field. A number of potential forms were considered to find an interaction that yielded the least error between MD energy predicted and the calculated ab initio data. The best fit was obtained using Equation 4-2, which is a modified Lennard-Jones potential. Because the Os-Pt interaction was maintained to be the same as that for Ow-Pt, a fitting was done for both the “strong” and “weak” H2O-Pt potentials. The parameters for each case are given in Table 4-3, and the fit is compared against QM data in Figure 4-4. Note, MD data are only included in the figure for the force field fit involving the weak Pt-H2O parameters, as the strong Pt-H2O data would overlie them.

\[
U_{pt-o}(r) = 4 \varepsilon \left( \frac{A}{r} \right)^B - \left( \frac{A}{r} \right)^C
\]

Equation 4-2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Strong</th>
<th>Weak</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\varepsilon) (kcal/mol)</td>
<td>1400</td>
<td>2200</td>
</tr>
<tr>
<td>A (Å)</td>
<td>3.215</td>
<td>3.250</td>
</tr>
<tr>
<td>B</td>
<td>5.800</td>
<td>5.430</td>
</tr>
<tr>
<td>C</td>
<td>4.900</td>
<td>4.960</td>
</tr>
</tbody>
</table>
Initial simulation of a full electrochemical system

Our electrochemical system consists of aqueous sulfuric acid between platinum electrodes. The MD simulations of our system were performed using a C++ code written within the research group to combine central force water with the electrode charge dynamics description of the metal surface. A snapshot of our simulation is shown in Figure 4-5. The coordinates are defined as such; x: into the paper, y: up-down, z: left-right.

Figure 4-5: Snapshot of our MD simulation of aqueous sulfuric acid between platinum electrodes

Because of the use of periodic boundary conditions in all directions, we chose a number of electrode layers that provides a “mirrored” FCC (111) stacking arrangement, which requires 3N+1 metal layers for the same surface to be exposed to both sides of the system, where N is any
integer value. We chose to simulate 7 (ABCABCA) layers of the electrode, as this allows for a distinct charge difference between two sides of an electrode, while simultaneously being more computationally efficient than larger systems and still providing enough metal layers to allow the charge to diffuse through the metal layers to a conserved value.

To determine the size of the box in the x and y directions, it was necessary to decide what cut-off distance would be implemented in our force field equations. Because periodic boundary conditions lead to “images” of all system particles, it is required that the cutoff distance for all forces be less than half of the box size, so that a particle cannot mathematically interact with its own “image.” The cutoff distance was chosen to be 9 Å, leading to a minimum box size in the x and y directions of 18 Å. Due to the stacking arrangement and bond distances in a Pt (111) layered structure, the x-y sizing is 19.204 Å x 19.406 Å. The sizing in the z-direction was chosen so as to allow for a sufficient region of bulk solution between the electrodes. To simulate a system with oppositely charged electrodes, enough bulk solution must be included so as to reach a region of neutral solution that is essentially unaffected by the presence of the electrodes [1,3,5,54,54]. To ensure that this bulk solution region was reached, we choose a z-direction length of 63 Å, corresponding to a length of 51.6 Å between the electrode surfaces. This box size also motivated the box size studied in LAMMPS simulations on aqueous sulfuric acid discussed previously, as the box was chosen to represent half of the occupied regions between the platinum surfaces (accounting for the ~2.5 Å between the metal and first layer of solution). All starting structures for the full electrochemical system were taken from a 6 ns simulation of aqueous H₂SO₄ carried out in LAMMPS. To use these structures in the new system, the boxes were doubled in the z-direction. This method allowed for a pre-equilibrated solution structure, which aided in computational efficiency because our LAMMPS simulations run over 100X faster than our ECD simulations.
Using this pre-equilibrated structure, we then carried out simulations of the acid/water/electrode system using our group code. Periodic boundary conditions were applied in all directions using a 3D Ewald summation for long range forces. A time step of 0.25 fs was imposed to allow the reactive bonds sufficiently fast updating. Before applying a potential across the electrodes, the system was run in a zero-charge system over a neutral electrode. The pre-equilibrated structure was started from a static state (no velocity on all particles). Metal atoms are fixed during the simulation, as movement of the electrode would not be expected. All simulations using charged electrodes were started from a structure obtained after 50 ps of simulation over a neutral electrode. We chose to analyze 6 different cases for charged systems; neutral, 0.8 V, 1.23 V, 4 V, 6 V, and 10 V. The 0.8 V and 1.23 V cases were chosen because they represent the typical operating potential and maximum theoretical voltage encountered in PEMFC’s. The latter three cases were chosen as extremes, which are not expected to be encountered in an actual PEMFC, to study the effect of very large electric fields.

For early times during the simulations, we monitored the distribution of solution species through the simulation box, charge density throughout the solution, and considered the charge on metal atoms. We expect, for runs with charged electrodes, to see a migration of charges toward their respective counter-electrodes, as well as a decrease in potential across the solution from one electrode to the other, as illustrated previously in Figure 1-1. We impose the potential difference between the layers at the ends of the simulation box, or the point at which the periodic boundary is defined normal to the electrode surface. In Figure 4-6, metal layers 1 and 7 are in contact with solution and metal layers 3 and 4 represent the far right side of our box and the far left side of our box, respectively, as seen in Figure 4-5. Platinum was shown to observe the expected behavior, in which metal layers show variation in charge due to nearby charges. Because the extreme potential difference is imposed between layers 3 and 4, a very negative and a very positive charge is
produced. The remaining layers alternate between positive and negative, giving the charge distribution shown in Figure 4-6.

![Figure 4-6: Average charges on metal layers in solution for a neutral run and a highly charged electrode case](image)

Despite the proper behavior shown in the electrode layers, structural data did not follow expected trends. For all cases, it would be expected for bisulfate anions to be attracted to the metal surfaces, and especially so in highly charged cases. Despite proving the charge on the metal atoms, there was no migration towards the electrodes in any of our simulations. This lack of migration can be seen when comparing density profiles for sulfur atoms in a simulation. The density profiles were generated from 47.25 ps time blocks. Figure 4-7 shows the sulfur atom density profile two separate time blocks for our most charged electrode case (10 V) averaged in the z-direction. Narrow peaks of high density indicate regions in which the atoms have little movement in the z-direction. Other peaks with a wider distribution indicate more mobile sulfate groups. In both time blocks, the sulfur atoms appear to be “locked” at a certain distance from the electrode, and cannot approach any closer. This sort of behavior may be reasonable in the case of
an adsorbed anion, but for an anion in bulk solution at a distance of ~10 Å from the electrode surface, the behavior is non-physical.

Figure 4-7: Sulfur density plots from different time blocks within a 10 V charged electrode simulation. Time block A: 40.5 – 87.75 ps. Time block B: 121.5 – 168.75 ps.

The behavior in Figure 4-7 led us to believe there was a force field coding error between the platinum electrode and sulfur atoms. Because the O₅ atoms had an identical interaction with platinum to that of the O₆ atoms, the problem was most likely in the Pt-S force field. To confirm that the problem existed between this pair, sulfate groups were forced closer to the surface. Two anionic sulfate groups were placed near the positive electrode, and one anion sulfate group was placed near the counter-electrode. In both cases the sulfate groups were placed outside of the first water layer, so as to not produce any undesired effects from an unstable surface structure. The new configuration was built using Materials Studio 4.6, to visually verify that no atoms were placed too close together and cause highly repulsive interaction behavior. All other run parameters remained the same, and the 10 V charged case was studied. After only a very brief simulation time (< 9 ps) it was seen that the sulfate groups had migrated away from both electrodes to the same distance seen in the peak locations in Figure 4-7. This test confirmed that
there was an unnatural repulsive behavior between the sulfate groups and electrode surfaces that needed to be corrected. Figure 4-8 shows snapshots of the initial simulation configuration (a) and the configuration that showed migration of sulfate groups away from the platinum surface (b). Platinum atoms have been removed from the image, however the positive electrode is to the left of solution and the negative electrode is to the right.

![Figure 4-8: Comparison of (a) initial configuration with sulfate groups forced towards the electrode surface, and (b) a 9ps snapshot showing migration away from both electrode surfaces.](image)

**Correcting the Pt/HSO₄⁻ force field interaction**

Motivated from the results seen in Figure 4-7 and Figure 4-8, a new force field was developed for platinum/bisulfate. A few initial coding errors were found in the development of the first interaction potential. The same QM data were used for force field fitting, and various potential forms were tested to determine the best description of the interaction. To minimize the mean-square error, a new interaction was simultaneously parameterized for Pt-O₅. Because a new
fitting was being used for Pt-O_S, it was unnecessary to fit sulfuric acid potentials for both the “strong” and “weak” water potentials. The potential form described in Equation 2-10 yielded the most accurate description for both interaction pairs, and their parameters are given in Table 4-4, and a comparison between the force field fitting and QM data is provided in Figure 4-9.

Table 4-4: Interaction parameters for final Pt-S and Pt-O_S interaction from Equation 2-10

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pt-S</th>
<th>Pt-O_S</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε (kcal/mol)</td>
<td>6.56</td>
<td>340.6</td>
</tr>
<tr>
<td>A (Å⁻¹)</td>
<td>0.651</td>
<td>1.382</td>
</tr>
<tr>
<td>r₀ (Å)</td>
<td>6.180</td>
<td>1.727</td>
</tr>
</tbody>
</table>

Figure 4-9: Comparison between MD and QM for the Pt/HSO₄⁻ energy for the final fitting

Simulation of an electrochemical interface

Using the revised force-field we fit to describe an electrochemical system, we have begun to simulate aqueous sulfuric acid between platinum electrodes. Due to the time limitations on this thesis, and the computational expense of the code, simulations have only been completed to 150 - 200 ps for all charged and uncharged simulation conditions. However, because the simulations
were started from equilibrated bulk structures, some information can be taken from these abbreviated run times. Additionally, in the original presentation of the ECD method, Wheeler’s simulation times were only 400 ps due to the computational expense of the code. Considering the shorter time steps required for a reactive water model, our run times are reasonable.

We showed previously that sulfuric acid tended to migrate away from the electrode surface very rapidly in our initial simulations. After developing the new interaction potential between sulfuric acid and platinum, this problem was resolved. A density profile of sulfur atoms as a function of distance away from the electrode surface is shown in Figure 4-10. This figure was developed using atomic coordinates between 54 – 101 ps in our most highly charged electrode case. Whereas previously we saw migration away from the electrode almost immediately, our current simulations show that the acid groups can maintain a close proximity to the electrode. To begin the simulation, two acid molecules were placed near the positive electrode and one acid molecule was placed near the negative electrode. Figure 4-10 shows that each acid finds an equilibrium-like position near each electrode at which the sulfur is less mobile. The wider peaks in solution are indicative of a more mobile bulk solution.
Performing the same density analysis on all species in solution gives the distribution of charges through the system. Poisson’s equation can be used to calculate the electric field from this distribution. The charge density distribution ($\rho$), according to Poisson’s equation, is the product of the second derivative of the charge density ($\varphi$) and the permittivity of the solution ($\varepsilon_o$). Equation 4-3 was used to determine the average potential in the Z-direction through solution for cases of different charge. This charge density distribution is due only to the electrolyte, and does not include the charges present in the electrode.

$$\nabla^2 \varphi = -\frac{\rho}{\varepsilon_o}$$  \hspace{1cm} \text{Equation 4-3}$$

This analysis is ongoing, in an effort to correctly define the integration constants, but the potential difference between electrodes and the variation in electric field with charge can be seen in Figure 4-11. Periodic oscillations in the z-direction are an artifact of the computational method. Because the z-length is greater than the x and y-lengths, the cutoff length in the Ewald summation must be adjusted in future simulations to dampen out these fluctuations. However, despite the presence of oscillating potential, the electric field can still be determined qualitatively.
Figure 4-11: Electric potential as a function of distance generated from Poisson’s equation for 3 different charged electrode cases (0 Å represent the surface of the positive electrode).

Because long simulation times are needed to see normal movement of the acid groups towards the electrode, there is no sufficient data to show the movement of SO₄ groups toward or away from either electrode. However, water does not require the same time scales to form ions near surfaces. Because water is the bulk species and is able to form ions through the movement of hydrogen bonds, an ionic analysis on the states of water shows a preference for ionic species to be located near their respective counter electrodes. We considered three forms for our ionic analysis. Two positive ions were considered, H⁺ and H₂O⁺, and one negative ion, OH⁻. To classify the existence of these species, cutoff distances were selected. The equilibrium distance for the O-H bond in water is 0.98 Å. A free proton, H⁺, was classified as a proton which was greater than 1.15 Å away from the nearest oxygen atom. A hydronium ion was classified as an oxygen atom with 3 hydrogen atoms within 1.115 Å. A shorter cutoff distance was chosen for the hydronium ion to differentiate truly cationic species from water molecules that were closely packed. Hydroxide anions were classified as oxygen atoms with only one neighboring hydrogen atom within 1.15 Å.
As stated, we began our simulations from a pre-equilibrated, bulk sulfuric acid solution. This solution had no positional dependence of ions in solution. To show this, the plots in Figure 4-12 show the number of instances of each water-derived ionic species. These data were taken from the first 4 ps of simulation in our 6 V charged electrode simulation. The time period considered is very short to demonstrate only the initial configuration with no effects from simulation. The x-axis denotes position through the box between electrodes, and the y-axis gives the number of times each configuration was found. There were 30 data snapshots considered, so numbers greater than 1 on the y-axis may refer to the same oxygen atom maintaining its configuration for multiple snapshots. Figure 4-12 shows that the instances of each water configuration were very low at the beginning of the simulation and, more importantly, that there was no positional bias to the location of ions in solution.

Figure 4-12: Distribution of water ions (H+, OH− and H2O+) through solution at the start of all simulations (taken from initial 30 snapshots of uncharged simulation).
After simulation, trends in the position of water-derived ions in solution were noticed. The positively charged ions have a preference to be located closer to the negative electrode (right hand side of the simulation box, and a higher z-coordinate), and the hydroxide ions tend toward the negative electrode. Figures 4-13 shows the same analysis as Figure 4-12 for the 6 V charged electrode case for the time period spanning 87.5 – 121.5 ps. The figures show a clear migration of charge toward counter electrodes in our electrochemical system.

Figure 4-13: Distribution of water ions (H⁺, OH⁻ and H₂O⁺) through solution during the 87.5 – 121.5 ps time block for the 6 V charged electrode simulation.

Application of an electric field has been shown to increase the dissociation of protons from sulfuric acid. Analysis of our systems has shown a similar trend thus far. For our 6 simulations, a different level of average sulfuric acid structure is observed. A similar analysis was
performed to find the average structure of sulfuric acid as was employed in classifying the ionic forms of water. A cutoff distance of 1.15 Å was chosen for the presence of a proton on an O$_3$ atom. Though longer simulation times are needed to confirm the results given here due to the time required for reactions to take place, trends show an increasing level of deprotonation from sulfuric acid with increased electrode potential. Table 4-5 summarizes the findings to this point.

All numbers given are in terms of the number of non-dissociated hydrogen atoms on each sulfuric acid cluster, using a cutoff distance of 1.15 Å.

Table 4-5: Statistical analysis of the proton dissociation from sulfuric acid in a charged environment. Averages given are the average number of protons bound to an SO$_4$ group during a 34 ps time block. A bond is defined as an O-S-H distance of less than 1.15 Å.

<table>
<thead>
<tr>
<th></th>
<th>0 V</th>
<th>0.8 V</th>
<th>1.23 V</th>
<th>4 V</th>
<th>6 V</th>
<th>10 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>1.377</td>
<td>1.266</td>
<td>1.110</td>
<td>1.249</td>
<td>1.241</td>
<td>0.982</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.215</td>
<td>0.198</td>
<td>0.185</td>
<td>0.189</td>
<td>0.180</td>
<td>0.178</td>
</tr>
<tr>
<td>Variance</td>
<td>0.554</td>
<td>0.471</td>
<td>0.413</td>
<td>0.429</td>
<td>0.390</td>
<td>0.378</td>
</tr>
</tbody>
</table>

All cases other than the 10 V simulation have an average sulfuric acid structure consisting of more than one proton per cluster. This finding contradicts what we saw from our radial distribution function analysis of sulfuric acid in bulk solution discussed in Chapter 3 of this thesis. The trend suggests that a greater number of protons are attached to a sulfate anion between electrodes than in our equilibrated bulk solution structure. A possible explanation is the higher level of dissociated water molecules in solution due to the presence of the electrodes. More free water-derived protons in solution may lead to a decrease in the ability of sulfuric acid protons to dissociate. However, longer simulation times are needed to confirm that this is a trend in the simulations and is not due to poor statistics.

For those protons that are bound to SO$_4$ groups, there is no clear trend in a positional dependence. We expect to simulate an electric field that is greater near the surface of the
electrodes, and less significant in bulk solution. This expectation, together with the knowledge that the application of an electric field leads to higher proton dissociation from sulfuric acid, would lead us to believe that the more deprotonated acid molecules would be nearer the positive surface. However, in analyzing the average coordination between O\textsubscript{S} atoms and hydrogen atoms throughout the simulation box, there is no clear trend which shows electric field dependence of proton dissociation. For the 10 V charged electrode case, we mapped the position of each O\textsubscript{S} atom, and the average number of protons to which it was bound for a 50 ps time block. The movement in the z-direction of O\textsubscript{S} atoms was no more than 3.5 Å for any atoms and it was neglected for graphical purposes. Figure 4-14 shows the average hydrogen coordination for each O\textsubscript{S} atom in the simulation. The positions plotted for each of the 48 atoms represent their positions at the end of the 50 ps time block. Though there is no clear trend in the bulk region, it does seem as if acid molecules closer to the positive electrode (left hand side of the figure) experience more deprotonation. The cluster about 10 Å represents 2 SO\textsubscript{4} groupings, and shows that the grouping spends the majority of the time block completely dissociated, with 1 O\textsubscript{S} atom protonated less than 25% of the time. There also seems to be less protonation on the right-most SO\textsubscript{4} group, which is nearest the negative electrode, but the data are less conclusive here.
Figure 4-14: Average number of H atoms bound to O₅ atoms as a function of distance for a 50 ps time block in the 10 V charged electrode simulation. Data are given as H atoms per O₅ atom. To determine the H atoms per S atom, the four O₅ atoms in a sulfate anion must be added.

Due to the different charge at each electrode surface, we also see a slight difference in the orientation of sulfuric acid at each platinum surface in charged systems. Near the positive electrode, sulfuric acid orients itself with three oxygen atoms pointing toward the surface, similarly to the preferred adsorption mechanism discussed earlier and seen in Figure 4-3. Because the oxygen atoms are negative and the core sulfur is positively charged, the orientation with 3 oxygen atoms towards the surface is electrostatically favored. At the negative electrode, the oxygen atoms are more repulsed from the surface, and they orient themselves farther away than at the positive electrode. This behavior, at both electrodes, is shown for the 10 V charged case in Figure 4-15, with a comparison to the uncharged electrode case. The top figure represents the 10 V charged electrode case. The 2 left-most SO₄ seem to prefer to have three oxygen atoms pointing towards the positive surface, whereas in the bottom image (uncharged) the same configuration is not seen. At the right-hand electrode, the top image shows clearly only one oxygen pointing toward the negative surface, with no straightforward conclusion drawn about the uncharged image.
Figure 4-15: Snapshot of SO$_4$ groups in solution for the 10 V charged electrode simulation (top) and uncharged electrode simulation (bottom) after 125 ps. In the charged electrode snapshot (top), the positive electrode is on the left and the negative electrode is on the right.

Though snapshots are not necessarily indicative of average simulation behavior, the O$_5$ density plots for each simulation seem to show the same trend over a time average of ~ 50 ps. These trends are difficult to ascertain solely from the density profiles, but together with the snapshot give the idea that charged electrodes force certain structural arrangements in sulfuric acid near the surface. We do not see the specific adsorption of anions demonstrated experimentally, but longer simulations times may allow for reorganization of surface layers to allow this adsorption to occur.

Figure 4-16 shows the density profiles for O$_5$ as a function of its z-coordinate for the same two cases explored in Figure 4-15. The peaks of note are the left-most and right-most peaks. In the charged electrode simulation, near the positive electrode (left), there are only two distinct peaks, suggesting a grouping of the oxygen atoms into two layers. The first of these distinct peaks is significantly wider, and is consistent with three oxygen atoms from each SO$_4$ group facing toward the surface. The next peak is much narrower, and is consistent with the one oxygen atom in the SO$_4$ group directed away from the surface.
Figure 4-16: O₃ distribution profiles for the 10 V charged electrode simulation (top) and the uncharged electrode simulation during a 50 ps time block.

The right-most grouping in the charged simulations’ density profile is consistent with the image of the SO₄ group with one oxygen atom directed toward the surface. There are three distinct peaks. The middle peak in this grouping is taller, and of a similar width to the peaks nearest to it, suggesting one oxygen atom is directed toward the surface, one oxygen atom is directed away from the surface, and two oxygen atoms share a plane nearly parallel to the surface. This orientation is consistent with the snapshot image seen in the right-most SO₄ group shown in the top figure of Figure 4-15.
These trends are not as distinct in the uncharged electrode case. Though similar arguments can be made for some of the structural features seen in the density profile for the uncharged electrode, there is no reason to assume an orientation was dictated by the electrode. Further simulations need to be carried out on the electrochemical system to validate the structural findings reported in this Chapter.

**Conclusions and future work**

In this thesis I have described the development of our atomistic modeling technique for electrochemical interfaces. The purpose of our work was to design a model capable of accurately predicting short range interactions at electrode surfaces and characterizing the resultant structure and electric field. The electrode/electrolyte interface plays a significant role in surface reaction kinetics impacting devices such as fuel cells, batteries and solar cells. We chose to study the cathode half-cell of the proton-exchange membrane fuel cell to determine what affects the interfacial structure can have on the oxygen reduction reaction kinetics.

We modeled aqueous sulfuric acid over a platinum (111) electrode surface as a first step towards modeling the aqueous behavior of Nafion in an electrochemical environment. We developed a novel modeling technique capable of describing aqueous sulfuric acid in a reactive manner over an electrode surface with atomistic resolution, as well as the capability to account for electronic polarizablity of the metal surface. We validated our aqueous acid model against previous *ab initio* molecular dynamics simulations of the same system.

Simulations of our full electrochemical systems have begun, and the initial results are promising. Currently, our method predicts some trends that would be expected of our system. We have seen migration of ions towards counter electrodes, and we observe proper trends in cell potential, with a decreasing electric field with distance away from the positive electrode.
Exposing aqueous sulfuric acid to an external electric field leads to more de-protonation of the acidic protons, which is a trend we have observed in our simulations with increased cell potential. Finally, we have observed changes in the interfacial structure in terms of the orientation of sulfuric acid groups near the electrode surface in the presence of an electric field.

To this point, we have proven that we are capable of modeling the chosen electrochemical system of interest using our developed modeling techniques. In the future, longer simulations must be performed to validate the results that have been discussed in this paper. The diffusion rate of sulfate groups is a problem which must be addressed. We have seen a certain level of sulfate movement in the bulk liquid away from the electrode surface, but the sulfate groups nearest the electrode surface are immobile in the Z-direction. These molecules maintain a fixed distance from the electrode surface in the second atomic layer. The lack of stronger molecular adsorption may be due to an over-predicted attraction of water molecules to the platinum surface. Analysis of the movement of species parallel to the surface may give insight as to the cause of this lack of movement in the Z-direction. Finally, with a solution to the value of the electric field from our charge distributions, we can classify the electric field quantitatively near the electrode surface, and analyze gas phase reaction energies to determine how the ORR kinetics are altered by the interfacial structures predicted by our MD simulations.
References


