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Author/s:

Wang, Peiyao

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Atomistic simulation-informed continuum models for ion distribution in water-filled graphene nanoslits and at graphene surfaces

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Atomistic simulation-informed continuum models for ion distribution in water-filled graphene nanoslits and at graphene surfaces

A thesis submitted in total fulfillment for
the degree of Doctor of Philosophy

Peiyao Wang

ORCID: 0000-0003-0406-4952

Department of Mechanical Engineering

The University of Melbourne

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Abstract

Aqueous electrolytes confined in nanoporous materials are involved in many biological and technological systems. Both atomistic simulation and experiments have revealed that the non-classical solvation state, ion spatial location, or in-pore density of electrolyte can emerge in nanoconfinement. The ability to develop quantitative models to describe the microscopic structure of nanoconfined electrolytes is crucial to allow the new nanoscience to be readily harvested for future engineering design. Although atomistic simulations can predict a detailed microscopic structure for nanoconfined aqueous electrolytes, the limited model size and time scale of atomistic simulations make it difficult to scale up the results for experimental design. By contrast, conventional continuum modelling is computationally efficient to describe and predict the behaviour or performance of a macroscale system. However, it is generally challenging to have atomic structure considered in continuum modelling, which will affect the accuracy of the resultant models. Continuum models that can describe the microscopic structure of aqueous electrolytes are so far very rare due to limited understanding of the crowdedly interplayed physical interactions in nanoconfinement and the lack of approaches for quantitatively measuring or parameterizing the interplayed physical interactions.

Using water-filled graphene nanoslits and a range of selected aqueous electrolytes as a model system, this PhD work aims to examine the critical role of nanoconfined water structure on the electrolyte ion structure and develop nanoscience-based continuum models to describe quantitatively the microscopic electrolyte structure that are parameterized with MD simulations. Such an approach enables the proposed continuum models to have the essential components necessary to reproduce the microscopic electrolyte structure observed in MD simulations, meanwhile, to maintain its capability to predict and design nanoconfined aqueous-electrolyte-based applications on a large scale. Specifically, the spatial density of aqueous electrolytes

including NaBF_4 , LiBF_4 , and CsBF_4 in non-electrified graphene nanoslits was first studied. By incorporating the non-electrostatic interaction energy between ions and graphene wall from the MD simulations, the modified Poisson-Boltzmann model can capture the oscillated layering of ion density profiles. The accuracy of the resultant continuum model can be further improved after the water distribution effect was considered through a new lattice-gas model. The conventional Poisson-Boltzmann model was then modified to improve the prediction of electric potential values in the electrified interface system. After the orientation of interfacial water molecules was considered, the modified continuum model can remedy the oversimplified surface potential values predicted by the Poisson-Boltzmann model and the artificial layer equipped by an implicit dielectric constant in the Poisson-Boltzmann-Stern model.

The continuum models developed were then combined with the nuclear magnetic resonance spectra of the aqueous electrolytes absorbed between graphene layers obtained by experimental collaborators to study the ion absorption density inside multilayered graphene membranes. The high simulation efficiency of the continuum modelling enabled the investigation of the membrane thickness effect on ion absorption density inside nanochannels. The prediction of the continuum model was in good agreement with experimental results when the slit sizes were relatively large ($> 1.2\text{nm}$). It also revealed that the electrical polarization of the graphene membrane contributed to the electroneutrality breakdown in nanochannels. In addition, the results show that not only the ion-graphene interaction strength but also the ion layered distribution structure played dominant roles in the ion accessibility inside nanochannels.

Declaration of Authorship

I, Peiyao Wang, declare that this thesis titled, ‘Nanoscience-based continuum models for ion distribution in water-filled nanoslits’ and the work presented in it are my own. I confirm that:

1. This thesis composes only my original work towards the PhD
2. Due acknowledgment has been made in the text to all other materials used.
3. This thesis is less than 100,000 words in length, exclusive of tables, figures, maps, bibliography, and appendices as approved by the Research Higher Degrees Committee.

Peiyao Wang

October 2020

Preface

1. **Chapter 3:** A new continuum model for ion-specific distribution in uncharged nanoslits.

- All the results in this chapter are my work.

2. **Chapter 4:** A refined continuum model for EDL structure at an electrified interface.

- All the results in this chapter are my work.

3. **Chapter 5:** Continuum model study of ion partition in multilayered graphene membranes in comparison with experiments.

- All the results in this chapter are my work except for the experimental characterization results provided by Dr. Diyan Liu.

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Abbreviation

CDC	carbide-derived carbons
EDL	electric double layer
ERDF	electron radial distribution functions
GCS	Gouy-Chapman-Stern
MD	molecular dynamics
MGMs	multi-layered graphene membranes
mPB	modified Poisson-Boltzmann
NICS	nucleus independent chemical shift
NMR	nuclear magnetic resonance
PB	Poisson Boltzmann
PMF	Potentials of mean force
PZC	potential of zero charges
QCM	quartz-crystal microbalance
RDF	radius distribution functions
SAMs	self-assembled monolayers
SAXS	small-angle X-ray scattering
TP ₁	first transit phrase
TP ₂	second transit phase
vdW	van der Waals
WHAM	weighted histogram analysis method

Symbols

c_i	the average cation or anion concentration
r_b	positive vector of boundary plane of system box
r_{int}	positive vector of graphene/electrolyte interface
A_p	plane area of the slit region
C_w	the capacitance of orientated water molecules by surface
E_0	the electric field strength of polarized water layer when the surface charge was zero
L_E	the thickness of electrolyte region
L_0	the thickness of orientational dipoles region
L_V	the thickness of vacuum region
N_-	the available sites of anions
N_+	the available sites of cations
$N_{\pm, \infty}$	available sites of cations or anions in the bulk state
N_∞	total available sites in the bulk state
N_s	the available sites of solvents
Q_{di}	areal ion number density
Q_i	total number of anions or cations in slit region
c_i	local ion concentration
c_i^0	bulk concentration of the ion species i
k_B	Boltzmann constant
q_i	the charge of ion species i
$r_\pm$	the bare radius of cations or anions
$r_\pm^*$	the radius of solvated cations or anions
r_w	the radius of a water molecule
ϵ_0	dielectric constant of vacuum
λ_-	the relative size of anion relative to a solvent molecule
λ_+	the relative size of cation relative to a solvent molecule
$\mu_\pm$	chemical potential of cations or anions
φ_{ion}	electric potential arising from ions
φ_{water}	electric potential arising from water molecules
$\epsilon_{r,g}$	the dielectric constant of graphene

$\epsilon_{r,s}$	dielectric constant of electrolyte solution
d	interlayer space
ε	depth of the potential well
F	Helmholtz free energy
L_G	the length of a graphene sheet
LJ	12-6 Lennard Jones Potential
n	the number solvated water molecules around an ion
N	the total available sites
Ng	total slit number formed by graphene sheets
r	the distance between the interacted particles
T	absolute temperature
t_G	thickness of graphene sheet
V_i^{PMF}	the non-electrostatic interaction energy between ion and surface
W	the number of microstates
ε	relative dielectric constant
σ	the surface charge density
σ_0	the interaction equilibrium distance
φ	electric potential

Chapter 1: Introduction

1.1 Background

Aqueous electrolytes are critical working fluids in biological systems and industrial applications ¹. The structure of aqueous electrolytes in nanoconfinement including both ions and solvent molecules can present distinctive features from the bulk solutions, such as ion species dependence ², inhomogeneous spatial density ^{3,4}, and reshaped hydration shell ⁵. Those microscopic structure features provide a vast potential to improve the macroscopic performance or functionality of applications from two aspects. First, some applications are fundamentally a nanoscale science by dealing with interface process within the electric double layers which are (sub)nanometers in thickness, such as electrochemical energy storage or conversion devices ⁶⁻⁷. Second, some applications are associated with the nanostructure of bulk nanoporous materials to achieve a selection or manipulation of molecules or ions in fluids, such as cell or desalination membranes and various nanofluidic devices ⁸. Indeed, some recent studies demonstrated several cases where the enhanced macroscopic performance was driven by the microscopic electrolyte structure ⁸⁻¹⁰. For example, Chmiola *et al.* achieved around three-time capacitance enhancement using sub-nanometer porous carbon as electrodes. They ascribed the underlying mechanism to the narrowed ion-wall distance because ions were dehydrated in such a small nanopore ¹⁰. To rationalize and establish the quantitative relationship between macroscale performance and confined electrolyte microstructure in nanopores, a theoretical model that can quantitatively describe the nanoscale structures and properties meanwhile can efficiently bridge to large length scale is imperative.

The microscopic electrolyte structure is determined by multiple interatomic physical interactions ¹¹. The atomistic simulations are preferable tools to investigate such electrolyte

structure as they explicitly involve most of the known physical interactions¹²⁻¹³. There are many successful applications¹⁴⁻¹⁶. However, atomistic simulations have two main limitations¹⁷. First, it has a very limited time-/length-scale, which makes its utilization very computational time-consuming for complex nanoporous material systems or under dynamic conditions. Second, it is challenging to extract/identify key physical factors and their quantitative influences on the observed phenomena from the obtained high-dimensional data in the atomistic simulations. It is a difficult task to distil understandable and implementable design guidelines with quantitative parameters for macroscopic engineering applications directly. A continuum model developed based on physics principles is an alternative choice. For example, the well-known Gouy-Chapman-Stern (GCS) model can semi-quantitatively predict the structure of the electric double layer (EDL)¹⁸ from several key physical factors, such as electrolyte concentration, dielectric constants, and temperature. However, the microscopic electrolyte structure in the nanometer-sized EDL region cannot be captured in the GCS model, owing to some adopted assumptions¹⁹. For example, the ions are treated as point charges and the solvent is described as a continuum dielectric background. An improved continuum model should include some essential atomistic scale physical interactions so that it can accurately describe the microstructure of electrolytes. Note that these essential physical interactions usually interplay and there are no simple additivity relationships between them²⁰. Such improved continuum models are rare.

Recently, researchers combined atomistic simulations and continuum models to capture some features of the microscopic electrolyte structure^{1, 17, 20-21}. The atomistic simulations were used to extract effective parameters to represent a part of interplayed interactions. The continuum model was then used to calculate the ion distribution profile by adopting those parameters and compared against the atomistic simulation results. For example, Lima *et al.* extracted the

potential of mean force (as extra interaction energy in Poisson-Boltzmann (PB) theory) for a single ion approaching the surface to represent the interplay of interfacial disperse, hydration, and image forces ²¹. Bonthuis *et al.* extracted the oscillated interaction potential between ions to present the interplay of steric, Coulomb, and hydration interactions ¹. McEldrew *et al.* extracted the effective ion radius considering the ion-specific hydration ability ¹⁷. In those works, the water molecules did not only serve as a uniform/non-uniform dielectric background but presented multiple means to affect ion spatial distributions. For example, the volume-exclusion mechanism allowed water molecules to reduce the available occupation sites of ions, but the hydration force would pull ions to absorb with water molecules. It is an open question of how water molecules will interplay with ions in the sub-2 nm nanopores or the interfacial region where the spatial distribution and the orientation of water molecules show significant deviations from the bulk condition ^{6, 22-23}.

This PhD thesis aims to develop nanoscience-based continuum models to describe the structure of electrolytes at the interface region and in the nanoslits. The effect of the water molecules on the microscopic electrolyte structure will be investigated with a comprehensive study of their spatial arrangement and orientations at the molecular level. Their polarization response to the electrified surface and ion distributions will also be investigated to derive their screening capability. The three research chapters will be: 1) A new continuum model for ion-specific distribution in uncharged nanoslits; 2) A refined continuum model for interface electric double layer (EDL) structure; 3) Continuum model study of ion accessibility inside multi-layered nanochannels embedded in graphene membranes in comparison with experiments. The continuum models developed in this thesis can serve as a ground for future engineering designs of the aqueous electrolyte-based large system from nanoscale.

1.2 Research Aims

1.2.1 A new continuum model for ion-specific distribution in uncharged nanoslits

Both MD simulation and experimental characterization results revealed the distinctive structure of interfacial water molecules. The water molecules showed an enhanced density (3-4 times of bulk density) and an ordered structure in the vicinity of the hydrophobic graphene surface due to the interruption of continuous hydrogen-bonding network ²⁴, forming the so-called ‘the first water layer’. This region usually extends around four angstroms from the surface. The significant water density oscillations were also suggested to present in nanoslits with a sub-2 nm size. The volume-exclusion effect will repulse ions to locate outside of ‘the first water layer’, but the solvation energy would attract ions to water molecules. It is an open question of how local ion density will accommodate such water oscillations.

We will investigate this question in Chapter 3 with molecular simulations and continuum theory. The microscopic electrolyte structure in a range of graphene slits (different slit sizes) will be obtained using molecular dynamics (MD) simulations. The interaction energy between ion and surface and the spatial structure of the water molecules will be calculated in MD simulations. The continuum theory will be then developed based on the obtained atomic insights to improve the description of the electrolyte microstructure in nanoconfinement.

1.2.2 A refined continuum model for EDL structure in the vicinity of an electrified surface

The microstructure of aqueous electrolytes in the vicinity of an electrified surface plays a fundamental role in electrochemical energy storage and conversion devices. Unlike ionic liquids, the microstructure of aqueous electrolytes and the recently developed water-in-salt electrolytes are subject to the additional effects of water molecules. At the interface region, the spatial distribution and orientation of water molecules would be modulated by both the charges

(e.g., electrolyte ions and surface charges) and the nature of the electrode surface, leading to a complicated dielectric screening of the ion-surface electrical interaction.

In Chapter 4, the MD simulation will be used to calculate the molecular-level electric potential profiles and density profiles of ions and water molecules in the electrified interface system. The electric potentials of water molecules will be decomposed into two components: 1) one induced by charges from the electrolyte ions; 2) the other one arising from the graphene wall with surface charge. The obtained molecular-level insights will then be used to refine the conventional Poisson-Boltzmann model to describe the electric double layer (EDL) structure and quantitatively predict some key performance parameters, such as the potential of zero charge and surface potentials at the electrified interface region.

1.2.3 Continuum model study of ion partition in multilayered graphene membranes in comparison with experiments

The in-pore ion density, spatial location, and ion-specificity are the key microstructure features of electrolyte to determine the performance in many engineering applications, such as energy density in bulk electrodes and ion selectivity of cell membranes. An effective theoretical model to elucidate and describe them in single nanoslit was developed in the first research aim. Because of the balance between the reservoir and in-pore space, the increased material volume will lead to deviations from those microscopic features predicted based on models for single nanoslits, particularly in bulk porous materials where concentration gradient and potential gradient exists between in-pore space and reservoir. A quantitative comparison between continuum models for large scale systems and the experimental results is expected. But it is a challenging task because the complex structure of bulk porous materials (such as amorphous

carbon) makes the experimental characterization and unambiguous theoretical model construction very difficult.

In Chapter 5, taking advantage of the relatively simple and quantifiable structure of graphene membranes, we will quantitatively compare the ion densities inside the nanochannels of multilayered graphene membranes between our theoretical model predictions and experimental characterizations. The influence of ion-specificity, slit-size, and thickness of membranes on the ion accessibility inside nanopores will be analysed quantitatively.

Chapter 2: Literature Review

The electrolyte features or properties present a high dependence on the degree of nanoconfinement (e.g., pore size) and electrolyte ion species in many electrolyte-based applications⁷. Those distinctive nanoconfined effects are determined by the complex interplay of the related interactions, such as steric force, disperse interactions, and electrostatic interactions), which may be different or complementary in the varied nanoconfined scenario. In the past two decades, many works investigated the underlying mechanisms by outlining molecular level pictures using computational simulation tools²⁵⁻²⁷. Some traditional theoretical models were also modified to interpret and predict the electrolyte nanoscale behaviours for applications and new designs²⁸⁻²⁹. Here, we try to summarize and analyse these works, aiming to identify key knowledge gaps in this field. In this chapter, we will start with the observable and measurable phenomena in experiments, revealing the interesting electrolyte microstructure and properties that the classic theory fails to predict. Then, we will move to the observations at the microscale. We will discuss the electrolyte structural organization features at the molecular level that were revealed by atomistic simulations. In the end, we will discuss the capabilities of current continuum models to predict the microstructure of electrolytes in nanoconfinement or in the interface region and then identify the challenges that will be addressed in this PhD thesis.

2.1 The experimental phenomena beyond the classic theory description

The aqueous electrolytes are the working solutions in diverse applications ranging from biology to colloids. The observed phenomena (driven by the electrolyte properties) and the properties of interests could vary depending on application systems^{2,30}. In this section, we will

choose ion storage devices as an application entry point to discuss/analyse the electrolyte properties at the nanoscale, which are often distinctive from bulk solutions.

Pore size sensitivity of the ion storage performance in nanoporous materials. The distribution of electrolyte ions at a charged surface was first modelled by Gouy and Chapman. They assumed that the ions were point charges embedded in a continuum of constant dielectric background. The ions are distributed following the Boltzmann statistics and they interact with all the other charges via a mean-field that is modelled by the Poisson equation. The differential capacitance calculated from the Gouy-Chapman model only depends on the electrode surface potential (φ_0) and electrolyte concentration (c_0). This model has the advantage of simplicity and good accuracy for univalent ions in dilute electrolytes (0.001-0.05M). But it has limited capability to describe some ion storage phenomena reported recently, particularly for the electrolyte microstructure in nanopores, which are different from those in the vicinity of the open surface.

The first case is a study of carbon EDL capacitance, which was optimized by controlling the electrode pore size in 2006³¹. Chmiola *et al.* showed that the capacitance was increased by around three times when the carbon pore size was decreased below 1 nm (smaller than the ion hydration radius) (Figure 2.1a). Their results challenged the conventional view arising from the Gouy-Chapman model, which does not consider the effects of ion finite size on the capacitance value. This study provided us with a solid clue that ions could be partially dehydrated to absorb in nanopores. It indicates that the electrolyte organizations at the nanoscale could be very different from the bulk solutions as well as in the vicinity of the open surface in terms of their hydration status. Accordingly, the enhanced capacitance in sub-nanopores was hypothesized to originate from a closer distance of electro-absorbed dehydrated ions to the electrode surface³¹.

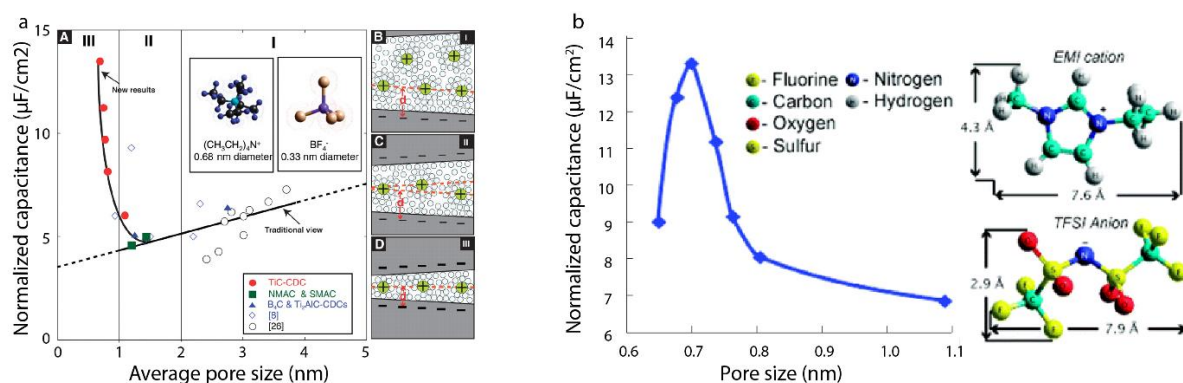


Figure 2.1 Normalized capacitance vs. the pore size of the carbide-derived carbons (CDC) samples. Normalized capacitance is obtained by dividing the specific capacitance by the specific surface area. **(a)** The figure was adopted from the work of Chmiola *et al.*³¹ It shows the normalized capacitance as a function of the pore size. The electrolyte is 1.5 M NEt_4BF_4 salt in acetonitrile. **(b)** The figure was adopted from the work of Largeot *et al.*³². In this work, the electrolyte is solvent-free electrolyte: the ionic liquid (EMI-TFSI). It shows the normalized capacitance as a function of the pore size.

However, the electrolyte organization in the nanopores seems beyond the simple argument of ion desolvation. In 2008, Largeot *et al.* also studied the carbon capacitance as a function of electrode pore size. The electrolyte they used is a solvent-free ionic liquid (*i.e.*, EMI-TFSI, the ion size in the longest dimension is around 0.79 nm and 0.76 nm for TFSI and EMI ions, respectively) (Figure 2.1b)³². They observed a similar trend as the study of Chmiola *et al.*, where a maximum capacitance was reached when the pore size narrowed to 0.7 nm down from 1.1 nm. They explained the observed phenomena from the viewpoint of the ion organization efficiency inside pore space. The spatial distribution of electrolytes in 0.7 nm pore is expected as the most efficient way by minimizing the free space available. For ions inside a larger pore, the average distance between the pore wall and centre of electrosorbed ions would increase when the pore size is increased³². Their explanation could make sense, provided that the packing density of electrolyte ions in such one-ion layer space remains at the same level (or

denser) as that in large pores. Although this work used the ionic liquids as a model electrolyte, the revealed ion organization efficiency would also present in solvent-contained electrolytes, and additionally there would be an issue of solvent organization efficiency. However, this explanation was challenged by later works. In some cases, the surface-area normalized capacitance was also experimentally measured to randomly fluctuate around a relatively constant when the pore size varied from 0.7 nm to 15 nm³³. Some MD simulation works reported an oscillated trend as the pore width is increasing as well³⁴. It seems that there are some other factors to balance (or compete) with the effect of narrowed pore volume (leading to a closer average ion-surface distance) in nanoconfinement. These experimental results clearly indicate that the pore size effect plays a vital role in ion organization in nanopores. However, the underlying mechanism could not be revealed easily from those experiment phenomena.

Ion-species dependence of ion storage performance in nanoporous materials. Apart from the pore size dependence of ion storage performance, researchers also observed that the charging behaviours and performances were sensitive to ion-species in recent years³⁵⁻³⁶. One representative work from Levi *et al.* in 2009³⁷. They used the quartz-crystal microbalance (QCM) to probe the concentration and compositional changes of electrolyte in the pore volume of microporous activated carbons. Then the supercapacitor charging mechanism was analysed via measuring simultaneously mass changes (can be transited to number ratio changes) of cations and anions during the dynamic charging conditions (*i.e.*, cyclic voltammetry) (Figure 2.2a)³⁷. The signals of both electrochemical and quartz-crystal microbalance measurements varied on electrolyte ion types (*i.e.*, LiCl, CsCl, BaCl₂, and TBACl), which is in contrast to the reported ion-type independent capacitance (measured in aqueous electrolytes) in the vicinity of graphene open surface²⁴. The LiCl and CsCl solutions present a similar cyclic

voltammogram in shape and the amount of reversible charge. But the cyclic voltammograms of BaCl_2 and especially TBACl solutions become gradually asymmetric (Figure 2.2a). The QCM data shows a nearly negligible mass peak of TBA^+ ions during charging cycles, while the mass peaks of Li^+ and Cs^+ are obvious. Their results indicate that the charging/discharging of the electrode in TBACl electrolyte is accompanied by insertions/disinsertion of solely the Cl^- anion (Figure 2.2b) ³⁷. They provided the first evidence that the supercapacitor charging mechanism depended on the electrolyte ion-species.

Such an ion-species dependence was also observed in non-charged nanopores by Luo *et al.* in 2015³⁸. They used a nuclear magnetic resonance (NMR) approach to characterize the electrolyte concentrations in graphitic-like nanoporous carbon (Figure 2.2c) ³⁸. They found that the concentration of some anions was higher than that of the paired cation (i.e., Na^+ for all studied anions) in carbon pores. Therefore, the electroneutrality breakdown in porous carbons was observed. In addition, the observed electroneutrality breakdown strongly depends on the anion-species. the degree of electroneutrality breakdown follows the anion ranking of the Hofmeister series (Figure 2.2d) ³⁸. The underlying mechanism they proposed is that the non-electrostatic interaction (i.e., van der Waals forces) between ions and carbon surface should be considered to capture different ion's affinities to carbon pores. Such short-ranged interactions were generally neglected in bulk solutions or at the macroscale. This work shed light on their critical role in electrolyte structural organizations at the nanoscale.

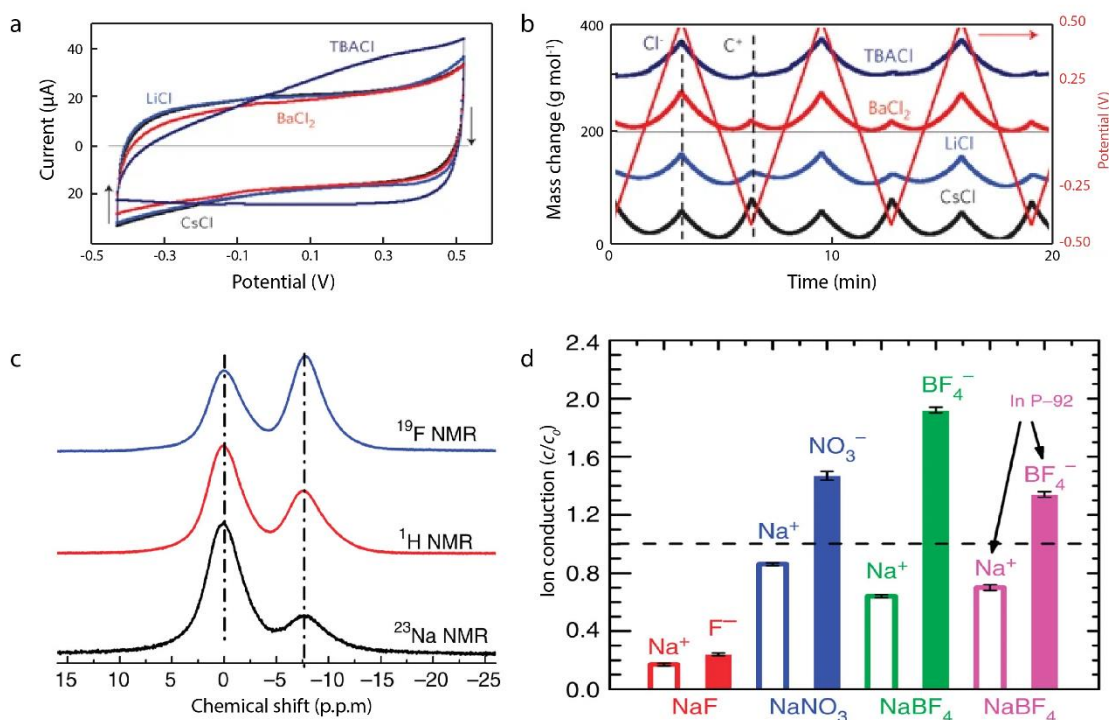


Figure 2.2 Ion specific effect in carbon nanopores. (a-b) the figures were adopted from the work of Levi et al.³⁷. They are the electrochemical characterization of a microporous activated carbon electrode for aqueous solutions of 0.5 M CsCl, LiCl, BaCl₂, and TBACl. (a) The cyclic voltammetry curves for typical electrolytes. (b) Simultaneously measured mass changes of cations and anions during the charging/discharging process³⁷. (c-d) the figures were adopted from the work of Luo et al., which characterized the ion concentrations c/c_0 inside uncharged carbon nanopores using NMR technology³⁸. (c) ¹⁹F, ¹H and ²³Na static NMR spectra of NaBF₄ electrolyte in carbon nanopores. (d) The ion (cations and anions) concentrations of NaF, NaNO₃, and NaBF₄ electrolytes inside carbon nanopores. The type of ion-species shows a clear influence. The pore size effect was also studied by using a larger nanopore sample (P-92) for NaBF₄ electrolyte.

2.2 The microstructure of electrolytes in nanoconfinement

In the previous section, the electrolytes in nanoconfinement demonstrated clear dependence of ion storage performances on pore-size (confined degree) and ion-species. They were attributed to the dependence of nanoconfined ion microstructure on pore-size and ion-species. Several critical parameters in the experiments suggest possible mechanisms. For example, 1) the pore size values of enhanced capacitance (sub-2nm, comparable to the ion hydration radius) suggest a potentially different ion hydration status in nanopores; 2) the oscillated capacitance as a function of pore size suggests the varied packing density of electrolytes in nanopores; 3) the ion-specific effect in uncharged nanopores indicates the critical role of non-electrostatic interactions. The molecular picture to visualize the microstructure of electrolytes is imperative to reveal or validate the hypotheses for those observed experimental results and thus to advance the understanding of the electrolyte behaviour in nanoconfinement. In this section, three microstructure features revealed by atomistic simulations will be discussed. They widely exist in nanoconfinement and provide solid molecular pictures to interpret the experimental observations.

Distorted solvation shell of ions in nanopores. The solvation of ions was suggested to play an important role in many processes. The work of Chmiola *et al.*, which is discussed in the previous section ³¹, observed the anomalous carbon capacitance when the pore size was comparable to the solvated ion radius. The solvation properties of ions have been used to interpret the electrolyte performance in nanoconfinement. For example, the solvated radius of electro-absorbed ions was used to parametrize the distance between parallel charged plates in the Helmholtz capacitor model and the thickness of the stern layer in the GCS model. Biological systems have also indicated a critical role in ion solvation. For example, the high selectivity of K^+ to Na^+ in the KcsA channel was ascribed to the differentiated hydration energy ³⁹. Motivated by those experimental phenomena, atomistic simulations were carried out to

study the structural characteristics of the hydration shell of ions in sub-2nm pores. The results include the ion-oxygen radial distribution functions, the coordination numbers, and the orientation distributions of the solvent molecules.

In an early work dated back to 1997, Lynden-Bell *et al.* studied the hydration of aqueous electrolyte ions inside a cylindrical micropore as a reference system. The channel wall was not a specific material but modelled as a steeply repulsive potential. Their study showed that the hydration of Na^+ ions in narrow pores was incomplete with a smaller coordination number. With a decreased channel radius, the number of neighbouring water molecules decreases from around 6 in the widest channel to 2 in the narrowest channel (Figure 2.3c)⁴⁰. The shape of the hydration shell has also been modulated in nanochannels. In the narrower channels (*i.e.*, with a radius up to 3.0 Å), the water molecules within the hydration shell only lie above and below the ions (Figure 2.3a and Figure 2.3b)⁴⁰. In later works, the distorted hydration shell has been widely observed in various nanochannels with different pore geometry (*e.g.*, nanopore, nanotube, slit, and 3D complex interconnected nanopore networks), wall materials (*e.g.*, carbon, clay, and protein), and charging conditions (*e.g.*, neutral, positive charging, and negative charging).

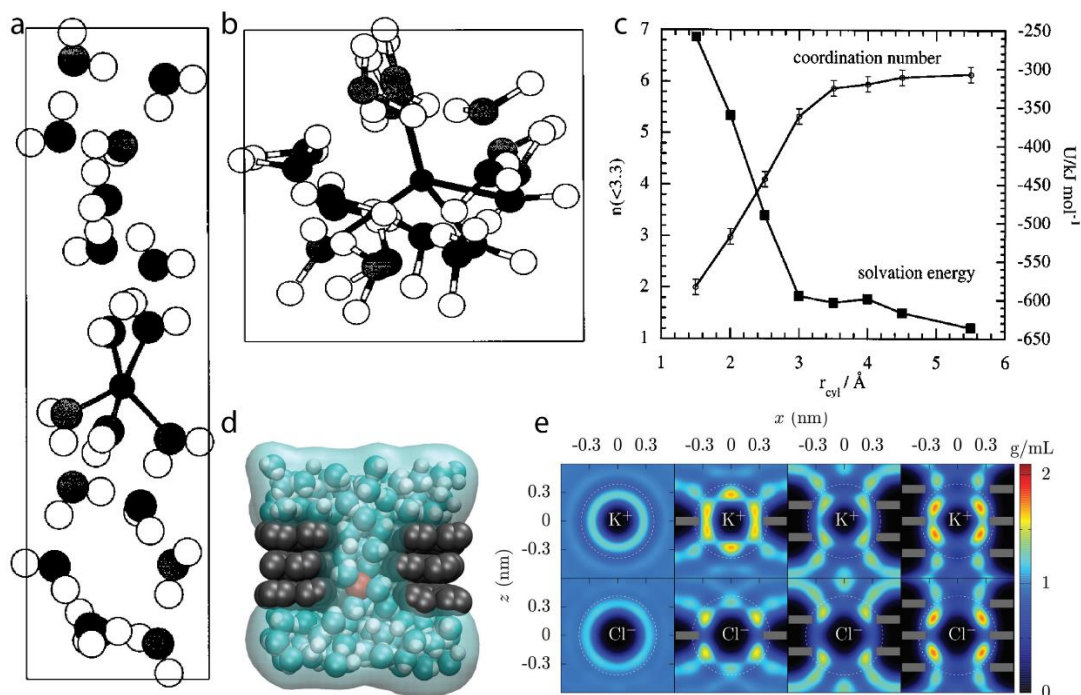


Figure 2.3 Ion hydration shell in nanopores. (a-c) the figures were adopted from the work of Lynden-Bell et al.⁴⁰ (a) and (b) are the two views of Na^+ hydrated configuration in the channel (radius of the channel is 3 Å) computed using molecular simulations. (a) Side view of the channel. Note the axis of the channel is vertical. (b) Top view of simulation boxes. The channel wall is a circle inscribed in the square shown. (c) The coordination number (the left-hand scale) and solvation energy (the right-hand scale) as a function of channel radius. (d-e) The figures were taken from the work of Sahu et al.⁴¹ (d) A typical schematic model of the molecular simulation. A nanopore composed of tri-layer graphene was immersed in KCl electrolyte. (e) The hydration shell profile of ions fixed in the centre of pores with a radius of 0.34 nm. The layer number of graphene for pores was varied. The hydration density of the water molecules was quantified by the position of the oxygen atom.

Note that such an often-observed feature might have multiple physical origins. An obvious or widely accepted factor is the confined pore geometry. The ions cannot bring their whole hydration shell when being admitted inside nanopores. In other words, the solvated ion volume

is larger than the pore volume. Sahu *et al.* have studied the volume effects on ion hydration by controlling the pore volumes where the nanopores were formed by a hole in one-, two-, or three-layer graphene, respectively (Figure 2.3d) ⁴¹. When the pore radius is fixed at 0.34 nm, the study showed that the hydration shell was slightly changed in a one-layer graphene pore. The monolayer graphene interfered little with the hydration in this pore. The water molecules could partially compensate for the dehydrated water sites by preferably orienting their dipole with respect to the ion. In contrast, for both bilayer and trilayer graphene, the dehydration of ions is more substantial (Figure 2.3e) ⁴¹.

Such a volume comparison could help us navigate whether ions would be desolvated when entering a pore. However, this understanding could not explain the partial desolvation of ions at the interface region, which is an open system and ions are dissolved in a large reservoir contacting a surface. Thereby instead of volume effect, ion desolvation in the vicinity of the open surface was understood from an interaction competition between ion-surface and ion-water molecules. ⁴² If ions present preferential affinities with the surface rather than water molecules, the ions would be partially desolvated to absorb with the surface (called ‘contact-absorption’). In contrast, if ions prefer to staying with solvent molecules, the ions would be solvated in the vicinity of the surface. In the open system, the ion solvation energy (the strength of ions interacted with solvent molecules) could be regarded as a standard value (same in bulk solution). The interactions between the ions and a surface can be manipulated via electrostatic interaction with varied surface charge densities. Therefore, the solvation of ions in the vicinity of the surface could be tuned under the hypothesis that ion solvation was the result of interaction competition. The work by Jia *et al.* has demonstrated it ⁴³. Their work showed that ions would bound with water molecules in the vicinity of a less charged surface but would directly absorb with a high-charged surface (Figure 2.4a). The work of Jiang *et al.* also

demonstrated similar point. Their work shows that the different ion species can show varied hydration status in the vicinity of the charged surface in the same charge density ²⁴.

Given that ion-surface interaction will play a vital role in ion solvation status, the detailed solvation structure of ions in nanopores could not be a simple volume comparison issue. It is a complicated question because these interactions interplayed crowdedly with each other in a ‘narrow room’ (i.e., limited pore volume) and the interactions could deviate from standard values or rules. For example, in an open system, the ion solvation energy was assumed to be the same as in the bulk state. However, such an assumption may not work in nanopores when the pore size is comparable with the ion solvated radius. Partial solvent molecules (e.g., outer hydration layer) will be peeled off when entering the pore. ⁴⁴ The actual solvation energy is undetermined, thereby challenging the comparison with the ion-surface interactions.

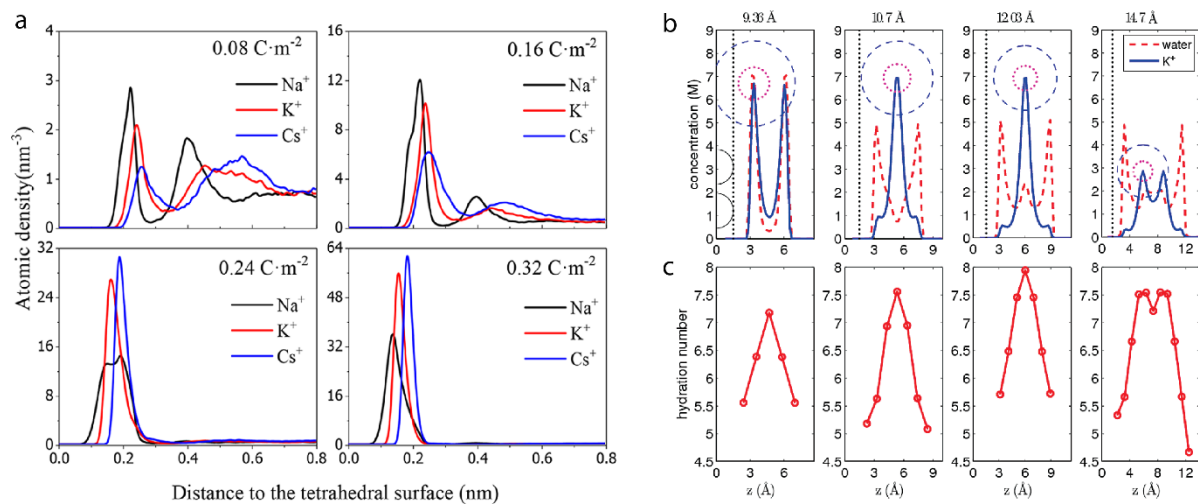


Figure 2.4 The ion distribution in the interfacial region and inside the nanopores. (a) The spatial density profiles of cations in NaCl, KCl, and CsCl aqueous electrolytes (0.5 M) near the mica surfaces with surface charge density equals 0.08, 0.16, 0.24, and 0.32 C m⁻², respectively ⁴³. **(b-c)** the figures were adopted from the work of Feng et al. ⁴⁴ **(b)** concentration profiles of K⁺ ions and water molecules inside slit pores with various widths (from 9.36 Å to

14.7 Å). Note that the concentration of water molecules was divided by a factor of 30. The dashed black line represents the effective boundary of the slit wall on one side. The dashed circles in red and blue colours represent the size of bare and hydrated K^+ ions, respectively. (c) The water coordination number of K^+ ions across slit pores with various widths. The surface charge density of all slit walls is $\sigma = -0.055 \text{ C m}^{-2}$.

For nanopores with large enough volumes to contain fully hydrated ions, the hydration shells could still be changed, as demonstrated by Feng *et al.*⁴⁴. They presented varied hydration shells of K^+ ions in graphene slits. The K^+ ions were fully hydrated in the slit of 10.7, 12.03, and 14.7 Å. In contrast, in the slit of 9.36 Å (larger than ionic hydrated width), K^+ ions instead of locating at the slit centre to keep a fully hydrated status like in slit of 10.7 Å, most of them were partially dehydrated in slit and formed into two ion layers in this slit (Figure 2.4b and Figure 2.4c)⁴⁴. Feng *et al.* found that water-water and ion-water interactions play a crucial role. They provide a comprehensive investigation for K^+ ion distribution in a negatively charged graphene slit. However, whether their proposed mechanism could be generalized in other nanopore systems is still an open question especially for uncharged systems. More efforts are still expected to understand the ion hydration in the nanopore, particularly to rationalize its sensitive dependence on pore size.

The electrolyte layering microstructure at the nanoscale. Profound layering is another microstructure feature of electrolytes in the nanopores or in the vicinity of the open surface. This feature was first proposed in the charged system to explain the discrepancy between experimental results and the classic continuum model predictions (i.e., GC model). The GC model often overestimated the capacitance values compared with experiments, particularly under highly charged states. Stern *et al.* proposed a discrete region to represent the absorbed ion layer near the charged surface so that the over-estimated capacitance by the GC model

could be corrected (the detailed information will be discussed in the next section). Such a ‘discrete’ concept was then observed in atomistic simulations, where counterions form an absorption layer with a certain distance from the charged surfaces and with a finite density due to the finite size of ions.

Figure 2.5a-d depicts a general trend in the electrolyte ion layering ⁴⁵. The first electrolyte absorption layer at an electrode delivers more counter-charges than the surface charge. The next electrolyte layer then shows a smaller opposite net charge. Such an alternation continues until electroneutrality is reached (Figure 2.5e) ⁴⁶. This phenomenon is called the ‘overscreening effect’, which commonly exists in the vicinity of a low charged surface. In the vicinity of the highly charged surface, there would be a thicker counterion layer absorbed at the charged surface and then followed by a co-ion layer, which is called the ‘crowding effect’ (Figure 2.5f) ⁴⁶. Thereby molecular-level picture from atomistic simulations for the electric double layer is multiple alternating layers of counterions and co-ions with the peak densities decaying exponentially into the corresponding bulk values. It is quite different from our conventional perception based on the classic continuum model prediction, where the concentration of counterions (co-ions) will accumulate (decay) monotonously from the surface to bulk electrolyte. The underlying mechanism was attributed to the ion-ion correlation interactions, which is a key feature for solvent-free electrolytes while such ion-ion correlation interactions would be much weaker in solvent-contained electrolytes. Such an oscillated ion/charge distribution profile was utilized by researchers to interpret the shape of differential capacitance vs. voltage ⁴⁵, the capacitance scaling relation with nanopore size ⁴⁴, and the charging mechanisms of supercapacitors ⁴⁷.

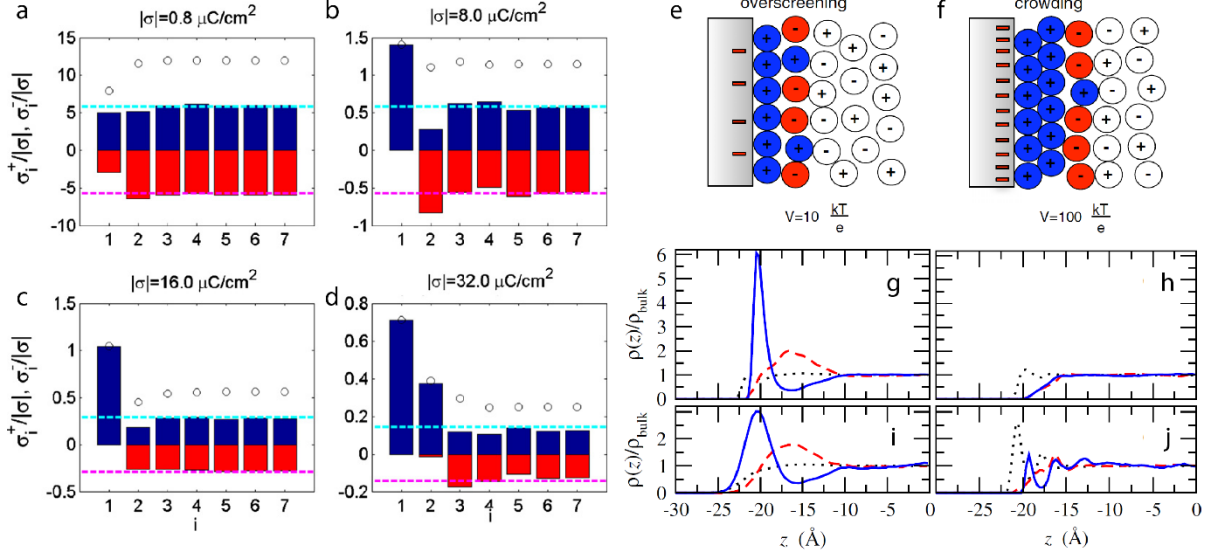


Figure 2.5 The overscreening phenomena near an electrified surface. (a-d) these figures were adopted from the work of Fedorov et al.⁴⁵ They present the rescaled charge density of cations (in blue colour) and anions (in red colour) in electrolyte near an electrified surface with various surface charge densities. The results are presented for the first seven monolayers of electrolyte near the surface. (e-f) these figures were adopted from the work of Bazant et al.⁴⁶ They are the schematics of the electric double layer for ionic liquid when the surface potential is moderate (e), and high (f). (g-j) these figures were adopted from the work of Huang et al.⁹, presenting the relative density profiles of anions (solid lines), cations (dashed lines), and water molecules (dotted lines) for 1M solutions of NaI (g) and NaCl (h) between neutral hydrophobic surfaces, NaI (i) at a vapour-liquid interface, and NaI (j) between neutral hydrophilic surfaces.

In the electrified system, although the alternating charge layers of EDL are beyond the conventional perception, the electrostatic interaction as a dominated force (in most cases) suggests the depletion and accumulation of counterions and coions at interface based on the Coulomb law. However, for an uncharged system, the ion spatial density oscillated in multiple ways since there are various competing interactions. If we only consider the Coulomb forces,

the cations and anions should be equally repelled from the uncharged interface due to the different dielectric properties of surface and solutions. For example, surface material with a smaller dielectric value case will lead to ion depletion at the surface⁹. However, experimental and atomistic simulation results were more complex than the trend as predicted and sometimes appear controversial. For example, the enhanced anion concentration of KI and KBr solutions was observed at the liquid/vapor interface of airborne saline droplets⁴⁸. The ion-specific effect (ion-species dependence, also called the Hofmeister effect) was also widely observed in uncharged systems (Figure 2.5g-j)⁹. It indicates that the nature of ions (e.g., ion finite size, polarisation, hydration ability, and so on) should play a critical role in ions distribution. However, at present, a well-accepted model to rationalize these phenomena is still missing. But it is clear that just considering the Coulomb interactions in the theoretical model is not enough.

The superionic state of electrolyte in highly confined nanopores. The superionic state is a more subtle microstructure feature of electrolytes, which was observed in sub-nm pores. It was first predicted theoretically by Kondrat *et al.* to clarify a different origin of the ‘anomalous’ EDL capacitance of porous electrodes⁴⁹. They proposed that the screened ion-ion Coulomb interaction via the image charge in the metallic walls of nanopore would lead to a denser ion density (the result of superionic state) in highly confined nanopores, and thus an enhanced capacitance density. To validate this hypothesis, they performed grand canonical Monte Carlo simulations of a restricted primitive model of ionic liquid in a metallic slit pore⁵⁰. In their simulation system, the electrostatic interaction between ions was modified using an exponential screening (the physical origin of the superionic state). An additional ion self-energy was also added into the system, which plays the role of an external field to bring the ions from bulk into the nanoslit. With those modifications, they calculated the accumulated total charge arising from the participation of ions inside the nanoslit as a function of voltage (Figure 2.6a)⁵⁰. Some

general trends were observed. The stored charges per area increased and then saturated at high voltage. The saturated charge value decreased with decreasing the pore width. Interestingly, the charge accumulation speed (upon voltage change) was faster in smaller pores at low voltages. As such, the differential capacitance was higher (Figure 2.6b) ⁵⁰. This trend is consistent with the experimental observations despite obvious quantitative discrepancy. The ion packing fraction also increased when the ratio of pore width over ion diameter was smaller than 1.5 (Figure 2.6c) ⁵⁰.

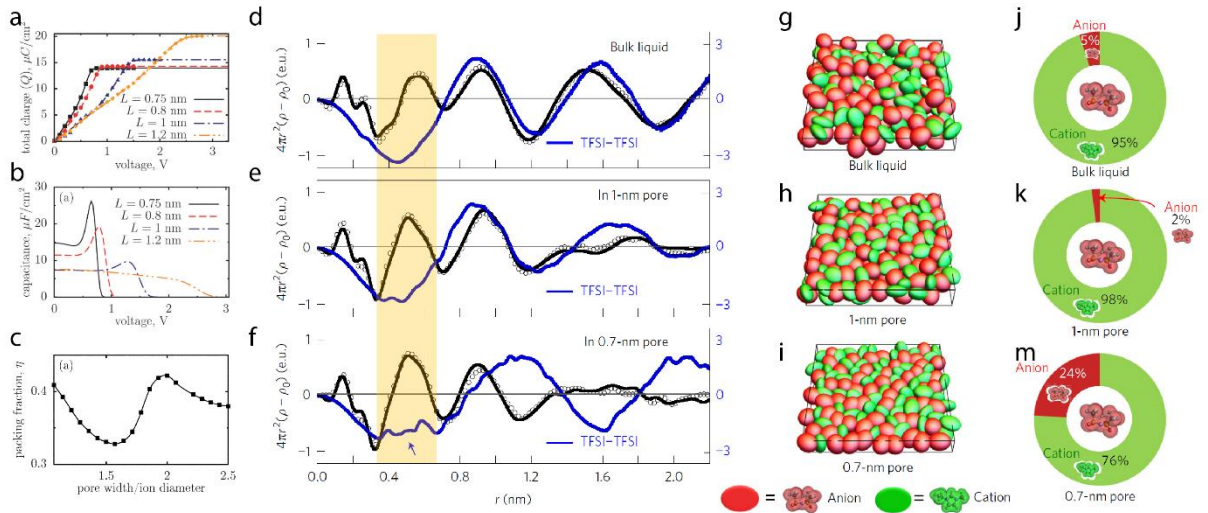


Figure 2.6 The superionic state in highly confined nanopores. (a-c) These figures were adopted from the work of Kondrat et al. ⁵⁰ (a) The stored total charges as a function of charging voltages with various pore widths (L). It presents saturation of the total charge with the increase of the voltages. (b) The differential capacitance (normalized by surface area) as a function of voltage for various pore width. (c) The packing fraction of the ions inside the pore as a function of rescaled pore width by the ion diameter. The packing fraction was calculated as such $\eta = \pi d^3 \rho / 6$, where $\rho = \rho_+ + \rho_-$ is the total ion density. (d-m) These figures were adopted from the work of Futamura et al. They present a pore size-dependent anion-anion structure in unpolarised carbon nanopores ⁵¹. (d-f) The comparison between experiment (dots) and simulation (black line) in terms of the electron radial distribution functions (ERDF) in

bulk liquid **(d)**, the 1-nm pore **(e)** and the 0.7 nm pore **(f)**. Besides, the blue line shows the simulated ERDF for the TFSI-TFSI correlations. **(g-i)** Atomistic picture of EMI-TFSI organizations in the bulk liquid **(g)**, the 1-nm pore **(h)** and the 0.7-nm pore **(i)** where the red and green ellipsoids are TFSI and EMI ions, respectively. **(j-m)** The fraction of EMI cations and TFSI anions in the first coordination shell of a TFSI ion in bulk liquid **(j)**, the 1-nm pore **(k)**, and the 0.7-nm pore **(m)**.

The experimental demonstration of superionic state was in 2017 by Futamura *et al.* with a combination of small-angle X-ray scattering (SAXS)) and the hybrid reverse Monte Carlo simulation ⁵¹. With the help of atomistic simulations, the signals change of experimental characterizations in nanopores was interpreted into the electrolyte structure at the nanoscale. Using this strategy, they recovered the structure of ionic liquids (EMI-TFSI) in nanopores of 0.7 nm and 1.0 nm ⁵¹. Their work showed deviations of electron radial distribution functions (ERDFs) for EMI-TFSI liquid in 0.7 nm pore from the bulk solution. In contrast, the ERDFs for EMI-TFSI in a 1.0 nm pore was similar to the bulk solution. The deviations of ERDFs observed in 0.7 nm are: 1) the positive peaks in 0.7 nm pores were shifted to larger values compared to bulk liquid, indicating an orientated alignment of anions in 0.7 nm pore; 2) the intensity of the negative peak was decreased in 0.7 nm pore, showing that the intrusion of anions into the cationic coordination shell surrounding a central anion. Accordingly, the partial breaking of the Coulombic ordering was evidenced in this work for the first time. This phenomenon arises from the proposed superionic effect (Figure 2.6 d-m) ⁵¹. The discovery of ‘superionic effect’ indicates the impact of non-conventional ion-wall interaction on the electrolyte microstructure in highly confined spaces.

2.3 Continuum models of electrolyte structure at the nanoscale

Although the microstructure of electrolytes described by atomistic simulations can be used to interpret experimental observations, however, atomistic simulations have two main limitations: First, it has very limited time-/length- scale. Its utilization is computational time-demanding for complex nanoporous material systems or under dynamic conditions. Second, it is challenging to extract/identify key physical factors and their quantitative influences on the observed phenomena from the obtained high-dimensional data in the atomistic simulations.⁵² It is not easy for atomistic simulations to provide implementable design parameters or design guidelines for quantitative design in macroscopic engineering applications. The continuum model developed based on physics principles is a complimentary choice.

Via incorporating the dominated interactions or nature of ions, the continuum models can capture some organization features at the nanoscale. The thermal motion of ions motivated Gouy and Chapman to develop a model (the conventional Poisson-Boltzmann theory, also called the GC model) where ions distribution follows a Boltzmann statistics with a screen length of $\sim$ nm near a charged surface. The GC model can capture the overlapping of the electric double layer in small pores. But a key disadvantage of the GC model is the overestimation of the counterion densities at highly charged surfaces and thus the overestimation of the capacitance. This is because the finite ion size effect is neglected⁵³.

The finite ion size was then considered by Stern via inserting a compact layer with a much reduced dielectric constant. A more explicit treatment of finite ion size was proposed by Bikerman within the lattice-gas scheme (Figure 2.7a)¹⁸. Besides the overall trend for capacitance value, some detailed electrolyte microstructure features were also captured by continuum models. For example, the alternative ion layers of EDL near the charged surface (overscreening effect) was captured qualitatively by Bazant's model (Figure 2.7b)⁵⁴, where the ion-ion correlations and finite ion size effect were incorporated into the conventional PB

model. The enhanced ion densities in highly confined nanopores (superionic state) were predicted by the models developed by Kondrat *et al.* (Figure 2.7c) ⁴⁹, where the ion-ion Coulomb interaction was exponentially screened. These cases demonstrate that by taking account of some newly revealed mechanisms or new driving forces, a continuum model can be developed to capture the essential microstructure of electrolytes.

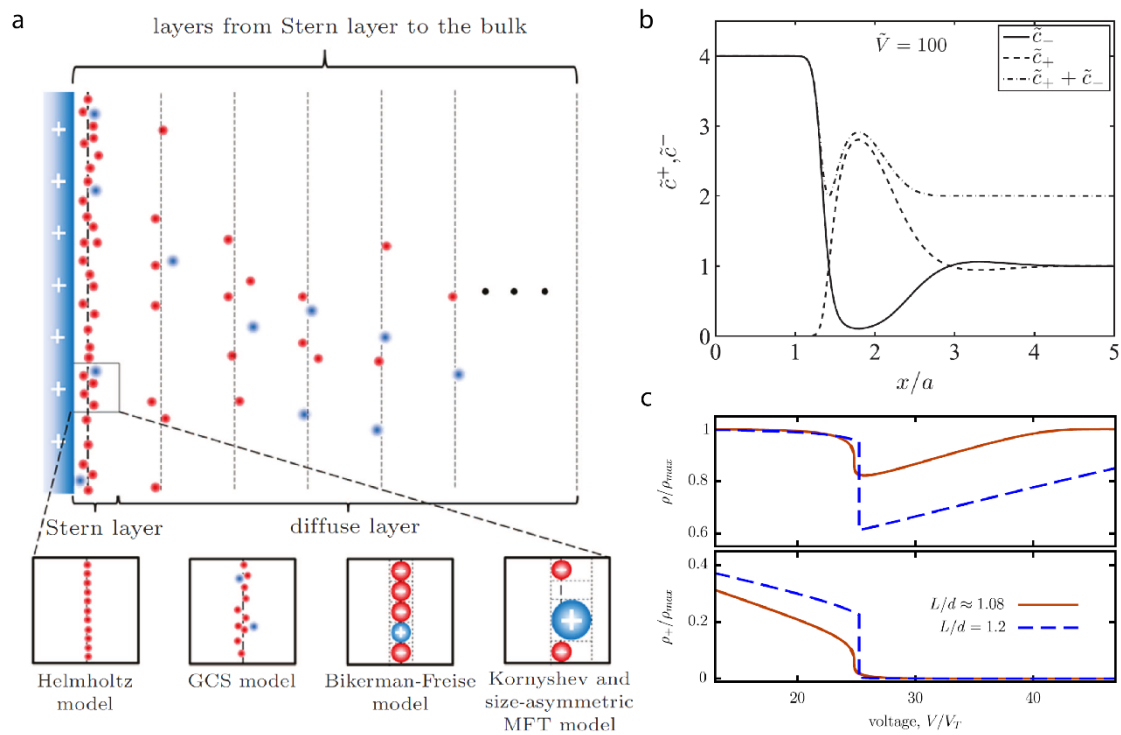


Figure 2.7 Some new or modified continuum models. (a) This figure was adopted from the work of Huang *et al.* ¹⁸ it presents the schematic structure of the electric double layer (EDL) using various models: Helmholtz model, Gouy-Chapman-Stern (GCS) model, Bikerman-Freise model, and Kornyshev model. (b) This figure was adopted from the work of Bazant *et al.* ⁵⁴ It shows the dimensionless concentration of anions and cations. The x-axis presents the distance of closet approach and scaled to the ion diameter a . (c) This figure was adopted from the work of Kondrat *et al.* ⁴⁹ It shows the relative density of total ions and cations (rescaled to maximum charge density ρ_{max}) as a function of rescaled voltage for the two pore widths.

Some microstructure features (e.g., ion-species dependence) are driven by multiple interactions including disperse interaction, ion-solvent interaction, image force and Coulomb interaction. In many cases, the driven forces underlying the observed electrolyte microstructure remain to be revealed. These interactions are comparable and interplay with each other in nanoconfinement or the close vicinity of surfaces. As such, many interesting electrolyte microstructure features emerge, e.g., ion-specificity and pore size dependence (sub-2nm). But it is a challenging task for theoretical models to involve these multiple interactions comprehensively and systematically. For example, the ion absorption distance (to the surface) is difficult to be quantitatively predicted by theoretical models that have already considered many interatomic interactions (e.g., steric force, hydration force, and disperse interaction). This is because of the correlations and interplay between them. The aqueous electrolytes and the water-in-salt electrolytes are good example systems. The ions could alter the orientation, spatial arrangement, and even molecular shape of solvent molecules. In return, the changes of solvent molecules would affect the ion distribution. Such interplay is particularly profound in nanopores. For example, bare ions in ionic liquids can have a fixed radius, while the radius of hydrated ions can be varied in sub-2nm pores as discussed in the last section.

In nanopores, the microstructure of water molecules is different from the bulk solution. The structurally altered water molecules can influence not only the effective distance between ions and surface but also the dielectric screening ability of solutions to the external electric field. Generally, continuum models use the ‘dielectric constant’ to describe the strength of the screening ability⁶. The Gouy-Chapman-Stern model is the first model to recognise that water in the interfacial region should have a much reduced dielectric constant (i.e., 3 or 4). This value is usually determined by fitting the experimental capacitance value¹⁸. Such reduced dielectric permittivity phenomena were then called ‘saturated dielectric’, and a series of continuum

models were developed to consider this feature explicitly. For example, Bockris introduced a 3-state model for the dielectric distribution of water at the electrode/electrolyte interface. The first layer of water dipoles was assumed to be strongly oriented by a surface with a dielectric constant of around 6⁵⁵. The rest part of the water molecules in Bockris model was divided into semi-oriented water and bulk water. The dielectric constant of the semi-oriented water molecules bridged the first layer and bulk water with an averaged value or a linear relation.

Some more delicate models relate the water dielectric constant to the contributed physical factors, not just using an estimated value. However, the relevant physical factors are diverse. Accordingly, models are developed from different viewpoints. Such as Booth derived a relationship between the dielectric constant of water and electric field strength⁵⁶. Schiby and Ruckenstein derived the water polarisation ability based on dipole-dipole interactions and related the dielectric constant to the dipole distribution structure⁵⁷. Bostrom et al., related the water dielectric constant to the water density profile near the surface⁵⁸. Some researchers also related the water dielectric constant to the ion concentrations considering the ion-solvent interaction⁵⁹. Those models could work well under specific conditions or for an electrolyte property particularly. But there is no consensus on which model comprehensively captured the features of water dipoles, not to mention their influence on the ion spatial distributions.

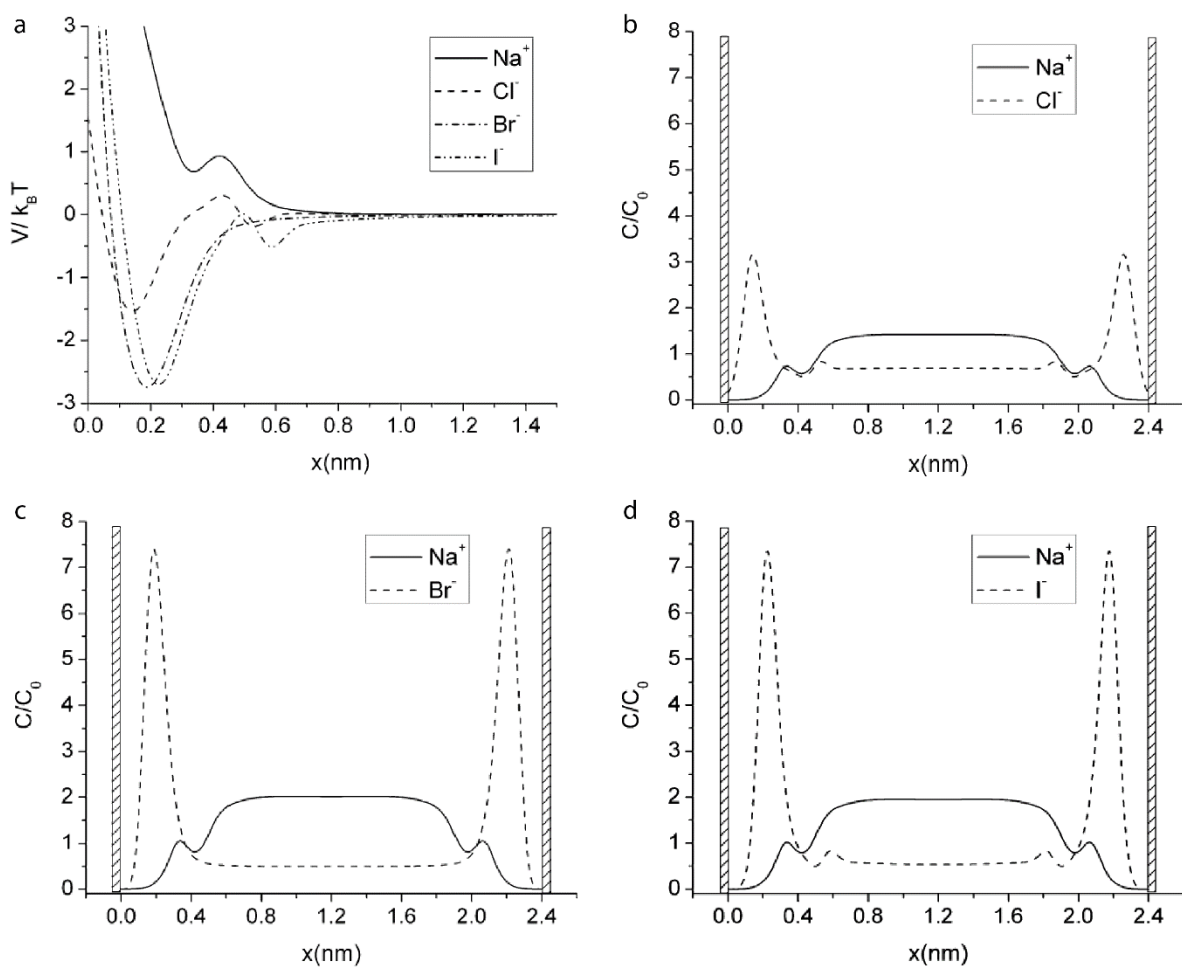


Figure 2.8 Continuum models considering the ion affinity to surface. These figures were adopted from the work of Bostrom et al.⁵⁸ **(a)** Potentials of mean force (PMF) for various ion species at the interface of self-assembled monolayers (SAMs)-water. **(b-d)** Rescaled concentration profile (by bulk concentration, $c_0 = 0.01$ mol/L) of cations and anions between two neutral SAM surfaces in aqueous electrolyte NaCl **(b)**, NaBr **(c)**, and NaI **(d)**. Note that the SAM surface location was represented as the hatched vertical bars.

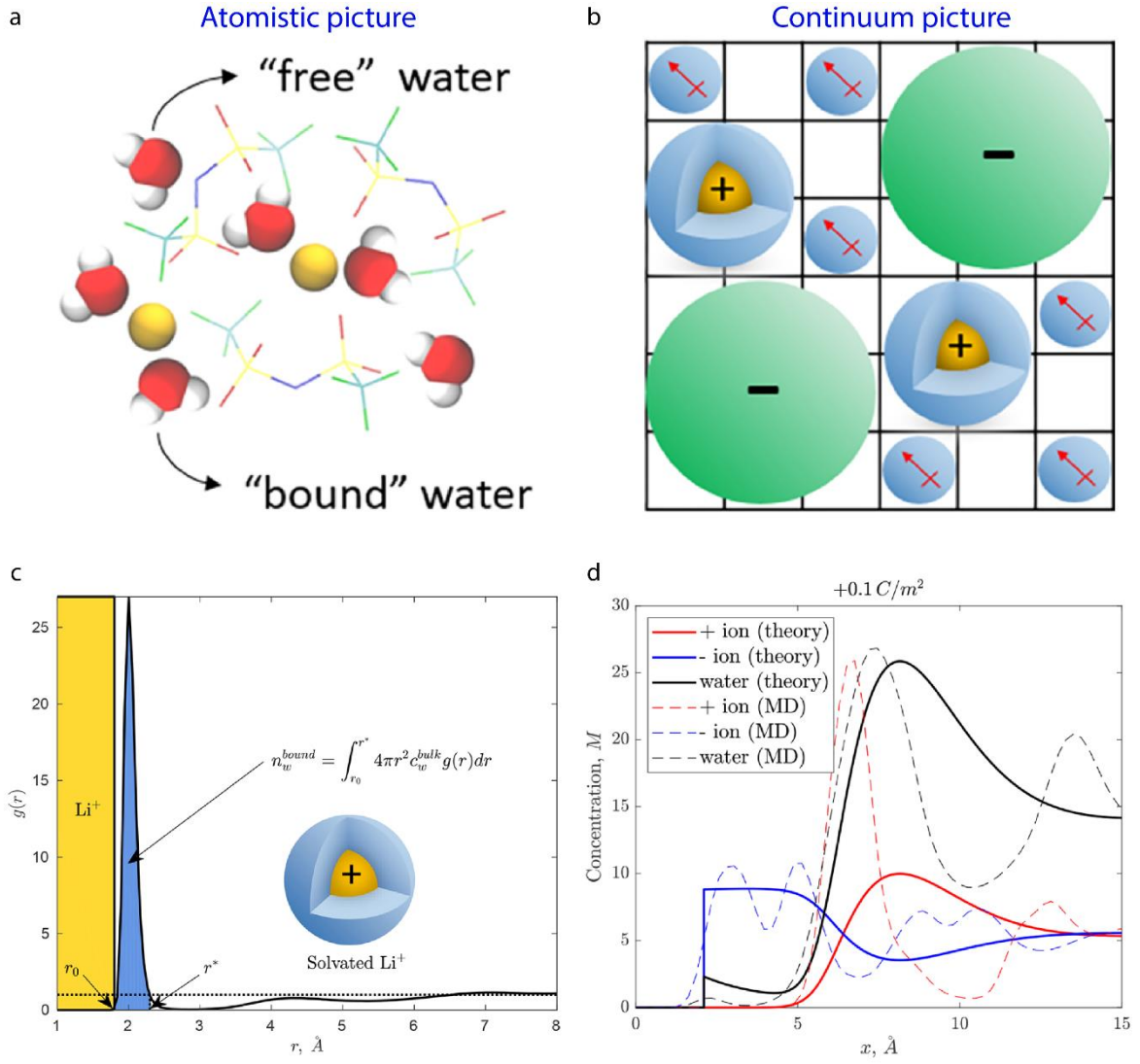


Figure 2.9 Continuum models considering the ion hydration shell. These figures were adopted from the work of McEldrew et al.¹⁷ **(a)** The atomistic structure of the water-in-salt electrolyte (21M LiTFSI). Two states of water were clarified: ‘bound’ or ‘free’. **(b)** A schematic lattice model of water-in-salt electrolyte with three components (cations with bounded water, anions, and free water). **(c)** The radius distribution functions of the water (represented by oxygen atom) around a Li^+ cation. **(d)** The results comparison between MD simulations and lattice models for the ion concentration profiles near the charged surface.

Recently, researchers proposed a strategy of combining the atomistic simulations and continuum models. The atomistic simulations were used to extract effective parameters to

represent part of interplayed interactions. The continuum model was used to predict microstructure by adopting those parameters. For example, Bostrom *et al.* extracted the potential of mean force for a single ion approaching the open surface to represent the interplay of interfacial disperse, hydration, and image forces and treated it as extra interaction energy in PB theory (Figure 2.8) ⁵⁸. Kalcher *et al.* extracted the oscillated interaction potential between ions in bulk solution to the interplay of steric, coulomb, and hydration interactions ⁶⁰. McEldrew *et al.* extracted the effective ion radius to considering the ion-specific hydration ability by calculating the water distribution function (Figure 2.9) ¹⁷. Those works provide a semi-quantitative prediction for electrolyte organizations in the bulk solution or open surface system. However, it is still an open question for the feasibility and quantitative accuracy of those models in nanopores.

In summary, the ion-species and pore-size dependent electrolyte microstructure and their influences on the ion storage performance are discussed in this chapter. The typical molecular picture is an inhomogeneous ion spatial distribution, manifested as an alternative cation and anion layering structure as well as the distorted ion solvation shell. Such a representative microstructure is a result of multiple comparable physical interactions that are crowdly at play in confined nanopores or the close vicinity of the surface. At present, there are no good continuum models that can quantitatively predict electrolyte microstructure from atomistic simulations and thus can model accurately the resultant properties, such as ion-specific and pore-size dependent ion storage. The literature review in this chapter also reveals the importance of ion solvation and the non-electrostatic interactions on the electrolyte microstructure. Therefore, this thesis will take the aqueous solutions as the model electrolyte and focus on the effect of water molecules on the electrolyte microstructure in nanopores or the close vicinity of the graphene surface by investigating the water structure and some related

non-electrostatic interactions. We will adopt the strategy of combining the atomistic simulations and continuum models, which has been proved successful in previous studies. We will carry out comprehensive atomistic simulations for some typical aqueous electrolytes in graphene membrane systems. Based on that, we will develop new theoretical models to quantitatively predict the ion-species and pore-size dependent electrolyte microstructure in either nanopores or the close vicinity of the surface.

Chapter 3: A new continuum model for ion-specific distribution in uncharged nanoslits

3.1 Introduction

The electrolyte structure in nanopores is important for a wide range of applications including nanofluidics, manipulation of biological membranes, and the design of desalination membranes⁶¹. The intrinsic feature of electrolyte microstructure in nanoconfinement is the inhomogeneous spatial distribution that depends on ion-species and pore-size.¹¹ Such microscopic structure is the basis to tailor/design the macroscale performance or functionality of many applications via controlling the electrolyte properties (e.g., surface tension, surface potential, and even the electrokinetic ability)^{42, 52, 62}. As we introduced in Chapter 1 and Chapter 2, experimental works have demonstrated the enhanced application performance (e.g., energy density of supercapacitor) benefiting from the anomalous electrolyte structure at the nanoscale³¹. For future macroscale performance design, an understanding and description of electrolyte microstructure are imperative.

Unlike ionic liquids, the solvent-contained electrolytes are subject to the additional effect of solvent molecules. In the vicinity of the substrate, the water molecules present a highly oscillated density distribution and then come to the standard density. Such heterogeneous water distribution comes from the interrupted hydrogen bonding by the substrate and would generally extend up to 1 nm from the substrate location. In bulk solutions or the open interface system, water molecules maintain a standard density in most regions and are generally treated as a uniform background. However, in nanopores, the heterogeneous water distribution could occupy a considerable volume fraction and thus, may have a different effect on the distribution of the ions from serving as a uniform background.

The solvent molecules influence the ion distributions from multiple means, such as dielectric screening on local ion packing density, steric exclusion effect on ion available volume, and solvation attraction to ions^{1, 12, 17, 43-44}. The recent atomistic results show that the ions can locate at a place with enhanced water density in nanopores, ascribing to the significant ion-water and water-water interactions, not just the ion-substrate interactions⁴⁴. This phenomenon is opposite to the trend of solvent-ion exclusion considering the water finite-size effect. These multiple solvent-ion interactions in many cases compete with each other and complicate the influence of water molecules on ions distribution. This is particularly true in the nanoconfined environment where the distribution of solvent molecules (orientation, spatial arrangement, and even molecular shape) is altered by the ions, surface, and confined geometry at the same time. Thereby a comprehensive understanding is required.

Previously, via an extension of the traditional PB theory to lattice gas, the obtained mPB theory (e.g., Fermi-Poisson) achieved a consideration of ion finite-size effect in a very simple and intuitive way since particles are not allowed to occupy the same lattice site. For electrolyte solutions, the solvent like water molecules is always randomly distributed with solvent-ion exclusion effect via assuming the overall lattice site is kept constant. However, as discussed before, the heterogenous water distribution would emerge in nanopores rather than a uniform/random distribution. In addition, the ion-water/water-water interaction energy is not captured in the classic lattice gas model. Those two important derivations derive us to carry out this work to investigate an effective way to consider the role of water molecules on the distribution of electrolyte ions in the lattice gas framework.

Recently, researchers combined atomistic simulations and continuum models to solve interplayed interaction issues. The atomistic simulations were used to extract effective parameters to represent some of the interplayed interactions. The continuum model then

adopted those parameters to predict the ion distribution profile. Some representative examples have been reviewed in the last chapter. These advances inspire us to systematically considering water contributions to electrolyte microscopic structure in continuum models with inputs from atomic properties conducting from atomistic simulations. In this Chapter, we use the molecular dynamics simulation to identify that the structure of water molecules in each nanoslit is almost unchanged no matter whether the ions are dissolved or what types of ions are dissolved. We then propose to directly account for the heterogeneous water distributions from MD simulations into the entropy term of the free energy in the lattice gas framework rather than explicitly involving the water-water interactions. The interaction between ions and water molecules was considered via refining the calculation of the effective ion relative size. A new model that accounts for the water structure was developed and achieved an improved description of the microscopic electrolyte structure.

3.2 Simulation systems and methods.

Figure 3.1a is a representative aqueous electrolyte-graphene system in our MD simulations. Five parallel graphene sheets as channel framework are assumed to be rigid, as in previous studies of ion adsorption in nanochannels⁶³⁻⁶⁴. The graphene slit walls measure 4.156×4.254 nm² laterally, and the width of the reservoir is around 12 nm. Periodic boundary conditions are applied in the lateral directions. The slit size (defined as the distance between the atomic centres of neighboured graphene sheets) is 1.0 nm, 1.2 nm, 1.5 nm, and 1.8 nm, respectively. We choose 0.8M NaBF₄, LiBF₄, and CsBF₄ as representative aqueous electrolytes. A recent experiment shows that the BF₄⁻ anions exhibit strong adsorption affinity in carbon nanopores in contrast to the paired cations Na⁺³⁸. As such, the NaBF₄ is a good aqueous electrolyte to study the ion specificity in carbon nanopores. We choose Li⁺ and Cs⁺ ions to compare the difference of cations in nanoconfinement. The adopted water model is TIP/3P and assumed to be rigid in

our simulations. The force field parameters of Na^+ ion and BF_4^- ion are taken from Ref. ⁶⁵, in which the all-atom force field parameters of various ionic systems (including Na^+ and BF_4^-) are updated and validated to reproduce experimental properties. In addition, the same parameters of BF_4^- ions have been used to study the dynamics of water molecules in NaBF_4 solutions (validated by the infrared spectrum), ion aggregation phenomena in highly concentrated NaBF_4 solutions, as well as the water structures near protein surface ⁶⁶⁻⁶⁸. The carbon atoms are modelled using the CHARMM27 parameter ²⁴. The parameters for Li^+ and Cs^+ ions are from the DANG force field ⁶⁹. They are widely used parameters for aqueous electrolyte-graphene systems, including our previous works for the EDL structure and capacitance in the vicinity of the electrified graphene ²⁴. The detailed force field parameters are summarized in Table 3.1.

To determine the thermal equilibrium number of water molecules in our systems, we run MD simulations under NVT ensemble and adjust the number of water molecules in the simulation box, meanwhile, we monitor the water density in a reservoir region that is 2 nm away from the graphene edges. Provided that the water number density in this region was equal to bulk water and remained steady for ~ 10 ns, we consider the system in the equilibrium condition. The determination of ion amounts in systems is similar to that of water molecules through the loops of ion number adjustment and concentration validation. The system is fulfilled initially with the determined equilibrium number of water molecules. To ensure the ion numbers in each system reach the equilibrium state (the reservoir part having concentration 0.8 M), each slit case is simulated twice with two different initial states: 1) ions being absent in the slit region initially (denoted as Mode 1), and 2) ions filled the slit region with an artificial concentration that is larger than 0.8 M initially (denoted as Mode 2). Our simulation time and system volumes are comparable to previous studies ⁶⁴ (40-90 ns vs. 50 ns; $27.5\text{-}49.4 \times 10^4 \text{ \AA}^3$ vs. $27 \times 10^4 \text{ \AA}^3$) to ensure reliable output statistics. The detailed simulation time for each system is summarized in

Table 3.2. To further check the variations, we compute the in-pore ion amounts at different time segments (each around 4-5 ns). Table 3.3 summarizes the in-pore amounts of ions and water molecules in each time segment during the data production period (15-33 ns). The variations are small, less than 7%.

Table 3.1 Atomic charges and Lennard-Jones potential parameters for carbon atoms, TIP3P water, and ions in our simulations

Atoms	ϵ (Kcal/mol)	σ (Å)	M (g/mol)	Valence (e)
C	0.070	3.550	12.01	0
O (TIP/3P)	0.152	3.151	15.99	-0.834
H (TIP/3P)	0.000	0.000	1.008	+0.417
Na	0.170	3.250	23.00	+1
B	0.095	3.581	10.80	+0.828
F	0.061	3.118	19.00	-0.457
Cs	0.100	3.884	39.00	+1
Li	0.165	1.506	7.00	+1

Table 3.2 Summary of MD simulation time for our molecular model systems

System	Time (ns)					
	Mode 1			Mode 2		
	Total	Pre-Equil.	Data Prod.	Total	Pre-Equil.	Data Prod.
Slit-1.0 nm	82.5	60.5	22.0	82.5	49.5	33.0
Slit-1.2 nm	88.0	71.5	16.5	58.5	31.5	27.0
Slit-1.5 nm	75.0	60.0	15.0	40.0	28.0	12.0

Slit-1.8 nm	50.0	35.0	15.0	40.0	20.0	20.0
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Table 3.3 The in-pore amounts of ions and water in different time segments

Slit size		Slit-1.0 nm					Slit-1.2 nm					Slit-1.5 nm					Slit-1.8 nm				
Time segment		Water	BF ₄ ⁻	Na ⁺	c(BF ₄ ⁻)	c(Na ⁺)	Water	BF ₄ ⁻	Na ⁺	c(BF ₄ ⁻)	c(Na ⁺)	Water	BF ₄ ⁻	Na ⁺	c(BF ₄ ⁻)	c(Na ⁺)	Water	BF ₄ ⁻	Na ⁺	c(BF ₄ ⁻)	c(Na ⁺)
Mode 1	No.1	1174.44	7.44	6.78	0.35	0.32	1499.69	24.57	24.45	0.91	0.90	2047.73	28.82	28.44	0.78	0.77	2589.24	35.94	36.08	0.77	0.77
	No.2	1168.73	9.92	9.6	0.47	0.46	1502.22	24.08	23.96	0.89	0.88	2039.64	33.13	32.43	0.90	0.88	2582.73	39.58	39.06	0.85	0.84
	No.3	1174.59	7.82	7.58	0.37	0.36	1497.75	25.24	25.08	0.93	0.93	2043.52	31.66	31.59	0.86	0.86	2582.42	39.51	39.68	0.85	0.85
	No.4	1171.04	9.09	8.17	0.43	0.39	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Mode 2	No.1	1186.92	6.12	6.35	0.29	0.30	1505.04	21.66	21.09	0.80	0.78	2036.83	33.00	33.26	0.90	0.90	2587.06	38.11	36.60	0.82	0.78
	No.2	1181.50	7.78	7.09	0.36	0.33	1508.74	20.84	20.66	0.77	0.76	2046.27	30.06	29.70	0.81	0.80	2597.67	40.18	40.55	0.86	0.86
	No.3	1176.18	9.72	8.32	0.46	0.39	1512.13	19.07	18.73	0.70	0.69	2037.72	32.77	33.63	0.89	0.91	2582.72	38.59	38.03	0.83	0.82
	No.4	1177.54	9.12	7.56	0.43	0.36	1506.47	21.29	20.31	0.78	0.75	2041.81	32.32	31.31	0.88	0.85	2592.05	35.72	35.78	0.76	0.76
	No.5	1188.48	5.48	6.71	0.26	0.31	1494.50	25.03	25.14	0.93	0.93	--	--	--	--	--	--	--	--	--	--
	No.6	1184.91	7.01	6.68	0.33	0.31	1505.67	21.27	20.90	0.78	0.77	--	--	--	--	--	--	--	--	--	--
Average		1178.433	7.884	7.55	0.37	0.36	1503.579	22.56	22.26	0.83	0.82	2041.931	31.68	31.48	0.86	0.85	2587.699	38.23	37.97	0.82	0.81
Deviation		±6.75	±1.54	±0.96	±0.07	±0.05	±5.57	±2.20	±2.39	±0.08	±0.09	±4.16	±1.65	±1.88	±0.05	±0.05	±5.75	±1.78	±1.87	±0.04	±0.04

Figure 3.1b summarizes the ion in-slit concentration for a slit size of 1.0 nm, 1.2 nm, 1.5 nm, and 1.8 nm, respectively. The ion in-slit concentrations are roughly equal to bulk concentration (0.8 M) for slits of 1.2 nm, 1.5 nm, and 1.8 nm. In contrast, the value is reduced to half (~ 0.4 M) for the 1.0 nm slit. With the slit size narrowing to 1.0 nm, our nanoslit becomes less accessible for ions. Similar trends were also observed in previous studies. For electrolyte NaPF₆ absorption in graphene slits, no ions were present in 0.85 nm, and one layer of the low concentration of Na⁺ and PF₆⁻ formed in the centre of the 1.02 nm slit ⁷⁰. In the study of electrolyte KCl in nanoslit, no ions entered the slits of < 0.6 nm ⁶³.

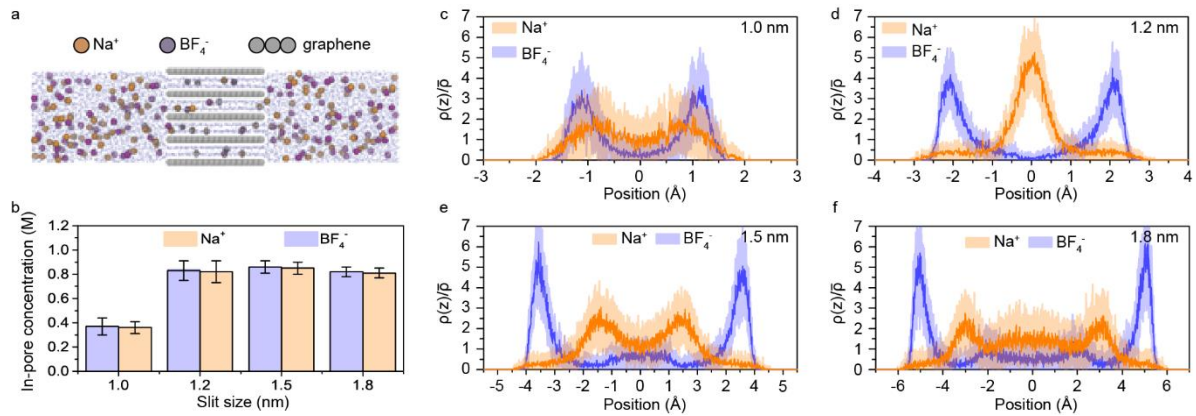


Figure 3.1 Equilibrium MD simulations of ion spatial distribution in graphene nanoslits. (a) The schematic of the MD simulation system. Four slits are enclosed between five parallel graphene sheets and the slits are connected to reservoirs. For clarity, the carbon atom, BF₄⁻ ion, and Na⁺ ion are represented by grey, orange, and purple spheres, respectively. The water molecules are represented by light blue points. Four slit-sizes (1.0 nm, 1.2 nm, 1.5 nm, and 1.8 nm) were simulated separately to obtain ion spatial profiles under different nanoconfined degrees. Here, the slit size was defined as the distance between atomic centers of adjacent graphene sheets. (b) The averaged ion concentration in the slit region as a function of slit size. The bulk concentration in the reservoir region was kept as 0.8 M. (c-f) The spatial rescaled density profile for BF₄⁻ ion (blue line) and Na⁺ ion (orange line) in slit size of 1.0 nm (c), 1.2

nm **(d)**, 1.5 nm **(e)**, and 1.8 nm **(f)**. Those profiles present an inhomogeneous spatial density. Generally, BF_4^- ion shows a closer and stronger absorption to the graphene surface than Na^+ ion.

3.3 Results and Discussions

3.3.1 Ion spatial density profiles from MD simulations

The density profiles ($\rho(z)$) of BF_4^- , Na^+ , and water with a spatial resolution of 0.01 Å on the z-axis (normal direction of graphene layer) in the nanoslit region are computed by counting the corresponding atom numbers (water molecules are represented by oxygen atom) in each bin. Then, we transfer the density profile of the four-slit configuration into one slit region. The rescaled density profile is computed via dividing the local density by the average ion density in the slit ($\rho(z)/\bar{\rho}$). Figure 3.1c-f show the rescaled density profiles of ions. The oscillated ion density profiles extend to the whole uncharged nanoslits. Similar oscillated features were reported in previous works in the interfacial region, the so-called Helmholtz layer⁷¹. We could also observe that such ion inhomogeneous spatial density profiles depend on ion-species. The BF_4^- ions have the absorption peaks (in 3-4 times of $\bar{\rho}$) near the surfaces in all slits, indicating anion enrichment at the interface (Figure 3.1c-f). Besides, in the larger slit (i.e., 1.8 nm), there are the 2nd absorption peaks of BF_4^- at around 7 Å from the wall. These smaller adsorption peaks merge into one peak in the 1.5 nm slit (Figure 3.1e) and disappear in the 1.2 nm and 1.0 nm slits (Figure 3.1d and Figure 3.1c). Na^+ ions show distinctive distribution profiles. In the 1.5 and 1.8 nm slits (Figure 3.1e and Figure 3.1f), a significant depletion of Na^+ is observed at the interface where anions show enrichment. The pronounced peaks of the Na^+ (2 times of $\bar{\rho}$) is observed at around 6 Å from the graphene wall centre. Such absorption distance is similar to the previous study of Na^+ (paired with Cl^-) in graphene slit (6.0 Å vs. 5.2 Å). The discrepancy may result from the different force model parameters⁷². With slit narrowing (Figure 3.1d), the

depletion region can still be observed, but the absorption peaks of Na^+ ion merge with enhanced intensity value (5 times of $\bar{\rho}$). Interestingly, when the slit size reduces to 1 nm (Figure 3.1c), the merged single density peak of Na^+ ions is split into two peaks again. These two peaks are located at the corresponding depletion region in those large slits. Our MD simulation results illustrate significant slit-size and ion-species dependence of ion spatial distribution profiles.

3.3.2 PB-PMF model to capture the layered ion distribution profile

The inhomogeneous spatial distribution of ions in nanoslits should result from multiple interplayed physical interactions (e.g., ion steric, disperse interaction, and hydrophobic interaction). The ion's potential of mean force (PMF) as it approaching a surface has been used to describe the effective ion-wall interaction^{42, 73-74}. Here, we apply the same strategy by incorporating the PMFs into the classic PB theory. Note that the classic PB theory only yields homogeneous ion distribution in the surface charge neutral nanoslits, which is distinctive from our MD simulations. To capture the intrinsic interaction between the ion and graphene surface, we calculate the ion's PMF for a single ion approaching a single graphene layer instead of in a slit region or concentrated solution. It is convenient to use such intrinsic electrolyte-wall property to predict ion's distribution in slits of varied sizes (i.e., 1.0 nm, 1.2 nm, 1.5 nm, and 1.8 nm in our work) in continuum models. The PMF for ions at the open surface may be different from in nanopore. This could lead to discrepancies between the PB-PMF and the MD results in small nanoslits. However, to calculate PMF for each ion and in each small nanoslits is highly undesirable for two reasons. First, it is too time demanding. Second, doing so will lose the generality virtue of theoretical model. We, therefore, aim to develop a new continuum model to mitigate such discrepancy. The system size is $4.156 \times 4.254 \times 8.208 \text{ nm}^2$, similar to the size in the previous study. Figure 3.2a shows the calculated PMFs for BF_4^- anions and a set of cations (Li^+ , Na^+ , and Cs^+). The observed general trend of PMFs is similar to previous simulations at air-water or hydrophobic surface-water interface⁷⁵⁻⁷⁶, where the heavy ion (BF

BF_4^-) prefers to adsorb, and smaller ions (Na^+ and Cs^+) are repelled from the surface. We then output the atomistic cartoon for each ion locating at the preferential absorption location (Figure 3.2b-e). Different hydration status of ions can be observed. The BF_4^- ion with low hydration ability (Figure 3.6b) is partially dehydrated/desolvated (Figure 3.2b). Na^+ or Cs^+ ions prefer to be fully bound with water (Figure 3.2c and e). Interestingly, Li^+ ions with the smallest bare size also do adsorb at the interface (Figure 3.2d). It might be attributed to its unique two hydration-shell structure (Figure 3.6e). Such different hydration abilities at interface are manifested as a various absorption distance in ion's PMFs (Li^+ (4 Å) $\approx$ BF_4^- (4 Å) < Na^+ (6 Å) $\approx$ Cs^+ (6 Å)). The order is not directly related to its bare or fully hydrated ion radius.

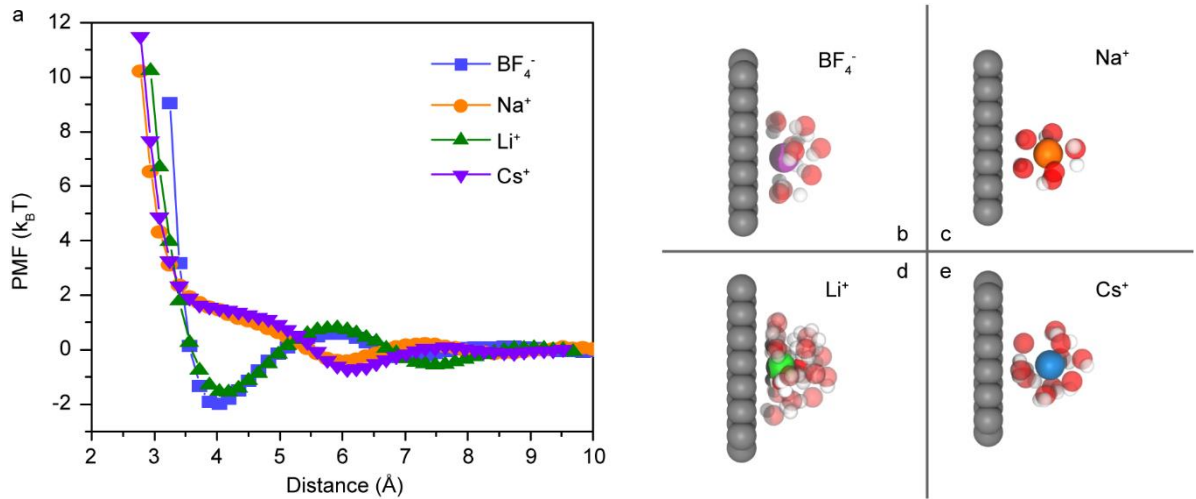


Figure 3.2 The calculated PMFs for a single ion approaching an open graphene surface. (a) the PMF curves for BF_4^- anion and several typical cations (Na^+ , Li^+ , and Cs^+). (b-e) the atomic snapshot of ion absorbing at graphene surface at its equilibrium location for BF_4^- anion (b), Na^+ cation (c), Li^+ cation (d), and Cs^+ cation (e), respectively.

Then the calculated PMF ($V_i^{\text{PMF}}(z)$) is incorporated in PB theory as

$$\varepsilon\varepsilon_0 \frac{d^2}{dz^2} \varphi(z) = - \sum_i q_i c_i^0 e^{-\frac{[V_i^{PMF}(z) + q_i \varphi(z)]}{k_B T}} \quad (3.1)$$

where $q_i = z_i e$ is the charge for ion species i (the valence z_i equals to 1 and -1 respectively in this work), φ is the electric potential, k_B is the Boltzmann constant, T is the absolute temperature, ε is the relative dielectric constant of the solvent, ε_0 is the dielectric constant of vacuum and c_i^0 is the bulk concentration of the ion species i . Note that we applied the $V_i^{PMF}(z)$ on both surfaces of the nanoslits. The superposition effect takes place. Under the zero surface charge condition ($\sigma(-d/2) = \sigma(d/2) = 0$), the solutions of Equation (3.1) are compared with MD results in Figure 3.3. Note that we employed the finite element method implemented in the multi-physics software COMSOL to solve our theoretical models.

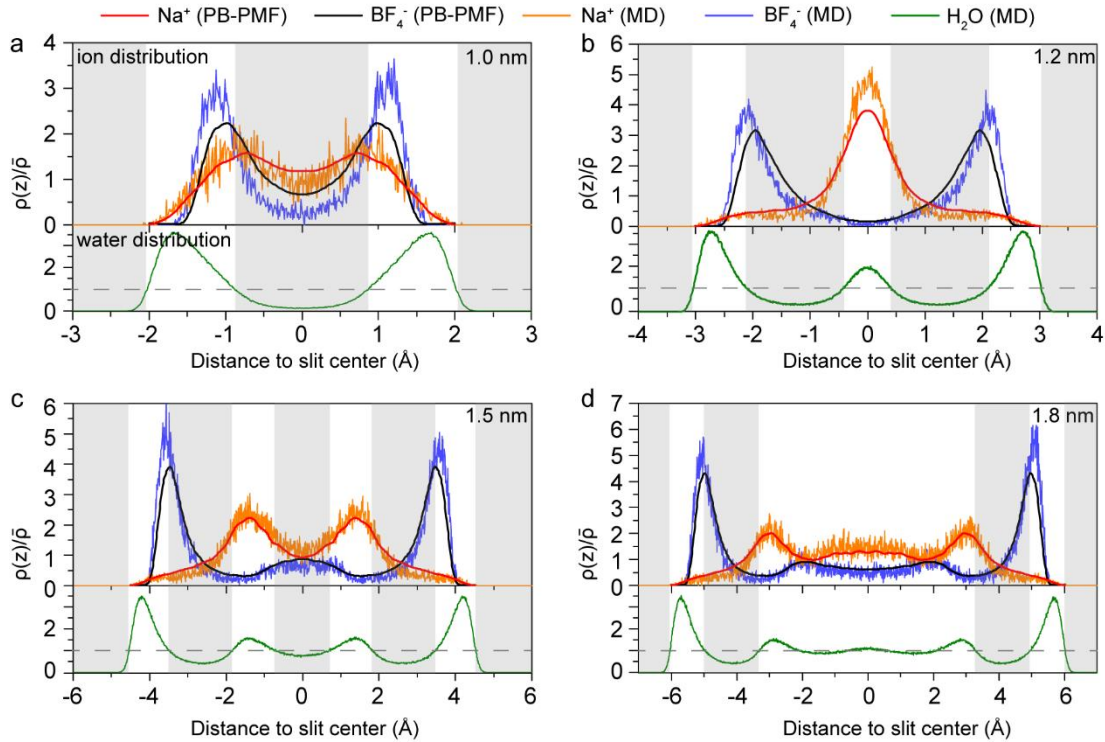


Figure 3.3 Comparison between MD and the PB-PMF model results. The spatial rescaled density profiles of BF_4^- ion and Na^+ ion calculated from MD simulations and continuum models (based on PB-PMF equation) are compared for slit size of 1.0 nm **(a)**, 1.2 nm **(b)**, 1.5 nm **(c)**,

and 1.8 nm (**d**). The discrepancy appears mainly in the interfacial region for larger slit sizes (i.e., 1.5 nm and 1.8 nm). For smaller slit sizes (i.e., 1.0 nm and 1.2 nm), significant discrepancy also appears in the middle region. The green line in each figure is the rescaled water spatial density profile with oscillated features. The underestimated ions densities via the PB-PMF model are accompanied by an enhanced water density (e.g., BF_4^- ions in the interfacial region in all present slits, and Na^+ ions in the middle region in 1.2 nm slit). In contrast, the overestimated ion densities overlap with the water depletion region (e.g., the middle region in the slit of 1.0 nm). This observation suggests a critical influence of water oscillated spatial density on ion distribution.

Figure 3.3 shows that the PB-PMF model results capture the ‘layering’ structure of ion distribution profile, which agrees well with MD simulation results. However, the adsorption peaks predicted by PB-PMF models are less pronounced than the MD simulation results, particularly in the interfacial region. A similar trend was also observed in the study of 1 M NaI electrolyte absorbing at the self-assembled alkane monolayer (SAM), where the PB-PMF modelling underestimated the absorption peak calculated from MD simulations for both Na^+ and I^- , and the discrepancy was attributed to the ion-ion correlation effect⁷⁶. Since the ion’s PMFs are calculated for a single ion where the concentration is diluted, the ion-ion correlation effect should be the obvious factor for the moderate concentration case (e.g., 1 M). Here, we incorporate a correlation length developed by the Bazant *et al.* into the PB-PMF model (denote as PB-PMF-Cor model) to examine the influence of ion-ion correlations⁵⁴. When the correlation length is 2 nm, the absorption intensity of BF_4^- ions is enhanced to a value close to the MD simulation results in an open system (single graphene sheet connecting with the solution) (Figure 3.4a). However, such enhancement does not exist in nanoslits, particularly in

1.0 nm and 1.2 nm slits (Figure 3.4c and Figure 3.4d). Significant deviations still exist between PB-PMF-Cor model results and MD simulation results.

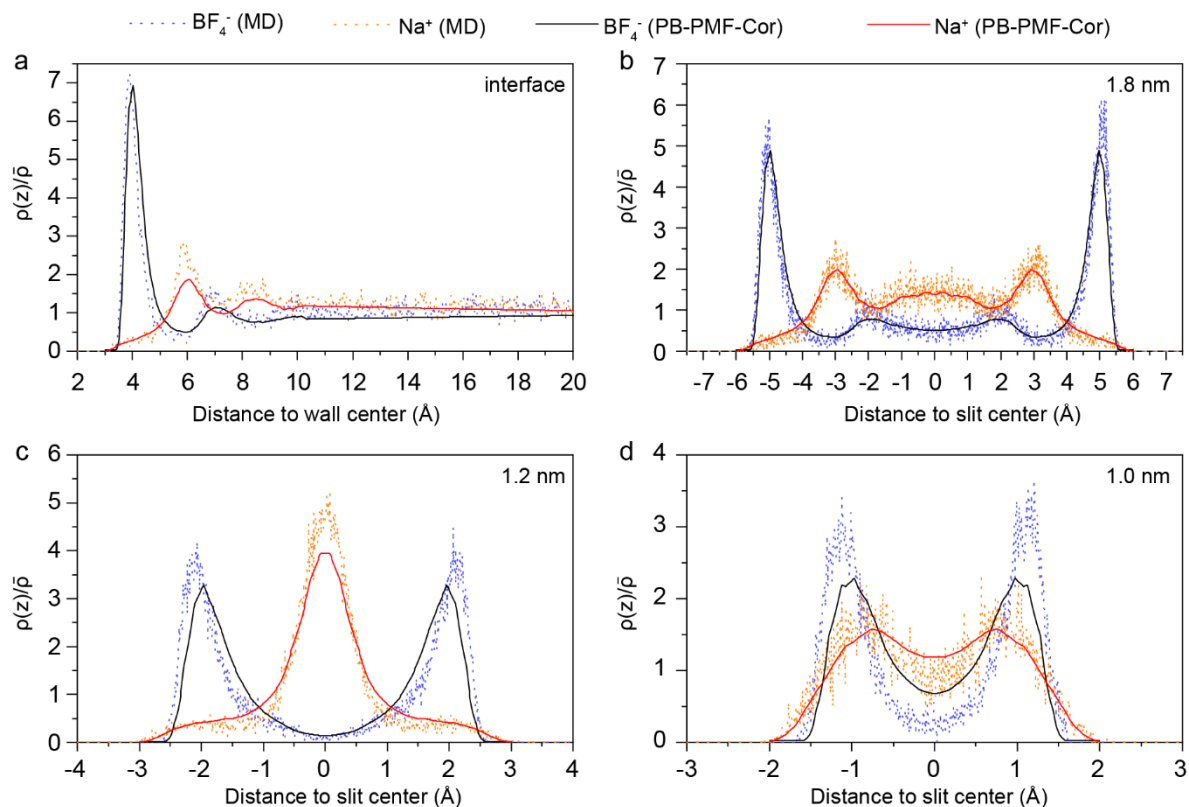


Figure 3.4 Comparison between MD and the PB-PMF-Cor model results. The rescaled spatial density profiles of BF_4^- ion and Na^+ ion calculated from MD simulations and the continuum models (based on PB-PMF-Cor equation) are compared at interface region of an open system (a) and in nanoslit of 1.8 nm (b), 1.2 nm (c), and 1.0 nm (d).

In light of the reorganized solvent structure in nanoconfinement, entropy change could also play a role. Via comparing the oscillations of the water spatial densities with that of the ions' spatial densities in nanoslits, we get some clues to understand the discrepancies between PB-PMF, PB-PMF-Cor, and MD results. As reported, significant water density oscillations present in nanoslits (green line in Figure 3.3a-d), where water-rich nanodomains appear at the interface, followed by a water depletion region. Such a depletion region is particularly pronounced in the

1.0 nm slit with a significant space fraction. In contrast, a 2nd strong water density peak is in the middle of the 1.2 nm slit. We further check the dependence of the water spatial density on the ion-species. It shows constant water distribution profiles, independent of electrolyte ion-species. Interestingly, we can observe that the underestimated ion's spatial density from the PB-PMF models present at the regions where the water shows enhanced local density (the regions with white background colour in Figure 3.3), *i.e.*, the interfacial region in all slits and middle region in the 1.2 nm slit. In contrast, for the water depletion region (background in grey colour), the PB-PMFs models predict an overestimated density. Our analysis implies a critical role of oscillated water spatial densities in the nanoslits. Incorporating the oscillated water density would be a necessary step to resolve the discrepancy in the PB-PMF and the PB_PMF-Cor theory.

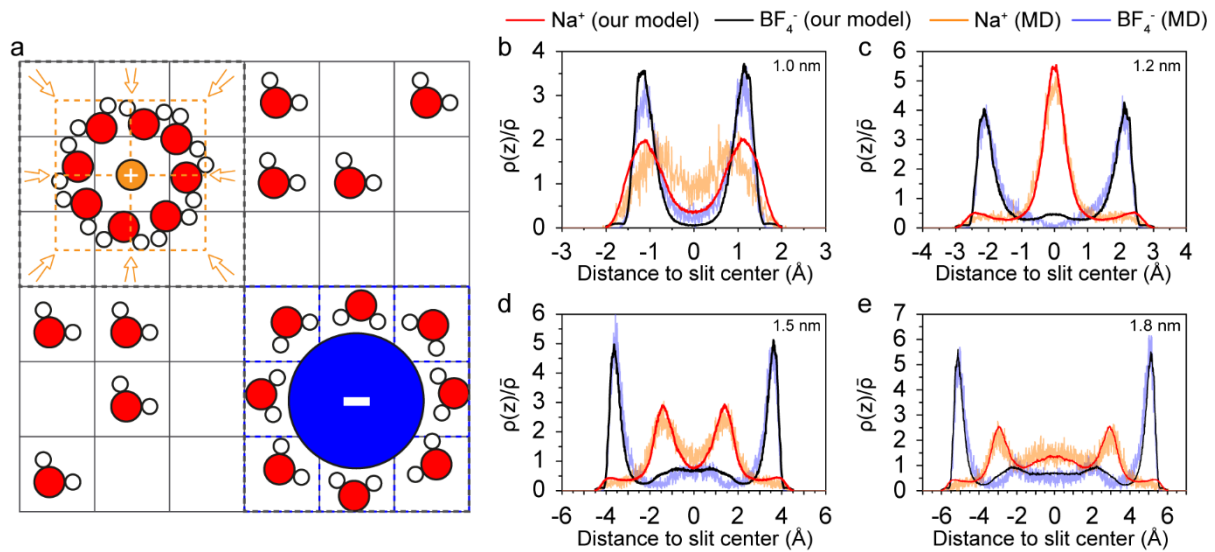


Figure 3.5 Schematic representation of the lattice gas model and ions spatial density profile described using our model. (a) three-component (anion, cation, and water molecules) lattice gas model description of the aqueous electrolyte. The volume of single water molecules is treated as the volume unit. The actual relative size of ions relative to the water molecules (denoted as λ_i) is calculated with considering the ion hydration. The orange (or blue) dashed

square represents the volume of corresponding hydrated positive (or negative) ion, and the dashed square represents the volume of an equal number of free water molecules without ionic attraction. Accordingly, the relative size parameter is the ratio of the orange (or blue) square area divided by the grey square area. **(b-e)** Via incorporating the spatial rescaled densities of water molecules calculated from MD simulations, our modified continuum model results (based on PB-PMF equation with considering the oscillated water spatial density) were compared with MD results for Na^+ and BF_4^- in nanoslits of 1.0 nm **(b)**, 1.2 nm **(c)**, 1.5 nm **(d)**, and 1.8 nm **(e)**.

3.3.3 The PB-PMF model with water distribution effect for ion-specific distribution in small nanoslits

In this section, we consider the structure of water molecules in the entropy term ($k_B T \ln W$) of the well-known lattice gas model. Considering our aqueous electrolyte system is composed of cations, anions, and water molecules with available sites N_+ , N_- , and N_s respectively, the Helmholtz free energy (F) for an aqueous electrolyte system in the mean-field approximation is

$$F = e(\varphi + V_{PMF}) (N_+ - N_-) - k_B T \ln W \quad (3.2)$$

where V_{PMF} is the non-electrostatic absorption potential of ions to surface (PMF curve), W is the number of microstates describing possible distributions for all ions and water molecules ($W = N! / (N_+! N_-! N_s!)$); N is the total available sites. Here we adopt the framework of Huang's lattice model that considers the asymmetric size of anion and cation⁷⁷,

$$N = \lambda_+ N_+ + \lambda_- N_- + N_s \quad (3.3)$$

where λ_+ and λ_- denotes the relative size of cation and anion with reference to the size of the solvent. In this work, different from the fixed N value that is widely adopted in previous works⁷⁸, we treat N_s as a constant value because the MD simulation results show that the spatial density of water molecules is nearly independent on ion-species and dissolved ion numbers (N_+ and N_-) in each slit. As such, the total lattice sites depend on anions and cations. Then the chemical potential is derived ($\mu_{\pm} = \partial F / \partial N_{\pm}$) using Stirling formula ($\ln M! \approx M \ln M + M$),

$$\frac{\partial N}{\partial N_{\pm}} = \lambda_{\pm} \quad (3.4)$$

$$\mu_{\pm} = e(\varphi + V_{PMF}) - k_B T (\lambda_{\pm} \ln N - \ln N_{\pm}) \quad (3.5)$$

Under thermal equilibrium, the chemical potential is constant. We can obtain $N_{\pm}$ in terms of ion available sites number and total available sites number in bulk states (denote as $N_{\pm, \omega}$ and N_{ω}),

$$N_{\pm} = N_{\pm, \omega} e^{\mp e(\varphi + V_{PMF}) / k_B T} \left(\frac{N}{N_{\omega}} \right)^{\lambda_{\pm}} \quad (3.6)$$

Here, we assume $\frac{N}{N_{\omega}} \sim \frac{N_s}{N_{s, \omega}}$ because the ion numbers are much smaller than the water numbers ($N_{\pm} \ll N_s$) in our MD simulation results. Even though the ion local number density can be 3-4 times of bulk value (0.8 M) in some regions of our nanoslit, the number ratio of N_s vs. $N_{\pm}$ is still larger than 20. The ion distribution at equilibrium is thus

$$N_{\pm} = N_{\pm, \infty} e^{\mp(\varphi + V_{PMF})/k_B T} \left(\frac{N_s}{N_{s, \infty}} \right)^{\lambda_{\pm}} \quad (3.7)$$

The value of $\frac{N_s}{N_{s, \infty}}$ can be directly adopted from our MD simulation (the water spatial density distribution, the green line in Figure 3.3), and the V_{PMF} is the calculated PMF curve from MD. The volume ratio (or relative size) $\lambda_{\pm}$ is the only parameter we should determine.

In previous works, this volume ratio was calculated in terms of the ion bare radius and water radius ($\lambda_{\pm} = \frac{r_{\pm}^3}{r_w^3}$), where $r_{\pm}$ is the bare radius of ion and r_w is the radius of the water molecule.

Such treatment works quite well for ionic liquids⁷⁹. But in an aqueous electrolyte system, the hydration force would enable ions to attract neighbored water molecules to form a solvated shell, leading to a volume shrink that depends on the ion-specific hydration abilities (Figure 3.5a). Considering this, here we calculate the volume ratio for a hydrated ion as: $\lambda_{\pm} = \frac{r_{\pm}^{*3}}{(n+1) \times r_w^3}$

where $r_{\pm}^*$ is the radius of the solvated ion, n is the number of the solvated water molecule surrounding the ion. The calculated volume ratio parameters are summarized in Table 3.4, in which the ion bare radius, solvated ion radius, and coordinated water numbers n are determined in MD simulation from the radial distribution function of ions in bulk solution (Figure 3.6). We can find when considering the coordinated water molecules, the volume ratio value (λ_2) varies in a narrower range than the value of λ_1 , that is calculated from ion bare radius. Besides, the λ_2 value of Li^+ ion becomes larger than the λ_2 value of Na^+ and Cs^+ ions, in contrast to the smallest λ_1 value calculated for Li^+ ion. It is more reasonable in aqueous electrolytes since the nature of the unique two water shells around Li^+ ion. Such a feature was also revealed in the study of ion behaviour in water-in-salt systems by McEldrew *et al.* recently⁵².

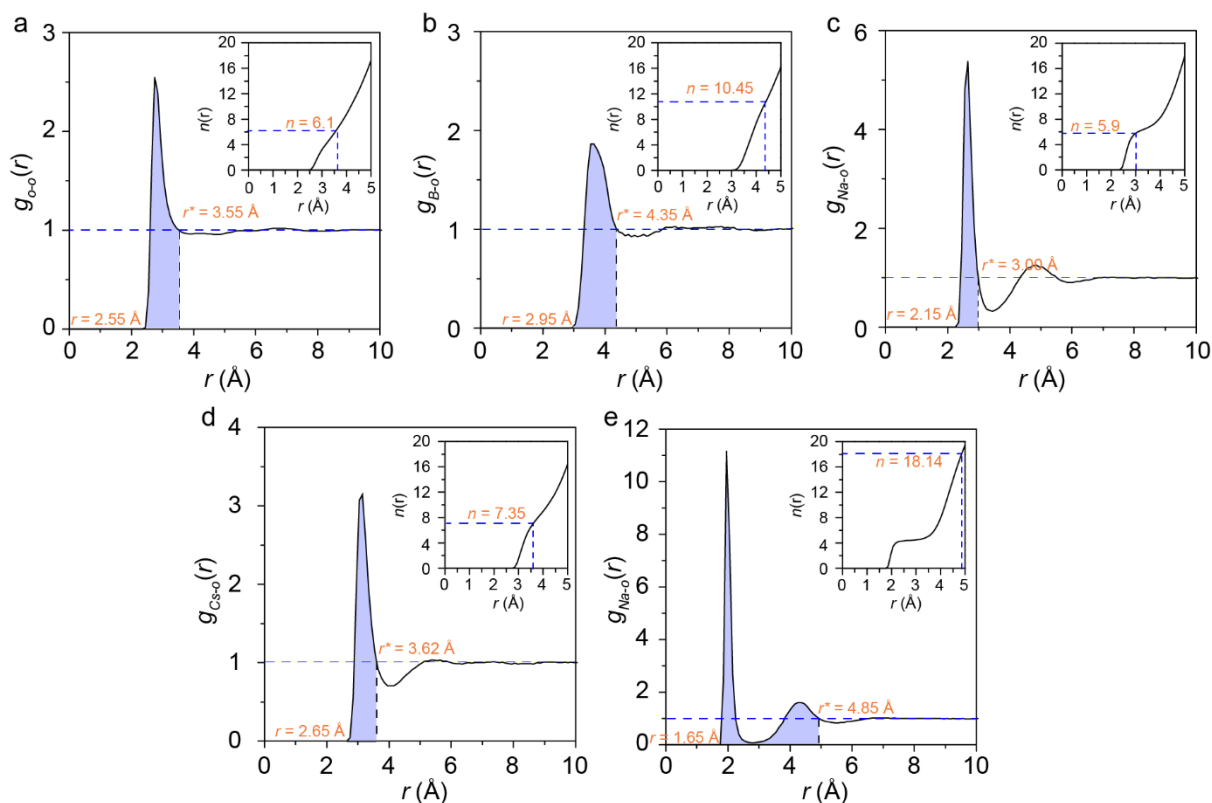


Figure 3.6 The radius distribution functions (RDF) of water (represented by oxygen atom) around the selected ion or water in 1 M electrolytes. (a) The RDF of water around water. (b) The RDF of water around B atom in BF_4^- anions. (c) the RDF of water around Na^+ cations. (d) the RDF of water around Cs^+ cation, and (e) the RDF of water around Li^+ cation.

Table 3.4 Parameters for volume ratio calculation

Ion type	BF_4^-	Li^+	Na^+	Cs^+
r (Å)	2.95	1.65	2.15	2.65
r^* (Å)	4.35	4.85	3.03	3.62
r_w (Å)	1.85	1.85	1.85	1.85
n	10.45	18.14	5.85	7.35
λ_1	4.05	0.71	1.57	2.94

λ_2	1.14	0.94	0.63	0.90
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Note: λ_1 was calculated using the bare ion radius and λ_2 was calculated using the ion hydrated radius.

We couple the Equation ((3.7) with the Poisson equation for a 1D slit model. The boundary conditions are the same as those in the PB-PMF equation in the last section. Figure 3.5 b-e show the results between MD simulation and our continuum models. Our new PB-PMF results agree with MD very well. At the interfacial region, the BF_4^- ions present enhanced number density in all slit size, and Na^+ ions also present enhanced density in the middle region in the slit of 1.2 nm. The main discrepancy in Figure 3.3 is resolved. These results indicate that more ions locate in the water-rich region. It is different from the volume-exclusion effect reported previously, where water molecules as a hard-sphere would reduce available sites of ions and leads to reduced ion number.

To test the feasibility of our models on other electrolyte ion types, we change the cation from Na^+ to Cs^+ or Li^+ . Figure 3.7 shows that the ion density profiles depend on electrolyte ion species in MD results. For example, the Li^+ ions show two distinct density peaks, and their locations are almost the same with BF_4^- ions in the slit of 1.0 nm and 1.2 nm. The Cs^+ ions show only one density peak in the 1.2 nm slit. But they have a similar profile in 1.0 nm slit with the Li^+ ions. All these ion-specific features are captured successfully in our new theoretical model without fitting. The excellent agreement in Fig. 3.5 and Fig. 3.7 indicates the generality of our model.

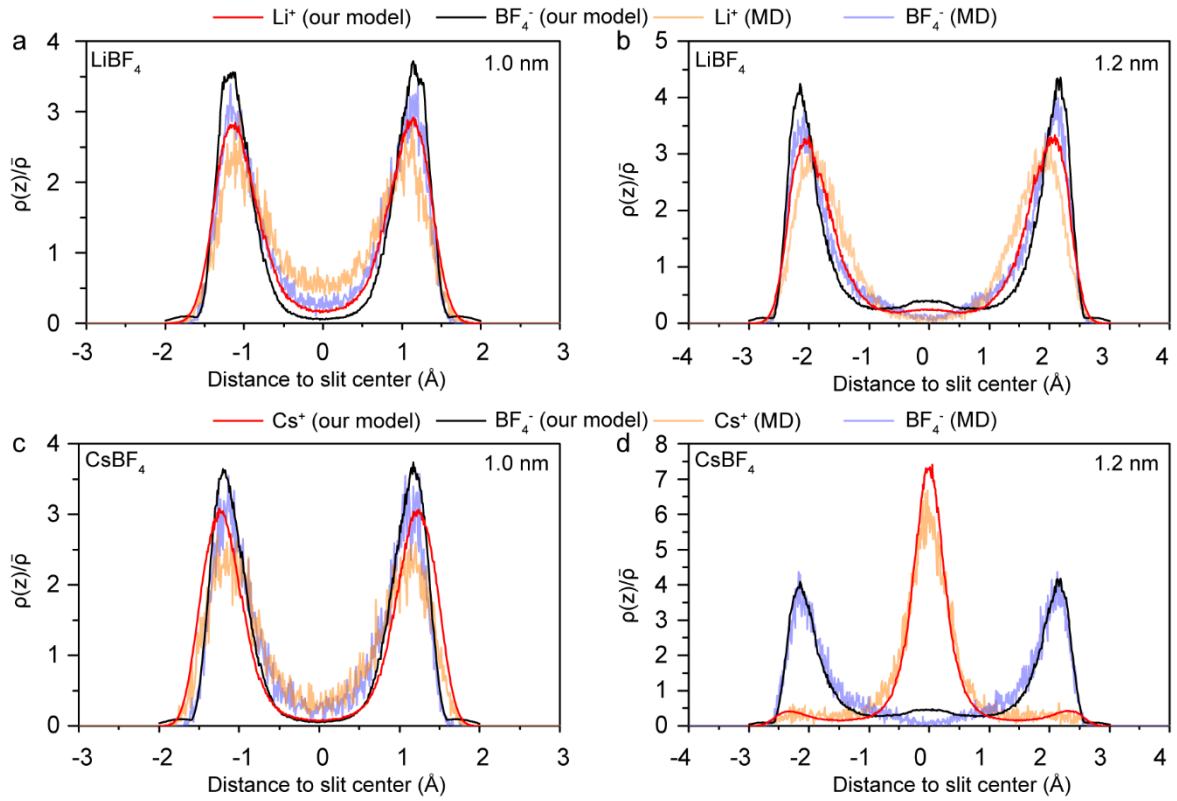


Figure 3.7 Comparison of ion distribution between our new model and MD for electrolyte ion LiBF_4 and CsBF_4 . (a) the electrolyte ion LiBF_4 in 1.0 nm slit; (b) the electrolyte ion LiBF_4 in 1.2 nm slit; (c) the electrolyte ion CsBF_4 in 1.0 nm slit; (d) the electrolyte ion CsBF_4 in 1.2 nm slit.

3.4 Conclusion

In this chapter, we propose a new continuum model for the spatial distribution of aqueous electrolyte ions in nanoconfinement. We incorporate the PMF between ion and graphene that are calculated from MD simulation in the classic PB theory. The modified model can reproduce the layering of density profiles observed in the MD simulation semi-quantitatively. After that, we consider the heterogeneous structure of water molecules in the PB-PMF model via a new lattice-gas model. An improved agreement is achieved between the new model and MD simulation. The critical role of the solvent distribution structure at the nanoscale is demonstrated. Our continuum model is promising to close the time and length scale gaps of the

atomistic simulation approaches for large length-scale simulations. Besides, it would also lay a ground for the development of continuum models to quantitatively describe the charging dynamics in complex nanoporous materials.

Chapter 4: A refined continuum model for EDL structure at an electrified interface

4.1 Introduction

Nanoporous electrodes have been widely used in energy storage devices in recent years. Their superior performance and interesting underlying physics are beyond the initial expectation of merely increased specific surface area³¹. The microstructure of electro-absorbed electrolytes inside nanoporous electrodes received intensive attention. Much experimental evidence indicates that they are significantly different from the bulk electrolyte and cannot be well described by the classic theories³⁷. The ionic liquids are frequently studied as an extreme case (dense electrolyte) to demonstrate the anomalous ion-storage phenomena and new physical mechanisms⁸⁰⁻⁸¹. One representative case has been introduced in Chapter 2⁵¹. The underlying mechanisms are the strong steric effect as well as the ion-ion correlations. They significantly affect the microstructure of the ionic liquids⁵¹. As for the solvent-contained electrolytes, many key features are different from the solvent-free electrolytes. They are treated generally as a middle case between the dilute electrolytes and the ionic liquids. They are assumed with a ‘moderate’ steric effect (ion density saturation at the surface) and the ‘possible’ ion-ion correlations.

However, recent experimental results revealed that the solvent-involved electrolytes are not just a moderate version of ionic liquids particularly at the open surface, where ions are fully solvated or only partially desolvated⁸³⁻⁸⁴. Here, we take the aqueous electrolytes as an example. The EDL capacitances are nearly a constant for commonly used monovalent electrolyte ions (e.g., LiCl, NaCl, KCl, and CsCl) and even divalent ions (e.g., CaCl₂)^{24, 80}. There is little ion-species dependence. In contrast, the ion-specific effect has been widely observed in ionic

liquids arising from either finite ion size or ion polarisation ⁸⁵. As such, it is reasonable to expect that the water molecules must have a critical role in the electrolyte ion structure and the electric potential values in the vicinity of an electrified surface. A comprehensive understanding and quantitative description are necessary. But it is a challenging task ⁸⁶. The water molecule distribution will be altered by both the ions and the charged graphene surfaces, subsequently modulating their screening ability to the external electric field ^{44, 87}. Several relevant studies provided some useful information on the pure water molecules (e.g., dielectric constant, organization) ¹ or the whole aqueous electrolyte (e.g., electric potential) ⁸⁰. More detailed understanding of how water molecules respond to either surface or ions individually as well as their interplay is highly desirable. It can serve as a basis to develop a quantitative model for EDL ion storage performance for aqueous electrolyte-based system design (e.g., multiscale porous structure of electrodes, positive/negative electrode matching, etc.).

In this chapter, we will use molecular dynamics (MD) simulations to investigate the aqueous electrolyte capacitance at the graphene open surface. Our simulations will simulate the ion-species independent capacitance value for two typical aqueous electrolytes with different affinity to the graphene surface. Our analysis will reveal the critical contributions of water molecules on capacitance values. We will investigate how water molecules respond to ions and graphene surfaces individually inside the electric double layer (EDL). Based on the obtained molecular insights, we propose a phenomenological EDL model to predict the microstructure of electrolytes at the electrified interface as well as the electric potential values in the system.

4.2 Simulation methods and systems

Our model supercapacitor system is composed of two flat graphene sheets as opposite electrodes. They are arranged in a parallel plate configuration and immersed in the aqueous

electrolyte (Figure 4.1). These two graphene sheets are placed at $z = \pm 4$ nm and have a lateral (x-y plane) dimension of 4.156×4.254 nm². The width of the whole simulation box is around 16 nm (along the z-axis). Periodic boundary conditions are applied in all three directions. As such, the width of the electrolyte bath between the two electrodes is sufficiently large (around 8 nm). This is to mimic an interfacial charging condition in experiments. The lateral size of graphene electrodes is comparable to or even larger than the typical electrodes simulated in previous works⁸⁸⁻⁹⁰. Two types of aqueous electrolytes are simulated in our work: 0.8 M NaBF₄ and 0.8 M NaCl. The BF₄⁻ anions exhibit strong adsorption affinity to the carbon surface, whereas Cl⁻ anions do not. The BF₄⁻ and Cl⁻ anions are paired with the same Na⁺ cations.

The force field parameters of BF₄⁻ and Na⁺ ions are taken from the Ref.⁶⁵, in which the all-atom force field parameters of various ionic systems were updated and validated to reproduce the experimental properties. The same force field parameters of BF₄⁻ ion were also adopted to study the properties of aqueous NaBF₄ solutions in previous studies⁶⁶⁻⁶⁸. The water model is TIP/3P and water molecules are assumed to be rigid in our MD simulations. The carbon atoms are modelled using the CHARMM27 parameters. Graphene sheets are assumed to be rigid in the system. The parameter of Cl⁻ ion is adopted from the DANG force field⁶⁹.

To determine the thermal equilibrium number of water molecules in the system, we run MD simulations under NVT ensemble and adjust the number of water molecules in the system, meanwhile, we monitor the water density in a reservoir region that is located 2 nm away from the graphene plane. Provided that the water density in this region was the same as the bulk solution and remained steady for ~10 ns, we consider the system under thermal equilibrium. The ion number is determined based on the ion concentration (0.8 M). As such, in our systems, the number of water molecules is about 9052, and the number of cation-anion pairs is 132. To simulate the electrified system, the two graphene sheets are fixed with a certain amount of

negative and positive charges. The total net charge of the system is zero (neutral system). Two charge densities, $\sigma_s = \pm 0.00938 \text{ e/C-atom}$ (i.e., $6.0 \text{ } \mu\text{C}/\text{cm}^2$) and 0, are considered in the simulation for each graphene sheet. Given the specific capacitance value of the graphene electrode is $\sim 5\text{-}10 \text{ } \mu\text{F}/\text{cm}^2$ at a typical voltage for an aqueous electrolyte of $\sim 1.0\text{-}1.2 \text{ V}$ ⁸⁰, the applied charge density fell in the typical range for EDLCs employing aqueous electrolytes.

The MD simulations are carried out under NVT ensemble at 300K using the LAMMPS code. The atomistic trajectories are integrated via the Verlet leapfrog algorithm using a time step of 1 fs. Each simulation case is carried out for more than 50 ns to ensure equilibrium, followed by a 50 ns production time slot in which ensemble averages are computed.

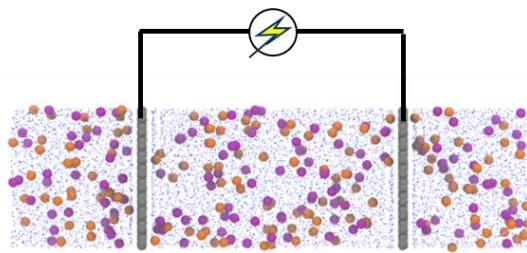


Figure 4.1 A schematic of our molecular system, where two graphene sheets (grey colour) were immersed in an aqueous electrolyte reservoir. The left graphene sheet is negatively charged (i.e., 0 or $-0.00938 \text{ e/C-atom}$), and the right graphene sheet is positively charged (i.e., 0 or $+0.00938 \text{ e/C-atom}$). The water molecules are represented by blue points. The anions are presented by the purple spheres. The cations are presented by orange spheres. Two types of electrolytes were simulated in our work: NaBF_4 and NaCl . The concentration of aqueous electrolytes is 0.8 M in our systems.

4.3 Results and Discussion

4.3.1 The spatial distribution of electrolyte ions from MD simulations

This section will present the microstructure of the electric double layer (EDL) in the vicinity of the graphene surfaces. The one-dimensional ion density profiles along the z -axis are computed across the EDL region by counting the corresponding ion numbers in each bin with a spatial resolution of 0.16 Å. For the water density profile, we count the O atoms. Figure 4.2 shows the relative density profiles of ions rescaled to the bulk density, where the surface charge density is varied (i.e., 0, +0.00938 e/C -atom, and -0.00938 e/C -atom). The oscillated ion density profiles extend to ~ 1.5 nm from the surface (the zero position is the centre of the carbon wall). Note that such ion density oscillations exist even for the zero-charge case. They depend on ion species. For the NaBF₄ electrolyte, the BF₄⁻ ions exhibit a large absorption density (~ 5.8 times of bulk density) next to the zero-charged surface, followed by much smaller Na⁺ density peaks (~ 2.1 times of bulk density). A gap of ~ 2.0 Å exists between the accumulation locations of BF₄⁻ (3.92 Å) and Na⁺ (5.84 Å), leading to a net charge unevenness in the vicinity of the interface. In contrast, for the NaCl electrolyte, the relative density profiles of Na⁺ and Cl⁻ are very similar in terms of both magnitude (~ 1.5 for Na⁺ and ~ 1.4 for Cl⁻) and locations (6.00 Å for Na⁺ and 6.48 Å for Cl⁻ from the surface).

The location of the first BF₄⁻ layer is much closer to the surface than all other ions. In fact, the first BF₄⁻ layer is located at the ion depletion region in the NaCl system. Such strong absorption of BF₄⁻ ions to the graphene was observed by researchers in recent years based on NMR characterization⁹¹. Interestingly, we also observe that the absorption intensity and locations of Na⁺ cations in the NaBF₄ and NaCl electrolytes are different, indicating clear cation-anion correlations. Similar ion-specific adsorption profiles in the vicinity of the zero-charged surface were used to explain the electrolyte equilibrium properties, such as the ion-species dependent surface tensions at the air-electrolyte interface. Here, we will focus on their influence on the

capacitance performance by examining the corresponding interfacial water structure and ion organizations.

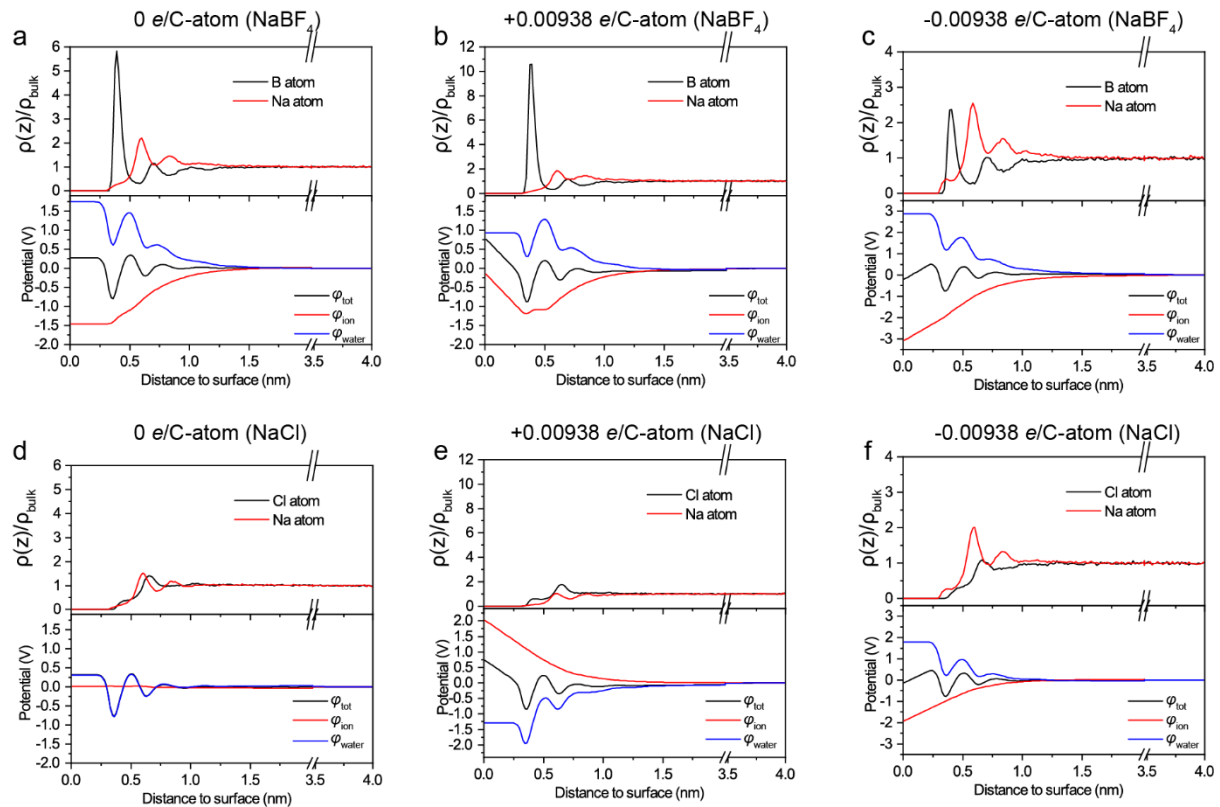


Figure 4.2 The relative density and electric potential profiles for two electrolytes (0.8 M NaBF_4 and NaCl) in the vicinity of electrified or non-electrified graphene surfaces. (a-c) show the results of NaBF_4 electrolyte under the surface charge density of 0, +0.00938, and -0.00938 e/C-atom, respectively. (d-f) are the results of NaCl electrolyte under surface charge density of 0, +0.00938, and -0.00938 e/C-atom, respectively. The upper plot in each graph is the ion relative density profiles, where the black line represents the anions and the red line represents the cations. The lower plot in each graph is the electric potential profiles, where the black line represents the total potential profile, the red line represents the potential profile of ions (including the surface charges), and the blue line represents the potential profile of water molecules.

When the surface is charged positively (*i.e.*, $+0.00938\ e/\text{C-atom}$), the relative density of BF_4^- ions increases from 5.8 to ~ 10.5 . The location of the adsorbed BF_4^- ions is nearly unchanged. The co-ion, Na^+ , shows slight desorption (magnitude change ~ 0.3) and nearly the same location. The charging mechanism of NaBF_4 electrolyte at the positively charged surface should be the counterion adsorption. The charging mechanism of NaCl electrolyte is different. They show an ion-exchange phenomenon when the surface is positively charged. Both Cl^- and Na^+ ions show significant changes upon surface charging. The Cl^- ions show a new absorption peak close to the positively charged surface ($4.08\ \text{\AA}$). The new absorption peak locates at the depletion region in the noncharged case. The distance between the graphene wall and the first Cl^- ion layer decreases from $6.48\ \text{\AA}$ to $4.08\ \text{\AA}$. The relative density peak of Na^+ ions also shows a significant reduction, from 1.5 to 1.03.

When the surface is negatively charged ($-0.00938\ e/\text{C-atom}$), the charging mechanism of NaBF_4 electrolyte becomes the co-ion desorption. BF_4^- ions present significant desorption. Na^+ ions again show a slight change. The NaCl electrolyte remains the ion exchange charging mechanism. The relative density of Na^+ ions increases from ~ 1.5 to ~ 2 and the relative density of Cl^- ions decreases from ~ 1.4 to ~ 1.08 . Our numerical observations reveal that the surface affiliated BF_4^- ions are more sensitive to the surface charges than Na^+ ions. They solely respond to the induced charges, leading to the counterion absorption and co-ion desorption at the positive and negative electrodes, respectively. In contrast, the Cl^- ions and Na^+ ions have a similar affinity to the graphene surface, which leads to the ion-exchange charging mechanism at both positive and negative electrodes. It seems to suggest that the specific ion adsorption could play a role in the EDL capacitance performance.

4.3.2 Electric potential profile and capacitance from MD simulations

The electric potential profiles in the system are calculated by integrating the spatial charge densities based on the Poisson equation. To identify the contributions of ions and water molecules in salt solution systems, we decompose the total electric potential φ_{tot} into two components, φ_{ion} and φ_{water} . The φ_{ion} arises from electrolyte ions (including surface charge). The water molecule dipoles determine the φ_{water} . In our calculations, the electric potential at the middle point of system (i.e., 4 nm from the graphene wall) is assumed as zero. This is reasonable assumption based on a recent work⁹². When the surface electric potential is not larger than 1.0 V, the surface potential is largely screened out by water. This assumption was made in order to coordinate with the boundary condition in the following Poisson-Boltzmann theories for the EDL structure near the surface. The results are summarised in Fig. 4.2.

The electric potential value at the electrode surface (called surface potential) is a key parameter to evaluate the charge storage ability (i.e., capacitance). Figure 4.2d shows that the surface potential of φ_{ion} in NaCl electrolyte is very close to zero (~ 0.01 V) at zero surface charge. In contrast, NaBF₄ ions exhibit a surface potential φ_{ion} of ~ -1.47 V (Figure 4.2a) as a result of the uneven absorption of ions. The ion uneven absorption in NaBF₄ electrolyte leads to a negative surface potential ($\varphi_{ion} \sim -0.16$ V) even when the surface is positively charged ($+0.00938$ e/C-atom). The NaCl ions present a surface potential of 2.0 V under this condition. If we only consider the ion distribution, the positive electrode capacitance is around 2.20 $\mu\text{F}/\text{cm}^2$ and 1.44 $\mu\text{F}/\text{cm}^2$ for NaBF₄ and NaCl electrolytes, respectively. For negative electrodes, the capacitance is around 1.79 $\mu\text{F}/\text{cm}^2$ and 1.51 $\mu\text{F}/\text{cm}^2$ for NaBF₄ and NaCl electrolytes, respectively. The ion-specific adsorption observed in NaBF₄ appears to benefit the capacitance values. It might be because of the thinner EDL thickness of NaBF₄ than that of Cl⁻ ions (3.92 Å vs. 6.48 Å). Note that the above analysis is just for us to gain some physical insights. The water

solvent screening effect is not considered. This is the reason why these calculated capacitance values are all significantly smaller than experiments (5-10 $\mu\text{F}/\text{cm}^2$).

Figure 4.2 shows that the decaying potential profiles of ions φ_{ions} are largely compensated by the water molecules φ_{water} , leading to reduced total potential values: $\varphi_{tot} < \varphi_{ions}$. In addition, the oscillations of the total electric potential profiles matched that of φ_{water} . The strong oscillated electric potentials indicate a heterogeneous structure of water molecules at the interface region. When the surface is neutral, the surface potentials of φ_{water} are 1.74 V and 0.32 V in NaBF_4 electrolyte and NaCl electrolyte, respectively. Thereby, the surface potentials of the whole electrolyte for the neutral surface (also called the potential of zero charges, PZC) are 0.27 V and 0.32 V, respectively, which is consistent with the previous results⁸⁰. When the surface is positively charged, the surface potentials of φ_{water} even show opposite values: 0.92 V in NaBF_4 electrolyte and -1.29 V in NaCl electrolyte. Such a large difference indicates that the orientations of water molecules could be modulated by ions significantly. Using $\varphi_{tot} = \varphi_{ion} + \varphi_{water}$, the positive electrode capacitances are 5.89 $\mu\text{F}/\text{cm}^2$ and 7.21 $\mu\text{F}/\text{cm}^2$ for NaBF_4 and NaCl electrolytes, respectively. The negative electrode capacitances are calculated as 6.14 $\mu\text{F}/\text{cm}^2$ and 6.27 $\mu\text{F}/\text{cm}^2$ for NaBF_4 and NaCl , respectively.

Compared with the calculated capacitance value using just φ_{ions} , the presence of water molecules enhances the capacitance values. This is reasonable since the larger dielectric constant of solutions compared with the vacuum. It should be emphasized that the ion-specific absorption effect is largely diminished by the solvent molecules. The negative electrode capacitance is nearly the same in NaBF_4 and NaCl electrolytes (6.14 $\mu\text{F}/\text{cm}^2$ vs. 6.27 $\mu\text{F}/\text{cm}^2$). Similar ion-species independence was also observed in previous research (e.g., LiCl , NaCl , KCl , and CsCl)^{80, 93}.

Table 4.1 The summary of surface potential and capacitance of each component in the system

		Surface charge state	Surface potential (V)	Capacitance ($\mu\text{F}/\text{cm}^2$)
NaBF₄ electrolyte	Ions	+	-0.16	2.20
		-	-3.08	1.79
		0	-1.47	-
	Water	+	0.92	-3.52
		-	2.88	-2.53
		0	1.74	-
	Whole electrolyte	+	0.76	5.89
		-	-0.20	6.14
		0	0.27	-
NaCl electrolyte	Ions	+	2.02	1.44
		-	-1.92	1.51
		0	0.01	-
	Water	+	-1.29	-1.76
		-	1.78	-1.98
		0	0.32	-
	Whole electrolyte	+	0.73	7.21
		-	-0.13	6.27
		0	0.33	-

However, NaCl electrolyte presents a larger anode capacitance than NaBF₄ electrolyte (7.21 $\mu\text{F}/\text{cm}^2$ vs. 5.89 $\mu\text{F}/\text{cm}^2$) after considering the contributions of water molecules (φ_{water}). This is opposite to the capacitance result calculated by just considering φ_{ion} . Such a change can be understood from some competitive effects arising from the ion electro-absorption in the parallel capacitor model: 1) the thinner EDL thickness as a result of smaller counterion absorption distance; 2) the dielectric reduction of solutions because more water molecules are bounded by the enhanced absorption density of ions. In previous studies, such two factors compete with (or cancel) each other²⁴, leading to an invariant cathode capacitance in commonly used monovalent electrolytes (LiCl, NaCl, KCl, and CsCl). For NaBF₄ electrolyte, such balance is broken down. This could be because the reduction of the dielectric constant is more significant than the ion-wall distance change. Figure 4.2a and Figure 4.2b show the increased absorption density of BF₄⁻ ions in the vicinity of the positively charged surface. However, the ion-wall distance of BF₄⁻ ions is unchanged, because the BF₄⁻ ions are dehydrated in the vicinity of the surface, even a zero-charged surface. As such, there is limited room for them to further move closer to the surface during the charging process to mitigate the dielectric reduction. For other typical electrolyte ions, they are not dehydrated or only partially dehydrated near the zero-charged surface. During the charging process, they could further lose their hydration shell to reduce the ion-wall distance. As a result, a new density peak gradually grows up in the original ion depletion region, or the density peaks move closer to the surface. These features can be found in the EDL structure of Cl⁻ ions, Na⁺ ions in this work, and other previous simulation works (e.g., Rb⁺, Cs⁺, F⁻ ions)²⁴. Our analysis concludes that the change of hydration and water dielectric screening in the close vicinity of surfaces upon surface charging are critical to determine the electric potential and the calculated capacitance.

Considering the graphene surface (either the charged or non-charged state) and ions will both alter the structure of water molecules (i.e., spatial arrangement and orientation) in the vicinity of the surface, contributing to the dielectric screening of water molecules. To decompose them, additional MD simulations are carried out for a system that is composed of only water molecules and graphene sheets (the model size, surface charge density, and calculation methods are the same as the previous system). It provides us the electric potential profiles of pure water molecules near the graphene surface (denoted as $\varphi_{\text{pure-water}}$). We then subtract it from the electric potential profiles of water in the ion-water-graphene system, to obtain the electric potential of water molecules influenced by ions ($\varphi_{\text{ion-water}} = \varphi_{\text{water}} - \varphi_{\text{pure-water}}$). Figure 4.3 shows the potential profiles of $\varphi_{\text{ion-water}}$, $\varphi_{\text{pure-water}}$, φ_{ion} , and φ_{tot} . Table 4.2 summarizes the surface potential values of these electric potentials. These results show that the $\varphi_{\text{pure-water}}$ plays a critical role in the final potential (φ_{tot}), in either magnitude or oscillations. In many cases, the $\varphi_{\text{pure-water}}$ dominates the quantitative values of the φ_{tot} . For example, when the graphene electrode is zero-charged or positively charged in both NaCl and NaBF₄ electrolytes, the electric potential of water molecules influenced by the ions ($\varphi_{\text{ion-water}}$) is almost a mirror of φ_{ion} , suggesting that the water molecules could largely screen the electric potential formed by ions. In the case of negatively charged graphene electrode, the $\varphi_{\text{pure-water}}$ still contributes at least 50% quantitative values of φ_{tot} . This observation is interesting and surprising. In previous works, researchers mainly focus on the ion effects on the relative dielectric constant of solvents, such as the proposed concept of ‘dielectric saturation’ when the electrolyte concentration increased. Here, our atomistic observation suggests the important role of water molecules modulated by graphene surface. These molecular insights provide us a basis to refine the conventional EDL model to improve the prediction of the surface potentials and ion distribution profiles.

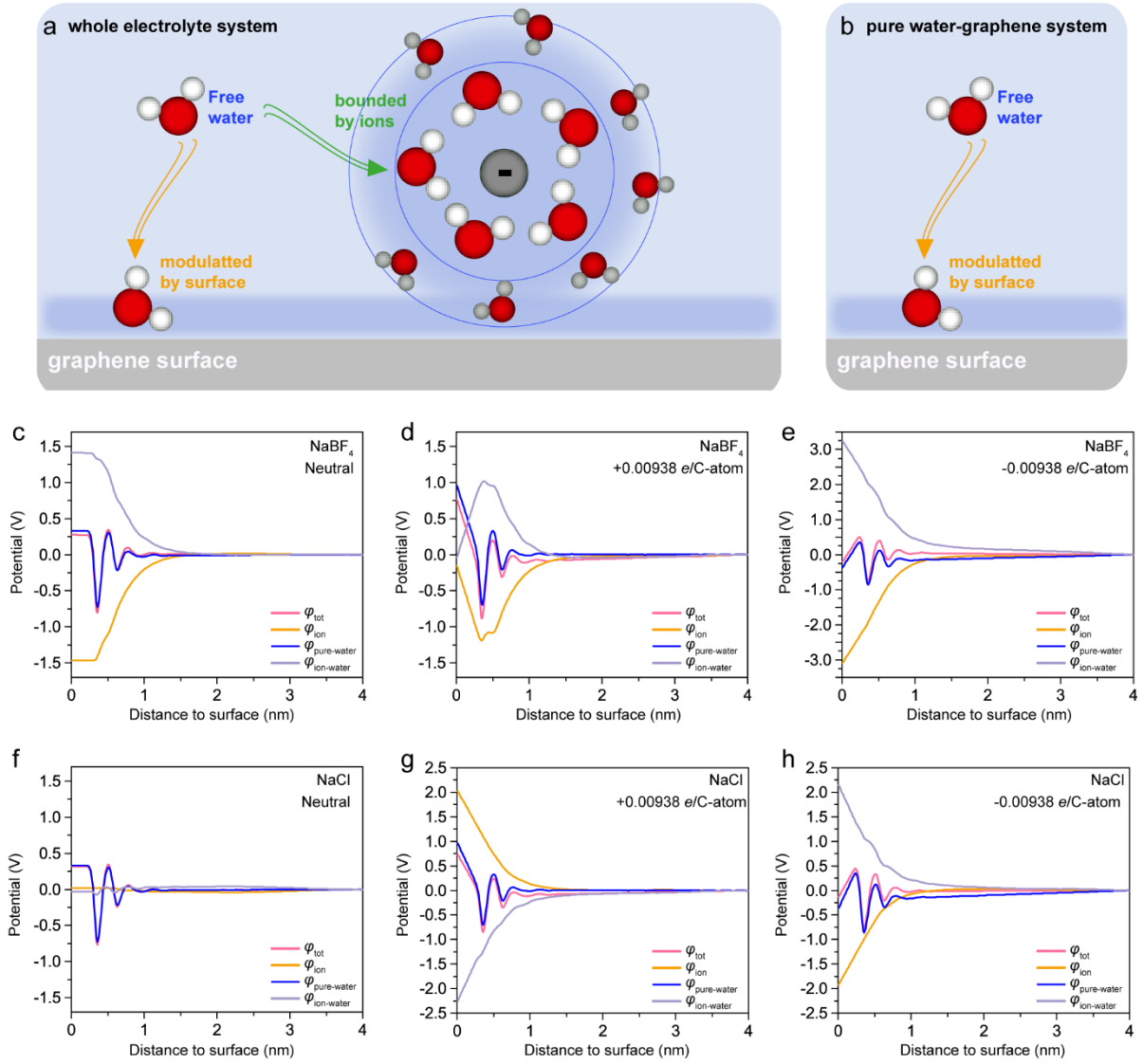


Figure 4.3 The electric potential profile comparison of the decomposed components near the electrified graphene surfaces. (a-b) schematic of water states in the interfacial region of electrolytes or pure solutions near the graphene surface. (c-h) the potential profiles of decomposed water components ($\phi_{pure-water}$ and $\phi_{ion-water}$) and compared with that of ions (ϕ_{ion}) and the whole system (ϕ_{tot}) for two electrolyte species (c-e for NaBF₄ and f-h for NaCl).

Table 4.2 The summary of surface potential of decomposed water components ($\varphi_{pure-water}$ and $\varphi_{ion-water}$) and compared with that of ions (φ_{ion}) and the whole system (φ_{tot}) for two electrolyte systems

Unit: V	Surface charge state	$\varphi_{pure-water}$ at surface	$\varphi_{ion-water}$ at surface	φ_{ion} at surface	φ_{tot} at surface
NaBF₄ electrolyte	+	0.96	-0.04	-0.16	0.76
	-	-0.36	3.24	-3.08	-0.20
	0	0.33	1.41	-1.46	0.27
NaCl electrolyte	+	0.96	-2.25	2.02	0.73
	-	-0.36	2.15	-1.92	-0.13
	0	0.33	-0.02	0.01	0.32

4.3.3 The refined electric double layer model

With knowing the critical role of water molecules modulated by the graphene surfaces in the system potential profile, here, we propose a phenomenological EDL model considering such interfacial features to predict the ion distribution profiles and surface potentials. We insert a region (denoted as orientational dipoles region) between the electrolyte ion region and the vacuum region (Figure 4.4). The vacuum region is identified due to a potential plateau of φ_{water} , which corresponds to a water depletion region. As such, three-domain regions are constructed for the electric double layer in an open interface space: vacuum region, orientational dipoles region, and electrolyte ion region.

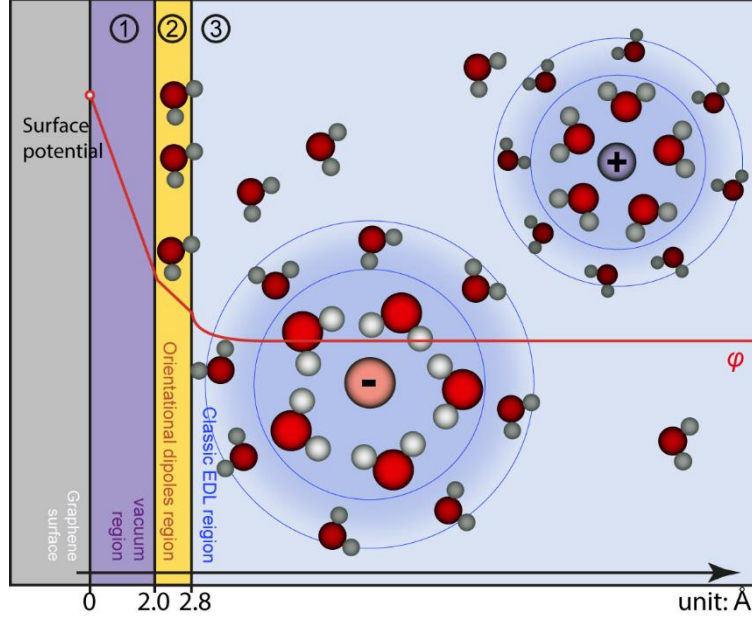


Figure 4.4 Phenomenological electric double layer model. It is composed of three regions: vacuum, orientational dipoles, and custom EDL regions. We propose this model based on our atomistic profiles of water molecules and electrolyte ions. The thickness of the vacuum region is assumed as 2.0 Å, locating at the interval of $[0.0 \text{ Å}, 2.0 \text{ Å}]$ of our 1D model. The orientational dipoles region locates at the interval of $[2.0 \text{ Å}, 2.8 \text{ Å}]$, and the conventional EDL region was in the interval $[2.8 \text{ Å}, 40 \text{ Å}]$. Two boundary conditions are set in terms of fixed charged values and potential values, respectively.

In the electrolyte ion region, the one-dimensional (1D) modified Poisson-Boltzmann (mPB) model is used to describe the potential profile considering the non-electrostatic interaction between ions and graphene surface:

$$\epsilon_{r,s}\epsilon_0\nabla^2\varphi = -\sum_i q_i c_\infty e^{-\frac{[V_i^{PMF}+q_i\varphi]}{k_B T}} \quad (4.1)$$

where ϵ_0 and $\epsilon_{r,s}$ are the free space permittivity ($\epsilon_0 = 8.854 \times 10^{-12} \text{ F/m}$) and relative permittivity of electrolyte, respectively. φ is the local electric potential. q_i is the charge of electrolyte ions for specie ‘i’ ($i = 1, 2$). c_∞ is the bulk molar concentration of electrolytes. V_i^{PMF}

is the local non-electrostatic interaction energy between ion species i and graphene surface. The k_B is the Boltzmann constant and T is the absolute temperature.

In the orientational dipoles region, the potential is described as:

$$\nabla\varphi = E_0 + \frac{\sigma}{L_O C_w} \quad (4.2)$$

where E_0 is the electric field strength of polarised water when graphene surface was at zero charge state, the σ is the surface charge density, C_w is the corresponding capacitance of orientated water molecules by surface, and L_O is thickness of orientational dipoles region. The value of E_0 is calculated via dividing the surface potential of pure water at zero surface charge over L_O .

In the vacuum region, the electric potential is governed by:

$$\nabla\varphi = -\frac{\sigma}{\epsilon_0} \quad (4.3)$$

The thickness of each region is denoted as L_V , L_O , and L_E . The boundary conditions of the model are summarized below.

The electric potential φ is continuous across the interface of vacuum region/orientational dipoles region ($x = L_V$) and the interface of the orientational dipoles region/electrolyte ion region ($x = L_V + L_O$):

$$\varphi(x = L_V^-) = \varphi(x = L_V^+) \quad (4.4)$$

$$\varphi (x = (L_V + L_O)^-) = \varphi (x = (L_V + L_O)^+) \quad (4.5)$$

At $x = L_V + L_O$, the surface charge density is fixed as the simulated values in MD simulations:

$$\epsilon_{r,s}\epsilon_0\nabla\varphi = \sigma \quad (4.6)$$

At $x = L_V + L_O + L_e$, the potential is assumed to decay to zero:

$$\varphi = 0 \quad (4.7)$$

The equations of our new refined model are solved using the finite element method implemented in the multi-physics COMSOL 5.2 software. The adopted parameters are listed in Table 4.3. Most of these parameters are determined based on the atomistic features in our MD simulation results. We assume that the inserted orientational dipoles region locates at the interval $[2.0 \text{ \AA}, 2.8 \text{ \AA}]$ along the z -axis ($L_O = 0.8 \text{ \AA}$), since the water depletion region extends to $2.0 \text{ \AA}$ from wall centre ($L_V = 2.0 \text{ \AA}$) and the electrolyte ions gradually appear at the location of $2.8 \text{ \AA}$ from the graphene surface.

Table 4.3 Parameters used in our new refined continuum modelling for EDL

Parameters	Physical Meaning	Value	Reference
L_V	Thickness of vacuum region	$2.0 \text{ \AA}$	From MD
L_O	Thickness of orientational dipoles region	$0.8 \text{ \AA}$	From MD
L_E	Thickness of electrolyte region	$37.2 \text{ \AA}$	From MD

C_w	Double-layer capacitance of orientated water by graphene surface	41.14 F/nm ² for neg. 240.0 F/nm ² for Pos.	From MD
E_0	Electric field strength of orientated water near the zero charged surface	0.41 V/Å	From MD
σ	Induced surface charge density	$\pm 3 \mu\text{C}/\text{cm}^2$	From MD
c_∞	Initial concentration of electrolyte	0.8 mol/L	Form MD
V_i^{PMF}	The non-static interaction between ion and graphene surface	PMFs	From MD
$\epsilon_{r,s}$	Relative dielectric constant of electrolyte	80	Assumed

Figure 4.5 presents the calculated results of our refined EDL models. One significant advantage of the refined model is that it captures the potential of zero charge (PZC) in MD simulation results. Both the classic PB model and PB-stern model predict the PZC was almost zero (Figure 4.5a). In the vicinity of the charged surface, the classic PB model underestimates the surface potential values significantly, whereas the PB-stern model could semi-quantitatively agree with surface potential values calculated by MD simulations. Thereby PB-stern models have been widely used previously to calculate the capacitance of systems. Besides the inaccurate PZC predicted by the PB-stern model, some other limitations of the PB-stern model are the ambiguous dielectric constant and thickness of the stern layer. Those values were commonly obtained by fitting the experimental results with a fixed thickness of the stern layer (pre-assumed). Such a stern layer with reduced dielectric constant considers the effect of absorbed finite-size ions at the interface. But it cannot provide a microstructure of electrolyte ions in this region. All these limitations come from the fact that the ‘stern layer’ is an artificial concept. It

involves multi-effects, such as the orientated water molecules at the interfacial region, the ion density saturation, and the contributions of the vacuum region. Our proposed model based on molecular insights from our MD simulations remedies these drawbacks. We use three regions in the continuum model to represent the vacuum, interfacial water molecules orientated by surface, and electrolyte ions, respectively. To obtain the layering of electrolyte distribution, the non-electrostatic interaction between ions and surface is considered. The ion distribution profiles predicted by the refined models agree well with the MD simulations, particularly within the ion accumulation regions.

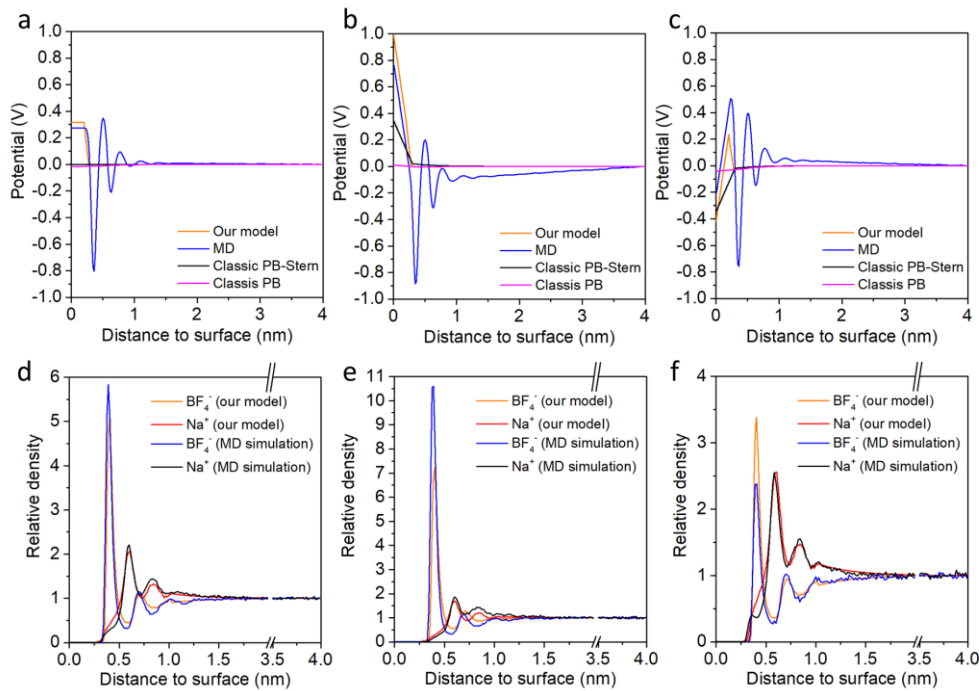


Figure 4.5 The results comparison between refined continuum EDL models and MD simulations. (a-c) shows the electric potential profiles at surface charge density of 0, +0.00938, and -0.00938 e/C-atom, respectively. (d-f) shows the ion distribution profiles at surface charge density of 0, +0.00938, and -0.00938 e/C-atom, respectively. The stern layer thickness in PB-stern models was assumed as 3 Å, and the dielectric constant was fixed as 3 in this region.

4.4 Conclusion

In summary, we use MD simulations to calculate the capacitance of NaBF_4 and NaCl aqueous electrolytes in the vicinity of charged graphene sheets. Their capacitance values of negative electrodes are similar, which is consistent with the observed ion-species independence of capacitance in other simple monovalent ions. But the NaBF_4 has a notably lower positive electrode capacitance. The difference originates from the unique absorption state of BF_4^- ion in the vicinity of the graphene surface, where they are dehydrated and thus directly absorb with the graphene surface. The restricted ion-wall distance space cannot mitigate the reduction of dielectric constant in the charging process, leading to a lower capacitance value.

Our comprehensive atomistic analysis of the electric potential profiles reveals a vital role of water molecules that are modulated by the graphene surface. In many cases, ions even play a minor role in the final capacitance value, which is interesting and surprising. Based on these understanding, we propose a refined EDL model to describe the potential profiles and ion spatial distributions. Our model breaks the EDL at the charged interface into three regions: vacuum region, orientational dipoles region, and electrolyte ion region. The vacuum and orientational dipoles region have clear physical meaning. They replace the conventional Stern layer and eliminate some ambiguity of the widely adopted Stern layer model. Our model results of the surface potentials (including PZC) and microstructure of aqueous electrolytes agree with MD simulation results quite well.

Chapter 5: Continuum model study of ion partition in multilayered graphene membranes in comparison with experiments

5.1 Introduction

The ion accessibility inside nanopores is the foundation for many important technical applications, such as supercapacitors ⁹⁴, batteries ⁹⁵⁻⁹⁶, and nanofluidics ⁶¹. The critical information for ion accessibility inside nanopores includes its in-pore density and distribution structure in light of its direct impacts on ionic applications ⁹⁷⁻⁹⁹. After continuous research in the past several decades, it is becoming clear that the pore size ^{34, 40}, ion-specificity ^{91, 100}, and surface chemistry ¹⁰¹ play an essential role in the ion density and microstructure in nanoconfined space. In Chapter 2, we provide some experiment evidence and understanding in this regard, such as the work of Luo *et al.* ⁹¹, giving rise to the surprising electroneutrality breakdown in carbon nanopores. In extreme nanoconfinement where only one layer of ions is admitted, Vella *et al.* reported that ion accessibility inside nanochannels is influenced by the ion-surface electrostatic/non-electrostatic interactions and ion solvation energies ⁹⁸. Via collaborative works between experiments and theory, Gogotsi, Simon, and co-workers found that pore size could change the microstructure of electrolyte, leading to a varied capacitance of supercapacitors ³¹. However, despite these advances in the past few years, we have limited methods to characterise the ion accessibility inside nanopores, not to mention a comprehensive understanding and quantitative description of the pore size effects and ion-specificity on ion accessibility.

A quantitative picture of the size confinement effects on ion accessibility would offer a benchmark for experimental design and developing/validation of new theoretical models ^{35, 102}.

The comprehensive relation of ion-specific density dependence versus pore size also allows a reliable classification of the distinctive ion accessibility behaviour in nanoconfinement. Analysing the comprehensive density/pore-size scaling relation could reveal the physical origins of distinctive ion accessibility and even establish a semi-quantitative guideline to classify them. However, current model materials used for exploring nanoconfined ion accessibility inside nanopores are mostly based on activated carbon, which usually has complex surface chemistry and irregular pore structure with broad size distribution. This limitation makes it challenging to probe the much-needed knowledge on this topic

In the past decades, various force-spectra techniques, including atomic force microscopy and surface force apparatus, have been used to characterize the electrolyte structure at the solid-liquid interfaces^{76, 103-104}. In the vicinity of a solid surface, the layering of the ionic liquid is observed under the interfacial driving forces³⁰. These techniques are well suited for open space. However, they are not capable of retrieving the electrolyte microstructure in the closed pore space in the nanoporous materials. Moreover, the electrolyte structure turns out to be remarkably complex in confined geometries. They would not be a result of simple superposition effect of electrolyte structures at the open surface because various physical interactions among ions and pore walls would be crowdedly at play under nanoconfinement. For example, in nanopores with a pore size of sub-2 nm, the adsorbed ion layers near the pore walls could overlap, resulting in some anomalous phenomena of ion packing, such as the aforementioned electroneutrality breakdown⁹¹ and Coulombic order breakdown⁴. On the theoretical side, the classic Gouy-Chapman-Stern model or Poisson-Boltzmann theory also fails to depict the accurate ion microstructure in sub-2 nm confinement⁵³. So far, it lacks experimental evidence and experimentally verified theoretical models to reveal the working mechanism for the intricate ion accessibility inside nanoporous materials at the sub-2 nm scale.

In this chapter, with the collaboration of Dr. Diyan Liu *et al.*, who provided the nuclear magnetic resonance (NMR) spectroscopy results of the electrolytes in multi-layered graphene membranes (MGMs), the continuum model developed in Chapter 3 is validated, for the description of the ion microstructure in nanopores, and the in-pore ion density dependence on pore size. Furthermore, the physical origins of distinctive ion accessibility behaviours in nanoconfinement are revealed and discussed. The influence of ion-specificity, slit-size, and membrane thickness on the ion accessibility in nanopores are investigated, to reveal the physical origins and establish a semi-quantitative guide to distinguish/manipulate them.

5.2 Methodology

5.2.1 Schematics of continuum models and assumptions

Figure 5.1 shows the schematic system of the porous structure of the graphene membrane immersed in an electrolyte reservoir. The graphene sheets (grey region) are parallel-aligned and have one shared end to mimic graphene membrane geometry that is composed of interconnected graphene sheets. Four parameters determine the geometry of the parallel graphene array: the length of the graphene sheet (L_G), interlayer spacing (d), the thickness of the graphene sheet (t_G), and the total slit number formed by graphene sheets (N_g). In this work, we adopted $L_G = 10$ nm, and $t_G = 0.3$ nm. The d values varied from 1.0 nm to 2.4 nm and N_g varied from 1 to 160, to investigate the effect of slit size and membrane thickness on the in-pore ion amounts and concentrations.

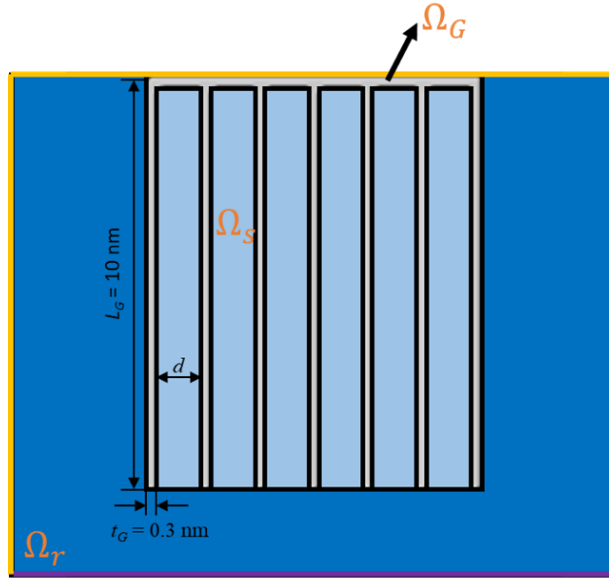


Figure 5.1 A schematic of the multilayer graphene membrane in the continuum model simulation. It shows a representative model of a 6-layer graphene membrane. The graphene region (section in grey color), slit region (section in light blue color), and the reservoir region (section in dark blue color) were denoted as Ω_G , Ω_S , and Ω_r , respectively. The length of graphene layer is 10 nm, the thickness of the graphene sheet is 0.3 nm, the reservoir box is larger than the membrane size for more than 2 nm on each side.

Here are several assumptions made on the simulated system: (1) the corrugation of graphene sheets in experiment membranes were not considered in this work; (2) the functional groups on graphene membranes were not considered; (3) The defects on graphene sheets were not considered (e.g., large pore, edges); (4) the electric potential was assumed to be the same across the solid phase of the graphene membrane (porous framework); (5) the graphene membrane was assumed to be metal that is polarizable by the absorbed ions; and (6) the electroneutrality was maintained for the whole system.

5.2.2 Governing equations and boundary conditions

For the electrolyte in the slit region, since ion-specific accessibility inside graphene membranes was observed in experiments, our continuum model developed in Chapter 3 was adopted. This model considers the non-electrostatic interaction between ions and graphene wall and the effects of heterogeneous solvent distribution:

$$\epsilon_{r,s}\epsilon_0\nabla^2\varphi = -\sum_i q_i c_\infty e^{-(\varphi q_i + V_{PMF})/k_B T} \left(\frac{N_s}{N_{s,\infty}}\right)^{\lambda_\pm} \quad (5.1)$$

Here ϵ_0 and $\epsilon_{r,s}$ are the free space permittivity ($\epsilon_0 = 8.854 \times 10^{-12}$ F/m) and relative permittivity of electrolyte, respectively. φ is the local electric potential. q_i is the charge of electrolyte ions for specie ‘ i ’ ($i = 1, 2$). c_∞ is the bulk molar concentration of electrolytes. V_i^{PMF} is the local non-electrostatic interaction energy between ion species i and graphene surface. k_B is the Boltzmann constant and T is the absolute temperature. N_s and $N_{s,\infty}$ are the local density of water molecules and water density in the bulk region, respectively. $\lambda_\pm$ are the volume ratio of cation and anion relative to a water molecule, respectively.

The electric potential φ in the electrode is governed by the Poisson equation:

$$\nabla^2\varphi = -\frac{\sigma}{\epsilon_{r,g}\epsilon_0} \quad (5.2)$$

where σ is the free charge density on the graphene membrane. In our system, no external charge was induced to porous materials. Some free charges could appear at graphene layers because of the graphene surface’s polarisation caused by ion’s absorption. The net charge in the whole graphene membrane/framework is equal to zero (e.g., opposite charges could distribute on the graphene membrane inner surfaces and the outer surfaces, respectively). $\epsilon_{r,g}$ is the relative permittivity of the graphene.

Moreover, the electric potential φ was continuous across the graphene/electrolyte interface so that,

$$\varphi(\mathbf{r}_{int}^-) = \varphi(\mathbf{r}_{int}^+) \quad (5.3)$$

In the boundary of the system box, the electric potential is fixed as,

$$\varphi(\mathbf{r}_b) = 0 \quad (5.4)$$

Here $\mathbf{r}_{int}$ and $\mathbf{r}_b$ denote the positive vectors of the graphene/electrolyte interface and the boundary plane of the system box, respectively.

5.2.3 Parameters and constitutive relations

To solve equations (5.1) to (5.4), the electrolyte properties $\epsilon_{r,s}$, q_i , c_∞ , V_i^{PMF} , $\frac{N_s}{N_{s,\omega}}$, $\lambda_\pm$ and graphene properties $\epsilon_{r,g}$ are needed. In this work, we focus on the accessibility of two typical aqueous electrolytes (0.8 M NaBF₄ and 0.8 M NaF) in multi-layered polarizable graphene membranes at room temperature. As such, the $\epsilon_{r,s} = 80$, $q_1 = -q_2 = 1 \times eN_A$ (e is the elementary charge, 1.602×10^{-19} C, and N_A is the Avogadro constant, 6.022×10^{23} mol⁻¹), $c_\infty = 0.8$ mol/L, $\epsilon_{r,g} = 100000$. The V_i^{PMF} , $\frac{N_s}{N_{s,\omega}}$, and $\lambda_\pm$ are obtained from MD simulations (details see Chapter 3). The ion's PMF to graphene surface (V_i^{PMF}) has two important features: the maximal absorption energy value and its distance to the surface. Besides incorporating the PMF in continuum model to predict ion adsorption density and profile in nanoslits, we want to investigate the influence of each PMF feature on ion adsorption inside nanoslits. Since we do not have a clear mathematic equation to describe the PMF with the lowest energy intensity and location identified, we adopted the 12-6 Lennard-Jones (LJ) potential to fit the PMF, though

there are some differences between the fitted LJ potential and PMF (Figure 5.2 c-d). The LJ potential is a widely used model that approximates the weak interaction between atoms. This potential model quantifies the interaction energy profile using two parameters, the interaction equilibrium distance (σ_0) and the depth of the potential well (ε) (Equation 5.5). Via artificially changing one parameter while maintaining the other one or rematching these parameters from different ion types (Figure 5.6e and f), we could get more insights into how the intensity and locations of ion's adsorption energy influence the ion adsorption inside nanoslits.

$$V_{LJ} = 4\varepsilon \left[\left(\frac{\sigma_0}{r} \right)^{12} - \left(\frac{\sigma_0}{r} \right)^6 \right] \quad (5.5)$$

where r is the distance between the interacted particles (*i.e.*, the perpendicular distance between ions and graphene surface). The parameters, σ_0 and ε , are determined via fitting the potential of mean force (PMF) curve calculated by our MD simulations (Figure 5.2). Table 5.1 summarizes these parameters. The purpose of using LJ potential instead of PMF is that we can easily tune the value of σ_0 and ε to investigate the ion adsorption position and ion-wall interaction strength on the ion density in graphene nanoslits (ion accessibility).

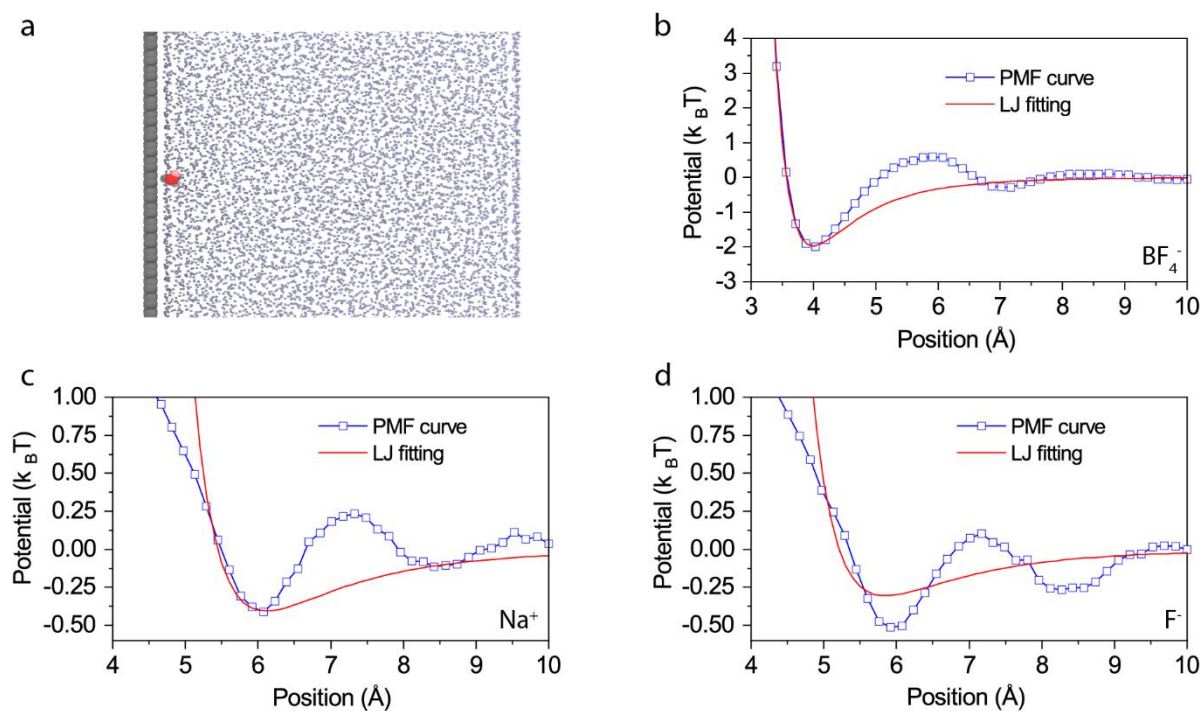


Figure 5.2 The potential of mean force curves (PMFs) and the fitted LJ potentials. (a) shows a typical atomic system in our MD simulations. (b-d) shows the PMF curves and fitted LJ potentials for BF_4^- ion (b), Na^+ ion (c), and F^- ion (d). For the detailed MD simulation methods please see the methods part in Chapter 3.

Table 5.1 The fitted parameters for the 12-6 LJ potential

Ions	ϵ ($k_B T$)	σ_0 ($\text{\AA}$)
BF_4^-	1.97	3.56
Na^+	0.40	5.45
F^-	0.31	5.21

5.2.4 Data processing

The model was solved using the commercial finite element solver COMSOL 5.2. The total number of anions or cations (Q_i , unit: mol/m) in the slit region was computed by integrating the local ion concentration (c_i) across the whole slit-region plane as,

$$Q_i = \int_{A_p} c_i dA \quad (5.6)$$

where A_p is the plane area of the slit region in the system. The areal ion number density (Q_{di} , unit: mol/m²) was calculated by dividing the Q_i by the length of the graphene sheet (L_G) as

$$Q_{di} = \frac{Q_i}{L_G} \quad (5.7)$$

The average anion or cation concentration ($\bar{c}_i$) in slit region was computed as,

$$\bar{c}_i = \frac{Q_i}{A_p} \quad (5.8)$$

The numerical convergence was assessed based on the ion amount Q_i in the slit region. The convergence criterion was chosen such that the maximum relative difference in Q_i was less than 2% when multiplying the total number of finite elements by at least two. The triangle elements were used to generate the finite element meshes. The mesh was refined near the graphene/electrolyte interface where the ion concentration gradient was large. In our work, the maximum element size was specified to be 0.02 nm at the interface and 1.2 nm in the rest of the domain.

5.3 Results and discussion

5.3.1 MD simulation results for ion-wall interaction

In the above experimental results, the graphene membranes are not electrified but the electrolytes accommodated in nanopores show a highly ion-species dependence either between anions and cations (e.g., Na^+ and BF_4^-) or between anions and anions (e.g., BF_4^- and F^-). The non-electrostatic interaction between ions and the graphene wall should play a critical role in those observed phenomena. The important role of such interactions is also reported in interfacial electrolyte ions distributions, leading to ion-specific surface tension at the interface of air-solutions. Therefore, we first use MD simulations to quantitatively determine the interaction energies between the electrolyte ions and the graphene wall as a function of ion-graphene perpendicular distance at a molecular scale.

The molecular system used in MD simulations is presented in Figure 5.2a. Using umbrella sampling and the weighted histogram analysis method (WHAM), the potential of mean force (PMF) is calculated to present the free energy variation as an ion approaching the graphene surface in electrolyte solutions (Figure 5.2 b-d). The PMF includes three physical components: the image potential due to the interfacial dielectric property, ion-graphene van der Waals (vdW) and steric interaction energy, and hydration energy. The most negative value in the PMF profiles quantifies the ion adsorption energy at the interface and the corresponding location represents the ionic preferable adsorption sites. Figure 5.2b shows that the BF_4^- anions have the lowest PMF value of $-2k_B T$ at around 4 Å (relative to the graphene wall centre). In contrast, Na^+ ion and F^- ion both present relatively smaller (absolute) energy values of $-0.4k_B T$ at around 6 Å. These results are consistent with NICS measurements, which reveal a smaller ion-graphene distance for BF_4^- anions than Na^+ cations and overlapped ion-graphene distance for Na^+ cations and F^- anions. Furthermore, the PMF curves show strong oscillations when the ion-

graphene distance is smaller than 10 Å, suggesting non-uniform ion distribution in graphene nanoslits.

5.3.2 Continuum model prediction and comparison with experiments

The obtained ion-graphene interaction energies are then incorporated into the continuum models. Here, three continuum models various on the governing equation for in-slit electrolyte description are compared, i.e., the proposed model in Chapter 3, the classic PB-PMF model, and the PB-LJ model. Compared with the classic PB-PMF model, the proposed model in Chapter 3 additionally considers the heterogeneous distribution of water in nanoslits. The PB-LJ model approximates the PMF curves in the PB-PMF model into a standard LJ potential formula. To consider the polarisation of the graphene surface and the resultant screening effect, the graphene sheets are assumed as a metal with a large dielectric constant. A range of slit sizes ($d = 1.2, 1.4$, and 1.8 nm) is simulated to investigate the effect of slit size on ion accessibility inside nanopores.

Figure 5.3 a-c show the ion distribution profiles in one slit of a 12-layer slit system predicted by our new model, the PB-PMF model, and the PB-LJ model, respectively. All these models capture the alternative layering of BF_4^- anions and Na^+ cations in graphene nanoslits as concluded in NMR experiments. Following the trend in PMFs results, BF_4^- anions show distinctive high concentration peaks close to the graphene surface at a distance of ~ 4 Å, whereas much weaker Na^+ concentration peaks are observed further away from the surface at a distance of ~ 6 Å. However, there are more profound oscillations of ion layering structure in our new model and PB-PMF model than results of the PB-LJ model. This can be attributed to the approximated LJ relation to replace the PMF curves. Compared with the PB-PMF model, our model shows an enhanced intensity of interfacial ion layers (i.e., BF_4^- anions).

Figure 5.3d shows the calculated average ion concentrations inside nanoslits. These three models all capture the features of electroneutrality breakdown inside nanoslit as observed in NMR results. There are more BF_4^- anions than Na^+ cations. Besides, these three models show a similar scaling relation of the in-pore ion average concentrations on slit size. When the slit size is larger than 1.2 nm, the in-pore concentration in these three models are comparable to each other and agree with the experimental results semi-quantitatively. Note that these results are for the 12-layer slit system. The thickness of the 12-layer slit is much smaller than the practical graphene membranes. The thickness effect will be discussed in the following. Deviations present for the 1.0 nm slit system. Different from the significant concentration drops that are predicted by the PB-PMF model and the PB-LJ model, the reduction of in-pore ion concentration from our new model is more moderate. However, the discrepancy still persists between our model and experimental results, which may come from some un-revealed physical mechanisms, such as the decomposition of water molecules.

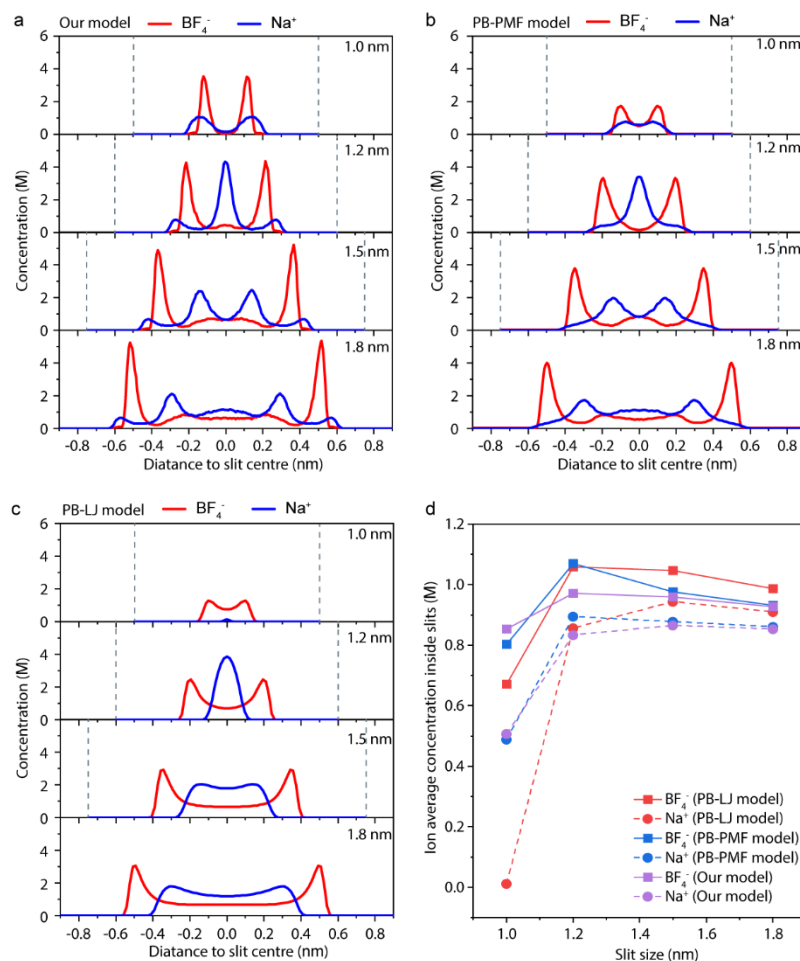


Figure 5.3 Ion spatial distributions in nanoslit from different theoretical models. (a-c) shows the concentration profile of NaBF_4 electrolyte in a slit of 1.2 nm, 1.4 nm, and 1.8 nm in a 12-layer slit model, which are predicted by our model (a), PB-PMF model (b), and PB-LJ model (c). (d) shows the scaling relation of ion average concentration inside the slit region on slit size.

To predict the ion-specific in-pore density in thick graphene membranes, the in-pore ion amounts for a range of membranes with different slit size and slit layers are simulated using the PB-LJ model. The PB-LJ model is adopted here due to its time-efficient for large geometry models (e.g., slit layer is 80 and 160) and the ease of manipulating ion-graphene interactions for in-depth discussion. Two types of aqueous electrolytes, i.e., 0.8 M NaBF_4 and 0.8 M NaF , are simulated. Figure 5.4 shows the microstructure of NaBF_4 and NaF electrolyte ions in one

slit predicted by the PB-LJ model in a 12-layer slit system. Different from BF_4^- anions, F^- anions show a similar location with Na^+ ions. These trends are consistent with the NICS results in Figure A1a-c. The order of ion-wall absorption distance ($\text{BF}_4^- < \text{Na}^+ \approx \text{F}^-$) is reverse to the order of ion hydration radius (F^- (3.52 Å) $\approx$ Na^+ (3.58 Å) $<$ BF_4^- (4.4 Å)). In addition, the ion-wall distance of BF_4^- anions is quite close to the sum of the ion bare radius and carbon atom radius (e.g., $\text{BF}_4^- \sim 3.0$ Å, carbon ~ 0.7 Å), implying that BF_4^- ions should be dehydrated near the graphene surface. Our MD atomic cartoon for ion absorbing near the graphene surface also confirms this point (Figure 3.2b and Figure 3.2c).

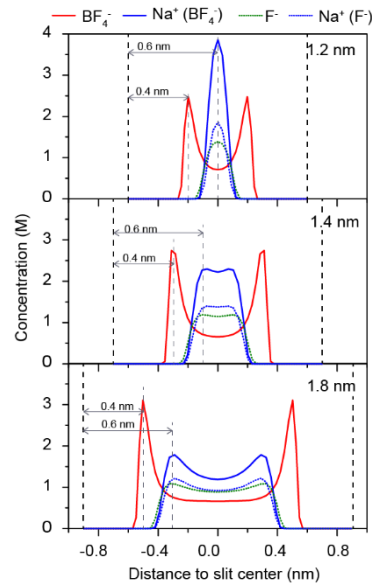


Figure 5.4 The local concentration of NaBF_4 and NaF electrolytes in a slit size of 1.2 nm, 1.4 nm, and 1.8 nm for the 12-layer slit model.

By integrating the ion local concentration across the slit region, we calculated the total number of anions or cations in the slit, Q_i (unit: mol/m) and the areal ion number density Q_{di} (unit: mol/m²) via dividing the Q_i by the graphene length (L_G). The linear dependence of Q_{di} on slit layers (N) can be observed (Figure 5.5c), which enables us to extrapolate the ion areal density in a 10000-layer slit system. Such a layer number $\sim 10,000$ is comparable to our membranes in

experiments (the thickness of 5.71 μm with a slit size of 0.48 nm). Figure 5.5d shows the areal ion density as a function of slit size, d , for $N_g = 10000$. We can observe a linear relationship for $d > 1.2$ nm. There are always more BF_4^- anions than Na^+ cations in the nanoslits, indicating the electroneutrality breakdown. In contrast, the number density of the F^- anions is almost equal to that of Na^+ cations in all slit sizes. The subsequently average ion concentration in the slit region agrees semi-quantitatively with NMR measurement (Figure 5.5d and Figure A1e). The average concentration of BF_4^- anions increases from ~ 0.8 to ~ 1.1 M when the slit size decreases from 2.0 nm to 1.2 nm while the concentration of Na^+ and F^- ions present a decreasing trend from ~ 0.8 to ~ 0.6 M. It validates the PB-LJ model for ion absorption in nanoslits of > 1.2 nm in thick membranes.

The average in-pore ion concentration in the 10000-layer slit system is nearly the same as the results of the 12-layer slit system from the PB-LJ model (Figure 5.5a and d), particularly for slit size of > 1.2 nm. But when the slit-layer N_g is smaller than 12, the in-pore ion concentration shows some obvious difference, particularly in the case of $1 < N_g < 6$ (Figure 5.5a). These results suggest that the increased thickness does not significantly affect ion-pore concentration for thick membranes where the membrane thickness is one order of magnitude larger than the slit size. But for thin membranes (membrane thickness is comparable to the slit size), the in-pore ion concentration sensitively depends on N_g . Our new model prediction in Fig. 5.4d is for $N_g = 12$. We expect similar results for thick membranes, which are also consistent with experimental results.

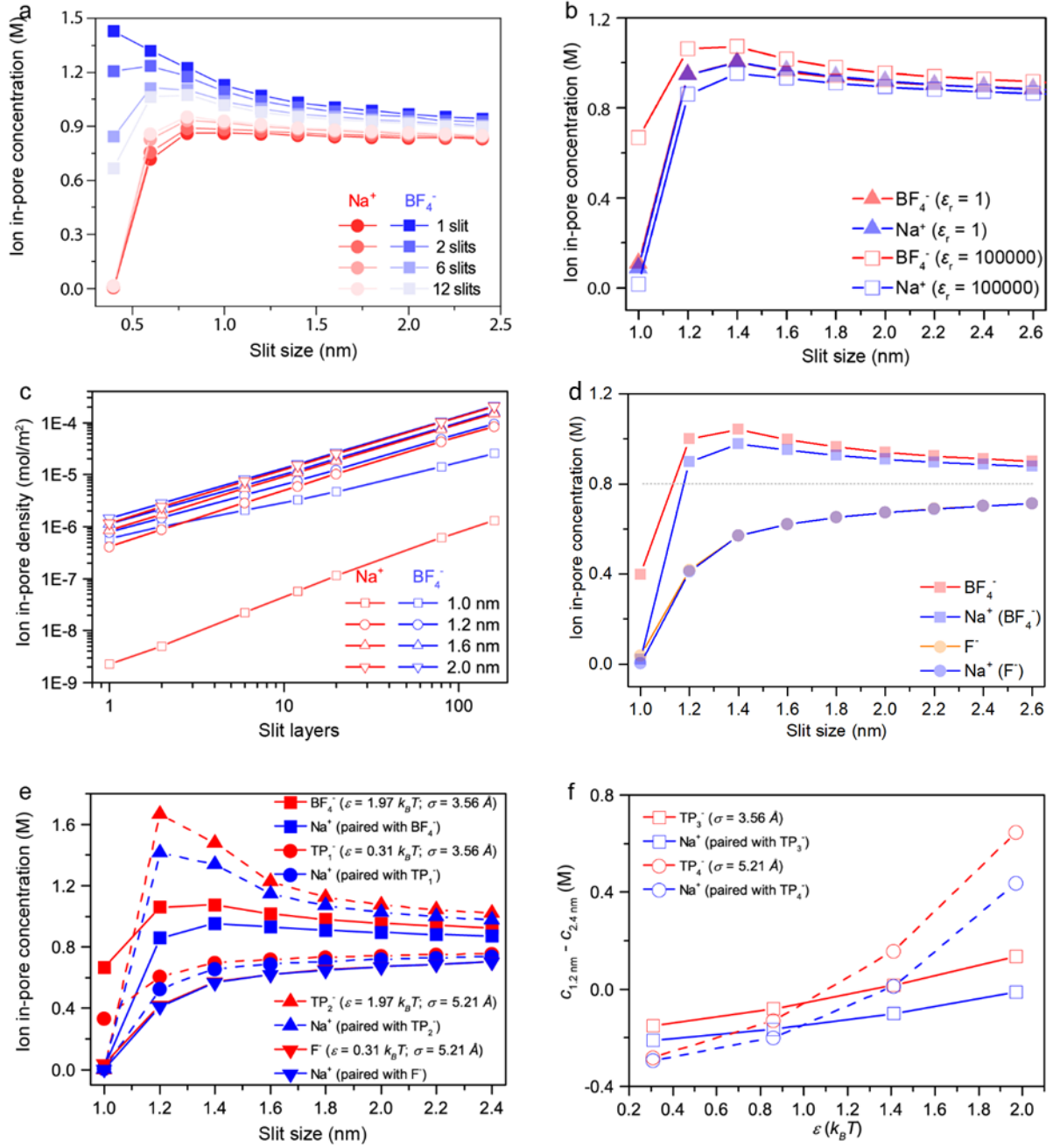


Figure 5.5 Physical origins discussion for ion accessibility in multi-layered nanoslits in graphene membranes. (a) The in-pore ion concentrations versus slit size for different slit layer number N_g (i.e., 1, 2, 6, and 12). **(b)** The in-pore ion concentration in the 12-layer slit model when the dielectric constant of graphene is 100000 and 1, respectively. **(c)** The in-pore ion areal density as a function of slit layers. **(d)** In-pore ion concentration as a function of slit size in 10000-layers slit model. **(e)** In-pore ion concentrations as a function of slit size for two transit phrases (TP_1^- and TP_2^-) and compared with $NaBF_4$ and NaF electrolytes. **(f)** The

concentration difference between 1.2 nm and 2.4 nm for transit phrases with varied interaction strength in the 12-layer slit model.

5.3.3 Physical origins of ion accessibility inside nanoslits

To interpret those observed phenomena, such as the electroneutrality breakdown, size-dependence, and the ion-species dependence of in-pore ion concentrations, some individual parameters in the PB-LJ model are manipulated to investigate their contributions. First, the relative dielectric constant of the graphene sheet is changed from 100000 (polarizable) to 1 (non-polarizable) to investigate the effect of the polarisation ability of the surface on in-pore ion concentrations (Figure 5.5b). It shows that when the surface is not polarizable, the concentration difference between BF_4^- anions and Na^+ cations disappears, suggesting that the screening effect arising from the surface plays a vital role in our observed electroneutrality breakdown.

Then, we investigate the influence of the non-electrostatic interaction between ions and the graphene surface. The ion-wall interaction energy (ion's PMF curve) is quantified via the two LJ potential parameters, i.e., the interaction strength (ε) and interaction equilibrium distance (σ_0). The BF_4^- anions have a stronger ε while a smaller σ_0 than the F^- ions (Table 5.1). Two transit phases via rematching the LJ potential parameters of BF_4^- ion and F^- ion are additionally stimulated. This is to investigate the influence of interaction distance and interaction strength separately on the in-pore ion concentration. The first transit phrase (denoted as TP_1) has the σ_0 value of BF_4^- ion and the ε value of F^- ion. Figure 5.5e shows that the in-pore ion concentration exhibits a similar trend as F^- ion where in-pore ion concentration is reduced when the slit size is decreased. The second phase (denoted as TP_2) has the σ_0 value of F^- ion and the ε value of BF_4^- ion. Its in-pore concentration exhibits a similar trend as BF_4^- ions with an enhanced

concentration at a smaller slit size. These results conclude that the ion-wall interaction strength plays a critical role to determine the variation of in-pore ion concentration in nanoconfinement.

The terms ‘ionophilic’ and ‘ionophobic’ are used recently to define the capacity level of extremely small nanopores to accommodate ions (or the ion accessibility). Inspired by the observed ion-specific effect, we focus on the effect of ion-wall interaction on the ion accessibility in nanopores. We varied the interaction strength ε with two fixed interaction distance σ_0 values. They are termed as TP₃ ($\sigma_0 = 3.56 \text{ \AA}$) and TP₄ ($\sigma_0 = 5.21 \text{ \AA}$). We calculated the difference of in-pore ion concentration between a large slit (2.4 nm) and a small slit (1.2 nm), $c_{1.2\text{nm}} - c_{2.4\text{nm}}$. A positive value represents feasible accessibility. Figure 5.5f shows that the calculated in-pore ion concentration using the PB-LJ model increases monotonously with ε . For TP₃ and TP₄, the accessibility transition points take place at 1.1 and 1.4 $k_B T$, respectively. A high ε leads to a feasible accessibility, which is reasonable to understand. The obtained semi-quantitative information could serve as a benchmark to classify the ion accessibility in confined pores. They could be useful for the selection of electrolyte ions in applications. Surprisingly, the larger ion-wall distance case (TP₃) needs a smaller ε value to yield feasible accessibility. This could be due to the location of the paired Na^+ cations. Such a phenomenon indicates the layering locations of anions and cations can also significantly influence the ion accessibility. The same location of anions and cations in nanoslits could further promote the ion density compared with the alternative layering of anions and cations.

5.4 Conclusion

In conclusion, the ion accessibility insides nanopores predicted by continuum models are compared with the NMR experiment results, including the in-pore ion density relation on pore size and the microstructure of electrolyte ions. For the slit size is larger than 1.2 nm, our new

theoretical model (in Chapter 3) could achieve a semi-quantitative agreement with experimental results. The oscillated ion distribution profile predicted by continuum models is consistent with NICSs signals of NMR results. Some physical origins of ion accessibility inside nanoslits are discussed. The polarisation effect of the graphene surface plays a vital role in the observed electroneutrality breakdown in nanoslits. Membrane thickness also significantly affects the in-pore ion concentration when the slit layer numbers are smaller than 12. Larger than this slit layer number, there is a minor effect from membrane thickness.

In addition, via varying the parameters that describe the non-electrostatic ion-wall interaction, we investigate how ion accessibility depends on the ion-wall interactions. We find that increasing the interaction energy strength ε will lead to a feasible ion accessibility in nanopores. The transition points have been determined. Interestingly, the electrolyte ion microstructure in nanoslits, i.e., the layering distribution of cations and anions, influences the transition point of ε . The overlapped cations and anions distribution benefits the in-pore ion density (accessibility) than the alternative layering of cations and anions. Our results should provide some valuable clues/benchmarks for the selection of electrolyte ions in nanopores electrode-based applications.

Chapter 6: Summary and outlook

This PhD work aims to develop nanoscience-based continuum models to describe quantitatively the microstructure of aqueous electrolytes in nanoconfinement. The ion-species and pore-size dependent microstructure of electrolytes is a result of multiple interplayed physical interactions (e.g., steric effect, hydration interaction, and non-electrostatic interaction). The literature review in Chapter 2 concludes that the effect of water molecules on the electrolyte microstructure requires particular attention. In contrast to the uniform dielectric background assumed in conventional continuum models, the microscopic structure of water molecules such as the dipole orientation and spatial arrangement is influenced by ions, surface, and neighbored water molecules, which in turn influence the microscopic ion distribution under nanoconfinement. A comprehensive investigation is required to obtain molecular-level insights. Based on them, new theoretical models for electrolyte microstructure can be developed.

6.1 Main findings

a) A two length-scale simulation framework was applied to involve the effect of water structure in continuum models, improving the description of the microstructure of electrolyte ions in uncharged nanoslits. The two simulation methods, the molecular dynamics (MD) simulation and continuum models, are combined in this PhD work. Via such a strategy, using 0.8 M NaBF₄, 0.8 M LiBF₄, and 0.8 M CsBF₄ as model electrolytes, we propose a new continuum model for the spatial distribution of aqueous electrolyte ion in nanoconfinement. We incorporated the PMF between ion and graphene that are calculated from MD simulation in the classic PB theory. The modified model can reproduce the layered density profile observed in the MD simulation semi-quantitatively. After that, we consider the nano-confined water distribution in the PB-PMF model via a new lattice-gas model. The excellent

quantitative agreement is achieved between the new model and MD simulation. The critical role of the solvent distribution structure at the nanoscale is demonstrated.

b) The atomistic analysis of interfacial water molecules on electric potential allows a refined EDL model for the electrified interface system. An atomistic system of two charged graphene sheets immersed in aqueous electrolytes (0.8 M NaBF₄ and 0.8M NaCl) was used as the model system. Our comprehensive atomistic analysis of the electric potential profiles reveals a vital role of water molecules that are modulated by the graphene surface. Based on these understanding, we propose a refined EDL model to describe the potential profiles and ion spatial distributions. Our model breaks the EDL at the charged interface into three regions: vacuum region, orientational dipoles region, and electrolyte ion region. The vacuum and orientational dipoles region have clear physical meaning. They replace the conventional Stern layer and eliminate some ambiguity of the widely adopted Stern layer model. Our model results of the surface potentials (including PZC) and microstructure of aqueous electrolytes agree with MD simulation results quite well.

c) The continuum modelling of ion accessibility inside the multi-layered slit in comparison to experimental results, allowing a validation of our new model and physical origins investigation for ion accessibility inside nanopores. The ion accessibility insides nanopores predicted by our continuum models are compared with the NMR experiment results, including the in-pore ion density scaling relation on pore size and the microstructure of electrolyte ions. Some physical origins of ion accessibility inside nanoslits are discussed. The polarisation effect of the graphene surface plays a vital role in the observed electroneutrality breakdown in nanoslits. Membrane thickness also significantly affects the in-pore ion

concentration when the slit numbers are smaller than 12. Larger than this slit number, there is a minor effect from membrane thickness.

Via approximating the non-electrostatic interaction between ion and graphene into the 12-6 LJ potential, the ion-graphene interaction was described mathematically by two parameters: interaction strength and interaction equilibrium distance. We find that increasing the interaction energy strength ϵ will lead to a feasible ion accessibility in nanopores. The locations of cations and anions would also influence the magnitude of in-pore density. The same location of cations and anions in nanoslit shows enhanced in-pore density than the alternative location of cations and anions in nanoslit.

6.2 Outlook

a) The extension of our new nanoscience-based continuum models to 2D or 3D systems and beyond graphene membrane. This PhD work focuses on the graphene-based systems. Since we do not make particular assumptions that are only valid for graphene membranes, we believe the developed models are readily extended to other 2D material membranes if the substrate-ions non-electrostatic interaction (i.e., PMF curve) and the water structure near the substrate can be updated based on the chosen materials. The extension of our continuum models to other nanoporous material systems and other non-aqueous electrolytes needs further investigation and is in our future work plan.

On the other hand, in this PhD work, nanoslits are used as a model system. Our new continuum models can produce the nanoconfined ion microstructures that are observed in atomistic simulations. In practical system, the nanoporous electrodes usually have a three-dimensional interconnected pore structure with varied pore sizes and geometries. Therefore, it is essential to extend the developed continuum models into higher geometric dimensions and nanoporous

structures with certain irregularities. The extended continuum models can be used to other porous structures in the widely used electrodes, such as the electrodes made of carbon particles. The model can be used to optimize electrode configurations (i.e., nanopores in particle, particle size, particle number, and inter-particle spaces) and selection of appropriate electrolytes to enhance energy density (either mass or volumetric energy density).

b) The extension of our new model to include a dynamic process. Our future work will also extend our current model to dynamics region, aiming to bridge the time scale gap between the nanoscale ion dynamics and the device/system dynamics that remains a huge challenge in our field. In this PhD work, we only investigate the ion equilibrium distributions either in a non-electrified nanoslit or electrified interface region. The dynamic ion transport processes, such as the electrolyte ion migration under cyclic charging in supercapacitors and the electrolyte diffusion in porous materials under concentration gradient, have not been considered in our developed model. Our model is developed under the framework of classic PB theory. The classic Poisson-Nernst-Planck (PNP) model is the extension of PB theory to incorporate the ion dynamics. The next step, therefore, is to extend our new model to include ion dynamics under the framework of the classic PNP theory.

c) Optimizing the practical performance of the electrochemical energy storage device. This thesis work shows that the enhanced water density will increase the local ion densities in nanoslit under equilibrium. Besides, the orientated water dipoles modulated by the graphene electrode surface dominate the electric potential in the electrified systems. The hydrophilic/hydrophobic property of materials can significantly affect the solvent density or orientations at the interface. In the future, it will be an interesting topic to utilize this property to manipulate the electrolyte spatial organizations and subsequently optimizing

electrochemical storage performance. It will be of practical importance to provide useful clues for selecting nanoporous materials beyond the pore size optimisation.

d) Optimizing the ion transport performance (e.g., flux, velocity, ion selectivity) via constructing a heterogeneous pore structure. Our work confirms the slit-size and ion-species dependent ion spatial densities in nanoconfinement. More importantly, we developed a new quantitative continuum model to describe these phenomena. Our model can be a powerful tool to predict and analyse ion dynamic transport performance in the different nanoporous structure at (pseudo-) steady state. It will be a promising topic to use our models to design a heterogeneous porous structure to optimize the ion transport performance for various engineering applications.

e) Un-resolved physical mechanisms for some ion storage performance in experiments. In Chapter 5, we compared our theoretical model prediction and experiments for ion storage in graphene membranes. Some clear discrepancy exists in small nanoslits ($d < 1.2$ nm). Our model results show dropped ion concentration in the extremely small nanoslits, which is opposite to experiment results. Since our MD simulations are carried out with the constant charge method, some physical factors are still not considered, such as the image force and superionic state, which may contribute to the discrepancy in nanoslits of smaller than 1.2 nm. In the future, the MD simulations with constant potential methods are desirable to investigate the effect of those neglected factors. More works (including atomistic simulation and theoretical models) should be carried out to uncover the physical mechanisms. The new discovery will advance our knowledge of ion storage in extreme nanoconfinement.

Appendix A: Experimental characterizations of aqueous electrolyte absorption in nanoporous graphene membranes

A.1 The structural parameters of the synthesised graphene membranes and the construction of the continuum models

Results in this section are provided by Dr. Diyan Liu. The multilayered graphene membranes (MGMs) with the interlayer spacing tuneable from 10 nm to sub-nanometre scale can be prepared through a soft wet chemical approach¹⁰⁵⁻¹⁰⁶. Using the same methods, five MGMs with sub-2nm pore size are fabricated. The measured membrane thickness and pore size are summarized in Table A1. All MGMs are cut into a rectangular across-shape (2 mm × 13 mm) in the NMR characterisation.

Since the nanopores in graphene membranes are mainly formed by the face-to-face graphene sheets, we use multilayered nanoslits to represent the porous graphene membranes. The pore size of each nanoslit is the same and kept as the measured pore size of the MGMs. To assemble the practical graphene, the layer number of multilayered nanoslits is expected to be around 10,000 and the across-area of each slit wall should be 2 mm × 13 mm. To directly simulation such a 3D system is very computationally expensive and thus, we simplified it into a 2D model (1D model is also OK) assuming that the across area of graphene wall plays a negligible role on ion adsorption density inside graphene membranes (i.e., the potential distinctive features of ion adsorption at pore entrance is negligible).

Here, we use a 2D model rather than a 1D model is for the ease of maintaining a constant potential throughout the multilayered graphene wall (in the 1D model, each graphene wall is discrete in the system). The slit-length is artificially set as 10 nm, which will be normalized in the calculation of the ion adsorption density. In previous work, the simplified 1D single-slit

model has been used to investigate the electroneutrality breakdown of aqueous NaBF₄ electrolytes inside activated porous carbons⁹¹. The underlying mechanism is ascribed to the polarization of carbons, which could balance the net-charges inside nanopores due to the unequal absorption of Na⁺ and BF₄⁻ ions. In our work, benefiting from the more uniform pore structure of graphene membranes, we try to investigate the thickness effect of multilayered graphene nanoslits on the unequal absorption of NaBF₄ electrolytes. Therefore, we constructed several continuum models with varied layer numbers (i.e., 1, 2, 6, 12, 20, 80, and 160). Then, via obtaining the relationship between layer-number and ion absorption density, the ion absorption density inside 10,000-layer multilayered slits will be derived/extracted and achieve a comparison with experimental results.

Table A2 Summary for the membrane thickness and pore size for the MGMs

Samples	Film thickness (μm)	Pore size (nm)
No.1	5.71	0.48
No.2	7.32	0.61
No.3	12.03	1.01
No.4	15.36	1.28
No.5	19.01	1.59

A.2 The structural parameters of the synthesised graphene membranes and the construction of the continuum models

The experimental data are summarized here for the convenience of comparison with the results of continuum models. Here are several features of electrolyte accessibility inside graphene membranes characterized by NMR. First, the nucleus independent chemical shift (NICS) signal is inversely proportional to the distance between the tested nucleus and aromatic domains (*i.e.*, the graphene wall in this work). Based on such a relationship, the extracted NICS show a varied

ion absorption distance to the graphene wall. Among Na^+ , BF_4^- , F^- , and PO_4^{3-} ions, they follow the order of $\text{BF}_4^- < \text{Na}^+ \approx \text{F}^- < \text{PO}_4^{3-}$ (Figure A1**Error! Reference source not found.**a-c). More information for the electrolyte ion spatial structure in nanoslits can be revealed by stacking the NMR spectra of anions and cations (Figure A1d). The minor overlapped NMR peaks of BF_4^- anions and Na^+ cations indicate an alternative layering of anions and cations for NaBF_4 electrolytes in nanopores (not shown here). In contrast, the nearly overlapped NMR peaks of F^- anions and Na^+ cations indicate a blurred boundary of cation and anion layers for NaF electrolyte (Figure A1d). The last key feature revealed by NMR is that the in-pore ion concentrations depend on ion-species and pore-sizes. The in-pore amounts of ions inside the graphene membrane are calculated by integrating the corresponding NMR resonance peaks. Figure A1e and Figure A1f show the scaling relation between the in-pore ion concentrations and slit size. BF_4^- anions present a continuous increase with the decrease of slit size, doubling from 1.2 M in 1.59 nm slit to 2.4 M in 0.48 nm slit. This is in stark contrast to the slightly varied concentration of the paired Na^+ cations and F^- , PO_4^{3-} , and Ac^- anions.

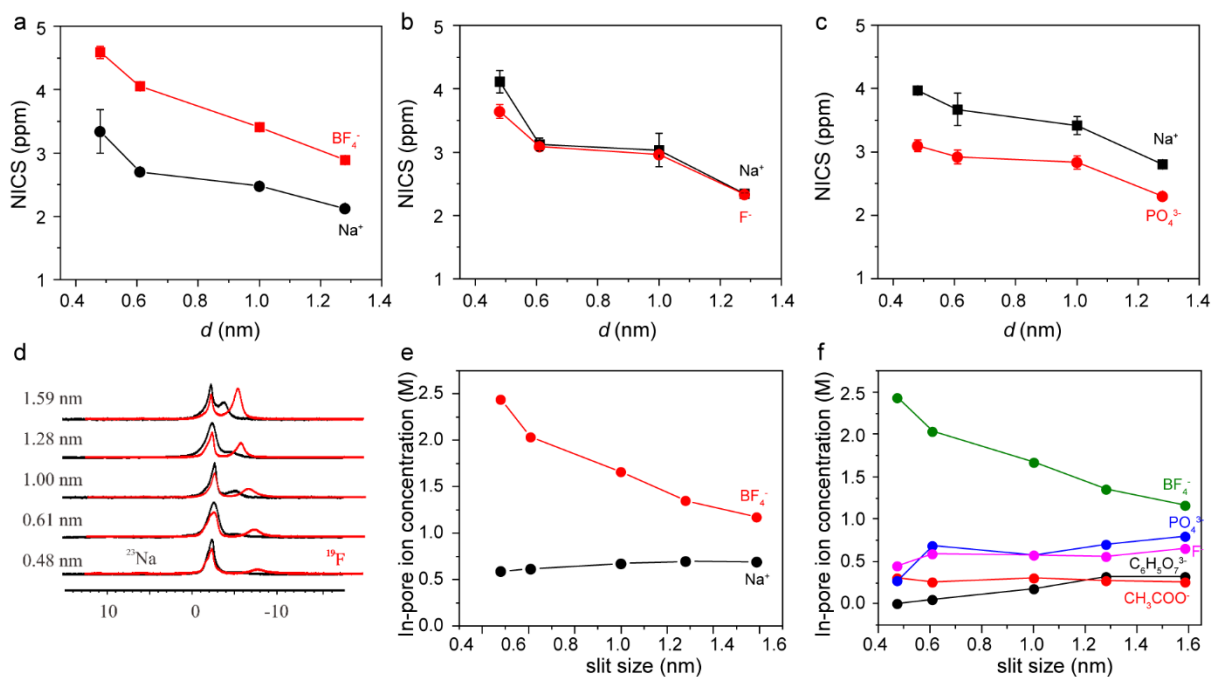


Figure A1. NMR results (Courtesy by Dr. Diyan Liu.) for various electrolytes confined in graphene membranes. (a-c) shows the NICS values extracted from NMR spectra in MGM with a slit size of 1 nm for NaBF_4 electrolyte (a), NaF electrolyte (b), and Na_3PO_4 electrolyte (c). (d) shows the stacked NMR spectra of cations and anions in NaF electrolyte. (e) shows the in-pore ion concentration of Na^+ and BF_4^- as a function of slit size. (f) The in-pore ion concentration of the other four anions as a function of slit size.

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