Structure and Dynamics of Molecules at Water/Silica and Water/Carbon Dioxide Interfaces

DISSERTATION

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By

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The interface between silica and water is one of the most technologically relevant surfaces. An especially important aspect of this system is its inherent negative charges at most pH values, and the resulting electrokinetic phenomena that take place in the fluid region. We have constructed a realistic model for the charged silica/water interface where many of these standard models can be tested. The model allows for undissociated and dissociated silanol groups. We have also conducted ab initio MD simulations of a smaller system consisting of a hydrated silica slab. The comparison of the radial distribution functions from the ab initio MD simulations and those obtained from the empirical model are favorable. The hydrophobic and hydrophilic nature of silanol-poor and silanol-rich regions of the amorphous silica surface observed in our empirical model is reproduced in the ab initio MD simulations of the smaller slab. In the initial stages of our ab initio MD simulations, we observe various chemical processes that represent different hydroxylation mechanisms of the surface.

To explain why dynamical properties of an aqueous electrolyte near a charged surface seem to be governed by a surface charge less than the actual one, the canonical Stern model supposes an interfacial layer of ions and immobile fluid. However, large ion mobilities within the Stern layer are needed to reconcile the Stern model with surface conduction measurements. Modeling the aqueous electrolyte/amorphous silica interface at typical charge densities, a prototypical double layer system, the flow
velocity does not vanish until right at the surface. The Stern model is a good effective model away from the surface, but cannot be taken literally near the surface. Indeed, simulations show no ion mobility where water is immobile, nor is such mobility necessary since the surface conductivity in the simulations is comparable to experimental values. Our studies suggest a richer, microscopic picture that allows for much greater mobility near the surface without a sharp boundary between mobile fluid and immobile ion layer, but still accounts for observed phenomena. The effect of salt concentration, surface charge density (which would be controlled experimentally by varying the pH) and local water viscosity on electrokinetic phenomena is explored.

The structural properties of the interface between water and carbon dioxide are very important in many areas of chemistry and physics, such as supercritical extraction and the formation of ice clathrates. In my study, the structural properties of the interface of water and CO$_2$ are investigated by means of molecular dynamics (MD) simulations. Capillary wave theory is used to identify a smooth, long wavelength boundary between the water and carbon dioxide phases. Density profiles are accumulated relative to the underlying capillary wave surface. The density profiles of CO$_2$ and water are extracted based on capillary wave theory. The density profiles are very helpful to calculate the surface excess and check whether there is a wetting transition when the pressure is increased. Molecular orientations of water and CO$_2$ are calculated to give detailed information of the interface structure. Both water and CO$_2$ molecules near the interface prefer to lay parallel to the surface. The preferred orientational distribution of molecules near the surface gives rise to the surface potential which is calculated to better understand the electrodynamics of the interface.
Dedicated to the continuation of human civilization
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CHAPTER 1

Introduction

An interface is defined as the boundary between phases, as the name suggests. Another term surface, which is often used, has almost the same meaning of interface. However, “interface” is preferred for the boundary separating two condensed phases which are named explicitly, such as liquid-solid interface and “surface” is usually applied to the boundary between a condensed phase and gas or vacuum, such as solid surface.\textsuperscript{7,8} The interfaces are usually a few molecular diameters thick, but the density and composition change rapidly across the interface, which gives the interface very special properties. The behavior of the molecules at interfaces can be quite different from that in the bulk phase because the molecules in the bulk “feel” the uniform interactions with its neighboring species. These interactions will be no longer uniform at the interface. Instead the molecules at interface “feel” the presence of their adjacent units as shown in Figure 1.1. The unique nature of interfaces and the related phenomena were not well described by existing classical theories of matter at the time when Wolfgang Ostwald called surface science “the world of neglected dimensions”.\textsuperscript{9} Even with the latest advanced techniques for probing the interface region,\textsuperscript{10} there are still lots of issues not well understood. For example, how do the water molecules and
ions behave near a hydrophobic or hydrophilic solid surface? What is the molecular structure of water/vapor interface?

Figure 1.1: The net force acting on the unit (hollow sphere) in the interior of bulk phase will be zero as shown in (a). The net forces acting on the unit at the interface is unbalanced due to the finite extent of one phase in (b).

We begin with the investigation of the structure and dynamics of aqueous solution/amorphous silica interface. Silica is one of the most abundant materials on the earth and has been widely used in many areas in science and industry.\textsuperscript{11–15} We are interested in the amorphous silica surface because of its potential use in biomedical devices for biomolecule delivery. Silica is also considered to play an important role during the chemical processes leading to the appearance of life. We are also interested in fundamental electrochemistry near the amorphous silica surface. The Gouy-Chapman-Stern model has been used for almost 80 years in most textbooks and publications to describe the structure of charged surfaces. In this model, there is an immobile layer of solvent with ions stuck to the surface, which can explain why the observed electroosmotic flow is less than what the surface charge could predict,
as shown in Figure 1.2. The “plane of shear”, “shear plane”, “slip plane”, “surface of shear” etc. is where hydrodynamic stick (no-slip) boundary conditions are enforced. It is idealized the plane that divides stagnant from flowing fluid. But our results indicate that water close to the surface is more susceptible to flow than considered in virtually all treatments of the double layer. While other simulations have shown mobility near the surface, none have used that information to tackle the interpretation of the Stern layer as we do.

Figure 1.2: Picture of the Gouy-Chapman-Stern model. The solid surface is negatively charged (blue curve for the surface charge distribution on the bottom-left plot). The line in the left picture shows the boundary between the Stern and diffuse layer. In the right picture, the fluid velocity approaches zero at the no-slip boundary.

Below are figures taken from review articles by, left to right, Schoch, Han and Renaud,16 Yuan, Garcia, Lopez and Petsev,17 and Delgado, Gonzalez-Caballero, Hunter, Koopal and Lyklema.18 One can see the “slip plane” or “shear plane” pushed out from the surface by one or several ion diameters. These articles are taken from the
recent physics (Rev. Mod. Phys., 2008), analytical chemistry (Electrophoresis, 2007), and colloid science (J. Colloid Int. Sci., 2007) literature, respectively. In two of the three figures, the slip or shear plane lies beyond the outer Helmholtz plane, the latter being the start of the diffuse layer.

Well-known and respected text books provide similar depictions of the Stern layer. Shown below, left to right, are figures from Adamson and Gast’s Physical Chemistry of Surfaces19 (1997), volume 2A of Bockris, Reddy and Gamboa-Aldeco’s Electrochemistry20 (2001), and Probstein’s Physicochemical Hydrodynamics21 (1994).

Again, the shear plane is one, and more often several, ion or water diameters from the surface. Other, more recent, texts are quite similar in their description of the Stern layer.22–25 A few sources also point out that the “plane of shear” or “slip plane” is an idealization in which the viscosity is assumed to fall from essentially infinity to its bulk value over a vanishingly short distance.26,27 Since, as Hunter puts it, this transition is believed to occur over a distance that is small compared to the diameter of a water molecule,28 this idealization is generally considered to be acceptable.
In the figure shown on the left of the next page, Lyklema\textsuperscript{29} draws the viscosity (top left) and fluid velocity (bottom left) expected for a stagnant layer with a rounded transition in $du/dz$ based on the viscoelectric theory of Lyklema and Overbeek\textsuperscript{26}. The corresponding quantities for the normal “plane of shear” picture are shown on the right in Lyklema’s figure. In Lyklema’s plot, the wall is moving and the asymptotic fluid is stationary, unlike any of the other figures here, so the reader needs to reflect the velocity profiles about a horizontal line to compare with all the other figures here. It is worth noting the Lyklema, Rovillard, and De Coninck\textsuperscript{30} eventually pronounced the viscoelectric theory, on which this figure is based, “not entirely adequate” because they came to a different conclusion about the origin of a presumed stagnant fluid layer near a charged surface.

Bazant \textit{et al.} propose that there might not be a stagnant layer at all for low surface charge (top of figure, below right), while a rounded profile similar to Lyklema’s (after it is flipped) would be observed at higher surface charges (bottom of figure, below right).\textsuperscript{27} The stagnant layer several molecular diameters thick drawn by Bazant \textit{et al.} is not what we observe in simulations which are rather high surface charge, nor is it seen in other simulations. Nevertheless, the two depictions given below is certainly more realistic than most others, and should be revised as more theory and experiment become available.

We believe that these authors are certainly on the right track, although further revision is needed. Furthermore, none of these authors (especially Lyklema) question the dynamic Stern model. Much still needs to be carefully considered. How sharp the transition is from stagnant to flowing, and whether such a stagnant layer is present at all, are separate issues. The degree of stagnancy can be overestimated because the
rise in viscosity at the surface tends to be more impressive than the fall in the flow velocity.\textsuperscript{31,32}

Our group has successfully constructed a realistic model for water/undissociated amorphous silica surface.\textsuperscript{33,34} The model was extended to treat the dissociated silanol groups on the surface. The model development and evaluation are described in chapter 2. Our model is used in molecular dynamics simulations on the aqueous solution/amorphous silica interface and the results of the model with regard to electrochemistry and electrokinetic phenomena are reported in chapter 3. Our results show that the solvent adjacent to the charged surface is not immobile, as shown in Figure 1.3. The classical view of the Stern model is challenged by our simulation results. We also investigate the increased viscosity of the solvent near the surface. In order to get the accurate prediction of the electroosmotic flow by Navier-Stokes equation, an inhomogeneous viscosity formula must be used.

Finally, we have studied the structure of water/CO\textsubscript{2} interface and the results are reported in chapter 4. Besides the fundamental scientific issues that make the
Figure 1.3: Water and Na\textsuperscript{+} density profiles and their velocity profiles.

water/CO\textsubscript{2} interface interesting, the characterization of the interface region is of importance in a variety of technological processes. CO\textsubscript{2} is perhaps the most famous gas in the world now because of its global warming effect. To reduce the CO\textsubscript{2} concentration in the atmosphere, CO\textsubscript{2} capture and storage are receiving wide concerns. Deep sea storage is one of the most attractive ways to store CO\textsubscript{2} since a stable clathrate hydrate forms in deep sea where CO\textsubscript{2} molecules are captured in the cage formed by water molecules.\textsuperscript{35–37} But there are concerns over the long term storage integrity of this approach because there might be CO\textsubscript{2} leakage from deep sea.\textsuperscript{37} In fact, the
interaction between CO$_2$ and water molecules and the structure of the interface between these two species play essential roles in the stability of the clathrate hydrate. On the other hand, CO$_2$ has been regarded as the potential substitute of the toxic organic solvents in separation processes and chemical reactions.$^{38}$ For example, supercritical CO$_2$ was used to extract the solute components from ionic liquids mixtures with little pollution and contamination. We have obtained the intrinsic structure of the water/CO$_2$ interface by accumulating number and orientational distribution relative to the capillary wave surface. The capillary wave surface is the surface that characterizes long wavelength interface fluctuations, and its properties depend on system size. Accumulating properties relative to the capillary wave surface removes the system size dependence. The wave-like interface is observed and density profiles are found to be more structured relative to capillary wave surface. Our results show that both water and CO$_2$ molecules have orientational preference at the interface. The surface potential of water is also calculated which is helpful in understanding the ion transport across the interface and the interfacial reactivity.
CHAPTER 2

The dissociated amorphous silica surface: Model development and evaluation

2.1 Introduction

Interfaces between amorphous silica and water are ubiquitous in chemical, biochemical and environmental settings.\textsuperscript{39,40} The strong interactions between silica, water, and adsorbates, such as biomolecules,\textsuperscript{41} make the amorphous silica surface an important and challenging system to model. These strong interactions between silica and analytes are often exploited in chromatographic applications.\textsuperscript{42,43} The interaction of silica and biomolecules is important in several arenas. Silica-DNA interactions are the basis of a standard purification scheme for nucleic acids,\textsuperscript{44,45} and novel microfabricated device applications.\textsuperscript{46,47} There has been recent interest in using silica nanochannels to stretch and sequence DNA.\textsuperscript{48,49} Silicates and silica exhibit widely varying health effects, with considerable effort devoted to elucidating mechanisms of toxicity.\textsuperscript{41,50} The importance of biomolecules at the water-silica interface in a variety of situations has prompted a number of fundamental investigations of the interactions of silica with nucleic acids\textsuperscript{51–57} and proteins.\textsuperscript{58–61} In addition to devices fabricated from silica, the amorphous silica-water interface is important in silicon-based devices.
where silicon acquires an oxide coating in contact with aqueous solution.\textsuperscript{62,63} At all but the lowest pH values, a silica surface in contact with water is negatively charged. Electrochemical and electrokinetic function of numerous practical devices depends not only on the overall surface charge, but also on the detailed microscopic properties of the silica-water interface. This is because the driving force for electroosmotic flow (EOF), even in fluidic channels of large dimension, originates in the electric double layer,\textsuperscript{1} the region of excess charge in the fluid that compensates the surface charge. Most of the excess charge of the double layer is typically located within a nanometer from the surface. There is a need for interaction potential models that can describe this region with some realism, and yet will be tractable for simulations that cover large spatial and time scales.

Recently our group has developed a model for the undissociated amorphous silica interface.\textsuperscript{33,34,64} In this chapter an extension to that model to include dissociated silanol groups on the surface will be described. The negative charge that develops at the water-silica interface arises from the deprotonation of silanol groups. As one illustration of the applications of this work, we have recently applied the model described herein, to study electrokinetic phenomena.\textsuperscript{65} Using non-equilibrium MD simulations of aqueous solvent containing Na\textsuperscript{+} and Cl\textsuperscript{−} ions near a realistically modeled surface, the classical Gouy-Chapman-Stern model\textsuperscript{66–69} and the dynamic Stern layer model,\textsuperscript{70–78} used extensively to account for surface ion conduction will be critically evaluated in Chapter 3. The heat of immersion calculated with our model for the undissociated surface is in good agreement with available experimental data.\textsuperscript{34} Silanol densities typical of common silica materials naturally arose in our annealing and hydroxylating procedure.\textsuperscript{34} Further calibration of the accuracy of this model, as extended in
this work, is supplied in the form of comparisons with *ab initio* molecular dynamics (AIMD) simulations.

Feuston and Garofalini\textsuperscript{79,80} have developed an impressive model for the water-amorphous silica interface. In their model, which has been applied and extended,\textsuperscript{81–84} the silicon, oxygen and hydrogen atoms are not fixed to any molecular unit such as a silanol or water group, but instead can spatially evolve over the course of the simulation based on the interaction potential. Garofalini and co-workers have recently developed an improved dissociative water potential for molecular dynamics simulations,\textsuperscript{85} and have applied it to study the chemisorption of water on silica surfaces yielding important insights into the surface chemistry of water near silica.\textsuperscript{83,84,86,87} To our knowledge, the applicability of this model to dissociated silica surfaces has not been assessed. Rustad and Hay\textsuperscript{88} have also developed a dissociated model that yields reasonable acid dissociation energies for orthosilicic acid in the gas and aqueous phase. The applicability of this model for very large scale simulations needed for device applications is however limited.

Schulten and co-workers\textsuperscript{89} have quite recently developed an empirical potential for the water-amorphous silica interface. Their model is exclusively for water interacting with a rigid silica prepared using other models. Their intended fitting procedure was to choose interaction parameters to match the water contact angle reported for quartz surface as a function of the degree of hydroxylation.\textsuperscript{90} The parameters for their surface without silanol groups were adjusted to reproduce the water contact angle for the corresponding quartz surface. However, Schulten and co-workers report that their model could not reproduce the experimental contacts angles of Lamb and Furlong\textsuperscript{90} for any finite degree of hydroxylation. However, contact angle measurements at low degrees of
hydroxylation are difficult because the dehydroxylated surface rapidly reacts with water, and other measurements report very different contact angles for dehydroxylated silica. Jenkins and co-workers simulated amorphous silica nanoparticles in water starting with initial configurations obtained from DMOL calculations. Then the simulation was continued using empirical potentials from the OPLS-AA force field and borrowed from a simulation of the quartz surface. Puibasset and Pelenq have modeled the adsorption of water in mesoporous silica from sub-monolayer coverage to saturation pressures using grand canonical Monte Carlo simulations. Treatment of quartz surfaces involves similar atom types, but compared to silica is considerably simplified by the regularity of the quartz surface. MacKerell and co-workers have developed a model for the quartz-water interface which is not designed to characterize dissociated silanol groups. Freund, and Qiao and Aluru have studied electrokinetic transport in electrokinetic channels where the negative charge is distributed on Lennard-Jones wall particles. In these simple models, the heterogeneity and surface roughness are not captured. Aluru and co-workers have also performed similar studies for the interface between water and a more realistic, electrically neutral quartz surface. Lorenz et al. have employed a modified version of the silica-water potential developed by Schulten and co-workers to study charge inversion in the presence of divalent cations and electrokinetic phenomena associated with mono- and divalent cations.

In addition to developing an empirical potential, we have used ab initio molecular dynamics (AIMD) simulations in this work, to test several features of our empirical model, including the strong variability in relative hydrophobicity/hydrophilicity with surface silanol density reported in our earlier work. The physisorption and
chemisorption of small numbers of water molecules near silica has also been examined previously by *ab initio* methods. Physisorption has been studied using quantum chemical fragment calculations by Saengsawang *et al.*\textsuperscript{109} Cheng *et al.* studied the reaction of an SiO$_2$ molecule in a cluster with up to six water molecules.\textsuperscript{110} Sutton and co-workers have studied the hydroxylation mechanisms of different silica clusters with *ab initio* optimization methods using DFT.\textsuperscript{111} These calculations shed important insight into the activation barriers for chemical reactions between water molecules and silica clusters, although thermal effects are not included in these calculations.\textsuperscript{111} Similar types of calculations have recently been performed by Konečný and Doren\textsuperscript{112} and Ugliengo and co-workers.\textsuperscript{113} With an eye toward dissolution of silica, Criscenti *et al* studied the reaction of a silanol-containing cluster with a hydronium ion in the presence of four water molecules.\textsuperscript{114} Ma *et al.*\textsuperscript{11} have conducted *ab initio* MD simulations of water near different defects found in silica clusters and find that several waters are needed for the hydroxylation mechanisms they observe. More recently Hamad, and Bromley\textsuperscript{115} have conducted longer thermal *ab initio* simulations to study the hydroxylation mechanisms of non-bridging oxygens (NBO’s) in small silica clusters. These results suggest that the NBO’s are a negatively charged, closed-shell species, whose hydroxylation is quite sensitive to the surface morphology. Du *et al.* have investigated the reaction of one or two water molecules with an amorphous silica surface using QM/MM techniques,\textsuperscript{116} yielding information about the initial steps of silica surface hydroxylation. *Ab initio* molecular dynamics have been used to study the reactions of water with the amorphous silica surface by Miasini and Bernasconi\textsuperscript{117} and Mischler *et al.*,\textsuperscript{118} and the pKa of silanol groups on crystalline silica surfaces by Leung *et al.*\textsuperscript{119} Tielens *et al.*\textsuperscript{120} initiated an AIMD simulation of a hydroxylated silica slab
using a starting point from Garofalini’s empirical potential models, and studied the
surface structure, making detailed comparisons with experiment. They calculated
the deprotonation energy of silanol groups and the binding energy of individual water
molecules. Trilocca and Cormack have reported AIMD studies of liquid water near the
related water-bioglass interface\textsuperscript{121} and Leung \textit{et al.} have reconstructed the bonding
arrangement on crystalline silicate surfaces to mimic the amorphous surface.\textsuperscript{119} To
our knowledge, \textit{ab initio} molecular dynamics of the amorphous silica-water interface,
along the lines of what we provide in section 2.3, have not been reported.

We have performed AIMD simulations on a small hydrated silica slab in which
one surface does not contain silanols and the other surface contains several silanols,
one of which is dissociated. The relative wetting properties of silanol-rich and silanol-
poor regions is confirmed, although the AIMD system was too small to quantitatively
compare radial density distributions. We also compared AIMD and empirical results
for a single orthosilicic acid molecule in water. Our potential was not designed to fit
the properties of orthosilicic acid, but at least the comparison is much more direct
because the size of the silicate system is not an issue. We find that the number
of waters in the first and second solvent shells compares well for orthosilicic acid,
although the radial densities of waters surrounding the silanol groups of orthosilicic
acid are more structured in the AIMD simulations. A direct comparison between
AIMD and empirical potential results is clouded by several factors. The empirical
potential simulations of a silica surface encompass much more surface variability
than the smaller, AIMD system. A further limit on our ability to benchmark our
empirical potential with AIMD is the limitation on the accuracy of currently available
density functionals and the numerical methods available for their implementation.
The BLYP\textsuperscript{122,123} and PBE\textsuperscript{124} functionals, as normally implemented, lead to over-structuring of the water, peaks in the radial distribution function of liquid water that are too high and narrow, and under-estimate the diffusion constant.\textsuperscript{125–127} The degree of over-structuring is sensitive to the details of the implementation, and system size.\textsuperscript{127} Lee and Tuckerman have shown that very accurate basis sets are needed to converge liquid state properties,\textsuperscript{128,129} including the diffusion constant.\textsuperscript{130} Exceptionally large charge-density cut-offs are needed to obtain a converged water density.\textsuperscript{131}

In section 2.2 we describe the potential form that is used to model our interface between the dissociated silica surface, water and salt. Within this section we provide all the parameters of the model for the use of interested readers. We also compare the quality of our empirical potentials to the \textit{ab initio} quantum chemistry cluster calculations that are used to generate our potentials. A comparison of some properties from the \textit{ab initio} MD simulations on the smaller system to those predicted from our empirical model are reported in section 2.3. We also describe specific chemical events that occur during the first few picoseconds of our AIMD simulations. Finally we end with a conclusion in section 2.4.

2.2 Development of a model for dissociated amorphous silica

2.2.1 Formulation of the potential

Our goal is to model the amorphous silica/water interface using a computationally inexpensive model with sufficient realism to capture essential features of the electrical double layer, electrokinetic phenomena and adsorbate binding. These phenomena require simulations that extend to large spatial and temporal scales. Models that can describe surface chemistry, either so-called dissociating potentials\textsuperscript{79–81,88,132–134}
or AIMD methods, are extremely valuable, but they are not sufficiently tractable for
the large-scale calculations we envision. The chemical bond structure will be fixed
in the model we propose, although the surface is not constrained to be rigid. For
example, the equilibrium between undissociated and dissociated silanols will not be
dynamic. For many purposes, the effects of the chemically diverse features of the
silica surface can be captured by a distribution of various species on a surface of
sufficient size, or a collection of different surface realizations.\textsuperscript{135}

Like our empirical potential for the undissociated amorphous silica surface,\textsuperscript{33,34} our
model for the hydrated dissociated amorphous silica surface extends the BKS model
for bulk silica\textsuperscript{136} and SPC/E model for water\textsuperscript{137} to describe the water-silica interface.
Hence the bulk silica and water regions are described by models that have been
tested in a variety of physical situations. The BKS and SPC/E potentials succeed
in describing physical properties of silicates, both crystalline and amorphous, and
water, respectively, but they also have limitations. Among the limitations, especially
for the BKS model, is unrealistically large partial charges, which are in place to
mimic other physical effects. Concern about the large partial charges was a major
motivation for us to compare with AIMD results. The simplicity of these models is
both a virtue and limitation: a virtue in the sense that large-scale simulations are
possible, but a limitation in that, even with the extensions put in place for surface
species, the functional form cannot fit all the available data obtained in fragment \textit{ab
initio} calculations.

In keeping with the BKS model,\textsuperscript{136} all silicon and oxygen atoms of the silica are
assigned charges of $+2.4$ and $-1.2$. The BKS potential is a sum of pair-wise Coulomb
and Buckingham (exponential repulsion $+r^{-6}$ attraction) interactions. In order to
avoid excessive overall attraction between water and our undissociated silica surface, we found it necessary to distinguish between silanol type and siloxane type oxygens, for the short range potentials.\textsuperscript{33,34} As shown before, an acceptable fit to \textit{ab initio} data could be achieved with these fixed charges\textsuperscript{34} for the water-silanol clusters. Charge neutrality of the undissociated surface requires that the charge on hydrogen atoms be $+0.6$. We have added a dissociated oxygen type, $O^{-}$ to include dissociated groups on the surface. The charge of the $O^{-}$ group was required to have a value of $-1.6$ to maintain a charge of $-1$ for each dissociated silanol generated in our simulations.

Without adjusting the charge on silicon atoms, the partial charges on silanol oxygen and hydrogen could be adjusted away from their BKS values of $-1.2$ and $+0.6$, respectively, as long as their sum is kept at $-0.6$, required to maintain charge neutrality of the undissociated surface.\textsuperscript{34} Further adjustment of the silanol group partial charges, or modification of the $O^{-}$ charge, would require distinguishing surface silicon atoms with charges different from interior silicons. However, retaining the BKS charges for all atoms greatly simplifies the construction of the hydroxylated amorphous silica (section 2.3.2) because the atoms that will eventually anneal to surface positions after cleavage of pure silica are not known in advance. Furthermore it should be noted that it is the sum of the Coulomb and short range interactions (Buckingham or Lennard-Jones) that is ultimately fit to \textit{ab initio} quantum chemistry calculations. While realistic partial charges are desirable, it is possible to compensate the unrealistic BKS partial charges with other parts of the complete interaction potential.

As mentioned above, our potential is designed to maintain a given bonded configuration, and not to predict making or breaking of chemical bonds. In some cases, the model has to be extended to prevent unintentional, and sometimes unphysical,
bond formation driven by strong Coulomb interactions. Our potential for the undisassociated surface included 3-body components that prevented the hydrogen atoms of silanols from binding to more than one oxygen atom.\textsuperscript{34} We refer to these components as “blocking potentials”. After the introduction of O\textsuperscript{−} groups, thermal simulations without the additional blocking potentials yielded species where the dissociated oxygen group (O\textsuperscript{−}) formed new bonds, either bonding to more than one silicon, mimicking a newly formed siloxane bond, or forming another (unphysical) species where the dissociated oxygen is divally bonded to a silanol hydrogen and a silicon atom.

We introduced two blocking potentials in addition to those used for the undisassociated surface, given below in Eqs. (2.1) and (2.2), which stabilized the chemical bond structure.

\begin{align*}
    u_{\text{SiO}_D\text{Si}}(r_{\text{SiO}_D}, r_{\text{O}_D\text{Si}}) &= k \exp \left[ -\rho^{-4}(r_{\text{SiO}_D}^4 + r_{\text{O}_D\text{Si}}^4) \right] \quad (2.1) \\
    u_{\text{SiO}_D\text{H}}(r_{\text{SiO}_D}, r_{\text{O}_D\text{H}}) &= k \exp \left[ -\rho^{-4}(r_{\text{SiO}_D}^4 + r_{\text{O}_D\text{H}}^4) \right] \quad (2.2)
\end{align*}

Eq. (2.1) is a 3-body interaction between the O\textsuperscript{−} of a dissociated silanol group (O\textsubscript{D}) and two Si atoms (Si, Si\textsuperscript{′}). Eq. (2.2) is a similar potential involving a Si atom, O\textsuperscript{−}, and the hydrogen of a nearby silanol group. The values of $k$ and $\rho$ in Eqs. (2.1-2.2), which control the strength and range, respectively, of the 3-body blocking potentials are given in Table 2.1.

Since the BKS potential\textsuperscript{136} consists of Buckingham potentials between the oxygen atoms, we also included three other Buckingham interaction potentials between each pair of O\textsuperscript{−} groups, a silanol oxygen and O\textsuperscript{−} group, and finally an O\textsuperscript{−} and siloxane oxygen. The total silica interaction potential including dissociated groups on the
surface is now of the following form,

\[ U = U_{\text{pair}} + U_{3-\text{body}} \]  \hspace{1cm} (2.3)

\[ U_{\text{pair}} = \sum_{i=2}^{N} \sum_{j=1}^{N-1} \left( \frac{q_i q_j}{r_{ij}} + u_{ij}(r_{ij}) \right) \]  \hspace{1cm} (2.4)

While Buckingham potentials are often used to describe inorganic solids like silica, Lennard-Jones potentials

\[ u_{\text{LJ}}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]  \hspace{1cm} (2.5)

are commonly used for water, as for SPC/E, ions in water, and biomolecules. Since we need to interface with common force fields, we employed Lennard-Jones potentials, denoted by the symbol “LJ”, for the salt, water and silica interactions described below. The procedure used to fit the potentials and the quality of fits are described in the following section. The Lennard-Jones potential parameters are collected in Table 2.3.

In Table 2.2 the parameters \( A, \rho \) and \( C_6 \) are obtained by fitting the \textit{ab initio} data to a Buckingham potential of the form,

\[ u_{B}(r) = A e^{-r/\rho} - \frac{C_6}{r^6} \]  \hspace{1cm} (2.6)

The Buckingham potential as shown in Eq. 2.6 has an unphysical maximum at small \( r \), and then plunges to \(-\infty\) at even smaller \( r \). It is thus standard to modify the Buckingham potential to eliminate the unphysical maximum and make it smoothly repulsive at small \( r \). Details of the small \( r \) patch is described in our previous work.\textsuperscript{34}

For the convenience of those wishing to use the potentials, the final parameters forming the interaction potentials \( U_{\text{pair}} \) and \( U_{3-\text{body}} \) for the extension of our undisassociated surface, are collected in Tables 2.2, 2.1 and 2.3. Readers are referred to our
previous work for the other interaction parameters that were unchanged in modeling the dissociated surface. In the tables, the subscript “X” refers to oxygen types that are not connected to hydrogens but different from dissociated types (i.e. O\(^-\)), the subscript “D” refers to oxygen types that are dissociated, and the subscript “H” refers to oxygens that are part of silanol OH groups.

\[\begin{array}{|c|c|c|}
\hline
\text{Atom Triplet} & k(eV) & \rho(A) \\
\hline
\text{Si-O\(_D\)-Si} & 1000.000 & 1.6 \\
\text{Si-O\(_D\)-H} & 100.0000 & 1.6 \\
\hline
\end{array}\]

Table 2.1: Interactions parameters for the 3-body potentials, Eqs. (2.1,2.2).

\[\begin{array}{|c|c|c|c|}
\hline
\text{atom pair} & A(eV) & \rho(A) & C_6(eVÅ^6) \\
\hline
\text{Si-O\(_D\)} & 13536.40 & 0.219247 & 128.344 \\
\text{O\(_D\)-O\(_D\)} & 1388.773 & 0.3623188 & 175.0000 \\
\text{O\(_D\)-H} & 5907.000 & 0.1254160 & 0.000000 \\
\text{O\(_D\)-O\(_W\)} & 6533.490 & 0.284692 & 336.7540 \\
\text{O\(_D\)-H\(_W\)} & 70.79500 & 0.306200 & 0.000000 \\
\text{Na\(^+\)-O\(_H\)} & 5151.600 & 0.2725004 & 60.44529 \\
\text{Na\(^+\)-O\(_X\)} & 5151.600 & 0.2763590 & 60.00000 \\
\text{Na\(^+\)-O\(_D\)} & 40286.40 & 0.2133588 & 70.40000 \\
\hline
\end{array}\]

Table 2.2: Pairwise potential Buckingham parameters

### 2.2.2 Parameter adjustment to match \textit{ab initio} data

Using fragments excised from a silica surface, \textit{ab initio} quantum mechanical calculations were performed from which we fit our empirical potentials. As in our previous work,\(^{34}\) the parameters of empirical potentials are adjusted to match \textit{ab initio} data.
### Table 2.3: Pairwise potential Leonard Jones parameters

<table>
<thead>
<tr>
<th>ion/atom pair</th>
<th>$\epsilon$ (eV)</th>
<th>$\sigma$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$-O$_W$</td>
<td>0.005406</td>
<td>2.8760000</td>
</tr>
<tr>
<td>Cl$^-$-Si</td>
<td>0.010823</td>
<td>3.8805759</td>
</tr>
<tr>
<td>Cl$^-$-O$_W$</td>
<td>0.005406</td>
<td>3.7840000</td>
</tr>
<tr>
<td>Cl$^-$-Na$^+$</td>
<td>0.004336</td>
<td>3.4920000</td>
</tr>
<tr>
<td>Cl$^-$-H</td>
<td>0.006378</td>
<td>3.6253307</td>
</tr>
</tbody>
</table>

generated for coordinate grids. This section is devoted to describing the quality of the match between our empirical potentials and *ab initio* data. The Born-Oppenheimer energy surface was obtained using MP2 perturbation theory$^{138-142}$ to account for electron correlation. We use the 6-311++G** basis set and all electronic structure calculations were performed using Gaussian03.$^{143}$

**Dissociated groups**

Figure 2.1: Fitted (solid line) vs. *ab initio* energies (solid black circles) for b) Si–O$^-$ stretch for fragment shown in a).
The potential for the dissociated groups Si–O\textsuperscript{−} consists of a single Si–O\textsuperscript{−} Buckingham plus Coulomb interactions. The Si–O\textsuperscript{−} distance in the fragment shown in Fig. 2.1a is varied between 0.7Å and 4.0Å, and the resulting energies used to fit the Buckingham potential form. The quality of the fit for the Si–O\textsuperscript{−} stretch is shown in Fig. 2.1b.

As indicated earlier, we found that thermal simulations without blocking potentials yielded configurations as seen in the left panel Figure 2.2 where an O\textsuperscript{−} is diva-
lently bonded to two silicons.

![Figure 2.2: Left panel shows the formation of a 2-membered ring involving a disso-
ociated oxygen that is divalentlly bonded to two silicons. The dotted white arrow points in both cases to the dissociated oxygen involved in the interaction. In the right panel, the dotted yellow arrow shows the hydrogen that originates from a one of the hydroxyl groups of a geminal silanol pair, which are attached to the same silicon atom.](image)

We also found that the hydrogens of silanol oxygens can transfer to dissociated oxygens during the simulations as seen in the right panel of Figure 2.2. In this defect, the hydrogen on the dissociated oxygen group originated via the deprotonation of
the silanol oxygen shown in translucent red. Our model is not intended to capture realistic deprotonation and protonation of oxygen species on the surface. In order to prevent new chemical structures from forming on the surface, we inserted three-body blocking potentials as described in Eqs. (2.1) and (2.2). These were not fit to \textit{ab initio} data. Instead, the parameters were adjusted by trial and error until these defects no longer occurred. Our potential form also includes the BKS Buckingham potential between the dissociated oxygen type and all other oxygens and silicons of the silica to ensure that the surface bond structure remains intact.

**Water-dissociated silica interactions**

![Figure 2.3: Paths of approach for water near a dissociated silanol](image)

The water-dissociated silica potentials were fit using a path of approach for a water molecule near a dissociated group shown in the left panel of Figure 2.3. The water-dissociated oxygen separation was varied from 1.8Å to approximately 13Å to obtain a comprehensive sweep of the potential energy surface. The water geometry
was fixed to that of the SPC/E model, and not allowed to relax as it approached the dissociated silanol. This scheme is similar to our design of a potential between water and undissociated silanols, for which the reader is referred to our previous work.\textsuperscript{33,34}

In most common water-water and water-ion potentials, only the water oxygen carries a non-Coulombic interaction, like a Lennard-Jones potential. The potential surface for these common water potentials contains basins where the potential diverges to $-\infty$ when a hydrogen is superimposed on an oxygen. These unphysical regions are never discovered in simulations. However, the dissociated silanol oxygen carries a large negative charge and the attractive Coulomb infinity was discovered in preliminary simulations. We found it necessary to include an exponential repulsive Buckingham between the dissociated oxygen and water hydrogen ($O_D-H_W$ potential).

In order to test the transferability of our water-dissociated silica potential to another path of approach, a water molecule was brought toward a dissociated oxygen shown in the right panel of Fig. 2.3. \textit{Ab initio} calculations indicate that path 1 (Fig. 2.3) is the more favorable path for approach of a water to a dissociated silanol. We were not successful in reproducing this feature in our empirical potential using the available flexibility in the Buckingham + Coulomb form of our potential, together with the many constraints on partial charges (BKS charges for silica Si and O, SPC/E charges for $H_W$ and $O_W$). Fig. 2.4 shows all the \textit{ab initio} energies for the two paths of approach, and the predictions of our empirical potential for each of these paths. Rather than “split the difference”, we chose to fit the \textit{ab initio} results along path 1 because preliminary simulations indicated that the binding geometry of path 1 was the preferred, even when the most stable orientation of an isolated water was the
Figure 2.4: Fitted (solid line) vs. *ab initio* (filled symbols) energies for the paths of approach shown in Fig. 2.3. On the left are path 1 energies and on the right path 2 energies.

bifurcated structure of path 2. This tendency is confirmed for the final form of the potential. Fig. 2.5 shows the distribution of the angle between the vectors $O_W-O_D$ and $O_W-H_W$ for waters within 3.5Å of each $O^-$ group on the dissociated surface. These results show that in the thermalized simulations the cosine of the angle of one of the two water hydrogens is close to 1, and hence path 1 is the most likely orientation on the surface despite the fact that our empirical potential predicts a higher binding energy for a single water molecule along path 2. In Fig. 2.5 there is a second peak near $\cos \theta = -\frac{1}{3}$ for the hydrogen not hydrogen bonding to the dissociated oxygen. The inset in Fig. 2.5 reveals a very small peak corresponding to the bifurcated structure.
Figure 2.5: Orientational distribution of water near dissociated oxygens. The distribution is given for the dot product between unit vectors linking water oxygens to a dissociated surface oxygen (O\textsubscript{W}-O\textsubscript{D}) within a distance of 3.5 Å, and vectors along each of the two hydrogen bonds. The data confirms that in the thermal simulations, path 1 (Fig. 2.3) is favored over path 2. Inset shows a small peak near the cosine of half the tetrahedral angle, the angle of the bifurcated structure of path 2.

Na\textsuperscript{+} and Cl\textsuperscript{−} silica and water interactions

Initial simulations indicated that the Na\textsuperscript{+} ions can strongly interact not only with dissociated silanols, but also silanol and siloxane oxygens. For this reason we selected fragments from our simulations with and without a dissociated silanol, where a Na\textsuperscript{+} ion interacts with all species in order to generate empirical potentials for these interactions.

Shown in Fig. 2.6 are the three fragments that were used for the \textit{ab initio} calculations. The first fragment consists of a sodium ion interacting with a single dissociated oxygen and siloxane oxygens. The second fragment consists of a sodium ion interacting with the silanol and siloxane oxygens while the third fragment consists of a sodium ion interacting with all three species of oxygens. The free parameters of the
sodium-oxygen Buckingham potential given in Table 2.2 were adjusted to match the *ab initio* binding energies.

For the fragments with a dissociated oxygen, it was not possible to generate a full potential energy surface representing the approach of a Na$^+$ ion to a surface fragment using ground state *ab initio* methods. Without solvent, the ground state of this system at large separations is a neutral sodium atom and neutral fragment. The ground state becomes ionic in character as the sodium approaches the fragment. Hence we relied on the binding energy to fix the non-Coulombic interaction parameters between the Na$^+$ ion and silica, the partial charges being constrained to the BKS values. The binding energy was calculated by separately calculating the energy of the ion-fragment complex, and then the energies of the isolated ion and fragment.

\[
\Delta E_{\text{bind}} = E(\text{fragment}/\text{Na}^+) - E(\text{fragment}) - E(\text{Na}^+) \quad (2.7)
\]

The comparison of the empirical and *ab initio* binding energies of a Na$^+$ ion to the three fragments shown in Fig. 2.6 are reported in Table 2.4. The Si-O bond length
and the position of the sodium ion was initially optimized with an *ab initio* calculation for the first fragment shown in Fig. 2.6a. The Si-O bond length used in the other two fragments was very close to the optimized bond length obtained for the first fragment.

<table>
<thead>
<tr>
<th>Fragment</th>
<th><em>ab initio</em> (eV)</th>
<th>empirical (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frag 1</td>
<td>-6.44</td>
<td>-5.59</td>
</tr>
<tr>
<td>Frag 2</td>
<td>-6.85</td>
<td>-7.35</td>
</tr>
<tr>
<td>Frag 3</td>
<td>-3.05</td>
<td>-2.98</td>
</tr>
</tbody>
</table>

Table 2.4: Fitted and *ab initio* binding energies for silica-Na\(^+\) fragments.

Chloride ions are repelled from a negatively charged silica surface and, compared to sodium, chloride ions will have considerably weaker interactions with the silica surface. Hence, the interactions between the chloride ions and the silica surface were calibrated without further quantum chemical calculations using available potentials in the GROMOS96 force field.\(^{144}\) Our preliminary simulations also indicated that the Cl\(^-\) ions quickly explore the Coulomb infinity between the Cl\(^-\) ions and positively charged silicon and silanol hydrogen atoms. For this reason short range LJ potentials were inserted between these species. These potentials were derived using combining rules with potentials from the GROMOS96 force field. The interaction parameters between the sodium and chloride ions and water were obtained from previous work by Dang.\(^{145}\) The parameters used in our simulations are shown in Table 2.3.
2.3 Comparison of \textit{ab initio} and empirical results

2.3.1 Simulation methods

In this section we describe the evaluation of our empirical potential using \textit{ab initio} MD simulations on a smaller hydrated slab system. Owing to computational feasibility, AIMD simulations were limited to rather small systems. The starting configuration for the AIMD simulations was generated by annealing a bulk crystalline silica tridymite structure with no free surfaces measuring $10.13\AA$ by $17.55\AA$ by $8.275\AA$, and consisting of 32 silicon atoms and 64 oxygen atoms using the BKS potential\textsuperscript{136} with dispersion interactions truncated to half of the shortest side of the box. The protocol that was used to generate amorphous silica from the starting material was adopted from cycle I-IV of Huff and co-workers,\textsuperscript{146} as in our previous work. We cleaved the surface by opening a gap in the $z$-dimension, followed by annealing for 5ps at $300K$. This small surface yielded one 2-membered ring on one surface and no structural features on the other surface that would lead to silanol groups. The 2-membered ring was opened with the addition of water to form two nearby silanol group in a process described below in section 2.3.2, initially yielding a total of 2 silanols on one of the surfaces and no silanols on the other. After hydroxylation a total of 71 waters were added to the system. This hydrated silica slab was then used as input for the \textit{ab initio} MD simulations. Further reaction of water with the surface during the \textit{ab initio} MD simulations led to the appearance of more silanol groups on the side that already contained silanols, and none on the other side of the slab. This is appealing because it furnished a means to test our findings\textsuperscript{34} that silanol groups make the silica surface hydrophilic, while surfaces depleted in silanols are relatively hydrophobic. Unfortunately, we were unsuccessful in conducting a classical
simulation of systems of the hydroxylated surface using our empirical potential due to technical limitations implementing 3-body interactions in the DL POLY package for a small system size. For this reason we could not use a starting configuration for the \textit{ab initio} MD simulations obtained by first equilibrating with our empirical potential, or compare data for AIMD and empirical simulations of exactly the same system. We emphasize that the 3-body interactions were omitted \textit{only} for the small system size that is used to generate a starting configuration for the \textit{ab initio} MD simulations. The 3-body interactions were implemented for the larger systems that are used in our production runs to compare the empirical and \textit{ab initio} MD results.

The AIMD simulations were conducted using Quickstep which is part of the CP2K package.\textsuperscript{147,148} In these calculations, \textit{ab initio} Born-Oppenheimer molecular dynamics is used for propagation of the classical nuclei. The electronic orbitals are converged to the Born-Oppenheimer surface at every step in the molecular dynamics simulation. The wave function was optimized using an orbital transformation method\textsuperscript{149} in conjunction with the DIIS scheme,\textsuperscript{150,151} as described in Ref.148. The convergence criterion for optimization of the wave function was set to $10^{-6}$. Using the Gaussian and plane waves (GPW) method, the wave function was expanded in the Gaussian DZVP basis set. While a triple-zeta basis set was not feasible for the silica slab, simulations using the larger TZV2P basis set were used to check convergence of our radial distribution functions with respect to basis set size for orthosilicic acid in water, as reported below. An auxiliary basis set of plane waves was used to expand the electron density up to a plane wave cutoff of 300 Ry. We used the Becke-Lee-Yang-Parr gradient correction\textsuperscript{122,123} to the local density approximation and Goddecker-Tetter-Hutter (GTH) pseudopotentials.\textsuperscript{152} A time step of 0.5 fs was used in all \textit{ab initio} simulations.
During the first 3\textit{ps} of the simulation, we observe several chemical processes that occur on the surface. These chemical processes will be documented in detail later. At this stage, reaction with water adds 3 silanols to the surface that already contained 2 silanols. Exchange of hydrogen and oxygen atoms between the water molecules and atoms on the silica surface results in the formation of an extra proton that, during the length of our simulations, fluctuates between two Eigen structures and samples a Zundel complex during the fluctuations. The presence of the excess proton in the solvent near the surface during the course of the simulation suggests that the silica slab is negatively charged, which is confirmed below. The simulation with the proton in the bulk was then run for a total of approximately 22\textit{ps}. For data analysis, the first 6\textit{ps} of this simulation was treated as equilibration. An additional simulation was begun from a configuration chosen from the first 3\textit{ps} of this simulation, where the proton was replaced by a Na\textsuperscript{+} ion. This simulation was run for a total of approximately 15\textit{ps}. For the data analysis, the first 4.5\textit{ps} of the run with Na\textsuperscript{+} was treated as equilibration. All the AIMD simulations described were conducted within the NVE ensemble.

We also conducted AIMD simulations of orthosilicic acid using the DZVP and TZV2P basis sets. These simulations consist of a single orthosilicic acid molecule (Si(OH)	extsubscript{4}) surrounded by 66 water molecules in a box of side length 12.75\text{Å}. Using the same methodology described above, AIMD simulations of length 20\textit{ps} were conducted using the DZVP basis set and 15\textit{ps} using the TZV2P basis set. Simulations of this system were also performed using our empirical model. All the simulations conducted with our empirical model and DFT \textit{ab initio} method, are summarized in Table 2.5.
Table 2.5: Summary of systems simulated in this work using both our empirical model and the ab initio MD method. The 9ns empirical model simulation was used to obtain the results presented in section 2.3. The small, 145ps empirical simulation provided the starting configuration for the AIMD simulations of a silica slab.

<table>
<thead>
<tr>
<th>System</th>
<th>Method</th>
<th>Simulation length</th>
<th>Cell dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large dissociated silica slab</td>
<td>empirical</td>
<td>9ns</td>
<td>$32.83 \times 32.84 \times 127.59 , \text{Å}^3$</td>
</tr>
<tr>
<td>Small silica slab (initial configuration for AIMD)</td>
<td>empirical</td>
<td>145ps</td>
<td>$10.13 \times 17.55 \times 8.275 , \text{Å}^3$</td>
</tr>
<tr>
<td>Small silica slab + excess proton</td>
<td>AIMD (DZVP)</td>
<td>22ps</td>
<td>$8.837 \times 15.309 \times 27.219 , \text{Å}^3$</td>
</tr>
<tr>
<td>Small silica slab + Na⁺</td>
<td>AIMD (DZVP)</td>
<td>15ps</td>
<td>$8.837 \times 15.309 \times 27.219 , \text{Å}^3$</td>
</tr>
<tr>
<td>Orthosilicic acid</td>
<td>empirical</td>
<td>2ns</td>
<td>$12.75 \times 12.75 \times 12.75 , \text{Å}^3$</td>
</tr>
<tr>
<td>Orthosilicic acid</td>
<td>AIMD (DZVP)</td>
<td>20ps</td>
<td>$12.75 \times 12.75 \times 12.75 , \text{Å}^3$</td>
</tr>
<tr>
<td>Orthosilicic acid</td>
<td>AIMD (TZV2P)</td>
<td>15ps</td>
<td>$12.75 \times 12.75 \times 12.75 , \text{Å}^3$</td>
</tr>
</tbody>
</table>

2.3.2 Construction of a dissociated silica surface

In our previous work, we described the method used to generate a hydroxylated silica surface. We will briefly review some of those procedures in this section. The starting configuration begins with crystalline tridymite with no free surfaces. The amorphous silica slab is then generated using a protocol adopted from cycle I-IV of Huff and co-workers. The slab is cleaved by opening up a gap in the $z$ dimension followed by annealing for a limited time at 300K. The silica surface consists of various species such as two-membered (2M) rings, nonbridging oxygens (NBOs), and three coordinated silicons. In Table 4 of our earlier work, we showed that the length of annealing time in the simulations controls the population of these species on the silica surface and consequently the silanol density of the silica surface. Thus the
concentration of silanols on the surface can be controlled in a systematic way to reproduce reported experimental values of the silanol density.\textsuperscript{39,153} The 2M rings were manually converted into a pair of vicinal silanols, i.e. two close by silanols, as seen below,

\begin{equation}
\text{Si}\text{O} \quad \text{O} \quad \text{Si} + \text{H}_2\text{O} \quad \rightarrow \quad \text{Si}\text{O} - \text{H} \quad \text{O} - \text{H} \quad \text{Si} \text{O} \quad \text{Si}.
\end{equation}

while the NBO’s were transformed into geminal silanols,

\begin{equation}
\text{Si}\text{O} \quad \text{Si} + \text{H}_2\text{O} \quad \rightarrow \quad \text{Si} - \text{H} \quad \text{O-H} \quad \text{Si},
\end{equation}

which are attached to the same silicon atom. These procedures follow likely hydroxylation reactions identified by previous \textit{ab initio} calculations\textsuperscript{117,118,154,155} as described in our previous work.\textsuperscript{34} The detailed structure of the aqueous silica surface, its mechanism of hydroxylation, and the distribution of isolated, vicinal and geminal silanols has not yet been conclusively established theoretically or experimentally and certainly more work is needed in this area.

Once the hydroxylated surface is formed, silanols on the surface need to be selected for deprotonation to form O\textsuperscript{−} groups. Due to the lack of any experimental or theoretical insight, the silanols are deprotonated in a random fashion except that we never deprotonate both hydroxyl groups of geminal silanols because we expect that charge repulsion will make doubly-dissociated geminals a high energy species. For the simulations reported here using our empirical model, dissociated sites are chosen so that they are separated by at least 6Å. Our empirical simulations for the dissociated surface consists of a box measuring 33.24Å by 33.24Å by 144.22Å. Along the box
height of 144.22Å, water occupies approximately 108Å and the silica slab fills the remainder. The charge density of the surface was $0.795 \, e \, nm^{-2}$.

Figure 2.7: Radial density of water (top row), and cumulative number of neighboring waters (bottom row) near silanol (solid line) and siloxanes (thick dashed lines) for empirical model shown in left panel, AIMD simulation with proton in middle panel and AIMD simulation with Na$^+$ shown in right panel. The green and red thick lines are radial densities near siloxanes in only hydrophilic and only hydrophobic regions respectively.

### 2.3.3 Radial densities near silanol groups of silica and orthosilicic acid

Shown in Fig. 2.7 is a comparison of the radial distribution functions for water near the silanol oxygens and siloxanes from our empirical model, and for the *ab initio*
simulations for the two systems described above. We note that the striking difference

in water density near silanol and siloxane oxygens, originally noted in our study of the undissociated surface,$^{34}$ is confirmed by AIMD. Previously we had reported$^{34}$ that our empirical model did not perform favorably in reproducing the paths of approach of a single water molecule to a siloxane group compared to ab initio results. This discrepancy does not appear to directly affect the hydrophobic/hydrophilic property of the surface. Water is depleted near siloxanes regardless of the proximity of silanol groups. It occurs on both sides of the AIMD slab, the side with no silanols and the side with 5 silanol groups (red and green curves in Fig. 2.7).

Figure 2.8: Radial density of water (top row), and cumulative number of neighboring waters (bottom row) near four individual silanol groups from empirical potential simulations.
The comparison between empirical and AIMD in Fig. 2.7 shows under-structuring by our empirical potential compared to AIMD in the form of lower and wider density peaks. Also, the radial distribution function (RDF) for the water oxygen-silanol oxygen peaks at about 3.0Å in our empirical model, but is peaked at about 2.7Å in the \textit{ab initio} simulations. Studies of orthosilicic acid reported below confirm that part of this trend can be attributed to the empirical potential parameters, which tend to under-structure water near silanol groups. However, very limited sampling of silanol group environments in the AIMD runs also contribute significantly to the difference between AIMD and empirical results in Fig. 2.7. As noted earlier, it was not possible to carry out empirical and AIMD simulations on exactly the same system. The empirical potential simulations were performed on a much larger sample. The surface area of the slab used in the empirical potential simulations is approximately 8 times that used in our AIMD simulations. Thus the empirical potential simulations encompass a much larger range of silanol environments. The variety of local environments is illustrated by radial density plots for water near four individual silanol groups in our empirical potential simulations shown in Fig. 2.8. A buried silanol group is found in the left-most plot, and the cumulative population plot beneath it shows that relatively few waters are surrounding it. All four examples exhibit a sharper first peak than the overall average for the empirical potential surface in Fig. 2.7, where such features are washed out. The right-most plot in Fig. 2.8 shows a silanol group with abundant exposure to water and a pronounced minimum between first and second peaks. In contrast to the diversity encompassed by the empirical simulation, the environments for the five silanol groups in the \textit{ab initio} simulations were relatively similar and individual radial water densities near individual silanol groups for the AIMD runs did
not show strong variation. In order to obtain a quantitative comparison of the radial distribution functions, larger AIMD system sizes over multiple realizations that have similar surface morphology to those used in our larger empirical model would be required.

In the left and right panels of Fig. 2.9 we compare the radial densities of sodium ions and water about dissociated groups and the radial density of water about sodium ions from our empirical model and AIMD simulations respectively. As mentioned before, the AIMD simulations consist of only a single sodium ion while the empirical model simulations are averaged over many sodium ions and dissociated O\(^-\) groups. As for silanol groups (see discussion of Fig. 2.7), we cannot make a direct comparison of O\(^-\) groups averaged over the entire empirical potential surfaces with a single O\(^-\) group in the AIMD simulation. With these caveats, a comparison of the positions of the maxima of the various densities suggests that our empirical model for the dissociated surface at least does not contradict the AIMD results. The O\(^-\)-Na\(^+\) density (over 10 dissociated oxygens) peaks at about 2.3\(\text{Å}\) in the AIMD simulations and 2.45\(\text{Å}\) for the single dissociated oxygen in our empirical model. The O\(_W\)-O\(^-\) density peaks at about 2.65\(\text{Å}\) in the AIMD simulations and 2.6\(\text{Å}\) in the empirical model and finally the Na\(^+\)-O\(_W\) density peaks at about 2.4\(\text{Å}\) in the AIMD and at 2.45\(\text{Å}\) in our empirical model. The empirical model qualitatively reproduces the trend observed in the AIMD simulations of a larger first peak position in the O\(_W\)-O\(^-\) radial density compared to the first peak positions in the O\(^-\)-Na\(^+\) and Na\(^+\)-O\(_W\) densities.

The radial densities of the water oxygens and atoms on orthosilicic acid are shown in the figure Fig. 2.10. The radial densities show good agreement between the DZVP and TZV2P basis sets suggesting that the radial densities in Fig. 2.7 confirming the
hydrophilic (hydrophobic) property of silanols (siloxanes), is at the very least qualitatively converged with respect to basis set. Convergence with respect to the charge density cut-off was not explored.\textsuperscript{131} We find that our empirical model, which was not designed to model orthosilicic acid, under-structures the water near the orthosilicic acid. However, the cumulative neighbor populations shown in the bottom row of Fig. 2.10 demonstrate that the number of waters near orthosilicic acid matches well between AIMD and our empirical model.

### 2.3.4 Description of surface chemistry in AIMD simulations

We observed interesting chemical processes occurring on the surface within the first 3\textit{ps} after a freshly cleaved silica surface was exposed to water in \textit{ab initio} simulations. This resulted in the formation of three more silanol groups on one surface. Some
of these important events will be reviewed in this section. These results should be viewed as preliminary information on processes that deserve much further study. It should be noted that the starting configuration for the AIMD simulations was not pre-equilibrated using our classical potential and hence represents a high energy starting configuration that is subject to significant surface relaxation. Further work is needed to show how sensitive the occurrence of these chemical events are to larger system sizes, and different initial surface morphologies that may arise from annealing and equilibration protocols using our classical model.
In the schematic shown in Fig. 2.11, three separate processes that occur on our surface are illustrated. The first process shows the conversion of an isolated silanol to a geminal silanol and another isolated silanol, resulting in the addition of two more silanols to the surface. The intermediate steps are seen more clearly in Fig. 2.12. As a water molecule binds strongly to the silicon atom of the isolated silanol, one of the Si-O bonds associated with the silicon atom lengthens resulting in a non-bridging oxygen (Fig. 2.12i). At the same time, the water molecule splits donating an OH group to the silicon, transiently forming a hydronium ion $\text{H}_3\text{O}^+$ (Fig. 2.12ii). The proton that forms the transient hydronium is then recaptured by the newly formed silanol. Simultaneously, the hydrogen that was originally added as part of the OH
group to the silicon, is transferred to the non-bridging oxygen (Fig. 2.12iii). The resulting product is a geminal silanol and an isolated silanol (Fig. 2.12iv). The role of the formation of transient hydronium ions during the chemisorption of small numbers of waters onto the silica surface has previously been observed by Du et al. in QM/MM simulations, by Mahadevan and Garofalini using a dissociating potential model, and, for large silica clusters, by Ma et al. with \textit{ab initio} MD simulations.

![Figure 2.12: Steps in the formation of a geminal and isolated silanol from an initial single silanol, process (1) in Fig. 2.11. The atoms of the water molecule that reacts with the surface are shown in blue in all four frames. i) Arrows point to water that attacks silicon atom and Si-O bond that begins to break. ii) Arrows point to the non-bridging oxygen formed after the Si-O bond breaks and the hydronium ion transiently formed. iii) Arrow points to the proton transferred from the newly formed silanol to the NBO. iv) Final products are a geminal and a single silanol.](image)

Snapshots from the second hydroxylation scheme of Fig. 2.11 are shown in Fig. 2.13. A two-coordinate silicon is transformed into an isolated silanol along with the transfer of a proton to the water. Ma and co-workers who have also conducted \textit{ab initio} MD simulations of water near silica clusters, found that the two-coordinate silicons in their simulations were highly unreactive with water. In our simulations we observe that as the water molecule strongly binds to the under-coordinated silicon, the OH group of the water is transferred to the silicon, and the proton is transferred to the
surrounding water forming a hydronium ion $\text{H}_3\text{O}^+$. During the transfer of the OH group from the water to the silicon, one of the Si-O bond lengths associated with the silicon increases by approximately 0.2 Å. This process involves charge separation between the slab and the solvent, as illustrated by the charges in Table 2.6 obtained using the DDAP charge partitioning method from 192 configurations after an excess proton is transferred to the solvent. The silica slab carries close to a full electron charge ($-0.923$), and the solvent a corresponding positive charge. All the oxygens of the silica slab have a charge close to $-0.8$, including NBOs. After a proton was transferred to the solvent and the surface was stabilized, we could identify a buried NBO within a cleft on the surface which was solvated by a single water molecule. This could be considered as the location of the excess charge on the silica slab.

<table>
<thead>
<tr>
<th>Species</th>
<th>Slab + excess proton</th>
<th>Slab + Na$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slab</td>
<td>$-0.923$</td>
<td>$-0.807$</td>
</tr>
<tr>
<td>O (Silanols)</td>
<td>$-0.659$</td>
<td>$-0.690$</td>
</tr>
<tr>
<td>O (Siloxanes, hydrophilic side)</td>
<td>$-0.830$</td>
<td>$-0.792$</td>
</tr>
<tr>
<td>O (Siloxanes, hydrophobic side)</td>
<td>$-0.782$</td>
<td>$-0.794$</td>
</tr>
<tr>
<td>NBO</td>
<td>$-0.832$</td>
<td>$-0.904$</td>
</tr>
</tbody>
</table>

Table 2.6: Average charges of species in AIMD simulations. Charges were obtained according to the DDAP charge partitioning scheme, which is based on the electron density.

The initial configuration for the AIMD simulation with the Na$^+$ was constructed by replacing a proton from the newly formed $\text{H}_3\text{O}^+$ (Fig. 2.13ii) with a Na$^+$. The newly formed silanol (Fig. 2.13ii) was deprotonated to form a non-bridging oxygen (NBO), and the proton transferred to a nearby siloxane oxygen which was converted thereafter into a silanol. The charge partitioning analysis was conducted for 192
Figure 2.13: The left and middle frames illustrate steps in the formation of an isolated silanol from an under-coordinated silicon, scheme 2 of Fig. 2.11. The atoms of the water molecule that reacts with the surface are shown in blue in these frames. i) Water attacks an undercoordinated silicon atom. ii) An OH group is added to silicon and hydronium ion formed. iii) The frame on the right shows a water molecule on the hydrophobic surface that binds to an exposed silicon atom without further reaction during the length of the AIMD simulation.

configurations sampled from our simulations with the Na\(^+\). The magnitude of the charges are shown in Table 2.6. The average charge of the Na\(^+\) in our simulations is +0.726 indicating that a significant amount of the positive charge has leaked to its surroundings. Furthermore the data also suggests that a significant proportion of the formal −1 charge of a singly-dissociated silica surface leaks out on to its environment. Charge transfer between solvated ions and solvent has already been reported in several systems. Klein and co-workers\(^ {156} \) conducted \textit{ab initio} simulations of a zwitterionic peptide, halide anions and alkali cations in water. They observed a substantial amount of charge transfer between the carboxylate terminus and the solvent (0.1e). Similar values were also found for K\(^+\) and Na\(^+\) ions. Chloride and bromine anions were found to transfer more electronic charge (0.26e) onto the surrounding solvent.
It is interesting that the charges of the oxygens of hydrophilic silanol groups are less than the oxygen from hydrophobic siloxane bonds in Table 2.6, once again confirming that hydrogen bonding interactions are not purely electrostatic. The magnitude of the density derived charges from the AIMD simulations, especially for silica atoms which follow the BKS model, are less than the charges used in our model. However, these differences do not preclude qualitative agreement between the empirical and AIMD predictions of the hydrophobic/hydrophilic property of the silica surface. Future work in the development and improvement of empirical models for amorphous silica may require adjustment of the charges in the empirical potential, guided by data shown in Table 2.6. Finally, we find that the oxygen of a single water molecule interacts intimately with a 4 coordinated silicon atom throughout the length of our simulation on the hydrophobic side of the silica surface (third scheme of Fig. 2.11 and right panel of Fig. 2.13). The Si−O\textsubscript{W} distance for this water molecule fluctuates between 1.8−2.0Å. Although the silicon atom is quite exposed to solvent, we do not observe any chemistry occurring at this site within the timescales of the simulations conducted. Perhaps longer simulations would lead to a hydroxylation event.

2.4 Conclusions

In contact with aqueous solution with pH greater than ∼3, the silica surface is negatively charged because a fraction of the silanol groups are dissociated, and an electrical double layer is present.\textsuperscript{39} In this chapter we extended our empirical model for the undissociated surface. The silica surface in this model is flexible, so it can be used to model heat transport in nanoscale devices. The extended model now includes deprotonated silanol groups, and specifies water, and sodium and chloride
ion interactions with the surface. We employed the same strategy that was used in
the previous model for the undissociated surface, fitting the parameters of our
empirical potential to accurate \textit{ab initio} cluster calculations.

We have made comparisons with experimental quantities, such as the heat of
immersion, where measurements are available. Otherwise, we have relied on com-
parisons with quantum chemical and \textit{ab initio} molecular dynamics results. We used
well-calibrated and widely used models, BKS\(^{136}\) and SPC/E,\(^{137}\) to describe bulk sil-
ica and water, respectively, away from the interface. However, these models employ
somewhat unrealistic partial charges to mimic other physical interactions. Therefore,
the benchmarking against quantum chemical and AIMD data is essential. We have
confirmed a key prediction of our empirical potential, the striking difference in water
density near silanol and siloxane groups. Despite the fact that the partial charges
of the empirical model, especially the BKS parameters, are larger than those pre-
dicted by electron density calculations, the data for orthosilicic acid suggests that,
if anything, our silica surface slightly under-structures nearby water. Populations of
neighboring water near the surface are in good agreement with AIMD results. The
evident under-structuring of our empirical potential compared to AIMD may be, in
part, attributed to the tendency of the BLYP density functional to over-structure
hydrogen bonding fluids, as discussed in the introductory section. The hydroxylation
of a freshly cleaved silica surface is poorly understood, as is the distribution of various
chemical groups on the surface.\(^{40}\) Further tests of the convergence of AIMD method-
ologies to this system are needed before quantitative benchmarks can be established.
We have provided an account of the reactions that occur in our AIMD simulations as
water comes in contact with silica, and general agreement is found with previous theoretical studies of water chemisorption using small numbers of water near silica.\textsuperscript{11,83,116} However, given the experimental difficulties in disentangling the complex structure of the silica surface, this is an area where extensive further AIMD investigations are needed.

In this chapter we have compared the distribution of water near silanol groups on a smaller amorphous silica slab using \textit{ab initio} MD simulations to silanols in our empirical simulations. We have also compared the radial density of water near orthosilicic acid. For the slab systems, the surface heterogeneity of the larger system simulations performed with our empirical model, complicates the comparison with the smaller \textit{ab initio} MD simulations (see Figs. 2.7 and 2.8 and corresponding discussion). When our model is applied to simulating orthosilic acid, we find that it results in the understructuring of water near the silanols. At this point we cannot conclusively determine whether this behavior is an artifact of the density functional used in the \textit{ab initio} MD simulations or whether our empirical model under-structures water near the silanols.

An interface between water and amorphous silica is found in many applications, ranging from chromatography to novel nanofluidic devices. Our potential model is designed to enable atomistic device simulations at large length and time scales, which is desirable for several reasons. Large length scales are needed to go beyond straight channels and model features like nozzles or bends. Long time scales are needed to model fluid flow. Typical flow velocities are many orders of magnitude smaller than a typical thermal velocity, $\sqrt{k_B T/m}$, where $m$ is the molecular mass. As a result, flow velocities in non-equilibrium simulations are obtained by averaging over much
larger numbers. The strategy in such simulations is to induce unrealistically large flow velocities to improve signal-to-noise, yet to keep the flow velocity below the point where non-linear effects arise. The largest tolerable flow rates are on the order of 10% of a thermal velocity,\textsuperscript{157} which means that extensive averaging is needed. Use of equilibrium simulations to evaluate Green-Kubo expressions has recently been advocated as an efficient alternative to non-equilibrium simulations for the calculations of transport coefficient\textsuperscript{158,159} and flow profiles.\textsuperscript{160,161} In either case, these calculations are demanding, underscoring the need for interaction models for the amorphous silica-water interface that combine computational efficiency with an acceptable level of realism, which is addressed in this chapter.
CHAPTER 3

Applications of the model: Electrokinetic Phenomena in a Silica Nanochannel

3.1 Introduction

In this chapter we will investigate the validity of the Gouy-Chapman-Stern model\textsuperscript{66–69} (Figure 3.1) and the dynamic Stern layer concept\textsuperscript{70–78} in a system to which these ideas have often been applied, aqueous electrolyte at the surface of amorphous silica. When applied to electrokinetic phenomena, this model dictates that the surface where hydrodynamic stick (no-slip) boundary conditions are enforced should reside near the boundary between an immobile layer of fluid and specifically bound ions adjacent to the surface, known as the Stern layer, and a mobile layer containing a diffuse charge distribution. The Stern model successfully rationalizes a very large body of experimental data.\textsuperscript{1} Placing a significant portion of the counter-charge in an immobile layer explains why the apparent charge driving electroosmotic flow is less than the actual surface charge. However, a completely static Stern layer model does not adequately account for surface conduction, the contribution to ionic current arising from the altered charge density near the surface.\textsuperscript{77,78,162} Surface conduction becomes increasingly important with smaller channel size and also with lower salt

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concentration, as the bulk region contributes less to the total current relative to the

Figure 3.1: Illustration of the Gouy-Chapman-Stern picture\(^1\) of the electrical double layer. If the surface (far left) is negatively charged, then cations will accumulate close to the surface. Counter-ions in the Stern layer are bound by specific interactions, while those further away, in the diffuse layer, are described using Poisson-Boltzmann theory. An electric field parallel to the surface induces electrophoresis of the ions, which in turn generates electroosmotic flow of the fluid. In the prevailing view, fluid in the Stern layer is not mobile, so the fluid velocity is zero (plot at bottom) until a distance from the surface close to the boundary between the Stern and diffuse layers.

surface. The observed surface conduction exceeds what could be produced by the ions remaining outside the Stern layer. Experimental evidence of the discrepancy for oxides like silica is based on the fact that conductance measurements indicate a substantially higher surface charge than electrophoretic mobilities.\(^{163–166}\) Retaining the Stern layer concept, it is required to postulate that ions within the immobile layer have mobilities near bulk values, a model known as the “dynamic Stern layer”,\(^{70–78}\) to describe the measured surface conduction. As described by Dukhin \textit{et al.},\(^{78}\) there
is no convective ion flux in the Stern layer, but according to these authors this does not exclude the possibility of conductive ion flux driven by tangential electric fields. The dynamic Stern layer model is widely accepted in the colloid community,¹ and is used, for example, in the physics literature to explain transport in nanochannels.¹⁶ In the following we will see that the Stern model does not furnish a realistic description of aqueous electrolyte adjacent to the surface of silica. It is best regarded as an effective model that produces the correct velocity profile far from the surface. A realistic picture of the surface region can reconcile electroosmotic flow with surface conduction without invoking the passage of ions through immobile solvent, which we show is untenable. Furthermore, the notion of a sharp boundary, or even somewhat rounded as, for example, Lyklema and Overbeek²⁶,¹⁶² have suggested, between mobile and immobile electrolyte near a surface is in need of revision.

In the widely used picture of the Stern layer (e.g. Figure 3.1 in this work, or Fig.1 of refs.18 and 167), hydrated counter-ions adsorbed to the surface are located a distance $d_β$ from the surface, which defines the inner Helmholtz plane. Ions from the diffuse layer approach to within a distance $d$, which defines the outer Helmholtz plane. Most accounts in the literature describe the distance from the surface to the inner edge of the diffuse layer (outer Helmholtz plane) as 1 to 2 ion, or hydrated ion, diameters.¹⁸–²⁰,²³,²⁴,²⁸,¹⁶⁸–¹⁷⁰ Depending on the ion and degree of hydration assumed near the surface,¹⁷¹ this implies a Stern layer thickness of 2-10Å. Potentiometric titration experiments for silica immersed in aqueous alkali chloride electrolyte, interpreted in terms of this model, yield a Stern layer thickness in this range.¹⁷²,¹⁷³ In particular, for sodium chloride, the salt used in our simulations, the thickness of the Stern layer has been estimated to be 5-6Å.¹⁷²,¹⁷³ While most authors subscribe to a width of 1-2
hydrated ions, much larger estimates for the Stern layer width have appeared in the literature, e.g. up to 63Å near pyrex\textsuperscript{174} and 81Å near rutile\textsuperscript{175}.

So far, these definitions are structural. Turning to dynamical properties in standard models, a plane of shear is located at $d_{ek}$, which is generally taken to be at, or slightly beyond the outer Helmholtz plane. The fluid is immobile from the surface to the plane of shear. The plane of shear concept is an idealization in which the viscosity is pictured to drop from an essentially infinite value to the bulk solution viscosity over a very limited distance range, and is the plane at which stick or no-slip boundary conditions are enforced in continuum equations of hydrodynamics. The concept of an immobile Stern layer extending 2-10Å from the surface is commonly found in the physics,\textsuperscript{16} electrochemistry,\textsuperscript{20} surface science,\textsuperscript{19} and colloid science\textsuperscript{22,25,162} literature. More realistic descriptions in which the viscosity drops continuously over a finite distance are available,\textsuperscript{26–28} but the rise is thought to occur over a fraction of the diameter of a water molecule,\textsuperscript{28} so the plane of shear concept continues to enjoy wide use.

Before Stern’s 1924 paper, it was well-known that that observed electroosmotic flow is generally less than the amount expected based on the measured surface charge, i.e., the apparent electrokinetic surface potential (the $\zeta$-potential) was less than the full potential difference between the solid surface and solution, and this was attributed to an immobile layer of strongly bound species adjacent to the surface. (See, e.g. pp. 341-343 of ref.176.) This was one motivation\textsuperscript{177} for Stern to work out the theoretical consequences of such an immobile layer. Separation of the ion atmosphere into the immobile Stern layer and a diffuse outer layer, the Gouy-Chapman-Stern model, has become a canonical part of the double layer literature, although certainly more elaborate models have been proposed.\textsuperscript{178–182} In 1941, Bikerman\textsuperscript{183} suggested that
surface roughness was the cause of a stagnant layer. Indeed, several decades after Bikerman’s work for quantitative theoretical investigations of flow velocity near rough surfaces confirmed that surface roughness pushes the effective plane of shear out from the surface. More recently, Lyklema, Rovillard and DeConinck, in reference to Lyklema and Overbeek’s viscoelectric theory and Bikerman’s notion of surface roughness, argue that “none of these interpretations can be entirely adequate” to explain hydrodynamically stagnant fluid layers near a surface. They cite the existence of stagnant layers near surfaces which are smooth and uncharged. Instead, they argue that the essential factor is layering of the fluid near the surface.

While introduction of the Stern layer remedies deficiencies of the Gouy-Chapman model, an apparent problem arises with regard to ion current. The ion current in a channel has a bulk convective component proportional to the cross sectional area $A$, and another contribution arising from modification of conductivity near channel walls that is proportional to the cross sectional perimeter $p$.

$$I_{\text{cond}} = (KA + K^\sigma p)E$$

In the above equation, $E$ is an electric field applied parallel to the channel walls, $K$ is the bulk conductivity, $K^\sigma$ is the surface conductivity, and $I_{\text{cond}}$ is the total current arising from ion conduction. In channels with large cross-sectional areas, bulk conduction dominates. However, when salt concentration is low in small pores, the extra conductivity from ions that collect near charged walls, the surface conductivity, provides a contribution to the overall current comparable to the bulk contribution.

Under the assumption of distinct Stern and diffuse layers, ion mobility in the diffuse region cannot account for the observed magnitude of the surface conductivity.
Many researchers in the colloid field have come to the conclusion that ions in the im-
mobile region near the surface must exhibit mobilities comparable to bulk conductivity
to fully account for the surface contribution to the total conduction.\textsuperscript{70–73,75,76,163,189}

The notion that an electrokinetically active surface has its own contribution to the
conductivity, distinct from the bulk fluid has roots that go far back in the litera-
ture.\textsuperscript{190–193} However, it was not until the 1980’s that the surface ion conductivity
was specifically assigned to the immobile fluid of the Stern layer.\textsuperscript{70–73,75–77,163,189} Van
Der Put and B. H. Bijsterbosch, in their analysis of electrokinetic phenomena near
polystyrene particles, used the concept of “anomalous conductance” of ions within
a “hairy layer” that is situated within the slip plane.\textsuperscript{70} Zukoski and Saville found
that $\zeta$-potentials inferred from the conductivity of a suspension of latex spheres was
consistently greater than that inferred from the electrophoretic mobility of the par-
ticles.\textsuperscript{71,72} Zukoski and Saville seem to be the first to coin the term “dynamic Stern
layer”. While they work out a complete theory on this premise, they are cautious
about its physical reality.\textsuperscript{194} However, other workers do take the notion of ions mov-
ing with bulk-like mobility through immobile water quite literally. Writing about the
Stern Layer in 1994, Lyklema states,\textsuperscript{162} “the [surface] layer is stagnant as far as the
macroscopic tangential flow is concerned, but nevertheless allows ions to migrate.”
(In this work we directly test this proposition in section 3.3.) In 1998, Lyklema and
Minor wrote,\textsuperscript{77} “…within the slip plane the fluid is hydrodynamically stagnant, so
that the electroosmotic contribution vanishes because the liquid is immobile.” They
also state, “Nowadays, convincing evidence is available for lateral ionic mobility in
the Stern layer, to an extent that depends on the system. Essentially the argument
stems from the observation that [the Bikerman formula for surface conduction in a
diffuse layer] underestimates the surface conduction.” The formula derived by Bikerman incorporates conductive and convective ion transports outside the Stern layer, but no transport within the Stern layer.\textsuperscript{195,196}

Initially, applications of the dynamic Stern layer concept were most common for polystyrene latex suspensions and other polymeric surfaces.\textsuperscript{70–73,197–200} Later, dielectric response experiments were performed that implicated a dynamic Stern layer for oxides.\textsuperscript{163–166} For example, low frequency dielectric response data shows that the $\zeta$-potentials for silica obtained by fitting dielectric data, which include the effects of surface conduction, are systematically greater than $\zeta$-potentials from the electrophoretic mobility of the silica particles.\textsuperscript{163} While the dynamic Stern layer concept does help reconcile theory with experiment and explain the differences between $\zeta$-potentials measured by different methods, not all experiments are in quantitative, or even qualitative agreement with the dynamic Stern layer picture.\textsuperscript{201} Several theoretical treatments of electrophoresis and response to time-varying electric fields incorporate a dynamic Stern layer.\textsuperscript{71,73,75,76,189,202,203}

The experimental and theoretical contributions in this area have been reviewed on several occasions by Lyklema and co-workers,\textsuperscript{77,162} who we have already quoted, and Dukhin and co-workers.\textsuperscript{74,78} In 1995, Dukhin\textsuperscript{74} defined alternatives to the standard electrokinetic model to be those cases where ion conduction occurs inside the slip plane, what he and Derjaguin had previous labeled anomalous surface conductivity.\textsuperscript{204,205} Part of the reason he felt the term “anomalous” should be discarded was that “disperse systems with additional surface conductivity probably occur more widely than those meeting the requirements of the SEM [standard electrokinetic
model].” Ion transport through a stagnant surface layer is attributed to the presence of a gel or porous region at the surface. Dukhin, Zimmermann and Werner discussed a surface stagnant layer and ion conduction, what they called stagnant layer conduction, or SLC, within that layer. By definition, convective ion flux, i.e. carried by fluid motion, is zero within the SL. However, ions may still move in response to electric fields tangential to the surface. The new model proposed by Dukhin, Zimmermann and Werner, the generalized standard electrokinetic model (GSEM) incorporates the effect of ion transport within the stagnant layer (SL). It applies to smooth and rough surfaces alike, although the GSEM looses its validity if the roughness is too large. According to Dukhin, Zimmermann and Werner, there are two mechanisms of liquid immobilization near a surface. First, there is an inherent immobilization near all surfaces that would give rise to a stagnant Stern layer near smooth surfaces. Dukhin et al subscribe to Lyklema's notion that layering near a surface is the physical origin of the inherent surface immobilization. This first effect is expected to produce a Stern layer of width less than a nanometer. The second cause of fluid immobilization near surfaces is roughness.

Finally, there are alternative explanations for the discrepancy between sol particle mobility and conductivity measurements. Some workers developed the consequences of finite ion size, demonstrating that finite ion size might explain experimental data without using a dynamic Stern layer model. Another alternative to dynamic Stern layer theory proposed by López-García, Grosse and Horno, the “charged layer” model, assumes that both surface charges (i.e. $\sigma_0$) and free ions inhabit the surface layer. The surface charges make the surface rough, and a parameter $\lambda$ quantifies the resistance to flow in the surface layer. Notably, in the charged layer model both
free ions and water are mobile in the surface layer. In a recent work, predictions of the charged-layer model were compared with those of the Mangelsdorf-White model.

In systems like oxide surfaces, most of the counter-charge resides within a nanometer of the surface. Direct experimental probes of the distribution of charge and flow velocity in this region are not available. Therefore, atomistic simulations can provide crucial insights into the mechanism of electrokinetic phenomena. Previous molecular dynamics simulations of electrokinetic phenomena have used widely different models. Generally, these models are highly idealized, with the surface represented as a perfectly flat and unstructured array of spherical particles. Regular, rectangular grooves have been introduced in models of this type to model surface roughness. Joseph and Aluru simulated electrokinetic effects near a flat, perfectly crystalline, and uncharged α-quartz surface. To our knowledge, the only realistic simulations of electrokinetic phenomena near the amorphous silica-water interface are the works of Lorenz et al. and our work.

Simulations based on different models have produced an assortment of results for the variation of water and ion densities as a function of distance from the surface, as well as corresponding profiles for the velocity, diffusion constant and viscosity. While these properties vary to some degree among the different simulations, the conclusions reached by the different research groups differ even more strongly, some offering confirmation of the traditional Stern model and dynamic Stern layer picture, and others seeing their results in clear conflict. Some, without clearly stating whether their results confirm or conflict with Stern layer models, note the conspicuous absence of a hydrodynamically stagnant layer in their simulations. With
few exceptions, simulations of electrokinetic phenomena have been performed using non-equilibrium molecular dynamics (NEMD). Long simulations are required to pick out sufficient “signal”, i.e. flow velocities of typically a 1-10 m/s in simulations, from the “noise”, the thermal velocities in the range of 400 m/s for water at room temperature. In NEMD simulations, rather large driving fields in the range of .1-.6 V/nm (1-8 × 10^{-11} N per ion) are employed to maximize signal. It is our experience that as long as the flow velocity is less than 10% of thermal velocities, the response is close to linear and the results can be extrapolated with acceptable error to the lower fields used in experiments.

Simulations in which the walls are smooth or simple, flat arrays of spherical particles are known to produce strong layering of solvent near the surface. Surfaces of this type in simulations of electroosmotic flow have tended to place the ions between water layers, and not adjacent to the surface. Of course, very strong ion-wall attractions would break this trend and pull the ions into the layer adjacent to the wall. However, such interactions were not used. Lyklema et al. set their water-wall particle interactions to be 3.8 times stronger than ion-wall interactions, favoring a strongly bound surface water layer and weaker adsorption of ions. There are no Coulombic interactions between any particles in the work of Lyklema et al., in keeping with their belief that the key to understanding Stern layer phenomena is fluid layering near the surface. In Freund’s simulations, the non-Coulombic attractions of ions and solvent to the wall were equal. He compared two types of wall charge distributions, a uniform distribution over all wall particles versus giving a fraction of wall particles a full elementary charge. In either case, the fluid was strongly layered near the wall and counter-ions were found between solvent layers. Again, Qiao and Aluru observed
the same pattern when the walls are modeled by perfectly flat arrays of spherical particles.

When channel walls are no longer flat and structureless, the nature of the water and ion densities begin to change. Joseph and Aluru simulated a potassium chloride solution near an α-quartz surface. The surface structure was free of defects and most of the surface was rigid, but the presence of silanol groups plus the fact that the silanols were not rigid introduced more realism than previous calculations. The ion density peaks near the surface calculated by Joseph and Aluru now line up with water density peaks. This is significant because Lyklema had proposed\textsuperscript{162} that the dynamic Stern layer model is explained by solvent density minima acting as conduits for ion motion. Lorenz \textit{et al.}\textsuperscript{108} do not report total ion densities as a function of perpendicular distance from their amorphous silica surface, but their water density is so unstructured (Fig.5 of ref.108) that the question of whether ions fall within or between solvent density maxima is moot. Our results for ion and solvent densities near an amorphous silica surface are reported below. We do observe weak layering of solvent near the surface. However the ion density peak lies somewhat closer to the surface than the solvent. The distribution of ions is sufficient broad to, once again, make the question of lining up with or between solvent density peaks moot.

To our knowledge, no molecular dynamics simulation of electroosmotic flow has found a region of hydrodynamically stagnant water near the surface that resembles a typical view of Stern layer (as found, for example, in Fig.4.11 of ref.29, Fig.1a of ref.17, or Fig.15 of ref.27). In our work, we only observe a weak immobile region, perhaps 2-3Å wide, when the silica surface is maximally charged by dissociating every
isolated silanol group and one of every geminal pair of silanols. A hypothetical stagnant region would be bounded by the surface on one end, and the slip plane on the other. Therefore, the width depends on the definition of the surface position, which we now discuss. In atomistic simulations, the position assigned to the wall is somewhat arbitrary because atoms at “fuzzy”. Although the wall position is sometimes assigned to be that of the centers of the outermost layer of wall atoms, this can never be a realistic choice because a fluid atom at this position would be occupying the same space as a wall atom. The furthest penetration of fluid to the wall is invariably far short of this position. Travis et al., in simulations of Poiseuille flow of particles interacting with a Lennard-Jones potential, suggested that the surface for stick (no-slip) boundary conditions should be placed one particle diameter from the wall atoms. In simulations of electroosmotic flow in a model system of Lennard-Jones particles, we have found this is a very reasonable choice.

The tangential fluid flow velocity as a function of distance from the channel walls obtained from molecular dynamics simulations is a crucial quantity in the analysis of electroosmotic phenomena. We briefly mention some previous results, excluding results that are specific for hydrophobic surfaces for which a stagnant region is not expected. Lyklema, Rovillard and De Coninck do not report the tangential velocity of fluid in response to a force on their ions. The only data of a dynamical nature to be presented in their work is the perpendicular distance from the wall of a single ion and single water molecule during a 200ps time interval. In that work, many conclusions are reached concerning flow parallel to the surface and the properties of a supposed stagnant layer, even though no results on tangential flow are presented. Freund provides tangential velocity profiles for the cases of charge evenly distributed among
wall atoms, where the flow velocity clearly goes to zero $\sim 3\,\text{Å}$ from the centers of
the wall atoms, roughly one wall atom/water diameter, and for discrete wall charges,
where the flow velocity exhibits an even gentler decrease to zero at the walls.\textsuperscript{31} He
comments that that the velocity “flattened out near the walls in a Stern-type layer,
though the molecules immediately adjacent to the wall were not completely fixed.
They had essentially zero mean streamwise velocity in the first layer only for the case
of uniformly distributed partial charges.” Similarly, in their 2003 work,\textsuperscript{104} Qiao and
Aluru found that the electroosmotic water flow velocity went to zero very close to the
walls, perhaps even exhibiting some slip, and that the decrease in velocity near the
walls was gentler than continuum hydrodynamics with constant viscosity would pre-
dict. Joseph and Aluru remark several times on the dynamic nature of water adjacent
to the $\alpha$-quartz surface.\textsuperscript{106} Lorenz \textit{et al}. (Fig.7 of ref.108) calculate electroosmotic
velocities for 0.4MNaCl that do not indicate a stagnant layer at the surface, and in
the case of 0.2MCaCl\textsubscript{2} even exhibits considerable slip. However, their interpretation
is quite different from ours.

One last set of issues concerns the local viscosity, diffusion tensor, and ionic mo-
bility as a function of distance from the surface. Lyklema \textit{et al}. mention that they
used the auto-correlation function of off-diagonal components of the pressure tensor
to calculate the local viscosity.\textsuperscript{30} No data is shown, but in the text they state that
the viscosity parallel to the surface (from off-diagonal pressure tensor components
with indices in directions parallel to the wall) rises softly, “by a factor of 1 to 2 in the
vicinity of the solid, as compared with the bulk value,” while “the ‘normal’ viscosity
is dramatically increased by a factor of 4 to 5 close to the wall.” Other workers
have also reported increased viscosity or decreased diffusivity in the perpendicular
direction compared to parallel. Kim and Darve also found that the parallel diffusion constant for water next to a smooth wall was larger than the perpendicular diffusion constant,\textsuperscript{218} although the drop near the walls and the difference between parallel and perpendicular was not as great as found by Lyklema \textit{et al.} In a simulation of water near rutile, Predota \textit{et al.} separately calculated parallel and perpendicular diffusivities.\textsuperscript{32} Both decreased to zero at the surface. At most distances from the surface the perpendicular diffusivity was 70-80\% of the parallel diffusivity. Water exhibited a strong and then a secondary density peak near the surface. At peaks in the water density, the perpendicular diffusivity dropped to roughly half of the parallel diffusivity. Freund reports diffusivities parallel and perpendicular to the walls in his simulations of electroosmotic flow.\textsuperscript{31} Freund’s data indicates little difference between the parallel and perpendicular directions, especially for the more realistic case of discrete wall charges. Freund carefully analyzed the electroosmotic velocity profile, showing that the velocity decreases to zero less rapidly than continuum hydrodynamics with constant bulk viscosity would predict and calculating the rise in viscosity needed to explain the velocity profile observed in MD simulations.\textsuperscript{31} Freund’s analysis influenced later works, and certainly influenced our own analysis. Joseph and Aluru determined the diffusion constant parallel to the surface of $\alpha$-quartz,\textsuperscript{106} finding that it decreased to 38\% of the bulk value at the walls, but did not go to zero. (The discrepancy of Freund’s results, where the diffusion constant approached zero at the surface, with those of Kim and Darve and Joseph and Aluru, where the diffusion constants did not approach zero at the surface, may be related to the larger bin widths used in the latter studies.) Turning to the behavior of ions, both the diffusion constant of ions and their mobilities seemed more clearly headed to zero at the surface in Joseph
and Aluru’s data, which seems at odds with the dynamic Stern model and Lyklema, Rovillard and De Conick’s report in their text that ions close to the substrate are slowed but not stuck.

In the previous chapter we described the development of a tractable model for the water/amorphous silica interface, and extended it to treat dissociation of the silanol groups, \[ \cdots \text{Si-O-H} \rightarrow \cdots \text{Si-O}^- + \text{H}^+ \], which gives the surface a negative charge. In this chapter we describe the applications of our amorphous silica/water model.

The simulation detail is described in section 3.2. In section 3.3, the application of our model in unraveling the molecular details of the Stern layer is presented. The electroosmotic flow described by the viscosity dependent Navier-Stokes equation is presented in section 3.4. Finally we end with a conclusion of our main results in section 3.5.

### 3.2 Simulation Detail

Electrokinetic phenomena have been very widely studied in aqueous electrolytes near the amorphous silica surface. The net charge density significantly departs from zero only in a crucial region, less than 1\( \text{nm} \) in thickness. This region supplies the driving force for electroosmotic flow and controls the flow characteristics over the entire width of the channel, even for macroscopic channels. We have previously developed a tractable model for molecular dynamics simulations of the water/amorphous silica interface, and recently extended it to treat dissociation of the silanol groups, \[ \cdots \text{Si-O-H} \rightarrow \cdots \text{Si-O}^- + \text{H}^+ \], which gives the surface its negative charge. The bulk water and amorphous silica regions are described by the SPC/E\(^{137} \) and BKS\(^{136} \) potentials, respectively. The complex hydroxylated amorphous silica surface depends on
preparation history, and has not been precisely characterized, either experimentally or theoretically.\textsuperscript{40} The calculated heat of immersion of our model agrees with experiment.\textsuperscript{34} Comparison with \textit{ab initio} molecular dynamics (AIMD) calculations confirms that our model captures enough features correctly to reproduce at least one important feature of surface-solvent interactions at the water/amorphous silica interface, the relative hydrophobicity of siloxane (\cdots Si-O-Si\cdots) compared to silanol (\cdots Si-O-H) groups.\textsuperscript{223} Qualitatively, the populations of water and ions near dissociated and undissociated silanol groups are in good agreement with AIMD benchmarks. The AIMD radial distributions are more structured than our empirical potential model,\textsuperscript{223} although part of this disparity arises from more extensive averaging over surface disorder in the larger empirical potential simulations. \textit{Ab initio} simulations are only feasible for smaller system sizes and run times, and would have to be repeated over many realizations of the disordered surface for a quantitative comparison.\textsuperscript{135} Detailed comparison of the distribution of water and ions from AIMD and empirical potential simulations near precisely the same surface is not possible because it was impossible to simulate the same system with the two methods. The empirical potential simulations require that the system size be larger than twice the van der Waals interaction cut-off, which precluded empirical simulations of systems as small as those used in the AIMD calculations.

Electroosmotic flow simulations in similar slit pores with different surface charge densities and amounts of added salt were constructed by varying the number of dissociated silanol groups, and including $N_{\text{Na}^+}$ sodium ions and $N_{\text{Cl}^-}$ chloride ions as given in Table 3.1. In every simulation, $N_{\text{Na}^+} - N_{\text{Cl}^-}$ equals the number of dissociated silanol groups. The periodic simulation cell measured 33\AA{} in the $x$- and $y$-directions,
Simulation| asymptotic salt concentration (M)| $N_{\text{Na}^+}$| $N_{\text{Cl}^-}$| electric field (V/m)
---|---|---|---|---
A| 0.55| 66| 48| $7 \times 10^8$
B| 0.30| 42| 24| $7 \times 10^8$
C| 0| 18| 0| $7 \times 10^8$
D| 0| 80| 0| $7 \times 10^7$

Table 3.1: Simulations with three different salt concentrations were constructed by equilibrating $N_{\text{Na}^+}$ sodium ions and $N_{\text{Cl}^-}$ chloride ions with sufficient water molecules to keep the water density near 1.0 g/cm$^3$. The asymptotic salt concentrations reported above were taken from the flat part of the sodium and chloride densities far from the surface after equilibration of the ion distribution.

parallel to the surface, and 144Å in the z-direction. These dimensions, principally the z-dimension, were adjusted by up to several Angstroms to maintain the experimental water density far from the channel walls. Of the total cell length in the z-direction, a slab of amorphous silica occupied roughly 35Å (as discussed in the previous section, the definition of the surface position is not unique), and the remainder occupied by aqueous solution. Each face had a total of 43 silanol groups, for an overall silanol density of 3.95 nm$^{-2}$, in good agreement with experiment.$^{153}$ In simulations A-C (Table 3.1), $N_{\text{Na}^+} - N_{\text{Cl}^-} = 18$, and 9 silanol groups on each side of the silica slab were dissociated, resulting in a surface charge density of $12.7 \mu C cm^{-2} = 0.793 enm^{-2}$. The silica slab used in the empirical simulations was generated from the undissociated silica slab previously described in our earlier work.$^{34}$ Silanol groups were randomly chosen for dissociation, except that dissociated silanols were always separated by at least 6Å, and both silanols belonging to the same geminal group were never dissociated. Since the surface morphology and distribution of dissociated silanols were different on the
two slab faces, the ion and velocity distributions were not symmetric across the channel. Simulation D was constructed to examine the limit of very large surface charge. One member of each geminal silanol group, and every other silanol was dissociated, producing a very large surface charge density of $58.7 \mu C \ cm^{-2} = 3.67e \ nm^{-2}$. This simulation contained a total of 80 dissociated silanol groups, 80 sodium ions, and no chloride ions.

To explore the dynamic properties of a partially dissociated silica surface, an electric field was introduced and a temperature of $300K$ in the non-equilibrium molecular dynamics simulation maintained with a Nosé-Hoover thermostat. The magnitude of the electric field was $7 \times 10^8 V/m$ when the total surface charge was 18 fundamental charges (simulations A-C of Table 3.1), and $7 \times 10^7 V/m$ for simulation D. These fields are much larger than typical experimental fields, and is used to enhance signal-to-noise from simulations. If the response, namely the induced ion and water velocities, depends linearly on the electric field, then using a very large field is an acceptable device for efficient calculation of electroosmotic mobility.

Even though the fields used in our simulations are much larger than realistic fields, the electroosmotic velocities still scale linearly with the driving field, and the electroosmotic mobilities (velocities divided by electric field strength) are independent of the field magnitude, as demonstrated in Figure 3.2. There it is shown that ion velocity profiles for the $0.55M$ NaCl system are 5 times smaller when the field is reduced by a factor of 5. Hence the mobility calculated with very large fields will be essentially the same as that calculated for realistic experimental field strengths. However, the calculation is far more efficient with larger fields for the following reason. Typical thermal velocities are on the order of $400m/s$. These thermal velocities
Figure 3.2: Comparison of ion velocity profiles from a simulations with asymptotic $[\text{NaCl}] = 0.55 M$ and electric field strength $7 \times 10^8 V/m$ (top) with an otherwise identical simulation but with field strength $1.4 \times 10^8 V/m$ (bottom), which is 5 times lower than the first simulation. The scale of the vertical axis of the lower figure is 5 times smaller that the upper plot, so the profiles would appear identical if the velocities were linear with the applied field.

constitute “noise” over which we attempt to accumulate “signal”, the flow velocity, from simulations. It would be very difficult to determine a signal corresponding to a realistic flow velocity, say $\sim 1 \text{ mm/s}$, by averaging over thermal noise in simulations lasting tens of nanoseconds. The same electroosmotic mobility can be calculated with less statistical error by employing a very large electric field, so long as the system is still responding linearly to the field.
Simulations A, B, and C in Table 3.1 were run for a total of 8, 10, and 9ns for data collection following an initial period of equilibration lasting at least 1ns. All of these simulations were performed using the DLPOLY molecular dynamics package.\textsuperscript{226} The simulation time step was 1fs. Coulomb interactions were treated with particle mesh Ewald\textsuperscript{227,228} setting the Ewald precision parameter to $10^{-8}$. Under this setting, the Ewald convergence parameter is $0.043\text{Å}^{-1}$, and 32, 32 and 128 reciprocal lattice vectors are used in the $x$, $y$ and $z$ directions. The silica slab was flexible in these calculations.

Simulation D was run for 100ns to acquire adequate statistics to converge the water and ion velocities near the silica surface and determine crucial issues concerning the dynamic Stern model. Because a very long simulation was required for simulation D, it was run using the GROMACS package,\textsuperscript{229} which was much faster because the silica slab was rigid except for azimuthal rotation of the silanol groups. All 3-body interactions, which are part of our flexible surface potential,\textsuperscript{34,223} were avoided in this run. Error bars are given for the water velocity in the crucial region near the surface in Figures 3.3-3.6, and 3.9, and for both water and ion velocities in Figure 3.10. These error bars represent one standard deviation, as estimated using the blocking method.\textsuperscript{230}

3.3 Stern Layer

3.3.1 Density and flow velocity of water and ions

Figures 3.3-3.5 provides the density of water, Na\textsuperscript{+} and Cl\textsuperscript{−} ions, and their velocities near the silica surface for simulations A-C. Only the first 20Å of aqueous solution on either side of the silica slab is shown to make the behavior of interfacial densities and velocities more apparent. We focus for the moment on the 0.55$M$ NaCl case,
Figure 3.3: The top panel shows a configuration taken from a non-equilibrium molecular dynamics simulation used to generate the data in the lower panels. The O$^-$ atoms of dissociated silanol groups are the large red spheres of the (centered) silica slab. Na$^+$ and Cl$^-$ ions are visible in solution. The lower panels depict the average velocities and densities of Na$^+$ ions, Cl$^+$ ions and water for simulation A of Table 3.1. The surface charge density is $12.7 \mu C \text{cm}^{-2} = 0.793 e \text{nm}^{-2}$, and an applied electric field of $7 \times 10^8 V \text{m}^{-1}$. Meaningless velocity spikes appear where densities are low and there is insufficient sampling to obtain reliable velocities. The vertical dashed lines are guides for the eye to facilitate comparison of the velocity and density profiles. Because the two faces of the silica slab are not identical, the densities and velocities on either side are not symmetric. A limited range of the aqueous solution is shown, so the densities and velocities on the far left and right do not match as would be expected from periodic boundary conditions if the full simulation cell was shown. Ion densities are scaled as indicated in the plots.

simulation A (Figure 3.3). In that figure, an image of the simulation system is included to clarify the meaning of Figures 3.3-3.5. Vertical dashed lines are included in the plots to help the reader align the density and velocity plots. Those vertical lines are
placed in the region where the water velocity appears to approach zero, although there is no precise theoretical formulation for the placement of those lines and they are best regarded as visual guides.

We are inevitably faced with sampling problems when accumulating flow velocities where densities are low. Thermal velocities are on the order of 400m/s. Therefore, it is difficult to average large numbers to obtain relatively small flow velocities in regions where densities are low. This is seen for the chloride ion concentration, which approaches zero near ±20Å in Figure 3.3. The chloride velocities for $z$ values less than 20Å from the center of the slab in Figure 3.3 are meaningless because finding chloride ions in this region is rare. The water and sodium ion densities are larger near the surface, so it is possible to obtain meaningful flow velocities up to the surface in those cases. However, the velocity exhibits meaningless spikes deeper into the surface in these cases which arise from water and sodium ions that occasionally make excursions into pockets of the surface. We chose to include all velocity data in our plots. An alternative would be to crop the velocity plots where the number of data points falls below a certain threshold.

Simulations B and C, intermediate and vanishing salt concentration, respectively, exhibit identical qualitative features to simulation A. Layering of water is visible, but not pronounced near the amorphous silica surface. The ion distribution does not reflect the density oscillations seen in the water density. As one moves in toward the surface, Figures 3.3-3.5 reveal that the water density falls from its maximum near the surface of about $0.04\AA^{-3}$ to zero over a range of about 4Å. The point where the water and $\text{Na}^+$ ion velocities approach zero generally falls in the middle of this range. The question of whether there is an immobile region at the surface depends to some
extent on which value of $z$ is taken to be the surface position. However, if there is an immobile region at the surface, it does not appear to be substantial and certainly not $10\,\text{Å}$ or more from the surface as in some Stern layer models (see discussion of section 3.3). Instead, the dynamic behavior of fluid near this charged surface seems similar to simple fluids, like the Lennard-Jones model, near an uncharged surface.\textsuperscript{222} Furthermore, the point where the sodium ion velocity approaches zero is, in all cases, very close to where the water velocity is zero. In other words, ions are not mobile where water is stagnant, in disagreement with the dynamic Stern model. A more precise analysis of the velocity profiles near the surface using comparisons with continuum theory is given below.

### 3.3.2 Analysis of flow velocity using continuum theory

The Stern model is generally employed to explain electrokinetic effects with continuum fluid mechanics using constant (position-independent) shear viscosity.\textsuperscript{29} Here
we explore the validity of this approach by solving the Navier-Stokes equation (identical to the Stokes equation for laminar flow in the slit pore geometry) using the electric field times the charge density \( q(z) = e(\rho_{Na^+} - \rho_{Cl^-}) \) from simulations as the body force.

\[
\frac{\partial^2 v_x}{\partial z^2} = -\frac{q(z)E_x}{\eta}
\] (3.2)

The charge density from molecular dynamics calculations reflects the statistical variations in the placement of charge groups in the simulation and is not symmetric across the channel, as reflected in the velocity profiles of Figures 3.3-3.5. Poisson-Boltzmann theory, although reasonably accurate, would not be adequate because the velocity profile, as shown below, is very sensitive to the charge density near the walls. The value of the shear viscosity of water at 298K, 0.891 cP, is used in all calculations reported here.
Figure 3.6: Comparison of velocity profiles from molecular dynamics ("noisy" black curve) with solutions to the Navier-Stokes equation (smooth solid blue curves) for simulation A of Table 3.1. The water density and net charge density are provided for reference. Stick boundary conditions are enforced at points \((z = -54.25, 55.17)\) that generated the best agreement with the molecular dynamics velocity profile across the channel. The water flow velocity from molecular dynamics is the same as in Figure 3.3, but now shown across the entire channel. The main discrepancy between molecular dynamics and continuum results near the channel walls is highlighted by red ellipses. Beyond this region, the water density vanishes and the molecular dynamics velocity is not statistically meaningful.

The close agreement between molecular dynamics and Navier-Stokes results in Figure 3.6 was achieved by adjusting the point where stick boundary conditions are enforced in the continuum theory calculations. Moving those points by even 1Å drastically degrades the agreement between continuum hydrodynamics and molecular dynamics simulations, as illustrated in Figure 3.7. Of the three choices for continuum boundary conditions in Figure 3.7, curve (c) is closest to where the molecular dynamics velocity goes to zero (but not quite reaching that point) yet it gives the
worst agreement with simulations. Focusing on the region near the walls, the circled

Figure 3.7: Demonstration of the sensitivity of the continuum theory results to choice of boundary conditions for simulation A of Table 3.1. (a) The best agreement between molecular dynamics and continuum theory is obtained by enforcing stick boundary conditions for the Stokes equation (3.2) at points \((z = -54.25, 55.17)\). Curves (b) and (c) are obtained by moving those points 1 and 2 Å closer to the surface respectively.

regions in Figure 3.6, one sees that near the silica surface the velocity decreases at a slower rate as the surface is approached compared to the Navier-Stokes predictions. To obtain agreement with the actual velocity profile from simulations, stick boundary conditions for the Navier-Stokes equation must be enforced at a point \(\sim 3\) Å into the fluid from where the actual velocity profile goes to zero. In other words, solving the equations of continuum theory with constant bulk viscosity the fluid must be considered immobile in a region near the surface even though both water and ions are still mobile in the calculations. Similar results are obtained for other salt concentrations. A comparison between molecular dynamics and continuum theory for a lower salt concentration (simulation B) is given in Figure 3.9. The sensitivity of the continuum theory results to boundary conditions in this case is demonstrated in Figure 3.8.
Once again, fluid must be considered immobile near the surface in continuum theory to agree with molecular dynamics.

Figure 3.8: Demonstration of the sensitivity of the continuum theory results to choice of boundary conditions for simulation B of Table 3.1. (a) The best agreement between molecular dynamics and continuum theory is obtained by enforcing stick boundary conditions for the Stokes equation (3.2) at points \((z = -52.76, 52.33)\). Curves (b) and (c) are obtained by moving those points 1 and 2 Å closer to the surface respectively.

The gradual decrease in mobility near the surface may be attributed to increased viscosity near the walls,\textsuperscript{26} to surface roughness,\textsuperscript{183} or a combination of these two effects. Freund\textsuperscript{31} and Qiao and Aluru\textsuperscript{104} have documented the increase in effective viscosity near idealized channel walls in the context of electroosmotic flow, although they did not interpret the Stern model in terms of these results. Since increased viscosity and surface roughness have many similar signatures, we may be able to eliminate or confirm certain mechanisms, but ultimately it may prove meaningless to distinguish between increased viscosity and roughness. Roughness is known to push the effective plane of shear away from the surface,\textsuperscript{184,185,187,188} as does increased viscosity, as we see in Figures 3.6 and 3.9. Hence roughness has the same effect on
Figure 3.9: Comparison of velocity profiles from molecular dynamics (“noisy” black curve) with solutions to the Navier-Stokes equation (smooth solid blue curves) for simulation B of Table 3.1. The water density and net charge density are provided for reference. Stick boundary conditions are enforced at points \(z = -52.76, 52.33\) that generated the best agreement with the molecular dynamics velocity profile across the channel. The water flow velocity from molecular dynamics is the same as in Figure 3.4, but now shown across the entire channel. The main discrepancy between molecular dynamics and continuum results near the channel walls is highlighted by red ellipses. Beyond this region, the water density vanishes and the molecular dynamics velocity is not statistically meaningful.

the plane of shear as increased viscosity near the surface, and their contributions may be difficult to disentangle.

### 3.3.3 The dynamic Stern model and surface conductivity

To test the central assumption of the dynamic Stern layer model, we increased the surface charge to extremely high values (simulation D of Table 3.1), which are the only conditions where anything resembling an immobile interfacial layer develops (Figure 3.10). However, there is still no evidence that ions are mobile within immobile solvent.
The difference in Na\(^+\) and water flow velocities for the highly charged surface in Figure 3.10, i.e. the total ion current minus its convective component, is proportional to the local ion mobility. The ion mobility, shown as the black line in the lower plot of Figure 3.10, does not maintain its bulk value or even level off at a reduced value, but instead vanishes where the solvent is not mobile. Simulations for more typical surface charges (Figures 3.3-3.9) also do not show evidence of anomalous ion mobility near the surface.

Figure 3.10: Densities (top) and flow velocities (bottom) near an almost completely dissociated silica surface with a large surface charge of 58.7 \(\mu\)C/cm\(^2\) = 3.67 \(\frac{\mu\text{C}}{\text{nm}^2}\) in the limit of low salt concentration. Because of the extremely large surface charge, the fluid is less mobile near the surface, which is apparent comparing the location of the dotted lines in this figure and Figure 3.5. The local ion mobility of sodium ions is proportional to \((v_{Na^+} - v_{H_2O})\).

The data in Figure 3.10 was generated from a 100\(ns\) run using the GROMACS simulation package using a surface with limited flexibility, as described in section 3.2. In addition, we performed a shorter run of length 11\(ns\) on the same high charge density system with the DLPOLY package using a fully flexible surface. Unlike the
Figure 3.11: Average velocities and densities of Na\(^+\) ions and water for simulation D of Table 3.1 obtained using the DLPOLY package with a fully flexible silica surface. The surface charge density is 58.7\(\mu\)C cm\(^{-2}\) = 3.67\(e\) nm\(^{-2}\), and an applied electric field of 7\(\times\)10\(^7\) V m\(^{-1}\). Ion densities are scaled as indicated in the plots. The dashed boxes indicate the regions where the sodium ion density is significant and the ion flow velocity is statistically meaningful.

results presented in Figure 3.10, these simulations are not of adequate length to obtain the sodium ion velocity profile where the sodium density is low, and to bring error bars in the flow velocity sufficiently low near the surface. However, even from this shorter run (actually comparable in length to simulations A-C of Table 3.1, it is clear that 1) giving up some of the silica surface flexibility did not have a qualitative effect on the results, and 2) just like the GROMACS results, the ion flow velocity using DLPOLY and a flexible silica surface is zero near the surface and vanishes where the water flow velocity vanishes.

In Figure 3.11 we present density and velocity profiles obtained for the 11\(ns\) run using DLPOLY, analogous to the 100\(ns\) GROMACS run presented in Figure 3.10.
The Na$^+$ ion velocity is statistically meaningful only inside the regions delimited with dashed boxes in Figure 3.11 where the sodium ions are concentrated. In this region, it is clear that the ion velocity flow is zero where the water velocity is zero, in agreement with the GROMACS results of Figure 3.10.

Even though there is no evidence of ion mobility through immobile water in molecular dynamics simulations, the surface conductivity calculated from the data is in qualitative agreement with experiment. The clearest comparison can be made with no added salt, as in Figure 3.5, where the entire ion current is the result of surface conduction and the surface conductivity can be calculated from the following equation,

$$K^\sigma = \frac{e}{2E} \int dz \rho_{Na^+}(z)v_{Na^+}(z),$$

where the factor of 2 is included because there are two surfaces driving ion transport in the simulations. The surface conductivity of Na$^+$ near silica in the limit of vanishing salt concentration calculated in this manner is $K^\sigma = 2.4 \pm 0.4\text{nS(nanoSiemens)}$. Establishing a precise experimental value for comparison is difficult, although the existence of the effect is clear under conditions where bulk conduction is suppressed.

One of the earliest measurements by Rutgers placed $K^\sigma$ in the limit of vanishing KCl concentration in the range of 10nS.$^{231}$ Jednacak-Biscan et al.’s measurements of $K^\sigma$ ranged from 1.78 to 4.63nS for water, and 6.46nS for $10^{-5}M\text{ NaCl}$ in contact with fused silica.$^{232}$ Most recently, Erickson, Li and Werner reported $K^\sigma$ to be 1.31nS for vanishing KCl concentration near silica.$^{233}$ Without invoking anomalous surface conduction, our calculated value of $K^\sigma$ is comparable to these experimental values.

The estimate of the surface conduction in the limit of zero salt concentration given in section 3.3.3 may be affected somewhat by overlap of the double layers from the
two sides of the silica slab. The error estimate given for the surface conductivity in section 3.3.3 does not reflect the systematic error that may arise from overlapping double layers, but here we give additional data that indicate that this effect should be minor.

Despite the diverging Debye length for zero salt, the Na\(^+\) ion density appears well-localized near the surface, as shown on the left in Figure 3.12, as would a plot of the Poisson-Boltzmann theory result. However, the data represented in this form does not reveal that several ions are loosely bound. (Of course, there is no strict separation of the ions into loosely or tightly bound groups. The distinction is only qualitative.) The 9 ions arising from each interface have somewhat different density profiles because the surfaces are different, and the binding strength depends sensitively on the surface morphology. The cumulative ion population is plotted on the right in Figure 3.12. There it can be seen that 5-7 Na\(^+\) ions are tightly bound on the right-hand surface, and 9-10 on the left. The remaining few ions drift in the center of the channel during this simulation.

The current density and cumulative contribution to the ion current [varying the upper limit of the integral in Eq. (3.3)] is provided in Figure 3.13. Because it binds its counter-ions less strongly, the contribution to the overall current from the left surface is more spread out than the contribution from the right side. The line separating 9 Na\(^+\) ions on the left from 9 on the right, as judged by where the cumulative ion population on the right-hand plot of Figure 3.12, is closer to the right-hand surface. The corresponding contributions to the current from equal numbers of counter-ions can be seen to be roughly equal. Despite having slightly different distributions, the ions
Figure 3.12: The left panel depicts the Na$^+$ ion density for simulation C. The four curves are averages over 2\textit{ns} from a simulation of total length 8\textit{ns}. The cumulative ion population is shown on the right. Horizontal lines at levels 5, 7, and 10 are provided to accompany the discussion in the text.

arising from each interface make similar contributions to the overall current. Therefore, we expect that these contributions would not change much if larger simulations could be done, better separating the double layers.

Figure 3.13: Current density (black) and cumulative current (red) for simulation D.
3.4 Viscosity Dependent Navier-Stokes Equation

In this section, we investigate the effect of local viscosity on the fluid flow velocity profile in nanochannel. When solving Navier-Stokes equations in the analysis above, we followed the vast majority of the literature and used constant viscosity for the bulk solvent. We have shown that this common procedure provides a remarkably good description of flow more than a few molecular diameters from the wall, but one boundary conditions near the walls where the fluid is actually still mobile. In this section we show that using position-dependent viscosity alleviates these problems.

In classical hydrodynamics, the flow velocity profile is obtained by solving the Navier-Stokes equation.\(^{25}\) For electroosmotic flow of a fluid confined between two walls, the steady state equation with inhomogeneous viscosity across the channel (for flow in \(x\)-direction) is:

\[
\frac{d}{dz} \left( \eta(z) \frac{u_x(z)}{dz} \right) = -\rho(z)E_x
\]  

(3.4)

where \(u_x(z)\), \(\eta(z)\) and \(\rho(z)\) are the flow velocity, local viscosity and charge density at position \(z\) across the channel with the electric field of \(E_x\). The flow velocity and charge density can be obtained from the simulation. By integrating the Eq.3.4 we can get:

\[
\eta(z) = -\int_{\eta_0}^{\eta(z)} \frac{\rho(z)E_x}{u_x(z)} dz
\]  

(3.5)

In our work, we make the local viscosity exponentially increase near the wall while remain constant in the center. Our trial position-dependent viscosity function is:

\[
\frac{\eta(z)}{\eta_0} = v_0 + \exp \left( -\frac{z - z_1}{\lambda_1} \right) + \exp \left( -\frac{z - z_2}{\lambda_2} \right) + \exp \left( \frac{z - z_3}{\lambda_3} \right) + \exp \left( \frac{z - z_4}{\lambda_4} \right),
\]  

(3.6)

where \(\eta_0\) is the experimental bulk viscosity of water and \(v_0, z_1, z_2, z_3, z_4, \lambda_1, \lambda_2, \lambda_3\) and \(\lambda_4\) are parameters which will be obtained by numerical fitting. \(z_1, z_2, z_3\) and
z_4 provide the positions where the viscosity increases and \( \lambda_1, \lambda_2, \lambda_3 \) and \( \lambda_4 \) give the magnitude of the increase. We set the center of the channel to be the origin of \( z \).

When \( v_0 = 1 \), the viscosity of water in the center of channel will be equal to the experimental bulk value. However, some previous work reported that the viscosity value was usually 11% lower than the experimental value when using SPC/E water model in simulations.\(^{31,32,234}\) Therefore, we chose \( v_0 = 0.89 \) in our work.

Figures 3.3-3.5 show the velocity profiles of water near a silica slab in simulation A, B and C in Table 3.1. As we have described in our previous work, the Na\(^+\) counterions accumulate near the surface and the ion and water velocity distribution as a function of distance from the surface shows they are mobile up to the channel walls. The velocity profile approaches zero right at the silica surface, and not 5-10 Å from the surface as commonly postulated in the Stern model. The velocity profile for three salt concentrations from molecular dynamics calculations (Table 3.1) are compared with the solutions of the Navier-Stokes equation of continuum hydrodynamics (Eq.3.2). The charge density from the simulations and the viscosity of bulk water (0.891 cP) were used as input in the solution of the Navier-Stokes equation. Close agreement between Navier-Stokes equation and molecular dynamics simulations can be achieved except within a few Angstroms of the channel walls. To obtain better agreement in the region near the walls (the red circles highlight in Figures 3.6,3.9) and 3.14, an inhomogeneous viscosity must be used.

The charge density distribution was interpolated to get a smooth profile and the velocity profile was fitted by polynomial function. After smoothing the smooth charge density and velocity profiles from simulations, we can solve for the viscosity distribution by using Eq.3.5. The resulting viscosity profile was then fitted by Eq.3.6. The
coefficients in Eq.3.6 were least square fitted and the results are shown in Table 3.2. In Eq.3.6, $\lambda_1$, $\lambda_2$, $\lambda_3$ and $\lambda_4$ were constrained to be positive. The viscosity obtained from Eq.3.5 and the fitted viscosity (Eq.3.6) are shown in Figure 3.15. The results of the solution from Navier-Stokes equation for simulation C in Table 3.1 are shown in Figure 3.16. The velocity profile was approximated with a polynomial and the derivative $dv_x(z)/dz$ was obtained.

We can see that viscosity starts to increase at about 8-10 Å from the silica wall. This result agrees with previous theoretical studies of fluid flow in confined geometries$^{31,222,235-237}$ and near interfaces.$^{238}$ When the fitted inhomogeneous viscosity is used to solve the Navier-Stokes equation using the charge density from simulations as input, the solution agrees well with the simulation result as shown in Figure 3.16.
Figure 3.15: The comparison of the viscosity obtained from the velocity profile in simulation C using Eq.3.5 and the fitted viscosity using Eq.3.6.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Fitted Value (Å)</th>
<th>Coefficient</th>
<th>Fitted Value (Å)</th>
</tr>
</thead>
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<td>$\lambda_1$</td>
<td>1.88</td>
</tr>
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<td>$\lambda_2$</td>
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<td>$z_4$</td>
<td>45.04</td>
<td>$\lambda_4$</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Table 3.2: Coefficients in Eq.3.6

Compared to Figures 3.6 and 3.9 in section 3.3.2 in which the continuum prediction only matches the molecular dynamics simulation velocity some distance away from the walls, the velocity profile can be predicted from the Navier-Stokes equation using inhomogeneous viscosity for the entire region of the channel by using our viscosity distribution.
Figure 3.16: Blue curve shows the viscosity distribution using Eq.3.6 across the silica channel. Navier-Stokes equation (Eq.3.5) is solved to get the velocity profile as the red curve shows. The vertical dashed lines are indicating approximately where the silica walls reside.

3.5 Conclusion

Solvent adjacent to the charged surface in the electrical double layer is not immobile, although the effective viscosity near the surface is greater than in the bulk. At typical charge densities for the silica surface we model, this effect leads to a velocity profile that approaches zero at the surface more gradually than if the viscosity maintained its bulk value. Our calculated flow velocities can be reproduced by continuum theory by assuming a viscosity that increases near the surface. In this chapter we examine the consequences of using constant bulk viscosity, as is done throughout the electrokinetics literature except in a few cases. The result is that stick boundary conditions must be enforced about 3Å in a direction away from the walls and toward
the bulk solvent from where the fluid velocity actually approaches zero. To obtain accurate electroosmotic flow rates from continuum theory with constant viscosity, the fluid must be considered immobile near the surface, even though it is not.

Except for extremely large surface charge density, the fluid located in the first few Angstroms from the surface (3 Å is what our simulations suggest for the silica surface) is a region of gradually reduced mobility. The classical Stern model is successful as an “effective” model that reproduces the fluid velocity far from the surface, but cannot be taken literally. The circled regions in Figures 3.6 and 3.9 that would be considered immobile in continuum theory are region of large charge density.

With regard to the dynamic Stern model, molecular simulations show no evidence that ions have enhanced mobility relative to solvent near a charged surface. Nevertheless, the simulations exhibit a surface conductivity similar to experiment, indicating that effects previously attributed to anomalously large surface conductivity through immobile water can be explained without anomalous transport near the surface. Furthermore, the fact that the effective ζ-potential can be very different or even of opposite sign from the potential at the surface, another important motivation for the Stern model, is captured in examples like simulation A (Figure 3.3,3.6).

We note recent efforts to reconcile measurements of the ζ-potential by different methods without the assumptions of the dynamic Stern layer model. Our analysis should provide guidance for the formulation of a unified model. It will also assist in the evaluation of recent reports of either ice-like or liquid-like water films and high-density premelting layers at the water-silica interface. With regard to device design, this research confirms that continuum hydrodynamics performs remarkably
well away from channel walls, but must be combined with a molecular perspective within a few Angstroms of the surface.
CHAPTER 4

Analysis of the subcritical CO$_2$/H$_2$O Interface

4.1 Introduction

The properties of aqueous interface are important in many areas of science. For example, hydrophobicity and hydrophillicity are phenomena which are determined by the structural properties of water at interfaces with other materials. Aqueous interfaces play crucial roles in material science, biology and chemistry.\textsuperscript{242-244} In atmospheric chemistry, the transport of molecules across the liquid/vapor interface is important in understanding heterogeneous chemical reactions in aqueous droplets.\textsuperscript{245} Ion behavior at aqueous interface plays an essential role in many chemical processes, biological systems and environmental issues.\textsuperscript{246,247}

Interface properties – for example, surface roughness, density profiles, molecular orientations – are the key to understand the problems as described above. However, compared to the bulk properties, interface properties are still not well understood. In experiments, the difficulty lies in the fact that there are not many effective techniques to probe the interface in molecular level.\textsuperscript{248} In the recently decades, the development of surface techniques such as scanning tunneling microscopy (STM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy enabled intensive study of
surface chemistry on the nanometer level. Non-linear optical spectroscopy, such as second-harmonic generation (SHG) and sum frequency generation (SFG) vibrational spectroscopy, are uniquely suited to investigate interfaces. In SFG, two input laser beams meet at an interface to generate an output beam with the frequency equal to the sum of the input frequencies. SHG is a special case of SFG where the frequency of the output beam is just twice of the input. The advantage of non-linear optical spectroscopy is their surface specificity since no signal arises from centrosymmetric media. They are now the preferred techniques to gather structural information about liquid-liquid, gas-liquid and gas-solid interfaces.

Early SHG investigations of the vapor/water surface by Goh et al concluded that surface water molecules are preferentially oriented. The first OH vibrational spectra of water molecules at the vapor/water surface was obtained by Du et al using SFG. They found that more than 20% of the water molecules at the surface have one OH group pointing into the vapor. The spectra of the vapor/water surface indicated that there were two peaks which could be characterized as bulk ice-like and liquid-like peaks due to their similarities to the IR and Raman spectra of ice and water. The dangling OH group is believed not to participate in H-bonding with other neighboring water molecules. Several groups have also performed SFG experiments on vapor/water surfaces in the last fifteen years. Their results reveal both order and disorder of H-bonding network at the surface. Other experiments on the vapor/solution surface indicate that ions near the surface influence the water vibrational spectrum via the reorientation of surface water molecules and hence these spectra provide information about the surface structure. The results of some experiments showed that the anions would be in excess at the surface while the cations
concentration would be depleted.\textsuperscript{248} However, \textit{ab initio} and classical molecular dynamics simulations by Buch \textit{et al}\textsuperscript{270} also indicated that the density of one particular cation, the excess proton, is enhanced at the surface. In their work, they found that the water surface is actually acidic meaning that $\text{H}_3\text{O}^+$ prefers surface sites. The enhanced hydronium concentration at the surface was also observed experimentally by Petersen \textit{et al} using SHG spectroscopy.\textsuperscript{271} They linked their observations to the existence of the anions at the surface, which decreases the repulsion of cations like hydronium from the surface. In general, the nature of the ions at the liquid water surface is still a matter of debate.

Optical surface techniques were also used to study the interface between liquid water and other materials. Richmond’s group performed SFG experiments to examine the adsorption and reaction of $\text{SO}_2$ and $\text{CO}_2$ at the water surface and found the formation of $\text{SO}_2$ complex at the surface. No $\text{CO}_2$ complex was observed, and $\text{CO}_2$ had little effect on the water molecules on the surface under the conditions of the study.\textsuperscript{260} The $\text{CO}_2$ pressure used in the experiments is not specified, but presumably much less than the upper range of our studies, which extend beyond 90% of the critical pressure of $\text{CO}_2$. Richmod and coworkers also combined molecular dynamics simulations and vibrational spectroscopy to study the $\text{CCl}_4$/water, 1,2-dichloroethane/water\textsuperscript{272} and oil/water interfaces.\textsuperscript{273} Miller \textit{et al} used SFG spectroscopy to obtain structural information about a monolayer lipid/water interface, and showed how the charged group on the lipid affected the layering of the interface water.\textsuperscript{274} The structure of a lipid/$\text{D}_2\text{O}$ water interface was also revealed by Allen \textit{et al} using SFG spectroscopy, and a dangling OD was observed even when the water surface was fully covered by lipid molecules.\textsuperscript{275}
Computer simulations have been used intensively to understand the structure of water interface in the past two decades. Density profiles, surface depth and molecular orientations are usually obtained from the simulations and compared with the experimental results. Vassilev et al performed \textit{ab initio} molecular dynamics simulations with Perdew-Wang 91 (PW91) exchange-correlation functional to calculate the structural and transport properties of liquid water and the water/vapor interface. Their results showed that the dipole of the interfacial water molecules preferred to point toward the vapor region. Although there is some early experimental and theoretical evidence supporting this water orientation preference, recently Alejandre et al used molecular dynamics simulations and showed that the water molecules on the middle and liquid sides of the surface prefer to be parallel to the surface while on the vapor side water dipole directed toward the liquid. Some other recent simulations support these results. Horvai et al also proposed a method to characterize the interfacial molecules in simulations that bears some similarities to the methods we use to identify a local interface position. They construct a bivariate distribution which describes the correlation interface height of two points on the interface. They argue that the interfacial water molecular orientation is not simply defined according to the overall density profile, and must be analyzed according to the local interface position and local curvature of the interface. They also applied their new method to analyze the CCl$_4$/water interface and similar orientational information concerning the interfacial water molecules was obtained. Other simulations also reported the existence of free OH bonds at the surface projecting toward the vapor side as observed in many experiments. Morita et al used molecular dynamics simulations to investigate the vapor/liquid interface of pure
water, NaCl and NaI solutions and found that the water molecular plane tends to lie on the surface. Moreover, the enhancement of anions at the surface slightly perturbed the water orientation due to the electrical double layer of Na\(^+\) and I\(^-\). They also compared their simulations with SFG experimental results. Several groups used both vibrational spectroscopy and molecular dynamics simulations to investigate the vapor/water and vapor/solution interfaces. The combination of simulations and experiments can provide further molecular-level information about the interface.

CO\(_2\) has attracted more and more attention as a useful solvent and as the principal greenhouse gas in recent years. CO\(_2\) as a compressible solvent has been used to replace toxic organic solvents for chemical reactions and separation processes. In these applications, CO\(_2\) can be used as the external phase of water-CO\(_2\) microemulsions. CO\(_2\) is also the main greenhouse gas responsible for global warming and climate change. The extraction and storage of CO\(_2\) have been proposed to slow the advance of global warming. Ocean sequestration may be one of the most attractive methods for storage of greenhouse gases. Clathrate hydrates form by the hydrogen bonded water molecules at deep sea and provide cages for guest molecules like CO\(_2\) and this process could happen at the interface of CO\(_2\) and sea water. Hence the fundamental understanding of the structure of CO\(_2\)/water interface is of great interest.

da Rocha et al used molecular dynamics simulations to investigate the structural properties of supercritical CO\(_2\)/water interface. The local dynamic interface definition method was used to identify the local surface position, and reveal intrinsic density profiles. The dipole of the water molecules at interface tends to be almost parallel to the interface and slightly point into the bulk water. The CO\(_2\) molecules at
the interface were also observed to be parallel to the interface. They also used molecular dynamics simulations to study the surfactant-modified CO$_2$/water interface with perfluoropolyether ammonium carboxylate (CF$_3$(OCF$_2$CF(CF$_3$))$_3$OCF$_2$COO$^-$NH$^+_4$) monolayer and found that CO$_2$ can penetrate into the surfactant and solvate the fluorinated tail-group due to the strong interactions between CO$_2$ and fluorinated tail group.$^{296}$ Surface tension and rheological measurements of CO$_2$/water interface were performed by Boury et al and the results showed that the hydrated CO$_2$ can diffuse into the water phase and then change the organization of the interface.$^{297}$ Trout et al used both Monte Carlo and molecular dynamics simulations to calculate the diffusivities of H$_2$O and CO$_2$ in clathrate hydrate and provide some insight into the mass transfer of CO$_2$ in clathrate hydrate.$^{298}$

Previous simulation studies of the CO$_2$/water interface have been performed in the limit of zero CO$_2$ pressure.$^{299-301}$ Investigations like those of Tewes and Boury$^{297}$ reveal a smooth progression of properties like the surface tension and CO$_2$ surface absorption (of course, related) as CO$_2$ pressure is increased from zero to its critical pressure. Our goal in this work is to furnish the first theoretical study of the CO$_2$/water interface between the zero-pressure and super-critical regions. To our knowledge, non-linear spectroscopic studies have not been attempted in this interesting subcritical region. It is our hope that our study will stimulate experimental investigations of the subcritical region.

In this work, the analysis of the structure of CO$_2$/water interface using molecular dynamics simulations is presented. The simulation details will be described in section 4.2. Capillary wave theory and its application in this work will be reported in section 4.3. We also investigate the molecular orientations at the interface in section 4.5 and
the surface potential in the interface systems in section 4.6. Finally we will end with
the conclusion in section 4.7.

4.2 Simulation Methods

The CO$_2$/water interface system was simulated using molecular dynamics package
DLPOLY 2. The SPC water model for water and EPM2 model for CO$_2$ were used
in the simulations. Harris and Yung showed that their EPM2 model, while simple and
computationally efficient, can successfully describe the liquid-vapor phase behavior of
CO$_2$ up to the critical point. While more recent water models like SPC/E give a
somewhat better account of the static and dynamic properties of pure water, the SPC water model
has been more extensively benchmarked, and shown to give a good account of water/CO$_2$ binary mixtures. For that reason, we have adopted
the combination of EPM2 and SPC models in our work. The EPM2 model consists
of three charge sites that are also centers for Lennard-Jones interactions.

\[
U_{ij} = \sum_{i,j} \left\{ 4\epsilon_{ij} \left[ \frac{\sigma_{ij}}{r_{ij}} \right]^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \right\} \quad (4.1)
\]

The SPC water model is in the same form, except that only the oxygen atom is a
center for Lennard-Jones interactions. As has been done in previous treatments of
CO$_2$/water mixtures, Lorenz-Berthelot combining rules were used to calculate
the dissimilar molecules.

\[
\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2} \quad \text{and} \quad \sigma_{ij} = (1/2)(\sigma_{ii} + \sigma_{jj}) \quad (4.2)
\]

Parameters for SPC and EPM2 models are summarized in Table 4.1.

19 different rectangular CO$_2$/water simulation cells were constructed with different
numbers of CO$_2$ molecules but the same number of water molecules. Larger systems
<table>
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<th>LJ parameters</th>
<th>$\epsilon/k_B$ (K)</th>
<th>$\sigma$ (Å)</th>
<th>point charges</th>
<th>$q$ (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_C C_C$</td>
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<td>2.757</td>
<td>$C_C$</td>
<td>+0.6512</td>
</tr>
<tr>
<td>$O_C O_C$</td>
<td>80.507</td>
<td>3.033</td>
<td>$O_C$</td>
<td>-0.3256</td>
</tr>
<tr>
<td>$C_O O_C$</td>
<td>47.588</td>
<td>2.892</td>
<td>$H_W$</td>
<td>+0.41</td>
</tr>
<tr>
<td>$O_W O_W$</td>
<td>78.208</td>
<td>3.166</td>
<td>$O_W$</td>
<td>-0.82</td>
</tr>
</tbody>
</table>

Table 4.1: LJ parameters for the EPM2 CO$_2$ and SPC water models. The C=O bond length is 1.149Å, and the O-H bond length is 1.0Å. The water bond angle is the tetrahedral angle.

were employed with increasing pressure as a film of increased density grew adjacent to the aqueous phase. The periodic simulation cells measured 74 Å in the x- and y-directions parallel to the surface. The dimension in z-direction ranged from 127 Å to 271 Å. 7722 water molecules occupied roughly 50 Å of the total cell length in the z-direction, the remainder of the system was occupied by the CO$_2$ molecules. Fig.4.1 shows the snapshot of one of the simulations, in which water slab is in the center of the cell. Detailed information of the simulated systems are given in Table 4.2.

Periodic boundary conditions were applied in all directions. The primary cell contained two CO$_2$/water interfaces. All simulations were run in the isothermal-isobaric (NPT) ensemble first for 200 ps to proceed to equilibration under 300K using the Berendsen thermostat and pressure coupling method.$^{308}$ After the equilibration run, the systems were run in the constant NVT ensemble for 5 ns to collect data. A time step of 1 fs was chosen. The thermostat relaxation time was 0.5 ps. Electrostatic interactions were calculated with the particle mesh Ewald method$^{227,228}$ setting the precision parameter to $1 \times 10^{-6}$ and convergence parameter to 0.3175. The maximum k-vector indices were 32, 32 and 64 in x-, y- and z-directions respectively. The SHAKE method$^{309}$ was used for distance constraints in the simulations.
Figure 4.1: Snapshot of the CO$_2$/water interface system in the simulation. Water molecules comprise the slab in the center of the figure.

4.3 Capillary wave analysis of CO$_2$/water interface

In three dimensions, long wavelength fluctuations of a liquid-vapor or liquid-liquid interface cause the interface width to diverge logarithmically with system size in the absence of additional restraints like a gravitational force.$^{310-312}$ Common physical properties, like the average number density tabulated along a direction perpendicular to the interface, will actually depend on system size. Our goal is to describe the
Table 4.2: Detailed information about the 19 simulations. Pressures were determined by plugging the asymptotic densities into the Bender equation of state. The intrinsic local structure of the water/CO$_2$ interface, which should be independent of simulated system size as long as the system is sufficiently large. This issue was tackled by previous authors. The various strategies devised in the past, which we follow here, is to track the long-wavelength fluctuations of the interface and accumulate local properties relative to the long-wavelength structure.

We use a Fourier description of the long-wavelength fluctuations of the water/CO$_2$ interface.

$$h(x, y) = \sum_n c_n \exp \left[ 2\pi i \left( \frac{n_x}{L_x} x + \frac{n_y}{L_y} y \right) \right]$$ (4.3)
Figure 4.2: Water and CO$_2$ density profiles from simulation 1, a low CO$_2$ pressure. Density profiles with respect to the capillary wave surface are shown on the left, while the right panel shows the density profiles relative to a space-fixed coordinate system.

$h(x, y)$ is the transverse displacement of the surface, $L_x$ and $L_y$ are the interface dimensions in the $x-$ and $y$-directions. $n_x$ and $n_y$ index the wave vector in the $xy$ plane and $c_n$ are the coefficients describing the instantaneous position of the interface obtained by a fitting procedure described below. The maximum $n_x$ and $n_y$ were chosen to be $n_{x,max} = n_{y,max} = 8$, which implies that a length of $\frac{L_x}{n_{x,max}} = \frac{L_y}{n_{y,max}} = 9.25\text{Å}$ is chosen to be the boundary that separates long wavelength interface fluctuations from local molecular displacements. In our analysis, the horizontal cross section is divided into an $13\times13$ fine grid. The $z$-coordinate of the highest (lowest) water molecule on the upper (lower) surface within each $13\times13$ parallelepipeds of height $L_z$ defines the local surface position. On rare occasions, a water molecule enters the CO$_2$-rich phase.
We did not consider water molecules if they were separated by a distance 6.5Å from the rest of the water. The coefficients $c_n$ in Eq. (4.3) are chosen by least-squares fit of $h(x, y)$ to the 13×13 interface positions.

![Density profiles](image)

**Figure 4.3:** Water and CO$_2$ density profiles from simulation 13, a CO$_2$ pressure close to the CO$_2$ critical point. Density profiles with respect to the capillary wave surface are shown on the left, while the right panel shows the density profiles relative to a space-fixed coordinate system.

Da Rocha et al., in their study of the water/supercritical CO$_2$ interface, used a similar grid scheme but based the interface height on both the highest water and lowest CO$_2$ molecule (for the upper surface). Our case is different, since we cover the range of CO$_2$ density from zero pressure to the critical region. At low density, the position of the CO$_2$ molecule closest to the interface is not strongly correlated to the
position of any well-defined interface. For this reason, we chose to define the interface solely with respect to water positions.

Structural properties can be obtained either in a space-fixed coordinate system, or using the definitions described above, relative to the capillary wave surface location, \( h(x, y) \) [Eq. (4.3)]. The density profiles are calculated using bins of width 0.35Å in the \( z \)-direction. Figures 4.2 and 4.3 compare the density profiles with and without capillary wave analysis in the limit of low and high CO\(_2\) pressure, simulations 1 and 13, respectively. An artifact of only using water to define the interface location is a very sharp density peak in the water density which reflects the position of water molecule that defines the interface position on the fine grid. Relative to the capillary wave surface, the density profiles are more structured. At low CO\(_2\) pressure (Fig. 4.2), the single CO\(_2\) density peak near the surface is significantly narrowed when accumulated with respect to the capillary wave surface. Despite the artifactual peak due to the interface-defining water, a smooth background rise in the water density upon entering the wave phase is clearly visible. The density profiles relative to a space-fixed frame are broadened, the result of convoluting local density profiles with the distribution of the capillary wave surface. As the system evolves from low to high CO\(_2\) pressure, the water density profile hardly changes as confirmed in Fig. 4.4. The same is true of the orientational distribution of water molecules, as we show below in section 4.5. However, the CO\(_2\) density exhibits major changes that go beyond a rescaling of the density profile with overall density. In particular, the CO\(_2\) density develops a secondary peak and a long-range tail. These features will be discussed below in
section 4.4. The CO$_2$ orientational distribution also change across the range of sub-critical pressures (section 4.5 below), although it is minor compared to the density change.

![Graph showing water density profiles in simulation 1 and 13.](image)

Figure 4.4: The comparison of water density profiles in simulation 1 and 13.

### 4.4 Evolution of the CO$_2$ density profile from low pressure to the critical region

Carbon dioxide density profiles from low pressure up to close to the critical point are shown in Fig. 4.5. Several features are readily apparent. The three density profiles at the lowest pressures all have similar shape. In this region the CO$_2$ density is simply scaling with the bulk density or pressure. This is the low density limit previously calculated by other workers.$^{299-301}$ The scaling with bulk density is verified
Figure 4.5: Carbon dioxide density profiles with respect to the capillary wave surface at various sub-critical pressures. The pressure associated with each curve (bar) is given in the figure legend.

In Fig. 4.6, where $\rho(z)/\rho_{\text{bulk}}$ is plotted. In the latter figure, the densities at 20.3, 29.3, and 36.2 bar are quite close to each other. Anticipating what will happen at higher pressure, the single density peak shows a very slight saturation effect and fails to grow linearly by a small amount. Therefore, when the density is normalized by $\rho_{\text{bulk}}$, the peak of $\rho(z)/\rho_{\text{bulk}}$ at 36.2 bar is slightly less than the peak at 20.3 bar in Fig. 4.6.

At pressures greater than $\sim 35\text{bar}$, saturation of the first peak becomes pronounced. In Fig. 4.5, it can be seen that the maximum of the first density peak is approaching a typical CO$_2$ liquid state density ($\sim .014\text{Å}^{-3}$). Beyond this point, further growth of the film of CO$_2$ on the water surface extends to a second and extended layers at larger $z$, and not a higher first peak. The saturation of the first peak
Figure 4.6: Carbon dioxide density profiles with respect to the capillary wave surface normalized by the asymptotic bulk density at various sub-critical pressures. All of the curves approach 1 asymptotically at large $z$. The pressure associated with each curve (bar) is given in the figure legend.

is quantified in Fig. 4.7, where the height of the density maximum is plotted as a function of the asymptotic bulk density.

As the pressure grows from $\sim P_c/2$ to $P_c$, a second density peak emerges, first visible as a shoulder, but then as a separate peak at the highest pressures. In this region the CO$_2$ molecules reach sufficient density to exhibit layering effects. In addition, a pronounced tail in the density appears at high pressures. To the numerical precision available in our simulations, the decay of the density at large $z$ is exponential. This is revealed in the plot of $\rho(z)/\rho_{\text{bulk}} - 1$ given in Fig. 4.8. At all but the highest pressure, the decay of $\rho(z)/\rho_{\text{bulk}} - 1$ with $z$ is a single exponential (linear behavior in Fig. 4.8).
Figure 4.7: The values of the first CO$_2$ density peak in different simulations. Here, the $x$ axes represent the bulk densities of CO$_2$ in 19 simulations; the $y$ axes represent the corresponding peak densities. The peak densities are fitted with an empirical equation $\rho_{\text{peak}} = \frac{a_0 \rho_{\text{bulk}} + a_1 \rho_{\text{bulk}}^2}{1 + a_2 \rho_{\text{bulk}} + a_3 \rho_{\text{bulk}}^2}$ (red curve).

At this time, it is not clear whether the slight curvature of the $P = 65.6\text{bar}$ plot in Fig. 4.8 can be taken as a departure from single-exponential decay, or just a numerical artifact.

The CO$_2$ density profiles of all the 19 simulations are shown in Figure 4.9. The second density peak appears only in simulations with relatively high CO$_2$ bulk densities.
Figure 4.8: $\rho(z)/\rho_{\text{bulk}} - 1$ on a logarithmic scale at various sub-critical pressures. The pressure associated with each curve (bar) is given in the figure legend. When $\rho(z)/\rho_{\text{bulk}} - 1$ falls below $\sim 0.1$, the simulation data lose sufficient precision to continue the plot.

4.5 Orientational order at the CO$_2$/water Interface

In this section, the orientational distribution of water and CO$_2$ molecules near the interface are presented. For water molecule, we examine the orientation of both the water dipole and OH vectors. For the CO$_2$ molecule, we track the orientation of CO vector. The orientation is defined relative to the unit vector normal to the interface and pointing into bulk CO$_2$. We focus on the orientational distributions from a low and high pressure case, simulations 1 and 15 (Table 4.2), respectively. The orientational distributions were accumulated in horizontal regions of width 1.4 Å.
Figure 4.9: 3D plot of the CO$_2$ density profile for all the 19 simulations.

Figure 4.10a shows the orientational distribution of water dipole vector ($\mu_{\text{H}_2\text{O}}$) in low pressure simulation 1 and high pressure simulation 15. It is clear that the orientational order of the water is barely affected as the CO$_2$ pressure rises from zero to 67.95 bar. At the surface (region 0 in Fig. 4.10), the distribution of the water symmetry axis peaks close to $\cos(\theta) = 0$, which means the angle between ($\mu_{\text{H}_2\text{O}}$) and surface normal is about 90 degree. The ($\mu_{\text{H}_2\text{O}}$) vector tends to lay parallel to the surface. In region 1, below the surface toward bulk water, the dipole vector has preference to point slightly into the bulk. There is a small amount of structure in region 2, further into the bulk water phase, and region 3 is almost perfectly isotropic. The distribution of water OH vectors in Fig. 4.11 is more structured than the distribution of dipole vectors in Fig. 4.10. A bimodal distribution is observed for the OH vector from region 0 at the surface down through region 2 toward bulk water. The two peaks
in the distribution represent the preferential direction of the two OH vectors of water molecule, in which one of the OH bonds points to the vapor side and the other one points toward the bulk liquid side. As was found for the dipole vector, there is no preferred orientation of OH vector in region 3. Our orientational results are similar to the previous simulations on the water/vapor and water/liquid interfaces.\textsuperscript{284–286,289,295}

The orientation distribution of CO vector in the \textit{CO}_2 molecule in simulation 1 is shown in Figure 4.12a. Region 0 is right at the density peak of \textit{CO}_2 density and there is a preferred orientation for \textit{CO}_2 molecules parallel to the surface and isotropic distribution is observed in region 1 and 2. The probability for the interaction between \textit{O}_C and \textit{H}_W could be maximized by the parallel orientation of the molecules as described in previous work.\textsuperscript{295}
Figure 4.11: a) The orientational distribution of OH vector with respect to the surface normal in simulation 1. Region 0, 1, 2 and 3 have the same meaning as in Figure 4.10. b) The orientational distribution of OH vector with respect to the surface normal in simulation 15.

Figure 4.12: a) Orientational distribution of CO vector with respect to the surface normal in simulation 1. b) The orientational distribution of CO vector with respect to the surface normal in simulation 15. The distribution is shown at the two density peaks of CO\(_2\) molecules near the surface and in between.
In Figure 4.10b and Figure 4.11b, we show the water orientational distribution in simulation 15, in which the asymptotic CO\(_2\) density is high and the surface excess is large. We didn’t see much difference between this one and the orientation in simulation 1. Still water dipole is preferably laying parallel to the interface and slightly pointing out to the bulk water with one O–H bond projecting into the vapor phase. To get the entire view of the water orientation near the surface, a 3D plot of the orientational distribution of OH vector is shown in Figure 4.13. The plot shows how the orientation distribution changes from the bulk CO\(_2\) phase to bulk water phase. The spikes in the bulk CO\(_2\) phase are due to the poor statistics of water in bulk CO\(_2\). The flat plane in the bulk water shows the isotropic distribution and anisotropicty is only observed near the surface. The similarity between the water orientational distribution of simulation 1 and 15 shows that the surface structure of water phase doesn’t change much with the increasing surface density of CO\(_2\). Our water orientational distribution results are quite similar to that at the hydrophobic surfaces as reported in previous works, such as water/CCl\(_4\), water/alkane and water/1,2-dichloroethane interfaces.\(^{283,284,295,317}\)

The orientational distribution of CO vector with respect to the surface normal in simulation 15 is shown in Figure 4.12b. The CO\(_2\) surface excess is very large in simulation 15, as we have shown in section 4.3, and there are two peaks of CO\(_2\) density near the surface. In Figure 4.12b, the orientational distributions were calculated for the regions with the two peaks and in between in order to obtain better statistics and give a better view of the surface structure. Similar to the orientation in simulation 1, CO\(_2\) molecules at the surface tend to lay parallel to the surface, as shown in the bottom plot. Isotropic distribution was observed in the bulk CO\(_2\). However, the
Figure 4.13: The 3D orientational distribution of OH vector with respect to the surface normal in simulation 15 in the entire surface region. Negative $z$ values correspond to layers into the bulk CO$_2$ and positive $z$ values correspond to the bulk water with the zero point as the surface position.

CO$_2$ molecules at the second density peak also show slightly orientational preference of being parallel to the surface; while the CO$_2$ molecules between the two density peaks show slightly orientational preference, but opposite to the orientation of CO$_2$ molecules at the two peaks. Figure 4.14 shows the full view of the CO$_2$ molecular orientational distribution near the surface. The small spikes in the water phase are due to the poor statistics of few CO$_2$ molecules in water. It can be seen clearly that the strong preference of CO$_2$ molecular orientation is observed at the surface region. Although the CO$_2$ molecules have orientational preference at the second density peak and between the two density peaks, the preference is very weak compared to that at the first density peak.
4.6 Surface Potential

In this section, we focus on the electrodynamics of the water/vapor interface, which plays an important role in electrochemistry, ion transport at surface and surface reactivity. For example, the behavior of ions near the interface can be influenced by the surface potential.\textsuperscript{318,319} There are two routes to the surface potential: thermodynamic and electrodynamic, here we only discuss the later, in which the surface potential is averaged over the underlying charge distribution. The surface potential ($\chi$) is defined as the difference between the gas-phase Volta potential ($\psi$) and the liquid-phase Galvani potential ($\phi$):\textsuperscript{320}

$$
\chi = \phi - \psi
$$

(4.4)

The Volta potential can be defined as the work to bring an ideal unit charge from infinity to the point just at the vapor side of the interface, and the Galvani
potential can be defined as the work to transfer an ideal unit charge from the vapor side through the interface and into the bulk liquid side. Here an ideal unit charge means the charge has no volume and is unperturbed. However, in practice a real physical charged particle is moved such as electron, ion and etc.

In section 4.5 we have shown that molecules are preferably oriented at the interface, as a result, molecular dipole distribution forms and surface potential occurs.\textsuperscript{321} Conventionally the surface potential of water at the vapor/water interface was thought to be positive since the hydrogen atoms prefer to pointing into the liquid side.\textsuperscript{320,321} However, Roux \textit{et al} argued that the determination of surface potential only from the orientation of the molecules would lead to quantitative error and the contribution of quadrupole should not be ignored.\textsuperscript{322} Some experiments gave the magnitudes of surface potential assuming certain molecular orientations at the surface and using some mathematical procedures, as reviewed by Paluch.\textsuperscript{321} But the surface potential can not be measured directly by experiments. Computer simulations using electrodynamics would be more appropriate to provide insight into the surface potential.

In electrodynamics, the surface potential can be obtained by integrating the total interfacial electric field $E(z)$ across the water/vapor interface:

$$
\Delta \chi = \chi(z) - \chi(z_0) = -\int_{z_0}^{z} dz' E(z') \quad (4.5)
$$

The $z$ direction is perpendicular to the surface and $z_0$ represents the position far away from the surface with the potential of zero, and the $x$ and $y$ contribution sum to zero due to the symmetry of the system. The electric field can be obtained by integrating the total charge distribution $\rho(z)$ obtained from the simulation across the
interface:

\[ E(z) - E(z_0) = \frac{1}{\varepsilon_r} \int_{z_0}^{z} dz' \rho(z') \]  

(4.6)

The surface potential of water at the interface has been calculated in recent years. Early works have been done by Pratt et al on the liquid/vapor interface of water and they showed the electric potential and electric field curve across the interface and the surface potential was predicted to be \(-(130 \pm 50)\) mV.\textsuperscript{318,319} Koper et al used classical molecular dynamics simulations to estimate the surface potential of water at vacuum/water interface and the result was approximately 560 mV.\textsuperscript{323} Roux et al proposed a simple model in which the molecules are isotropically oriented with a Gaussian distributed charge density. The surface potential of vacuum/water interface predicted from the model was about \(-400\) mV.\textsuperscript{322} Recently Patel et al used a modified water model (TIP4P-QDP) with charge dependent polarizability to compute the surface potential of water and their result was about \(-500\) mV.\textsuperscript{5} They also investigated the surface potential under different temperatures and in different sodium halide solutions.\textsuperscript{324,325} Mundy et al reported the first calculation of surface potential of water/vapor interface from \textit{ab initio} molecular dynamics simulation and the result was \(+3.1\) V, which is quite different from the results from classical molecular dynamic simulations.\textsuperscript{4,320} Recently, Leung reported his calculation of surface potential at air/water interface using density functional theory and the result is \(+3.63\) V.\textsuperscript{6} The surface potentials calculated from different water models are compared in Table 4.3.

As we have shown in Eq.4.5 and 4.6, the surface potential and electric field are sensitive to the charge distribution \(\rho(z)\). How to accurately calculate the charge distribution becomes the central issue here. In \textit{ab initio} molecular dynamics simulations, electron density and nuclear distribution can be obtained to calculate the total charge.
Table 4.3: Comparison of surface potential calculated from different water models.\(^4\)\(^-\)\(^6\)

<table>
<thead>
<tr>
<th>Water model</th>
<th>(\chi) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ab\ initio)</td>
<td>+3100</td>
</tr>
<tr>
<td>SPC</td>
<td>-530</td>
</tr>
<tr>
<td>SPC/E</td>
<td>-546</td>
</tr>
<tr>
<td>TIP4P</td>
<td>-510</td>
</tr>
<tr>
<td>TIP4P-QDP</td>
<td>-500</td>
</tr>
<tr>
<td>TIPS2</td>
<td>-890</td>
</tr>
<tr>
<td>D-C</td>
<td>-480</td>
</tr>
<tr>
<td>CC</td>
<td>-600</td>
</tr>
<tr>
<td>RWL</td>
<td>-530</td>
</tr>
<tr>
<td>DFT</td>
<td>+3630</td>
</tr>
</tbody>
</table>

density.\(^{320}\) In our work, since we performed classical molecular dynamics simulations, point charge was used to represent the charge on each atom, the charge distribution was simply represented by the product of atomic density distribution and the atomic partial charge.

Figure 4.15 shows the charge distribution of water/CO\(_2\) in simulation 13. In the surface region, positive charge distribution is observed close to the CO\(_2\) phase, which is consistent with the molecular orientation results described in section 4.5 that one of the O–H bonds in water molecule tends to project into the gas phase. The electric field and surface potential distribution integrated over the total charge distribution by using Eq.4.6 is shown in Figure 4.16. The electric field is positive in the interface region and comes to zero in the water phase where the potential approaches its minimum. When a test charge is moving from the vapor into the liquid, it passes the positive charge layer first. This always gives rise to the electric field and thus the maximum electric field occurs in the outer layer of the surface. The maximum magnitude of the electric field is about \(1\times10^9\) V/m, which is in the
same magnitude of the electric field of pure water/vapor interface reported by other works.\textsuperscript{4,318,320} The surface potential here is found to be -665 mV. This value is close to all the reported surface potential of pure water/vapor interface in Table 4.3 except the \textit{ab initio} ones. However, in simulation 1, when the CO\textsubscript{2} density is much lower than that in simulation 13, the surface potential is found to be -615 mV. We can see that the surface potential keeps fairly the same level of magnitude in these simulations, even when the density of CO\textsubscript{2} near the surface increases in significant amount. From the surface potential profiles in Figures 4.16 and 4.17, we can also see that the surface width in simulation 13 is obviously larger than that in simulation 1.

![Figure 4.15: The total charge distribution of water and CO\textsubscript{2} in simulation 13. Water slab is located in the center.](image-url)
Figure 4.16: The electric field (black) and surface potential (red) profiles of water/CO$_2$ in simulation 13. Only one surface is shown here due to the symmetry of the system. Bulk CO$_2$ is on the left side and water is on the right.

4.7 Conclusions

The water/CO$_2$ interface is studied with the capillary wave theory to get the intrinsic surface position. The structure of water near the interface is more layered when using capillary wave theory. Near the interface region, water dipole vectors tend to lay parallel with respect to the surface with one hydrogen projecting into the liquid phase and the other hydrogen pointing toward the vapor phase. This orientation preference is also convinced by the result of electric field calculation. CO$_2$ molecules near the interface also tends to lay parallel to the surface so that CO$_2$ molecules can interact with the water molecules with the greatest probability. The surface excess of CO$_2$ in different simulations indicate no phase transition when the
Figure 4.17: The electric field (black) and surface potential (red) profiles of water/CO$_2$ in simulation 1. Only one surface is shown here due to the symmetry of the system.

CO$_2$ density approaches critical value under 300K. The results of electric field and surface potential of water are both smaller than those of pure water/vapor interface.
CHAPTER 5

Summary

The central theme of my dissertation is the use of detailed theoretical simulations to provide a more accurate picture of molecular behavior at two common and important interfaces: the amorphous silica-water interface and the carbon dioxide-water interface. The surface properties of amorphous silica play important roles in a variety of applications, ranging from the mundane (laboratory glassware) to exotic new micro- and nano-scale devices. One of the fundamental properties of the silica surface in contact with water is the presence of electrically charged groups on the surface. At all but the lowest pH values, the silica surface is negatively charged.\(^{39,40}\) The charged surface, and the counter-ions in solution whose charge compensates the charge of the surface, are together known as an electrical double layer.\(^1\) The double layer, and its electrokinetic properties, has been a prominent topic in physical chemistry and colloid science for almost a century. Recent interest has developed because the electrical charge of the fluid part of the double layer adjacent to a silica surface has been exploited to drive flow in silica-based devices by applying an electrical potential.\(^{63,326-328}\) Our research tests some of the venerable theories, such as the Gouy-Chapman-Stern model,\(^{19-25,66-69}\) that are commonly used to describe the
double layer and its electrokinetic properties. We developed and evaluated an inter-
action model that provides an atomistic description of the silica-water double layer,
and then analyzed simulations of electrokinetic phenomena using that model.

The negative charge of the silica surface results from the dissociation of surface
silanol groups. The model we developed for the dissociated silica surface is an ex-
tension of our previous model developed for undissociated silica/water interface. Our empirical model has been calibrated by ab initio calculations and is able to be
used for large scale device-type simulations. For example, we are currently model-
ing electrically driven flow through a nanonozzle device as shown in Figure.5.1. The
nanonozzle walls are made of silica using our empirical model. The interactions be-
tween silica and biomolecules are also important in many applications. For example,
silica is recently considered to be used to stretch and sequence DNA. Silica could
also have played an important role in the appearance of life (prebiotic chemistry).
Therefore, our group has also extended our empirical model to interface with the
GROMOS96 biomolecular forcefield and provided some preliminary predictions of
the binding modes of peptides near silica surface, as shown in Figure.5.2. However,
more investigations on a wide variety of biomolecules near silica surface should be
performed to be compared with experiments to make improvement for our models.

In chapter 3 we describe application of our empirical model to electrokinetic phe-
nomena in silica nanochannel. With the realistic description of amorphous silica
surface, we can shed some insight into the foundations of the venerable Stern layer
model. The Stern model stipulates that an immobile layer of water exists next to a
charged surface like silica. In our simulations, we find that water and ions are mo-
bile right up to the silica surface. We find that the Stern model is only an “effective”
Figure 5.1: Nanonozzle made of silica walls (yellow part) with our empirical model. The red and white part is the water solvent, while dark blue particles are sodium ions and light blue particles are chloride ions.

Figure 5.2: Left and right panels show snapshots of a single EWE tripeptide bound to the silica surface. Different regions of the tripeptide can bind to the surface. For visual clarity the solvent is not shown.

model that can reproduce the pattern of fluid flow away from the surface using the bulk fluid viscosity throughout the channel. While the original Gouy-Chapman-Stern model adequately accounts for electroosmotic flow, it predicts too little ion conduction near the surface. To rescue the Stern model, colloid scientists have postulated that ions move with bulk-like mobility through the immobile fluid layer adjacent to the surface. The revised model is known as the dynamic Stern model. We have shown that the dynamic Stern model is both inaccurate, and unnecessary once the
local viscosity variation near the surface is taken into account. Our analysis should be able to provide guidance in nanoscale device design, combining both continuum theory of hydrodynamics away from the surface and molecular description near the surface.

Our study of the CO$_2$/water interface stems from fundamental scientific interest, as well as relevance to technological and environment problems. There have been intensive studies on liquid/gas interfaces, both experimentally$^{262,264,265}$ and theoretically.$^{270,279,301}$ As CO$_2$ is the major greenhouse gas, the strategies for CO$_2$ capture and storage have been considered to be the great challenge to our planet.$^{35}$ It was proposed to be safe and economically favorable to inject CO$_2$ into deep geological strata such as deep ocean and gas field.$^{37}$ It is believed that CO$_2$-water clathrate hydrate would rapidly form at the interface between these two species at low temperature and high pressure.$^{36}$ Detailed information about the CO$_2$/water interface will play an important role in understanding the mechanism of the formation of CO$_2$-water clathrate. In chapter 4 we used molecular dynamics simulations to investigate the structural properties of CO$_2$/water interface. Capillary wave theory helps us to separate out the effects of long wavelength interface fluctuations, which depend on system size, and obtain the intrinsic features of CO$_2$/water interface. Previous research on the CO$_2$/water interface has been performed in the limit of zero CO$_2$ pressure$^{299-301}$ and super-critical CO$_2$ pressures.$^{295}$ Our analysis is the first simulation research linking these two regimes. We find that with increasing CO$_2$ pressure, a layer of carbon dioxide forms on the water surface, and rises to liquid-like density before saturating around 67 bar. At higher pressures, a second discrete layer of CO$_2$ is also observed. As the CO$_2$ pressure climbs to its critical value, the film on the
surface of water also develops an extended tail. The width of the tail region grows with increasing pressure, evidently diverging as the critical point is approached, as expected. More calculations of interfacial properties, such as surface tension at different CO₂ pressures, are needed to make closer comparisons with experiments and other simulations.
BIBLIOGRAPHY


[64] As written, the first two terms on the right side of Eq.(7) in Ref. 34 involve sums over the silanol oxygens of the silica. They should include a sum over all oxygens of the silica, including both silanol and siloxane types.


Another important reason motivating the Stern layer is the unreasonably large concentration of ions at the surface predicted by the Gouy-Chapman model for large surface potentials.


In Ref. 71, Zukoski and Saville write, “...it appears prudent to avoid taking the adsorption terminology too literally. Much more needs to be known about the structure of the Stern layer before the strict validity of different models can be assessed. For the present we view this sort of description simply as one that allows introduction of certain functional relationships which reproduce the empirical results. The details of any adsorption processes, including the role of the surface itself and interactions between different constituents of the Stern layer, remain subjects for further investigation.”.


Ho Teng and Akihiro Yamasaki. Pressure-mole fraction phase diagrams for CO2-pure water system under temperatures and pressures corresponding to ocean waters at depth to 3000 m. *Chemical Engineering Communications*, 189(11):1485, 2002.


[324] Brad A. Bauer and Sandeep Patel. Properties of water along the liquid-vapor coexistence curve via molecular dynamics simulations using the polarizable


