Monte Carlo simulation of ion transport of high strain ionomeric polymer transducers

by

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Abstract

Ionomeric polymer transducers exhibit electromechanical coupling capabilities. The transport of charge due to electric stimulus is the primary mechanism of actuation for a class of polymeric active materials known as ionomeric polymer transducers (IPTs). The research presented in this dissertation focuses on modeling the cation transport and cation steady state distribution due to the actuation of an IPT.

Ionomeric polymer transducers exhibit electromechanical coupling capabilities. The transport of charge due to electric stimulus is the primary mechanism of actuation for a class of polymeric active materials known as ionomeric polymer transducers (IPTs). The research presented in this dissertation focuses on modeling the cation transport and cation steady state distribution due to the actuation of an IPT.

Ion transport in the IPT depends on the morphology of the hydrated Nafion membrane and the morphology of the metal electrodes. Recent experimental findings show that adding conducting powders at the polymer-conductor interface increases the displacement output. However, it is difficult for a traditional continuum model based on transport theory to include morphology in the model. In this dissertation, a two-dimensional Monte Carlo simulation of ion hopping has been developed to describe ion transport in materials that have fixed and mobile charge similar to the structure of the ionic polymer transducer. In the simulation, cations can hop around in a square lattice. A step voltage is applied between the electrodes of the IPT, causing the thermally-activated hopping between multiwell energy structures. By sampling the ion transition time interval as a random variable, the system evolution is obtained.

Conducting powder spheres have been incorporated into the Monte Carlo simulation. Simulation results demonstrate that conducting powders increase the ion conductivity. Successful implementation of parallel computation makes it possible for the simulation to include more powder spheres to find out the saturation percentage of conducting powders for the ion conductivity. To compare simulation results with experimental data, a mul-

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A multiscale model has been developed to increase the scale of Monte Carlo simulation. Both transient responses and steady state responses show good agreement with experimental measurements.
To my mother Shouqiong Tang,
my father Guanyin He
and all of my friends
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Chapter 1

Introduction and Literature Survey

1.1 Background of the ionic polymer transducer and mechanisms behind its nonlinear behavior

An ionic polymer transducer (IPT) is fabricated by an ionomer membrane, such as Nafion\textsuperscript{TM}(a trade mark of DuPont’s ionomer and a perfluorinated sulfonic acid polymer \cite{4}) sandwiched by two noble metal electrodes. Certain cations, such as Li\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, Cs\textsuperscript{+}, etc., are doped into the IPT to neutralize the sulfonate groups fixed to the membrane. In the early 1990s, it was documented that ionic polymer transducer can exhibit coupling between the electrical and mechanical domains as sensors or actuators. Sadeghipourt et al. developed a novel vibration sensor based on the metallized Nafion\textsuperscript{TM} membrane \cite{10}. It was reported that Nafion\textsuperscript{TM} sandwiched between two electrodes can sense mechanical vibrations and generate a voltage response. Oguro et al. were the first to report that mechanical deformation is produced in the polymer transducer with platinum electrolyte in response to electric stimuli \cite{11}.

Following this work, there were numerous studies of the potential applications of the 'smartness' of ionic polymer transducers based on their electromechanical coupling capabilities. Buecheler and Leo proposed an active mirror used in outer space \cite{12}. This circular disk was fabricated from the ionic polymer material so that shape and vibration control can be accomplished through electrical boundary conditions applied to the ionic polymer rather than by adding external actuators. Etebari et al. has demonstrated the potential of ionic polymer transducers for measuring skin friction as a wall shear stress sensor.
Figure 1.1: Actuation behavior of ionic polymer transducer

in liquid flows [13]. Ionic polymer transducers have shown more accurate measurements over a large range of fluid velocity fluctuation scales than conventional technologies. Keshavarzi et al. used ionic polymer transducer sensors to measure blood pressure, pulse rate and rhythm [14]. Typically, the IPT sensors are installed on the inner surface of a cuff. After the load is applied, it can produce larger voltage output than a typical pulse rate sensor. K. Kim et al. proposed to expand the use of IPT for fuel cells, electrolysis and hydrogen sensors [15]. Bar-Cohen introduced a gripper consisting of four IPT finger-strips with hooks at the bottom to grab rocks similarly to human hand [16]. B. Kim et al. presented a wireless undulatory tadpole robot using an ionic polymer transducer as its fin tail [17]. The motion of the tadpole microrobot can be accurately controlled by changing the frequency and duty ratio of the input voltage. Nakano et al. [18] designed a haptic interface device usually used in virtual reality, so that users would be able to feel the shape or even the surface texture of an object in the computer as a means of kinesthetic feedback or tactile feedback. The deformable device is made by an IPT actuator array (a strip consisting of four actuators arranged in line) and the deformation is derived by monitoring the potential of the electrodes.

Figure 1.1 illustrates the properties of ionic polymer transducer as actuators. When a low step voltage (usually 1-4V) is applied, the IPT bends toward the anode. Conversely, when the IPT is suddenly bent a voltage is produced across its surface. The transducer shown in the figure consists of a Nafion™ membrane that has been hydrated and plated with a conductive electrode on both surfaces. Nafion™ in the hydrated state exhibits high conductivity and permselectivity for counter ions. Its chemical structure is shown in Figure 1.2 where the value of m can be as low as 1 and the value of n varies from

...
Figure 1.2: The chemical structure of Nafion™ with counter ion of Lithium

![Chemical structure of Nafion™ with counter ion of Lithium]

Figure 1.3: The simplified schematic cross-sectional diagram for ionic polymer transducer without external field.

5 to 11. The Nafion™ membranes show inherent chemical and thermal stability because of the Teflon™-like backbone; relatively short side-chains are terminated by the sulfonic acid group where $SO_3^-$ is the strongly acidic cation exchange site. The lithium counter ions in Figure 1.2 can be exchanged by proton or other metal ions in appropriate aqueous solutions. The equivalent weight (EW) and material thickness are used to describe most commercially available Nafion™ membranes. For example, Nafion 117 films have 1100 EW and a nominal thickness of 185-200 microns. The EW is defined as the average weight in grams of unhydrolyzed polymer per mole of exchange sites and is related to $n$ by $EW = 100n + 446$ [19]. For example, the side chains are separated by around 14 CF₂ units ($n=7$) in a membrane of 1100 EW. Moreover, the equivalent is equal to 1000 divided by the exchange capacity in milliequivalents per gram[2].
The simplified cross-sectional diagram of an ionic polymer transducer without external field is presented in Figure 1.3. For a Nafion-based ionomer, the metal electrodes at the boundary can be platinum with a layer of finishing gold to improve surface conductivity, with the thickness of platinum diffusion zone up to 25 µm and the gold overlay of 1 µm [20]. The fluorocarbon backbone is hydrophobic while the sulfonate group at the end of a side-chain is extremely hydrophilic and can absorb as much as 30 water molecules per exchange site and more than double its volume [21]. This dissolution frees the cations associated with each pendant chain so that unbound cations can roam within the water in the membrane while the anions, the sulfonic acidic groups, remain attached to the fluorocarbon matrix. In the electrically neutral state, cations, water and neighboring sulfonic groups aggregate into small cross-linked clusters to remain in their lowest energy state [2]. The most accepted mechanism behind IPT actuation until recently is illustrated in Figure 1.4. Under the applied step voltage, cations carrying water move across to the cathode, which results in the local deformation of the transducer, specific to the anode and cathode boundary layers. Direct measurements have revealed continued cation depletion from the anode and accumulation into the cathode boundary layers [22]. As shown in Figure 1.4, the accumulation of cations and water at the cathode causes the expansion of the cathode and the contraction of the anode. This cations and water transport mechanism is identified by Nemat-Nasser through the observations of an experiment using an ethylene-glycol based transducer [23]. The step response of the ionomer lasts for a longer time by using this much more viscous solvent. The phenomenon was observed that the anode surface of
the transducer dried out during the actuation. This laboratory observation established the presence of water movement due to the migration of cations. Therefore it is one of the key issues to track cations and water during the actuation.

Figure 1.5: Illustration of back relaxation of ionic polymer transducers under stepped DC voltage.

Followed by the initial fast motion toward the anode, a Nafion™-based IPT often exhibits slow back relaxation toward the cathode; while a Flemion™-based IPT, in which the ionic side group is made up with weakly acidic carboxylate, has the slow relaxation toward anode. As seen in Figure 1.5, the tip movement from point A to B is its fast actuation stage; while the step voltage is still applied, the movement of the tip reverses slowly from point B to C and in this back-relaxation point C is usually beyond the starting point A; finally the actuator stops at point D. The mechanism behind the relaxation has not been modeled yet and the attempted explanations includes the back diffusion of water and the reorganization of cations at the cathode [23]. This dissertation will only focus on modeling of the fast actuation stage.

Several groups of researchers have started exploring the mechanism behind the sensing ability of ionic polymer transducers. According to the work by Nemat-Nasser and Li [24], polarization response plays a significant role in sensing. The imposed deformation
displaces the effective anion and cation charge centers within each cluster, producing an effective dipole; the average electric field in the membrane is the sum of the contributions from all the dipoles along the thickness direction. Based on the demonstration of reciprocity between actuation and sensing [25], Farinholt and Leo [26] studied the charge sensing properties in a manner similar to the actuation. The hypothesis is that the charge density at the surface of the polymer is proportional to the induced stress and this assumption was applied in the description of actuation mechanism [24].

1.2 Factors that influence the performance of IPTs

Since the cation transport and redistribution ultimately causes actuation, actuation performance is first attributed to Nafion membrane morphology, including the morphology of Nafion backbone and the organization and distribution of ionic clusters. Nafion membrane is found to possess little or no cross-linking which means individual polymer chains are not linked together by covalent bonds to form one giant molecule [4]. This lack of chemical cross-links in polymer chains generates a dynamic morphology for Nafion [27]. Otherwise, the presence of hydrophobic polymer chains retards ions by increasing the tortuosity of the diffusion path [28]. On the other hand, ionic clusters and ion channels offer the path for cation transport. These ionic cluster regions may be a major factor in ionic transport properties. Thus, a wealth of morphological information from numerous scattering and diffraction studies has been obtained and reported and will be discussed later in this chapter. This section will focus on the factors that influence performance that are measurable from experiments and their physical explanations.

Considerable efforts have been taken on to improve the performance of ionic polymer transducers. Some efforts focus on the morphology and conductivity of the metal electrodes. Shahinpoor et al. has reported that lower surface-electrode resistance generates higher actuation capability in the ionomers [29]. The reduced surface-electrode resistance was achieved by depositing a thin layer of silver (or copper) on top of the platinum electrode. As a result, up to 20% improved forces were obtained. While electrolysis is introduced with the applied voltage at levels above 1.23V, Fujiwara et al. [30] has described the construction of a gold-composite actuator. No gas evolution was observed up to the maximum applied voltage (above 2.0 V), due to the much higher overvoltage for hydrogen and oxygen evolution.
on gold than platinum.

Akle et al. [31] discussed a series of experiments that characterized the actuation response of three families of ionomers including Nafion. The analysis focused on the response at frequencies higher than 1 Hz to approximately 200 Hz to avoid the influence from relaxation in the ionomers on the charge-to-deflection relationships. A linear correlation, which was independent of the polymer composition and the plating parameters, was obtained between the strain response and the capacitance of the material. Since the low-frequency capacitance of an ionomer is strongly related to charge accumulation at the blocking electrodes, this correlation suggests a strong relationship between charge accumulation at the cathode and mechanical deformation. Based on this correlation, Akle et al. developed ionic electroactive hybrid transducers with the increased capacitance to increase the maximum displacement [32]. The direct assembly process was used to mix an ionic polymer dispersion with a fine conducting powder and attach it to the membrane as an electrode. Capacitance in such ionomers can be described as an electric double layer so that ions accumulated in a thin boundary layer close to the metal-polymer interface [9]. Therefore, when the conducting powder with a large surface area was incorporated as electrode materials of the ionomers, capacitance was increased by increasing the conductor-ionomer interfacial surface area or surface area-to-volume ratio of the metal particulate. It is reported that electrodes applied using this method of mixing RuO$_2$ particles and Nafion$^{\text{TM}}$ dispersion provided 5 times the displacement and 10 times the force compared to a transducer made with conventional methods. Strain rate in the ionic polymer transducer correlates to the conductivity of the electrode.

Another study focuses on the form of cations. Nemat-Nasser and Wu [33] studied IPTs in various Na-TBA cation compositions under direct current. Various actuation behaviors, including the duration, speed and the maximum amplitude of the initial bending toward the anode and the speed of the subsequent relaxation, can be controlled by properly adjusting the corresponding cation content. The effects of cations on the performance of IPTs in sensing and actuation were discussed by Shahinpoor et al. [34, 35]. Among samples containing various monovalent and divalent metal cations including Na$^+$, Li$^+$, K$^+$, H$^+$, Ca$^{++}$, Mg$^{++}$ and Ba$^{++}$, the IPT with Li$^+$ shows the best performance in terms of the maximum force generated under a given voltage as well as force density per given power input. Li$^+$ is the smallest bare ion in the set but has much larger hydration capability.
hydration process refers to the formation of a tightly held sheath of water molecules bound around counter ions and this hydration shell was mentioned as well in the modeling work by Nemat-Nasser [22]. It is concluded that the cations with higher hydration numbers should produce larger displacement and more force and this hydration process predominates rather than electrostatic field interaction. The lowest mobility of Li\(^+\) is explained by the the viscous drag it experiences. Farinholt et al. [36] found that when the sensing and actuation response was normalized with respect to the electrical impedance, the electric potential to strain relationship is much more consistent between various cation species. Cations tend to change the transducer’s impedance or the resistive nature, changing the performance of actuation and sensing.

Solvent viscosity can affect the speed of ion transport. Its dielectric property is one of the key factors to determine the performance by varying the electrostatic interaction between ions. Bennett et al. [37, 1] explored the use of highly stable ionic liquids to replace water. Ionic liquids are non-volatile and have greater electrochemical stability than water which has a chemical breakdown at relatively low operating voltages. It has been demonstrated that the ionic liquid-swollen IPTs based on Nafion\(^{\text{TM}}\)- based membranes exhibit enhanced stability in their performance when operated for long periods of time in air. Moreover, they are observed to not exhibit the characteristic back-relaxation which limits the low frequency response of IPTs. The main drawback is the decrease of the magnitude and the speed of the response due to the fact that ionic liquids are viscous diluents. Figure 1.6 shows the chemical structure of two types of ionic liquid. Spectroscopic

![Figure 1.6: Chemical structure of the (a) EMI-Tf ionic liquid, (b) EMI-Im ionic liquid [1]](image)
investigations show that the ionic liquid displaces the counter ions away from the exchange sites by associating the sulfonate groups with its cations and associating the counter ions with its anions. A model for charge transport in ionic liquid-swollen IPTs is proposed in which the counter ions hop along the free anions of ionic liquid not in association with another ion of the polymer. Trends relating the actuation speed to the counter ion size and uptake of ionic liquid predicted by the model agree with experimental results.

Hydration is another factor to influence the performance of IPTs. Stiffness of the transducer decreases as water hydration increases until fully hydrated [22] due to the stiffness change of ionic polymer chains. The cation diffusion increases as the solvent swells because of a decrease in the volume fraction of the hydrophobic polymer matrix and the increase in the ability of cations to move between clusters. The hydration process from ion insulator-to-conductor transition can be described by a percolation model [38, 6]. At low water content, the membrane consists of isolated ionic clusters as revealed by the extremely low value of the ionic conductivity. By increasing the water content, clusters swell and more clusters are connected leading to the large increase of the ionic conductivity which indicates a percolation of the ionic aggregates. Diffusion coefficients vary dramatically for small changes in swelling as well [28].

In conclusion, the performance of the ionomeric depends on the structural morphology of the membrane, morphology at the electrodes, cation forms, hydration and properties of the solvent.

1.3 Motivation

Many aspects of electromechanical performance features of the IPT remain only partially understood impeding its widespread use and the development of new properties. For ionomeric polymer transducers, transport of charge due to electric stimulus is the primary mechanism of actuation. Therefore, one of the key issues to understand actuation performance, including the maximum achievable strain and strain rate, is to track the distribution and dynamics of cations.

Given a certain cation form and water content, the transport of cations depends on the morphological structures inside the ionomeric and at the electrodes. For example, if a cluster-network model is assumed, hydrophilic ionic clusters and connected ion channels
will facilitate the transport of ions and water in the membrane while ionic exchange sites which make up the clusters are constrained by the fluorocarbon matrix. Strain rate in the ionic polymer transducer depends on the conductivity of the electrodes and the viscosity of the solvent. The conductor-ionomer interfacial surface area plays an important role in charge accumulation at the cathode which correlates to the deformation and energy density of the ionomeric. Moreover, hydration changes the morphology of the hydrophilic phase and the properties (e.g. stiffness) of the hydrophobic pendant chains.

Obviously, those correlations involve interactions with morphologies at microscopic, mesoscopic and macroscopic levels. This feature produces tremendous uncertainty for modeling and prediction of the ionic polymer transducer. Thus a model needs to be designed to cover multiple scales: On one hand, the simulation has to be carried out as a function of the morphology of electrodes and the morphology of ionic cluster regions. Those atomic level descriptions can be included in Monte Carlo simulations of ion hopping model. On the other hand, a hand-shaking algorithm is needed to bridge the Monte Carlo simulation and a continuum model to obtain macroscopic quantities and compare with experimental measurements.

The rest of the chapter is organized as follows: first Nafion\textsuperscript{TM} membrane morphology is discussed based on a variety of experimental techniques. The next section will focus on the modeling works of the ionic polymer transducer. Finally, the Monte Carlo method and ion hopping model are introduced.

### 1.4 Morphological studies of Nafion\textsuperscript{TM} membrane

The prominent morphological studies of Nafion are presented from numerous scattering and diffraction studies, such as small-angle X-ray scattering (SAXS), wide-angle X-ray diffraction (WAXD), small-angle neutron scattering (SANS), atomic force microscopy (AFM), transmission electron microscopy (TEM) and nuclear magnetic resonance (NMR) microscopy. Many groups evaluate the influence of environmental perturbations, e.g. solvent swelling and varying cation forms, for comparison and validation of morphological models. Mauritz and Moore \cite{39} conducted a comprehensive survey of the morphological characterization of Nafion. The scope of this section is to emphasize those potential morphological structures which may be used in the future computational model. The first section describes the ionic
domains, where a model of interconnected ionic clusters has been widely accepted though still debated. The second section concentrates on structural characterizations of the membrane, whereas a universally accepted structural model has not been defined. Quite a few morphological models, though established with substantially different structural descriptions have been presented and still remain debated, because it is complicated to separate or obtain morphological information from scattering and diffraction data [39].

1.4.1 The morphology of ionic domains

The existence of ionic clustering was proposed by Gierke [2] in 1981. The results from Small angle X-ray scattering on hydrolyzed Nafion show a wide range reflection with an equivalent Bragg spacing of 3 to 5 nm. This reflection is interpreted by Gierke as ionic clustering in Nafion, referring to nano-scale hydrated ionic aggregates at a distance with each other and embedded in the fluorocarbon matrix, even though there is much concerning whether this SAXS signal is related to the interparticle spacing or the intraparticle dimension. With reference to the cluster structure, Gierke suggested a nearly spherical, “inverted micellar” model as shown in Figure 1.7. Sulfonic acid sites are located close to the surface of the sphere for ion exchange sites are inclined to be highly hydrated and meanwhile their positions can reduce unfavorable interactions between water and the fluorocarbon matrix. The cations create an inner circle corresponding to the outer shell of anions and form associations of ion pairs or pseudo dipoles with anions. This geometric arrangement enables any counter ion traveling inside to be repulsed by the cation circle and to be pushed and attracted close to the cluster surface.

Over the years, ion cluster morphology has been in agreement with the results from the studies using other techniques. Elliott [40] evaluated the shape and spatial distribution of ionic domains under the application of uniaxial extension, based on a maximum entropy analysis of SAXS data. The results support ion clustered morphology with a hierarchical scale of structure. The smallest scale consists of a collection of roughly spherical ionic clusters. Either the clusters or the mean separation between clusters are anisotropically coherent. The clusters are agglomerated into higher order structures. Their shapes are decided by the spatial coherence of the clusters, and they are responsible for the low angle upturn in the SAXS.

Atomic force microscopy (AFM) is a useful tool for the examination of surface tex-
Figure 1.7: A visual depiction of inverted micellar structure by Gierke[2]

tural features and McLean et al. [3] demonstrated the ability of AFM to characterize the surface and near-surface morphology of the ionic domains in Nafion membranes. In contrast to SAXS techniques which can resolve individual ionic cluster relatively well because SAXS has good contrast for ionic domains, AFM is better at detecting the fluorine-rich crystallites in addition to deciding the relative morphological position of the ionic species and domains. Fluorocarbon crystalline domains and ionic domains were imaged using tapping AFM by the normal “stiffness” contrast. Phase data for Nafion 117 exhibits a broad level of uniformly spread ionic domains which are likely individual ionic clusters or “clumps of multiple ionic domains” with a “clump” size of about 4-10 nm in diameter. Those “clumps” are most probably agglomerates of a few ionic clusters. After soaked in deionized water, the clusters and cluster agglomerates have the approximately enlarged sizes of 7-11 nm. Most of the cluster agglomerates were observed as large channels making up the ionic cluster rich phase. The data support the model of Gierke et al. though cluster shapes cannot be conclusive other than approximately spherical. Surface morphology was reported as illustrated in Figure 1.8 consisting of fluorocarbon crystallite, ionic clusters and few angstroms of surface excess layer containing mostly fluorocarbon with very few ionic species. James et al. studied hydrated Nafion membrane with AFM and SAXS combined with a maximum entropy (MaxEnt) reconstruction [41]. Individual clusters ranging from 3 to 5 nm were
observed and the dimension of cluster agglomerates varied from 5 to 30 nm.

Figure 1.8: Schematic picture of Nafion surface morphology based on AFM studies by McLean et al. [3]

Transmission electron microscopy has been used to investigate the Nafion membrane. Ceynowa [42] examined ultra-thin sections (60 - 80 nm) of Nafion 125 membrane with stained lead ions. The results show uniformly distributed “dark points” 3-6 nm in diameter, which were interpreted as ionic groups. The interpretation was verified by the exchange of the Pb\(^{2+}\) ions with the H\(^+\) ions and no previous features were observed. Porat et al. [43] studied the microstructure of Nafion EW 1100, especially its crystallinity, using TEM and electron diffraction. Homogeneously distributed ion clusters with 5 nm in diameter were exhibited, consistent with the ion clustering proposed by Gierke et al. [2] again. The results from electron diffraction showed randomly distributed single crystals with an average distance of several microns. The diffraction pattern suggested that the fluorocarbon backbone of Nafion is in the form of a linear zigzag chain instead of a twisted chain.

Gierke et al. [2] have also discussed the effect of equivalent weight, cation form and water content. Based on the assumption of spherical aggregates, Gierke estimates cluster dimensions using simple geometric variable elements, for example, for EW 1100, there are 84 ion exchange sites and 1200 water molecules within each cluster. The cluster diameter calculated is 4.31 nm compared with 4.78 nm from Bragg spacing. With decreasing equivalent weight at the given water content, Gierke suggested a steep increase in \(N_p\), the average number of ionic exchange sites per cluster. The calculation results show as water swelling, both the cluster diameter and exchange sites per cluster increase, which suggests that the cluster dimension grow not only by an expansion of the original cluster but also by a reorganization of exchange sites. Therefore, the number of clusters decreases in the fully hydrated membrane. This allowance of cluster reorganization strongly indicates an inhomogeneous distribution of clusters in ionic domains [39].
However, the prediction of change in the number of ions per cluster $N_p$ due to varied EW and water content proposed by Gierke et al. have been questioned by Kumar et al. [44] through the interpretation of small-angle X-ray and neutron scattering. Kumar et al. assumed that the ionic clusters were noninteracting hard spheres and the closest approach distance between clusters is equal to the diameter of the cluster. The calculations showed only a small change from 48.2 to 53.5 in $N_p$ with decreasing EW compared with the results from Gierke et al. [2], where the value of $N_p$ changed from 43 to 95. Moreover, Kumar et al. suggested a small increase in $N_p$ with initial increase in water content and a decrease in $N_p$ at higher water content. This behavior was explained as the increased elastic forces on the chains from stretching, which forces some ions out of the existing clusters. The ions forced out of the cluster have chances to form another cluster. Therefore, Kumar indicated a more complicated recombination for ions during water swelling while Gierke et al. only suggested a simple regroup of neighboring sulfonate groups.

Based on SAXS study, except the spherical ion cluster model there were two prevalent models for the morphology of ionic domains, including a core-shell model and a lamellar model. Fujimura et al. [45, 46] examined the swelling behavior of Nafion membrane and reported that the microscopic degree of swelling determined by SAXS was much larger than the macroscopic degree of swelling. Fujimura et al. concluded that this experimental evidence favored an intraparticle core-shell model rather than an interparticle, spherical ionic domain model. In this particular core-shell model, ion-rich core is surrounded by a shell of fluorocarbon chains and these core-shell particles are dispersed in a matrix of fluorocarbon chains. A computer simulation was carried out to predict the changes of the SAXS profiles with water uptake and deformation based upon the two models, however, the two models turned out to give similar effects on the variation of the profiles and qualitatively account for general features of the experimental observations. Furthermore, the core-shell model was questioned owing to “the unfavorable electrostatic energetics of having isolated ion-dipole pairs imbedded in a fluorocarbon medium with a very low dielectric constant” [2]. According to the core-shell model, the number of clusters has to hold constant during water absorption which violates the experimental observation [44]. The number density of ionic clusters varies as a function of water content [41]. For the spherical cluster model, the difference in microscopic and macroscopic swelling has been the focus of debate over the years. James et al. [41] explained that the decreased number of clusters as water
increased caused the observation that the bulk volumetric swelling is significantly less than the swelling inferred from scattering measurements. Kumar et al. [44] have even pointed out this comparison is invalid because Bragg’s equation cannot be applied to the system where the scattering peak determines interparticle distance instead of intraparticle distance.

In conclusion, fluorocarbon chains inside Nafion membranes appear semicrystalline character consisting of both crystalline and amorphous region; for ionic domains, the existence of ionic clusters has been observed using SAXS, SANS, TEM and AFM techniques, however, the spherical cluster model proposed by Gierke is inadequate to explain the observed swelling data. The ion organization within each cluster, including the number of ion exchange sites etc., remains inconclusive. It is the opinion of the author that further description of the cluster reorganization during the swelling is the key issue to answer these related questions, though this reorganization is a dynamic process.

1.4.2 Structural morphological models

Following the morphological characterization for Nafion membranes, numerous efforts have attempted to define a structural morphological model for the ionomer. Generally speaking, there are a two-phase model proposed by Marx et al. [47], containing a hydrophobic phase and a hydrophilic phase and a three-phase model proposed by Yeager [4] (see Figure 1.9) which includes (A) a fluorocarbon backbone, part of which is microcrystalline, (B) an interfacial region containing pendant chains, water and cations which are not in clusters, (C)
the clustered regions where the majority of the ionic exchange sites, cations and absorbed water exist. The principal models, which have involved nano scale structure geometry and have considered spacial distribution of ionic domains for ion transport, include a cluster-network proposed by Gierke et al., a sandwich like model proposed by Haubold et al., a local-order model porposed by Dreyfus et al., a rodlike model proposed by Gebel et al. and a ribbon like model proposed by Rubatat et al.

Based on the morphology determined by SAXS studies, Gierke [5] proposed a cluster-network model shown in Figure 1.10. The model suggests that hydrated Nafion separates into fluorocarbon matrix and spherical ion clusters which are connected by short channels for ion transport. In Figure 1.10, the cluster separation between two centers (5 nm), or the interparticle distance, matches the SAXS maximum. Cluster size and the length of ion channel were deduced by a simple geometric model. The location of sulfonic acid groups can minimize the interaction between backbone and water, minimize the electrostatic repulsion of sulfonate groups and help ion permselectivity. The spacial distribution of clusters on a paracrystalline lattice was assumed for space-filling calculations. However, the observed spatial cluster distribution was not paracrystalline [39]. Since the existence of channels has not been demonstrated by any experimental evidence, Orfino and Holdcroft [48] suggested clusters could be simply bridged by single ionic sites for their calculations showed the separation distance between two clusters matched the size of a single, hydrated ionic group. Despite this model by Gierke et al. has based on various assumptions and not suitable for a definitive description; a great number of papers have referred this model as a principle basis to analyze the properties of Nafion membranes.

Dreyfus et al. [49] proposed a new model based on the existence of a local order
between ionic clusters and a long-range gas-like disorder. Each ionic cluster is assumed to be spherical and surrounded by four clusters in a tetrahedral coordination. The four first neighbors of an ionic cluster are positioned at a well-defined distance while the rest of clusters are assumed to be randomly distributed. This arrangement of ionic clusters in hypercrystallites with a diamond structure is accounted for by electrostatic interactions and allows for the interpretation of the peak observed in diffraction experiments. Gebel et al. [50] recorded the SAXS and SANS spectra of water swollen Nafion 117 membranes and demonstrated that the local order model is able to adequately reproduce the shape and the intensity of the scattering curves. Gebel et al. [51] also studied the membranes using SAXS and SANS over a comparable range of equivalent weights. The local order model is found to reproduce the scattering profiles depending on the EW. The discrepancy for large EWs is due to the presence of crystalline component modifying both the position and the intensity of the ionomer peak while the contribution of crystalline component has been ignored in the model. The model was not able to fit the scattering curve for the lowest EW membrane neither, due to the large water uptake up to 80%. Under this large degree of swelling, the membrane was described as a connected rodlike [52, 53] network. This rodlike network was also suggested by Lee et al. [54]. Lee et al. measured the H-H and O-H correlations within the nickel form of Nafion membrane using a combination of SAXS and SANS. The comparison with those for bulk water leads to the preliminary conclusion that when the water content is high, the local water structure is similar to that of bulk water. At lower water contents, water structure is likely to be influenced by H₂O - SO₃ interactions. The H-H correlation function, however, contains information about both the shape and the distribution of clusters. Average cluster radius of 1.85 nm was obtained and from the long-range behavior of H-H correlation, mean center to center distance of clusters was 7 nm. The experimental data do not support a series of isolated aqueous clusters by simple space-filling calculations. “Only a network, consisting, for example, of rodlike structure, can be consistent with the experimental data”. Like ion channels with 1 nm in diameter proposed by Gierke et al. [2], the existence of connecting cylinders has never been directly evidenced by scattering techniques and electron microscopy in swollen membranes [6].

Spherical ionic clusters with local order and inter-connected rods, though appear far from each other in geometry, are not mutually exclusive. It is possible to convert one model into the other through a proper variation of parameters. Gebel studied the structural
Figure 1.11: Schematic description of structural evolution during water swelling by Gebel [6]

evolution depending on the water content using SAXS and SANS techniques as well as ionic conductivity and swelling properties [6]. As depicted in Figure 1.11, the dry membrane consists of isolated spherical ionic clusters with a diameter around 1.5 nm and an inter-cluster distance of 2.7 nm. By a light swelling, clusters become isolated small water pools at the polymer water interface, the spherical shape is assumed to minimize the interfacial energy and ionic conductivity has extremely low value. The author suggested the local order model to describe the cluster spatial distribution at this stage. When water volume fraction $\phi_w$ increases to 0.2, the large increase of the ionic conductivity indicates a percolation of clusters. The continuous evolution of the SAXS and SANS spectra stresses that the geometrical constraints from the polymer chains are severe and govern the structural evolution. Between $\phi_w = 0.3$ and $\phi_w = 0.5$, the increase of the ionic conductivity as water content increases implies that both the connectivity and the diameter increase. Spherical ionic clusters with
4 to 5 nm in diameter are connected with channels with the lengths and the diameters unknown. No significant change in scattered intensity; thus the structure is still formed of clusters in local order. The polymer reorganization is suggested to be facilitated above the percolation threshold. When \( \phi_w \) values larger than 0.5, a spherical shape is not favorable to minimize the interfacial energy for the polymer volume associated with the ionic group is much larger than the average distance between ionic groups along the polymer chains. Therefore, an inversion of the structure occurs by the formation of connected cylindrical particles. Between \( \phi_w = 0.5 \) and \( \phi_w =0.9 \), the rod-like network swells and the ionic conductivity decreases due to the dilution of the ionic groups. This structural evolution model presented a persuasive mechanism which involved two different types of morphology for the hydrophilic phase over a wide range of water content, in agreement with a dynamic process, however, the phase inversion lacked support of both thermodynamic justification and the scattering profiles.

### 1.4.3 Computer simulations for Nafion morphology

In this section, efforts using computer simulations to construct the structure of hydrated Nafion will be introduced and the conclusion will be given for the literature survey of hydrated Nafion morphology. In the work of Khalatur et al. \[55\], semi-empirical quantum mechanical calculations were carried out to investigate the aggregation process of sulfonic acid groups with water. The results support an irregularly shaped cluster surfaces which are favorable to the formation of long channels of connected water-containing aggregates. Blake et al. \[56\] have investigated the structural properties of the hydrophilic phase as a function of the hydration level using molecular dynamics. The hydration energies and the electrostatic interactions, rather than the influence of Teflon chains or the water-water interaction, are the main factors to control the structure. In the percolating structure, the water forms irregular curvilinear channels branching in all directions. At all levels of hydration the pendant chains hug the walls of the channel and the sulfonate groups point to the center of hydrophilic phase to increase the degree of solvation of \(-\text{SO}_3^−\). Compared with bulk water, the distribution of the number of water neighbors is significantly broader in the Nafion. For example, there are fewer water neighbors for water molecules near the walls of domain than those residing in the second solvation shell. It is accounted for as the highly inhomogeneous nature of the material.
Yamamoto et al. [7] presented a multi-scale simulation to study the proton-conducting polyelectrolyte membrane Nafion for a fuel cell. A mesoscopic structure of the hydrated Nafion was first built. Initially, polymer particles and water particles having the same size of 0.61 nm in diameter are randomly distributed in a unit cell with side length of about 28.4 nm. Those soft particles correspond to groups of several atoms, as illustrated in Figure 1.12 where particles A, B and C represent -CF$_2$CF$_2$CF$_2$-, -OCF$_2$C(CF$_3$)FO-, and -CF$_2$CF$_2$SO$_3$H respectively. A dissipative particle dynamics simulation was carried out to study the dynamics of the soft particles interacting by repulsive forces between particles, hydrodynamic drag, random forces due to thermal noise and spring forces from the bead-spring structure. Equilibrium states were displayed as a sponge-like structure which is essentially identical to the cluster-network model. However, the shape of the water clusters is not spherical and the water regions are indistinguishable structures of water clusters and channels. Based on this mesoscopic structure, a molecular structure is generated by mapping atoms to the position at the corresponding particles using a Monte Carlo technique. Then molecular mechanics and molecular dynamics simulations were performed to obtain a stable structure without stress. The self-diffusion coefficients of water molecules are in good agreement with experimental study in terms of magnitude and dependence on the water content. The hydronium ion is found to be more stabilized in the middle of a water cluster than close to the cluster surface because of the dielectric polarization effect of the mesoscopic structure. On the other hand, it is seen that detailed molecular dynamics simulations of ionic channels are currently limited to short time equilibrium simulations [57].

In conclusion, a clear 3D description of the morphology throughout the hydrated
Nafion membrane supported by scattering data has not been defined yet. The consensus among groups includes the ionic clustering in nano scale and the separation between hydrophilic and hydrophobic phase. The shape of clusters, the organization inside and the connection between clusters still remain debated. The degree of hydration and EWs can affect the morphology as well as ion transport properties and have been used to validate any proposed model. It is the opinion of author that the irregularity shown in computer simulations matches the inhomogeneous nature of the membrane rather than a model composed of single patterns or uniform structural elements.

1.5 Modeling of ionic polymer transducers

There have been many attempts to devise models for the electromechanical coupling properties of ionic polymer transducers. Since the governing mechanism behind actuation, relaxation and sensing of ionic polymer transducers have not been fully understood, these models use different assumptions of dominant mechanisms as a basis. Much of the modeling work offers enlightening understanding for the material, help to optimize the material at the molecular level for better performance or to design new materials and devices.

The first category of models introduced here will describe the IPT with equivalent circuit for the IPT is both inherently resistive and capacitive which allows for the material to be modeled using RC circuit. Kanno et al. [58] proposed the first gray box model in which the ionic polymer was modeled as a network of a capacitor and resistor in series. Based on the experimental observation, the current through the membrane differentiated with time was believed to be proportional to the internal stress for the bending motion. A finite element model was used to transform the internal stress into the expansion and contraction of the corresponding surface. Newbury and Leo [59] have developed a linear electromechanical model for ionic polymer materials. It is based on an equivalent circuit representation similar to equivalent circuit models for piezoelectric elements. All of the terms can be frequency dependent, mechanical impedance derived from beam theory and electrical impedance is modeled as a series combination of resistive and capacitive elements. The coupling relationship was derived using sample geometry and three measured parameters including the effective permittivity, elastic modulus and effective strain coefficient. Both sensing and actuation were modeled in a single set of expressions and a reciprocity
was stressed between sensing and actuation. This dynamic model can be used for the design of new devices and material systems that utilize ionic polymer materials as either sensors or actuators. Paquette et al. [60] used two sets of R||C circuit to model the upper and lower surface of the IPT, respectively. Another resistor was set in between to describe the resistance of the membrane. The expressions obtained from the concept were substituted into the linear irreversible thermodynamic relationship developed by De Gennes et al. [61].

Bao et al. [8] used a simple clumped RC model for actuation response of the IPT. The model could not produce the time response of current to fit well with the measured data. It was due to a fractal-like structure of the gold electrode diffusing into the polymer instead of a simple uniform metal layer. The fractal-like structure is schematically described as shown in Figure 1.13 (a), each level of “stickers” is associated with a capacitance and connected to each other by corresponding resistance. A distributed RC line model in 1.13 (b) has been constructed to represent the double-layer capacitance of the fractal-like electrode. The result shows the current response decreases exponentially with time as $t^{-0.5}$ which is close to the best fit of the experimental data as $t^{-0.45}$. The distributed RC line model considering the fractal morphology of the gold electrode is more accurate than the clumped RC model. However, the integration of this circuit model with the actuation model is still
under study. In this work, Bao et al. also developed a four-lumped parameter system to express the relaxation phenomena.

Modeling the IPT by using the equivalent circuit captures the feature of double layers at the polymer-metal interface, however, those models depend on empirical fits of experimental data rather than on the analysis of the fundamental physics. Efforts have emerged to focus on the micro-physicochemical process inside the membrane and the mechanisms behind the unique response of the IPT subjected to an electric field. Several groups believe the water redistribution produces the swelling at the cathode. Tadokoro et al. \[62\] proposed a white-box actuator model which assumed that travel of cations and water generated eigenstrains causing the deformation of IPTs. Electrostatic interaction was modeled showing a minor influence compared with the water movement. Nakano et al. \[18\] introduced a simple model to simulate the deformation of an IPT using finite element methods. In the model, the cation concentration is obtained by solving the Nernst-Planck and Poisson equations. Nernst-Planck equation considers three mechanisms for ion movement: Brownian motion, drift due to the potential field and diffusion due to the concentration gradient. Then water concentration is assumed in analogy with the cation concentration profile. From these results the thickness of the shrinking layer close to the anode is estimated and the strain is calculated. Lee et al. \[63\] has mentioned it is impossible to quantitatively measure the concentration distribution of water or ions during the dynamic actuation process. They suggested a hydraulic mechanical model in which the deformation are associated not only with water migration, but also with mechanical properties such as the modulus of hydrated polymer film, the modulus of platinum, the expansion coefficient of moisture and the geometric arrangement of composite layers. The classical lamination theory (CLT) was applied by dividing the membrane into 20 layers with equal thickness, each having different water content linearly increasing from the anode to the cathode. The deformation, bending moment and residual stress distribution of the IPT was quantitatively compared well with experimental results. However, the model is not suitable for transient response.

Many models have included the morphology of Nafion membranes and most of them based on the cluster-network proposed by Gierke et al. \[2\]. Hsu et al. \[64\] applied percolation theory to investigate ion transport occurring in the system of ionic insulator-to-conductor transition in Nafion. On a two dimensional grid, empty and occupied sites correspond to the ionic insulator phase (fluorocarbon matrix) and the ion conducting clus-
ter phase. An experiment to measure ion conductivity was used and the threshold volume fraction of the aqueous phase at the insulator-to-conductor transition was obtained. This threshold is less than the value for a completely random system in percolation theory, which demonstrates that ion clusters tend to spread out into an extended conductive network for ion transport. Datye et al. [65] presented a model for clustering and transport in ionomer membranes. The neutralizing counter-ions form a dipole layer at the surface of an ionic cluster. The orientations for dipoles are treated as parameters that must be allowed to vary as the system minimizes its free energy and seeks its most favorable configuration. The equilibrium size of the ionic clusters is determined by balancing the electrostatic and elastic forces. Current efficiency through the membrane was computed by using site percolation theory. Compared with the work by Hsu et al. [64], Datye et al. introduced the influence of dipole layers inside clusters, though the results cannot make quantitative comparison with experiment for the treatment of the system as a uniform dielectric. Datye [66] also extended the previous work and studied the electrostatic energy as a function of temperature and cluster size. In the high-temperature phase, the orientations of the dipoles would be disordered; the electrostatic energy did not show major difference when the cluster shape was changed. Nemat-Nasser and Li [67] studied ionic clustering using a micromechanics approach. The cluster size is decided by minimizing the free energy including electrostatic dipole interaction energy, elastic energy due to the reorganization of polymer chains and the cluster surface energy. The results support that the cluster shape is spherical in the absence of an electric field and becomes oblate under an applied electric field. The cluster size as a function EW and water content is in accord with experimental observations.

Moreover, Nemat-Nasser and Li have developed the first comprehensive micromechanical model to predict the response of ionic polymer transducer [24]. Uniformly distributed ionic clusters and ion pairs inside clusters are assumed. Compared with those hydraulic descriptions of actuation response of IPT, Nemat-Nasser and Li suggest that the electrostatic forces are dominant in fast actuation. Therefore, the cations accumulated at the cathode cause a microscopic, locally imbalanced net charge density which yields internal stresses acting on the fluorocarbon backbone. In the linearized approximation, the charge density is zero inside the membrane; thin boundary layers contain most of the imbalanced charges which will induce the electro-static stress and a bending moment over the membrane. The prediction of the tip displacement is in good correlation with experimental data.
In their later work [22], effects produced at the boundary layers were discussed in detail. Those effects include the change in the effective stiffness, electrostatic force, effective electric permittivity, the amount of water molecules and osmotic pressure. It is also mentioned in this work that when bending stiffness is given, maximizing the capacitance and surface conductivity of the IPT is necessary to increase the tip displacement.

Nemat-Nasser et al. have accomplished considerable investigation toward the understanding of the actuation response. However, the assumption of the complete ion pairing inside clusters has been questioned by Weiland and Leo [68]. Within a given cluster, a computational micromechanics model has been designed to track the position of each ion by considering the influences of ion-ion interaction, mechanical stiffness of the pendant chain, cluster surface energy and external electric field. The results predict incomplete ion pairing which can assist cations transport. Therefore, the classic assumption will underevaluate the actuation response. Regarding the mechanisms behind the initial fast actuation, Weiland and Leo [69] also assume the interplay of mechanisms including elastic, electrostatic and osmotic effects as studied by Nemat-Nasser and Li [24]. The model bases on the balance of forces acting on each dipole; dipole orientation and distortion are obtained. It is believed that the dipole distortion directly leads to the distortion of clusters which results in the fast initial deformation. The work proves the hypothesis that a polarization mechanism dominates the actuation response.

Wallmersperger et al. [70] developed a computational model of transport and electromechanical transduction. Ion transport was calculated by solving a coupled chemo-electrical multi-field formulation subjected to the electric potential and zero flux boundary conditions. The spatio-temporal charge density profile was obtained and the bending moment was assumed to be a summation of linear and quadratic functions of the charge density. The deflection was calculated using an Euler-Bernoulli beam theory. Basically, the authors believe the deformation in the actuation is directly related to the charge density profile.

1.6 Research objectives

This modeling work is based on the hypothesis that the actuation response is directly related to properties of ion transport in IPTs and will focus on the morphological influence to improve the actuation performance. The technical objectives are outlined as follows:
• Develop a spatio-temporal Monte Carlo simulation to track cations movement when the IPT is subjected to an electric field.

• Develop a Monte Carlo simulation to model how the morphology influences the actuation performance.

• Use multi-scale modeling to increase the thickness of the substrate to 200µm for both the steady state response and the dynamic response.

• Compare the simulation results with experimental data.

Based on recent experimental findings, the morphology of conducting powders is important for obtaining more ion accumulation at the cathode, maximizing the capacitance and surface conductivity and increasing the generated strain. Compared with existing continuum models, the current model is able to investigate the complicated geometry of conducting powders at the polymer-metal interface. For example, mechanical strain of the ionic polymer transducer can be increased by adding conducting powders at boundary layers. However, there is a saturation point when mechanical strain starts to decrease because too many added powders slow down or even block the ion movement at the polymer-metal interface. It is difficult for a continuum model to predict this saturation point since the finite size of conducting powders is not easy to include as a parameter in a continuum model. However, Monte Carlo simulations can easily incorporate the information of powders geometry for calculations. On the other hand, the model bridges the ion transport description at the level of nanometers and the measurable macroscopic performance such as current, tip displacement, etc., therefore, the model enables experimental validation.
Chapter 2

Monte Carlo Simulation of the Ionic Polymer Transducer

Although the understanding of fundamental mechanisms that cause actuation in the ionic polymer transducer is still under debate, the previous research results relate actuation mechanisms to ion conduction across the Nafion$^\text{TM}$ membrane. Leo et al. [70] modeled the electromechanical coupling by the expansion form:

\[ \sigma(x,t) = \alpha \rho(x,t) + \beta \rho^2(x,t), \]  

(2.1)

where \( \alpha \) and \( \beta \) are coefficients that define the linear and quadratic terms of the transduction model, \( \sigma \) denotes the stress and \( \rho \) is the space-temporal charge density. Akle [9] wrote a similar model by using mechanical strain and charge density:

\[ \varepsilon = \alpha Q + \beta Q^2, \]  

(2.2)

where \( \varepsilon \) represents the strain and \( Q \) is defined as the charge per unit area. From equation 2.2 we see the existence of a correlation between the surface charge accumulation and the mechanical deformation in ionomeric actuators. Therefore, the goal of this chapter is to use a Monte Carlo simulation of ion hopping to model the charge density and current density for ionic polymer transducers.

The chapter is organized as follows: the background of Monte Carlo simulation is introduced first and the sampling techniques used in ion hopping model is described as well. The next section will describe the ion hopping model in detail. And then simulation results
and parameter studies are presented. The last section explains the parallel computation to speed up Monte Carlo simulation by using the Message Passing Interface library.

2.1 An introduction to Monte Carlo simulation

The Monte Carlo method can be described as a statistical method since it uses sequences of random numbers to perform the simulation. Credit for inventing the Monte Carlo method often goes to three individuals, i.e. Stanislaw Ulam, John von Neuman and Nicholas Metropolis. They are early pioneers in the field and applied the Monte Carlo method to simulate neutron diffusion for the atomic bomb during the second World War[71]. The method was invented in 1946 and later the first paper on the topic was published in 1949 by Ulam and Metropolis[72]. Their contribution was not to invent statistical sampling. Instead they utilized the newly invented electronic computer to automate such sampling, developed algorithms for computer implementations and first found means of transforming non-random problems into random forms which can be solved via statistical sampling. Metropolis named the method after the famous casino in Monaco because of the similarity of statistical sampling to games of chance.

Roughly speaking, we can categorize problems handled by Monte Carlo methods into two broad types [73]: 1) Direct simulation of random processes. 2) Monte Carlo methods which recast deterministic problems in probabilistic terms.

Direct simulation can be used to study a naturally random system, e.g. a queueing system consisting of a group of random variables such as the arrival time, the service time, etc. Another example is its application to the control of floodwater and the construction of dams on the Nile [74]. This is a random problem because the quantity of water in the river is a random variable which varies from season to season. The goal is to simulate the water level by using direct Monte Carlo method when certain dams are built and certain policies of water control are exercised under extreme meteorological conditions. In finance, Monte Carlo method can be exploited to simulate standard European options pricing [75] for a stock price is a stochastic process. Additional applications can be found in various fields, such as reliability theory[76, 77], statistics[78], physical, biological and social sciences[79, 80, 81], etc.

The rest of the section will focus on the applications of Monte Carlo methods falling
into class II since Monte Carlo simulation of ion hopping is counted in this category. In these applications, the underlying problem is represented as part of another random system and then one performs a direct simulation of this new system. First of all, Monte Carlo integration is introduced for it is a standard way to introduce the associated sampling techniques in sophisticated Monte Carlo methods. In the second subsection, the related probability theory is reviewed and then ion hopping is considered as ions’ random walk to its neighboring sites and the probability density function for the random variable, i.e. the transition time interval is deduced. The last subsection explains how the transition time interval can be sampled by using a random variable that is uniformly distributed on \([0, 1]\) when direct sampling of its probability density function fails.

### 2.1.1 Monte Carlo Integration

Numerical integration is a simple problem that illustrates the use of the Monte Carlo method. Consider the evaluation of the following definite integral:

\[
I = \int_{a}^{b} f(x)dx, \tag{2.3}
\]

where \(f(x)\) is real-valued. As shown in Figure 2.1, the definite integral of \(f(x)dx\) from \(a\) to \(b\) is equal to the shaded area \(I\) under the curve \(y = f(x)\) bounded by the lines \(x = a, x = b\) and \(y = 0\).

![Figure 2.1: Monte Carlo Integration](image)

According to the mean value theorem:

\[
I = \int_{a}^{b} f(x)dx = (b - a)\bar{f} \approx (b - a)\frac{1}{n} \sum_{i=0}^{n-1} f(x_i), \tag{2.4}
\]

29
where $\bar{f}$ represents the average value of $f(x)$ in the interval $[a, b]$ and it is plotted as the red dash line in Figure 2.1.

Thus, we can use Monte Carlo simulation to sample $x$ as a random variable which is uniformly distributed over the interval $[a, b]$. For each $x_i$ there is a corresponding value of $f(x_i)$. After taking the average of $N$ observations of $f(x_i)$, the true value of the integral area $I$ on $[a, b]$ can be estimated by equation 2.4.

As the same concepts are expanded into a two-dimensional integral, Monte Carlo method can be used to approximate $\pi$. For example, the famous mathematics problem Buffon’s needle is essentially solved by Monte Carlo integration. Buffon’s needle problem is first posed in the 18th century by French naturalist Buffon: suppose we drop a needle onto a board plotted with parallel straight lines with the same width. What is the probability that the needle will lie across one of the lines on the board? The remarkable result is that the probability is directly related to the value of $\pi$.

In the simplest case shown in Figure 2.2, the length of the needle is unit one and the distance between lines is unit one as well. Whether the needle will lie across the line depends on two variables, the angle $\theta$ at which the needle falls against a line parallel to the lines on the board and the distance $D$ from the center of the needle to the nearest line. The angle $\theta$ varies from 0 to 180 degree and $D$ can be no more than half of a unit. As illustrated in Figure 2.2, both the needle (b) and (c) hit a line while the needle (a) does not. The needle will only hit the line if $D \leq \frac{1}{2} \sin \theta$. In Figure 2.3, if $D$ falls into the area bounded by the curve $f(\theta) = \frac{1}{2} \sin \theta$ and $D = 0$ (e.g. $D_0$ in Figure 2.3), the needle will hit the line. Otherwise the needle will miss the line (e.g. $D_1$ in Figure 2.3). Thus the probability of hitting a line is equal to the ratio of the bounded area to the entire rectangle:

$$P = \frac{\int_0^\pi \frac{1}{2} \sin \theta d\theta}{\frac{1}{2} \pi} = \frac{2}{\pi}. \quad (2.5)$$

We can use random numbers to perform a simulation that solves this problem. We will generate a series of pairs ($\theta, D$) where $\theta$ is taken from a uniform random distribution between 0 and $\pi$ and $D$ between 0 and $\frac{1}{2}$. Each pair represents a point inside the rectangular in Figure 2.3. We keep track of the fraction $g$ of points falling inside the curve $f(\theta) = \frac{1}{2} \sin \theta$; that is, the points for which $D \leq \frac{1}{2} \sin \theta$. Since $g \approx 2/\pi$, we know $\pi \approx 2/g$.

To explain why Monte Carlo works, we will use the mean value theorem as well.
Based on the mean value theorem, the volume in Figure 2.4 (a) and (b) are identical. Object (a) is within the rectangle bounded by $0 \leq \theta \leq \pi$ and $0 \leq D \leq 1/2$. The height of the surface is 1 where $D \leq f(\theta) = \frac{1}{2} \sin \theta$ and 0 otherwise. Object (b) is within the rectangle bounded by $0 \leq \theta \leq \pi$ and $0 \leq D \leq 1/2$ with the height of the surface is $2/\pi$. Both (a) and (b) have the value of volume equal to 1 by some simple calculations. In Monte Carlo simulation, we set an accumulator to 0, randomly generate pairs of points $\theta, D$ from the rectangle, add 1 to the accumulator if $D \leq f(\theta) = \frac{1}{2} \sin \theta$ and add nothing to the accumulator otherwise. We are sampling from the surface in Figure 2.4 (a). After $n$ samples, we divide the contents of the accumulator by $n$, we produce an expectation for $2/\pi$. Recall the one dimensional integral in Figure 2.1, the value of $\bar{f}$ is obtained by sampling from the curve $f(x)$. Now in this two dimensional integration problem, the curve $f(x)$ becomes a surface $f(\theta, D)$ (see the shaded area in Figure 2.4 (a)) with the value:

$$f(\theta, D) = \begin{cases} 
1 & D \leq \frac{1}{2} \sin \theta \\
0 & D > \frac{1}{2} \sin \theta
\end{cases}. \quad (2.6)$$
Hence 2 over the calculated mean yields a Monte Carlo estimate of $\pi$.

![Diagram](image)

Figure 2.4: Two dimensional integral and the mean value theorem

By extending the previous two examples, it is apparent that one could use Monte Carlo methods to estimate multi-dimensional definite integrals. For low dimensional problems, standard (deterministic) numerical integration methods are more efficient than Monte Carlo. However, Monte Carlo is better in high dimensions because the rate of its convergence is independent of the dimension of the integrand compared with deterministic numerical integration methods, which have a rate of convergence that decreases as the dimension increases. Therefore, the Monte Carlo method is the only practical way to calculate integrals of arbitrary functions in six or more dimensions [82].

2.1.2 Definition of the Probability Density Function

This section will describe Monte Carlo stochastic dynamics method [83, 84, 85] used in the ion hopping model. The related basic properties and terminology from probability and statistics will be reviewed first.

In probability theory[86], a random variable is a quantity whose values are random and it is a measurable function defined on the sample space. For instance, when tossing a dice the outcome is a discrete random variable whose possible values range from 1 to 6. The random variable can also be continuous (the rest of discussion will only focus on the continuous random variables) and let $X$ be such a random variable. A nonnegative probability density function (p.d.f) $f(x)$ is assigned to $X$ to represent its probability distribution.
Hence the total integral of $f(x)$ must be 1:

$$P(-\infty \leq X \leq \infty) = \int_{-\infty}^{\infty} f(x)dx = 1. \quad (2.7)$$

The cumulative distribution function (c.d.f) of $X$ is the function $F$, with the range of $[0, 1]$, defined by

$$F(t) = P(X \leq t) = \int_{-\infty}^{t} f(x)dx. \quad (2.8)$$

Figure 2.5: Probability density function

Consider the ion hopping events inside the ionic polymer transducer. Since ion transitions occur randomly in space and time, the time taken for another transition to happen since the last hopping event is a random variable. For this random variable $t'$, the corresponding probability density function $f(t')$ needs to be specified. For any given $f(t')$, as shown in Figure 2.5:

$$dP = f(t)dt, \quad (2.9)$$

where $dP$ is the probability that the random variable $t'$ occurs between $[t, t + dt]$. Suppose no transition occurs before $t$ since the last transition, but exactly one transition occurs in the interval $[t, t + dt]$. The probability for a transition during this $dt$ is

$$w\,dt = \frac{1}{\tau} dt, \quad (2.10)$$

where $w$ is the ion hopping rate and $\tau$ is the average transition time, which depends on the temperature and the energy barrier height of the system. This probability is also a conditional probability which based on the condition that no transition occurs between $[0, t]$ so that: $\tau = \tau_0 = \tau_k = \tau_l$, ($0 < k < t$). Thus the joint probability that another new transition happens in the time interval $[t, t + dt]$ is:

$$dP = P(t) \times \left(\frac{1}{\tau} dt\right), \quad (2.11)$$
where $\bar{P}(t)$ is the probability that no ion moves between $[0,t]$ after the last transition. Correspondingly, $\bar{P}(t + dt)$ is the probability for no transition in the interval $[0, t + dt]$. Based on equation 2.10, the relationship between $\bar{P}(t + dt)$ and $\bar{P}(t)$ can be described as:

$$\bar{P}(t + dt) = \bar{P}(t) \times \left( 1 - \frac{1}{\tau} dt \right) = \bar{P}(t) - \bar{P}(t) \frac{1}{\tau} dt$$

(2.12)

or in differential form

$$\frac{\bar{P}(t + dt) - \bar{P}(t)}{dt} = \dot{\bar{P}}(t) = -\frac{1}{\tau} \bar{P}(t).$$

(2.13)

$\bar{P}(t)$ can be solved as:

$$\bar{P}(t) = e^{-t/\tau}.$$ 

(2.14)

Substituting the value of $\bar{P}(t)$ into equation 2.11 combined with equation 2.9, the expression for the probability density function can be obtained:

$$f(t) = \frac{1}{\tau} e^{-t/\tau}.$$ 

(2.15)

### 2.1.3 Sampling from Probability Density Function

As described in the previous subsection, ion transport inside the ionic polymer transducer is described in terms of the probability distribution functions (p.d.f’s) for the random time interval between two transitions. The goal of the Monte Carlo method is to describe the system evolution by random sampling from these p.d.f’s. However, it is not realistic to directly sample the p.d.f’s in equation 2.15 and to calculate the expectation value of the random time interval by using $E(t) = \int_0^\infty f(t')t'dt'$. There’s a more sophisticated way: "one may start from the given probabilistic problem, formulate it in theoretical terms, discern a second probabilistic problem described by the resulting theory, and finally solve the first probabilistic problem by simulating the second [71]." In other words, we will solve $t'$ by sampling a second p.d.f which statistically depends on $f(t')$. In order to explain this process, we need to explain transformation rules for p.d.f’s [87].

Given a p.d.f $f(x)$, one defines a new variable $y = y(x)$, and the goal is to find the p.d.f $g(y)$ for the random variable $y$. $x$ and $y$ are restricted to a 1-to-1 relationship. That is, a given value of $x$ corresponds to only one value of $y$. Since the 1-to-1 relationship between $x$ and $y$ necessitates that $y$ appears when $x$ occurs, the probability of the random variable $x'$ occurring in $dx$ about $x$, i.e. $Pr(x \leq x' \leq x + dx)$, must be the same as the probability
of the random variable $y'$ occurring in $dy$ about $y$, i.e. $Pr(y \leq y' \leq y + dy)$. The equality yields

$$f(x)dx = g(y)dy.$$  \hspace{1cm} (2.16)

Equation 2.16 holds for the monotone increasing function $y(x)$. If the monotone decreasing function $y(x)$ is considered as well, the transformation rule for p.d.f’s has the following expression

$$|f(x)dx| = |g(y)dy|.$$ \hspace{1cm} (2.17)

One of the most important transformations occurs in equation 2.17 when $y(x)$ is the cumulative distribution function (c.d.f). Any value for the c.d.f occurs equally likely on the interval $[0, 1]$. Therefore, instead of directly sampling $x$ from its p.d.f, one can first sample its c.d.f: $y = F(x)$ and then solve for $x$ by inverting $F(x)$, i.e. $x = F^{-1}(y)$. This sampling rule is sometimes called the "Golden Rule for Sampling" and it was first suggested by von Neumann in 1947 [88]. The steps for sampling by inversion of the c.d.f are summarized as follows:

- Sample a random number $\xi$ from $U[0, 1]$ by using a random number generator
- Equate this random number $\xi$ with the c.d.f: $F(x)=\xi$
- Invert the c.d.f to solve for $x$: $x=F^{-1}(\xi)$

Consider the sampling techniques in the ion hopping model again. Equation 2.15 gives the form of the p.d.f and therefore the c.d.f can be calculated as

$$F(t) = \int_0^t \frac{1}{\tau} e^{-t' / \tau} dt' = e^{-t' / \tau} \bigg|_0^t = 1 - e^{-t / \tau}.$$ \hspace{1cm} (2.18)

Notice that both $F(t)$ and $1 - F(t)$ are uniformly distributed on $[0, 1]$. The random time interval between two transitions can be solved as follows:

$$e^{-\frac{t}{\tau}} = \xi \Rightarrow t = -\tau \ln(\xi),$$ \hspace{1cm} (2.19)

where $\xi$ is a random number with the distribution density function $q(\xi) \equiv 1$ in the interval $0 \leq \xi \leq 1$.

Equation 2.19 is used to formulate the Monte Carlo algorithm for the ion hopping model. In conclusion, this section presents two applications of sophisticated MC methods, i.e. Monte Carlo integration and MC simulation of ion hopping.
2.2 Monte Carlo simulation of ion hopping

In our current model, ion transport inside an ionic polymer transducer is described by a thermally-activated hopping in a two-dimensional multi-well energy structure [85]. The ion hopping model consists of a square lattice with each site empty or occupied by a single cation. The dynamics consist of cations hopping randomly to nearest neighbor sites at an equilibrium state. At a non-equilibrium state such as the application of an external electric field, cation hops are biased. At each time step, every hopping event has a rate calculated and the individual rate acts as probability for each event.

Figure 2.6 presents a one-dimensional energy barrier hopping model. The arrows indicate two possible ion jumps. The following assumptions have been made in the simulation:

1. Energy barrier wells are located on cubic lattice sites.
2. Each lattice cell can only contain one cation.
3. Cations can only hop to the neighboring cells which are not occupied by another cation.
4. Ion-ion interaction does not consider the field caused by the ion itself or by the ion in the neighboring cells.
5. Periodic boundary conditions are applied when ions hop in the direction perpendicular to the electric field, so ion-ion interaction is only considered in the range within 24 lattice cells. Though Coulomb interaction is a long-range force, due to the dielectric screening which can reduce this interaction, Coulomb potential is ignored outside the cutoff range. When the hopping event happens in the direction of electrical field, the interaction between all charges and all image charges will be included.

Three types of energy contribute to the energy barrier wells: intrinsic energy, external electric potential energy and Coulomb potential energy. Intrinsic energy barrier height $W_0$ can be assumed to be constant as $W_0 = 25kT$ or a normal distribution due to the disorder in the ionomer membrane. For the assumption of normal distribution, average energy height of $W_m = 25kT$ and standard deviation energy of $W_{SD} = 2kT$ are adopted, where $k$ is the Boltzmann constant and $T$ is the temperature [85]. Scarle et al. [89] have shown that the Gumbel distribution is better than the Gaussian to describe the distribution of site energies for ion hopping model. However, it greatly complicates the mathematics in the simulation.
without giving significantly improved results for the modeling of ion transport. Energy barrier height due to the externally applied field $E$ is calculated by $\delta W = qEl$, where $q$ is the electric charge, $l$ is the distance between two neighboring lattice cells and $l = 1 \ nm$ in the simulation since each lattice cell is a one-nanometer cube.

The third energy barrier height is due to ion interaction, namely, Coulomb potential energy that consists of ion-ion interaction and the interaction between ions and electrodes. In Figure 2.7, a point charge is close to a conducting plane. Physically, the point charge would induce opposite sign charges on the surface of the conductor, resulting in a surface charge density $\rho_s$ [90]. Hence the potential at the point with coordinates $(x, y, z)$ would be:

$$V(x, y, z) = \frac{Q}{4\pi \varepsilon_0 \sqrt{x^2 + (y - d)^2 + z^2}} + \frac{1}{4\pi \varepsilon_0} \int_S \frac{\rho_s ds}{R_1},$$

where $R_1$ is the distribution from $ds$ to the point under consideration and $S$ is the surface of the entire conducting plane. The induced surface charge density $\rho_s$ must be determined from the boundary condition $V(x, 0, z) = 0$. Moreover, the calculation of the indicated surface integral is non-trivial. An alternative way is the method of images. Instead of directly solving the governing Laplace’s equation with boundary conditions, the method of image charges offers a straightforward manner to satisfy boundary conditions by placing
image charges of suitable size into the region which is not under consideration. Figure 2.7 shows a point charge located at a distance \( d \) above a grounded conducting plane. The potential at a point \( P(x, y, z) \) in the \( y > 0 \) region is

\[
V(x, y, z) = \frac{Q}{4\pi\varepsilon_0} \left( \frac{1}{R_+} - \frac{1}{R_-} \right)
\]

(2.21)

where

\[
R_+ = \left[ x^2 + (y - d)^2 + z^2 \right]^{1/2},
\]

(2.22)

\[
R_- = \left[ x^2 + (y + d)^2 + z^2 \right]^{1/2}
\]

(2.23)

For IPTs applied with direct current, electric potential at the electrodes stays constant and the potential contribution from cations is considered to be zero at the cathode and anode. To meet this boundary condition, image charges are appropriately placed by mirroring ions multiple times outside the region in which the field is to be determined. In the simulation, all the ions are mirrored twice. Figure 2.8 shows original positive charge +Q and its four image charges. +Q and -Q1, -Q2 and +Q3 are symmetric along electrode 1 respectively. +Q and -Q2, -Q1 and +Q4 are symmetric along electrode 2.

![Figure 2.8: Method of image used in the simulation to meet the potential boundary condition at the electrode](image)

After three types of energy barrier heights were obtained, the thermally activated hopping rate is calculated as:

\[
w = \nu_0 \exp\left( -\frac{W_0}{kT} + \frac{\delta W}{2kT} + \frac{\Delta W}{2kT} \right),
\]

(2.24)

where \( \nu_0 \) is the attempt to escape frequency, which is set to \( 10^{20} \) Hz so that the diffusion coefficient is equal to \( 2 \times 10^{-10} \text{m}^2/\text{s} \). The terms \( W_0 \), \( \delta W \) and \( \Delta W \) represent the energy difference between the original position and the next possible position of a cation. The term \( W_0 \) describes the intrinsic energy difference, \( \delta W \) is for external electric potential energy
difference and $\Delta W$ denotes ion-ion interaction energy difference. In two dimensional lattice cells, each cation could possibly jump to the left, to the right, up or down as long as the neighboring cell is not occupied by another cation. For example, assume that the electric field has the direction from bottom to top and a cation could hop to its four neighboring cells. The corresponding hopping rates in four directions are described as:

$$w_1 = \nu_0 \exp\left(-\frac{W_{01}}{kT} + \frac{\delta W_1}{2kT} + \Delta W_1}{2kT}\right),$$  \hspace{1cm} (2.25)

$$w_2 = \nu_0 \exp\left(-\frac{W_{02}}{kT} - \frac{\delta W_2}{2kT} + \Delta W_2}{2kT}\right),$$  \hspace{1cm} (2.26)

$$w_3 = \nu_0 \exp\left(-\frac{W_{03}}{kT} + \frac{\Delta W_3}{2kT}\right),$$  \hspace{1cm} (2.27)

$$w_4 = \nu_0 \exp\left(-\frac{W_{04}}{kT} + \frac{\Delta W_4}{2kT}\right),$$  \hspace{1cm} (2.28)

where $w_1$, $w_2$, $w_3$ and $w_4$ are the hopping rates toward the cathode (top), toward the anode (bottom), to the left and to the right; $W_{01}$, $W_{02}$, $W_{03}$ and $W_{04}$ are the intrinsic energy differences in four directions respectively; $\Delta W_1$, $\Delta W_2$, $\Delta W_3$ and $\Delta W_4$ are ion-ion interaction energy difference in four directions. For each possible hopping event, the corresponding average transition time is given as: $\tau = 1/w$. From Monte Carlo simulation algorithm (equation 2.19), transition time interval $t$ can be sampled by using the following formula:

$$t = -\frac{1}{w} \times \ln(x),$$ \hspace{1cm} (2.29)

where $w$ is hopping rate and $x$ is a random number between zero and one. Finally all the possible hopping is compared by its random transition time and the ion with minimum transition time $t_{\min}$ is chosen to hop during the current simulation step. After this hopping event is accomplished, the system time is updated by increasing $t_{\min}$ and the new cation positions are recorded for the calculation of the next loop. The procedure continues by repeating the recalculation of the energy structure. The simulation stops when the system reaches the equilibrium state where current density drops to zero. Current density is calculated by its definition [91]:

$$J = pq\vec{v} = \frac{n}{V} \times q \times \frac{a}{dt} \left(\sum_{i=1}^{n} (j_i - k_i) \right) \cdot \frac{1}{n} = \frac{a}{V} \times q \times \frac{\sum_{i=1}^{n} (j_i - k_i)}{dt},$$ \hspace{1cm} (2.30)
where $p$ is particle density, $q$ is the basic electric charge, $v$ is average particle velocity, $n$ is the number of particles, $a$ is the hopping distance, $V$ is the volume, $j_i$ is the count (how many times) for the ion $i$ to move in the direction of electric field during a small time interval $dt$ and $k_i$ is the count to move in the opposite direction.

Charge density and electric field are computed from the distribution of positive and negative ions. All the ions staying in the same layer are assumed to belong to one single ensemble. For example, in $50 \times 30 \times 1$ lattice cells, there will be 30 layers in the direction of electric field each with size of $50 \times 1 \times 1$. Normalized charge density can be defined as:

$$Q_{Nm} = \frac{C_{m+} - \overline{C}}{\overline{C}} = \frac{N_{m+} - N_{m-}}{N_{m-}},$$

(2.31)

where $C_{m+}$ is the positive ion concentration at layer $m$, $\overline{C}$ is the average negative charge concentration, $N_{m+}$ is the number of cations in layer $m$, $N_{m-}$ is the average number of negative charges in each layer, $q$ is $1.60 \times 10^{-19}$ C for each ion is assumed to carry a basic electron charge and $k$ is the volume of layer $m$. Because each layer can hold 50 cations at most for either $50 \times 50 \times 1$ or $50 \times 30 \times 1$ lattice cells, there will be a maximum normalized charge density for each layer. For $50 \times 50 \times 1$ lattice cells with 200 cations:

$$Q_{N_{\text{max}}} = \frac{C_{m+} - \overline{C}}{\overline{C}} = \frac{50 - 4}{4} = 11.5.$$  

(2.32)

For $50 \times 30 \times 1$ lattice cells with 120 cations:

$$Q_{N_{\text{max}}} = \frac{C_{m+} - \overline{C}}{\overline{C}} = \frac{50 - 4}{4} = 11.5.$$  

(2.33)

Hopping model in one dimension is compatible to a continuum model. The macroscopic quantity, the mobility $\mu$ and the diffusion coefficient $D$, can be derived from the ion hopping model [85]. The mobility has the following form:

$$\mu = \nu_0 \frac{q \ell^2}{kT} \exp \left( - \frac{W_0}{kT} \right),$$

(2.34)

where $\nu_0$ is the escape frequency in the ion hopping model, $T$ is the temperature, $k$ is the Boltzmann constant, $\ell$ is the length of each lattice layer, i.e. each hopping distance and $W_0$ is the intrinsic energy. The expression for diffusion coefficient is given as:

$$D = \nu_0 \ell^2 \exp \left( - \frac{W_0}{kT} \right) = \frac{\mu kT}{q},$$

(2.35)

As summary, Figure 2.9 presents the flow chart of the calculation algorithm used in Monte Carlo simulation of ion hopping model. Based on this basic flow chart, the simulation
Figure 2.9: Flow chart of Monte Carlo simulation
has been improved in two ways to reduce the simulation time. By removing the code from MATLAB to C, the simulation time required to reach the same amount of calculation has been reduced by a factor of 60. For $50 \times 50 \times 1$ lattice cells with 200 cations, part of the

```plaintext
old_position=i  new_position=i+1
neighbor_energy[i+1]=0
If neighbor_energy[i-1] != 0
    If there is an ion at i-2
        Do nothing
    else
        neighbor_energy[i-1]=0
    End If
End If
For m = 1 to the number of cells
    If neighbor_energy[m] != 0
        neighbor_energy[m] = neighbor_energy[m] – potential caused by ion at i
        + potential caused by ion at i+1
    End If
End For
neighbor_energy[i] = potential caused by all the ions
If neighbor_energy[i+2] = 0
    neighbor_energy[i+2] = potential caused by all the ions
End If
```

**Figure 2.10: Pseudo code**

algorithm has been optimized because more calculation is required as the increased system size. The new algorithm is designed to only change the data sets locally according to the previous ion hopping event. Suppose one ion hopped from an old position $i$ to a new neighboring position $j$; instead of starting over to recalculate the electric potential energy and ion-ion interaction energy at each site, the algorithm accesses the previous data and only changes the energy at the sites around and at $i$ and $j$. All the energy calculated elsewhere will minus the effect caused by the ion at the lattice $i$ and add the effect caused by the ion appearing at the new position; mirrored image charges of the ion at lattice $i$ disappear while images of the ion at the new position show up, etc. The pseudo code for the algorithm in one dimension ion hopping is given in Figure 2.10 and it shows how the
algorithm updates energy values for the neighboring sites of ions. The simulation time can be reduced to 1/3 by using this improved algorithm.

2.3 Simulation results and parameter study

Monte Carlo simulation of ion hopping model has been performed and simulation results are discussed in this section. As seen in Figure 2.11, initially 200 cations each with a positive electrical charge are uniformly distributed on $50 \times 50 \times 1$ lattice cells. Each lattice location physically represents a 1nm $\times$ 1nm region. To provide charge neutrality, 200 negative charges are uniformly scattered as well. In each simulation step, there is one cation hopping between lattice cells while negative charges are fixed in their initial positions. Therefore, the ion hopping model concerns the motion of completely non-collision ions. For simulation results, three types of responses are interested. Normalized charge density at steady state (see equation 2.31) exhibits the stationary ion distribution in the direction of electric field. Current density (see equation 2.30) plot shows the dynamic response of the...
material. Another result is the charge density versus time plot, which is the integration of the current density plot. Charge density vs time plots can not only show the dynamic response but also display the peak charge density at steady state. In parameter study, discussion on two important parameters, i.e. permittivity and diffusion coefficient, are included because of the direct influence on the stationary and dynamic response respectively.

2.3.1 Simulation results

![Normalized charge density with 0V input at steady state](image1)

![Current density plot for 0V](image2)

Figure 2.12: Stationary and dynamic response when 0 V is applied: (a) Normalized charge density plot at steady state with anode located at 0nm and cathode at 50nm. (b) Current density plot vs. time

For the external electric field, a step voltage function is used in the simulation though in principle any arbitrary test function can be used. In experiments IPTs can be activated by a low step voltage from 0 to approximately 4V. For the $50 \times 50 \times 1$ lattice cells with 200 ions, step voltage levels of 0V, 0.05V, 0.1V, 0.2V and 0.4V were applied along one side with 50 lattice cells and both transient and stationary results are presented. For the $50 \times 30 \times 1$ lattice cells with 120 ions, step voltage levels of 0.05V and 0.1V were applied along the side with 30 lattice cells. In these simulations, the permittivity of water is used and diffusion coefficient is set as $1 \times 10^{-10} \text{ m}^2/\text{s}$.

Figure 2.12 presents the normalized charge density at steady state (see Figure 2.12(a)) and current density plot (see Figure 2.12 (b)) when 0 volt is applied in a $50 \times 50 \times 1$ lattice. Both quantities are approximately zero which suggests that when there is no electric stimulus, ion transport toward each direction is equally likely.
Figure 2.13: Normalized charge density plots for 50×50×1 lattice cells at (a) 0.05V and (b) 0.1V (c) 0.2V and (d) 0.4V. The anode is located at 0 nm and cathode at 50 nm.

Normalized charge density plots at steady state are presented when a voltage of 0.05V, 0.1V, 0.2V and 0.4V is applied respectively (see Figure 2.13). Plots (a), (b), (c) and (d) all show three regions in the direction of electric field: a depletion region close to anode, charge neutralization region in the middle and a very thin layer of ion accumulation region close to the cathode. Though the ion charge density plot cannot be verified by experimental results, it can be compared with other models. Li and Nasser [22] developed a continuum-based model and found the steady-state charge distribution due to ion conduction. In their results, charge density also shows charge neutrality over the most central part of the membrane and the charge imbalance over narrow boundary layer close to the anode and cathode. The properties of charge density plots from Monte Carlo simulations show
agreement with Li and Nasser’s model. As the applied voltage increases, the depletion region width increases as well and in this region, the normalized charge density has a value of $-1$, which represents that all the positive ions have moved away and there are only fixed negative ions left. Another trend is evident in Figure 2.13 that higher values of voltage result in an increase of peak value in the ion accumulation region before saturation happens.

Figure 2.14: Normalized charge density plots for $50 \times 30 \times 1$ lattice cells at (a) $0.05\text{V}$ and (b) $0.1\text{V}$. The anode is located at $0\text{nm}$ and cathode at $50\text{nm}$.

Next Monte Carlo simulations are performed on a $50 \times 30 \times 1$ lattice with 120 cations/ions. The distance in the electric field is reduced from $50\text{nm}$ to $30\text{nm}$ while the ion concentration maintains the same. Figure 2.14 displays the normalized charge density plots at steady state when $0.05\text{V}$ (Figure 2.14 (a)) and $0.1\text{V}$ (Figure 2.14 (b)) is applied correspondingly. Three distinct regions, i.e. depletion region, neutrality region and accumulation region, can also be observed in both plots. If we compare Figure 2.14 (a) with Figure 2.13 (a) and compare Figure 2.14 (b) with Figure 2.13 (b), looking more closely at these results it must be noted that both ion depletion region and accumulation region are almost identical to those seen in our previous study when the same amount of voltage is applied on a $50 \times 50 \times 1$ lattice. The observation is very interesting since the thickness of the material has been varied, yet they both seem to produce the same normalized charge density on two boundary layers. This observation can be explained as follows. At steady state, the redistribution of cations results in an internal electric field that balances the applied external field. Therefore, for a given applied voltage, in spite of the thickness change the same ion


distribution profile will be formed at boundary layers for the charge density is equal to zero for the central part.

The transient response is studied for a $50 \times 50 \times 1$ lattice with 200 cations/anions (see Figure 2.15). Current density plots for different voltages are shown in Figure 2.15 (a). Each current density profile approximates an exponential decay and current density drops to zero which indicates the system has reached the steady state. Correspondingly, plots of charge density versus time, the integral of the current density versus time, are shown in Figure 2.15 (b). Charge density keeps increasing and becomes a straight line at steady state. The peak charge density represents the total transported charges per unit area. The trend is very clearly that the peak current density and the peak charge density increase for the increasing applied potential.

### 2.3.2 Parameter study

In the previous section, Monte Carlo simulation of ion hopping model has enabled us to predict the ionomer’s induced current and stationary ion distribution in a small time and length scale as a function of an applied potential. With this modeling capability, we now want to consider the influence of parameters within the ionic polymer transducer. We are interested in two macroscopic quantities: the diffusion coefficient ($D$) and the electrical
permittivity ($\varepsilon$). The two variables are chosen because they govern the polymer’s ability to transport ions ($D$) and its ability to store charges ($\varepsilon$). All the simulations discussed in this section were performed on a 50\textit{nm}×50\textit{nm} lattice with 200 cations/anions.

Trends between current and charge densities as a function of the permittivity is shown in Figure 2.16 and 2.17. The diffusion coefficient $D = 2 \times 10^{-10} \text{m}^2/\text{s}$ and the applied voltage $U = 0.2 \text{V}$ are held constant. As it can be noticed that higher values of permittivity result in an increase in both the peak current density and the peak charge density. In other words, there will be more ion accumulation at the cathode with increasing permittivity. However, the peak current density and charge density scale nonlinearly with the permittivity. Therefore, for larger permittivity the increase of the peak current density and charge density become smaller.

Another parameter considered in this analysis is the diffusion coefficient and results are shown in Figure 2.18 and 2.19. The permittivity $\varepsilon = 20$ is held constant for both plots. Diffusion coefficient defines the cation’s ability to move within and through the Nafion$^{\text{TM}}$ membrane. It is evident in Figure 2.18 that the rate of decrease of the peak current density is faster for larger diffusion coefficient. This is also demonstrated in Figure 2.19. It takes a longer time for smaller diffusion coefficient to reach the steady state. From a physical standpoint we see that the results make sense because a decreased diffusion coefficient means that cations diffuse through the material at a lower rate. Another major finding is the total transported charge density, the integral of the current density, remains the same independently of the diffusion coefficient. Therefore diffusion coefficient will affect transient response instead of stationary response.

In conclusion, the parameters diffusion coefficient and permittivity provide us with the ability to independently tune the transient and stationary responses of the ionic polymer transducer. This feature will be beneficial in the comparison with experimental measurements later.

2.4 Parallel programming

In order to reduce the simulation time, parallel computation of Monte Carlo simulation is utilized by using Message Passing Interface (MPI) library. The performance of parallel programming also depends on the development of good parallel random number generators.
Figure 2.16: Current density plots for different permittivity

Figure 2.17: Charge density plots versus time for different permittivity
Figure 2.18: Current density plots for different Diffusion Coefficient with permittivity of 20

Figure 2.19: Charge density plots versus time for different Diffusion Coefficient with permittivity of 20
Thus the scalable parallel pseudo random number generator (SPRNG) standard library is implemented to generate statistically independent random numbers when multiple processors are involved. Finally, results from parallel and sequential code are compared and the performance of parallel computation is evaluated.

### 2.4.1 Message Passing Interface

Message passing interface (MPI) [92] is a language-independent communications library designed for use with high-performance computing on computer clusters or multiprocessor systems. Compared with the library of OpenMP, which is mostly used on shared memory machines, MPI is mainly used on distributed memory machines. It consists of over 120 functions [93] and every function has been defined for C/C++ and Fortran programs. The basic purpose of these MPI functions is to transmit the data from one processor to another. There are two types of MPI communication: point-to-point and collective communication. Point-to-point communication is between one processor to another. Collective communication, however, can send/receive the data from/to one processor to/from many processors. This subsection is not aimed to be an exhaustive reference for those functions, however, the functions used for parallel computing of Monte Carlo simulation will be introduced in detail.

Although MPI has many functions, communicator is one of a few very important concepts. Communicators are groups of processors in the MPI session. All communicators have a size, which is the number of processors in the group. Each processor has its own unique numeric rank and has its own communication ability for point-to-point operations. `MPI_COMM_WORLD` is a default communicator that consists of all the processes running the program when the execution begins.

To develop a parallel simulation, the next step is the domain decomposition, which means the data and the calculation load must be distributed across multiple processors. For the application of parallel computation to Monte Carlo simulation, two processors in the default communicator are used, i.e. the domain of $50 \times 50$ nm is divided by two and each processor is in charge of the data in one sub-domain. For example, in Figure 2.20, in the direction of electric field, the first half domain is assigned to processor 1 and the other half to processor 2. Therefore, at each simulation step, processor 1 will calculate the transition time intervals for any possible hopping events from row 1 to row 25 and then pick the
minimum time interval; on the other hand, processor 2 will do the same for row 26 to row 50. To figure out the minimum time interval for the whole domain and the corresponding ion that will conduct hopping, data from two processors must be collected and compared by using the collective function $\textit{MPI\_Allreduce()}$.

![1d domain decomposition](image)

**Figure 2.20: 1d domain decomposition**

$\textit{MPI\_Allreduce()}$ combines values from all processes in the communicator and distributes the result back to all processes. The MPI implementation of this operation takes a source buffer address, a destination buffer address, the number of elements, the data type of those elements, an operation to perform, and a communicator. For the application of Monte Carlo simulation, each processor saves the value of the minimum transition time interval and the rank of the processor into a structure. The function $\textit{MPI\_Allreduce()}$ collects the addresses of these structures, compares and chooses the minimum value of transition time interval, saves the results into a destination buffer, i.e. another structure in this case and sends back the address of the destination buffer to each processor in the communicator.

Once the rank of the processor, which holds the minimum transition time interval, e.g. processor with rank 1, is known, this processor has to broadcast the information about the ion which will conduct hopping at the current step. This operation can be accomplished by using function $\textit{MPI\_BCast()}$. $\textit{MPI\_BCast()}$ is a function that broadcasts data from one process to many other processes (see Figure 2.21). It is called by the process sending the data as well as every process receiving the data. Its input parameters include a source buffer address, the number of entries in the buffer, the data type of the buffer, the rank
of broadcast root and the communicator. For the application of Monte Carlo simulation, the processor with rank 1 as mentioned at the beginning of this paragraph will save the data, including the hopping direction, x/y coordinates values of the current ion location and of the next possible ion location corresponding to the minimum transition time interval, into a structure. \textit{MPI \_ BCast()} takes the address of this structure as a source buffer and meanwhile the rank of broadcast root is set to 1. \textit{MPI \_ BCast()} is called by each processor in the communicator and each will receive a copy of data sent by processor 1. The parallel algorithm continues by repeating all steps starting from recalculation of the energy structure and the minimum transition time interval in each sub-domain. In this way the temporal evolution of the complete system can be simulated.

![Figure 2.21: Data broadcast](image)

### 2.4.2 Parallel random number generators

Random numbers used for the random variable in Monte Carlo simulations are produced by pseudo-random number generators. There are various algorithms for those generators [82]. The linear congruential method is the most popular one using the following formula:

\[
X_i = (a \times X_{i-1} + c) \mod M, \tag{2.36}
\]

where \(a\) is called the multiplier, \(c\) is called the additive constant and \(M\) is called the modulus. Another generator with the rising popularity is called lagged Fibonacci generator. It is defined as follows:

\[
X_i = X_{i-p} \times X_{i-q}, \tag{2.37}
\]
where $p$ and $q$ are the lags, $p > q$, and $\ast$ is any binary arithmetic operation. Both methods can generate uncorrelated and uniformly distributed (i.e. each possible number is equally probable) numbers. No matter which method is used, the particular sequence of values produced by generators depends on the initial value $X_0$, which is called the "seed". Since the operation to generate random numbers is deterministic, the produced sequences are predictable. The generated random numbers will begin to repeat themselves at a certain point where the generator has completed a cycle. The period of a random number generator is the length of this cycle.

The performance of the parallel Monte Carlo algorithm introduced in the previous section also depends on the ability to generate a large number of high-quality parallel random number sequences. In another word, the goal is to generate a sequence of random numbers by multiple processors and this sequence should be the same as the one generated by one processor if the same "seed" is given initially. As shown in Figure 2.22, each processor generates one stream starting from different initial states in a random number sequence.

![Figure 2.22: Parallel random number sequences](image)

The ideal parallel random number generator would have the following properties:

- There are no correlations among the numbers in different sequences
- Scalability, that is, it should be possible to handle a large number of processes, each with its own stream
- Locality, which means a process should be able to spawn a new sequence of random numbers without communication between processors.

To generate such sequences on parallel computers, the scalable parallel pseudo random
number generators (SPRNG) standard library [94] has been included in Monte Carlo simulations. SPRNG 1.0 uses a multiplicative lagged Fibonacci generator, whose recurrence relation for random numbers is given by the following equation:

$$X_n = X_{n-k} \ast X_{n-l} \mod M,$$

(2.38)

where \(l\) and \(k\) are called the lags of the generator and \(l > k\). \(M\) is the modulus chosen to be \(2^{64}\). The period of the generator is \(2^{61}(2^l-1)\) where \(l\) is the lag. For the default generator with lag \(l = 17\), the period is approximately \(2^{81}\). The number of distinct streams available is \(2^{63(l-1)-1}\). For the default generator this gives around \(2^{1008}\) different streams. The seed used during initialization for this generator returns a distinct sequence. The seeding algorithms ensures that for the same used seed, all streams obtained on every processes are independent. Therefore, for the application of Monte Carlo simulations, the seed is shared by every processors by using the MPI function \texttt{MPI	extunderscore{B}Cast()} at the initialization.

### 2.4.3 Results and discussion

<table>
<thead>
<tr>
<th></th>
<th>Minimum time for each run of simulation (min)</th>
<th>Maximum time for each run of simulation (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Computation by sequential code</td>
<td>40</td>
<td>72</td>
</tr>
<tr>
<td>Computation by parallel code on 2 processors</td>
<td>22</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 2.1: Simulation time comparison between sequential code and parallel code

The parallel computation of Monte Carlo simulations were conducted either on a linux cluster with 40 processors or on the System X at Virginia Tech. System X has 1100 cluster nodes and each node has dual 2.3 GHz PowerPC 970FX processors. Figure 2.23 shows the comparison between the results obtained by using sequential code and parallel code. Normalized charge density in steady state is presented when 0.2 \(V\) is applied in a \(50 \times 50\) lattice with 200 cations inside. As shown in the figure, both simulation results match well especially for both ion depletion region and accumulation region close to the boundary layers. The mean value of the difference between two data sets is \(4 \times 10^{-8}\) with a standard deviation of 0.142. The correlation between two results is 0.991 (when correlation
coefficient is equal to 1, two vectors are exactly the same). Good correlation between the results demonstrates that the parallel computation of Monte Carlo simulation is reliable.

Figure 2.23: Results comparison by using sequential code and parallel code: 0.2 V is applied in a 50 × 50 lattice with 200 cations

Table 2.1 presented the execution time for both the sequential code and parallel code. Both simulations were executed for 20 runs and the minimum and maximum time for each run were recorded. There are a couple of quantities to describe the performance of parallel computations. Speedup is the ratio between sequential execution time and parallel execution time:

\[
Speedup = \frac{\text{Sequential execution time}}{\text{Parallel execution time}}.
\]  

(2.39)

And the efficiency of a parallel program is a measure of processor utilization:

\[
Efficiency = \frac{\text{Sequential execution time}}{\text{Processors used} \times \text{Parallel execution time}}.
\]  

(2.40)

Since the performance also depends on other usages of the processors, the minimum time is used to calculate the performance. For the application of Monte Carlo simulations with 2 processors, speedup is equal to 1.82 and efficiency is 91% while the rest of 9% is spent on the parallel overhead which includes communication operations and redundant computations.
In conclusion, parallel computation with 2 processors speeds up the execution time with the current parallel algorithm and both simulation results have very good correlation.

2.5 Chapter summary

In this chapter a Monte Carlo simulation of ion hopping model has been performed for the ionic polymer transducer. By sampling the ion transition time interval as a random variable, the system evolution is obtained. Current density approximates an exponential decay and charge density at steady state displays distinct three regions which agree with other continuum models. Higher values of voltage or permittivity result in more ion accumulation at the cathode. Increasing the diffusion coefficient results in a smaller time constant while the steady charge density remains constant. Parallel computation has been successfully implemented to speed up the simulation.
Chapter 3

Monte Carlo Simulation of the Morphology of the Ionic Polymer Transducer

Chapter 2 presented the Monte Carlo simulation of ion hopping and studies the parameters that are expected to influence charge density and current responses. Chapter 3 will investigate the influence of morphologies inside the ionic polymer transducer by looking at three applications of Monte Carlo simulation of ion hopping. (1) First, stationary ion accumulation close to a flat electrode and that close to a zigzag-shaped electrode are compared. (2) Next, responses are compared when the simulation starts from different initial ion distributions. (3) Finally, conducting powder electrodes are included in the simulation and the resulting impacts are discussed.

3.1 Model application at the polymer-metal interface

Bao et al. [8] state that the fractal-like structure of gold electrodes and the porous platinum particles exist inside ionic polymer transducers. Charges accumulate along the entire surface at the polymer-metal interface. For these reasons the effective area of electrodes is much larger than the cross-sectional area of the bulk polymer. Moore [95] measured these areas experimentally using a hydrogen adsorption and desorption method. It’s reported that the area of the platinum electrode is 9.2 times larger than the cross-sectional area of the bulk
Figure 3.1: Illustration of zigzag shape electrodes inside lattice cells. Black dots are positive ions which are able to hop between neighboring cells polymer. In this section, Monte Carlo simulation has been conducted to look into the effects of polymer-metal contact area on charge migration and charge accumulation.

3.1.1 Approximation of zigzag-shaped electrodes

Figure 3.2: Comparison of zigzag-shaped electrodes: substrate square (a) and flat electrodes: substrate square (b)

Zigzag-shaped electrodes with geometry shown in Figure 3.1 are introduced to the model. In the simulation, a small square of substrate close at cathode is considered (illustration can be seen in Figure 3.2). Each square is divided into 50×50×1 lattice cells with 200 cations inside. Therefore lattice (a) and (b) in Figure 3.2 have the same area, the same number of lattice cells assigned and the same applied electric field. The same ion hopping rules mentioned in the previous chapter are applied for both lattice (a) and (b). Since those two tiny squares are distant from anode, the influence of positive electrode will not be
Figure 3.3: Distribution of cations (red sphere) and anions (blue pin head) at initial state: (a1) and (b1); after $1 \times 10^{-6}$ sec of simulation time: (a2) and (b2); after $4 \times 10^{-6}$ sec of simulation time: (a3) and (b3) and after $6 \times 10^{-6}$ sec of simulation time: (a4) and (b4). The squares represent the material with flat shaped cathode at the top while the diamonds have zigzag shaped cathode at the top.

counted; therefore image charges mirrored by positive electrode are ignored. However, lattice (a) has the negative electrode angled at 90 degrees and lattice (b) has the flat negative electrode at the top. The method for computing the image charges will be different for these two cases. As shown in Figure 3.2, each cation in lattice (a) has three image charges: image a1 and image a2 with negative sign and image a3 with positive sign. In lattice (b), each cation has only one negative image charge which is positioned symmetrically with respect to cathode. For lattice (a), boundary conditions cannot be applied and therefore the ion interaction caused by all charges will be counted during each simulation step. In conclusion, the previous code still can be used for simulation in square (a) after three changes: first no boundary conditions will be applied; secondly, positions of image charges have been changed; thirdly, the electric field vector has to be divided into the direction perpendicular and parallel to electrodes.

Simulations have been carried out with external applied potential of 0.2 V for lattice (a) and (b) in Figure 3.2, respectively. Figure 3.3 presents the results of ion distribution. The squares in the first row represent the material with flat-shaped cathode at the top.
while the diamonds in the second row in the plot have zigzag-shaped cathode at the top. In (a1) and (b1), ions are randomly distributed initially. After $1 \times 10^{-6}$ seconds of simulation time, ion accumulation emerges in the diamond (Figure 3.3 (b2)) while it is not obvious in the square (Figure 3.3 (a2)). After $4 \times 10^{-6}$ or $6 \times 10^{-6}$ second of simulation time, ion accumulation in diamonds (Figure 3.3 (b3) and (b4)) is much more prevailing than in squares (Figure 3.3 (a4) and (a4)). In other words, simulation results demonstrate that more and faster ion accumulation at the cathode can be obtained in the ionic polymer transducer with zigzag-shaped electrodes than with flat-shaped electrodes. The results can be explained as follows. One reason is that obviously larger contact area leads to less steps for cations to reach an electrode. The other reason lies in that zigzag-shaped electrodes result in calculations change between cations and image charges, that is the interaction between cations and electrodes. Image charges formed by zigzag-shaped electrodes attract more cations to the cathode.

### 3.2 Simulation of cluster morphology

The second application of Monte Carlo simulation is to investigate the relation between the ion transport and initial ion distribution. Four different patterns of initial ion distribution are arranged before the application of a step voltage (see Figure 3.4). Each substrate consists of 200 anions and 200 cations. Figure 3.4 (a) shows a random uniform distribution for both cations and anions; the other three patterns involve cluster morphology (see Figure 3.4 (b), (c) and (d)). The model of ionic clustering employs an approximately spherical, “inverted micellar structure” proposed by Gierke [2]. Phase separation and ion channels have not been considered in the present model.

#### 3.2.1 Simulation design

According to the work done by Orfino et al.[48], initially 89% ions remain in the spherical cluster domains in a wet membrane. Complete ion pairing within each cluster is assumed for the initial state. Table 3.1 summarizes the ions and clusters arrangements for pattern (b), (c) and (d). In pattern (b), 15 clusters are uniformly distributed; in pattern (c), clusters with higher charge density and with the decreased cluster-to-cluster distance form rod-like channels from anode (at the bottom) to the cathode (at the top). Each cluster in pattern
Figure 3.4: Initial distribution of cations (red sphere) and anions (blue pin head). Pattern (a): random distribution; Pattern (b): 15 clusters; Pattern (c) rod-like 8 clusters and Pattern (d): 4 clusters. In (b2), (c2) and (d2), squares denote anions and dots denote cations.

(d) can be considered as the regroup or the combination of a few smaller clusters in pattern (b). For each initial pattern, the same amount of step voltage as 0.2V is applied. For each simulation, the diffusion coefficient $D = 2 \times 10^{-10} \text{m}^2/\text{s}$ and the permittivity of water $\varepsilon = 78$ are held constant. The results of charge density versus time plots and stationary ion distributions are presented and discussed. For charge density plots, we average over several runs to reduce the noise of the data.

3.2.2 The influence of initial ion distributions

Figure 3.5 displays the charge density versus time plots for different initial ion distribution patterns. Four plots present the same trend: the charge density, which is the integral of the current density, first increases as time increases and then remains constant when steady state is reached. Consider the values of charge density at steady state, i.e. the peak charge density: the initial distribution with uniform random ion distribution has the highest peak charge density, the pattern with 15 clusters has slightly lower peak charge density, the pattern with 4 clusters ranks third highest and the pattern with 8 clusters ranks the lowest. The difference in peak charge density indicates that the morphology does contribute to
<table>
<thead>
<tr>
<th>Patterns</th>
<th>Cluster numbers</th>
<th>Number of ions per cluster</th>
<th>Total number of ions within cluster domains</th>
<th>Cluster-to-cluster spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pattern (b)</td>
<td>15</td>
<td>12 ion pairs</td>
<td>180 ion pairs</td>
<td>11</td>
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<td>Pattern (c)</td>
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<td>22 ion pairs</td>
<td>176 ion pairs</td>
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</tr>
<tr>
<td>Pattern (d)</td>
<td>4</td>
<td>44 ion pairs</td>
<td>176 ion pairs</td>
<td>21</td>
</tr>
</tbody>
</table>

Table 3.1: Cluster definition in Pattern (b), (c) and (d)

influence the amount of ion transport inside the material.

Figure 3.5: Charge density plots when 0.2V is applied for simulations starting with (1) uniformly distributed anions (2) anions in 15 clusters (3) anions in 8 clusters and (4) anions in 4 clusters

Ion distributions are investigated, as shown in Figure 3.6. The images in the first row show initial ion distributions and those in the second row show ion distributions at steady state. Comparatively, at steady state, the substrate with the uniform initial distribution (see Figure 3.6 (b1)) has more cations accumulated close to the cathode than the other three substrates. Looking more closely at these results it must be noted that the initial
distribution with higher peak charge density in Figure 3.5 corresponds to that with more cation accumulation at the cathode in Figure 3.6 (b1), (b2), (b3) and (b4).

![Figure 3.6: Distribution of cations (red sphere) and anions (blue pin head). (a1), (b1), (c1) and (d1) are at initial state; (b1), (b2), (b3) and (b4) are at steady state. In (a1) and (b1) anions are in uniform distribution; in (a2) and (b2) are anions in 15 clusters; in (a3) and (b3) are anions in 8 clusters; (a4) and (d4) are anions in 4 clusters.](image)

Interestingly, it can be observed in Figure 3.6 (b3) that most cations stay within the region covered by the eight anions circles. Even though in the model there is no restriction set to prevent cations from hopping outside clusters, cations still show up close to the anions due to the electrostatic attraction. This stationary cation distribution indicates the path of cation transport follows the fixed anions. Therefore, for uniformly distributed anions in Figure 3.6 (b1), there is plenty of space for cations to move around. For anions in 15 clusters shown in Figure 3.6 (b2), since small anion clusters are uniformly distributed inside the substrate, responses of this pattern are very close to those of the uniformly distributed anions. However, for anions in eight clusters shown in Figure 3.6 (b3), the comparably limited space restricts cation movement and reduces the cation accumulation at the cathode.

The arrangement in Figure 3.6 (a4) is designed to simulate the cluster reorganization during water swelling. According to the work of Gierke et al. [2], as the polymer absorbs more water, several clusters nearby could be redistributed to form a new cluster without
significant spatial translation of polymer chains. However, the simulation result of this
design did not show any advantage for ion transport. One main reason is because the
current model only uses one hydrophilic phase to describe the whole material where cations
are free to hop around as long as its neighboring lattice has not been occupied by another
cation. In the cluster-network model proposed by Gierke et al., ion transport between
clusters through ion channels. If ion channels are introduced for cation to enter one cluster
from another and if hydrophobic phase of Nafion is added in, the arrangement of anions in
4 and 8 clusters shall show the advantage of facilitating ion transport.

In conclusion, a two dimensional Monte Carlo simulation of ion hopping has been
carried out for anions in four different arrangements: random distribution, 15 uniformly
distributed clusters, 8 clusters which form the rod-like channels and 4 uniformly distributed
clusters. Charge density versus time plots and ion distribution plots are recorded and
compared. In this one hydrophilic phase model, the simulation starting with uniform ion
distribution has the best performance: it has the highest peak value in charge density
plot; in ion distribution plot, it is observed to have the most cation accumulation close to
the cathode at steady state. It is evident that the initial ion distribution influences the
stationary response. It is also observed that the anion distribution influences the path of
cation hopping.

3.3 Simulation of conducting powder electrodes

The last application of Monte Carlo simulation of ion hopping in this chapter considers the
influence of conducting powder electrodes. The first subsection will focus on the motivation
to simulate the ionic polymer transducer with conducting powders. The second subsection
introduces the method to obtain the external electric potential distribution when conducting
powders are added into the material. The following subsection develops the mathematical
formula for the calculation of image charges induced on the surface of flat electrodes and
powder electrodes. Finally simulation results are presented and compared.

3.3.1 Ionomer-conductor interface

The simulations presented in this section build upon the experimental findings by Akle
et al. [9]. In his work, the mechanical strain of ionic polymer transducers is improved
by incorporating conducting powders, such as platinum particles, gold flakes, single-walled carbon nanotubes and high surface area RuO$_2$, in the electrode. As shown in Figure 3.7 (b), a 10-µm layer of large surface area electrode made of RuO$_2$ / Nafion mix has been added at the ionomer-conductor interface by a novel Direct Assembly Process (DAP). Conducting powders are dispersed evenly and the thickness of the powder electrode is controllable by DAP. The reason for conducting powders to improve the mechanical strain of the IPT can be illustrated in Figure 3.7 (c). Mobile ions diffuse through the ionomer electrolyte, accumulate in a thin boundary layer close to the metal-polymer interface and form the electric double layer around the particles. According to the double layer theory, specifically the Helmholtz model, the capacitance of the double layer is given by the following equation [96]:

$$C = \frac{\varepsilon A}{4\pi \delta},$$

(3.1)

where $\varepsilon$ is the dielectric constant of the electrolyte, $\delta$ is the distance from the electrode interface to the center of the ion, and $A$ is the effective surface area of the electrode interface. Equation 3.1 indicates that the capacitance increases linearly with the surface area of the electrode interface. Experimental results also demonstrate that there is an approximately linear relationship between capacitance and bending performance [31]. That is, the more cations accumulate at the cathode the more mechanical strain will be obtained. Therefore, the larger surface area formed by conducting powders leads to the larger mechanical strain. However, there is a saturation point when mechanical strain starts to decrease because too much added powder slows down or even blocks the ion movement at the polymer-metal interface. As a result, the morphology of conducting powders is an important parameter in modeling the ion transport at the electrodes. For Monte Carlo simulation, it is easy to incorporate the powder geometry for calculations. For example, as shown in Figure 3.8, the anode is at $y = 0$ and the cathode at $y = 50$ in two substrates. A powder sphere of 10nm diameter is centered at (25, 45) in Figure 3.8 (a) and the other powder sphere is centered at (25, 5) in Figure 3.8 (b). Comparably, the finite size of conducting powders is not easy to be included as a parameter in a continuum model.

### 3.3.2 External electric potential

After adding the powder sphere into the simulation, the boundary condition of the external field becomes non-uniform. Therefore, the electric potential distribution inside the IPT is...
Figure 3.7: Ionomer conductor interface: (a) the top cross-section of a Nafion 117 plated with platinum following 6 layers of impregnation-reduction, (b) the top cross-section of a Nafion 117 ionomer painted with 6 layers of Ruthenium oxide and Nafion mix (c) Interaction between cations and conducting powders at the boundary layer [9]
Figure 3.8: The initial state of a two dimensional ion hopping model with one conducting powder (a) at the cathode and (b) at the anode. H-shape represents fixed anions and spheres represent mobile ions.

analyzed by using Finite Element Method (FEM) software - ANSYS. For static electric field analysis ANSYS uses Laplace equation as the basis:

$$\nabla^2 V = 0$$  \hspace{1cm} (3.2)

with boundary conditions:

$$V(y = 0) = a_1,$$ \hspace{1cm} (3.3)

$$V = a_1 \text{ on } \partial \Omega_1,$$ \hspace{1cm} (3.4)

$$V(y = 50) = a_2,$$ \hspace{1cm} (3.5)

$$V = a_2 \text{ on } \partial \Omega_2,$$ \hspace{1cm} (3.6)

where $V$ is the potential, $a_1$ and $a_2$ are constant since constant voltage is applied, $\Omega_1$ and $\Omega_2$ are domains covered by conducting powders at two electrodes respectively and $\partial \Omega_1$ and $\partial \Omega_2$ denote the corresponding boundary. FEM turns a boundary value problem into a variation problem and then into an extreme problem of the ordinary function by dissection interpolation and discretization. Finally, several algebraic equations are obtained and the relevant numerical solution is solved [97]. Figure 3.9 presents the electric potential contour plots for Figure 3.8 when 0.2V is applied. From this figure it is apparent that boundary
conditions at the powder sphere have been satisfied. The conducting powder sphere expands
the potential at the electrode into the material. The calculated potential data has been
incorporated in the Monte Carlo simulation.

Figure 3.9: Electric potential contour plot with 0.2V applied and with one
powder sphere of 10nm in diameter (a) at the cathode and (b) at the anode.

3.3.3 Induced surface charges on the conducting powder

The interaction between ions and electrodes is calculated by the method of images. Com-
pared with the images calculation shown in Figure 2.8, the calculation becomes more com-
pllicated when conducting powders are considered. First we start analyzing the situation
when there is only one ion and one powder sphere. Suppose a positive point charge $Q$ is
located at a distance $d$ from the center of a grounded conducting sphere of radius $a$ ($a<d$)
(see Figure 3.10). The image charge generated $Q_i$ is situated inside the sphere and on the
line joining $O$ and $Q$. The electric charge carried by $Q_i$ is decreased compared with by
the original charge $Q$. Respectively, $Q_i$ and its distance from the sphere center $O$ can be
expressed as:

$$Q_i = -\frac{r}{d}Q,$$  \hspace{1cm} (3.7)

$$d_i = \frac{r^2}{d}.$$  \hspace{1cm} (3.8)
Figure 3.10: Point charge and its image in the presence of a conducting sphere

When two flat electrodes and powder spheres are considered, the basic idea to generate images is that once there is an image generated by one electrode, we investigate its disturbance on the other two electrodes. If this disturbance is above the threshold, there will be another image charge created to balance the disturbance. Therefore the first step is to decide an ignorable potential threshold. As shown in Figure 3.11, the distance between the Electrode 1 at \((x_0, 0)\) and the Electrode 2 at \((x_0 + a, 0)\) is a nm. The center coordinates of the powder sphere with radius of \(r\) are given as \((x_0 + a - r, 0)\). A positive ion \(+Q_0\) located at \((x, 0)\) is mirrored twice by the Electrode 1 and the Electrode 2, producing image charges of \(-Q_{0,1}, -Q_{0,2}, +Q_{0,1,2}\) and \(+Q_{0,2,1}\) (In the expression of image \(Q_{m,n}\), \(m\) represents the original charge and \(n\) represents the electrode being mirrored by). \(+Q_{0,2,1}\) does not need to be mirrored by the Electrode 2 and its potential on the Electrode 2, \(|U| = \frac{1}{4\pi\varepsilon} \frac{Q}{2a} < \frac{1}{4\pi\varepsilon} \frac{Q}{2a}\); \(+Q_{0,1,2}\) does not need to be mirrored by the Electrode 1 and its potential on the Electrode 1, \(|U| = \frac{1}{4\pi\varepsilon} \frac{Q}{3a-x} < \frac{1}{4\pi\varepsilon} \frac{Q}{2a}\). Hence if \(|U| < \frac{1}{4\pi\varepsilon} \frac{Q}{2a}\) we assume the potential is ignorable.

Next, consider the influence caused by five charges in 3.11 on the powder sphere. Because we ignore the disturbance by \(+Q_{0,2,1}\) on the Electrode 2, we can also ignore its potential on the sphere. Therefore we’ll have 4 new image charges inside the sphere.

The image of \(Q_0\): \[ Q_1 = -\frac{Q \cdot r}{a - r - x}, \quad d_1 = x_0 + a - r - \frac{r^2}{a - x - r} \quad (3.9) \]

The image of \(Q_{0,1}\): \[ Q_2 = +\frac{Q \cdot r}{a - r + x}, \quad d_2 = x_0 + a - r - \frac{r^2}{a - r + x} \quad (3.10) \]

The image of \(Q_{0,2}\): \[ Q_3 = +\frac{Q \cdot r}{a + r - x}, \quad d_3 = x_0 + a - r + \frac{r^2}{a + r - x} \quad (3.11) \]

The image of \(Q_{0,1,2}\): \[ Q_4 = -\frac{Q \cdot r}{a + r + x}, \quad d_4 = x_0 + a - r + \frac{r^2}{a + r + x} \quad (3.12) \]

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Figure 3.11: Illustration of the method of images for two electrodes and one powder sphere: four images are generated by the Electrode 1 and 2.

Those 4 images, \(Q_1 - Q_4\), will be mirrored by the Electrode 2:

\[
Q_{1,2} = +\frac{Q\cdot r}{a - r - x}, \quad d_{1,2} = x_0 + a + r + \frac{r^2}{a - x - r} \quad (3.13)
\]

\[
Q_{2,2} = -\frac{Q\cdot r}{a - r + x}, \quad d_{2,2} = x_0 + a + r + \frac{r^2}{a - r + x} \quad (3.14)
\]

\[
Q_{3,2} = -\frac{Q\cdot r}{a + r - x}, \quad d_{3,2} = x_0 + a + r - \frac{r^2}{a + r - x} \quad (3.15)
\]

\[
Q_{4,2} = +\frac{Q\cdot r}{a + r + x}, \quad d_{4,2} = x_0 + a + r - \frac{r^2}{a + r + x} \quad (3.16)
\]

Now check if \(Q_1 - Q_4\) will disturb the Electrode 1. Consider the potential generated by \(Q_1\) on the Electrode 1:

\[
|U_{Q1,1}| < \frac{1}{4\pi \varepsilon} Q \cdot r \cdot \frac{1}{a - r - x} \cdot \frac{1}{a - 2r}, \quad (3.17)
\]

Since

\[
x < a - 2r \Rightarrow \min(a - r - x) \approx r, \quad (3.18)
\]

we have

\[
\text{max}(|U_{Q1,1}|) = \frac{1}{4\pi \varepsilon} Q \cdot r \cdot \frac{1}{r(a - 2r)} = \frac{1}{4\pi \varepsilon} \frac{Q}{a - 2r} \quad (3.19)
\]

and so \(Q_1\) cannot be ignored by the Electrode 1. Consider the potential generated by \(Q_2\) on the Electrode 1:

\[
|U_{Q2,1}| < \frac{1}{4\pi \varepsilon} \frac{Q \cdot r}{a - r + x} \cdot \frac{1}{a - 2r} = \frac{1}{4\pi \varepsilon} \frac{Q}{(a + x - r)(\frac{a}{r} - 2)}. \quad (3.20)
\]
Since \( \frac{a}{r} - 2 > 2 \), \( a + x - r \geq a \) (3.21)

we have

\[
|U_{Q2,1}| < \frac{1}{4\pi \varepsilon} \frac{Q}{2a}
\]

and so \( Q_2 \) can be ignored by the Electrode 1. Consider the potential generated by \( Q_3 \) on the Electrode 1:

\[
|U_{Q3,1}| < \frac{1}{4\pi \varepsilon} \frac{Q \cdot r}{a + r - x} \frac{1}{a - r} = \frac{1}{4\pi \varepsilon} \frac{Q}{(a + r - x)(\frac{a}{r} - 1)}.
\]

(3.23)

Since

\[
x < a - 2r \Rightarrow a + r - x > 3r, \quad 3r(\frac{a}{r} - 1) = 3a - 3r = 2a + (a - 3r) > 2a
\]

(3.24)

we have

\[
|U_{Q3,1}| < \frac{1}{4\pi \varepsilon} \frac{Q}{2a}
\]

(3.25)

and so \( Q_3 \) can be ignored by the Electrode 1. Finally, consider the potential generated by \( Q_4 \) on the Electrode 1:

\[
|U_{Q4,1}| < \frac{1}{4\pi \varepsilon} \frac{Q \cdot r}{a + r + x} \frac{1}{a - r}.
\]

(3.26)

Since

\[
(\frac{a}{r} - 1) > 2, \quad a + r + x > a
\]

(3.27)

we have

\[
|U_{Q4,1}| < \frac{1}{4\pi \varepsilon} \frac{Q}{2a}
\]

(3.28)

and so \( Q_4 \) can be ignored by the Electrode 1.

In conclusion, only \( Q_1 \) will disturb the boundary condition at the Electrode 1. Another image \( Q_{1,1} \) is added to balance the potential on the Electrode 1:

\[
Q_{1,1} = +\frac{Q \cdot r}{a - r - x}, \quad d_{1,1} = x_0 - a + r + \frac{r^2}{50 - x - r}.
\]

(3.29)

Until now 5 more image charges \( Q_{1,1}, Q_{1,2} - Q_{4,2} \) have been added into the system (see Figure 3.12). The influence of \( Q_{1,1} \) on the conducting sphere and the Electrode 2 and the influence of \( Q_{1,2} - Q_{4,2} \) on the conducting sphere and the Electrode 1 need to be investigated respectively. By following the analysis shown in Equation 3.17 – Equation 3.28, we have
obtained all the images charges (see Figure 3.13). Images inside the conducting sphere have the forms as follows:

\[ Q_{4n+1} = (-1)^n + 1 \frac{Q\alpha_1}{n + 1 + n\alpha_1}, \quad n = 0, 1, 2..., \quad \alpha_1 = \frac{r}{a - r - x} \]  

(3.30)

\[ Q_{4n+2} = (-1)^n \frac{Q\alpha_2}{n + 1 + n\alpha_2}, \quad \alpha_2 = \frac{r}{a - r + x} \]  

(3.31)

\[ Q_{4n+3} = (-1)^n \frac{Q\alpha_3}{n + 1 + n\alpha_3}, \quad \alpha_3 = \frac{r}{a + r - x} \]  

(3.32)

\[ Q_{4n+4} = (-1)^n + 1 \frac{Q\alpha_4}{n + 1 + n\alpha_4}, \quad \alpha_4 = \frac{r}{a + r + x} \]  

(3.33)

with coordinates of

\[ d_0 = x_0 + a - r + \frac{r\alpha}{1 + 0 \cdot \alpha}, \quad \alpha = \alpha_1, \alpha_2, \alpha_3 \text{ or } \alpha_4 \]  

(3.34)

\[ d_n = x_0 + a - r + \frac{r[n + (n - 1)\alpha]}{n + 1 + n\alpha}, \quad n > 0. \]  

(3.35)

Additionally, \( Q_1 \) has image \( Q_{1,1} \) and \( Q_{1,2} \) has image \( Q_{(1,2),1} \) mirrored by the Electrode 1.

\[ Q_{1,1} = + \frac{Q \cdot r}{a - r - x}, \quad d_{1,1} = x_0 - a + r + \frac{r^2}{a - x - r} \]  

(3.36)

\[ Q_{(1,2),1} = - \frac{Q \cdot r}{a - r - x}, \quad d_{(1,2),1} = x_0 - a - r - \frac{r^2}{a - x - r} \]  

(3.37)

After image charges \( Q_n \) are mirrored by the Electrode 2, another group of images are obtained:

\[ Q_{4n+1,2} = (-1)^n \frac{Q\alpha_1}{n + 1 + n\alpha_1}, \quad n = 0, 1, 2... \]  

(3.38)
\[ Q_{4n+2,2} = (-1)^{n+1} \frac{Q\alpha_2}{n + 1 + n\alpha_2} \quad (3.39) \]
\[ Q_{4n+3,2} = (-1)^{n+1} \frac{Q\alpha_3}{n + 1 + n\alpha_3} \quad (3.40) \]
\[ Q_{4n+4,2} = (-1)^n \frac{Q\alpha_4}{n + 1 + n\alpha_4} \quad (3.41) \]

with coordinates of
\[
d_{0,2} = x_0 + a + r - \frac{r\alpha}{1 + 0 \cdot \alpha}, \quad \alpha = \alpha_1, \alpha_2, \alpha_3 \text{ or } \alpha_4 \quad (3.42) \\
d_{n,2} = x_0 + a + r - \frac{r[n + (n-1)\alpha]}{n + 1 + n\alpha}, \quad n > 0. \quad (3.43) \\
\]

Figure 3.13: Illustration of the method of images for two electrodes and one powder sphere

The definition of images in equation 3.30 - 3.33 and equation 3.38 - 3.39 indicates that infinite numbers of image charges are involved. From equation 3.7 we see that the amount of charge carried by an image decreases when it is reflected by the powder sphere. The ignorable threshold of \( n \) can be determined when the summation of the potential caused by \( Q_{4n+1} \), \( Q_{4n+2} \), \( Q_{4n+3} \) and \( Q_{4n+4} \) at any considered point inside the material meets the ignorable potential criterion. The formula can be represented as:
\[
\frac{1}{r} \frac{2n+2}{(2n+1)(4n+3)} < \frac{1}{2a}. \quad (3.44) 
\]

At this point, we finished analyzing the generation of images for one dimension. In a two dimensional case, when a charge is reflected by either electrode 1 or electrode 2, the \( y \) value of its image shall not be changed. Therefore, both ignorable potential threshold and equation 3.44 can be applied in two-dimensions as well.
3.3.4 Results and discussion

Several groups of simulations have been conducted to study the effects of location, size and amount of conducting powder spheres on the actuation response of ionic polymer transducers. The stationary charge density plots will be studied and compared. In each simulation, $0.2\, V$ is applied in a $50 \times 50$ lattice with 200 cations (anions). Anode is at $y = 0$ and cathode is at $y = 50$. The first group of simulations was designed to incorporate a conducting powder sphere at the cathode with different diameters. As shown in Figure 3.14 (a), a powder sphere with 8nm in diameter is centered at $(25, 46)$; in Figure 3.14 (b), a powder sphere with 10 nm in diameter is centered at $(25, 45)$; in Figure 3.14 (c), a powder sphere with 14 nm in diameter is centered at $(25, 43)$. Similarly, the second group of simulations has one powder sphere of 8nm, 10 nm and 14 nm in diameter, respectively, situated at the anode. Correspondingly, their center coordinates are $(25, 4)$, $(25, 5)$ and $(25, 7)$. The third group of simulation has two powder spheres of 10 nm in diameter. One is centered at $(25, 45)$ and the other is centered at $(25, 5)$.

![Figure 3.14: Ion distribution at steady state with one conducting powder sphere of (a) 8nm (b) 10nm (c) 14nm in diameter at the cathode. H-shape represents fixed anions and spheres represent mobile ions. The coordinates in plot (a) are also applied to plot (b) and (c).](image)

Figure 3.14 presents the snapshots of ion distribution at steady state for varied powder sphere dimensions. From this figure, it can be clearly seen that 3 plots have the cation depletion region close to the anode, the cation accumulation region close to the cathode and particularly the cation accumulation around the powder sphere. As the powder sphere size increases, it is more apparent to see the accumulation around the sphere. This
finding indicates that conducting powder sphere with bigger surface area can attach more ions around itself.

Figure 3.15 quantitatively presents the ion distribution shown in Figure 3.14 by the normalized charge density with respect to the distance to the anode. In three plots, red straight lines represent the charge density of the IPT without any powder sphere to provide the baseline; blue dash lines represent the charge density of the IPT with one powder sphere of 8 nm in (a), 10 nm in (b) and 14 nm in (c). Three regions are apparent to be seen: ion depletion region close to the anode corresponds to the negative values of charge density; charge neutrality region in the middle corresponds to zero value in charge density.
plots; charge accumulation region close to the cathode corresponds to peak value in charge density plots. One difference in the charge density plot between the case of without any powder and with one powder sphere is a small peak which appears at the distance to the anode of 42 nm in Figure 3.15 (a), of 39 nm in Figure 3.15 (b) and of 36 nm in Figure 3.15 (c). Those small peak values represent the ion accumulation around the powder sphere because the location of the small peak value matches the location of the powder sphere. As far as the peak value, as shown in Figure 3.15 (a), it is less in the IPT with an 8nm-diameter sphere than that in the IPT without any powder. This is thought to be the function of the disturbance of the powder sphere, namely, by the attraction to cations, the powder sphere prevents ion accumulation at the flat cathode. As the dimension of the sphere increases, the peak value increases as well. In Figure 3.15 (c), the peak value in the IPT with a 14nm-diameter sphere is even higher than that in the IPT without a powder. Comparison of this group of simulations reveals that the conducting powder sphere has a pulling function on cations toward the cathode.

The second group of simulations investigates the IPT actuation response when one conducting powder sphere is located at the anode. The results of normalized charge density are presented in Figure 3.16. It is apparent that the charge density peak value in the IPT with one powder sphere is higher than in the IPT without any powder. This feature is attributed to the pushing function of the powder sphere on cations, resulting in more depletion region close to the anode and then more ion accumulation close to the cathode. As the dimension of the sphere increases, the peak value of charge density increases correspondingly. The results indicate that the bigger dimension of the sphere creates the stronger pushing force on cations. From another point of view, we may reason that the presence of a powder sphere in a bigger dimension reduces the effective distance between the cathode and the anode for cations.

The last simulation investigates the IPT with two powder spheres. Figure 3.17 presents the charge density plots of three cases for comparison: (1) no powder sphere included (2) one 10nm diameter powder sphere at the anode and (3) two 10 nm diameter powder spheres with one at the cathode and the other at the anode. The case with two powder spheres possesses the highest peak value in charge density plot.

In conclusion, for the first time, the ionic polymer transducer with finite size of the conducting powder sphere at the boundary layers was studied by the Monte Carlo
Figure 3.16: Stationary normalized charge density with respect to the distance to the anode for four cases: without any powder, with one powder of 8 nm diameter, of 10 nm diameter and of 14 nm diameter at the anode.

Figure 3.17: Stationary normalized charge density with respect to the distance to the anode for 3 cases: no powder involved, one powder of 10 nm in diameter at the anode and two 10 nm diameter powder spheres with one at the anode and the other at the cathode.
simulation of ion hopping. The external electric field is analyzed by FEM software - ANSYS. Images charges reflected by two flat electrodes and the powder electrode are incorporated in the simulation. We focus on three groups of simulations: one conducting powder sphere with varied sizes located at the cathode; one conducting powder sphere with varied sizes located at the anode; two conducting powder spheres of 10 nm in diameter with one at the anode and the other at the cathode. Convincing simulation results support the fact that conducting powder spheres increase ion conduction. Comparison of these simulations reveals a consistent trend that ion accumulation at the cathode increases when the powder sphere diameter rises.

### 3.4 Chapter summary

In this chapter, Monte Carlo simulation of ion hopping has been used to investigate the influence of morphologies of ionic polymer transducers. Three types of morphology include a zigzag-shaped electrode, initial ion distributions and the conducting powder electrodes. A zigzag-shaped electrode attracts more ion accumulated at the cathode that a flat electrode. The path of cation hopping follows the fixed anions. Conducting powder spheres increase the ion conduction. Simulation results demonstrate that the morphology plays an important role in ion transport inside the ionic polymer transducer.
Chapter 4

Multiscale Modeling

In Chapter 3, we investigated the microscale morphologies of ionic polymer transducers using Monte Carlo simulation of ion hopping. However, Monte Carlo simulation is used for systems with comparably small scales. For example, the length scale studied in Chapter 2 and Chapter 3 for Monte Carlo simulation is up to 50nm and the time scale is up to micro seconds. It is impractical to model the whole Nafion membrane with 200 $\mu$m by using Monte Carlo simulation. In order to compare with experimental results, we develop a multiscale model to link a continuum model with Monte Carlo simulation.

4.1 Method of multiscale modeling

Multiscale modeling, used in many areas such as fluid dynamics [98], polymer science [99] and materials science, is the field of solving physical problems which have important features at multiple scales. Figure 4.1 presents the characteristic time and length scales for the main types of simulation models used in materials science [100][101]. For many systems, those different length and time scales are essential to tailor the macroscopic physical and mechanical properties and those scales strongly interact and cannot be modeled separately. Therefore, the challenges in this field include the coupling and linking of models in different scales. A brief introduction to three typical hybrid multiscale techniques to couple atomistic and continuum models will be given in the following subsection.
4.1.1 Introduction to hybrid multiscale techniques

Broadly defined, there are three typical multiscale modeling strategies: top-down, bottom-up and direct coupling approaches [102]. Top-down approaches solve the continuum equations by extracting constitutive laws from the underlying atomistic descriptions. Quasicontinuum method is one of the top-down approaches and it was first performed by Tadmor, Ortiz and Phillips [103]. In this approach, the entire domain is divided into finite element meshes down to the atomic dimensions. Inside each element, a small relevant subset of atoms is selected, the energies of individual “representative atoms” are computed and the finite element solution follows by energy minimization. The elements in the model behave locally or non-locally. A local element is away from defects, has uniform deformation and its computation befits a continuum model while a non-local element is highly deformed with inhomogeneous structural features and the straightforward atomistic methodology is used for the energy calculation. Other top-down approaches include the bridging scale method [104] and the heterogeneous multiscale method [105].

In contrast, bottom-up methods coarse-grain (the procedure of grouping neighboring atoms into single interaction ensembles, thus drastically reducing the number of particles and interactions in the calculations) the atoms of the system into macro-atoms and the
fundamental equations defined on the atoms are coarse-grained into equivalent macroscale equations. For example, Rudd and Broughton proposed a coarse-grained molecular dynamics method [106]. They model the important regions of the system by using molecular dynamics (MD) while the far-field regions are coarse grained recovering the continuum elasticity equations. For the coarse-grain (CG) system, the energy functional is defined as a constrained ensemble average of the atomistic energy. The equations of motion are Hamilton’s equations. When the mesh nodes and the atomic sites are identical, the CGMD equations of motion agree with the atomistic equations of motion and therefore, MD regions are coupled seamlessly to CG regions. This method reduces the computational overhead of MD, however, the seamless coupling of length scales is achieved with high computational costs.

For direct coupling methods [107, 108, 109], the physical domain is decomposed into atomistic, continuum and interface regions. The atomistic region and continuum region are calculated separately and the interface region is used to exchange information between the atomistic and continuum regions. For example, three regions of interest proposed by Broughton etc. [107] include: continuum mechanics, that is elasticity theory in this case, implemented by finite elements; atomistic statistical mechanics via molecular dynamics; and quantum mechanics described by using semi-empirical tight-binding method. To seamlessly couple different length scales, the appropriate handshaking algorithms have been designed at the interface. Figure 4.2 shows the FE/MD handshake region, that is the overlapping region between the FE and MD region. The FE mesh has been refined down to the atomic

Figure 4.2: FE/MD handshake region: particles are hybrid nodes/atoms; and triangles are finite element meshes
scale such that each FE node coincides with an MD atom, establishing a one-to-one correspondence between the atoms and the nodes at equilibrium. Therefore, as long as there is no diffusion, atomic motion may be viewed as displacement of a node and the displacement field may be viewed as motion of an atom away from its equilibrium position. In order to achieve the dynamic coupling between the MD and FE regions, an explicit energy function or Hamiltonian has been defined for the transition zone so that the potential energy is taken to have both FE and MD contributions while the lumped mass approximation in FE brings the FE kinetic energy into agreement with the MD kinetic energy. In the result the FE and MD displacements would obey the same equations of motion and the dynamics at the interface are well behaved. Similarly, Aktas and Aluru [110] used a handshaking algorithm to couple the direct simulation Monte Carlo method and a continuum region treated by Stokes equations for multiscale analysis of microfluidic filters.

The linking scheme used for the ionic polymer transducer will be different from those methods mentioned above. Based on the unique properties of the ionic polymer transducer, we propose a novel methodology to couple Monte Carlo simulation and a continuum method to obtain the transient and stationary responses.

4.1.2 The multiscale model used for ionic polymer transducers

First of all, periodic boundary conditions can be applied in Monte Carlo simulation to increase the length scale in the direction perpendicular to the electric field. A periodic boundary is usually used in molecular dynamics simulations. As an assumption, it makes a simulation that consists of only a few hundred atoms behave as if it was infinite in size. Figure 4.3 illustrates the concept of periodic boundary conditions. The shaded box represents the simulation system which is replicated to fill the whole of space. Virtual copies of all particles exist in surrounding boxes. Every particle in the shaded box has an exact duplicate in each of the surrounding boxes in every detail, including location, velocity, etc. For example, when periodic boundary conditions are applied in the direction perpendicular to the electric field (e.g. in $x$ direction), if a particle is located at position vector $\mathbf{r}$ in the original lattice, the identical particles are assumed to be located at $\mathbf{r}+iL$, where $i$ is integer numbers varied from $-\infty$ to $+\infty$ and $L$ is the lattice length. As particles moves in the shaded box, its periodic image moves in all of the boxes in exactly the same way. As particles leave the shaded box on one of its sides immediately re-enter it on the opposite
side. Therefore, periodic boundary conditions can only be applied for zero flux or insulation boundary conditions. For periodic boundary conditions (PBCs), a so-called cutoff distance can be introduced to reduce computational demands. When this cutoff is employed, all the interactions between all pairs of particles that are further apart than a specified cutoff value are set to zero. The simulation box size is at least twice the cut-off radius without a particle being able to sense the symmetry of the periodic lattice.

In the direction of electric field, the periodic boundaries must be abandoned because the external potential does not have the same periodicity as the simulation unit. PBCs are not adapted to far-from-equilibrium problems and another method is needed to deal with the thickness between electrodes. The inspiration comes from observations of charge density plots at steady state. As shown in Figure 2.13 and Figure 2.14, obviously, each charge density plot at steady state has three regions, a cation depletion region close to the anode, an accumulation region close to the cathode and an approximate zero charge density region for the middle part. Due to the zero charge density in the middle, it is assumed that once there is a cation leaving the anode boundary layer, there will be another cation entering into the cathode boundary layer (see the illustration in Figure 4.4). Therefore two boundary layers can be simulated, as if they were connected directly without the central part of the material, to obtain the steady state response.
There are two ways to demonstrate that the thickness of the material will not affect the steady state response. Firstly, surface charge accumulated at the interface between the ionomer and the conducting electrode is decided by the applied voltage and the capacitance of the electric double layer. Equation 3.1, \( C = \frac{εA}{4πh} \), shows that the capacitance of the double layer is related to the dielectric constant of the electrolyte, the distance from the electrode interface to the center of the ion and the effective surface area of the electrode interface. Since the thickness of the membrane will not affect the capacitance, it will not affect the amount of surface charge at the cathode. Secondly, if we look at the normalized charge density plots at steady state for the substrate with different thickness (compare Figure 2.13 (a) and Figure 2.14 (a) and compare Figure 2.13 (b) and Figure 2.14 (b)), when the same voltage is applied across the substrate, very similar boundary layer close to the cathode is obtained.

Based on the assumption that steady state response can be simulated by using a much thinner substrate, Monte Carlo simulation overhead is reduced dramatically. The next question is, how much thickness shall be simulated for two boundary layers? Figure 2.13 illustrates that as the applied potential increases, the thickness of the zero charge density region in the middle decreases. In another word, the thickness of two boundary layers increases as the applied potential increases. In Figure 2.14, if higher potential (e.g. \( > 0.2V \)) is applied across this membrane in 30 nm thick, the zero charge density region in the middle can be expected to disappear. And then this 30 nm thick substrate will not be thick enough to completely represent two boundary layers. Therefore the minimum thickness required for the simulated substrate shall lead to three regions in a stationary charge density plot.

Figure 4.4: Illustration of large scale simulation. Red dots represent cations inside anode block and blue dots represent cations in cathode block
The second assumption made in this multiscale model is that the transient response only depends on the ion transport in the central part of the membrane. For the transient response, a continuum model is solved separately from Monte Carlo simulation and it is linked with Monte Carlo simulation by the conservation of the net charge transported across the membrane. For the steady state response, the same code and results in Chapter 2 for the substrate of 50 nm thick can be used when 0.1 V, 0.2 V and 0.5 V is applied, respectively. In the next section, Monte Carlo simulation results for the steady state response will be compared with experimental data.

4.2 Simulation of two connected boundary layers

The simulation results of two connected boundary layers have been compared with experimental data. Experiments were conducted by Barbar Akle, who graduated from CIMSS at Virginia Tech in 2005. For the comparison, flat plate electrodes are considered. In the experimental setup flat plates of gold with an area of 2cm × 2cm were prepared. A Nafion sample 200 µm thick is sandwiched by the flat electrodes. The area becomes approximately 2.4cm × 2.4cm after the sample is hydrated by water. The current is measured for 0.1V, 0.2V and 0.5V applied step potential. In all the experiments the Nafion sample is submerged in de-ionised water. The current density \( i(t) \) is computed as

\[
    i(t) = \frac{i_m(t)}{A}, \tag{4.1}
\]

where \( i_m(t) \) is the measured current and \( A \) is the area of the electrodes. The charge density \( q(t) \) is computed as

\[
    q(t) = \int_0^t (i(\tau) - i_{ss}) d\tau, \tag{4.2}
\]

where \( i_{ss} \) is the steady state value of the current density. The steady state value needs to be subtracted from the original current density due to ion transport with blocking electrodes so that \( i(\tau) - i_{ss} = 0 \) at steady state.

Figure 4.5 shows the steady state charge density comparison. When the ion hopping distance \( l \) of 1.4 nm is used in the Monte Carlo simulation shown in Chapter 2, the prediction at 0.1V and 0.2V are very promising. At a larger potential such as 0.5V, the simulation result underestimates the experimental steady state value. Wallmersperger explains this underestimation by the fact that “redox reactions at the electrode occur which are not
Figure 4.5: A comparison of peak charge density between experimental data and Monte Carlo simulation results with the applied electric potentials $U = 0.1V; 0.2V; 0.5V$

captured by the model” when the higher voltage is applied. Table 4.1 records the steady state charge density values from Monte Carlo simulation when $l = 1nm$. Those data will be used later in the calculation of transient responses.

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>0.1V</th>
<th>0.2V</th>
<th>0.5V</th>
</tr>
</thead>
<tbody>
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<td>Peak charge density from MC ($\mu C/cm^2$) when $l=1.4nm$</td>
<td>3.5</td>
<td>6.3</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Table 4.1: Peak charge density values from Monte Carlo simulation with hopping size of $1.4nm$ for the applied electric potentials $U = 0.1V; 0.2V; 0.5V$
4.3 Transient response

4.3.1 Continuum model for the central part

In this subsection, we will derive the continuum model hybrid with Monte Carlo simulation. In describing the transport of ions through ion-exchange membranes such as Nafion, the Nernst-Planck development serves as the most common approach [36]. By substituting the Nernst-Planck equation into the continuity equation, the ion drift and diffusion are taken into account for calculating the ion concentration as function of time and space and the convection-diffusion equation [85] for cations in one dimension can be expressed as:

$$\frac{\partial n(x,t)}{\partial t} = \frac{\partial n(x,t)}{\partial x} \mu E(x,t) + n(x,t) \mu \frac{\partial E(x,t)}{\partial x} - D \frac{\partial^2 n(x,t)}{\partial x^2},$$

(4.3)

where $n$ denotes the cation concentration, $x$ is the dimension in the direction of electric field, $\mu$ is the cation mobility, $E$ the local electric field and $D$ is the diffusion coefficient. The mobility $\mu$ and the diffusion coefficient $D$ meet the Nernst Einstein relation

$$\mu = \frac{Dq}{kT} = \frac{FD}{RT},$$

(4.4)

where $q$ is the electric charge, $k$ is Boltzmann constant, $T$ is the absolute temperature, $R$ is gas constant and $F$ is the Faraday constant.

Zero-flux boundary conditions are prescribed so that the summation of drift current and diffusion current is equal to zero. In another word, the Nernst-Planck equation is equal to zero

$$-D \frac{\partial n(x,t)}{\partial x} - \frac{F}{RT} Dn(x,t) \frac{\partial \phi(x,t)}{\partial x} = 0,$$

(4.5)

where $\phi$ is the electric potential. In the modeling work of Wallmersperger [111], nonlinear partial differential equations 4.3 and 4.5 have been solved by using numerical methods such as finite element method. However, in order to couple with Monte Carlo simulation results and to obtain the transient response, we reduce the system to a linearized continuity expression for ion transport in the central part of the transducer. This is achieved by ignoring the electric potential influenced by ions and by considering the electric field as a constant which is equal to the external field. At this point, there is

$$\frac{\partial E(x,t)}{\partial x} = 0$$

(4.6)

and the governing equation 4.3 turns into

$$-\frac{\partial n(x,t)}{\partial t} = \frac{\partial n(x,t)}{\partial x} \mu E - D \frac{\partial^2 n(x,t)}{\partial x^2},$$

(4.7)
where $E$ is a constant. For boundary conditions, Equation 4.5 will not have zero flux on the right side. Instead, the expression becomes

$$-D \frac{\partial n(x, t)}{\partial x} + \frac{F}{RT} D n(x, t) E = \frac{f(t)}{F},$$

(4.8)

where $f(t)$ is the ion current density flowing between the central part of the material and two boundary layers. The system has initial condition

$$n(x, 0) = 0.$$

(4.9)

In conclusion, Equations 4.7 - 4.9 will be used to solve the transient response for the middle part of the ionic polymer transducer.

### 4.3.2 Scaling and dimensionless variables

Before solving equations 4.7 - 4.9 by using the finite difference method, dimensionless independent and dependent variables are introduced so that the number of physical parameters can be reduced because only certain combinations of the parameters appear in the resulting equations. In general, a quantity $q$ is made dimensionless by [112]

$$\bar{q} = \frac{q - q_0}{q_c},$$

(4.10)

where $q_0$ is a characteristic reference value and $q_c$ is a characteristic magnitude of $q - q_0$. Note that $q$, $q_c$ and $q_0$ are measured in the same unit. Thus, the units cancel and $\bar{q}$ becomes dimensionless. The right scale $q_c$ is required because the ultimate goal of the scaling is to obtain a unit magnitude of $\bar{q}$. In the continuum model (Equations 4.7 - 4.9) we can introduce

$$\bar{x} = \frac{x}{b}, \quad \bar{n} = \frac{n}{n_c}, \quad \bar{t} = \frac{t}{t_c}, \quad \text{and} \quad \bar{\psi} = \frac{\psi}{\psi_c},$$

(4.11)

where $\bar{x}$, $\bar{n}$, $\bar{t}$ and $\bar{\psi}$ are scaled dimensionless variables for coordinate, ion concentration, time and current density, respectively. $b$ is the thickness of the material. $n_c$, $t_c$ and $\psi_c$ is the scale for ion concentration, time and current density, respectively. We will postpone the precise estimation of some scales and perform the scaling first. Noting that

$$\frac{\partial n}{\partial t} = \frac{n_c}{t_c} \frac{\partial \bar{n}}{\partial \bar{t}}, \quad \frac{\partial n}{\partial x} = \frac{n_c}{b} \frac{\partial \bar{n}}{\partial \bar{x}}, \quad \frac{\partial^2 n}{\partial x^2} = \frac{n_c}{b^2} \frac{\partial^2 \bar{n}}{\partial \bar{x}^2},$$

(4.12)

substitute Equation 4.12 into the governing equation (Equation 4.7)

$$\frac{\partial \bar{n}}{\partial \bar{t}} = D \frac{t_c}{b^2} \frac{\partial^2 \bar{n}}{\partial \bar{x}^2} - \mu E \frac{t_c}{b} \frac{\partial \bar{n}}{\partial \bar{x}},$$

(4.13)
and substitute Equation 4.12 into the boundary conditions (Equation 4.8)

\[ \frac{\partial \bar{n}}{\partial \bar{x}} - \mu E \frac{b}{D} \bar{n} = -\frac{b\psi_c}{Dn_c} \bar{\psi}(t). \]  
(4.14)

Let

\[ D \frac{t_c}{b^2} = 1 \Rightarrow t_c = b^2 ; \quad \mu E \frac{t_c}{b} = \mu E \frac{b}{D} = M ; \quad \frac{b\psi_c}{Dn_c} = 1 \Rightarrow \psi_c = \frac{Dn_c}{b}. \]  
(4.15)

Finally the governing equation becomes

\[ \frac{\partial \bar{n}}{\partial \bar{t}} = \frac{\partial^2 \bar{n}}{\partial \bar{x}^2} - M \frac{\partial \bar{n}}{\partial \bar{x}}, \]  
(4.16)

with boundary condition

\[ \frac{\partial \bar{n}}{\partial \bar{x}} - M \bar{n} = -\bar{\psi}(t), \]  
(4.17)

and initial condition

\[ \bar{n}(\bar{x},0) = 0. \]  
(4.18)

### 4.3.3 Finite Difference method

In this section, ‘\( n \)' will be used as an index so we replace ‘\( n \)' in Equations 4.16 - 4.18 by ‘\( u \)’. After the scaling is carried out, it is common to ignore the bars in the dimensionless quantities. That is, scaling leads to the following model problem for the transient ion transport equation in the middle part of the membrane:

\[ \frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} - M \frac{\partial u}{\partial x}, \]  
(4.19)

\[ \frac{\partial u}{\partial x} - M u = -\psi(t), \]  
(4.20)

\[ u(x,0) = 0. \]  
(4.21)

For this one-dimensional model, we introduce a uniform grid in \( x \) and \( t \) directions in a finite difference method. The grid points are then \( 0 = x_1 < x_2 < ... < x_n = 1 \) in space and \( 0 = t_0 < t_1 < ... \) in time. Set \( h \) as the space interval and \( \Delta t \) as the time interval. The goal is to compute \( u(x,t) \) at the grid point and the numerical approximation to \( u(x_i,t_l) \) is written as \( u_i^l \). The derivatives at the grid point \( (x_i,t_l) \) are approximated by finite differences. The first-order and the second-order spatial derivatives can be approximated as

\[ \frac{\partial}{\partial x} u(x_i,t_l) \approx \frac{u_i^l - u_{i-1}^l}{h}, \]  
(4.22)

\[ \frac{\partial^2}{\partial x^2} u(x_i,t_l) \approx \frac{u_{i-1}^l - 2u_i^l + u_{i+1}^l}{h^2}. \]  
(4.23)
For the time derivative, different choices are considered. One possibility is to apply a forward difference
\[
\frac{\partial}{\partial t} u(x_i, t_l) \approx \frac{u_{l+1}^i - u_l^i}{\Delta t}.
\] (4.24)

A backward difference could be used as well
\[
\frac{\partial}{\partial t} u(x_i, t_l) \approx \frac{u_l^i - u_{l-1}^i}{\Delta t}.
\] (4.25)

Another difference, a centered difference, approximate the partial differential equation at the space-time point \((x_i, t_{l-\frac{1}{2}})\). Among these three differences, the forward difference yields an explicit updating formula from which new values of the unknown can be computed while both the backward and the centered differences are the counterpart, implicit schemes. After applying the finite difference if we write the system in matrix form:
\[
Au_l^i = b(u_{l-1}^i),
\] (4.26)

the coefficient matrix \(A\) is diagonal for explicit schemes and the linear system of equations can be solved by hand. Provided the computed values at time level \(l\), the new values \(u_{l+1}^i\) are obtained. For implicit schemes the matrix \(A\) will be tridiagonal and solution of the linear system of equations at each time level is required. The forward difference will only be stable when the time step \(\Delta t\) is small. More precisely, it will be stable when \(\Delta t \leq h^2/2\) [112]. For the backward difference, the computations are numerically stable for any choice of \(\Delta t\). However, as \(\Delta t\) increases, the accuracy decreases because its numerical error is of order \(\Delta t\) in time. For the centered difference, the computations are stable for all \(\Delta t\) and the accuracy is of order \(\Delta t^2\).

These three methods can be combined and written in a unified form by the so-called \(\theta\)-rule [112]. That is, the partial differential equation is sampled at the space-time point \((x_i, t_{l-1+\theta})\), where \(\theta\) is a parameter in \([0, 1]\). Obviously when \(\theta = 0\), the forward difference is used; when \(\theta = 1\), the backward difference is used; when \(\theta = 0.5\), the centered difference is used. We employ
\[
\frac{\partial}{\partial t} u(x_i, t_{l-1+\theta}) \approx \frac{u_l^i - u_{l-1}^i}{\Delta t}.
\] (4.27)

Quantities at time level \(t_{l-1+\theta}\) are approximated by a weighted average of the same quantities at levels \(l\) and \(l - 1\),
\[
u_{l-1+\theta}^i = \theta u_l^i + (1 - \theta) u_{l-1}^i.
\] (4.28)
Therefore, the spatial derivatives become:

\[
\frac{\partial}{\partial x} u(x_i, t_{i-1+\theta}) = \theta \frac{\partial}{\partial x} u(x_i, t_i) + (1 - \theta) \frac{\partial}{\partial x} u(x_i, t_{i-1}),
\]

(4.29)

\[
\frac{\partial^2}{\partial x^2} u(x_i, t_{i-1+\theta}) = \theta \frac{\partial^2}{\partial x^2} u(x_i, t_i) + (1 - \theta) \frac{\partial^2}{\partial x^2} u(x_i, t_{i-1}).
\]

(4.30)

The resulting differences can be written

\[
\frac{\partial}{\partial x} u(x_i, t_{i-1+\theta}) = \theta \frac{u^l_i - u^l_{i-1}}{h} + (1 - \theta) \frac{u^l_{i-1} - u^l_{i-1}}{h},
\]

(4.31)

\[
\frac{\partial^2}{\partial x^2} u(x_i, t_{i-1+\theta}) = \theta \frac{u^l_i - 2u^l_i + u^l_{i+1}}{h^2} + (1 - \theta) \frac{u^l_{i-1} - 2u^l_{i-1} + u^l_{i+1}}{h^2}.
\]

(4.32)

Substituting Equation 4.27, 4.31 and 4.32 into the governing equation 4.19 yields

\[
\frac{u^l_i - u^l_{i-1}}{\Delta t} = \theta \frac{u^l_{i-1} - 2u^l_i + u^l_{i+1}}{h^2} + (1 - \theta) \frac{u^l_{i-1} - 2u^l_{i-1} + u^l_{i+1}}{h^2} - M\theta \frac{u^l_i - u^l_{i-1}}{h} - M(1 - \theta) \frac{u^l_i - u^l_{i-1}}{h},
\]

(4.33)

which can be sorted as:

\[
\left( -\theta \frac{\Delta t}{h^2} - M\theta \frac{\Delta t}{h} \right) u^l_{i-1} + \left( 1 + 2\theta \frac{\Delta t}{h} + M\theta \frac{\Delta t}{h} + 2M\theta \Delta t \right) u^l_i - \theta \frac{\Delta t}{h} u^l_{i+1} =
\]

(4.34)

\[
u^l_{i+1} = \left( 1 - \theta \right) \frac{\Delta t}{h} \left( 2u^l_{i-1} - 2u^l_{i-1} + u^l_{i+1} \right) - M(1 - \theta) \frac{\Delta t}{h} \left( u^l_{i-1} - u^l_{i-1} \right).
\]

The system implied by Equation 4.34 can be written in matrix form shown as Equation 4.26 and solved by using Gaussian elimination procedure.

Boundary condition at x=0 has:

\[
\frac{u_2 - u_0}{2h} - Mu_1 = -\psi \Rightarrow u_0 = u_2 - 2hMu_1 + 2h\psi.
\]

(4.35)

Substitute equation 4.35 into the governing equation in finite difference form 4.34:

\[
\left( -\theta \frac{\Delta t}{h^2} - M\theta \frac{\Delta t}{h} \right) u^l_2 + \left( 1 + 2\theta \frac{\Delta t}{h} + M\theta \frac{\Delta t}{h} + 2M\theta \Delta t \right) u^l_1 =
\]

(4.36)

\[
u^l_{i+1} = \left( 1 - \theta \right) \frac{\Delta t}{h} \left( 2u^l_{i-1} - 2hMu^l_{i-1} + 2h\psi^l - 2u^l_{i-1} \right)
\]

Boundary condition at x=1 has:

\[
\frac{u_{n-1} - u_{n+1}}{2h} - Mu_n = \psi \Rightarrow u_{n+1} = u_{n-1} - 2hMu_n - 2h\psi.
\]

(4.37)

Substitute equation 4.37 into the governing equation in finite difference form 4.34

\[
\left( -\theta \frac{\Delta t}{h^2} - M\theta \frac{\Delta t}{h} \right) u^l_{n-1} + \left( 1 + 2\theta \frac{\Delta t}{h} + 3M\theta \frac{\Delta t}{h} \right) u^l_n + \theta \frac{\Delta t}{h} \left( 2h\psi^l \right) =
\]

(4.38)

Equations 4.34, 4.36 and 4.38 will be used in the programming code. \( \theta = 0.5 \) is taken in the simulation and so the scheme is based on centered differences.
4.3.4 Linking between Monte Carlo simulation and the continuum model

Recall that in section 4.1.2 we discuss a multiscale approach assuming ion movement in boundary layers governs the steady state response and ion transport in the middle part governs the transient response. Monte Carlo simulation is performed to simulate two connected boundary layers and a continuum model is used for the ion transport in the middle part of the IPT. No dynamic linking is needed since the solutions of two models do not influence each other. In fact, two models are connected by the conservation of the net charge transported:

$$\int_{0}^{\infty} f(t) dt = \int_{0}^{\infty} I(t) dt = Q,$$  \hspace{1cm} (4.39)

where $f(t)$ is the cation current density flowing from the anode boundary layer and meanwhile flowing into the cathode boundary layer. $f(t)$ shows up in boundary conditions for the continuum model (see Equation 4.8) and this quantity is the transient response for the whole system. $Q$ denotes the peak charge density or the total charge transported. $I(t)$ is the current density from Monte Carlo simulation.

The peak charge density can be obtained from Monte Carlo simulation for different voltages as shown in Figure 4.5 and as listed in table 4.1. Therefore, for transient response, we are looking for the solution of $f(t)$, whose integration is known, from equations 4.7 - 4.9. Based on the results from Monte Carlo simulation (see Figure 2.15 and Figure 2.16) and from experimental measurements [113], the current density response should be approximately an exponential decay. We employ

$$f(t) = a \cdot e^{-bt},$$  \hspace{1cm} (4.40)

where $a$ and $b$ are real numbers. Note that

$$\int_{0}^{\infty} f(t) dt = -\frac{a}{b} e^{-bt} \bigg|_{0}^{\infty} = -\frac{a}{b} (0 - 1) = \frac{a}{b},$$  \hspace{1cm} (4.41)

which means the integration of an exponential decay function such as $f(t)$ will only depend on the ratio of two parameters, that is the ratio of $a$ to $b$. For example, in Figure 4.6, three current density functions $f_1(t) = 6e^{-500t}$, $f_2(t) = 4.5e^{-375t}$ and $f_3(t) = 3e^{-250t}$ are exponential decay functions as shown in Equation 4.40. According to Equation 4.41, the integration of three current density functions, that is the peak charge density, remains the same due to the constant ratio of $a$ to $b$. In other words, if we keep the constant ratio of $a$ to $b$, by adjusting one of the parameters, $a$ or $b$, the different peak current density and time
constant can be obtained while the peak charge density stays the same. We will implement this idea in the simulation for the continuum model to find the current density response \( f(t) \).

\[
\begin{align*}
0.01 & = 500 \cdot \text{etf}^t \\
0.015 & = 375 \cdot \text{etf}^t \\
0.02 & = 250 \cdot \text{etf}^t
\end{align*}
\]

\( f_1(t) = 6e^{-500t} \)

\( f_2(t) = 4.5e^{-375t} \)

\( f_3(t) = 3e^{-250t} \)

Figure 4.6: Exponential decay functions with the same integration

4.3.5 DIFFPACK and algorithm to obtain the current response

Considering the special boundary conditions in the model, instead of using the software with built-in functions, such as MATLAB, to solve the PDEs by using the finite difference method, we choose Diffpack for its flexibility to build a specialized simulator. Diffpack [114] is a sophisticated tool for developing numerical software, with main focus on numerical solution of partial differential equations. Diffpack works as a numerical library consisting of C++ classes and those C++ classes can be combined into application codes to solve problems in diverse fields. In general, Diffpack contains a large collection of useful abstractions, such as vectors, matrices, couplings to visualization tools, representation of linear systems, iterative methods for sparse linear systems, finite difference, element and volume grids, adaptive grids, numerous examples on simulators for problems like heat transfer, elasticity, and fluid flow, etc.

At this point, we shall create a simulator for the continuum model, which here means developing a computer program that generates and solves the discrete equations 4.34, 4.36.
and 4.38. The program will be implemented in Diffpack/C++, adopting a coding style close
to plain C. For the initial condition \( n(x,0) = 0 \), we set \( u_0 = 0 \). The discrete equations 4.34, 4.36 and 4.38 can be written in matrix form

\[
Au^l = b(u^{l-1}),
\]

(4.42)

where \( A \) is an \( n \times n \) matrix defined as

\[
A = \begin{bmatrix}
A_{1,1} & A_{1,2} & 0 & \ldots & \ldots & \ldots & 0 \\
A_{2,1} & A_{2,2} & A_{2,3} & 0 & A_{3,2} & A_{3,3} & A_{3,4} & \ldots & A_{i,i-1} & A_{i,i} & A_{i,i+1} & \ldots & 0 \\
0 & A_{n-1,n-2} & A_{n-1,n-1} & A_{n-1,n} & 0 & A_{n,n-1} & A_{n,n} \\
\end{bmatrix}
\] (4.43)

The entries \( A_{i,j} \) are easily identified from equations 4.34, 4.36 and 4.38:

\[
A_{1,1} = 1 + 2\theta \frac{\Delta t}{h^2} + M\theta \frac{\Delta t}{h} + 2M^2\theta \Delta t, \quad A_{1,2} = -2\theta \frac{\Delta t}{h^2} - M\theta \frac{\Delta t}{h},
\]

(4.44)

for \( i = 2, \ldots, n-1 \),

\[
A_{i,i-1} = -\theta \frac{\Delta t}{h^2} - M\theta \frac{\Delta t}{h}, \quad A_{i,i} = 1 + 2\theta \frac{\Delta t}{h^2} + M\theta \frac{\Delta t}{h}, \quad A_{i,i+1} = -\theta \frac{\Delta t}{h^2},
\]

(4.45)

and

\[
A_{n,n-1} = -2\theta \frac{\Delta t}{h^2} - M\theta \frac{\Delta t}{h}, \quad A_{n,n} = 1 + 2\theta \frac{\Delta t}{h^2} + 3M\theta \frac{\Delta t}{h}.
\]

(4.46)

The expression for the matrix \( A \) is tridiagonal, that is, each row has at most three nonzero entries. Matrices where most of the entries are zero are classified as sparse matrices. Diffpack specifies a tridiagonal matrix class with the declaration of MatTri(real) A(n), which allocates memory for a full \( n \times n \) matrix. A MatTri object assumes indices of the form \( A(i,k) \) for \( k=-1, 0, 1 \), where \( k=-1 \) corresponds to \( A_{i,i-1} \), \( k=0 \) refers to the main diagonal \( A_{i,i} \), and \( k=1 \) corresponds to \( A_{i,i+1} \). Solving a system of \( n \) equations using Gaussian elimination (LU factorization) on a standard dense matrix needs the order \( n^3 \) arithmetic operations. However, if we know that the matrix is tridiagonal, the Gaussian elimination algorithm
requires operation only on the nonzero entries and the total work becomes of order $n$. By utilizing the MatTri object, the efficiency of the algorithm can be dramatically improved.

The main steps in the algorithm to solve the continuum model for ion transport in the middle part of the membrane are summarized in Figure 4.7. Initially, the calibration is

\[ \theta - \text{rule scheme for the continuum model to simulate ion transport in the middle part of the membrane} \]

Define $u_i$ and $u_i^-$ as $u_i^0$ and $u_i^{-1}$, respectively

SET THE INITIAL CONDITIONS:

$u_i = 0, \quad \text{for } i = 1, ..., n$

$t = 0; \quad f(t) = a_i e^{-b_i t}$

while time $t \leq t_{\text{max}}$

$t \leftarrow t + \Delta t$

Define tridiagonal system:

$Au = b, \quad \text{where}$

$u = (u_1, ..., u_n)^T$,

Solve the system $Au = b$

Initialize for next step:

$u_i^- = u_i, \quad \text{for } i = 1, ..., n$

dump the solution $(u_i, i = 1, ... n)$ to file

if $e^{-b_i} < 10^{-5}$

break while loop and stop the simulation

Figure 4.7: Algorithm implemented in a Diffpack program to solve the continuum model

performed at 0.2V to decide the value of the diffusion coefficient. Before running the simulation, the current density function for 0.2V is constructed: $f(t) = 9 \times e^{-1429t}$. The time constant and peak current value of this function agrees with the experimental data shown in Figure 4.8 (b). And the integration of this function is equal to the peak charge density from Monte Carlo simulation shown in Table 4.1. Substituting $f(t)$ into the boundary con-
ditions, the system is solved and the simulation stops when $e^{-b_1t}$ is less than a specified tolerance value. The calibration variable diffusion coefficient is adjusted so that when the simulation stops, there is $\sum_{i=1}^{n} u_i \to 0$, where $u_i$ is the ion concentration at each node in the finite difference.

For another applied voltage, the default values of two parameters, $a_1$ and $b_1$, in current density function $f(t)$, are chosen randomly with the condition that the value of $a_1/b_1$ is equal to the peak charge density from Monte Carlo simulation shown in Table 4.1. The current density function is substituted into the boundary conditions and the system is solved. If $\sum_{i=1}^{n} u_i \to 0$ before the simulation stops, increase $a_1$ and change $b_1$ to keep $a_1/b_1$ as a constant; if $\sum_{i=1}^{n} u_i > 0$ or non-ignorable when the simulation stops, decrease $a_1$ and change $b_1$ to keep $a_1/b_1$ as a constant. This method has been employed to find current density functions and results are presented in the following section.

### 4.4 Current density plots and discussion

The algorithm mentioned in the previous section has been implemented in a Diffpack program. The parameter values used for the numerical simulations are provided in Table 4.2 in which the diffusion coefficient is the calibration variable. Figure 4.8 shows the comparison between the experimental measurement of current density and the current density functions obtained from the continuum model. Experimental data in Figure 4.8 is the corresponding transient response for the steady state response shown in Figure 4.5. In numerical simulation, with the applied voltage of 0.2V, the calibration is performed to decide the diffusion coefficient. Obviously, for the applied electric potentials $U = 0.1V$ and $0.2V$, the peak value and time constant of current density functions obtained from numerical simulation are in good agreement with experimental results. At 0.5V, the peak current density is lower

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scale for the ion concentration</td>
<td>$n_c$</td>
<td>1200mol/m$^3$</td>
</tr>
<tr>
<td>Thickness of the membrane</td>
<td>$b$</td>
<td>200µm</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>$D$</td>
<td>$2.5 \times 10^{-6}m^2/s$</td>
</tr>
</tbody>
</table>

**Table 4.2: Simulation parameters in Diffpack program**
than the experimental result because the peak charge density in Figure 4.5 from the model underestimates the experimental result. Table 4.3 quantitatively lists three current density functions for simulation results in Figure 4.8. The integration of the current density function is equal to the peak charge density calculated from Monte Carlo simulation and provided in Table 4.1. The total amount of transported ions is conserved between two scales.

![Figure 4.8](image)

**Figure 4.8:** A comparison between the measured and numerical current density for the applied electric potentials $U = (a)\, 0.1\, V$; (b) $0.2\, V$; and (c) $0.5\, V$

Figure 4.9 presents the time response of normalized charge density for the central part of the material with the applied voltage of $0.1\, V$ (see Figure 4.9 (a)), $0.2\, V$ (see Figure 4.9 (b)) and $0.5\, V$ (see Figure 4.9 (c)), respectively. For three plots, initially, charge density is
<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Current density ($mA/cm^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1V</td>
<td>$6 \times e^{-1714t}$</td>
</tr>
<tr>
<td>0.2V</td>
<td>$9 \times e^{-1429t}$</td>
</tr>
<tr>
<td>0.5V</td>
<td>$14 \times e^{-1273t}$</td>
</tr>
</tbody>
</table>

Table 4.3: Expressions for current density plots in continuum model in Figure 4.8 with the applied electric potentials $U = 0.1V; 0.2V; 0.5V$

zero through the dimension. As time increases, there is ion flux entering into one boundary $x = 0$ and the same amount of ion flux leaving out from the other boundary $x = 1$. All three plots show positive normalized charge density close to $x = 0$ and negative charge density close to $x = 1$ and at the end of the simulation, normalized charge density becomes zero through the dimension. In fact, at the end of the simulation, the summation of the absolute value at each node in finite difference is around 1% of its peak value during the simulation time. As the applied voltage increases, the peak value in charge density during the simulation time increases correspondingly. Figure 4.9 (a) shows that it takes 0.0067 second to stop the simulation and the charge density becomes zero everywhere for 0.1V, Figure 4.9 (b) shows that it takes 0.0081 second for 0.2V and Figure 4.9 (c) shows that it takes more than 0.0091 second for 0.5V. Obviously, as the applied voltage increases, the simulation time increases correspondingly.

4.5 Chapter summary

In this chapter, a novel multiscale model has been developed for the ion transport inside the ionic polymer transducer. The steady state response is obtained by using Monte Carlo simulation to simulate two boundary layers as if they were connected directly. The transient response is calculated by numerically solving a linearized continuum model with the assumption that the transient response is an exponential decay function. Two scales are linked by the conservation of the total amount of transported ions. Both transient responses and steady state responses show good agreement with experimental measurements.
Figure 4.9: Time responses of ion transport through the middle part of the membrane with the applied voltage (a) 0.1V (b) 0.2V and (c) 0.5V
Chapter 5

Summary and Conclusions

Throughout this research, the primary objective has been the development of a model which describes the ion transport of ionomeric polymer transducers. This chapter provides a summary of the major research results, conclusions and contribution of this work. The most important results are presented first, followed by a discussion of the significant contributions to the field. Finally, recommendations for future work are presented at the end of this chapter.

5.1 Research Conclusions

In this dissertation, Monte Carlo simulation of ion hopping has been developed to model the actuation behavior of ionomeric polymer transducers under a direct current electric field. Based on the electromechanical coupling model developed by Leo et al. [70], we see the existence of a correlation between the surface charge accumulation and the mechanical deformation in ionomeric actuators. Therefore, results of charge density and current density are produced by the simulation. In normalized charge density plots, three distinct regions are observed: the cation depletion region close to the anode, the charge neutrality region for the central part of the material and the cation accumulation region close to the cathode. The influences of two macroscopic parameters, the diffusion coefficient and the electrical permittivity, are studied. Simulation results show that higher values of permittivity result in an increase in both the peak current density and the peak charge density. Diffusion coefficient influences the transient response, that is, the rate of decrease of the peak current density. However, diffusion coefficient will not affect the value of the peak charge density.
which is the stationary response. By using Message Passing Interface (MPI) library, parallel computation of Monte Carlo simulation is utilized to reduce the simulation time. By using two processors, the speedup is equal to 1.82 and efficiency is 91%. The scalable parallel pseudo random number generator (SPRNG) standard library is implemented to generate statistically independent random numbers when multiple processors are involved. When two processors are used for the parallel computation, the correlation between the result from sequential code and that from parallel code is 0.991 and the speedup is 1.82.

In chapter 3, Monte Carlo simulation has been utilized to study the morphologies of the ionic polymer transducer. First, stationary ion accumulation close to a flat electrode and that close to a zigzag-shaped electrode are compared. More and faster ion accumulation at the cathode can be obtained in the ionic polymer transducer with zigzag-shaped electrodes than with flat-shaped electrodes. Next, responses are compared when the simulation starts from different initial ion distributions. The difference in charge density plots demonstrates that Monte Carlo simulation is sensitive to study the morphologies of the ionic polymer transducer. Finally, for the first time, conducting powders with finite size were simulated. In Monte Carlo simulation, conducting powders are represented by spheres. The external potential distribution inside the ionic polymer transducer is calculated by using finite element method software, ANSYS. The interaction between ions and electrodes, including flat electrodes and powder spheres, is calculated by the method of images. When the powder spheres are added in, the formula to compute the generated image charges has been deduced. We focus on three groups of simulation: (1) There is one conducting powder sphere with varied sizes located at the anode. Both charge density plots and the ion distribution snapshot at steady state show ion accumulation around the powder sphere. (2) There is one conducting powder sphere with varied sizes located at the anode. As the dimension of the powder sphere increases, the peak value of charge density increases correspondingly. Conducting powders located at the anode are suggested to have a pushing function on cations, resulting in more depletion region close to the anode and then more ion accumulation close to the cathode. (3) There are two powder spheres with one at the anode and the other at the cathode. Compared with the simulation with one powder sphere and without powder sphere, the simulation with two powder spheres has the highest peak value in charge density plot. Convincing simulation results demonstrate that conducting powder spheres increase ion conduction.
In chapter 4, a multiscale model has been developed to increase the scale of Monte Carlo simulation and to compare with the experimental data. Periodic boundary conditions are applied to increase the length scale in the direction perpendicular to the electric field. In the direction of electric field, the stationary response and transient response are computed separately. Due to the charge neutrality region in the central part for every charge density plots at steady state, it is assumed that once there is a cation leaving the anode boundary layer, there will be another cation entering into the cathode boundary layer. Therefore, the stationary response can be obtained by simulating two boundary layers as if they were connected directly without the central part of the material by using Monte Carlo simulation. The second assumption made in this multiscale model is that the transient response depends on the ion transport in the central part of the membrane. For the transient response, a linearized continuum model has been solved separately from Monte Carlo simulation and it is linked with Monte Carlo simulation by the conservation of the net charge transported across the membrane. The transient response, current density function, is approximated as an exponential decay and is substituted into the boundary conditions of the continuum model. The continuum model is solved in software DIFFPACK by using finite difference method so that the parameters in the current density function can be adjusted while the integration of the current density function, that is the peak charge density holds constant. Both transient responses and steady state responses show good agreement with experimental measurements.

5.2 Research Contributions

This dissertation has three major contributions to the modeling of ionic polymer transducers. These contributions better the understanding of ionic polymer transducers, develop a model to predict the actuation and provide a tool to help enhance the performance of ionic polymer transducers. The following is a list of these contributions:

- The development of a Monte Carlo simulation of ion hopping for ionic polymer transducers. The ion transport due to electric stimulus is the primary mechanism of actuation and the simulation can track the ion movement directly. Successful implementation of parallel computation reduces the simulation time and makes it possible to increase the scale to some extent or to study more complicated systems.
• Studies of morphologies of ionic polymer transducers by using Monte Carlo simulation, especially the study of conducting powders applied at the polymer-conductor interface. In the simulation for conducting powders, the external electric field was analyzed by finite element method and the formula to compute the image charges has been derived. Convincing simulation results demonstrate that conducting powders increase ion conduction. The model can be applied to calculate the conducting powder volume percentage at the saturation point to better the material performance.

• A novel multiscale model has been built for ionic polymer transducers. This multiscale model enables the study of the morphologies in nano/micron scale close to the boundary layers of ionic polymer transducers. And meanwhile the simulation results can be compared with and validated by experimental data.

5.3 Recommendations for Future Work

Three main recommendations for future works will be presented in this section.

• The first recommendation is to optimize the volume percent of the conducting powders by using the developed multiscale model. More conducting powders can be added into Monte Carlo simulation to find the saturation point for the maximum generated mechanical strain. The strain rate can be computed through the transient response in the multiscale model. A larger lattice and higher ion concentration can be simulated by using the parallel computation.

• A second idea is to study other morphologies of ionic polymer transducers by using Monte Carlo simulation. In this dissertation we focused on the conducting powders applied at the polymer-conductor interface, while other morphologies, such as hydrophilic and hydrophobic phases, various solvents, etc., are also very important for the performance of ionic polymer transducers.

• The last future work recommendation is to simulate ion transport during the back relaxation or sensing stage of ionic polymer transducers.
Vita

The author, Xingxi He was born on May 25, 1979 in Sichuan province, China. She received a BE in Mechanical Engineering in August, 2001 from Beijing University of Aero & Astro in China. After her undergraduate study, Xingxi went to United States to pursue her advanced degrees in Mechanical Engineering. She graduated from Ohio University in August, 2003 with her MS degree and her Master’s work was focusing on Robotics/Haptics (virtual reality force feedback). She started her PhD study at Virginia Tech since August, 2003. In the first year at VT she was a graduate teaching assistant for Machine Design course in the mechanical engineering department. Over the next three and half years, she worked on the research in modeling of ionic polymer transducers under the advisement of Dr. Donald Leo in the Center for Intelligent Material Systems and Structures. Her research interest will always be computer programing, modeling and simulation for understanding and prediction.

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