



Master of Science

## ATOMIC BOUNDARY POSITION AND STERIC EFFECTS ON ION TRANSPORT AND SEPARATION THROUGH NANO POROUS GRAPHENE MEMBRANE

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# ATOMIC BOUNDARY POSITION AND STERIC EFFECTS ON ION TRANSPORT AND SEPARATION THROUGH NANO POROUS GRAPHENE MEMBRANE

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A Master's Thesis

Submitted to

the Graduate School of the University of Ulsan In partial fulfillment of the requirements for the degree of Master of Science

by

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May 2022

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## Acknowledgement

First of all, I would like to convey my sincere gratitude to my advisor Dr. BoHung Kim of the School of Mechanical and Automotive Engineering at the University of Ulsan, for his supervision, advice, continuous support, and constant encouragement throughout my M.Sc. study and academic life. His patience, motivation, immense knowledge, and continuous guidance supported me to build the foundation of my research skills. Apart from research, his moral and ethical guidelines helped me grow up as a person in practical life.

I am very much thankful to the University of Ulsan for giving me an outstanding research environment and financial support. I am also grateful Dr. Yoon Ho Lee and Dr. Dong Kim for being the honorable judge of my thesis defense. This university allowed me to conduct several practical courses with excellent instructors that will enable me to think and work properly for the rest of my life. My special thanks go to National Research Foundation (NRF) Korea for its contribution and financial support during my study.

I would also like to express my gratitude to my lab mate, MD. Masuduzzaman, Kazi Ehsanul Karim, Jaber Al Hossain in Micro-Nano Scale Thermal Fluid Laboratory for their friendship and immense support in my master's life. Besides, I am also really grateful to my former Korean lab mate, Kim Sunghwan and Yeyoungmeyong. They assisted in many cases that were priceless concerning their effort.

I am ever grateful to my parents for raising me and helping me achieve all that I have in my life. They gave me endless support from my home country during my whole academic life. I also express my gratefulness for my brothers in Ulsan Atish Bhattacharjee, Shovon Talukder, Nasim Al Islam, Md. Junayed Hasan, and special thanks to my roommate Md. Jashim Uddin Shehab. Last but not least, I would like to express gratitude to my friend Takia Maliha and Md. Rafi-Ur Rahman for their mental support in my abroad life.

## Abstract

Atomic boundary position and steric effects on ion transport and separation through Nano porous graphene membrane

(May 2022)

#### Morshed Mahmud

The electrostatic attraction between ion and water is the primary concern of changing the ion's bare diameter. The modification in ion shape is known as the steric effect that plays a crucial role in the desalination approaches using nanoporous graphene membranes. Utilizing molecular dynamics (MD), a pressure-driven flow is generated using specular reflection wall movement at a constant speed to analyze the saltwater transport through a nanoporous graphene membrane. This study signifies pore diameter's atomic boundary position impact on single-ion transportation and the steric influence of ions on the water mass flow rate and velocity profile. Due to the Columbic interaction between ions and water, ions hinder the water molecules from their regular velocity, which also lessens the flow rate of water molecules. For the different atomic boundary positions of pore diameter, we propose the ratio of the input energy of the total ion and the energy barrier of ion dehydration as the theoretical ion transportation. Interestingly, a significant deviation for different atomic boundary positions is observed for ion rejection at less than 1 nm pore diameter. The ion rejection drops considerably if all hydration layers break off due to high critical pressure. However, at more than 1nm pore diameter, the ion rejection closely matches the atomic boundary position specified to the 2% water density drop inside the nanopore.

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## I. Introduction

The expanding human populace combined with exploitation of water assets for household purposes, industry, and irrigation has come about in a deficiency of new water supply in numerous parts of the world. It is anticipated that 40–50% development in human populace over the next 50 a long time, coupled with industrialization and urbanization, will result in an expanding request on the accessible water resources(1).Since only 3% of the world's water is fresh water, it is becoming difficult to meet the water demands of the expanding population of the world(2,3). However, ocean water can meet this demand if it is desalinated. In this regard, it is necessary to assess the significance of salt water desalination as a permanent water supply option (4).In the salt water desalination, the most effective method is the reverse osmosis system. Reverse osmosis (RO) is the process in which contaminating particles such as ions and minerals are removed from water by a pressure driven flow. The water molecules are squeezed through the membrane, but the other substances stay behind.



Semi permeable membrane

## Figure 1.1: Reverse osmosis concept

The birth of pressure driven membrane desalination took put about 100 a long time prior. Early improvements in this technology stay covered in a few riddle, particularly with regard to application of the osmotic wonder to desalination(5). The challenges in the desalination industry incorporate nourish water characterization, prepare advancement, materials improvement, renewable energy source, rigid water standard and brine administration. Considering the worldwide normal water utilization per capita of  $1243m^3$  year<sup>-1</sup> (5% for household utilize, 85% for agrarian water system, and 10% for mechanical utilize), this plant can supply new water to less than 100,000 individuals. Thus mega-sized desalination plants must be created on the off chance that we are to supply unused clean water supplies to billions of individuals. In this setting, the greatest challenge would be making RO desalination reasonable for poorer nations(6).Despite the fact that the reverse osmosis (RO) system is the most common desalination process due to low energy consumption, it needs to be advanced in terms of cost and efficiency(7–9).

Advances in nanotechnology opened up a new door for water desalination. Whereas nanoscale wonders have been distinguished and examined for a few decades, critical advance within the capacity to control matter at the nanometer length scale happened within the to begin with decade of the 21st century. These advancements have opened the plausibility of making gadgets and frameworks utilizing nanostructured materials counting carbon nanotubes, nanowires, graphene, quantum dabs, super lattices, and Nano shells, among other materials. In expansion to the center on applications such as vitality change, medicate conveyance, hardware, computing, auxiliary materials, photonics, bio imaging, and bio sensing, researchers have as of late begun examining nanostructured materials within the setting of water desalination(1). When the Nano pore diameter is less than the size of the hydrated diameter of ion (the entire boundary of the hydrated ion along with the hydration sphere around it), that ion can be excluded from the transportation by this size exclusion mechanism(10). Ion's dehydration barriers along with this size exclusion mechanism can lead to effective water desalination(11-13). RO layers were at first created utilizing cellulose acetate and commercialized within the 1960s, but advertised moderately Ion fluxes and were subject to natural debasement.

Current state-of- the art RO layers are deviated polyamide and thin film composite layers created polymerization. These layers comprise of a various leveled structure where a lean (100–1000 nm) polyamide particular layer is created on a porous polysulfide layer that gives mechanical back and minimizes weight drop (1). In fact, choosing a membrane material for the Nano pore is a delicate task because the membrane material needs to withstand against the pressure that will create by the flow. Also, the membrane surface required to be impermeable except the Nano pore area. Among all the candidate materials, graphene has these unique characteristics. Graphene blocks all kinds of molecules as it is composed of  $sp^2$ hybridized carbon atoms with another in a 2D honeycomb lattice with a high electron density in its aromatic rings. The high carbon-carbon bond energy and intrinsic mechanical strength make graphene the supreme impermeable membrane(14). Since the lattice constant of graphene is smaller than the molecular diameter of water, graphene is impermeable to ionic aqueous solution(15). Having the  $sp^2$  hybridized carbon atoms structured like a hexagonal lattice structure, this single atom thickness (0.34nm) material is considered a critical material due to its remarkable mechanical strength and robustness(Fig 1.2)(16,17). Due to this fact, specifically engineered graphene sheets have become the most promising new material for polymer electrolyte membrane fuel cells (PEMFC) applications(18). Besides this, graphene-based fuel cell catalysts are also very efficient for both anode and cathode fabrication (19).

Given the above facts, creating a Nano pore on a graphene membrane can effectively retain the increased size of hydrated ions due to the steric effect while the water molecules can pass through the Nano pore successfully. Graphene membrane are still durable to face a pressure-driven flow after crafting the pore. In fact, the Nano porous graphene (NPG) membrane can withstand pressures exceeding 57 MPa when having a Nano pore smaller than 1  $\mu$ m(20). These Nano pore can be functionalized and the Nano porous membrane can be used in multilayers, but the water permeability depends on the pore spacing in that case(21). Hypothetical expectations propose that artificial pores in graphene can increment its penetrability and permeation-selectivity (14). For instance, a nitrogen functionalized pore in graphene can open up an effective gap of 3A° with a selectivity of 10<sup>8</sup> while the hydrogen terminated vacancy can space up to 2.5 A° with a selectivity of 10. As like that, periodic pores on graphene can yield different barrier heights for transmissions of various gas as well.



**Figure 1.2:** Graphene lattice structure: sp2 hybridized carbon atoms arranged in a 2D honeycomb lattice (14)

The low energy consumption effect of Nano porous graphene membranes allows the flow of the desired molecules while blocking the contaminated particles. Hence, sea water ions can be effectively rejected by using this single layer or multi-layer NPG membranes while purifying a significant amount of water(7). Actually, the NPG membranes are already used as effective filters for desalination in a lot of molecular dynamics studies in recent days focusing on saltwater transport driven by pressure. However, the desalination efficiency of the NPG membrane is highly dependent on selective pore size, selective pressure, and pore hydrophobicity(22).

A lot of conflicts are going on in selecting the pore diameter for desalination in recent studies. For example, Cohen-Tanugi et al. mentioned that a maximum pore diameter of 5.5 Å was necessary to prevent salt ion transport in their MD model of reverse osmosis water desalination process using NPG membrane while Konatham et al. reported that a maximum pore diameter of 7.5 Å was needed to retard the salt ions(23,24). Later on, Nguyen et al. achieved 100% salt rejection with a 9.90 Å pore diameter using a 35.02 MPa pressure drop (15). This ongoing discussion on how to select the Nano pore diameter remains since the definition of the Nano pore diameter (visually the pore width) is still a debatable issue. The pore radius are defined in diverse ways on the nanoscale for different reasons(25). The deep impact of the hydrated ion's boundary can have a great influence on determining the pore diameter for effective water desalination. In fact, the hydration layer beyond the first hydration layer is also responsible for retaining the ion transport through the Nano pore. The internal energy barrier for ion transport depends on the pore radius which can be effected on the proper boundary position of Nano pore. The effective pore radius was also defined by the width that forces the hydration layer to be partially broken for ion transportation(26,27)By investigating the hydration properties, it is possible to evaluate the hydrated solute steric hindrance and so predict an approximate pore size that may work properly for effective water filtration(28). Thus, it is necessary to intensely understand the pore boundary position relation with the hydration layers for predicting the saltwater transportation.

The most natural way to halt a particle from passing through a limit pore is to form the pore smaller than the size of the particle; that's, to form utilize of estimate prevention [fig 1.3 (a)]. Through the dehydration barriers Ion exclusion can be explained more vividly. In the salt water solution, ions attract a shell of nearby water molecules due to the long range columbic

interaction between charge on the ion and the water dipole. This hydration sphere broadens the size of the ion [fig.1.3 (b)]. When the pore is smaller than the size of the hydration sphere, the hydration sphere will not go through the pore. To transport through the pore, water molecules need to adjust their geometry around the ion, allowing it to squeeze into slightly smaller spaces at a small energy cost(10).

In figure 1.3, (a) Size exclusion, in which the ion is larger function of the position of the ion within car than the size of the pore, (b) dehydration barriers created by the necessity to remove water bon nanotubes with different diameters. In the form an ion to enter the pore, and (c) electrostatic repulsion between the ion and the pore. The ion is shown in orange in each case (29). Ion mobility in the pore is smaller than the bulk ion mobility because they have a layered liquid structure in the pore axial direction (30). When an ion hits the pore and wants to leave the bulk, it requires sufficient energy to overcome the energetic penalty. The energetic penalties progressions are subjected to the ion hydration, ion charge, pore chemical characteristics, pore size, and pore geometry(31–33). Deformation of the reactive zone can happen when the sterically demanding group is close to the reactive center (34). Ions show a gel-like property in aqueous form and the shape of this gel can change under pressure. Moreover, the strength of the ion's hydration depends on the ionic concentration and other environmental factors like ionic strength, pH, and temperature(35).



Figure 1.3: Physical mechanisms of ion rejection (36).

Due to these factors when ion's the hydration strength became weak, the ion partially dehydrated. These partially or fully dehydrated ions are transported through the Nano pore. This dehydration is the primary contribution of the ion energy barrier for transportation in narrow pores.(36). The water molecules around small cations remain practically at a fixed distance, forming a shell where bulk water molecules continuously replace individual water molecules in nanoseconds(37,38). Because of the electric field of the ion, the solvent dipoles in the first hydration layer are highly structured and the diploes around it do not act linearly (39,40). For this reason, transporting the cation for a pore radius of 1.2nm, the first layer of the hydration layer can be intact whereas the second layer can be partially dehydrated due to the pore wall(27). When the ion is at the pore center, the hydration sphere around the ion will be dehydrated depending on the pore radius(41).Therefore, for predicting ion transportation, it is necessary to assess the energy barrier for dehydration relation with the atomic boundary position of pore diameter more extensively.

There are lot of tools and numerical simulation method considering the system scale as like in figure 1.4.



Figure 1.4: Approximate length and time scales for the commonly used computational methods(42).

For example, from Nano scale to meso-scale there has been several scale like firstprinciples Boltzmann transport equations (BTE), molecular dynamics (MD) simulations, nonequilibrium Green's function (NEGF), numerical solution of phonon BTE, and hybrid methods. First-principles BTE strategies can be used for nonparametric expectations by exploring BTE using the interatomic drive constants (IFCs) of the Density Functional Theory (DFT). The computational acquisition of first-principles BTEs is so expensive that framework estimates are limited to hundreds of particles, but the driving force of today's high-execution computing makes the application of first-principles BTEs significant. MD simulation is based on Integral of Newton's equation for a population of atoms, usually described atomically using empirical potential interaction. Despite the classic nature of MD simulation, it Effective for treating nanostructures, interfaces and other flow phenomenon. Among all the methods we choose MD simulation since it is much less computationally intensive and also it can calculate the evolution of the system in time.

This paper mainly aims to investigate the atomic boundary position of pore diameter impact on water and ion transportation prediction with molecular dynamics (MD) study. The molecular dynamics is The steric effect of ion on water transportation has been studied in this study. The main objective of see the influence of the atomic boundary position of pore diameter on chlorine ion transportation has been analyzed with a theoretical ion rejection proposed method with the MD predicted ion rejection.

## II. Theoretical background

#### **2.1 Molecular Dynamics Simulation**

Due to the vast expansion of nanotechnology in the recent scientific age, nanofabrication is a common to proceed for the nanotech. For that reason, many nanostructure fabrication processes have been developed. Especially, chemical vapor deposition (CVD) is one of promising fabrication process, CVD process can be used to make carbon nanotubes (CNT) (43–45). However, still lot of difficulty has been faced to experimentally model in Nano scale system such as desalination by Nano pore or ion separation by nonporous graphene membrane due to expensive cost or harness of making complex structures.

To overcome these boundaries, molecular dynamics (MD) has been emerged as alternative method to experiment for Nano scale research following rapid development of computer, Molecular dynamics is computational method to simulate of a set of molecules with interact. MD is theoretically based on statistical thermodynamics. In MD simulation, velocity and positions were calculated by numerically solving the Newton's equation of motion and by using intermolecular potentials, thus MD can provide all trajectories of atoms, Also, MD simulations with statistical concepts, such as ensembles, local thermodynamic equilibrium, etc. We can obtain properties of materials. In this regard, many researchers conducted MD simulations to study on fluidics or to investigate thermal, mechanical properties. And MD has been gained trustworthiness from many research papers.

In fact, for ion separation and transportation, many MD research papers have been published in recent days. The ion rejection and the mechanism behind it were actively studied by the molecular dynamics simulation and statistical thermodynamics (15,23,24).

#### 2.2 Maxwell – Boltzmann Distribution

Maxwell –Boltzmann distribution is the most crucial part to establish statistical thermodynamics concepts in molecular dynamics. Maxwell –Boltzmann distribution is basically based on the kinetic energy theory of molecules. Thus, the MB distribution is also maintaining the assumption that follows the kinetic theory. The assumptions are:

- Number of gas is huge and the particle size is much smaller than the average distance between molecules 2) with the random movement each molecule follows Newton's Law
   same type molecules have same mass. 4) The molecules collide with walls of container and among themselves. Since all the collisions are perfectly elastic, energy is conserved.
  - 5) Without collisions, the interactions among molecules are negligible.

Maxwell-Boltzmann distribution defines the velocity in idealized gases where the particles move randomly inside a stationary system in state of thermodynamic equilibrium.

Maxwell-Boltzmann distribution is given by:

$$f(v) = \sqrt{\left(\frac{M}{2\pi k_B T}\right)^3 4\pi v^2 e^{-\frac{mv^2}{2k_B T}}}....(1)$$

Where m = the particle mass,  $k_B$  = Boltzmann constant T = absolute temperature



Figure 2.1: The speed variation of the Maxwell Boltzmann velocity Distribution

From figure 2.1, it can be seen there are three meaningful speeds: peak speed  $(v_p)$ , mean speed (v) and root mean square speed  $(v_{rms})$ . Each speed can be found as follow:

$$(v) = \int_0^\infty v f(v) dv = \sqrt{\frac{8k_B T}{\pi m}}....(2)$$

$$v_{rms} = \sqrt{(\int_0^\infty v^2 f(v) dv)} = \sqrt{\frac{3k_B T}{m}}....(3)$$

The relationship between the kinetic energy and thermal energy can be established from Maxwell Boltzmann relationship:

$$E_k = \frac{1}{2}mv^2 = \frac{3}{2}K_BT.$$
 (4)

The relationship indicates the average kinetic energy of molecules is proportional to absolute temperature. The shape of Boltzmann distribution depends on temperature and molecular mas. When the temperature is inclined with some molecular mass, the Boltzmann distribution becomes more flat and the average speed increases. On the other hand, when molecular mass is upwards with equal temperature, the Boltzmann distribution become steeper and average speed is decreased.

#### 2.3 Local Thermodynamic Equilibrium

The relationship between kinetic energy and thermal energy as equation (4) is only satisfied in equilibrium system. In several cases, we need local temperature to obtain detailed temperature profile in materials to calculate thermodynamic properties. To establish local temperature, we need concept of local thermodynamic equilibrium. However, Local thermodynamic equilibrium is valid only when the velocities of molecules are distributed following the Maxwell-Boltzmann distribution.

Local equilibrium thermodynamics is concerned with the time courses and rates of advance of irreversible forms in frameworks that are easily spatially inhomogeneous. It concedes time as a crucial amount, but as it were in a limited way. Instead of considering timeinvariant streams as long-term normal rates of cyclic forms, nearby balance thermodynamics considers time-varying streams in frameworks that are portrayed by states of neighborhood thermodynamic balance. Neighborhood balance thermodynamics considers forms that include the time-dependent generation of entropy by dissipative forms, in which active vitality of bulk stream and chemical potential vitality are changed over into inside vitality at time rates that are expressly accounted for. Time-varying bulk streams and particular diffusional streams are considered, but they are required to be subordinate factors, inferred as it were from fabric properties portrayed as it were by inactive plainly visible balance states of little nearby locales(46).

#### 2.4 Ergogodic hypothesis

Summing the suitable attributes of the molecules in the volume element over a prolonged time interval is called a time average. Ensemble average, on the other hand, is an instantaneous average of the molecules in a certain volume element. There are an endless number of such systems.MD simulations numerically solve Newton's equation of motion. . It indicates that Molecular dynamics calculations are obtained from the collecting of particles trajectories of systems with time. The temporal average of particles in the volume element is used to deal with this result. However, Ensemble average is what we want to obtain out of MD simulation, and ensemble average requires infinitely large number of similar systems. In this way, it is difficult to obtain ensemble normal by MD reenactment since computational taken a toll is restricted. In this way, we need a bridge to interface these two midpoints to get ensemble average. In this respect, ergodic speculation is profoundly imperative concept in MD recreation to handle MD result. Ergodic theory could be a key to associate time normal and ensemble average. Ergodic theory means that the time normal and gathering normal can be identical. Due to ergodic theory, we are able get this ensured for MD simulation and able to calculate bulk property, such as warm conductivity, thickness, and etc. from MD recreation comes about. We are able get time normal from MD recreations easily, and able to get gathering normal from time usual with little computational cost. In any case to realize ergodic theory, we ought to get time averaging over long time enough.

#### 2.5 Ensemble

In statistical mechanics, an ensemble is a concept of involving of a large number of virtual copies of system, one of which represents a possible state the system could be in. There are three ensembles widely used in MD simulations: Micro- canonical ensemble (NVE), Canonical Ensemble (NVT), and Isothermal-isobaric ensemble (NPT). The NVE ensemble is a statistical ensemble where number of particles, volume of system, and total energy are each fixed. This ensemble regenerate's isolated system which is called as micro-canonical ensemble. The NVT ensemble is a statistical ensemble where number of particles, volume of system, and temperature are fixed, instead of energy fixing. This ensemble is linked to isothermal system. Thermostat is employed to maintain temperature of system constant which rescales the velocities at each time step. This NVT ensemble is called as canonical ensemble. The NPT ensemble fixes number of particle and maintains temperature and pressure constant. This is achieved by utilizing thermostat for temperature and barostat for pressure. This ensemble is useful to systems that the correct system temperature and pressure is required. This ensemble is called as isothermal-isobaric ensemble.

#### 2.6 Particle Particle Mesh

The number of particles is important factor in MD simulations. The more reliable result can be obtained if more particles are included. For that reason, large size of system is required in MD simulation. However, the computational cost would become more costly. This difficulty is in practical in gas-solid interface system. In fact, gas system needs large volume size comparing to other phase states. To meet this condition, large number of solid atoms need be included. In this cases, periodic boundary condition (PBC) can be on solution to deal with such problem. Periodic boundary condition allows us to run large (infinite) system simulation with a small simulation box containing particles in which we are interest.

In arrange to reassure the consider of bulk framework behavior utilizing Nano scale simulations, intermittent boundary conditions (PBCs) appeared in Figure 2.2 are regularly utilized, whereas the framework arrangement within the simulation box is occasionally imitated in an interminable cross section. In this manner, the simulation box must be space filling and commensurate with a three-dimensional (3D) grid. For case, simulation box can be cubic but not spherical, as the last mentioned isn't space filling. In fact, PBC presents certain finite-size artifacts due to the presumption of a "crystalline" arrange at length scales above the framework measure and the reenactment must be performed for system sizes huge sufficient in order to play down such artifacts. This will be guaranteed by performing recreations at different framework sizes until the properties of intrigued converge with framework estimate(47).



**Figure 2.2** Two-dimensional representation of periodic boundary condition. The middle cell (filled with yellow) represents the simulation box whereas filled circles indicate particles in the simulation box and open circles represent their

periodic picture in other cells. Bold and dashed lines shows movement of two particles near the boundary; as a particle leaves the simulation box, its image enters the box from the opposite end(47)

## **2.7 Interatomic Potential**

In this study, we deal with the interface between solid, liquid and ions. Therefore, we need potentials for solid, liquid, solid-ion, liquid-ion and solid-liquid interface. In section 2.7 the Van der Waals interaction is explained first after that the Leonard Jones and Leonard Jones columbic interaction and lastly the AIRBO Potential for graphene membrane.

#### 2.7.1 Van der walls

Van der Waals intuitive happens when adjoining particles come near sufficient that their external electron clouds fair scarcely touch. This activity actuates charge variances that result in a nonspecific, non-directional fascination. These intuitive are profoundly separate subordinate, diminishing in extent to the 6th control of the partition. The vitality of each interaction is as it were almost 4 kJ mol-1 (exceptionally frail when compared with the normal motor vitality of a particle in arrangement, which is around 2.5 kJ mol-1) and is critical as it were when numerous intelligent are combined (as in intuitive of complementary surfaces). Beneath ideal circumstances, van der Waals intuitive can accomplish holding energies as tall as 40 kJ mol-1. When two particles get as well near, they emphatically repulse each other. Thus, imperfect fits between connection atoms are enthusiastically exceptionally costly, avoiding affiliation in the event that surface bunches meddled sterically with each other.

## 2.7.2 Lennard Jones Potential

The LJ potential is typically used to simply mimic the interatomic interaction (Van der Waals potential) due to its simple approximation. The Lennard-Jones model has two 'parts'; a

steep repulsive term, and smoother attractive part indicating the London dispersion forces. Other than being an important model in itself, the Lennard-Jones potential frequently forms one of 'building blocks' of many force fields. In fact the 12-6 Lennard-Jones model is not the most reliable representation of the potential energy surface, but rather its use is commonly due to its computational efficiency. The Lennard-Jones Potential is given by the following equation:

Where, V is the intermolecular potential between the two atoms or molecules. $\epsilon$  is the well depth and a measure of how strongly the two particles attract each other is the distance at which the intermolecular potential between the two particles is zero(Figure 2.3).  $\sigma$  gives a measurement of how close two nonbonding particles can get and is thus referred to as the van der Waals radius. It is equal to one-half of inter nuclear distance between nonbonding particles. 'r' is the distance of separation between both particles (measured from the center of one particle to the center of the other particle).

The Coulomb potential is which decays slowly with the distance between particles. The Coulomb potential presents the electrostatic interaction between point charges. The mathematical expression for the Coulomb potential is:



**Figure 2.3:** Lennard–Jones 12–6 potential and Coulomb potential of the Silicon–Oxygen interaction in the a-quartz(48).

In differentiate to short-range interaction, long-range interaction effects need to be considered for the Coulomb possibilities. Notwithstanding, it isn't attainable to calculate the long-range interactions directly due to unsatisfactory computational costs. Different approximation methods have been proposed to bargain with the long-range potentials. The Ewald summation method may be a broadly adopted approximation method which reorganizes the interactions into a particular form that can be effortlessly assesse.

#### 2.7.3 AIRBO Potential

The Airebo pair style computes the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) Potential of (Stuart) for a system of carbon and/or hydrogen atoms. The rebo pair style computes the Reactive Empirical Bond Order (REBO) Potential. REBO is closely related to the initial AIREBO; it is just a subset of the potential energy terms with a few slightly different parameters. The AIRBO Potential has three terms:

$$E = \frac{1}{2} \sum_{i} \sum_{j \neq i} \left[ E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{k \neq i} \sum_{l \neq i, j, k} E_{ki j ll}^{TORSION} \dots \right]$$
(7)

#### 2.7.4 Mixing Rule

At the time of dealing l with different molecules together (e.g., binary gas system or solid-Liquid interface), the LJ potential parameters between them need to calculate. Mixing rule provide different potential result which could play a different result in the Molecular dynamics. The Lorentz-Berthelot (LB) rule is extensively used in Molecular Dynamics. Lorentz proposed an arithmetic average for the collision diameter, a considering a hard-sphere atom model whereas Berthelot projected a geometric average is used for the well depth  $\varepsilon$ .

$$\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j)....(8)$$
$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}...(9)$$

#### 2.8 The Sampson Flow Equation

For a flow a through an infinity thin circular pore with a low Reynolds number, uniform velocity and no-slip condition Sampson derived an analytical solution in 1891 in continuum hydrodynamics form the Stoke's equation.

If the pressure drop across the system is  $\Delta P = Pf - Pp$ . The volumetric flow rate can be expressed as:

$$q = \frac{\Delta P \, a^3}{3\mu}....(10)$$

Where "q" denotes the volumetric flow rate, "a" denotes the pore radius and  $\mu$  denotes the viscosity of the liquid.

Utilizing the Sampson's stream function solution in cylindrical coordinates, the velocity profile inside the pore can be written as follows:



**Figure 2.4:** Sampson flow through a circular pore in an infinitely thin plate. The pore radius is denoted by 'a' and flow rate by 'q'(49).

## 2.9 Steric effect & approaching hydration Boundary

The structural configuration of water molecules induces polarity. As a result of their polarity and the strong local electric field around the ion, water molecules arranged themselves around the ions to form hydration layers(26). In saltwater, positively charged Na<sup>+</sup> attracts the negatively charged oxygen atoms, while Cl<sup>-</sup> attracts the positively charged hydrogen atoms of water molecules. The size of the ionic diameter is increased due to this hydration sphere (sum of the entire hydration layer) which is known as the steric effect of ions in an aqueous solution.

Among all the ion transport and sepration mechanism , the steric effect have been choosen because it is related with the different hydration shell dehydration. So with choosing this mechanism for our research will allow us to study with different pore diamter and the phenomenon of ion transport with that different pore diameter. Therefore, Steric effect more specifically size exclusion method has been choosen for this research.



- $\frac{L_{h1}}{2}$  =Distance between ion center & primary(first) hydration layer
- $\frac{L_{h2}}{2}$  = Distance between ion center & secondary hydration layer

 $\frac{L_{h(n)}}{2}$  = Distance between ion center & 'N' number of secondary hydration layer (total hydration sphere radius due to steric effect)



**Figure 2.5:** Typical illustration of the hydration layer of ion due to steric attraction for Na+ and Cl- ion (b) Approaching hydration boundary concept with different pore diameter.

Figure 2.5 illustrates of the hydration sphere in saltwater for Na<sup>+</sup> and Cl<sup>-</sup>. The first hydration layer of ions due to the strong attraction is known as the primary hydration layer. The second shell up to an 'N' number of hydration layers is known as the secondary hydration layer(35). Here, the distance from the ion center to the primary hydration boundary is defined as  $\frac{L_{h1}}{2}$ , whereas  $L_{h1}$  is the diameter for the first hydration layer. Similarly as like that, for the second hydration layer,  $L_{h2}$  is the diameter for the secondary hydration layer. In this way, for an 'N' number of secondary hydration layers, the boundary is denoted as  $\frac{L_{h(n)}}{2}$  from the ion center. In figure 2.6, we denoted the nearest hydration layer outside the pore diameter as approached hydrated diameter needs to be bigger than the pore diameter. Hence, when the pore diameter is increased, the hydration diameters that approach the pore edges membrane need to be uplifted to reject the ion transportation.

#### **2.10** Computational Details

In Figure 2.6(a), the simulation domain has saltwater on the left side (feed side) and pure water on the right side (permeate side). The volumes of both of these regions are kept static using the specular reflection wall as represented in Figure 2.6(c). In the beginning, two of the specular reflection boundaries were made rigid at Z=-4.4925 nm and Z=4.4925 nm, while the x and y directions in the simulation domain were periodic with lengths of 3.192 nm and 2.952 nm. The graphene membrane was placed at the center at 0.0nm in the z-direction, and a circular pore of 0.99 nm diameter was generated by removing the carbon atoms, as shown in Figure 2.6(b).



**Figure 2.6:** (a)Schematics of the simulation domain (b) Denoting the initially considered diameter L of graphene Nanopores (c) physical description of the specular reflection wall.
Initially, this pore diameter L was considered from the atomic center to the center of carbon atoms inside the pore. The typical wall works like a piston to incite pressure-driven flow and may interrupt the bulk pressure in the feed and permeate regions in the atomic level framework because of the van der Walls interaction between the fluid and piston(50-52). Nonetheless, the specular reflection wall with genuinely forthright and computationally compelling strategies settles the issue(15,52). Thus, to avoid imprecise pressure drop across the simulation domain, a specular reflection wall is chosen instead of using a piston. The extended simple point charge (SPC/E) model was picked for water molecules due to its simplicity and efficient computational cost (53). Besides, it can also be depicted as an active rigid pair potential, including Lennard-Jones (LJ) and Columbic terms(54). The three atoms of water molecules have three interaction spots while they are allocated a point charge to induce the long-range Columbic interactions. Moreover, oxygen atoms also show a Lennard Jones (LJ) potential to model the van der Waals (VDW) forces. As per the SPC/E model, oxygen and hydrogen atoms are allotted partial charges of qo=0.-8476e and q<sub>H</sub>=0.4328e. Meanwhile, the H-O-H angle of 109.47° and O-H bond length of 0.1nm were kept constant using the SHAKE algorithm.(55)

To measure the interatomic interaction of oxygen atoms of water molecules, salt ions, and carbon atoms in the graphene membrane, a Truncated Lennard Jones (LJ) (12-6) potential was used as follows equation 5; where,  $\varepsilon$  is the potential well depth,  $\sigma$  is the finite molecular distance at which point the interatomic potential is zero,  $r_{ij}$  is the intermolecular distance and lastly  $r_c$  is the cutoff distance. The intermolecular forces are curtailed at a distance of  $r_c = 1.0$ nm in this work. The AIREBO potential was applied to model the planar interatomic interactions between carbon atoms in the graphene membrane(56). Although the interaction parameters of Na<sup>+</sup> and Cl<sup>-</sup> in the aqueous solutions were occupied based on quantum calculations, oxygen atom interaction parameters were taken from the SPC/E model(57). On the other hand, the interaction parameters between carbon and oxygen atoms are estimated from the Lorentz-Brethelot (L-B) mixing rule(58). For any atomic molecules with charge, columbic interactions were also employed. Correspondingly, the dissolved salt ions Na<sup>+</sup> and  $Cl^{-}$  are assigned charges of  $q_{Na}$  = 1.0e and  $q_{Cl}$  = -1.0e. The interaction parameters used in this study are presented in Table 1(15). The particle-particle particle-mesh (PPPM) method was utilized to ensure precise long-range electrostatic interactions between all charged atomic types(58). Newton's equations of motion were coordinated in the VERLET calculation with a simulation time step of 1.0 fs. All simulations were performed using LAMMPS(59). The Maxwell-Boltzmann velocity distribution at 300 K was applied for assigning initial conditions of fluids. NVT (constant number of molecules, volume, and temperature) ensembles were initially used with a Nose-Hoover thermostat to preserve the system at 300K in the equilibrium MD simulations. Individually, the feed and permeate side have 1584 water molecules to meet the water density at 1 g/cm<sup>3</sup>. Meanwhile, the feed side has 20 Na<sup>+</sup> and 20 Cl<sup>-</sup> ions which result in the salt concentration in the feed region of 0.6 M. For the first NVT ensemble, no pore was created and was equilibrated for 20 ns. After that, the pore of 0.99 nm diameter has created and equilibrated for additional 3ns.For all the four cases, these two steps have been followed before pursuing to NEMD simulations. After the EMD, in NEMD simulations were conducted to maintain flow for four different pore sizes of 0.568 nm, 0.994 nm, 1.420 nm, 1.9884 nm by moving the two specular reflection boundaries with the same velocity (1.5 ms<sup>-1</sup>) in the zdirection through the fixed graphene membrane. The preferred velocity was 1.5 ms<sup>-1</sup> because it coordinated well the molecular level with the continuum level properties for fluid in the previous studies(52). Using a higher specular reflection, the wall velocity may considerably disrupt the fluid thermodynamic properties, while applying a low velocity can increase the total computational time unreasonably.

Interaction	$\epsilon(ev)$	$\sigma(\dot{A})$
C-Cl	0.003619748	3.9240
C-Na	0.001350014	2.9876
C-0	0.00403278	3.283
С-Н	0.0	0.0
Na-Cl	0.001702700	3.5116
Cl-O	0.005575083	3.8068
Cl-H	0.0	0.0
Na-O	0.002079272	2.8704
Na-H	0.0	0.0
Cl-Cl	0.004613823	4.4480
Na-Na	0.000641772	2.5752
H-H	0.0	0.0
0-0	0.006739	3.166
О-Н	0	0.0

Table 1. Details of the interaction parameters used in this work

# 2.11 Selecting the SRW velocity

While selecting the SRW velocity, we need to consider two type of parameter. At first, we need to ensure that using that specific velocity doesn't disrupt the flow phenomenon along with preserving the thermodynamic property smoothly. For that reason, we cannot use a SRW velocity here more than 1.5 ms<sup>-1.</sup> However, another thing need to consider the too low SRW velocity. If we choose a velocity that is very low, then it will increase the computational cost a lot. Although using a lower SRW velocity less than 1.5 ms<sup>-1.</sup> could be effective, it could a long time to take the data with that time. Therefore, considering these facts the SRW velocity has been chosen here in this research.

# **III.** Result and Discussion



3.1 Density distributions of water and ions in the district of the porous membrane

Figure 3.1: Mass density distribution of water

In figure 3.1, Equilibrium molecular dynamics were used to determine the density distribution of water when the pore plug is off. The local density of water and salt ion concentrations were averaged for 20 ns by dividing the computational domain into slab bins with a length of 0.115 nm along the z-direction. Bin thickness was chosen to be ten times smaller than the molecular diameter of water to get a better visualization of the separation distance from the solid to the liquid region. The liquid transport and the liquid's property were greatly influenced by both the molecular structure and intermolecular force of liquid(52). Clearly, the bulk density of water on both sides of the membrane was almost 1g/cm<sup>3</sup> in Figure 3.1 as anticipated.



Figure 3.2: Determining pore boundary L' using water's radial density peak.

The density peak for water near the NPG membrane was observed due to the wellknown density layering(60). Due to the surface force and liquid-liquid strength in the nanoscale domain, liquid atoms adjacent to the solid surface drive in freezing mode and generate a solidlike liquid layering at the dissimilar molecular interface(61). Though the layered liquid structure near the solid surface is not reflected at the continuum level, this can significantly influence the flow phenomena at the nanoscale due to the increase in interfacial density, viscosity, and pressure(62–64). The density distribution of water molecules inside the Nanopore was shown in figure 3.2 for a pore diameter of 1.98 nm. In figure 3.2, the atomic boundary position L' of pore diameter was depicted where the water molecule's density dropped 2% from its bulk density(65). After that, (L -  $2\sigma_{c-c}$ ) was defined as the atomic boundary position L' of pore diameter whereas  $\sigma_c$  is atomic radius of the carbon atom. From the density distribution inside the Nanopore, L'' was found 0.3124 nm, 0.7426 nm, 1.20 nm, 1.83 nm for the pore diameter of 0.568 nm,0.99 nm, 1.42 nm, and 1.92 nm, respectively.

# 3.1 Pressure distribution of saltwater across the system

A pressure was developed in the feed and permeate region by the movement of the SRW at a constant speed ( $1.5 \text{ ms}^{-1}$ ). For conciseness, the pressure distribution for only one pore diameter (L) of 0.994 nm is shown in Figure 3.3 for a system of LJ + Columbic interaction between ion and water. The average of the three symmetrical ordinary stress segments in the Cartesian coordinate system from the IK expression was used to determine pressure(66,67). The bin size for the pressure distribution was also chosen as 0.115 nm to better describe the molecular interaction in compliance with the density distribution.

Figure 3.3 shows the pressure distribution in the z-direction, which displays ambivalence close to the interface. As a consequence of the density layering near the membrane, the local shear stress near the interface is increased, which eventually generates a pressure peak close to the interface on both sides of the system. In earlier studies, it was established that getting an anisotropic type of pressure close to the interface is very fundamental(15,51).

To find the pressure difference, the constant bulk pressure on the feed  $(P_f)$  and permeate  $(P_p)$  sides are given as follows:



**Figure 3.3:** Pressure distribution along the z-axis direction while two specular reflection boundaries are moving at 1.5ms<sup>-1</sup>



**Figure 3.4:** Pressure difference varied for various pore sizes for LJ and LJ+ Columbic interaction between ion and water molecules

From Figure 3.4, it is observed that the pressure difference along the z-direction is reduced in a non-linear way when the pore diameter is increased, although the specular

reflective wall velocity is the same for all cases. However, for the Lj+ Columbic interaction between water and ion, the pressure difference is less than in the cases of LJ interaction between water and ion. With the increment of the pore diameter, the saltwater flow area was increased. As a consequence, the shear stress between the molecules of saltwater was decreased on the feed side. Due to the decreasing shear stress in the feed side, the pressure drop of the system is decreased with increasing the pore diameter.

# **3.2** Comparison of water mass flow rate

The water cluster around the ion or the steric effect is formed due to the Columbic interaction between the ion and water molecules(10). At first, to visualize the steric effect on water flow rate, we have depicted the water mass flow rate separately both for LJ interaction and LJ+ Columbic interaction between the water and ion along with atomic boundary position of pore diameter in figure 3.5(a) and (b). For both cases, the interaction and all other parameters are the same except the ion-water interaction. The MD flow rate was calculated from the time rate of change of water molecules along the feed reservoir and then multiplied with the single water molecules that filled up the volume. Each water molecule filled up a volume 0f 0.03231 nm<sup>3</sup> in each reservoir. Interestingly, the water mass flow rate is reduced when the steric effect is present (Lj + columbic interaction between water and ion). The possible explanation for this phenomenon is linked up with water cluster formation around the ions due to the electrostatic interaction. In the presence of a steric effect, the ion tries to hinder the water molecules from moving freely, which ultimately reduces the water flow rate.



**Figure 3.5:** (a) Water mass flow rate relation with pore diameter with atomic boundary position for LJ interaction between ion and water (b)Water mass flow rate relation with pore diameter with atomic boundary position for LJ|+ Coulomb interaction between ion and water.

In addition to that, for three different boundary positions of pore diameter, the Sampson flow prediction was calculated from the Sampson flow equation that was solved from the Stokes equations for a pressure-driven flow through an infinitely thin circular orifice(68). The mass flow rate from the Sampson flow rate equation could be obtained from equation 10. Where 'q' denotes the volumetric flow rate, 'a' denotes the pore radius and ' $\mu$ ' denotes the viscosity of the fluid. The viscosity of saltwater is 850-860 µPa was used in the Sampson flow rate calculation (69). For the Sampson flow rate prediction, the water flow rate was also reduced for the steric affected case as the MD predicted result. It is apparent that as the pressure difference was decreased for each pore diameter of the steric affected case, the predicted Sampson flow rate also needs to be reduced due to the linear relationship between pressure and mass flow rate. However, there is no linear pattern found for the difference between the steric effect and non-steric affected case for MD and Sampson flow prediction with the pore diameter. In both steric and non-steric affected cases, the Sampson flow rate prediction is lower than the MD predicted magnitude. Since the Sampson flow over predicts the hydrodynamic resistance of the graphene Nanopore, the water mass flow rate decreased for the Sampson flow prediction from the MD (70). Moreover, when the atomic boundary position of L' and L'' applied to the Sampson flow rate prediction, it starts to deviate more from the MD predicted result. This result denotes that applying the atomic boundary position of Nanopore in the Sampson flow model doesn't hold the same prediction for water mass flow rate as it holds for a simple fluid flow(71). The long-range Columbic interaction of the water molecules itself could play the key role here in this variance.

#### **3.3 Comparison of water velocity profile**

To investigate the cause of the mass flow rate reduction of the water molecule in the presence of a steric effect, we analyzed the velocity distribution of water molecules at the pore and also for the overall system.



Figure 3.6: Water velocity distribution for pore diameter of 1.42 nm

To maintain the brevity, only the velocity distribution of 1.42nm pore diameter has been shown in figure 3.6, figure 3.7(a) and (b). Figure 3.6 illustrates the comparison between the velocity of water molecules for the entire system for LJ and LJ+ Columbic interaction between water and ion. When the ion-water has a Columbic interaction, the ion attracts the water molecules, strongly holding back their usual movement. As a result, the water velocity became lower for the steric affected case, and this difference between these two cases is more apparent at the center of the pore.

To acquire the complete view, the velocity profile at the pore center showed from the MD simulation along with the Sampson flow equation with a different boundary position of pore diameter. Applying Sampson's stream function solution in cylindrical coordinates, the velocity profile for r position inside the pore can be expressed as follows equation 11.



**Figure 3.7:** (a) Water velocity inside the Nanopore for LJ interaction between ion and water for pore diameter of 1.42 nm (b): Water velocity inside the Nanopore for LJ+ Columbic interaction between ion and water for pore diameter of 1.42 nm.

In figure 3.7(a) and (b), to calculate the velocity profile of water from MD, a cylindrical bin was used with a radius equal to the pore radius and length equal to the diameter of a single carbon atom. The cylindrical bin axis was set along the Z direction of the pore center, and the bin was also divided into multiple concentric circle bins to gather the velocity data in the radial direction of the pore. The multiple concentric circle bins were divided to get the maximum water molecules in each bin. The data were averaged for 0.4ns when the water flow was established across the Nanopore for a 1.42nm diameter Nanopore. The velocity profile is also reduced for different boundary conditions with the Sampson flow model for the steric-affected system case, and it also deviates from the MD value, maintaining consistency with the flow rate results

# 3.4 Defining the primary hydration boundary of ions

The ionic concentration distribution is represented in Figure 3.8, along the z-direction while ensuring that no ion has been passed through the Nanopore in EMD without applying pressure. The bulk ionic concentrations for Na<sup>+</sup> and Cl<sup>-</sup> were almost equal and matched with the theoretically calculated value of 0.6M. Although our focus was to investigate any ions transportations impact with the shift of the atomic boundary position of pore diameter, equal concentrated sodium, and chlorine ion is presented in this system due to maintaining the charge neutrality for added charge in the system.

Using the radial distribution function (RDF), the primary hydration layer boundary  $[L_{h1}]$  can be measured precisely. In Figure 3.9 (a) and (b), the radius of the primary shell boundary  $[\frac{L_{h1}}{2}]$  was determined using the RDF.



The first density peak in the radial distribution function indicates the starting region of the primary hydration layer, while the first minimum after the first density peak was considered as the radius of the primary hydration layer from the ion center. For Na<sup>+</sup>, the peak in the RDF indicates the strong electrostatic interactions with O<sup>-</sup> atoms of the primary hydration layer. For Cl<sup>-</sup>, it defines the strong electrostatic interactions with H<sup>+</sup> atoms of its primary hydration layer. The first minimum density drop indicates the strong repulsion between the atoms of the same charge. The primary hydration layer radii of Na<sup>+</sup> and Cl<sup>-</sup> were reported in this study as 0.37nm and 0.39 nm, respectively, which matched closely with the previous studies (30,72). After the first hydration layer, the second and the third hydration layer was found to be 0.62 nm and 0.85 nm from the chlorine ion center, respectively. For sodium, the second and the third hydration layer were found at 0.62 nm and 0.84 nm from the ion center, respectively. According to the literature, it is expected that the subsequent layer after the innermost layer is spaced at 0.2-0.23 nm (27)



**Figure 3.9:** (a) Defining hydration radius of sodium ions with the radial distribution function of water molecules around sodium ions (b) around chlorine ions.

## 3.5 Relating water and ion flow paths for various nanopore diameters

In this part of analysis, to observe the salt ion and water flow, the percentage of the salt and water on the feed side is tracked for pore diameters (L) of 0.994 nm, 1.4203 nm, 1.989 nm and 2.22nm. In figure 3.10 (a-d), the water and ion track down has been depicted. We add specifically pore diameter 2.2nm for this analysis over 0.55nm since for water and ion flow comparison, 0.99 nm to 2.22nm is considerable range. A reference time was needed to compare the percentage of the remaining molecule of water with salt ions. For each simulation, we characterized a period T<sub>f</sub> that is illustrative of the end of the simulation because the water flow rate generally shifted depending on the nanopore size.(73) For each pore case, T<sub>f</sub> has been selected when 160 of the water molecules passed from the feed side. After that, the salt ion passing percentage is compared with the water molecule flow percentage. For a larger pore diameter like 2.2 nm, salt ion flow proportion was almost the same as the water molecules. For example, for a pore diameter of 2.2 nm, both Na<sup>+</sup> and Cl<sup>-</sup> ions were passed at almost 20% while the water molecule flow holds constant at 20%. In contrast with this, when the pore diameter decreased, the difference between the salt ions and water molecules flow proportionality became larger for the smallest pore diameter like 0.99 nm. As a result of these facts, it can be said that the salt ions and water molecule's flow proportionality differences are inversely proportional to the pore boundary size. Alongside this, the Na<sup>+</sup> flow proportion difference with respect to water was lower compared to Cl<sup>-</sup> for the initial case pore boundary. Since cations hold their hydration shells less strongly than anions at a given charge density, it is easy for Na<sup>+</sup> ions to pass through the smaller nanopore by shedding the hydration shell close to the ion center(35). However, this is difficult for Cl<sup>-</sup> for its higher electrostatic attraction. Nevertheless, after the initial pore boundary, the flow proportion difference between Na<sup>+</sup> and Cl<sup>-</sup> and water molecules was observed to be insignificant due to the probable action of a weakly attracted hydration shell far from the ion center. Interestingly, the ions fluctuate around the feed and permeate the side through the pore before going permanently to the permeate side. The probable cause of this is that ion acts like free radicals at nanoscale, so they circulate in the pore region before going permanently to the permeate side. This flow proportionality difference between water and salt ions for different pore cases in saltwater transportation induces desalination. In actual fact, the free energy obstruction of ions is inversely proportional to the pore boundary size. Indeed, the free energy profile of ions is additionally influenced by the ion's hydration structure that in has an overall impact on ion transportation. (74)

From the above observation, it is presumed that the ions have trouble translocating when the steric impact boundary is greater than the pore boundary. Once an ion encounters the membrane, its secondary hydration shell may start to fall apart due to the pressure. In fact, the water molecules are separated from the ion during ion transportation by decreasing the first ion hydration number and increasing the energy of the ion(75). In this way, the steric limit ( $L_{h(n)}$ ) likely decreases, and when that limit was not greater than the pore limit size, the ion moved to the permeate region. For ion transportation through a small pore, ion hydration shells near the ion center must detach to reduce the steric effect boundary due to small pore boundary. This detachment requires an extremely high pressure since the hydration shell closest to the ion center has higher long-range columbic attraction. This is a plausible reason why ion transportation is lower in smaller pores, though they have higher pressure difference. In larger pores, ion transport is smooth as the secondary hydration shells far away from the ion center are only weakly attracted by the electrostatic force and can be separated even at low pressure.







**Figure 3.10:** Water molecules and salts remain proportional in the feed at a constant speed (1.5 ms<sup>-1</sup>) for (a) L=0.99nm (b) L=0.1.42 nm (c) L=0.1.98 nm (d) L=2.22 nm

Furthermore, the remaining percentage of salt ions in the feed side indicates the salt rejection of the saltwater as noted in earlier literary works. However, the salt rejection rate is highly dependent on the reference time  $T_f$ , which is the time salt rejection was determined. In previous works, the salt rejection was measured when the water molecules filtration was between 10% to 50% depending on the pore size(13,73). However, it should be noted that allowing for higher water molecules filtration will moderate the salt rejection rate. Accordingly, as various sizes of pores are considered in this study, a constant minimum amount of water flux filtration is designated so that even the smallest pore can have adequate water filtration with a lower computational cost. That constant minimum amount of water flux purification is used here to define the reference time  $(T_f)$  for each pore case.

After comparing the transportation for water and ions in Figure 3.10 (a-d) it is obvious that ion transportation isn't united with water for more modest nanopores due to their steric impact. To visualize the phenomenon, the anticipated transportation pathway is shown in Figure 3.11 (a-d) for salt ions and water by the linear least square method by utilizing the transportation information from Figure (3.10). As shown in Figure (3.10), the flow was considered up to the reference time. Here in Figure 3.11 (a-d), the flow was mathematically predicted until the water flow ended. The total salt ion vs. water flow path is represented to obtain total salt rejection. As estimated, there is a significant gap between the water and ion transport path for the first three pore cases (0.9942 nm, 1.4203 nm, 1.988 nm) due to the steric effect. The mathematically predicted salt rejection is obtained by measuring the percentage of salt that remains on the feed side when the remaining water is almost empty on the feed side. For pore diameters (L) of 0.9942 nm, 1.4203 nm, 1.988 nm, the mathematically predicted salt rejection were calculated to be 52.53%, 45.32%, 18.32%, respectively.





**Figure 3.11:** Generalized predicted comparison for water and ion flow with mathematically predicted salt rejection for (a) L=0.99nm (b) L=0.1.42 nm (c) L=0.1.98 nm (d) L=2.22 nm

This predicted salt rejection is not as high as the salt rejection that was directly gained from MD. However, this is not an issue for this study because our main focus was to identify the pore boundary where salt rejection is happening and where it is not. In Figure 3.11(d), for L=2.274 nm, the ion and water flow matched for a certain time, and then ions started to pass faster than water molecules. As shown, all the ions are translocated to the permeate side even before the water flow is finished. For this reason, salt rejection tends to zero percent when L= 2.274 nm. This also provides a comprehensive overview of the flow paths of ion and water molecules for the small and large-scale pore boundaries of this study. Smaller pore sizes with closer solvated hydration shells near the ion would encounter the carbon atoms at the pore edge. Hence, the ions are more hindered because water molecules close to the ion in the solvated hydration shell are more strongly attracted, and the shell is likely to collapse except at a very high pressure. This is the probable reason why the salt rejection is high for the small size nanopore diameters. It can be said from these results, that ion flow behavior will be similar to fluids like water when the pore boundary starts to reach the continuum scale, and the ion rejection phenomenon will not be effective for a continuum scale pore boundary. This also implies that the steric boundary will not interfere with ion transport after a certain nanopore boundary.

## 3.6 Investigating the salt rejection dependence and the steric impact limit region

In this section, to determine the steric boundary while transporting ions through a nanopore, the predicted salt ion rejection needs to be analyzed with respect to the pore boundary. This depends on the pore boundary definition since defining the pore boundary at nanoscale is very difficult. Initially, the pore boundary (L) was considered using the distance between the atomic centers of carbon for visual simplicity (as suggested by Thomas and McGaughey(76)). However, to check whether water has entered up to the distance of the edge of nanopore, the radial density of water inside the nanopore was measured as shown in Figure 3.12. The radial density distribution for a nanopore diameter (L) of 1.98 nm is shown as an example. The radial density distribution was obtained from the center of the nanopore up to the atomic center of the nanopore edge's carbon atoms while the bin size was ten times smaller than the carbon atomic diameter for better visualization. There is a density peak inside the nanopore on the radial density distribution of water. After the peak, the significant density drop indicates that the liquid water does not enter up to the center of the nanopore edge carbon atoms due to the density layering of water. The strong repulsion effect among the molecules at the nanoscale created this density layering gap between the solid and liquid molecules(77). Thus defining the center to a center atomic distance of the nanopore edge carbon atoms as the pore diameter is not a useful way to define the absolute steric boundary as the encircled water molecules around the ions do not enter up to the diameter L. When the density drops below 2% of the bulk density, another pore diameter definition was defined in previous literature which is denoted here as L' (25). For the four diameter cases in this study, L' was found to be 0.7456 nm,1.2072 nm,1.8223 nm,2.1708 nm respectively for 0.99 nm, 1.420 nm, 1.9884 nm, and 2.274 nm that were considered initially.



Figure 3.12 : Exponential decrease of (L - L') with L.

As shown in Figure 3.12, the gap between L and L' is defined here as the interfacial solid-liquid gap due to water's density layering which exponentially decreases with the increase in the pore diameter. Interestingly, in Figure 3.13, when this interfacial solid-liquid gap (L - L') is three times lower than the interatomic distance ( $\sigma_{oc}$ ) of carbon and water, the salt rejection started to diminish. In fact, after a certain value of  $\frac{\sigma_{oc}}{L-L'}$ , the salt rejection started to increase exponentially and the ratio was 3.13. The probable cause of this exponential increase in salt rejection is related to the repulsion effect of the (LJ) (12-6) potential between solid carbon and liquid water(58). When the (L- L') tends to reach close to the  $\sigma_{oc}$ , the salt rejection will approach to be higher because on that case the repulsion region of interfacial solid-liquid will approach to be greater by lowering the accessible area for ion translocation. Though this magnitude of this ratio is not universal because of the change in L' with the wettability of the solid surface, this gives an unprecedented insight into salt rejection that it is also vastly affected by the liquid-solid interaction(78).



**Figure 3.13 :** Exponential relationship of salt rejection with  $\frac{\sigma_{oc}}{L-L'}$ , where  $\sigma_{oc}$  is the intermolecular interaction distance between solid and fluid

Figure 3.13 shows, the predicted salt rejection obtained from the Figure 3.12 with respect to the pore diameter (L') and this demonstration visibly displaying how salt rejection is inversely proportional to the pore boundary. From Figure 3.14, we can conclude that the salt rejection tends to zero when the pore diameter (L') is 2.1708 nm. The theoretically measured salt rejection tends to zero percent for a specific pore diameter, indicating that the steric effect is a nanoscale property, and it should not influence ion transportation when the pore diameter inclines to expand to a continuum scale. It is obvious that salt ions will not pass like fluids due to the steric effect when  $L' < L_{h(n)}$ , where L' is the pore boundary and  $L_{h(n)}$  is the steric boundary. In contrast, ion flow will be like fluids having almost no salt rejection when  $L_{h(n)} < L'$ . Figure 3.14 shows that this transition of ions passing and not passing likes fluids happens in between the region for pore diameters of 1.8223 nm and 2.1708 nm. Therefore, from this perspective concerning the initial parameters defined., the steric boundary region

 $(L_{h(n)})$  is expected to remain in between the region 1.8223 nm<  $L_{h(n)}$ <2.1708 nm. From the data fitting in Figure 3.14, we show that

Salt Rejection= 
$$C L' + 84.851....(13)$$

For this study, C is  $-37.552 \text{ nm}^{-1}$  by a linear least square method. However, figuring out this steric boundary region depending on the salt rejection is not general as the pore diameter (L') is varied depending on the initially defined flow parameters. Here we analyzed the salt rejection with the assistance of Sampson flow model. From the Sampson flow model,

$$L' = \left(\frac{3q\mu}{\Delta P}\right)^{\frac{1}{3}}....(14)$$

where,  $\Delta P$ , q,  $\mu$  are the pressure difference, flowrate, and viscosity of saltwater respectively(79).

Equating Equation (13) and (14) gives:

Salt Rejection = 
$$C \left(\frac{3q\mu}{\Delta P}\right)^{\frac{1}{3}} + 84.851....(15)$$

From Equations (14) and (15), the salt rejection is not only depending on the pore diameter but also depend on the pressure difference, viscosity, and flowrate used for a specific pore diameter in that saltwater system. Increasing the pressure difference probably will reduce the density peak drop region for water inside the nanopore and by this ion's translocation space inside the pore can be increased. This is the likely reason of why salt rejection is reduced for a specific pore boundary when the pressure is increased(13).



Figure 3.14 : Salt rejection with pore boundary (L') representing the steric effect region of salt ions.

Fluid flow rate and viscosity can play a vital role in increasing the salt rejection rate for a specific pore boundary. When the flow rate is high, fluid transport can be high compared to ion transport. This can create a higher flow path gap between water and ions regarding the pore boundary and by that ultimately the predicted salt rejection could be high in that case. Besides this, more viscous saltwater results in a higher repulsion region for water inside the nanopore. This can actually provide a shorter ion translocation space inside the nanopore. Hence, the salt rejection could be comparatively high for a specific pore diameter with more viscous salt water. As salt rejection is dependent on the parameters discussed above, the steric boundary region of ion transportation through the nanoporous membrane also can be shifted based on these parameters

This steric boundary region effectively eliminates misperceptions when selecting the pore diameters for water desalination using a nanoporous membrane. Nguyen et al. already

used a larger pore diameter than previous studies of 0.99 nm and acquired a 100% salt rejection(15). The steric boundary limit and the salt rejection dependence on pressure is the reason why they obtained 100% salt rejection with a larger pore boundary in that work though this was not mentioned. It should be noted that Nguyen et al. used a very low-pressure difference (35.02 MPa) for that specific pore boundary which helped to obtain the highest salt rejection. This can be understood in light of our discussion above on how salt rejection is crucially dependent on pressure for a specific pore boundary. It can be assumed using a realistic pressure difference (<10 MPa) at the RO process, that water desalination for a larger pore boundaries than 0.99 nm can be achieved successfully by utilizing the steric boundary concept from this study. It is also already proved that water is also permeable through the nanopore at low pressures as in the RO process(80). Therefore, applying a low-pressure difference with a large nanopore diameter that is still less than our predicted steric boundary region can be investigated in future works to achieve more efficient desalinated water through an NPG membrane.

# 3.7 Relating atomic boundary positon of pore diameter with ion transportation

When the pore diameter is smaller than the hydration shell of the ion, the hydration shell would not be fit inside the pore. However, to fit inside a smaller diameter pore, some water molecules can be removed from the hydration shell at an energy cost(10,27). This phenomenon can change the initial total hydration diameter of the ion. We denoted the approached hydration boundary as the closest hydration layer to the pore edge, which needs to be dehydrated so that the ion can be transported through the pore. Therefore, the change of the approached hydration diameter will depend on the pore diameter. For example, to fit and transport through a diameter of 0.56 nm, chlorine's first hydration layer (0.76 nm) needs to be dehydrated. However, while transporting through the pore diameter of 0.99 nm, up to chlorine's second hydration layer needs to be dehydrated and the first hydration layer can be present during transportation. In that case, the approached hydration diameter changed to the length of the second hydration shell (1.24 nm). In figure 3.15, due to the dehydration in ion transportation, this tendency of changing the approached hydration boundary with the pore diameter has been depicted. To be specific on our goal of atomic boundary position of pore diameter effect on ion transportation and for maintaining the brevity, we have shown our analysis only for the chlorine since the consideration is the same for the others ion too(27). It is observed that the approached hydration boundary is appeared to be longer with the pore diameter increment. However, in that case, the attraction between the ion and the water molecules on that specific layer has been decreased according to the coulombs law. Therefore, the energy cost to remove the water molecules from the longer hydration layer should be less compared to the hydration layer nearest to the ion.



Figure 3.15: Approached hydrated boundary relation with the pore diameter

To observe our thoughts, we used the model proposed by Zwolak et.al. where the energy barrier to dehydrate the water molecules from the hydrated layer is presented as a function of pore radius(27). That model was assumed to be valid for an ion concentration less than 1M and with the absence of surface within the pore, which are also mutual with our system. In the model, the internal energy contained in a partially intact hydration layer as  $U_i$ =  $f_i U_i^o$ ; where  $f_i$  denotes for the fraction of the hydration layer present inside the pore area. Here,  $f_i$  represents for a specific pore radius  $R_p$  by:

$$f_i = 1 - \sqrt{1 - (\frac{R_p}{R_i})^2}$$
 .....(17)

 $U_i^o$  is the energy difference between the hydration layer and water in the bulk. Here,



**Figure 3.16**: Energy barrier for chlorine ion with pore diameter by applying the atomic boundary position

Where K represents the dielectric constant of water and  $R_i^{o/I}$  denotes the presenting the hydrated layers for outer and inner of the pore area. After that, the internal energy barrier as a function of pore radius denoted by

From this model and figure 3.16, it is evident that our initial thought about the decrement of the energy cost for dehydration with the pore boundary increment is valid. However, to see the impact of different atomic boundary positions on ion transportation, we have applied the atomic boundary position of pore diameter L, L'and L'' here. Interestingly, when the pore diameter was below 1 nm, the energy barrier of ion for a pore diameter has deviated largely for the different atomic boundary positions of pore diameter. However, a vice versa situation happens when the pore diameter. In fact, it almost matches for L, L'and L'' when the pore diameter becomes 1.988 nm. Due to the scale effect, the energy barrier difference



Figure 3.17: Critical Pressure of chlorine ion to transport through a nanopore.

becomes more apparent for different atomic boundary position of pore diameter when the pore diameter becomes less than 2 nm (71,81)

The energy barrier related with the critical pressure that was developed in the system to break hydration shells. For a specific pore diameter, this critical pressure is varying since different approached hydration shell need to break for different type of pore diameter. However, for a pore diameter of 0.568 nm this critical pressure will be the highest as that critical pressure will tend to break the strongly attracted first hydration shell.

To see that impact of the deviation of the energy barrier of an ion on ion transportation, we calculated the critical pressure (figure 3.17) for the chlorine ion in the feed side from the MD simulation. The critical pressure was found at 68.67 MPa, 8.5 MPa, 2.50 MPa, 2.37 MPa for the pore diameter of 0.568 nm, 0.99nm, 1.42 nm, 1.94 nm, respectively, considering the kinetic and virial stress of chlorine to the flow axis. The input energy of chlorine ion was

averaged for each pore diameter up to the time when there were at least more than 160 water molecules transported. To predict the chlorine ion transportation theoretically for different atomic boundary positions of pore diameter, we proposed the ion transportation prediction as to the ratio of the total chlorine ions input energy and the total energy barrier of chlorine ion as a function of pore radius.

Therefore, the ion rejection (I) for different atomic boundaries becomes:

However, to maintain the comparison consistency for our theoretical and MD prediction, the chlorine ion rejection from MD was also calculated for the time when more than 160 water molecules transportation through the Nanoporous graphene membrane for all the pore diameter cases. This reference time is selected to get a considerable computational time and have a proper view of the ion rejection from a small to a big pore diameter. In figure 3.17, apparently, it has been observed that the ion rejection prediction could be shifted for the different atomic pore boundary positions. Due to the atomic boundary position towards the pore center, the resistance to the ion transportation was inclined, which ultimately affected the ion rejection. The difference between the MD predicted ion rejection and our theoretically predicted ion rejection is more visible when the pore diameters become less than 1 nm. The possible explanation is linked with the van der walls and columbic interaction between the ion and the membrane. When the pore is very narrow with boundary conditions, the ion faces exponentially increased high repulsion from the graphene membrane. For that, either the ion needs to move away to the feed side or the permeate side, depending on the input energy.



**Figure 3.18:** Chlorine ion rejection prediction for different atomic boundary position of pore diameter and from MD simulation.

If the input energy is high enough, then the ion is pushed through the Nanopore and goes to permeate side. Considering this hypothesis, it is observed that when the pore diameter becomes 0.568 nm, to transport through this pore, all the hydration shells, including the first hydration shells, need to be dehydrated with higher input energy. It was noticed that for the 0.568 nm pore, the input energy is far high (8 times higher) than the closest pore diameter 0.99 nm case. Therefore, if at least one chlorine ion was transported through this pore diameter, it was detached from the entire hydration layer with this input energy. A similar phenomenon could be started with all the chlorine ions of the system, and they started to transport more rapidly only with their bare ion diameter (0.34nm) along with a partial hydration shell (82). As a consequence of transport with a much lower diameter than the size, including the first hydration shell, the ion rejection for the 0.568 nm pore goes against the increasing trend of ion rejection with the pore diameter decrement.

One important calculation point that need to be addressed is the ion passing calculation through a nanopore. The ion passage has been calculated in this type of system for a specific period time. When the movement of the specular reflection wall was started, the volume has been reduced in the front reservoir. For that reason, the pressure will be increased and that increased pressure will tend to break the hydration shell. Moreover, if the volume is reduced but the density tries to be constant (i.g. very small pore diameter), then the overall pressure become too high. That high pressure acted even up to the first hydration shell and could break that. Therefore, to get a reasonable ion separation percentage, we need to choose an appropriate time frame which require a minimum amount of the pressure allowing with a considerable amount of water molecules.

The most noticeable point from figure 3.17 is that the MD prediction ion rejection value is most closely matched for the atomic boundary position of L' for the pore diameter case 1.42 nm and 1.98 nm. The center to center atomic boundary position (L) predicts low resistance for ion transportation, whereas L'' over predicts the higher resistance for ion transportation. Therefore, for these two atomic boundary positions, the ion rejection could be less approximate than the atomic boundary position of L'. The effective pore diameter for ion rejection is that which forces the hydration layer to be partially broken off (27). According to this thought and the observed result from the pore diameter of 1.42 nm and 1.98 nm, L' might be the approximate atomic boundary position for ion rejection since it is also denoted the dense core area of water molecules inside the Nanopore. However, when the pore diameter becomes less than 1nm denoting the atomic boundary position is too high there to precise an approximate boundary position of pore diameter with the comparison of theoretical and MD magnitude.
However, the similarity of the theoretical and MD predicted ion rejection when the pore diameter is increased to 2nm indicates the atomic boundary position effect, which was previously addressed for a simple fluid flow(71). As to the water flow rate deviation from the MD predicted result, the ion rejection also can be significantly changed due to the atomic boundary position effect of pore diameter when the scale becomes less than 2nm. In synopsis, since the van der Waals force and the Columbic interaction of the molecules becomes significantly apparent at the molecular level; a small change in the atomic boundary position could lead to a greater change in the resistance of water and ion transportation. That shift in the resistance of Nanopore diameter due to the atomic boundary position could significantly impact the flow phenomenon of ions along with water transportation.

#### **IV.** Conclusion

In recapitulation, this study has emphasized the impact of the pore diameter's atomic boundary position on ion transportation by using a pressure-driven flow through a nanoporous graphene membrane. The effect of the atomic boundary position of pore diameter is delicately related to the ion's hydrations layers. Moreover, the hydration layer is the outcome of the steric effect of ions, which also modifies the water velocity and flow rate from their particular activity.

This impact of the steric effect on water flow properties has been visualized by alternating the LJ and LJ+ Columbic force interaction between the water and ion. Apart from that, according to the Sampson flow model, the velocity and flow rate are lower than MD predicted result for both steric and non-steric-affected cases. In the time of water and ion transportation, the hypothesis of the approached hydration boundary connection with the pore diameter has been defined. Employing this assumption, the energy barrier of the ion transport as a function of the pore diameter has been illustrated for each of the atomic boundary positions of pore diameter. Consequently, the theoretical ion transport as a function of the pore diameter.

The theoretical ion rejection is compared with the MD predicted ion rejection to observe the importance of the pore diameter's atomic boundary position on ion transportation. It is noticed that the theoretical ion rejection significantly deviated for the different atomic boundary positions of pore diameter when the pore diameter is less than 1 nm. However, at more than 1nm of pore diameter, the theoretical ion rejection is identical to the MD predicted result for the atomic boundary position stated to the 2% water density drop inside the nanopore. Moreover, it is also observed that if the entire hydration layer is broken, the ion rejection is significantly reduced by going against the inversely proportional relationship with pore diameter.

However, this hydration layer disruption is directly related with the critical pressure that is responsible to break a specific hydration shell. The critical pressure created in the front reservoir is

depended with the pore diameter. Since if the pore diameter is small, then the front reservoir pressure will be high and it will tend to reach the critical pressure where the approached hydration layer will be broken to pass an ion through a the nanopores graphene membrane. Depending on this critical pressure, the theoretical ion rejection has been illustrated in this work.

In future outcomes, we would like to see the theoretical ion rejection prediction with lower input energy which is not assessed in this work regarding the computational time frame. Discussing proper atomic boundary position for ion transportation and separation through our investigations will have severe implications for the desalination experiments and the reverse osmosis plants for water purification. Also, the thermodynamic and the mechanical property of the graphene membrane has not been considered in this research due avoid the complication and the computational cost. In the upcoming work, the thermodynamic and mechanical property of the graphene membrane need to be considered to predict the ion transportation more accurately for the implication in practical field.

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#### **Research Interest**

Research michest	
	Micro fluids- Nano fluids
	Nanoscale Flow Modelling and Interfacial Phenomenon
	• Ion transport and separation through porous membrane
	• Electric double layer effects in nanoscale flow
	• Heat transfer in nanoscale
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## ATOMIC BOUNDARY POSITION AND STERIC EFFECTS ON ION TRANSPORT AND SEPARATION THROUGH NANO POROUS GRAPHENE MEMBRANE

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Morshed Mahmud

## ATOMIC BOUNDARY POSITION AND STERIC EFFECTS ON ION TRANSPORT AND SEPARATION THROUGH NANO POROUS GRAPHENE MEMBRANE

Academic Advisor: Dr. BoHung Kim

A Master's Thesis

Submitted to

the Graduate School of the University of Ulsan In partial fulfillment of the requirements for the degree of Master of Science

> by Morshed Mahmud

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May 2022

## ATOMIC BOUNDARY POSITION AND STERIC EFFECTS ON ION TRANSPORT AND SEPARATION THROUGH NANO POROUS GRAPHENE MEMBRANE

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#### Acknowledgement

First of all, I would like to convey my sincere gratitude to my advisor Dr. BoHung Kim of the School of Mechanical and Automotive Engineering at the University of Ulsan, for his supervision, advice, continuous support, and constant encouragement throughout my M.Sc. study and academic life. His patience, motivation, immense knowledge, and continuous guidance supported me to build the foundation of my research skills. Apart from research, his moral and ethical guidelines helped me grow up as a person in practical life.

I am very much thankful to the University of Ulsan for giving me an outstanding research environment and financial support. I am also grateful Dr. Yoon Ho Lee and Dr. Dong Kim for being the honorable judge of my thesis defense. This university allowed me to conduct several practical courses with excellent instructors that will enable me to think and work properly for the rest of my life. My special thanks go to National Research Foundation (NRF) Korea for its contribution and financial support during my study.

I would also like to express my gratitude to my lab mate, MD. Masuduzzaman, Kazi Ehsanul Karim, Jaber Al Hossain in Micro-Nano Scale Thermal Fluid Laboratory for their friendship and immense support in my master's life. Besides, I am also really grateful to my former Korean lab mate, Kim Sunghwan and Yeyoungmeyong. They assisted in many cases that were priceless concerning their effort.

I am ever grateful to my parents for raising me and helping me achieve all that I have in my life. They gave me endless support from my home country during my whole academic life. I also express my gratefulness for my brothers in Ulsan Atish Bhattacharjee, Shovon Talukder, Nasim Al Islam, Md. Junayed Hasan, and special thanks to my roommate Md. Jashim Uddin Shehab. Last but not least, I would like to express gratitude to my friend Takia Maliha and Md. Rafi-Ur Rahman for their mental support in my abroad life.

#### Abstract

Atomic boundary position and steric effects on ion transport and separation through Nano porous graphene membrane

(May 2022)

#### Morshed Mahmud

The electrostatic attraction between ion and water is the primary concern of changing the ion's bare diameter. The modification in ion shape is known as the steric effect that plays a crucial role in the desalination approaches using nanoporous graphene membranes. Utilizing molecular dynamics (MD), a pressure-driven flow is generated using specular reflection wall movement at a constant speed to analyze the saltwater transport through a nanoporous graphene membrane. This study signifies pore diameter's atomic boundary position impact on single-ion transportation and the steric influence of ions on the water mass flow rate and velocity profile. Due to the Columbic interaction between ions and water, ions hinder the water molecules from their regular velocity, which also lessens the flow rate of water molecules. For the different atomic boundary positions of pore diameter, we propose the ratio of the input energy of the total ion and the energy barrier of ion dehydration as the theoretical ion transportation. Interestingly, a significant deviation for different atomic boundary positions is observed for ion rejection at less than 1 nm pore diameter. The ion rejection drops considerably if all hydration layers break off due to high critical pressure. However, at more than 1nm pore diameter, the ion rejection closely matches the atomic boundary position specified to the 2% water density drop inside the nanopore.

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#### I. Introduction

The expanding human populace combined with exploitation of water assets for household purposes, industry, and irrigation has come about in a deficiency of new water supply in numerous parts of the world. It is anticipated that 40–50% development in human populace over the next 50 a long time, coupled with industrialization and urbanization, will result in an expanding request on the accessible water resources(1).Since only 3% of the world's water is fresh water, it is becoming difficult to meet the water demands of the expanding population of the world(2,3). However, ocean water can meet this demand if it is desalinated. In this regard, it is necessary to assess the significance of salt water desalination as a permanent water supply option (4).In the salt water desalination, the most effective method is the reverse osmosis system. Reverse osmosis (RO) is the process in which contaminating particles such as ions and minerals are removed from water by a pressure driven flow. The water molecules are squeezed through the membrane, but the other substances stay behind.



Semi permeable membrane

#### Figure 1.1: Reverse osmosis concept

The birth of pressure driven membrane desalination took put about 100 a long time prior. Early improvements in this technology stay covered in a few riddle, particularly with regard to application of the osmotic wonder to desalination(5). The challenges in the desalination industry incorporate nourish water characterization, prepare advancement, materials improvement, renewable energy source, rigid water standard and brine administration. Considering the worldwide normal water utilization per capita of  $1243 \text{m}^3 \text{ year}^{-1}$  (5% for household utilize, 85% for agrarian water system, and 10% for mechanical utilize), this plant can supply new water to less than 100,000 individuals. Thus mega-sized desalination plants must be created on the off chance that we are to supply unused clean water supplies to billions of individuals. In this setting, the greatest challenge would be making RO desalination reasonable for poorer nations(6).Despite the fact that the reverse osmosis (RO) system is the most common desalination process due to low energy consumption, it needs to be advanced in terms of cost and efficiency(7–9).

Advances in nanotechnology opened up a new door for water desalination. Whereas nanoscale wonders have been distinguished and examined for a few decades, critical advance within the capacity to control matter at the nanometer length scale happened within the to begin with decade of the 21st century. These advancements have opened the plausibility of making gadgets and frameworks utilizing nanostructured materials counting carbon nanotubes, nanowires, graphene, quantum dabs, super lattices, and Nano shells, among other materials. In expansion to the center on applications such as vitality change, medicate conveyance, hardware, computing, auxiliary materials, photonics, bio imaging, and bio sensing, researchers have as of late begun examining nanostructured materials within the setting of water desalination(1). When the Nano pore diameter is less than the size of the hydrated diameter of ion (the entire boundary of the hydrated ion along with the hydration sphere around it), that ion can be excluded from the transportation by this size exclusion mechanism(10). Ion's dehydration barriers along with this size exclusion mechanism can lead to effective water RO layers were at first created utilizing cellulose desalination(11-13). and acetate

commercialized within the 1960s, but advertised moderately Ion fluxes and were subject to natural debasement.

Current state-of- the art RO layers are deviated polyamide and thin film composite layers created polymerization. These layers comprise of a various leveled structure where a lean (100–1000 nm) polyamide particular layer is created on a porous polysulfide layer that gives mechanical back and minimizes weight drop (1). In fact, choosing a membrane material for the Nano pore is a delicate task because the membrane material needs to withstand against the pressure that will create by the flow. Also, the membrane surface required to be impermeable except the Nano pore area. Among all the candidate materials, graphene has these unique characteristics. Graphene blocks all kinds of molecules as it is composed of sp<sup>2</sup> hybridized carbon atoms with another in a 2D honeycomb lattice with a high electron density in its aromatic rings. The high carbon-carbon bond energy and intrinsic mechanical strength make graphene the supreme impermeable membrane(14). Since the lattice constant of graphene is smaller than the molecular diameter of water, graphene is impermeable to ionic aqueous solution(15). Having the  $sp^2$  hybridized carbon atoms structured like a hexagonal lattice structure, this single atom thickness (0.34nm) material is considered a critical material due to its remarkable mechanical strength and robustness(Fig 1.2)(16,17). Due to this fact, specifically engineered graphene sheets have become the most promising new material for polymer electrolyte membrane fuel cells (PEMFC) applications(18). Besides this, graphene-based fuel cell catalysts are also very efficient for both anode and cathode fabrication (19).

Given the above facts, creating a Nano pore on a graphene membrane can effectively retain the increased size of hydrated ions due to the steric effect while the water molecules can pass through the Nano pore successfully. Graphene membrane are still durable to face a pressure-driven flow after crafting the pore. In fact, the Nano porous graphene (NPG) membrane can withstand pressures exceeding 57 MPa when having a Nano pore smaller than 1  $\mu$ m(20). These Nano pore can be functionalized and the Nano porous membrane can be used in multilayers, but the water permeability depends on the pore spacing in that case(21). Hypothetical expectations propose that artificial pores in graphene can increment its penetrability and permeation-selectivity (14). For instance, a nitrogen functionalized pore in graphene can open up an effective gap of 3A° with a selectivity of 10<sup>8</sup> while the hydrogen terminated vacancy can space up to 2.5 A° with a selectivity of 10. As like that, periodic pores on graphene can yield different barrier heights for transmissions of various gas as well.



**Figure 1.2:** Graphene lattice structure: sp2 hybridized carbon atoms arranged in a 2D honeycomb lattice (14)

The low energy consumption effect of Nano porous graphene membranes allows the flow of the desired molecules while blocking the contaminated particles. Hence, sea water ions can be effectively rejected by using this single layer or multi-layer NPG membranes while purifying a significant amount of water(7). Actually, the NPG membranes are already used as effective filters for desalination in a lot of molecular dynamics studies in recent days focusing on saltwater transport driven by pressure. However, the desalination efficiency of the NPG membrane is highly dependent on selective pore size, selective pressure, and pore hydrophobicity(22).

A lot of conflicts are going on in selecting the pore diameter for desalination in recent studies. For example, Cohen-Tanugi et al. mentioned that a maximum pore diameter of 5.5 Å was necessary to prevent salt ion transport in their MD model of reverse osmosis water desalination process using NPG membrane while Konatham et al. reported that a maximum pore diameter of 7.5 Å was needed to retard the salt ions(23,24). Later on, Nguyen et al. achieved 100% salt rejection with a 9.90 Å pore diameter using a 35.02 MPa pressure drop (15). This ongoing discussion on how to select the Nano pore diameter remains since the definition of the Nano pore diameter (visually the pore width) is still a debatable issue. The pore radius are defined in diverse ways on the nanoscale for different reasons(25). The deep impact of the hydrated ion's boundary can have a great influence on determining the pore diameter for effective water desalination. In fact, the hydration layer beyond the first hydration layer is also responsible for retaining the ion transport through the Nano pore. The internal energy barrier for ion transport depends on the pore radius which can be effected on the proper boundary position of Nano pore. The effective pore radius was also defined by the width that forces the hydration layer to be partially broken for ion transportation(26,27)By investigating the hydration properties, it is possible to evaluate the hydrated solute steric hindrance and so predict an approximate pore size that may work properly for effective water filtration(28). Thus, it is necessary to intensely understand the pore boundary position relation with the hydration layers for predicting the saltwater transportation.

The most natural way to halt a particle from passing through a limit pore is to form the pore smaller than the size of the particle; that's, to form utilize of estimate prevention [fig 1.3 (a)]. Through the dehydration barriers Ion exclusion can be explained more vividly. In the salt water solution, ions attract a shell of nearby water molecules due to the long range columbic

interaction between charge on the ion and the water dipole. This hydration sphere broadens the size of the ion [fig.1.3 (b)]. When the pore is smaller than the size of the hydration sphere, the hydration sphere will not go through the pore. To transport through the pore, water molecules need to adjust their geometry around the ion, allowing it to squeeze into slightly smaller spaces at a small energy cost(10).

In figure 1.3, (a) Size exclusion, in which the ion is larger function of the position of the ion within car than the size of the pore, (b) dehydration barriers created by the necessity to remove water bon nanotubes with different diameters. In the form an ion to enter the pore, and (c) electrostatic repulsion between the ion and the pore. The ion is shown in orange in each case (29). Ion mobility in the pore is smaller than the bulk ion mobility because they have a layered liquid structure in the pore axial direction (30). When an ion hits the pore and wants to leave the bulk, it requires sufficient energy to overcome the energetic penalty. The energetic penalties progressions are subjected to the ion hydration, ion charge, pore chemical characteristics, pore size, and pore geometry(31–33). Deformation of the reactive zone can happen when the sterically demanding group is close to the reactive center (34). Ions show a gel-like property in aqueous form and the shape of this gel can change under pressure. Moreover, the strength of the ion's hydration depends on the ionic concentration and other environmental factors like ionic strength, pH, and temperature(35).



Figure 1.3: Physical mechanisms of ion rejection (36).

Due to these factors when ion's the hydration strength became weak, the ion partially dehydrated. These partially or fully dehydrated ions are transported through the Nano pore. This dehydration is the primary contribution of the ion energy barrier for transportation in narrow pores.(36). The water molecules around small cations remain practically at a fixed distance, forming a shell where bulk water molecules continuously replace individual water molecules in nanoseconds(37,38). Because of the electric field of the ion, the solvent dipoles in the first hydration layer are highly structured and the diploes around it do not act linearly (39,40). For this reason, transporting the cation for a pore radius of 1.2nm, the first layer of the hydration layer can be intact whereas the second layer can be partially dehydrated due to the pore wall(27). When the ion is at the pore center, the hydration sphere around the ion will be dehydrated depending on the pore radius(41). Therefore, for predicting ion transportation, it is necessary to assess the energy barrier for dehydration relation with the atomic boundary position of pore diameter more extensively.

There are lot of tools and numerical simulation method considering the system scale as like in figure 1.4.



Figure 1.4: Approximate length and time scales for the commonly used computational methods(42).

For example, from Nano scale to meso-scale there has been several scale like firstprinciples Boltzmann transport equations (BTE), molecular dynamics (MD) simulations, nonequilibrium Green's function (NEGF), numerical solution of phonon BTE, and hybrid methods. First-principles BTE strategies can be used for nonparametric expectations by exploring BTE using the interatomic drive constants (IFCs) of the Density Functional Theory (DFT). The computational acquisition of first-principles BTEs is so expensive that framework estimates are limited to hundreds of particles, but the driving force of today's high-execution computing makes the application of first-principles BTEs significant. MD simulation is based on Integral of Newton's equation for a population of atoms, usually described atomically using empirical potential interaction. Despite the classic nature of MD simulation, it Effective for treating nanostructures, interfaces and other flow phenomenon. Among all the methods we choose MD simulation since it is much less computationally intensive and also it can calculate the evolution of the system in time.

This paper mainly aims to investigate the atomic boundary position of pore diameter impact on water and ion transportation prediction with molecular dynamics (MD) study. The molecular dynamics is The steric effect of ion on water transportation has been studied in this study. The main objective of see the influence of the atomic boundary position of pore diameter on chlorine ion transportation has been analyzed with a theoretical ion rejection proposed method with the MD predicted ion rejection.

#### **II.** Theoretical background

#### 2.1 Molecular Dynamics Simulation

Due to the vast expansion of nanotechnology in the recent scientific age, nanofabrication is a common to proceed for the nanotech. For that reason, many nanostructure fabrication processes have been developed. Especially, chemical vapor deposition (CVD) is one of promising fabrication process, CVD process can be used to make carbon nanotubes (CNT) (43–45). However, still lot of difficulty has been faced to experimentally model in Nano scale system such as desalination by Nano pore or ion separation by nonporous graphene membrane due to expensive cost or harness of making complex structures.

To overcome these boundaries, molecular dynamics (MD) has been emerged as alternative method to experiment for Nano scale research following rapid development of computer, Molecular dynamics is computational method to simulate of a set of molecules with interact. MD is theoretically based on statistical thermodynamics. In MD simulation, velocity and positions were calculated by numerically solving the Newton's equation of motion and by using intermolecular potentials, thus MD can provide all trajectories of atoms, Also, MD simulations with statistical concepts, such as ensembles, local thermodynamic equilibrium, etc. We can obtain properties of materials. In this regard, many researchers conducted MD simulations to study on fluidics or to investigate thermal, mechanical properties. And MD has been gained trustworthiness from many research papers.

In fact, for ion separation and transportation, many MD research papers have been published in recent days. The ion rejection and the mechanism behind it were actively studied by the molecular dynamics simulation and statistical thermodynamics (15,23,24).

#### 2.2 Maxwell – Boltzmann Distribution

Maxwell –Boltzmann distribution is the most crucial part to establish statistical thermodynamics concepts in molecular dynamics. Maxwell –Boltzmann distribution is basically based on the kinetic energy theory of molecules. Thus, the MB distribution is also maintaining the assumption that follows the kinetic theory. The assumptions are:

- Number of gas is huge and the particle size is much smaller than the average distance between molecules 2) with the random movement each molecule follows Newton's Law
   same type molecules have same mass. 4) The molecules collide with walls of container and among themselves. Since all the collisions are perfectly elastic, energy is conserved.
  - 5) Without collisions, the interactions among molecules are negligible.

Maxwell-Boltzmann distribution defines the velocity in idealized gases where the particles move randomly inside a stationary system in state of thermodynamic equilibrium.

Maxwell-Boltzmann distribution is given by:

$$f(v) = \sqrt{\left(\frac{M}{2\pi k_B T}\right)^3 4\pi v^2 e^{-\frac{mv^2}{2k_B T}}}.$$
(1)

Where m = the particle mass,  $k_B$  = Boltzmann constant T = absolute temperature



Figure 2.1: The speed variation of the Maxwell Boltzmann velocity Distribution

From figure 2.1, it can be seen there are three meaningful speeds: peak speed  $(v_p)$ , mean speed (v) and root mean square speed  $(v_{rms})$ . Each speed can be found as follow:

$$(v) = \int_{0}^{\infty} vf(v) dv = \sqrt{\frac{8k_{B}T}{\pi m}}....(2)$$

$$v_{rms} = \sqrt{\left(\int_{0}^{\infty} v^{2}f(v) dv\right)} = \sqrt{\frac{3k_{B}T}{m}}...(3)$$

The relationship between the kinetic energy and thermal energy can be established from Maxwell Boltzmann relationship:

$$E_k = \frac{1}{2}mv^2 = \frac{3}{2}K_BT.$$
 (4)

The relationship indicates the average kinetic energy of molecules is proportional to absolute temperature. The shape of Boltzmann distribution depends on temperature and molecular mas. When the temperature is inclined with some molecular mass, the Boltzmann distribution becomes more flat and the average speed increases. On the other hand, when molecular mass is upwards with equal temperature, the Boltzmann distribution become steeper and average speed is decreased.

#### 2.3 Local Thermodynamic Equilibrium

The relationship between kinetic energy and thermal energy as equation (4) is only satisfied in equilibrium system. In several cases, we need local temperature to obtain detailed temperature profile in materials to calculate thermodynamic properties. To establish local temperature, we need concept of local thermodynamic equilibrium. However, Local thermodynamic equilibrium is valid only when the velocities of molecules are distributed following the Maxwell-Boltzmann distribution.

Local equilibrium thermodynamics is concerned with the time courses and rates of advance of irreversible forms in frameworks that are easily spatially inhomogeneous. It concedes time as a crucial amount, but as it were in a limited way. Instead of considering timeinvariant streams as long-term normal rates of cyclic forms, nearby balance thermodynamics considers time-varying streams in frameworks that are portrayed by states of neighborhood thermodynamic balance. Neighborhood balance thermodynamics considers forms that include the time-dependent generation of entropy by dissipative forms, in which active vitality of bulk stream and chemical potential vitality are changed over into inside vitality at time rates that are expressly accounted for. Time-varying bulk streams and particular diffusional streams are considered, but they are required to be subordinate factors, inferred as it were from fabric properties portrayed as it were by inactive plainly visible balance states of little nearby locales(46).
## 2.4 Ergogodic hypothesis

Summing the suitable attributes of the molecules in the volume element over a prolonged time interval is called a time average. Ensemble average, on the other hand, is an instantaneous average of the molecules in a certain volume element. There are an endless number of such systems.MD simulations numerically solve Newton's equation of motion. It indicates that Molecular dynamics calculations are obtained from the collecting of particles trajectories of systems with time. The temporal average of particles in the volume element is used to deal with this result. However, Ensemble average is what we want to obtain out of MD simulation, and ensemble average requires infinitely large number of similar systems. In this way, it is difficult to obtain ensemble normal by MD reenactment since computational taken a toll is restricted. In this way, we need a bridge to interface these two midpoints to get ensemble average. In this respect, ergodic speculation is profoundly imperative concept in MD recreation to handle MD result. Ergodic theory could be a key to associate time normal and ensemble average. Ergodic theory means that the time normal and gathering normal can be identical. Due to ergodic theory, we are able get this ensured for MD simulation and able to calculate bulk property, such as warm conductivity, thickness, and etc. from MD recreation comes about. We are able get time normal from MD recreations easily, and able to get gathering normal from time usual with little computational cost. In any case to realize ergodic theory, we ought to get time averaging over long time enough.

## 2.5 Ensemble

In statistical mechanics, an ensemble is a concept of involving of a large number of virtual copies of system, one of which represents a possible state the system could be in. There are three ensembles widely used in MD simulations: Micro- canonical ensemble (NVE), Canonical Ensemble (NVT), and Isothermal-isobaric ensemble (NPT). The NVE ensemble is a statistical ensemble where number of particles, volume of system, and total energy are each fixed. This ensemble regenerate's isolated system which is called as micro-canonical ensemble. The NVT ensemble is a statistical ensemble where number of particles, volume of system, and temperature are fixed, instead of energy fixing. This ensemble is linked to isothermal system. Thermostat is employed to maintain temperature of system constant which rescales the velocities at each time step. This NVT ensemble is called as canonical ensemble. The NPT ensemble fixes number of particle and maintains temperature and pressure constant. This is achieved by utilizing thermostat for temperature and barostat for pressure. This ensemble is useful to systems that the correct system temperature and pressure is required. This ensemble is called as isothermal-isobaric ensemble.

#### 2.6 Particle Particle Mesh

The number of particles is important factor in MD simulations. The more reliable result can be obtained if more particles are included. For that reason, large size of system is required in MD simulation. However, the computational cost would become more costly. This difficulty is in practical in gas-solid interface system. In fact, gas system needs large volume size comparing to other phase states. To meet this condition, large number of solid atoms need be included. In this cases, periodic boundary condition (PBC) can be on solution to deal with such problem. Periodic boundary condition allows us to run large (infinite) system simulation with a small simulation box containing particles in which we are interest.

In arrange to reassure the consider of bulk framework behavior utilizing Nano scale simulations, intermittent boundary conditions (PBCs) appeared in Figure 2.2 are regularly utilized, whereas the framework arrangement within the simulation box is occasionally imitated in an interminable cross section. In this manner, the simulation box must be space filling and commensurate with a three-dimensional (3D) grid. For case, simulation box can be cubic but not spherical, as the last mentioned isn't space filling. In fact, PBC presents certain finite-size artifacts due to the presumption of a "crystalline" arrange at length scales above the framework measure and the reenactment must be performed for system sizes huge sufficient in order to play down such artifacts. This will be guaranteed by performing recreations at different framework sizes until the properties of intrigued converge with framework estimate(47).



**Figure 2.2** Two-dimensional representation of periodic boundary condition. The middle cell (filled with yellow) represents the simulation box whereas filled circles indicate particles in the simulation box and open circles represent their

periodic picture in other cells. Bold and dashed lines shows movement of two particles near the boundary; as a particle leaves the simulation box, its image enters the box from the opposite end(47)

## 2.7 Interatomic Potential

In this study, we deal with the interface between solid, liquid and ions. Therefore, we need potentials for solid, liquid, solid-ion, liquid-ion and solid-liquid interface. In section 2.7 the Van der Waals interaction is explained first after that the Leonard Jones and Leonard Jones columbic interaction and lastly the AIRBO Potential for graphene membrane.

### 2.7.1 Van der walls

Van der Waals intuitive happens when adjoining particles come near sufficient that their external electron clouds fair scarcely touch. This activity actuates charge variances that result in a nonspecific, non-directional fascination. These intuitive are profoundly separate subordinate, diminishing in extent to the 6th control of the partition. The vitality of each interaction is as it were almost 4 kJ mol–1 (exceptionally frail when compared with the normal motor vitality of a particle in arrangement, which is around 2.5 kJ mol–1) and is critical as it were when numerous intelligent are combined (as in intuitive of complementary surfaces). Beneath ideal circumstances, van der Waals intuitive can accomplish holding energies as tall as 40 kJ mol–1. When two particles get as well near, they emphatically repulse each other. Thus, imperfect fits between connection atoms are enthusiastically exceptionally costly, avoiding affiliation in the event that surface bunches meddled sterically with each other.

# 2.7.2 Lennard Jones Potential

The LJ potential is typically used to simply mimic the interatomic interaction (Van der Waals potential) due to its simple approximation. The Lennard-Jones model has two 'parts'; a

steep repulsive term, and smoother attractive part indicating the London dispersion forces. Other than being an important model in itself, the Lennard-Jones potential frequently forms one of 'building blocks' of many force fields. In fact the 12-6 Lennard-Jones model is not the most reliable representation of the potential energy surface, but rather its use is commonly due to its computational efficiency. The Lennard-Jones Potential is given by the following equation:

$$V_{ij} = 4 \in (\frac{\sigma}{r_{ij}})^{12} - (\frac{\sigma}{r_{ij}})^6 \dots (5)$$

Where, V is the intermolecular potential between the two atoms or molecules. $\epsilon$  is the well depth and a measure of how strongly the two particles attract each other is the distance at which the intermolecular potential between the two particles is zero(Figure 2.3).  $\sigma$  gives a measurement of how close two nonbonding particles can get and is thus referred to as the van der Waals radius. It is equal to one-half of inter nuclear distance between nonbonding particles. 'r' is the distance of separation between both particles (measured from the center of one particle to the center of the other particle).

The Coulomb potential is which decays slowly with the distance between particles. The Coulomb potential presents the electrostatic interaction between point charges. The mathematical expression for the Coulomb potential is:



**Figure 2.3:** Lennard–Jones 12–6 potential and Coulomb potential of the Silicon–Oxygen interaction in the a-quartz(48).

In differentiate to short-range interaction, long-range interaction effects need to be considered for the Coulomb possibilities. Notwithstanding, it isn't attainable to calculate the long-range interactions directly due to unsatisfactory computational costs. Different approximation methods have been proposed to bargain with the long-range potentials. The Ewald summation method may be a broadly adopted approximation method which reorganizes the interactions into a particular form that can be effortlessly assesse.

# 2.7.3 AIRBO Potential

The Airebo pair style computes the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) Potential of (Stuart) for a system of carbon and/or hydrogen atoms. The rebo pair style computes the Reactive Empirical Bond Order (REBO) Potential. REBO is closely related to the initial AIREBO; it is just a subset of the potential energy terms with a few slightly different parameters. The AIRBO Potential has three terms:

$$E = \frac{1}{2} \sum_{i} \sum_{j \neq i} [E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{k \neq i} \sum_{l \neq i,j,k} E_{ki jil}^{TORSION} \dots$$
(7)

### 2.7.4 Mixing Rule

At the time of dealing l with different molecules together (e.g., binary gas system or solid-Liquid interface), the LJ potential parameters between them need to calculate. Mixing rule provide different potential result which could play a different result in the Molecular dynamics. The Lorentz-Berthelot (LB) rule is extensively used in Molecular Dynamics. Lorentz proposed an arithmetic average for the collision diameter, a considering a hard-sphere atom model whereas Berthelot projected a geometric average is used for the well depth  $\varepsilon$ .

$$\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j)....(8)$$
$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}...(9)$$

## 2.8 The Sampson Flow Equation

For a flow a through an infinity thin circular pore with a low Reynolds number, uniform velocity and no-slip condition Sampson derived an analytical solution in 1891 in continuum hydrodynamics form the Stoke's equation.

If the pressure drop across the system is  $\Delta P = Pf - Pp$ . The volumetric flow rate can be expressed as:

$$q = \frac{\Delta P \, a^3}{3\mu}.$$
(10)

Where "q" denotes the volumetric flow rate, "a" denotes the pore radius and  $\mu$  denotes the viscosity of the liquid.

Utilizing the Sampson's stream function solution in cylindrical coordinates, the velocity profile inside the pore can be written as follows:

$$V_{z,r} = \frac{a\Delta P}{2\pi\mu} \sqrt{1 - (\frac{r}{a})^2}$$
....(11)



Figure 2.4: Sampson flow through a circular pore in an infinitely thin plate. The pore radius is denoted by 'a' and flow rate by 'q'(49).

## 2.9 Steric effect & approaching hydration Boundary

The structural configuration of water molecules induces polarity. As a result of their polarity and the strong local electric field around the ion, water molecules arranged themselves around the ions to form hydration layers(26). In saltwater, positively charged Na<sup>+</sup> attracts the negatively charged oxygen atoms, while Cl<sup>-</sup> attracts the positively charged hydrogen atoms of water molecules. The size of the ionic diameter is increased due to this hydration sphere (sum of the entire hydration layer) which is known as the steric effect of ions in an aqueous solution.

Among all the ion transport and sepration mechanism, the steric effect have been choosen because it is related with the different hydration shell dehydration. So with choosing this mechanism for our research will allow us to study with different pore diamter and the phenomenon of ion transport with that different pore diameter. Therefore, Steric effect more specifically size exclusion method has been choosen for this research.



- $\frac{L_{h1}}{2}$  =Distance between ion center & primary(first) hydration layer
- $\frac{L_{h2}}{2}$  = Distance between ion center & secondary hydration layer

 $\frac{L_{h(n)}}{2}$  = Distance between ion center & 'N' number of secondary hydration layer (total hydration sphere radius due to steric effect)



**Figure 2.5:** Typical illustration of the hydration layer of ion due to steric attraction for Na+ and Cl- ion (b) Approaching hydration boundary concept with different pore diameter.

Figure 2.5 illustrates of the hydration sphere in saltwater for Na<sup>+</sup> and Cl<sup>-</sup>. The first hydration layer of ions due to the strong attraction is known as the primary hydration layer. The second shell up to an 'N' number of hydration layers is known as the secondary hydration layer(35). Here, the distance from the ion center to the primary hydration boundary is defined as  $\frac{L_{h1}}{2}$ , whereas  $L_{h1}$  is the diameter for the first hydration layer. Similarly as like that, for the second hydration layer,  $L_{h2}$  is the diameter for the secondary hydration layer. In this way, for an 'N' number of secondary hydration layers, the boundary is denoted as  $\frac{L_{h(n)}}{2}$  from the ion center. In figure 2.6, we denoted the nearest hydration layer outside the pore diameter as approached hydrated diameter needs to be bigger than the pore diameter. Hence, when the pore diameter is increased, the hydration diameters that approach the pore edges membrane need to be uplifted to reject the ion transportation.

## 2.10 Computational Details

In Figure 2.6(a), the simulation domain has saltwater on the left side (feed side) and pure water on the right side (permeate side). The volumes of both of these regions are kept static using the specular reflection wall as represented in Figure 2.6(c). In the beginning, two of the specular reflection boundaries were made rigid at Z= -4.4925 nm and Z=4.4925 nm, while the x and y directions in the simulation domain were periodic with lengths of 3.192 nm and 2.952 nm. The graphene membrane was placed at the center at 0.0nm in the z-direction, and a circular pore of 0.99 nm diameter was generated by removing the carbon atoms, as shown in Figure 2.6(b).



**Figure 2.6:** (a)Schematics of the simulation domain (b) Denoting the initially considered diameter L of graphene Nanopores (c) physical description of the specular reflection wall.

Initially, this pore diameter L was considered from the atomic center to the center of carbon atoms inside the pore. The typical wall works like a piston to incite pressure-driven flow and may interrupt the bulk pressure in the feed and permeate regions in the atomic level framework because of the van der Walls interaction between the fluid and piston(50-52). Nonetheless, the specular reflection wall with genuinely forthright and computationally compelling strategies settles the issue(15,52). Thus, to avoid imprecise pressure drop across the simulation domain, a specular reflection wall is chosen instead of using a piston. The extended simple point charge (SPC/E) model was picked for water molecules due to its simplicity and efficient computational cost (53). Besides, it can also be depicted as an active rigid pair potential, including Lennard-Jones (LJ) and Columbic terms(54). The three atoms of water molecules have three interaction spots while they are allocated a point charge to induce the long-range Columbic interactions. Moreover, oxygen atoms also show a Lennard Jones (LJ) potential to model the van der Waals (VDW) forces. As per the SPC/E model, oxygen and hydrogen atoms are allotted partial charges of  $q_0=0.-8476e$  and  $q_H=0.4328e$ . Meanwhile, the H-O-H angle of 109.47° and O-H bond length of 0.1nm were kept constant using the SHAKE algorithm.(55)

To measure the interatomic interaction of oxygen atoms of water molecules, salt ions, and carbon atoms in the graphene membrane, a Truncated Lennard Jones (LJ) (12-6) potential was used as follows equation 5; where,  $\varepsilon$  is the potential well depth,  $\sigma$  is the finite molecular distance at which point the interatomic potential is zero,  $r_{ij}$  is the intermolecular distance and lastly  $r_c$  is the cutoff distance. The intermolecular forces are curtailed at a distance of  $r_c = 1.0$ nm in this work. The AIREBO potential was applied to model the planar interatomic interactions between carbon atoms in the graphene membrane(56). Although the interaction parameters of Na<sup>+</sup> and Cl<sup>-</sup> in the aqueous solutions were occupied based on quantum

calculations, oxygen atom interaction parameters were taken from the SPC/E model(57). On the other hand, the interaction parameters between carbon and oxygen atoms are estimated from the Lorentz-Brethelot (L-B) mixing rule(58). For any atomic molecules with charge, columbic interactions were also employed. Correspondingly, the dissolved salt ions Na<sup>+</sup> and Cl<sup>-</sup> are assigned charges of  $q_{Na}$  = 1.0e and  $q_{Cl}$  = -1.0e. The interaction parameters used in this study are presented in Table 1(15). The particle-particle particle-mesh (PPPM) method was utilized to ensure precise long-range electrostatic interactions between all charged atomic types(58). Newton's equations of motion were coordinated in the VERLET calculation with a simulation time step of 1.0 fs. All simulations were performed using LAMMPS(59). The Maxwell-Boltzmann velocity distribution at 300 K was applied for assigning initial conditions of fluids. NVT (constant number of molecules, volume, and temperature) ensembles were initially used with a Nose-Hoover thermostat to preserve the system at 300K in the equilibrium MD simulations. Individually, the feed and permeate side have 1584 water molecules to meet the water density at 1 g/cm<sup>3.</sup> Meanwhile, the feed side has 20 Na<sup>+</sup> and 20 Cl<sup>-</sup> ions which result in the salt concentration in the feed region of 0.6 M. For the first NVT ensemble, no pore was created and was equilibrated for 20 ns. After that, the pore of 0.99 nm diameter has created and equilibrated for additional 3ns.For all the four cases, these two steps have been followed before pursuing to NEMD simulations. After the EMD, in NEMD simulations were conducted to maintain flow for four different pore sizes of 0.568 nm, 0.994 nm, 1.420 nm, 1.9884 nm by moving the two specular reflection boundaries with the same velocity (1.5 ms<sup>-1</sup>) in the zdirection through the fixed graphene membrane. The preferred velocity was 1.5 ms<sup>-1</sup> because it coordinated well the molecular level with the continuum level properties for fluid in the previous studies(52). Using a higher specular reflection, the wall velocity may considerably disrupt the fluid thermodynamic properties, while applying a low velocity can increase the total computational time unreasonably.

Interaction	$\epsilon(ev)$	$\sigma(\dot{A})$
C-Cl	0.003619748	3.9240
C-Na	0.001350014	2.9876
C-0	0.00403278	3.283
С-Н	0.0	0.0
Na-Cl	0.001702700	3.5116
Cl-O	0.005575083	3.8068
Cl-H	0.0	0.0
Na-O	0.002079272	2.8704
Na-H	0.0	0.0
Cl-Cl	0.004613823	4.4480
Na-Na	0.000641772	2.5752
H-H	0.0	0.0
0-0	0.006739	3.166
О-Н	0	0.0

Table 1. Details of the interaction parameters used in this work

# 2.11 Selecting the SRW velocity

While selecting the SRW velocity, we need to consider two type of parameter. At first, we need to ensure that using that specific velocity doesn't disrupt the flow phenomenon along with preserving the thermodynamic property smoothly. For that reason, we cannot use a SRW velocity here more than 1.5 ms<sup>-1.</sup> However, another thing need to consider the too low SRW velocity. If we choose a velocity that is very low, then it will increase the computational cost a lot. Although using a lower SRW velocity less than 1.5 ms<sup>-1.</sup> could be effective, it could a long time to take the data with that time. Therefore, considering these facts the SRW velocity has been chosen here in this research.

# **III.** Result and Discussion



3.1 Density distributions of water and ions in the district of the porous membrane

Figure 3.1: Mass density distribution of water

In figure 3.1, Equilibrium molecular dynamics were used to determine the density distribution of water when the pore plug is off. The local density of water and salt ion concentrations were averaged for 20 ns by dividing the computational domain into slab bins with a length of 0.115 nm along the z-direction. Bin thickness was chosen to be ten times smaller than the molecular diameter of water to get a better visualization of the separation distance from the solid to the liquid region. The liquid transport and the liquid's property were greatly influenced by both the molecular structure and intermolecular force of liquid(52). Clearly, the bulk density of water on both sides of the membrane was almost 1g/cm<sup>3</sup> in Figure 3.1 as anticipated.



Figure 3.2: Determining pore boundary L' using water's radial density peak.

The density peak for water near the NPG membrane was observed due to the wellknown density layering(60). Due to the surface force and liquid-liquid strength in the nanoscale domain, liquid atoms adjacent to the solid surface drive in freezing mode and generate a solidlike liquid layering at the dissimilar molecular interface(61). Though the layered liquid structure near the solid surface is not reflected at the continuum level, this can significantly influence the flow phenomena at the nanoscale due to the increase in interfacial density, viscosity, and pressure(62–64). The density distribution of water molecules inside the Nanopore was shown in figure 3.2 for a pore diameter of 1.98 nm. In figure 3.2, the atomic boundary position L' of pore diameter was depicted where the water molecule's density dropped 2% from its bulk density(65). After that, (L -  $2\sigma_{c-c}$ ) was defined as the atomic boundary position L'' of pore diameter whereas  $\sigma_c$  is atomic radius of the carbon atom. From the density distribution inside the Nanopore, L'' was found 0.3124 nm, 0.7426 nm, 1.20 nm, 1.83 nm for the pore diameter of 0.568 nm,0.99 nm, 1.42 nm, and 1.92 nm, respectively.

# 3.1 Pressure distribution of saltwater across the system

A pressure was developed in the feed and permeate region by the movement of the SRW at a constant speed ( $1.5 \text{ ms}^{-1}$ ). For conciseness, the pressure distribution for only one pore diameter (L) of 0.994 nm is shown in Figure 3.3 for a system of LJ + Columbic interaction between ion and water. The average of the three symmetrical ordinary stress segments in the Cartesian coordinate system from the IK expression was used to determine pressure(66,67). The bin size for the pressure distribution was also chosen as 0.115 nm to better describe the molecular interaction in compliance with the density distribution.

Figure 3.3 shows the pressure distribution in the z-direction, which displays ambivalence close to the interface. As a consequence of the density layering near the membrane, the local shear stress near the interface is increased, which eventually generates a pressure peak close to the interface on both sides of the system. In earlier studies, it was established that getting an anisotropic type of pressure close to the interface is very fundamental(15,51).

To find the pressure difference, the constant bulk pressure on the feed  $(P_f)$  and permeate  $(P_p)$  sides are given as follows:



**Figure 3.3:** Pressure distribution along the z-axis direction while two specular reflection boundaries are moving at 1.5ms<sup>-1</sup>



**Figure 3.4:** Pressure difference varied for various pore sizes for LJ and LJ+ Columbic interaction between ion and water molecules

From Figure 3.4, it is observed that the pressure difference along the z-direction is reduced in a non-linear way when the pore diameter is increased, although the specular

reflective wall velocity is the same for all cases. However, for the Lj+ Columbic interaction between water and ion, the pressure difference is less than in the cases of LJ interaction between water and ion. With the increment of the pore diameter, the saltwater flow area was increased. As a consequence, the shear stress between the molecules of saltwater was decreased on the feed side. Due to the decreasing shear stress in the feed side, the pressure drop of the system is decreased with increasing the pore diameter.

#### **3.2** Comparison of water mass flow rate

The water cluster around the ion or the steric effect is formed due to the Columbic interaction between the ion and water molecules(10). At first, to visualize the steric effect on water flow rate, we have depicted the water mass flow rate separately both for LJ interaction and LJ+ Columbic interaction between the water and ion along with atomic boundary position of pore diameter in figure 3.5(a) and (b). For both cases, the interaction and all other parameters are the same except the ion-water interaction. The MD flow rate was calculated from the time rate of change of water molecules along the feed reservoir and then multiplied with the single water molecules that filled up the volume. Each water molecule filled up a volume 0f 0.03231 nm<sup>3</sup> in each reservoir. Interestingly, the water mass flow rate is reduced when the steric effect is present (Lj + columbic interaction between water and ion). The possible explanation for this phenomenon is linked up with water cluster formation around the ions due to the electrostatic interaction. In the presence of a steric effect, the ion tries to hinder the water molecules from moving freely, which ultimately reduces the water flow rate.



Figure 3.5: (a) Water mass flow rate relation with pore diameter with atomic boundary position for LJ interaction between ion and water (b)Water mass flow rate relation with pore diameter with atomic boundary position for LJ|+ Coulomb interaction between ion and water.

In addition to that, for three different boundary positions of pore diameter, the Sampson flow prediction was calculated from the Sampson flow equation that was solved from the Stokes equations for a pressure-driven flow through an infinitely thin circular orifice(68). The mass flow rate from the Sampson flow rate equation could be obtained from equation 10. Where 'q' denotes the volumetric flow rate, 'a' denotes the pore radius and ' $\mu$ ' denotes the viscosity of the fluid. The viscosity of saltwater is 850-860 µPa was used in the Sampson flow rate calculation (69). For the Sampson flow rate prediction, the water flow rate was also reduced for the steric affected case as the MD predicted result. It is apparent that as the pressure difference was decreased for each pore diameter of the steric affected case, the predicted Sampson flow rate also needs to be reduced due to the linear relationship between pressure and mass flow rate. However, there is no linear pattern found for the difference between the steric effect and non-steric affected case for MD and Sampson flow prediction with the pore diameter. In both steric and non-steric affected cases, the Sampson flow rate prediction is lower than the MD predicted magnitude. Since the Sampson flow over predicts the hydrodynamic resistance of the graphene Nanopore, the water mass flow rate decreased for the Sampson flow prediction from the MD (70). Moreover, when the atomic boundary position of L' and L'' applied to the Sampson flow rate prediction, it starts to deviate more from the MD predicted result. This result denotes that applying the atomic boundary position of Nanopore in the Sampson flow model doesn't hold the same prediction for water mass flow rate as it holds for a simple fluid flow(71). The long-range Columbic interaction of the water molecules itself could play the key role here in this variance.

#### 3.3 Comparison of water velocity profile

To investigate the cause of the mass flow rate reduction of the water molecule in the presence of a steric effect, we analyzed the velocity distribution of water molecules at the pore and also for the overall system.



Figure 3.6: Water velocity distribution for pore diameter of 1.42 nm

To maintain the brevity, only the velocity distribution of 1.42nm pore diameter has been shown in figure 3.6, figure 3.7(a) and (b). Figure 3.6 illustrates the comparison between the velocity of water molecules for the entire system for LJ and LJ+ Columbic interaction between water and ion. When the ion-water has a Columbic interaction, the ion attracts the water molecules, strongly holding back their usual movement. As a result, the water velocity became lower for the steric affected case, and this difference between these two cases is more apparent at the center of the pore.

To acquire the complete view, the velocity profile at the pore center showed from the MD simulation along with the Sampson flow equation with a different boundary position of pore diameter. Applying Sampson's stream function solution in cylindrical coordinates, the velocity profile for r position inside the pore can be expressed as follows equation 11.



**Figure 3.7: (a)** Water velocity inside the Nanopore for LJ interaction between ion and water for pore diameter of 1.42 nm (b): Water velocity inside the Nanopore for LJ+ Columbic interaction between ion and water for pore diameter of 1.42 nm.

In figure 3.7(a) and (b), to calculate the velocity profile of water from MD, a cylindrical bin was used with a radius equal to the pore radius and length equal to the diameter of a single carbon atom. The cylindrical bin axis was set along the Z direction of the pore center, and the bin was also divided into multiple concentric circle bins to gather the velocity data in the radial direction of the pore. The multiple concentric circle bins were divided to get the maximum water molecules in each bin. The data were averaged for 0.4ns when the water flow was established across the Nanopore for a 1.42nm diameter Nanopore. The velocity profile is also reduced for different boundary conditions with the Sampson flow model for the steric-affected system case, and it also deviates from the MD value, maintaining consistency with the flow rate results

# 3.4 Defining the primary hydration boundary of ions

The ionic concentration distribution is represented in Figure 3.8, along the z-direction while ensuring that no ion has been passed through the Nanopore in EMD without applying pressure. The bulk ionic concentrations for Na<sup>+</sup> and Cl<sup>-</sup> were almost equal and matched with the theoretically calculated value of 0.6M. Although our focus was to investigate any ions transportations impact with the shift of the atomic boundary position of pore diameter, equal concentrated sodium, and chlorine ion is presented in this system due to maintaining the charge neutrality for added charge in the system.

Using the radial distribution function (RDF), the primary hydration layer boundary [L<sub>h1</sub>] can be measured precisely. In Figure 3.9 (a) and (b), the radius of the primary shell boundary  $\left[\frac{L_{h1}}{2}\right]$  was determined using the RDF.



The first density peak in the radial distribution function indicates the starting region of the primary hydration layer, while the first minimum after the first density peak was considered as the radius of the primary hydration layer from the ion center. For Na<sup>+</sup>, the peak in the RDF indicates the strong electrostatic interactions with O<sup>-</sup> atoms of the primary hydration layer. For Cl<sup>-</sup>, it defines the strong electrostatic interactions with H<sup>+</sup> atoms of its primary hydration layer. The first minimum density drop indicates the strong repulsion between the atoms of the same charge. The primary hydration layer radii of Na<sup>+</sup> and Cl<sup>-</sup> were reported in this study as 0.37nm and 0.39 nm, respectively, which matched closely with the previous studies (30,72). After the first hydration layer, the second and the third hydration layer was found to be 0.62 nm and 0.85 nm from the chlorine ion center, respectively. For sodium, the second and the third hydration layer were found at 0.62 nm and 0.84 nm from the ion center, respectively. According to the literature, it is expected that the subsequent layer after the innermost layer is spaced at 0.2-0.23 nm (27)



**Figure 3.9: (a)** Defining hydration radius of sodium ions with the radial distribution function of water molecules around sodium ions (b) around chlorine ions.

### 3.5 Relating water and ion flow paths for various nanopore diameters

In this part of analysis, to observe the salt ion and water flow, the percentage of the salt and water on the feed side is tracked for pore diameters (L) of 0.994 nm, 1.4203 nm, 1.989 nm and 2.22nm. In figure 3.10 (a-d), the water and ion track down has been depicted. We add specifically pore diameter 2.2nm for this analysis over 0.55nm since for water and ion flow comparison, 0.99 nm to 2.22nm is considerable range. A reference time was needed to compare the percentage of the remaining molecule of water with salt ions. For each simulation, we characterized a period  $T_f$  that is illustrative of the end of the simulation because the water flow rate generally shifted depending on the nanopore size.(73) For each pore case, T<sub>f</sub> has been selected when 160 of the water molecules passed from the feed side. After that, the salt ion passing percentage is compared with the water molecule flow percentage. For a larger pore diameter like 2.2 nm, salt ion flow proportion was almost the same as the water molecules. For example, for a pore diameter of 2.2 nm, both Na<sup>+</sup> and Cl<sup>-</sup> ions were passed at almost 20% while the water molecule flow holds constant at 20%. In contrast with this, when the pore diameter decreased, the difference between the salt ions and water molecules flow proportionality became larger for the smallest pore diameter like 0.99 nm. As a result of these facts, it can be said that the salt ions and water molecule's flow proportionality differences are inversely proportional to the pore boundary size. Alongside this, the Na<sup>+</sup> flow proportion difference with respect to water was lower compared to Cl<sup>-</sup> for the initial case pore boundary. Since cations hold their hydration shells less strongly than anions at a given charge density, it is easy for Na<sup>+</sup> ions to pass through the smaller nanopore by shedding the hydration shell close to the ion center(35). However, this is difficult for Cl<sup>-</sup> for its higher electrostatic attraction. Nevertheless, after the initial pore boundary, the flow proportion difference between Na<sup>+</sup> and Cl and water molecules was observed to be insignificant due to the probable action of a weakly attracted hydration shell far from the ion center. Interestingly, the ions fluctuate around

the feed and permeate the side through the pore before going permanently to the permeate side. The probable cause of this is that ion acts like free radicals at nanoscale, so they circulate in the pore region before going permanently to the permeate side. This flow proportionality difference between water and salt ions for different pore cases in saltwater transportation induces desalination. In actual fact, the free energy obstruction of ions is inversely proportional to the pore boundary size. Indeed, the free energy profile of ions is additionally influenced by the ion's hydration structure that in has an overall impact on ion transportation. (74)

From the above observation, it is presumed that the ions have trouble translocating when the steric impact boundary is greater than the pore boundary. Once an ion encounters the membrane, its secondary hydration shell may start to fall apart due to the pressure. In fact, the water molecules are separated from the ion during ion transportation by decreasing the first ion hydration number and increasing the energy of the ion(75). In this way, the steric limit ( $L_{h(n)}$ ) likely decreases, and when that limit was not greater than the pore limit size, the ion moved to the permeate region. For ion transportation through a small pore, ion hydration shells near the ion center must detach to reduce the steric effect boundary due to small pore boundary. This detachment requires an extremely high pressure since the hydration shell closest to the ion center has higher long-range columbic attraction. This is a plausible reason why ion transportation is lower in smaller pores, though they have higher pressure difference. In larger pores, ion transport is smooth as the secondary hydration shells far away from the ion center are only weakly attracted by the electrostatic force and can be separated even at low pressure.







Figure 3.10: Water molecules and salts remain proportional in the feed at a constant speed (1.5 ms<sup>-1</sup>) for (a) L=0.99nm (b) L=0.1.42 nm (c) L=0.1.98 nm (d) L=2.22 nm

Furthermore, the remaining percentage of salt ions in the feed side indicates the salt rejection of the saltwater as noted in earlier literary works. However, the salt rejection rate is highly dependent on the reference time  $T_f$ , which is the time salt rejection was determined. In previous works, the salt rejection was measured when the water molecules filtration was between 10% to 50% depending on the pore size(13,73). However, it should be noted that allowing for higher water molecules filtration will moderate the salt rejection rate. Accordingly, as various sizes of pores are considered in this study, a constant minimum amount of water flux filtration with a lower computational cost. That constant minimum amount of water flux purification is used here to define the reference time ( $T_f$ ) for each pore case.

After comparing the transportation for water and ions in Figure 3.10 (a-d) it is obvious that ion transportation isn't united with water for more modest nanopores due to their steric impact. To visualize the phenomenon, the anticipated transportation pathway is shown in Figure 3.11 (a-d) for salt ions and water by the linear least square method by utilizing the transportation information from Figure (3.10). As shown in Figure (3.10), the flow was considered up to the reference time. Here in Figure 3.11 (a-d), the flow was mathematically predicted until the water flow ended. The total salt ion vs. water flow path is represented to obtain total salt rejection. As estimated, there is a significant gap between the water and ion transport path for the first three pore cases (0.9942 nm, 1.4203 nm, 1.988 nm) due to the steric effect. The mathematically predicted salt rejection is obtained by measuring the percentage of salt that remains on the feed side when the remaining water is almost empty on the feed side. For pore diameters (L) of 0.9942 nm, 1.4203 nm, 1.988 nm, the mathematically predicted salt rejection were calculated to be 52.53%, 45.32%, 18.32%, respectively.





Figure 3.11: Generalized predicted comparison for water and ion flow with mathematically predicted salt rejection for (a) L=0.99nm (b) L=0.1.42 nm (c) L=0.1.98 nm (d) L=2.22 nm

This predicted salt rejection is not as high as the salt rejection that was directly gained from MD. However, this is not an issue for this study because our main focus was to identify the pore boundary where salt rejection is happening and where it is not. In Figure 3.11(d), for L=2.274 nm, the ion and water flow matched for a certain time, and then ions started to pass faster than water molecules. As shown, all the ions are translocated to the permeate side even before the water flow is finished. For this reason, salt rejection tends to zero percent when L= 2.274 nm. This also provides a comprehensive overview of the flow paths of ion and water molecules for the small and large-scale pore boundaries of this study. Smaller pore sizes with closer solvated hydration shells near the ion would encounter the carbon atoms at the pore edge. Hence, the ions are more hindered because water molecules close to the ion in the solvated hydration shell are more strongly attracted, and the shell is likely to collapse except at a very high pressure. This is the probable reason why the salt rejection is high for the small size nanopore diameters. It can be said from these results, that ion flow behavior will be similar to fluids like water when the pore boundary starts to reach the continuum scale, and the ion rejection phenomenon will not be effective for a continuum scale pore boundary. This also implies that the steric boundary will not interfere with ion transport after a certain nanopore boundary.

#### 3.6 Investigating the salt rejection dependence and the steric impact limit region

In this section to determine the steric boundary while transporting ions through a nanopore, the predicted salt ion rejection needs to be analyzed with respect to the pore boundary. This depends on the pore boundary definition since defining the pore boundary at nanoscale is very difficult. Initially, the pore boundary (L) was considered using the distance between the atomic centers of carbon for visual simplicity (as suggested by Thomas and McGaughey(76)). However, to check whether water has entered up to the distance of the edge of nanopore, the radial density of water inside the nanopore was measured as shown in Figure 3.12. The radial density distribution for a nanopore diameter (L) of 1.98 nm is shown as an example. The radial density distribution was obtained from the center of the nanopore up to the atomic center of the nanopore edge's carbon atoms while the bin size was ten times smaller than the carbon atomic diameter for better visualization. There is a density peak inside the nanopore on the radial density distribution of water. After the peak, the significant density drop indicates that the liquid water does not enter up to the center of the nanopore edge carbon atoms due to the density layering of water. The strong repulsion effect among the molecules at the nanoscale created this density layering gap between the solid and liquid molecules (77). Thus defining the center to a center atomic distance of the nanopore edge carbon atoms as the pore diameter is not a useful way to define the absolute steric boundary as the encircled water molecules around the ions do not enter up to the diameter L. When the density drops below 2% of the bulk density, another pore diameter definition was defined in previous literature which is denoted here as L' (25). For the four diameter cases in this study, L' was found to be 0.7456 nm, 1.2072 nm,1.8223 nm,2.1708 nm respectively for 0.99 nm, 1.420 nm, 1.9884 nm, and 2.274 nm that were considered initially.



Figure 3.12 : Exponential decrease of (L - L') with L.

As shown in Figure 3.12, the gap between L and L' is defined here as the interfacial solid-liquid gap due to water's density layering which exponentially decreases with the increase in the pore diameter. Interestingly, in Figure 3.13, when this interfacial solid-liquid gap (L - L') is three times lower than the interatomic distance ( $\sigma_{oc}$ ) of carbon and water, the salt rejection started to diminish. In fact, after a certain value of  $\frac{\sigma_{oc}}{L-L'}$ , the salt rejection started to increase exponentially and the ratio was 3.13. The probable cause of this exponential increase in salt rejection is related to the repulsion effect of the (LJ) (12-6) potential between solid carbon and liquid water(58). When the (L- L') tends to reach close to the  $\sigma_{oc}$ , the salt rejection will approach to be higher because on that case the repulsion region of interfacial solid-liquid will approach to be greater by lowering the accessible area for ion translocation. Though this magnitude of this ratio is not universal because of the change in L' with the wettability of the solid surface, this gives an unprecedented insight into salt rejection that it is also vastly affected by the liquid-solid interaction(78).


**Figure 3.13 :** Exponential relationship of salt rejection with  $\frac{\sigma_{oc}}{L-L'}$ , where  $\sigma_{oc}$  is the intermolecular interaction distance between solid and fluid

Figure 3.13 shows, the predicted salt rejection obtained from the Figure 3.12 with respect to the pore diameter (L') and this demonstration visibly displaying how salt rejection is inversely proportional to the pore boundary. From Figure 3.14, we can conclude that the salt rejection tends to zero when the pore diameter (L') is 2.1708 nm. The theoretically measured salt rejection tends to zero percent for a specific pore diameter, indicating that the steric effect is a nanoscale property, and it should not influence ion transportation when the pore diameter inclines to expand to a continuum scale. It is obvious that salt ions will not pass like fluids due to the steric effect when  $L' < L_{h(n)}$ , where L' is the pore boundary and  $L_{h(n)}$  is the steric boundary. In contrast, ion flow will be like fluids having almost no salt rejection when  $L_{h(n)} < L'$ . Figure 3.14 shows that this transition of ions passing and not passing likes fluids happens in between the region for pore diameters of 1.8223 nm and 2.1708 nm. Therefore, from this perspective concerning the initial parameters defined.

 $(L_{h(n)})$  is expected to remain in between the region 1.8223 nm<  $L_{h(n)}$ <2.1708 nm. From the data fitting in Figure 3.14, we show that

Salt Rejection= 
$$C L' + 84.851....(13)$$

For this study, C is  $-37.552 \text{ nm}^{-1}$  by a linear least square method. However, figuring out this steric boundary region depending on the salt rejection is not general as the pore diameter (L') is varied depending on the initially defined flow parameters. Here we analyzed the salt rejection with the assistance of Sampson flow model. From the Sampson flow model,

$$L' = \left(\frac{3q\mu}{\Delta P}\right)^{\frac{1}{3}}$$
.....(14)

where,  $\Delta P$ , q,  $\mu$  are the pressure difference, flowrate, and viscosity of saltwater respectively(79).

Equating Equation (13) and (14) gives:

Salt Rejection = 
$$C \left(\frac{3q\mu}{\Delta P}\right)^{\frac{1}{3}} + 84.851....(15)$$

From Equations (14) and (15), the salt rejection is not only depending on the pore diameter but also depend on the pressure difference, viscosity, and flowrate used for a specific pore diameter in that saltwater system. Increasing the pressure difference probably will reduce the density peak drop region for water inside the nanopore and by this ion's translocation space inside the pore can be increased. This is the likely reason of why salt rejection is reduced for a specific pore boundary when the pressure is increased(13).



Figure 3.14 : Salt rejection with pore boundary (L') representing the steric effect region of salt ions.

Fluid flow rate and viscosity can play a vital role in increasing the salt rejection rate for a specific pore boundary. When the flow rate is high, fluid transport can be high compared to ion transport. This can create a higher flow path gap between water and ions regarding the pore boundary and by that ultimately the predicted salt rejection could be high in that case. Besides this, more viscous saltwater results in a higher repulsion region for water inside the nanopore. This can actually provide a shorter ion translocation space inside the nanopore. Hence, the salt rejection could be comparatively high for a specific pore diameter with more viscous salt water. As salt rejection is dependent on the parameters discussed above, the steric boundary region of ion transportation through the nanoporous membrane also can be shifted based on these parameters

This steric boundary region effectively eliminates misperceptions when selecting the pore diameters for water desalination using a nanoporous membrane. Nguyen et al. already

used a larger pore diameter than previous studies of 0.99 nm and acquired a 100% salt rejection(15). The steric boundary limit and the salt rejection dependence on pressure is the reason why they obtained 100% salt rejection with a larger pore boundary in that work though this was not mentioned. It should be noted that Nguyen et al. used a very low-pressure difference (35.02 MPa) for that specific pore boundary which helped to obtain the highest salt rejection. This can be understood in light of our discussion above on how salt rejection is crucially dependent on pressure for a specific pore boundary. It can be assumed using a realistic pressure difference (<10 MPa) at the RO process, that water desalination for a larger pore boundaries than 0.99 nm can be achieved successfully by utilizing the steric boundary concept from this study. It is also already proved that water is also permeable through the nanopore at low pressures as in the RO process(80). Therefore, applying a low-pressure difference with a large nanopore diameter that is still less than our predicted steric boundary region can be investigated in future works to achieve more efficient desalinated water through an NPG membrane.

#### 3.7 Relating atomic boundary positon of pore diameter with ion transportation

When the pore diameter is smaller than the hydration shell of the ion, the hydration shell would not be fit inside the pore. However, to fit inside a smaller diameter pore, some water molecules can be removed from the hydration shell at an energy cost(10,27). This phenomenon can change the initial total hydration diameter of the ion. We denoted the approached hydration boundary as the closest hydration layer to the pore edge, which needs to be dehydrated so that the ion can be transported through the pore. Therefore, the change of the approached hydration diameter will depend on the pore diameter. For example, to fit and transport through a diameter of 0.56 nm, chlorine's first hydration layer (0.76 nm) needs to be dehydrated. However, while transporting through the pore diameter of 0.99 nm, up to chlorine's second hydration layer needs to be dehydrated and the first hydration layer can be present during transportation. In that case, the approached hydration diameter changed to the length of the second hydration shell (1.24 nm). In figure 3.15, due to the dehydration in ion transportation, this tendency of changing the approached hydration boundary with the pore diameter has been depicted. To be specific on our goal of atomic boundary position of pore diameter effect on ion transportation and for maintaining the brevity, we have shown our analysis only for the chlorine since the consideration is the same for the others ion too(27). It is observed that the approached hydration boundary is appeared to be longer with the pore diameter increment. However, in that case, the attraction between the ion and the water molecules on that specific layer has been decreased according to the coulombs law. Therefore, the energy cost to remove the water molecules from the longer hydration layer should be less compared to the hydration layer nearest to the ion.



Figure 3.15: Approached hydrated boundary relation with the pore diameter

To observe our thoughts, we used the model proposed by Zwolak et.al. where the energy barrier to dehydrate the water molecules from the hydrated layer is presented as a function of pore radius(27). That model was assumed to be valid for an ion concentration less than 1M and with the absence of surface within the pore, which are also mutual with our system. In the model, the internal energy contained in a partially intact hydration layer as  $U_i = f_i U_i^o$ ; where  $f_i$  denotes for the fraction of the hydration layer present inside the pore area. Here,  $f_i$  represents for a specific pore radius  $R_p$  by:

$$f_i = 1 - \sqrt{1 - (\frac{R_p}{R_i})^2}$$
 .....(17)

U<sup>o</sup><sub>i</sub> is the energy difference between the hydration layer and water in the bulk. Here,



**Figure 3.16**: Energy barrier for chlorine ion with pore diameter by applying the atomic boundary position

Where K represents the dielectric constant of water and  $R_i^{o/I}$  denotes the presenting the hydrated layers for outer and inner of the pore area. After that, the internal energy barrier as a function of pore radius denoted by

From this model and figure 3.16, it is evident that our initial thought about the decrement of the energy cost for dehydration with the pore boundary increment is valid. However, to see the impact of different atomic boundary positions on ion transportation, we have applied the atomic boundary position of pore diameter L, L'and L'' here. Interestingly, when the pore diameter was below 1 nm, the energy barrier of ion for a pore diameter has deviated largely for the different atomic boundary positions of pore diameter. However, a vice versa situation happens when the pore diameter. In fact, it almost matches for L, L'and L'' when the pore diameter becomes 1.988 nm. Due to the scale effect, the energy barrier difference



Figure 3.17: Critical Pressure of chlorine ion to transport through a nanopore.

becomes more apparent for different atomic boundary position of pore diameter when the pore diameter becomes less than 2 nm (71,81)

The energy barrier related with the critical pressure that was developed in the system to break hydration shells. For a specific pore diameter, this critical pressure is varying since different approached hydration shell need to break for different type of pore diameter. However, for a pore diameter of 0.568 nm this critical pressure will be the highest as that critical pressure will tend to break the strongly attracted first hydration shell.

To see that impact of the deviation of the energy barrier of an ion on ion transportation, we calculated the critical pressure (figure 3.17) for the chlorine ion in the feed side from the MD simulation. The critical pressure was found at 68.67 MPa, 8.5 MPa, 2.50 MPa, 2.37 MPa for the pore diameter of 0.568 nm, 0.99nm, 1.42 nm, 1.94 nm, respectively, considering the kinetic and virial stress of chlorine to the flow axis. The input energy of chlorine ion was

averaged for each pore diameter up to the time when there were at least more than 160 water molecules transported. To predict the chlorine ion transportation theoretically for different atomic boundary positions of pore diameter, we proposed the ion transportation prediction as to the ratio of the total chlorine ions input energy and the total energy barrier of chlorine ion as a function of pore radius.

Therefore, the ion rejection (I) for different atomic boundaries becomes:

However, to maintain the comparison consistency for our theoretical and MD prediction, the chlorine ion rejection from MD was also calculated for the time when more than 160 water molecules transportation through the Nanoporous graphene membrane for all the pore diameter cases. This reference time is selected to get a considerable computational time and have a proper view of the ion rejection from a small to a big pore diameter. In figure 3.17, apparently, it has been observed that the ion rejection prediction could be shifted for the different atomic pore boundary positions. Due to the atomic boundary position towards the pore center, the resistance to the ion transportation was inclined, which ultimately affected the ion rejection. The difference between the MD predicted ion rejection and our theoretically predicted ion rejection is more visible when the pore diameters become less than 1 nm. The possible explanation is linked with the van der walls and columbic interaction between the ion and the membrane. When the pore is very narrow with boundary conditions, the ion faces exponentially increased high repulsion from the graphene membrane. For that, either the ion needs to move away to the feed side or the permeate side, depending on the input energy.



**Figure 3.18:** Chlorine ion rejection prediction for different atomic boundary position of pore diameter and from MD simulation.

If the input energy is high enough, then the ion is pushed through the Nanopore and goes to permeate side. Considering this hypothesis, it is observed that when the pore diameter becomes 0.568 nm, to transport through this pore, all the hydration shells, including the first hydration shells, need to be dehydrated with higher input energy. It was noticed that for the 0.568 nm pore, the input energy is far high (8 times higher) than the closest pore diameter 0.99 nm case. Therefore, if at least one chlorine ion was transported through this pore diameter, it was detached from the entire hydration layer with this input energy. A similar phenomenon could be started with all the chlorine ions of the system, and they started to transport more rapidly only with their bare ion diameter (0.34nm) along with a partial hydration shell (82). As a consequence of transport with a much lower diameter than the size, including the first hydration shell, the ion rejection for the 0.568 nm pore goes against the increasing trend of ion rejection with the pore diameter decrement.

One important calculation point that need to be addressed is the ion passing calculation through a nanopore. The ion passage has been calculated in this type of system for a specific period time. When the movement of the specular reflection wall was started, the volume has been reduced in the front reservoir. For that reason, the pressure will be increased and that increased pressure will tend to break the hydration shell. Moreover, if the volume is reduced but the density tries to be constant (i.g. very small pore diameter), then the overall pressure become too high. That high pressure acted even up to the first hydration shell and could break that. Therefore, to get a reasonable ion separation percentage, we need to choose an appropriate time frame which require a minimum amount of the pressure allowing with a considerable amount of water molecules.

The most noticeable point from figure 3.17 is that the MD prediction ion rejection value is most closely matched for the atomic boundary position of L' for the pore diameter case 1.42 nm and 1.98 nm. The center to center atomic boundary position (L) predicts low resistance for ion transportation, whereas L'' over predicts the higher resistance for ion transportation. Therefore, for these two atomic boundary positions, the ion rejection could be less approximate than the atomic boundary position of L'. The effective pore diameter for ion rejection is that which forces the hydration layer to be partially broken off (27). According to this thought and the observed result from the pore diameter of 1.42 nm and 1.98 nm, L' might be the approximate atomic boundary position for ion rejection since it is also denoted the dense core area of water molecules inside the Nanopore. However, when the pore diameter becomes less than 1nm denoting the atomic boundary position becomes more difficult to approximate for ion rejection. The van der walls repulsion is too high there to precise an approximate boundary position of pore diameter with the comparison of theoretical and MD magnitude.

However, the similarity of the theoretical and MD predicted ion rejection when the pore diameter is increased to 2nm indicates the atomic boundary position effect, which was previously addressed for a simple fluid flow(71). As to the water flow rate deviation from the MD predicted result, the ion rejection also can be significantly changed due to the atomic boundary position effect of pore diameter when the scale becomes less than 2nm. In synopsis, since the van der Waals force and the Columbic interaction of the molecules becomes significantly apparent at the molecular level; a small change in the atomic boundary position could lead to a greater change in the resistance of water and ion transportation. That shift in the resistance of Nanopore diameter due to the atomic boundary position could significantly impact the flow phenomenon of ions along with water transportation.

#### IV. Conclusion

In recapitulation, this study has emphasized the impact of the pore diameter's atomic boundary position on ion transportation by using a pressure-driven flow through a nanoporous graphene membrane. The effect of the atomic boundary position of pore diameter is delicately related to the ion's hydrations layers. Moreover, the hydration layer is the outcome of the steric effect of ions, which also modifies the water velocity and flow rate from their particular activity.

This impact of the steric effect on water flow properties has been visualized by alternating the LJ and LJ+ Columbic force interaction between the water and ion. Apart from that, according to the Sampson flow model, the velocity and flow rate are lower than MD predicted result for both steric and non-steric-affected cases. In the time of water and ion transportation, the hypothesis of the approached hydration boundary connection with the pore diameter has been defined. Employing this assumption, the energy barrier of the ion transport as a function of the pore diameter has been illustrated for each of the atomic boundary positions of pore diameter. Consequently, the theoretical ion transport as a function of the pore diameter.

The theoretical ion rejection is compared with the MD predicted ion rejection to observe the importance of the pore diameter's atomic boundary position on ion transportation. It is noticed that the theoretical ion rejection significantly deviated for the different atomic boundary positions of pore diameter when the pore diameter is less than 1 nm. However, at more than 1nm of pore diameter, the theoretical ion rejection is identical to the MD predicted result for the atomic boundary position stated to the 2% water density drop inside the nanopore. Moreover, it is also observed that if the entire hydration layer is broken, the ion rejection is significantly reduced by going against the inversely proportional relationship with pore diameter.

However, this hydration layer disruption is directly related with the critical pressure that is responsible to break a specific hydration shell. The critical pressure created in the front reservoir is

depended with the pore diameter. Since if the pore diameter is small, then the front reservoir pressure will be high and it will tend to reach the critical pressure where the approached hydration layer will be broken to pass an ion through a the nanopores graphene membrane. Depending on this critical pressure, the theoretical ion rejection has been illustrated in this work.

In future outcomes, we would like to see the theoretical ion rejection prediction with lower input energy which is not assessed in this work regarding the computational time frame. Discussing proper atomic boundary position for ion transportation and separation through our investigations will have severe implications for the desalination experiments and the reverse osmosis plants for water purification. Also, the thermodynamic and the mechanical property of the graphene membrane has not been considered in this research due avoid the complication and the computational cost. In the upcoming work, the thermodynamic and mechanical property of the graphene membrane need to be considered to predict the ion transportation more accurately for the implication in practical field.

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## **Research Interest**

	Micro fluids- Nano fluids
	Nanoscale Flow Modelling and Interfacial Phenomenon
	• Ion transport and separation through porous membrane
	<ul> <li>Electric double layer effects in paposcale flow</li> </ul>
	Heat transfer in nenegoals
	Heat transfer in nanoscale
	• Molecular dynamics
Academic Background	
March 2020- August 2022	M.Sc. in Mechanical Engineering, CGPA: 4.31/4.5 (97.83 %)
C C	University of Ulsan ,93 Daehak-ro, Nam-gu, Ulsan (44610),
	Republic of Korea
	B.Sc. in Aeronautical Engineering, CGPA: 3.12/4.00.
February 2015-April 2019	Military Institute of Science & Technology (MIST), Bangladesh
	University of Professionals (BUP); Mirpur Cantonment, Dhaka-
	1216, Bangladesh
<b>Research Experience</b>	
March 2020-Present	Graduate Research Assistant in "Micro and Nano-scale Thermal
	Fluid Lab
	Analysis Technique: Molecular Dynamics Simulation (EMD and
	NEMD)
	<b>Performed analysis:</b> Ion Transport and Separation across pristine
	and charged nanopore, Flow modeling (Shear Dirven, Pressure
	Driven, Sampson flow model in nanopore), Interfacial phenomena,
	Thermodynamics Properties and Local thermodynamics
	equilibrium
2010	
2018	Undergraduate thesis on "Sheet molding compound (SMC) from carbon nanotubes"
	<b>Analysis:</b> Investigate the effect on mechanical properties of SMC after using various formulation of resin with carbon panotubes &
	other additives like hollow glass microspheres

Submitted:	Influence of Steric Effects on Ion transport and separation through
	nanoporous graphene membrane; BoHung Kim, Morshed Mahmud

# Conference Proceeding

Abstract submitted and Oral Presentation:	2021 Spring Conference of Korean Society of Mechanical Engineers (KSME)
Published:	Mahmud, M., Washir, M.R., Islam, M.K. and Dhar, N.R., 2021, February. Comparison study of different formulation effect on the mechanical behavior of sheet molding compound (SMC). In AIP Conference Proceedings (Vol. 2324, No. 1, p. 030002). AIP Publishing LLC
Skills	
	Molecular Modeling: Material studio, LAMMPS
	Molecular Analysis: LAMMPS
	Visualization: OVITO, VMD
	Post Processing: Origin, MATLAB Plot

- CFD Analysis: Ansys FLUENT
- **Design:** Solidworks

# **Professional Experience**

2020-Present	National Science and Technology Information Service ( <b>NTIS</b> ) (Korean Researcher Number: 12585836)
2021-Present	Content Developer at 'Sabash Fakibaj'' [Trade License no. TRAD/DSCC/258135/2019, USA License no. 803751949 and under the Copyrights Act, 2006]
2021-Present	Course Instructor at "Abartan" [Trade License no. TRAD/DSCC/061040/2020]
2017	Internship on "Biman Bangladesh Airlines"

# Scholarships 2020-Present

AF-1 Scholarship (full tuition fee) awarded by Mechanical and Automotive Engineering Department ,University of Ulsan and Research grant by National Research Foundation of Korea (NRF)

# **Projects and Participation**

2016	UAV drone racing on TECHFEST at Independent University of
	Bangladesh (IUB)
2017	Rob riot on MECCELERATION at Islamic University of
	Technology, Dhaka, Bangladesh.
2016	UAV drone racing & Bot fighting on ROBOLUTION at Military
	Institute of Science and Technology (MIST), Dhaka, Bangladesh

Test Score	
IELTS	Overall 7.00 (Listening 7.5, Reading 7.5, Speaking 7.0, Writing 6.0)
GRE	Quant: 156 ; Verbal : 147 ; AWA: 3.0

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