PROTON HOPPING IN A SINGLE LAYER WATER BETWEEN MXENE LAYERS USING REAXFF MOLECULAR DYNAMICS SIMULATION

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by

Gunwoo Jo

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The thesis of Gunwoo Jo was reviewed and approved* by the following:

Adri van Duin  
Professor of Mechanical Engineering  
Thesis Advisor  

Donghai Wang  
Associate Professor of Mechanical Engineering  

Mary Frecker  
Professor of Mechanical Engineering  
Head of the Department of Mechanical Engineering  

*Signatures are on file in the Graduate School
ABSTRACT

The purpose of this thesis is to analyze proton migrations in single layer water which is located between two MXene layers with nine different temperatures (200K, 250K, 260K, 270K, 280K, 290K, 300K, 350K, and 400K) by molecular dynamics (MD) simulations using the ReaxFF Reactive Force Field. MXenes, a recently discovered two-dimensional (2D) material, attract great interest as one of the leading candidates for high energy storage applications such as super capacitors, lithium ion batteries, and fuel cells because of their exceptional electronic conductivities [1-6]. Due to the hydrophilic nature on the surface and the weakness of hydrogen bond and van der Waals force between the MXene layers, MXenes can easily trap water molecules between the 2D material layers. Those water molecules significantly affect the electrical potential of MXenes [7]. In order to provide insight into proton conduction in MXene-trapped water layers, we simulated proton diffusion in this water layer to investigate how protons hop around in terms of time and, temperature and compare this simulation with the electrical potential found in bulk water diffusion. In our simulations on three independently-created MXene-water models, we found unusual trends of proton diffusion constant changes with temperature rise. This thesis seeks to elucidate these trends by developing analysis tools to track effective movement of the protons.
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Chapter 1

Introduction

Because of its unique mechanical, electronical, and thermal properties, graphene, a two-dimensional material, has drawn major attentions from researchers in the material science field [8-18]. At the beginning of this decade, MXenes, composed with a group of 2D early transition metal carbides and carbonitrides, were discovered by the MAX/MXene Research Group at Drexel University [1] [19]. Since MXenes have been reported that have hydroxyl or oxygen surface groups, they exhibit a higher electrical conductivity than graphene layers [1] [7]. As such, MXenes are a promising candidate for applications such as energy storage, electronic devices, polymer, and conductive thin films due to their special properties [20-23]. Within several years, a significantly amount of experimental research has been performed in this area. The rising interest of this 2D material motivated us to study MXenes’ electrical potential.

The next sections introduce the fundamental background for my thesis research. Since I performed one of the computer simulation techniques called Molecular Dynamic (MD), let me begin with a short summary of that method. Three other aspects for this simulation, ReaxFF Reactive Force Field, MXene, and proton mobility, are described in the subsequent sections.
1.1 Molecular Dynamics

In the middle of the 20th century, the computer with its tremendous computational power enabled, amongst others, Molecular Dynamics (MD) simulations. MD is an atomic scale computer simulation method that calculates the time dependent changes of a molecular system. As the power of the computer has improved, so has the ability of MD to simulate complex systems. In the late 1950’s, Alder and Wainwright firstly tried to use the MD method to explain the elastic collision of rigid spheres [24]. In the beginning of the 1960’s, the first real solid (Cu) and liquid (argon) MD simulations were performed [25] [26]. In 1970’s, scientists have been using MD simulation more widely in larger and more complex materials such as proteins [27]. From that point on, MD steadily extended its application to fields such as biochemistry, material science, semiconductors, and batteries, all of which benefit from this type of atomic scale phenomena and interactions study.

1.1.1 Algorithm of the Molecular Dynamics

To examine the atomic-level motion as a function of time, in a MD simulation, we use the Newton’s equation of motion [1.1] for the system [28].

\[ F = m \frac{d^2 r (t)}{dt^2} \]  

[1.1]

The algorithm of the MD mainly consists of 3 steps, initialization of the system, force calculation, and integration of the equation of motion. Figure 1-1 is a simplified schematic of the MD algorithm
1.1.2 Initialization of System

First, we give particles initial positions and velocities to perform the appropriate simulation as shown in the Figure 1-1. In this initialization procedure, positions for the atoms are assigned with proper distance to avoid overlap of each other. Next, by using a Maxwellian distribution, we set the initial velocities with zero total momentum of the system. Subsequently, for the initial setting of the temperature, the velocities are scaled to
match the desired temperature. After that step, we approximate the particle’s positions from the previous positions by using following equation:

\[ x_{i-1} = x_i - v dt \]  \[1.2\]

The left side of the equation represents the previous position of a particle and the first term of the right hand side is the next position at next time step.

### 1.1.3 The Force Calculation

After the initialization, to integrate Newton’s equation of motion, the calculation of the particle interaction forces is required using equation [1.3]:

\[ F(R_{ab}) = \frac{\partial \varphi(R_{ab})}{\partial R_{ab}} \]  \[1.3\]

As shown in the above equation, to calculate forces interacting between atoms, we need the potential energy function \( \varphi(R_{ab}) \). The potential energy represents non-bonded interactions and bonded interactions with all particles. There are a wide range of potentials to be used for the potential energy calculation, including hard spheres, Lennard-Jones, and Morse potentials but you can also use more complex potentials –like ReaxFF. Equation 1.4 shows the Lennard-Jones potential:

\[ \varphi(R_{ab}) = 4\varepsilon \left( \frac{\sigma}{R_{ab}} \right)^{12} - \left( \frac{\sigma}{R_{ab}} \right)^{6} \]  \[1.4\]

Where \( \varepsilon \) indicates the well depth and \( \sigma \) is the diameter. Figure 1-2 shows the Lennard-Jones potential.
1.1.4 Integration of the Equation of Motion

The preceding steps are performed in preparation for this next step, which is the integration of Newton’s equation of motion. There are many numerical algorithms to integrate the Newton’s equation of motion such as Verlet algorithm, Leap-frog algorithm, and Beeman’s algorithm. To find the positions $r(t+\Delta t)$, we use one of the simplest and stable algorithms called the Verlet algorithm [29]. This algorithm is derived from Taylor series expansion for the known positions at time $t$. 

Figure 1-2. Lennard-Jones Potential
Equation [1.5] expresses the positions:

\[
  r(t + \Delta t) = 2r(t) - r(t - \Delta t) + \frac{F(t)}{m} \Delta t^2
\]  

[1.5]

This expression is fourth order accurate and provides accurate calculation of velocities from the positions. With this process which find new positions at each time step, we are able to calculate present temperature, potential energy, total energy, and trajectories.

1.1.5 MD Ensembles

To run MD simulations, boundary conditions play a pivotal role in affecting interactions amongst particles. The following three types of Molecular Dynamics ensembles are mostly used in MD simulation: Micro-canonical ensemble (NVE), Canonical ensemble (NVT), and Isothermal-isobaric (NPT) ensemble.

The Micro-canonical ensemble or NVE ensemble has a constant number of atoms (N), a volume (V), and a total energy (E) which means the system’s total energy is conserved by exchanging the particles’ kinetic and potential energy during the simulation. This ensemble was introduced in the previous section with the simplified schematic of the MD algorithm, Figure 1-1. In NVE ensemble, we cannot control the temperature and pressure of the system. Thus, pressure and temperature may change during a NVE MD simulation.

The Canonical ensemble (NVT) is an ensemble that can control the temperature (T) of the system with constant number of atoms and volume. In this NVT ensemble,
temperature is conserved and we are able to reach the desired temperature. In comparison to NVE, NVT’s control of temperature assists in getting the model closer to properly simulate the observations of the lab experiment.

If, we want to keep the pressure constant in the system in order to imitate the experimental conditions. Isothermal-isobaric (NPT) ensemble allows control of the pressure (P) and Temperature during the simulation. Since this ensemble has constant pressure and temperature, its conditions are more analogous to real experimental conditions than NVE and NVT ensembles.

1.2 ReaxFF Reactive Force Field

The ReaxFF Reactive Force Field was invented by van Duin and coworkers [32]. ReaxFF is a computational chemical method that allows us to perform MD simulations on chemically reactive systems, thus bridging the gap between quantum chemical computational methods and empirical force field computational methods.

As shown in Figure 1-3, the ReaxFF takes a position between the quantum methods and the empirical force field as far as accessible time- and size-scales are concerned. Quantum mechanics (QM) methods have high accuracy but limitations in time scale and the size of systems due to its computational cost. On the other hand, the empirical methods, which are based on classical principles, enable us to simulate sufficiently large systems up to million atoms with a time ranging up to the nanoscales. When non-reactive force fields are applied to empirical methods, however, they often fail to express reactive events such as chemical reactions and transition states. ReaxFF, on the
other hand, gives a path to overcome these limitations from the two aforementioned methods: it deals with long ranges of time (~ns) and large systems (~100,000 atoms) by expressing details of the chemical events without QM methods’ expensive computational cost [30].

This section will present short overview of the basic concept of the ReaxFF potential and its applications. Further more details of ReaxFF are described in this recent review article [30].

![Hierarchy of different computational simulation methods](image)

Figure 1-3. Hierarchy of different computational simulation methods [31]

### 1.2.1 Overview of the ReaxFF potential

The overall ReaxFF system energy is described in the following equation:

\[
E_{system} = E_{bond} + E_{over} + E_{angle} + E_{tors} + E_{vdWaals} + E_{Coulomb} + E_{specific} \quad [1.6]
\]
where $E_{\text{bond}}$ indicates bond energy that is directly derived from bond orders. $E_{\text{over}}$ is an overcoordination energy which is a penalty for overcoordinating atoms. $E_{\text{angle}}$ is a valence angle strain energy which is a bond-order dependent three-body term. $E_{\text{tors}}$ is a bond-order dependent four-body torsion energy term. Also, $E_{\text{vdWaals}}$ and $E_{\text{Coulomb}}$ are bond-order independent energy terms which are calculated between every atoms, indicating van der Waals energy and Coulomb interaction energy respectively. The term $E_{\text{specific}}$ indicates a special case of energy that does not generally occur and includes Lone pair, undercoordination, angle conjugation, hydrogen bond, torsion conjugation and $C_2$-correction energies.

The bond orders are calculated from the interatomic distance and updated every iteration. To calculate bond order, ReaxFF uses the following empirical equation:

$$BO_{ij} = \exp[p_{bo,1}\left(\frac{r_{ij}}{r_0}\right)^{p_{bo,2}}] + \exp[p_{bo,3}\left(\frac{r_{ij}}{\pi\sigma}\right)^{p_{bo,4}}] + \exp[p_{bo,1}\left(\frac{r_{ij}}{r_0^{\pi\pi}}\right)^{p_{bo,6}}] \quad [1.7]$$

Where $i$ and $j$ indicate $i^{th}$ and $j^{th}$ atom. $p_{bo}$ is parameter that is typically derived from fitting against QM-data, $r$ is distance between atoms, and $r_0$ is equilibrium bond length.

The van der Waals and Coulomb energy non-bonded interaction terms are included in all atom pairs and are calculated independently [30].

The elements currently supported by ReaxFF are shown on a periodic table in Figure 1-4.
1.2.2 Applications

The ReaxFF was initially developed for hydrocarbon systems [32]. After then, silicon and silicon oxide chemical systems were successfully developed in 2003 [33]. As shown in Figure 1-5, there are two available main applications: the combustion and the aqueous. The combustion branch contains hydrocarbon and oxygen systems [34], coal combustion [35], Mo-based alloys [36], carbon nanotubes [37], and etc. The aqueous branch possesses transition metals and metal oxides [38-41], silica-water interface [42], and etc. The ReaxFF has been successfully applied and demonstrated for those systems. More details for the applications of the ReaxFF are presented in a recent review paper [30].

Figure 1-4. Current elements described by ReaxFF [31]
1.3 Introduction of MXenes

In the beginning of the 2000s, the first two-dimensional material, graphene, was discovered and attracted great interest due to its exceptional characteristic. From then on, 2D materials including graphene have been expected to be used in semiconductors, batteries, and electronics. MXenes are recently being developed 2D layers of early transition metal carbides and carbonitrides with hydrophilic surfaces such as hydroxyl. In this section, a short introduction for MAX phases and MXenes will be presented.
1.3.1 MAX Phases

MXenes are created by removing A elements from the MAX phases [43]. MAX Phases are layers of metal carbide composites, the composites comprised of three elements. Figure 1-6 shows what MAX stands for in a periodic table.

![Figure 1-6. MAX elements on a periodic table](image)

As shown in Figure 1-6, “M” is an early transition metal, “A” is an A group element (usually either Al, Si), and “X” is Carbon and/or Nitrogen. MAX phases can be expressed by the general formula: $M_{n+1}AX_n$ where $n=1$ to 3. Many studies in search of new combination of MAX phases have been performed and so far, more than 70 MAX phases have been synthesized [44].
1.3.2 MXenes

From the MAX phases, selective etching to remove “A” elements is implemented to synthesize MXenes. Figure 1-7 [45] shows an example of the process to make MXene layers and Figure 1-8 [45] is SEM pictures of Ti$_2$AlC$_2$ MAX phase and MXene layers.

Figure 1-7. Schematic description to form MXenes from MAX phases [45]
Figure 1-8. SEM pictures showing a (A) Ti$_3$AlC$_2$ particle before treatment (MAX phase), (B) Ti$_3$AlC$_2$ after HF treatment [45]

Depending on the elements of the MXene, different properties of the MXene are obtained. Due to their structure, which is composed with early transition metal carbide and nitride inside and hydrophilic natured surface group such as –OH, -O, and –F outside, the MXenes possess metallic properties and they are thought of as electrically conductive particles [46].

Because of this structural potential with high electrical conductivities, they are expected to be an attractive candidate for many applications. One of the promising fields of application in Lithium-ion battery (LIB). MXenes show their possibility to be a great candidate as an anode material with high capacity [4]. MXenes are expected to provide a solution to find an anode source for LIBs—a problem to which a large amount of research has been dedicated [47]. Polymer nanocomposites are one of the promising applications as well. The intercalative characteristic of MXenes facilitates its possession of high conductivity and flexibility [22]. Also, as a 2D material of flexible thin film with high conductivity, an experiment with Ti$_3$C$_2$, which is one of the compositions of MXenes, was performed in 2016 and it reported that MXene layers can be prospective in
the field [23]. Besides these applications, extensive research has been conducted in many fields such as nanoelectronics, electromagnetic shielding, water purification and others, [21] [48-49].

1.4 Proton Mobility in Water

Proton mobility in water molecules is a phenomenon by which an excess proton hops to adjacent water molecules by a combination of the Grotthuss mechanism and a vehicular mechanism. The Grotthuss mechanism involves two formations, the Eigen cation (H₅O₄⁺) [50] and the Zundel cation (H₅O₂⁺) [51] for the reactive transport [52]. This reactive transport is faster than the vehicular mechanism, which is a non-reactive diffusion whereby the whole H₃O molecule diffuses by itself to the space between the water molecules [53]. The Grotthuss mechanism process is described from left to right in Figure 1-9: two water molecules share a proton and the proton from a water molecule transports to the other water molecule and forms a H₃O molecule.

Figure 1-9. The Grotthuss mechanism or the proton hopping mechanism (Red balls are oxygen atoms and white balls are hydrogen atoms) [54]
In our study, to describe the proton hopping, we used a script to track an oxygen atom which has three hydrogen bonds in the water layer. At each iteration, the script searches oxygen atoms with three hydrogen bonds and calculates O-H bond lengths of the molecules. Thereafter, an oxygen atom with the shortest bond length amongst the calculations is identified as a H$_3$O molecule. With this process, we analyzed the proton migrations in the water layer.
Chapter 2

ReaxFF MD Simulation Details

MXenes, a promising 2D early transition metal carbide, have been intensively studied in the past decade due to their structure and outstanding properties [8-18]. Especially, in a field of high energy storage, MXenes are considered as electrode materials with high electrical conductivity. Hence, they are expected to be used in many applications such as lithium-ion batteries, super capacitors and fuel cells [1-6]. In 2016, Naresh C. Osti and coworkers utilized X-ray and neutron scattering techniques along with ReaxFF-molecular dynamics to elucidate the structural influence of potassium ion water trapped between two MXene layers [55]. Additionally, these techniques were used to investigate the behavior of the ionized water itself [55]. Using ReaxFF simulation they reported that the diffusion constant of the intercalated water layer is $5.33 \times 10^{-10}$ m$^2$s$^{-1}$ and the constant of the potassium or K$^+$ in the water layer is $9.77 \times 10^{-12}$ m$^2$s$^{-1}$ at 300K. These results gave our group motivation to investigate how the addition of protons to a similar system, instead of potassium, will affect the diffusion coefficient at various temperatures.

In this study, we determined the diffusion constant of protons that lie within the intercalated single layer of water molecules that are in between the MXene layers to observe the proton diffusion. This calculation of the proton diffusion constant was made by using the computational ReaxFF method and comparing that diffusion constant with the constant from self-diffusion of the water layer as well as the constant from the measurement of bulk water. Three different water configurations were used for the diffusion constant calculation. Figure 2-1 shows an initial model of MXene system with 9
protons in a water layer. Annealing processes were applied two obtain additional initial water/MXene configurations.

Figure 2-1. A snapshot of the MXene, Ti$_3$C$_2$(OH)$_2$, contained within a MXene system using ReaxFF

### 2.1 Simulation Procedure

Initially, we added 9 protons to a system that consisted of 324 Ti$_3$C$_2$(OH)$_2$ MXene molecules and 252 H$_2$O molecules in a 48.81×27.72×24.96 nm sized simulation box. This nine proton addition created a system with 324 Ti$_3$C$_2$(OH)$_2$ molecules, 243 H$_2$O molecules, and 9 H$_3$O molecules; here we will call this system the initial model. Subsequently, to have two other different structures from the initial structure, melting (300K) and cooling (200K) procedures were done before adding the protons to the system; we will call these two systems annealed model 1 and annealed model 2. The annealing is a process done by NVT simulation, and it consist of heating the structure to 300K for 7.5 ps with a temperature damping constant of 100 fs and then refreezing the structure to 200K for same period of time with same damping constant. A total of three...
different systems configurations were prepared for this study: initial model, annealed model 1, and annealed model 2. All models have different distributions of the water molecules and different locations of the H$_3$O molecules within their box; those boxes each have the same periodic boundary condition. After preparing the models, energy minimization procedures were conducted and canonical ensemble (NVT) molecular dynamics for equilibration were implemented for 10 picoseconds (ps) with damping constant of 100 femtoseconds (fs) at 9 different temperatures (200K, 250K, 260K, 270K, 280K, 300K, 350K, and 400K). Then, we simulated the systems with micro-canonical ensemble (NVE) for 125 ps to determine the proton and water mean square displacement (MSD), from which we can calculate the diffusion coefficient. The MSD or average squared displacement is calculated from the following equation:

$$MSD = \langle x^2 \rangle = \frac{1}{N} \sum_{n=1}^{N} (x_n(t) - x_n(0))^2$$  \[2.1\]

Where $N$ indicates the number of atoms, $x_n(t)$ is the position of $n^{th}$ atom at time $t$, and $x_n(0)$ is the initial position of the atom. The relationship between the MSD and the diffusion coefficient is expressed by equation \[2.2\]:

$$\langle x^2 \rangle = q_i D t$$  \[2.2\]

Where $\langle x^2 \rangle$ is the MSD, $i$ is the dimension of the diffusion: $i = 1, 2, \text{ or } 3$, $q_i$ is the dimensional constant: $q_i = 2, 4, \text{ or } 6$, $D$ is the diffusion coefficient, and $t$ is time. In this study, $q_i = 6$ was chosen because we treated the investigated systems as 3D structures.
However, there could be an argument that the systems should be treated as 2D structures. If we select $q_i = 4$, the diffusion constants will be 1.5 times greater than our results.

In addition, we simulated the same systems without the addition of protons, only a single layer of water between the MXene layers, at the same temperatures to compare their coefficients with the results from the proton added systems.

### 2.2 Results and Discussion

Generally, the water diffusion constant exhibits the trend of gradually going up with increasing temperatures. However, the research performed by our group indicates that the diffusion constants’ relation to temperature shows unusual trends; details will be presented with graphs in this section. To explain the results, we counted total number of times any proton hops and the number of oxygen atoms in the water molecules used for diffusion of protons. The locations of these oxygen atoms define a boundary that puts a limit on the area any proton can hop into. For purpose of this paper, we will call this “the total area of proton migration.”

The site-site radial distribution function (RDF) was used to evaluate the structure of homogeneous phases of the systems. Figure 2-2 and Figure 2-3 show O-O (oxygen-oxygen) radial distribution functions for the water with protons at 200K and 300K respectively. Compared with previous work done by A.K Soper in 2000 [56], our systems have frustrated water structures: they do not have perfect crystalized structures at 200K, and they also show different graphs in liquid phases at 300K. Figure 2-4 (a)’s O-O RDF,
$g_{oo}(r)$ (—), shows more complicate configuration than Figure 2-2 graphs. The graphs in Figure 2-2 have smoother trends like liquid water, and the highest peak in the figure is displayed at 3.1 Å while Figure 2-4 (a) shows the highest peak at 2.8 Å. In the liquid phase, our models in Figure 2-3 show different graphs from Figure 2-4 (b)’s $g_{oo}(r)$ (—): the RDFs of our models have also smoother configurations than Figure 2-4 (b) shows.
Figure 2-2. O-O RDFs of the systems at 200K

Figure 2-3. O-O RDFs of the systems at 300K
2.2.1 Diffusion constant

Figure 2-5 presents the overall trends of proton and pure water layer diffusion constant changes of each model and bulk water diffusion constant changes depending on temperature rise. The normal trend of the diffusion constant of bulk water that is gradually increased with temperature, is also shown in the graphs. The results from our systems, show unusual behavior for all the systems: initial, annealed 1, and annealed 2 models. Figure 2-5 only shows 400K simulation results for the annealed models. We observed some reactions in which H$_3$O molecule combined with O-H from one of the
MXene layers and formed two water molecules at 350K and 400K in the initial model and 400K in the annealed models; the Figure 2-6 shows the process of the reaction at 400K in the initial model. Therefore, the proton diffusion constants at 350K and 400K for initial model and the constants at 400K for annealed models are not displayed in the Figure 2-5 graphs. Also, we observed that the proton diffusion constants are greater than the water self-diffusion constants at many temperatures: initial model (200K, 250K, 260K, 270K, 300K), annealed model 1 (200K, 260K, 270K, 280K), and annealed model 2 (200K, 250K, 260K, 270K, 280K, 300K).
Figure 2-5. Diffusion constant comparison graphs (a) proton and pure water layer diffusion constants of the initial model with bulk water diffusion constant, (b) proton and pure water layer diffusion constants of the annealed model 1 with bulk water diffusion constant, (c) proton and pure water layer diffusion constants of the annealed model 2 with bulk water diffusion constant
Figure 2-6. H$_2$O generation reaction process between the H$_3$O and O-H on the MXene surface at 400K (Yellow: Ti atoms, Green: C atoms, Red: O atoms, White: H atoms)

To provide more details, Figure 2-7 and 2-8 show with the exact values of diffusion constants. Figure 2-7 displays proton diffusion constants in each systems with increasing temperature. The graph shows significantly different diffusion constants of each model at 270K and 280K: the diffusion constant in the initial model at 280K was increased by $2.72 \times 10^{-10}$ m$^2$s$^{-1}$ and the diffusion constants of annealed model 1 and 2 at 280K were decreased by $1.27 \times 10^{-10}$ m$^2$s$^{-1}$ and $3.78 \times 10^{-10}$ m$^2$s$^{-1}$ respectively. Also, the annealed models have different trends in comparison to the initial model, especially, at 270K and 280K.

In the case of pure water diffusion which is expressed in Figure 2-8, the diffusion constants in the initial model increased with the temperature rise except in the cases of 280K and 300K. On the other hand, in the annealed models case, which display a similar tendency of diffusion constant, the graph shows a little drop at 280K. Since the models
have significantly different trends in diffusion constant changes, particularly, at 280K both in proton and pure water diffusion, we calculated the average of potential energy and standard deviation to figure out which system has the highest thermodynamic stability.

Figure 2-7. Proton diffusion constants of the three models depending on temperature changes
Figure 2-8. Water diffusion constants of the three models depending on temperature changes.

As shown in the Figure 2-9, the averages of potential energy of the annealed model 1 and 2 are 82 kcal and 69 kcal lower than that of initial model, respectively. The standard deviations of the systems at 280K are displayed in the Table 2-1. Although the three models have similar magnitude of standard deviation, the annealed models seem to be more stable and as such their diffusion constant results are more relevant.

To obtain a clear explanation for the different diffusion trends, we analyzed the proton hopping by counting the total number of proton hops and the number of oxygen atoms in the water molecules which were used for this proton diffusion.
Figure 2-9. Averages of the potential energy of each model graph at 280K

<table>
<thead>
<tr>
<th></th>
<th>Initial Model</th>
<th>Annealed Model 1</th>
<th>Annealed Model 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Standard Deviation</strong></td>
<td>32.0431</td>
<td>27.70952</td>
<td>33.53616</td>
</tr>
</tbody>
</table>

Table 2-1. Standard deviation table of the potential energy of each model at 280K

2.2.2 Proton Diffusion Analysis

2.2.2.1 Total Number of Hopping

To elucidate the trends of the diffusion constants of each model, we counted total number of hops of all protons within the systems. In the Figure 2-10, these hops are presented visually by bar graphs at the temperatures of 200K, 250K, 270K, 280K, and 300K. There are significant differences in the diffusion constant at the low temperatures of 200K and 250K and very different trends at 270K and 280K between the initial and
annealed models. At the temperature of 200K and 300K, the total number of the protons’ hopping is reflected in the diffusion coefficient of the models. However, at the other temperatures, the number of hops fails to produce a correlation with the diffusion constant. This could be related to the contribution of ineffective proton migrations, for example, protons move back and forth between two same oxygens. Table 2-2 contains the exact values of the counted number of total migrations including the ineffective migrations. It is clear that the count of total hopping is insufficient to explain the proton diffusion constants of each model, thus we tried to calculate the effective hopping. Counting the number of different oxygen atoms that are used for proton diffusion was expected to be an effective solution to find a correlation with the diffusion constant.
Figure 2-10. Bar graphs of diffusion constant (left) and total number of times of all the protons hopping (right) at each of the following temperatures: 200K, 250K, 270K, 280K, and 300K
Table 2-2. The counted number of total proton migrations at each temperature and their correlation with the diffusion constants

<table>
<thead>
<tr>
<th>Total number of hopping</th>
<th>Initial Model</th>
<th>Annealed Model 1</th>
<th>Annealed Model 2</th>
<th>Correlation with Diffusion constant</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>200K</strong></td>
<td>4474</td>
<td>3236</td>
<td>2316</td>
<td>Yes</td>
</tr>
<tr>
<td><strong>250K</strong></td>
<td>6509</td>
<td>6349</td>
<td>6079</td>
<td>No</td>
</tr>
<tr>
<td><strong>270K</strong></td>
<td>7036</td>
<td>6546</td>
<td>6774</td>
<td>No</td>
</tr>
<tr>
<td><strong>280K</strong></td>
<td>6709</td>
<td>6654</td>
<td>7431</td>
<td>No</td>
</tr>
<tr>
<td><strong>300K</strong></td>
<td>7509</td>
<td>6587</td>
<td>7503</td>
<td>Yes</td>
</tr>
</tbody>
</table>

2.2.2.2 Number of Oxygen for Diffusion

The bar graphs in the Figure 2-11 shows the trends in the number of oxygen atoms (O) used for proton diffusion of each model. The exact number of O is in the table 2-3 as well as a judgement of its correlation with the diffusion constant. As shown in the Figure 2-11, the number of oxygens involved in proton hopping at 200K, 250K, and 280K display a similar trend with the diffusion constant of each model. However, at 270K and 300K, it is difficult to determine the correlation with the diffusion coefficient with this number. For example, at 270K, the diffusion constant of the initial model is lower than the annealed model 1, but the initial model used more oxygens for diffusion. Additionally, at 300K, though the annealed model 1 has the highest diffusion constant value, it used the least number of O for the proton diffusion.
Figure 2-11. Bar graphs of diffusion constant (left) and number of O used for diffusion (right) at each of the following temperatures: 200K, 250K, 270K, 280K, and 300K
<table>
<thead>
<tr>
<th>Number of oxygen atoms used for diffusion</th>
<th>Initial Model</th>
<th>Annealed Model 1</th>
<th>Annealed Model 2</th>
<th>Correlation with Diffusion constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>200K</td>
<td>45</td>
<td>29</td>
<td>27</td>
<td>Yes</td>
</tr>
<tr>
<td>250K</td>
<td>85</td>
<td>58</td>
<td>60</td>
<td>Yes</td>
</tr>
<tr>
<td>270K</td>
<td>87</td>
<td>85</td>
<td>100</td>
<td>No</td>
</tr>
<tr>
<td>280K</td>
<td>106</td>
<td>88</td>
<td>82</td>
<td>Yes</td>
</tr>
<tr>
<td>300K</td>
<td>124</td>
<td>125</td>
<td>121</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 2-3. Number of oxygen atoms (in water molecules) used for proton diffusion and their correlation with the diffusion constant at each temperature

To count the number of oxygens involved in proton hopping, we selected 2.0 Å as a cut-off distance for our models’ O index search. From the RDFs in Figure 2-2 and Figure 2-3, we can see the peaks start at the 2.45 Å, thus the cut-off distance for oxygen index search should be sufficiently less than 2.45 Å to avoid oxygen overlap. Also, because the bond length of O-H in a water molecule is approximately 1.0 Å, the cut-off distance should be greater than 1.0 Å. A small cut-off distance can cause over count of the number of diffusion involved oxygens because the water molecules can move out of the cut-off distance during the simulation. Therefore, we selected 2.0 Å as the cut-off distance. In the calculation process, we neglect the proton migrations between the same oxygens and only display the oxygen xy-coordinate when a new oxygen is visited by a proton. Since we used single layer water, the oxygens are presented on a xy-coordinate. Figure 2-12, 13, 14, 15, and 16 display the oxygens that are used for diffusion on a xy-plane at varying temperatures. The nine protons in our modeled systems migrate through the waters’ oxygens. In the Figure 2-12, 13, 14, 15, and 16 diagram, those oxygen atoms
are represented by different colors on a xy-plane, and the number of circles indicates the oxygen atoms that are involved for diffusion. At the low temperatures of 200K and 250K, we are easily able to count which model has the greatest population of O and figure out the active and inactive protons in the system. Additionally, at 270K, even though the used number of O in the annealed model 1 (b) is smaller than that of the initial model (a), the oxygens in the annealed model 1 (b) seem to be more widely dispersed. However, at high temperatures, evaluating the figures from only visual analysis is unachievable.

Figure 2-12. Oxygen atoms used for diffusion on xy-coordinates at 200K (a) initial model, (b) annealed model, and (c) annealed model 2

Figure 2-13. Oxygen atoms used for diffusion on xy-coordinates at 250K (a) initial model, (b) annealed model, and (c) annealed model 2
Figure 2-14. Oxygen atoms used for diffusion on xy-coordinates at 270K (a) initial model, (b) annealed model, and (c) annealed model 2

Figure 2-15. Oxygen atoms used for diffusion on xy-coordinates at 280K (a) initial model, (b) annealed model, and (c) annealed model 2

Figure 2-16. Oxygen atoms used for diffusion on xy-coordinates at 300K (a) initial model, (b) annealed model, and (c) annealed model 2
The used number of oxygens cannot completely reflect the diffusion constant trends because some protons migrated only to adjacent water molecules such as in Figure 2-16’s (b), brown, orange and yellow colored oxygens. Thus, we tried to calculate the total area of proton migration in the next step.

### 2.2.2.3 Total Area of Protons Migration

In the preceding sections, we found that the total proton hopping and number of oxygens visited by the protons can explain the systems’ diffusion constant to a certain degree, but they cannot fully explain all trends observed in the diffusion constant. In the data represented in the Figure 2-12, 13, 14, 15, and 16, we focused on figuring out how far the protons migrated from the first oxygen in a xy-plane.

As displayed in Figure 2-17, 18, 19, 20, and 21, we plotted the polygons with outer points of each color and calculated the total area of them to find the total migration range of the protons. An area of a rectangle with height of 0.05 Å is used if only two oxygen atoms are used for diffusion such as in Figure 2-17’s (b) yellow points. The calculated total area of the polygons of each system is presented in the Table 2-4.

At 200K, in Figure 2-17, the calculated area of the polygons shows the same trend with that of the number of used O. The initial model has a larger range of proton movement than the two annealed models: the initial model’s total area of proton movement is 122.8207 Å², while annealed model 1 has 40.2978 Å², and annealed model 2 used only 35.3638 Å². The results at 250K also have the same trend: the initial model
has the highest value while annealed model 1 has the lowest value of polygon area, Figure 2-18.

In the case of the models at 270K, Figure 2-19, they present different results from the number of used O calculation. The number of O in the initial system is 87 which is greater than the value of 85 in the annealed model 1, but the annealed model 1 has 368.1069 Å² of total area that is greater than the initial model’s, 367.5397 Å². This trend well reflects the trend of the diffusion constant at 270K.

Still, at relatively high temperature, such as 300K, it is difficult to investigate the result by visual analysis because some overlapped area of polygons are generated as shown in Figure 2-21.

Figure 2-17. Area used for diffusion at 200K expressed by polygons on a xy-plane (a) initial model, (b) annealed model 1, and (c) annealed model 2

Figure 2-18. Area used for diffusion at 250K expressed by polygons on a xy-plane (a) initial model, (b) annealed model 1, and (c) annealed model 2
Figure 2-19. Area used for diffusion at 270K expressed by polygons on a xy-plane (a) initial model, (b) annealed model 1, and (c) annealed model 2

Figure 2-20. Area used for diffusion at 280K expressed by polygons on a xy-plane (a) initial model, (b) annealed model 1, and (c) annealed model 2

Figure 2-21. Area used for diffusion at 300K expressed by polygons on a xy-plane (a) initial model, (b) annealed model 1, and (c) annealed model 2
The trends of the total area of proton migration at each temperature (200K, 250K, 270K, 280K, and 300K) are displayed in Figure 2-22 with bar graphs for the diffusion constants. The two sets of figures showing both the diffusion constant and area of polygons shows similar trends at the same temperatures. As such, we found that the area covered by the proton diffusion agrees with the diffusion constant at each temperature. Additionally, the water self-diffusion coefficients of the three models (initial model, annealed model 1, and annealed model 2) at 300K are $7.24 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, $10.73 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, and $10.73 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ respectively, whereas the proton diffusion coefficients of the three systems are $12.15 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, $8.87 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, and $11.43 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ respectively. The proton diffusion coefficients values are close to the water self-diffusion coefficient of $11.01 \pm 1.2 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, which was calculated by experimental work from the previous research [55].
Figure 2-22. Bar graphs of the diffusion constant (left) and total used area for diffusion (right) at each of the following temperatures: 200K, 250K, 270K, 280K, and 300K
<table>
<thead>
<tr>
<th>Total Area of Proton Migration (Å²)</th>
<th>Initial Model</th>
<th>Annealed Model 1</th>
<th>Annealed Model 2</th>
<th>Correlation with Diffusion constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>200K</td>
<td>122.8207</td>
<td>40.2978</td>
<td>35.3638</td>
<td>Yes</td>
</tr>
<tr>
<td>250K</td>
<td>356.0532</td>
<td>186.5283</td>
<td>237.3771</td>
<td>Yes</td>
</tr>
<tr>
<td>270K</td>
<td>367.5397</td>
<td>368.1069</td>
<td>542.9223</td>
<td>Yes</td>
</tr>
<tr>
<td>280K</td>
<td>488.1849</td>
<td>374.5658</td>
<td>359.331</td>
<td>Yes</td>
</tr>
<tr>
<td>300K</td>
<td>725.0956</td>
<td>635.447</td>
<td>688.8712</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 2-4. Calculated total used area of each of the polygons at each temperature and their correlation with diffusion constant
Chapter 3

Summary, conclusion and future work

3.1 Summary and conclusion

In summary, we investigated the diffusion of the protons which are in a single layer of water trapped between the MXene layers using ReaxFF MD simulation. There were three systems of different initial configurations, each differentiated by annealing procedure: initial model, annealed model 1, and annealed model 2. Each system exhibited unusual trends in the proton and water self-diffusion constant. To explain these trends we tried three methods: counting of the total number of protons hops, counting the number of oxygen atoms used for diffusion, and measuring of the total area of proton migration. We found a correlation between the total area of proton migration and the proton diffusion constant, Table 3-1. The more area the protons moved about in, the higher the diffusion constant was calculated to be.

<table>
<thead>
<tr>
<th>Correlation with Diffusion Constant</th>
<th>Total number of hopping</th>
<th>Number of O used for diffusion</th>
<th>Total area of pentagons</th>
</tr>
</thead>
<tbody>
<tr>
<td>200K</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>250K</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>270K</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>280K</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>300K</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 3-1. Correlation between the diffusion constant and the three methods (Total number of hopping, Number of O used for diffusion, and Total area of proton migration)
3.2 Future work

To draw more accurate results from this study, another model with different configuration will be needed. Thus, we will build another system by using the annealing process and simulate the model. Also, a longer simulation time will be a useful to improve accuracy. In addition, we will investigate a system consisting of a double layer of water intercalated between the MXene layers. The difference between the single layer water system and the double layer water system is expected to be a good source to understand the MXenes’ properties.
References


