Molecular Dynamics Of Ionic Liquids In Nanoporous Electrodes

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MOLECULAR DYNAMICS OF IONIC LIQUIDS IN NANOPOROUS ELECTRODES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agriculture and Mechanical College
in partial fulfillment of the
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Doctor in Philosophy

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by

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ABSTRACT

Molecular dynamics simulations were performed to investigate structural, dynamical and electrical properties of ionic liquids (ILs) confined inside different nanoporous materials. These systems have potential uses in environmental and energy applications. The main goal is to understand how these IL properties are affected by a) characteristics of nanoporous materials such as chemical nature of the pore walls (e.g., carbon, titania), pore size and pore morphology, and b) characteristics of electrolyte, such as amount of IL inside the pores (pore loading) and concentration of organic solvent, in the case of mixtures of ILs with organic solvents. The results obtained in this work indicate that the properties of the nanoporous materials have a profound effect on the structure and dynamics of ILs. Formation of layers of ILs near the interface is observed in all systems studied, however density and thickness of these layers depends on variations in pore size, amount of IL inside the nanopores, density of electrical charges in the porous walls, pore morphology, the material of the pore walls, and concentration of solvent (in the case of mixtures of ILs with organic solvents). Our results indicate that variation in pore size, pore loading and pore morphology induce only slight changes in the local structure of liquid, but other variables such as variations in surface charge density and changing the material in the porous walls has a significant effect on the structure of the confined ions. In all systems the structure of ions far away from the pore walls closely resembles that of the bulk IL. We observed that the cations have faster dynamics than the anions in each system studied, except in very small slit graphitic pores. Dynamics of ions near the pore walls are slower as compared to those of the ions in the center regions of the pores. Varying pore loading of ions have pronounced effects on the dynamics of the ions in the center of the pore, with slight effect on the ions close to the pore surfaces. We observed that increases the density of electrical charges in the pore walls lead to an
important reduction in the mobility of the ions, especially in the direction perpendicular to the pore walls. The slow dynamics of ILs can be enhanced by increasing pore sizes, or by adding organic solvents such as acetonitrile
CHAPTER 1 INTRODUCTION AND REVIEW OF LITERATURE

1.1 Motivation

Search of efficient, clean and renewable energy resources has a high degree of precedence due to environmental concerns and depleting fossil fuels. Electrochemical devices such as batteries, electrochemical-double layer capacitors (EDLCs), dye-sensitized solar cells (DSSCs), Li-ion batteries, and fuel cells are capable of providing an alternative to fossil fuels, particularly in transportation and other industrial applications. Electrochemical double layer capacitors (EDLCs) have attracted extensive attention in recent years as an attractive technology for high power delivery applications. EDLCs are charge storage devices with structure similar to batteries, but differ from those in that it stores electrostatic charge using reversible adsorption of ions in a thin layer formed at the interface of a porous electrode and electrolyte. It typically consists of two electrodes immersed in an electrolyte and an ion-permeable separator as shown in Figure 1.1. The thin layer formed at the interface is known as electrochemical double layer (EDL) and it has a crucial role in deciding the performance of EDLCs. Reversible adsorption of ions at the electrode interface give EDLCs high power density and longer cycle life as compared to batteries and fuel cells, which make them suitable for applications that demand rapid storage and fast release of energy.[1, 2] However, limited capacitance of electrodes and small potential window of electrolytes give them moderate energy density which is typically lower (<10 Wh/kg) than that of batteries (200 Wh/kg).

Demand of batteries and EDLCs based on green electrolytes has increased in Electric Vehicles (EVs), Hybrid Electric Vehicles (HEVs), electric planes and many other industries. EDLCs and batteries can complement each other in these applications (Figure 1.2), with EDLCs supplying boosts of energy when needed, as well as helping to recover energy during braking.
Organic electrolytes such as acetonitrile and propylene carbonate are widely used in EDLCs due to their better performance and wide electrochemical stability window (>2 V), but they suffer from low ion conductivity and high toxic nature. On the other hand aqueous electrolytes such as sulfuric acid and potassium hydroxide show low decomposition voltage (ca.1 V) hence lower specific energy. One of the solutions to overcome this problem is to use solvent-free ionic liquids (ILs) as electrolytes, which provides wider electrochemical stability window, high thermal stability and low volatility as compared to traditional electrolytes.

DSSCs have attracted much attention recently for conversion of solar energy.[4-15] They are photovoltaic devices based on a semiconductor formed between a photo-sensitized anode and an electrolyte. However use of volatile organic solvents in DSSCs in one of the major concern regarding their safety and lifespan.[13] Traditional organic solvent used in DSSCs are explosive and evaporate with time. Hence, ILs are being considered by researchers as alternative electrolytes. ILs are potentially safe and ‘green’ electrolytes. Their low volatility and high thermal stability make them a suitable candidate for long term outdoor DSSC applications.
Figure 1.2. Ragone plot showing approximate relations of specific energy and specific power for several energy storage and conversion devices. Adapted from[2]

Ionic liquids (ILs) are salts comprised entirely of ions and are fluid at temperature as low as -96°C. [16] The bulky structure and loose packing of organic cations and organic or inorganic anions decreases the columbic interaction between ions hence preventing them from crystallization. [17] More than a million ILs can be synthesized by selecting proper combinations of cations and anions based on desired applications. However it is not possible to characterize all possible combinations of ILs experimentally, hence it is essential to have molecular level understanding of properties of ILs. [18] Molecular simulations are well suited to determine properties of ILs at molecular level hence giving a better understanding of these salts for their implementation in industries. Remarkable thermo dynamical properties, such as thermal, chemical, and electrochemical stability and non-volatile nature of ILs have gained them immense attention in recent years and also increased their demand in wide industrial applications such as catalysis, nuclear fuel processing, biomedical applications and as a potential electrolyte for energy applications in electrochemistry. [17-30] Various experiments have shown that ILs are better and safer than traditional volatile organic compounds such as methylene chloride, ethylene carbonate, acetonitrile etc. Hence use of ILs as a solvent and electrolyte in industrial applications
is a step toward decreasing the amount of volatile organic compounds in environment. ILs as solvent-free electrolytes exhibit high ionic conductivity and wider electrochemical stability window (up to 6 V) as compared to traditional organic electrolytes (up to 2 V). In electrochemistry applications, ILs typically interact with solid or porous surfaces hence it is important to study these solid/liquid interfaces. Furthermore, inserting ILs inside nanopores is one step in the synthesis of nanomaterials based on ILs. These materials were dubbed GUMBOS (Group of Uniform Materials Based on Organic Salts). These IL-based nanomaterials look promising in biomedical, analytical and optoelectronic applications. [31-34] Previous studies have shown that confinement breaks the uniform environment of bulk ILs causing interesting changes in properties which are of great importance for industrial applications such as electrochemistry, catalytic process and tribological systems.[35, 36] These heterogeneous systems are very complicated and require an in-depth molecular level understanding. Higher performance and safety can be achieved by advancing our understanding of pore morphology, surface characteristics, diffusion kinetics, behavior of ions in sub-nanometer pores and developing new electrode materials with high specific surface area (SSA), high capacitance and electrical conductivity.[35] The electrodes used in EDLCs are typically made of porous carbons, mainly activated carbons blended with carbon blacks or graphite, carbon aerogels, glassy carbons, ordered mesoporous carbons, and carbon nanotubes and their composites with conducting polymers because of their low cost, high surface area, high capacitance and long cycle life.[37-41]. Different semiconductor materials such as TiO2, ZnO and CuO are commonly used in DSSCs as anode due to their commercial availability and unique chemical, electrical, and photochemical properties [10, 11, 42-45]. Molecular simulations will be the key for studying the
molecular level properties of ILs at the interface of nanopores leading to advancement in designing tomorrow’s high performance devices.[46]

Previous simulation studies on ILs and molten salts confined inside ‘ideal’ nanopores of simple geometry i.e., slit-like [14, 47-56] and cylindrical.[56-60] have provided important insights suggesting that confinement affects the properties of ILs. Nevertheless, a fundamental understanding of variables such as surface charge density, surface corrugation in nanoporous materials, surface chemistry and presence of other organic solvents that have practical importance to electrochemical devices is still in its infancy.

In this work molecular dynamics simulations are performed to investigate the structural, dynamical and electrostatic properties of ionic liquids (ILs) confined inside different nanoporous materials. The simulations were performed using GROMACS MD package[61] in the canonical ensemble (constant NVT). This work focusses on the interfacial behavior and confinement effects of ILs inside carbon nanopores, namely slit-graphitic pores, activated carbons, carbon nanotubes, CMK-3 and rutile nanopores. The objective is to understand the effect of different variables such as pore size, pore loading, pore morphology, density of electrical charges in the pore walls, and concentration of solvents (in the case of mixtures of ILs with organic solvent), on the molecular-level properties of the confined ions. These properties are difficult to obtain through experiments. Such fundamental understanding is crucial to optimize the performance of alternative energy devices such as EDLCs and DSSCs, as the molecular level properties of the electrolytes influence the macroscopic properties such as capacitance and resistance. In this work, imidazolium-based ILs are studied as they possess unique features such as negligible vapor pressure, high chemical and thermal stability and high ionic conductivity which make them suitable for their application in electrochemical devices. [35] All the systems studied in this
work contain a nanoporous material in contact with electrolyte, mimicking a small section of an electrode immersed in the electrolyte. We study two different kinds of setups (Figure 1.3). In setup A (closed system), the electrolyte is placed inside the nanoporous material and their density is varied to study the effect of pore loading on properties of ILs. In setup B (open system), the nanoporous material is placed into a simulation box containing bulk electrolyte, ions are then allowed to fill the pores at the desired temperature. The results obtained in this work indicate that characteristics of electrode and electrolyte play a crucial role in determining the properties of ILs. Hence their optimization is important for the rational design of electrochemical devices with optimal properties.

![Figure 1.3. Schemes of simulation setups (A) closed system and (B) open system](image)

**Figure 1.3.** Schemes of simulation setups (A) closed system and (B) open system

**1.2 Outline of Dissertation**

The rest of this document is structured as follows.

**Chapter 2** is published work (N. N. Rajput, J. Monk, R. Singh and F. R. Hung. “On the Influence of Pore Size and Pore Loading on Structural and Dynamical Heterogeneities of an Ionic Liquid Confined in a Slit Nanopore”, *J. Phys. Chem. C* 2012, 116, 5169) in which we performed molecular dynamics simulations to study the effect of pore size and pore loadings on
the structural and dynamical properties of the IL [EMIM$^+$][TFMSI$^-$] confined inside slit-like graphitic pores. We studied four systems with pore size of 1.9, 2.5, 4.0, 5.2 nm and three pore loadings of $\rho = \rho_{\text{bulk}}, \rho = 0.8\rho_{\text{bulk}},$ and $\rho = 0.6\rho_{\text{bulk}}$.

**Chapter 3** is published work (N. N. Rajput, J. Monk and F. R. Hung. “Structure and Dynamics of an Ionic Liquid Confined Inside a Charged Slit Graphitic Nanopore”, *J. Phys. Chem. C* 2012, 116, 14504). In this work we performed MD simulations to study the structure and dynamics of the IL [EMIM$^+$][TFMSI$^-$] confined inside slit-like graphitic pore of width 5.2 nm, where the pore walls have different surface charge density. We compared two kinds of systems. In the first system we distributed equal and opposite charges on the walls of the graphitic slit nanopores. In the second system we considered the case where both top and bottom walls had charges of the same sign.

**Chapter 4** includes work on comparing the properties of the IL [BMIM$^+$][PF$_6^-$] confined inside different morphologies of carbon nanopores namely slit-graphitic pore, multi-walled carbon nanotubes and ordered mesoporous carbon CMK3. The results indicate that varying the pore morphologies and pore size have a profound influence on the structure and dynamics of the confined IL.

**Chapter 5** includes work in which we used rutile (110) surface as electrodes for its application in dye-sensitized solar cells. We studied two different models with pore size of 5.2 nm at 333 K. Model A (Open system) ions were placed outside the pore and then the pore was allowed to be filled completely at the desired temperature. In model B (closed system) we vary the density of ions inside the pore from $\rho = 0.6\rho_{\text{bulk}}$ to $\rho = \rho_{\text{bulk}}$. 
Chapter 6 includes work on a realistic model of coconut shell activated carbon and the IL [EMIM$^+$][TFMSI$^-$] using MD simulations. Activated carbon model used in this work incorporates true morphology of activated carbon. We studied three different pore size distributions for activated carbon model and compared the results qualitatively with ideal slit-like graphite pore model.

Chapter 7 includes work on the binary mixture of the IL [EMIM$^+$][TFMSI$^-$] with the organic solvent acetonitrile confined inside coconut shell activated carbon model. We aim at understanding the effect of molar concentration of IL and surface charge density of electrodes on the structure and dynamics of ions and acetonitrile molecules.

Chapter 8 includes conclusions and idea for future research.
2.1. Introduction

Ionic liquids (ILs) are salts composed of an organic cation and an organic or inorganic anion with melting point below 100°C.[62] Their unique properties such as great thermal, chemical, and electrochemical stability and their non-volatile, non-explosive and non-flammable nature have gained them immense attention in recent years.[62-64] Due to their numerous applications and unique properties, there is a rapidly growing scientific and commercial interest in ILs. In particular, understanding the behavior of ILs when confined inside materials with nm-sized pores is relevant for a number of applications. Several groups[20, 26, 65-78] have recently attempted to use ILs as alternative electrolytes in electrochemical double-layer capacitors (EDLCs),[3, 39, 46, 65, 78-85] motivated by their excellent thermal stability, non-volatility, high ion density and wide electrochemical window. ILs have also been proposed as alternative electrolytes in dye-sensitized solar cells (DSSCs)[65, 86, 87] for conversion of solar energy. ILs have also been used very recently in the development of ionogels,[88-92] a new class of hybrid materials involving a solid-like network formed by immobilizing ILs within nanoporous solids (e.g., carbon nanotubes, porous silicas, organic gelators, polyethylene oxide, cellulose, etc.); functional molecules can also be encapsulated into the IL phase. Ionogels have potential applications as solid electrolyte membranes in lithium batteries, fuel cells and DSSCs, in optics, catalysis and biocatalysis, drug delivery and sensing and biosensing.[88-92] The macroscopic performance of IL-based EDLCs and DSSCs, as well as the macroscopic properties of ionogels,

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are determined by the structural, dynamical and electrical properties of the IL confined inside the nanopores. Nevertheless, a fundamental understanding of the properties of ILs inside nanopores is still in its infancy. Such knowledge is crucial for the rational design of EDLCs, DSSCs and ionogels with optimal properties. Molecular simulations, in close interplay with experiments, are well positioned to provide such fundamental understanding and advance those technologies well beyond their current state of the art.

Several authors have reported simulation studies of ILs and molten salts adsorbed on surfaces such as rutile, graphite, quartz and sapphire.[47, 56, 93-101] A few simulation reports have been published on ILs confined inside nanopores with slit-like[14, 47-56, 102-115] and cylindrical[56-60, 114-116] geometries, as well as inside model CMK-3 nanoporous carbon materials.[117] These studies have provided important insights about the properties of ILs at the interfaces with solid walls and when confined inside pores of simple geometries. A number of these simulation studies have considered the presence of charges in the pore walls, and their effects on the properties of the electric double layer and the capacitance. Some of these simulations[52-57, 103-107, 110, 111] suggest that the electrode capacitance attains maxima at certain specific conditions of pore size, pore geometry, surface charge density and electrode potential. These simulation and theoretical studies also supported and provided rational explanations to the experimental findings that the specific (or area-normalized) capacitance of nanopores filled with organic electrolytes or ILs increased anomalously as the pore size decreased[75, 76, 118-120] (however, a recent experimental study[121] reports a relatively constant specific capacitance for the electrolyte (C$_2$H$_5$)$_4$NBF$_4$/acetonitrile inside carbons with pore sizes ranging between 0.7 and 15 nm). Furthermore, very recent simulation and theoretical
studies[103-105] suggest that the specific capacitance has a decaying oscillatory behavior as the pore size increases.

In two recent papers,[60, 112] we studied the structural and dynamical properties of [BMIM$^+$][PF$_6^-$] confined inside MWCNTs and slit graphitic pores at several temperatures. The structural properties of an IL confined inside a nanoporous electrode affect the macroscopic capacitance of an EDLC; and the dynamical properties of the confined IL is one of the factors that determines the macroscopic electrical resistance in these electrochemical devices. Results from these studies suggest that the local liquid structure and the local dynamics of the confined cations and anions are very complex and heterogeneous, and depend strongly on the distance of the ions to the pore walls. In the present study we further explore the effect of variations of pore size and pore loading (i.e., the amount of IL inside the nanopores as compared to the density of the IL in the bulk at the same temperature) on these structural and dynamical heterogeneities. For example, in an experimental setup, the amount of IL inside a nanoporous material could vary depending on variables such as temperature, pressure and the nature of the porous material (for example, it might be difficult to completely fill a material with very tortuous pores; also, the strength of interactions between the pore walls and the ions of the IL could also affect the amount of IL inside the nanopores). For the present study we have performed molecular dynamics (MD) simulations for the IL [EMIM$^+$][TFMSI$^-$] confined inside an uncharged slit-like graphite pore. This IL has been used in several experimental studies involving EDLC applications,[26, 67, 68, 75, 78] and a very recent simulation study involving this IL inside slit pores focused on the effect of pore size on the capacitance.[104] The rest of this document is structured as follows. Section 2.2 contains details about the computational models and methods
used in this study. The main results and discussion from this study are presented in Section 2.3, and concluding remarks are included in Section 2.4.

2.2. Computational Details

MD simulations were performed to study the properties of the IL [EMIM$^+$][TFMSI$^-$] confined inside a slit-like graphitic pore at 333 K (Fig. 2.1). The simulations were performed using the GROMACS MD package [61] version 4.0.5 in the canonical ensemble (constant $NVT$). The force field parameters for the cations [EMIM$^+$] and anions [TFMSI$^-$] were taken from Kelkar and Maginn. [122] These force field parameters reproduced adequately the experimental density, heat of vaporization and dynamical properties (viscosities, diffusivities) of the bulk IL. [122-124]

![Figure 2.1. Schematic representation of the ions in the IL [EMIM$^+$][TFMSI$^-$].](image)

The slit graphitic nanopore consisted of two carbon walls separated by a pore width $H$ (Fig. 2.4). Each pore wall was modeled as three sheets of graphene separated by a distance $\Delta=0.335$ nm and fixed in space. The carbon atoms in the graphene sheets were modeled as Lennard-Jones particles corresponding to sp$^2$ carbon atoms with $\epsilon_c/k = 28.0$ K and $\sigma_c = 0.340$ nm; the positions of these carbon atoms are kept fixed throughout our simulations. We only considered the case of uncharged pore walls in this study. This model system is a simple representation of a slit-shaped nanopore in an electrode, which is in contact with an IL electrolyte. All systems contained equal
number of cations and anions with a charge of +1 and -1 respectively, so that the net charge of the system is zero.

The improved velocity-rescaling algorithm recently proposed by Parrinello et al.[125, 126] was used to mimic weak coupling at different temperatures with a time constant of 0.1 ps. Lennard-Jones interactions were truncated at the cutoff distance of 1.0 nm, and the Particle-Mesh Ewald (PME) method[127] was used to handle long range electrostatic interactions with a cutoff of 1.2 nm and a grid spacing of 0.1 nm. Periodic boundary conditions were applied in all three directions. To avoid artificial influence from periodic images, the slit pore filled with IL was kept in the center of an orthorhombic box with vacuum on both sides separating it from the next periodic image in Z direction. The total length of the simulation box in the Z direction was 10 nm, which was large enough to avoid any interaction between the adsorbed ions and its nearest periodic image in that direction. The two sides of the box were equal to the X and Y dimensions of the graphene sheets. The initial atomic positions of the [EMIM]$^+$ and [TFMSI]$^-$ ions were generated using PRODRG.[128]

Simulations were started from an initial configuration in which a given amount of cations and anions were placed in an arbitrary lattice structure inside the slit graphitic nanopore. To relax strained contacts in the initial configuration, the systems were energy-minimized twice, first using steepest descent and then using conjugated-gradient energy minimization schemes. All the systems were then melted to 600 K for 1 ns and subsequently annealed from 600 to 333 K in three steps for 2 ns. Afterwards, a 50-ns MD simulation run with an integration time step of 0.5 fs was performed at a temperature of 333 K to equilibrate and sample properties of interest. This simulation time is long enough to adequately sample the Fickian (diffusive) regime of all systems (see, e.g., the mean squared displacement (MSD) results shown in Figure 2.8). This
simulation time is also long enough to decorrelate the rotational motion of the cations (Figure 2.7). After finishing this first production run, we took the final configuration of our system and repeated the above steps (melting, annealing, equilibration, and averaging) at least one additional time. Our reported results were averaged over at least two independent realizations of the same system.

In our simulations we considered four different pore sizes $H = 1.9$, 2.5, 4.0, and 5.2 nm. The pore width $H$ was defined as the minimum surface-to-surface distance between the two graphitic walls in the $z$ direction. We initially included a suitable number of ion pairs inside the graphitic slit pores, such that all systems have a density of $\sim$1.56 g cm$^{-3}$, which is similar to the bulk density of the IL at 333 K. The effect of pore loading in our systems was studied by varying the amount of IL inside the pores to 80% and 60% of the IL bulk density. To ensure that our results were not affected by finite size effects in the $x$ and $y$ directions, for each pore size we considered graphite sheets of different areas. For example, for a pore size of 1.9 nm, two systems were considered, $5.289 \times 5.577 \times 10$ nm$^3$, and $8.8 \times 8.58 \times 10$ nm$^3$. Similarly, for a pore size of 2.5 and 5.2 nm two systems of $6.83 \times 6.45 \times 10$ nm$^3$ and $8.68 \times 8.28 \times 10$ nm$^3$ were considered. For these area sizes considered, we observed negligible differences in the structural and dynamical properties of the confined IL.

2.3. Results and Discussion

2.3.1. Structural Properties

In Figure 2.2 we present the number density profile $\rho(z)$ in molecules nm$^{-3}$ for the cations and anions confined inside slit-like graphitic nanopores of different widths $H$ at 333 K. In all cases the amount of IL inside the nanopores is such that the confined IL has a density similar to
that of the bulk IL at the same temperature ($\rho = \rho_{\text{bulk}}$). Layering effects are noticeable for all pore sizes, with the number of peaks increasing as the pore size increases. For larger pore sizes, the local density profiles near the walls exhibit pronounced oscillations, but a uniform density distribution is observed in the center of the pore starting at distances of about 1.5 nm from the pore walls (Fig. 2.2).

**Figure 2.2** Number density profiles $\rho(z)$ of [EMIM$^+\,$] (blue, solid lines) and [TFMSI$^-\,$] (red, dashed lines) confined in slit graphitic nanopores of different widths ($H = 1.9, 2.5, 4.0, 5.2$ nm) at 333 K. In all cases $\rho = \rho_{\text{bulk}}$. The vertical dotted lines indicate how the confined ions were divided into different layers/regions for further study.

The effect of variations in pore loading in the local density profiles $\rho(z)$ of the IL ions confined inside slit-like graphitic pores of different widths is shown in Figure 2.3. It is observed that a reduction in pore loading causes a decrease in the local density of ions in the layers close to the pore walls, as well as in the center regions of the pores. For smaller pore sizes the reduction in local density is larger in the layers close to the pore walls. In contrast, for larger pore sizes, the drop in local density is larger in the center regions of the pore (Fig. 2.3). Reduction in the total
amount of IL inside a slit pore of width $H = 5.2$ nm makes the ion to cluster together, which leads to the formation of regions of low local density (i.e., cavities without ILs) that might be partially depleted of IL at pore loadings approaching 60% of $\rho_{\text{bulk}}$ (Figure 2.4). At $\rho = 0.8\rho_{\text{bulk}}$, the low-density and high-density regions in the center of the pore have densities of 1.21 and 2.08 molecules/nm$^3$; at $\rho = 0.6\rho_{\text{bulk}}$, the corresponding densities are 0.90 and 1.89 molecules/nm$^3$. These results agree with our previous findings for varying amounts of ILs inside carbon nanopores of different geometries.[60, 117] These result also indicates that at low pore loadings, the density profiles measured along the $Z$ direction will depend strongly on the values of the $x$ and $y$ coordinates, and therefore may differ significantly from the density profiles averaged over the whole $z$ direction (e.g., Fig. 2.3).

To further investigate the local structure of the IL confined in slit pores, we computed the cation-cation, anion-anion and cation-anion radial distribution functions $g(r)$. First, for all pore sizes considered, we computed the $g(r)$ in 3-D considering all the confined ions inside the slit nanopores, and compared those against similar 3-D $g(r)$ computed for the simulated bulk IL at the same temperature (333 K). These results (see Fig. B-1 and B-2, Appendix B) indicate that variations in pore size lead to increases in the height of the peaks of $g(r)$ as compared to those of the bulk IL. Some of the peaks in the overall cation-cation $g(r)$ are slightly displaced to different values of $r$ with reductions in pore size, but new peaks in $g(r)$ are not observed for the confined IL as compared to that of the bulk IL. Therefore, variations in pore size does not cause appreciable changes in the overall, average 3-D liquid structure of the IL confined inside the slit nanopores, i.e., in average the overall 3-D liquid structure is similar to that of the bulk IL at the same temperature.
Figure 2.3. Number density profiles $\rho(z)$ of cations (left panel) and anions (right panel) for $[\text{EMIM}^+][\text{TFMSI}^-]$ at 333 K confined in slit graphitic pores of different widths: (a) $H = 1.9$ nm, (b) $H = 2.5$ nm, and (c) $H = 5.2$ nm, with different pore loadings. The vertical dotted lines indicate how the confined ions were divided into different layers/regions for further study.

Nevertheless, in our previous MD study for $[\text{BMIM}^+][\text{PF}_6^-]$ inside a slit graphitic nanopore of $H = 5.4$ nm,[112] we computed the $g(r)$ for the ions in the different layers/regions of the pore, and we found that the structure of $[\text{BMIM}^+][\text{PF}_6^-]$ in the center of the pore is similar to that observed for the bulk IL at the same temperature. However, significant structural differences were observed between the ions near the pore walls and those in the center of the pore. Those results were obtained for a pore loading such that the confined IL has a density similar to that of
the bulk IL at the same temperature ($\rho = \rho_{\text{bulk}}$). In Figure 2.5 we show the effect of varying pore loadings on the local structure of the different layers/regions of the IL confined inside a slit graphitic nanopore of width $H = 5.2$ nm. From the density profile (Figs. 2.2 and 2.3), the confined ions were divided into three different layers/regions: the first layers (closest to the pore walls), the second layers and the center region. The results shown in Fig. 2.5 suggest that a decrease in pore loading leads to increases in the height of the peaks of $g(r)$ in the second layer and in the center region; the increases are not very marked in the $g(r)$ of the first layers. These effects are due to significant decreases in the density of ions in the second layers and center of the pore as the pore loading is reduced. These reductions in density can be observed in Figs. 2.2-2.4, and also in Figure 2.6, where snapshots of the different layers of IL inside a slit pore of $H = 5.2$ nm at different pore loadings are presented. Variations in pore loading lead to formation of regions that are partially depleted of IL in the second layer and center regions, but do not produce very large changes in the IL in the first layers.

**Figure 2.4.** Representative simulation snapshots of [EMIM$^+$][TFMSI$^-$] at 333 K confined in a slit graphitic nanopore of width $H = 5.2$ nm and different pore loadings: (a) $\rho = \rho_{\text{bulk}}$, (b) $\rho = 0.8 \rho_{\text{bulk}}$, and (c) $\rho = 0.6 \rho_{\text{bulk}}$. Cations and anions are depicted in green and red. In (c), the horizontal dashed black lines indicate how ions were divided according to their distance to the pore walls into first layers, second layers and center regions. The vertical dashed black line indicates a further division of the center regions into a ‘dense’ region (left) and a ‘vapor’ region (right) (see Figure 2.10 and text for further details).
Figure 2.5. Radial distribution functions $g(r)$ of (a) cation-cation, (b) cation-anion and (c) anion-anion for the different layers of [EMIM+] [TFMSI-] confined inside a slit pore of $H = 5.2$ nm and different pore loadings at 333 K. The same $g(r)$ for the bulk IL are also shown.

In Fig. 2.5, if we compare the positions of the peaks of $g(r)$ between the bulk and the confined ions in the different layers/regions, we conclude that the structure of [EMIM$^+$][TFMSI$^-$] in the second layer and center region within the slit pore is not very different from the structure of the bulk IL. Furthermore, the structure of the confined IL in the first layer differs only slightly from that of the bulk IL (more correlations in $g(r)$ are present at longer distances, and the first peaks in the cation-cation and anion-anion $g(r)$ are observed at slightly shorter distances in the first layers as compared to the bulk). In particular, in the cation-anion $g(r)$, the first peak is somewhat smaller than the second peak for the bulk IL, but for the confined IL, as the pore loading decreases, the first peak becomes larger than the second peak. We also compared the $g(r)$ of the
ions in the different layers/regions inside two slit pores, \( H = 5.2 \, \text{nm} \) and \( 2.5 \, \text{nm} \), when the confined IL has a density similar to that of the bulk IL at the same temperature (\( \rho = \rho_{\text{bulk}} \)).

Figure 2.6. Representative simulation snapshots of the first layers (top), second layers (center) and center regions (bottom) of \([\text{EMIM}^+][\text{TFMSI}^-]\) inside a slit pore, \( H = 5.2 \, \text{nm} \) at different pore loadings: (a) \( \rho = \rho_{\text{bulk}} \), (b) \( \rho = 0.8 \, \rho_{\text{bulk}} \), and (c) \( \rho = 0.6 \, \rho_{\text{bulk}} \). Cations and anions are depicted in green and red.

The ions inside a pore of \( H = 2.5 \, \text{nm} \) were divided into two different layers based on the data shown in Fig. 2.2. These results (see Fig. B-3, Appendix B) suggest that, apart to increases in the height of the peaks, varying the pore size between \( H = 5.2 \, \text{nm} \) and \( 2.5 \, \text{nm} \) while keeping the pore loading constant does not lead to drastic changes in the liquid structure of the IL within the different layers/regions; the liquid structure resembles closely that of the bulk IL. The slight
changes in structure described above for confined [EMIM\textsuperscript{+}][TFMSI\textsuperscript{-}] contrast to what we observed in our previous study for [BMIM\textsuperscript{+}][PF\textsubscript{6}\textsuperscript{-}] inside a slit pore,[112] where the IL in the center of the pore had a liquid structure similar to that of the bulk IL, but the first and second layers had structures that were markedly different from that of the bulk IL. Therefore, changes in liquid structure upon confinement in slit-like nanopores seem to depend strongly on the specific IL.

In our simulations we also monitored the orientation of the ions inside the slit graphitic nanopores. These results (not shown for brevity) indicate that the imidazolium ring of the cations closest to the pore walls remain parallel to the surfaces; similarly, the CJ-CJ vector of the anions (Fig. 2.1) closest to the surfaces tend to lie parallel to the pore walls. More variations in the average orientations are observed as the ions get farther from the pore walls. These results agree with previous simulation studies involving confined imidazolium ILs.[14, 50, 60, 112, 117] Variations in pore size do not induce significant changes in the trends described above. When pore loading is varied, no significant changes were observed in the orientations of the cations; however, smaller pore loadings cause the anions closest to the pore walls to show more variations in their orientations (see Fig. B-4, Appendix B).

2.3.2. Dynamical Properties

This section presents results for single particle dynamics such as mean squared displacements (MSD), rotational autocorrelation functions, self-part of the van Hove correlation functions, and incoherent intermediate scattering functions. Studying translational dynamics is important for fundamental understanding of mass transfer, conductivity, interfacial and mixing behavior and rheology of liquids. In addition, the dynamics of ions inside nanopores is one of the factors that determine the electrical resistance in devices such as EDLCs. In Figure 2.7 we
present the parallel ($x$ and $y$) components of the mean squared displacements (MSD) for [EMIM$^+$][TFMSI$^-$] confined inside slit graphitic nanopores of width 1.9, 2.5, and 5.2 nm and for the bulk liquid at 333 K. In all cases, the density of the confined IL is similar to the bulk density of the simulated bulk IL. These results indicate that the bulk IL have the fastest dynamics, and the mobility of the confined ions increases monotonically with increasing pore size from 1.9 nm to 5.2 nm. For this last pore size, the cations exhibit similar MSD as the bulk cations, but the confined anions still move slower than the bulk anions. In all cases, the cations exhibit faster dynamics than the anions, as observed in previous studies involving ILs with imidazolium cations.[60, 112, 117, 129-133] The differences in the dynamics of cations and anions become smaller as pore size is reduced. As expected, the MSD component of the ions in the parallel ($x$ and $y$) directions is larger than the $z$-component of the MSD (data not shown for brevity). In Figure 2.7 we also present single-particle time correlation functions for the reorientation of the cations around an axis perpendicular to the imidazolium ring (Fig. 2.1). This function decorrelated in less than 500 ps for the bulk cations; longer times were needed for decorrelation as the pore sizes become smaller.

The parallel components of the MSD as a function of time in log-log scale for [EMIM$^+$][TFMSI$^-$] confined in slit graphitic nanopores of widths $H = 5.2$ nm and 2.5 nm are shown in Figure 2.8. The density of the confined IL is similar to that of the bulk IL at the same temperature, 333 K. As described above, the ions within a pore of $H = 5.2$ nm were split into three different layers/regions based on the density profile (Fig. 2.2); likewise, the IL inside a pore of $H = 2.5$ nm were divided into two different layers based on the data shown in Fig. 2.2.
Figure 2.7. (a) Parallel (x and y) components of the mean squared displacements (MSD) of [EMIM⁺][TFMSI⁻] confined inside slit graphitic nanopores of width 1.9, 2.5, and 5.2 nm and for the bulk liquid at 333 K, and (b) single-particle time correlation function for the reorientation of the cations around an axis perpendicular to the imidazolium ring (see Fig. 2.1) for the same systems. In all cases, \( \rho = \rho_{\text{bulk}} \).

The MSD of the ions in these layers/regions was compared to that of the bulk IL. As expected, three regimes are observed in the MSDs reported in Fig. 2.8: ballistic at early times when the ions have not interacted much with their neighbors (MSD \( \propto t^2 \)); sub-diffusive at intermediate times where ions rattle inside a cage formed by their neighbors (MSD \( \propto t^{1/2} \)); and when the ions escape from these cages, they reach the diffusive or Fickian regime at larger times (MSD \( \propto t \)).

For \( H = 5.2 \) nm, the dynamics of cations and anions in the first layers closest to the surface are slower as compared to the dynamics of the ions in the center of the pore, which in turn have similar mobility as the bulk IL. These trends agree with what we observed in our previous study\cite{112} for [BMIM⁺][PF₆⁻], but in this latter case the difference in dynamics between the different layers of IL were more marked than in the case of [EMIM⁺][TFMSI⁻]. Likewise, for \( H = 2.5 \) nm, the ions in the first layers have slower dynamics than those in the second layers, which in turn move slower than the bulk ions. Therefore, the MSD depends on the distance of the ions
from the pore walls. The overall self-diffusion coefficient of the IL confined inside a slit pore size of 5.2 nm is ~5.0E-7 and 2.7E-7 cm² s⁻¹ for [EMIM⁺] and [TFMSI⁻] respectively. In comparison, experimental diffusion coefficients for cations and anions at the same temperature are 13.7E-7 and 9.0E-7 cm² s⁻¹, respectively.[134, 135] Similar trends were observed for the other pore sizes considered in this study at a pore loading such that \( \rho = \rho_{\text{bulk}}. \)

The effect of pore loading on the parallel component of the MSDs of the confined cations in the different regions of a slit pore of width \( H = 5.2 \) nm is studied in Figure 2.9. In analogy to what we observed in Figs. 2.7-2.8, the cations in the center of pore exhibit the fastest dynamics, whereas the cations close to pore walls move the slowest. Slight differences in dynamics are observed for the cations in the first and second layers as the pore loading varies. In contrast, large variations in the dynamics of the cations are observed in the center of the pore, which are related to the important variations in densities that take place as pore loading decreases (Figs. 2.3, 2.4 and 2.6). Overall, the fastest dynamics are observed when \( \rho = 0.8 \rho_{\text{bulk}}, \) followed by \( \rho = \rho_{\text{bulk}} \) and \( \rho = 0.6 \rho_{\text{bulk}}. \) These trends are consistent with results reported in our previous studies for different ILs inside carbon nanotubes[60] and CMK-3 carbons.[117] Interestingly, the results shown in Fig. 2.9c suggest that when \( \rho = 0.8 \rho_{\text{bulk}}, \) the cations in the center of the pore seem to have significantly high MSDs, even larger than those observed in a bulk IL. Such a behavior might be induced by the local heterogeneities (regions of high and low density) observed at lower pore loadings.

We have looked in more detail at the MSD of the cations and anions in the system \( H = 5.2 \) nm, \( \rho = 0.6 \rho_{\text{bulk}}. \) For this particular system, in addition to dividing the ions according to their distance to the pore walls into first layers, second layers and center regions, we further divided the ions in the center regions of the pore into two regions, a ‘liquid’ side and a ‘vacuum’ side, as
depicted in Fig. 2.4c. We further analyzed the parallel component of the MSD of the ions in the liquid and vacuum side, and compared those against similar results observed for the first and second layers of ions, as well as for a bulk IL.

**Figure 2.8.** Log-log scale plot of the parallel (x and y) components of the MSDs of [EMIM$^+$] (left) and [TFMSI$^-$] (right) confined inside slit graphitic nanopores of $H = 5.2$ nm (top) and $H = 2.5$ nm (bottom). Data are presented for the ions based on their distance to the pore walls, and compared against the MSD of the bulk ions at the same temperature (333 K). In all cases, $\rho = \rho_{\text{bulk}}$. 
Figure 2.9. Effect of pore loading on the parallel component of the MSD of cations in the different layers/regions within a slit pore of $H = 5.2$ nm. (a) First layers, (b) second layers, and (c) center region. In (c), the parallel component of the MSD of all confined cations at different pore loadings (dashed lines) and the MSD of the cations in the bulk IL (purple continuous line) are also shown.

Figure 2.10. Parallel component of the MSD of cations (left) and anions (right) in the different layers/regions within a slit pore of $H = 5.2$ nm and a pore loading $\rho = 0.6 \rho_{\text{bulk}}$. In addition to the division of ions according to their distance to the pore walls into first layers, second layers and center regions, we further divided the ions in the center regions of the pore into two regions, a ‘liquid’ side and a ‘vacuum’ side (as depicted in Fig. 2.4c). MSD of ions in the bulk are also presented.

Further insights on dynamical heterogeneities can be obtained by studying the time dependence of the self-part of the van Hove correlation function $G_s(r,t)$ of the ions:[136, 137]

$$G_s(r,t) = \frac{1}{N} \sum_{i=1}^{N} \delta[r + r_i(t) - r_i(0)] >$$

(1)
The space Fourier transform of \( G_s(r,t) \), the incoherent or self-intermediate scattering function, \( F_s(q,t) \), can be measured experimentally, for example using inelastic neutron scattering:

\[
F_s(q, t) = \langle \frac{1}{N} \sum_{i=1}^{N} \exp(iq[r_i(t) - r_i(0)]) \rangle
\]  

\[ (2) \]

\( G_s(r,t) \) gives a detailed description of the motion of particle in a fluid, and is defined as the probability of finding a particle \( i \) in a region \( dr \) around a point \( r \) at time \( t \), provided that particle \( i \) was at the origin (0) at \( t = 0 \) at a particular temperature.\[136, 137\] In Figure 2.11 we show \( G_s(r,t) \) for the cations and anions in the different layers of fluid inside two slit graphitic pores, \( H = 2.5 \) and 5.2 nm at three different simulation times and a pore loading such that \( \rho = \rho_{\text{bulk}} \). These results are compared against \( G_s(r,t) \) for the bulk IL at the same temperature. At short times, \( t = 0.2 \) ps (such that the ions are in the ballistic regime, Figure 2.8), all \( G_s(r,t) \) decays to zero at a very short distance of about 0.15 nm for the cations (slightly less for the anions). \( G_s(r,t) \) for all ions in the different regions of the two pores and in the bulk are very similar, suggesting that at this short simulation time, the dynamics are very similar for the cations or anions independently of pore size and distance to the pore walls. However, at \( t = 100 \) ps (where all ions are in the sub-diffusive regime, Figure 2.8), the \( G_s(r,t) \) show different behaviors depending on the pore size and the distance of the ions from the pore walls. For \( H = 5.2 \) nm, the \( G_s(r,t) \) functions of cations in the first layers, second layers and the center region peak at 0.1, 0.15 and 0.21 nm respectively, but for anions all peaks are localized at approximately 0.1 nm for all three layers. Similar trends are observed for \( H = 2.5 \) nm. These trends indicate that at this particular time, the dynamics of the cations show more dependence on distance from the walls as compared to the anions. All \( G_s(r,t) \) functions decay to zero within 0.7 nm, suggesting that the particles are still inside the cage formed by neighboring ions. As observed in our previous study,\[112\] \( G_s(r,t) \) for the ions in the first layers (closest to the pore walls) have their peaks and decay to zero at shorter distances as
compared to the $G_s(r,t)$ of the ions in the second layers and in the center regions. At $t = 100$ ps, when comparing the $G_s(r,t)$ distributions for the cations in first layers at the different pore sizes, it is observed that $G_s(r,t)$ become wider as the pore size decreases; similar trends are observed for the cations in the second layers. These effects are less pronounced when comparing $G_s(r,t)$ of the anions in the first layers and second layers for the two different pore sizes considered. These observations suggest that, at this particular time, the ions in the first and second layers inside a pore of $H = 5.2$ nm move slower than the ions in the same layers inside a pore of $H = 2.5$ nm. However, at longer times, 20 ns (when all ions are in the diffusive regime, see Figure 2.8), the $G_s(r,t)$ curves for the ions in the first and second layers inside a pore of $H = 2.5$ nm reach their peaks and decay to zero at much shorter distances than those observed for the ions in the first and second layers inside a pore of $H = 5.2$ nm. This observation indicates that, in the diffusive regime, the ions in the first and second layers inside a pore of $H = 5.2$ nm move faster than the ions in the same layers inside a pore of $H = 2.5$ nm. The dynamics become slower and relaxation times become larger as pore size decreases, consistent with the results shown in Fig. 2.7. Back in Fig. 2.11, at $t = 20$ ns for $H = 5.2$ nm, $G_s(r,t)$ for the ions in the first layers are significantly different from those of the ions in the second layer, which in turn are very different from $G_s(r,t)$ for the ions in the center of the pore. In particular, small secondary peaks were observed in the $G_s(r,t)$ of the ions in the first and second layers for both pore sizes. Similar secondary peaks in $G_s(r,t)$ were also observed for a supercooled LJ fluid inside a slit pore with rough walls,[138] and suggests that the particles in the layers close to the wall do not move continuously but ‘hop’ to a new position (within the same layer of fluid) that has a typical distance equal to the position of second peak from the initial site. Scheidler et al.[138] rationalized this behavior by stating that the rough pore walls give rise to a local potential energy landscape with several energy minima,
and the observed peaks in $G_s(r,t)$ for particles near the pore walls represent the motion of the particles between these local minima within the same layer of fluid. For both pore sizes and within each layer/region, $G_s(r,t)$ for the cations reach their peaks and decay to zero at larger distances than the anions, confirming that the cations have faster dynamics than the anions.

**Figure 2.11.** Self-part of the van Hove correlation function $G_s(r,t)$ of [EMIM$^+$] (left) and [TFMSI$^-$] (right) confined in slit graphitic nanopores of $H = 5.2$ nm (continuous lines) and $H = 2.5$ nm (dashed lines) at three different time scales (a) $t = 0.2$ ps (b) $t = 100$ ps (c) $t = 20,000$ ps. Data are presented for the ions based on their distance to the pore walls, and compared against data of the bulk ions at the same temperature (333 K). In all cases, $\rho = \rho_{\text{bulk}}$.

In Figure 2.12 we show the effect of pore loading on $G_s(r,t)$ of the cations in the different layers/regions in a slit pore of $H = 5.2$ nm at three times, $t = 0.2, 100$ and $20,000$ ps. At $t = 0.2$ ps, decreases in pore loading lead to slight reductions in the height of the peaks and slight
increases in the width of $G_s(r,t)$ of the cations in the different layers/regions. These effects are more evident at $t = 100$ ps, especially for the cations in the center of the pore, for which the peaks in $G_s(r,t)$ are observed at larger distances and small secondary peaks arise when $\rho = 0.8 \rho_{\text{bulk}}$ and $0.6 \rho_{\text{bulk}}$. At longer times, $t = 20$ ns, we observe important differences in $G_s(r,t)$ of the cations in the different layers/regions as the pore loading decreases. In particular, small secondary peaks in $G_s(r,t)$ are observed with reductions in the pore loading.

**Figure 2.12.** Effect of pore loading on the self-part of the van Hove correlation function $G_s(r,t)$ of [EMIM$^+$] in the different layers/regions in a slit graphitic nanopore of $H = 5.2$ nm. First layers = left, second layers = center, center region = right. Data at three different times are depicted: $t = 0.2$ ps (top), $t = 100$ ps (center) and $t = 20,000$ ps (bottom).
These complex dynamics can be induced due to a combination of effects from the pore walls, the clustering of the ions and the formation of regions depleted of ions at lower pore loadings. The observed peaks in $G_s(r,t)$ in the different layers represent the motion of the particles between the local energy minima caused by these effects. Similar trends were observed for the anions. The incoherent or self-intermediate scattering function $F_s(q,t)$, is the space Fourier transform of $G_s(r,t)$ and can be determined experimentally from scattering measurements. $F_s(q,t)$ is typically measured in simulations of ILs and other subcooled liquids\cite{112,138,139} to further understand dynamical heterogeneities at the molecular level. In particular, $F_s(q,t)$ exhibits several dynamic regimes in subcooled liquids, namely a fast relaxation process at short timescales (the so-called $\beta$-relaxation), which is followed by a plateau associated with caging effects, where the ions are temporarily trapped in a cage formed by their neighbors. At longer timescales, the particles escape this cage ($\alpha$-relaxation). Furthermore, $F_s(q,t)$ can be compared against experimental measurements via quasielastic neutron scattering. In Figure 2.13 we show $F_s(q,t)$ of the center of the mass of the ions in the different layers of two slit pores, $H = 5.2$ and 2.5 nm, as a function of time at 333 K. In all cases, $\rho = \rho_{\text{bulk}}$. In Fig. 2.13, the plateau corresponds to $\beta$-relaxation is not very well developed due to the relatively high temperature considered (333 K).

Following previous studies, \cite{112,139} $F_s(q,t)$ was determined at the wave vector $q = 15.0$ nm$^{-1}$ (maximum of the structure factor for the bulk IL). These results indicate that the ions in the first layers of both pores take the longest time for $F_s(q,t)$ to decay to zero, in agreement with the data shown for $G_s(r,t)$ at $t = 100$ ps (Fig. 2.11). The first and second layers of ions in the pore of $H = 2.5$ nm exhibit slightly faster relaxation (i.e., $F_s(q,t)$ decays to zero faster) as compared to the first and second layers of ions in the pore of $H = 5.2$ nm, again in agreement with the trends shown for $G_s(r,t)$ at $t = 100$ ps (Fig. 2.11). These results also indicate that at short times, the ions
in the bulk show the fastest relaxation, but at times approaching \( t = 100 \) ps, the ions in the center of the pore of \( H = 5.2 \) nm exhibit slightly faster relaxation than the bulk ions, in agreement to what was presented in Fig. 2.11(b). In Figure 2.14 we studied the effect of pore loading on \( F_s(q,t) \) of the ions in the different layers inside a pore of \( H = 5.2 \) nm. In agreement with the results shown in Fig. 2.12, the ions in all the layers of systems with \( \rho = 0.6 \rho_{\text{bulk}} \) and \( 0.8 \rho_{\text{bulk}} \) exhibit \( F_s(q,t) \) that decay faster as compared to the system where \( \rho = \rho_{\text{bulk}} \).

**Figure 2.13.** Incoherent scattering function \( F_s(q,t) \) of cations (left panel) and anions (right panel) in the bulk and in the different layers of slit pores of \( H = 5.2 \) nm (continuous lines) and \( H = 2.5 \) nm (dashed lines). \( F_s(q,t) \) is calculated at the wave vector \( q = 15.0 \) nm\(^{-1} \) at 333 K. In all cases \( \rho = \rho_{\text{bulk}} \).

**Figure 2.14.** Incoherent scattering function \( F_s(q,t) \) of cations in the different layers of slit pores of \( H = 5.2 \) nm at different pore loadings. \( F_s(q,t) \) is calculated at the wave vector \( q = 15.0 \) nm\(^{-1} \) at 333 K.
2.4. Concluding Remarks

We performed MD simulations of varying amounts of the IL [EMIM$^+$/][TFMSI$^-$] confined inside uncharged, slit-like graphitic nanopores of different widths $H$. The structural and dynamical properties of the confined IL were studied as a function of pore size and pore loading. Naturally, the number of layers of ions observed in the density profiles depends on pore size, and because the pore walls are uncharged, the peaks in density of cations and anions are observed at similar values of the $z$ coordinate. Reductions in pore loading make the ions to cluster together into high-density regions, which lead to the formation of low-density regions in the center of the pore. Variations in pore size do not cause marked changes in the overall 3-D liquid structure of the confined IL as compared to that of the bulk IL. Furthermore, variations in pore size and pore loading seem to induce slight changes in the local liquid structure of [EMIM$^+$/][TFMSI$^-$] with respect to that of the bulk IL, as determined by measuring $g(r)$ for the ions in the different layers/regions inside the slit pores (i.e., the first layers that are closest to the walls, the second layers and the center regions, for a pore of $H = 5.2$ nm). These findings, when compared to the drastic changes in local liquid structure observed in our previous study[112] of [BMIM$^+$/][PF$_6^-$] in slit pores, suggest that confinement inside slit-like nanopores may or may not induce changes in the local liquid structure depending on the specific IL.

In contrast, pore size and pore loading seem to have a deeper influence on the dynamics of confined [EMIM$^+$/][TFMSI$^-$], as characterized by mean squared displacements, the self-part of the van Hove correlation functions $G_s(r,t)$ and the incoherent scattering functions $F_s(q,t)$. When $\rho = \rho_{\text{bulk}}$, the overall dynamics of the confined ions increase monotonically with increasing pore size. As found in our previous study for [BMIM$^+$/][PF$_6^-$] in slit pores,[112] the local dynamics of [EMIM$^+$/][TFMSI$^-$] are heterogeneous and depend on the distance of the ions to the pore walls;
the ions tend to have less mobility as they get closer to the pore walls. When $\rho = \rho_{\text{bulk}}$ and pore size is varied, at long times when the confined IL is in the diffusive regime, the ions in the first layers (closest to the pore walls) and in the second layers of a pore of $H = 5.2$ nm have faster dynamics than those in the same layers of a pore of $H = 2.5$ nm; the ions in the center of a pore of $H = 5.2$ nm have dynamics similar to that of the bulk IL. However, in parts of the sub-diffusive regime, the ions in the first and second layers in a pore of $H = 2.5$ nm move faster than the ions in the same layers in a pore of $H = 5.2$ nm. For varying amounts of $[\text{EMIM}^+][\text{TFMSI}^-]$ inside a pore of $H = 5.2$ nm, MSD results indicate slight differences in the dynamics of the ions in the first and second layers. In contrast, the dynamics of the ions in the center of the pore change markedly, with the fastest dynamics observed when $\rho = 0.8\rho_{\text{bulk}}$ (these dynamics are even faster than those observed in bulk systems). These observations might be associated with the formation of regions partially depleted of IL as pore loading decreases. Marked deviations from Gaussian behavior (e.g., large secondary peaks) arise in $G_s(r,t)$ with reductions in pore loading, which suggest that the local dynamics become more complex as the ions cluster together when pore loading is reduced.

The structural properties of an IL confined inside a nanoporous electrode affect the macroscopic capacitance of an EDLC; and the dynamical properties of the confined IL is one of the factors that determines the macroscopic electrical resistance in these electrochemical devices. The results obtained in this paper indicate that variations in pore size and pore loading seem to induce slight changes in the local liquid structure and have a deeper influence on the dynamics of confined $[\text{EMIM}^+][\text{TFMSI}^-]$. In particular, dynamics tend to become slower as the pore size is reduced. Therefore, while a reduction in pore size might lead to an increase in the capacitance according to several experimental studies, the slowing down in the dynamics of the confined IL
might affect the electrical resistance. A factor that needs to be considered in future simulation studies in this area is how electrical charges in the pore walls, as well as variations in the charge density affects the dynamics of the confined IL. These studies are currently in progress and will be described in detail in an upcoming paper.
3.1. Introduction

Electrochemical double-layer capacitors (EDLCs), or supercapacitors, are devices that have a structure similar to that of batteries, but differ from those in that electrical energy is stored physically at the interface between a nanoporous electrode and an electrolyte.[3, 79] EDLCs exhibit fast charge/discharge times and can provide bursts of energy very quickly, but cannot store as much energy as batteries. However, recent experiments involving nanopores filled with organic electrolytes or ionic liquids (ILs) suggest that a reduction in pore size can lead to anomalous increases in the capacitance of these systems.[75, 76, 118-120] These studies suggest that carefully controlling the properties of the nanoporous electrodes and the electrolytes can lead to significant improvements in the energy storage in EDLCs (see, e.g.,[3, 39, 46, 65, 79-85, 140]). However, a recent experimental study[121] reported that the capacitance of the electrolyte [(C$_2$H$_5$)$_4$N$^+$][BF$_4^-$]/acetonitrile inside carbons remains relatively constant upon variation of the pore size. This apparent controversy suggests that much remains to be fundamentally understood regarding the behavior of systems of electrolytes such as ILs inside nanopores. Molecular simulations, in close interplay with experiments, are well positioned to provide such fundamental understanding and advance those technologies well beyond their current state of the art.

Recent simulation studies have focused on ILs confined inside nanopores with slit-like[14, 47-56, 102-115, 141-143] and cylindrical[56-60, 114-116] geometries, as well as inside model CMK-3 nanoporous carbon materials[117] and realistic model carbons.[144] Some of these

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simulation studies have considered the presence of charges in the pore walls, and their effects on the properties of the electric double layer and the capacitance. Some of these simulations[52-57, 103-107, 110, 111, 144] suggest that the capacitance reaches maxima at certain specific conditions of pore size, pore geometry, surface charge density and electrode potential. For example, molecular dynamics (MD) results from Wu et al.[103] for systems of charged slit-shaped nanopores of different sizes in contact with an IL electrolyte, show that the capacitance of these IL-filled nanopores has a U-shaped behavior with pore size, with a minimum around 0.9 nm. Further reductions in pore size leads to increases in the capacitance, in agreement with recent experiments.[75, 76, 118-120] Increases in pore size was also found to lead to increases in the capacitance; a couple of recent studies suggest that the specific capacitance has a decaying oscillatory behavior as the pore size increases.[104, 105] In particular, the results reported in ref.[105] were obtained using classical density functional theory, which is able to capture the structure of the electrical double layer of ILs near solid interfaces better than classical electrochemical theories (e.g., the Helmholtz model, the Gouy-Chapman model, and the so-called “layer model”[145]). These classical models have important assumptions that do not apply to ILs near walls (e.g., two important assumptions are that the ions are extremely diluted in the electrolyte, and that the IL-electrode interface is only one ion-layer thick).[114, 146] Several theoretical models that relax these assumptions have been proposed recently,[146, 147] but these are based on mean-field approximations that neglect Coulomb correlations between the ions, which are adequately captured with classical density functional theory. Finally, recent simulation results from our group[117] for ILs inside a realistic model of CMK-3 carbon materials, as well as the recent simulation results of Merlet et al.[144] for an IL inside a realistic model of carbide-
derived porous carbons developed by Palmer et al.,[148] provides further insights on the structure of ILs inside carbons with complex pore geometries.

Most of these simulation studies on ILs inside nanopores have mainly focused on their structural and electrostatic properties; in sharp contrast, the dynamics of these systems have not been studied in detail. The dynamics of ILs inside nanoporous electrodes is one of the factors that determine the macroscopic electrical resistance in EDLCs; the structure of the confined IL affects the macroscopic capacitance in these electrochemical devices.[3, 79] In four recent papers,[60, 112, 117, 141] we studied the structural and dynamical properties of ILs confined inside uncharged carbon nanotubes, slit graphitic pores and CMK-3 carbon materials at several temperatures. Results from these studies suggest that the liquid structure and the dynamics of the confined cations and anions are heterogeneous and depend strongly on the distance of the ions to the pore walls. In the present study we explore the effect of variations in the density of electrical charges on the pore walls on the structure and dynamics of an IL, [EMIM⁺][NTf₂⁻] (Figure 3.1a), confined in a slit graphitic nanopore of width $H = 5.2$ nm. This IL has been used in several experimental studies involving EDLC applications,[26, 67, 68, 75, 78] and a very recent simulation study involving this IL inside slit pores focused on the effect of pore size on the capacitance.[104] The rest of this document is structured as follows. Section 3.2 contains details about the computational models and methods used in this study. The main results and discussion from this study are presented in Section 3.3, and concluding remarks are included in Section 3.4.

3.2. Computational Details

Molecular dynamics (MD) simulations were performed to study the liquid state properties of the ionic liquid [emim⁺][TFMS⁻] (Fig. 3.1a) confined inside a slit graphitic nanopore of size $H = 5.2$ nm with rigid charged walls. A charged nanoporous material is
modeled in our simulations by uniformly distributing a constant charge $q = \pm ne$ among the wall atoms (where $e$ is the charge of one electron; $n = 0$ for an uncharged porous material).

The total charge $q$ is kept fixed throughout the simulations. This constant-charge approach has been used extensively in previous simulation studies,[14, 48, 52, 54, 57, 58] however the effect of surface charge density $\sigma$ on the dynamical properties of the confined IL has not been studied before. This constant-charge model is not a completely realistic representation of a charged electrode, especially in materials with pores of complex geometry.[55, 56, 102] Local fluctuations in the structure of the IL near the pore walls can induce a non-uniform distribution of charges among the atoms in the wall. In addition, when using fixed-charge distribution in the nanoporous walls, the electrostatic potential in the simulation cell can vary. Several groups have considered simulation approaches where the charges in the atoms of the electrode can vary, based on the imposed electrostatic potential (which is kept fixed in the simulation), and on variations in the local structure of the electrolyte at the interface.[55, 56, 102, 103, 109, 113, 144, 149] Nevertheless, a recent simulation study by Merlet $et$ $al.$[102] concluded...
that, for the case of IL confined in a slit graphitic pore, the constant-charge approach yields results similar to those obtained with a constant-potential approach. Likewise, capacitance results obtained recently for ILs inside slit nanopores by Feng and Cummings,[104] and by Jiang et al.[105] using a constant-charge approach exhibit the same trends and scaling as those obtained by Wu et al.[103] using a constant-potential approach.

In our first series of simulations, we distributed equal and opposite charges on the walls of the graphitic slit nanopore (Figure 3.1b); the three graphene sheets of the bottom walls were negatively charged (cathode), and the three graphene sheets of the top walls were positively charged (anode). Five different systems were studied with surface charge density $\sigma = 0, 5.3, 8.9, 12.4 \text{ and } 16.0 \mu\text{C/cm}^2$, which are comparable to those used in previous simulation studies (e.g.,[48, 52, 57]). A total of 504 IL ion pairs were placed inside the nanopore, yielding a density of $\sim1.56 \text{ g/cm}^3$ (similar to the bulk density of the IL at 333 K). We also carried out a second series of simulations where we considered the case where both the top and bottom walls had charges of the same sign. Four different systems were studied with surface charge density of $\pm2.8 \text{ and } \pm7.2 \mu\text{C/cm}^2$. To ensure that these systems were electrically neutral, we removed 8 and 20 anions (for the case of negatively charged walls), and 8 and 20 cations (positively charged walls). In both series of simulations, we conducted long runs of at least 30 ns in order to make sure that the results are statistically converged. Different single particle time correlation functions (not shown for brevity) were monitored to make sure that the simulations run are long enough. The force field and the rest of the simulation procedure used in this work are the same as those described in detail in our previous paper.[141]
3.3. Results and Discussion

3.3.1. Structural Properties

In Figure 3.2 we show the number density profile $\rho(z)$ of [emim$^+$][TFMS$^-$] inside a slit graphitic nanopore with five different surface charge densities ($\sigma = 5.3$, 8.9, 12.4 and 16.0 $\mu$C/cm$^2$), where the bottom wall is charged negatively and the top wall is charged positively (Fig. 3.1b). No density oscillations are observed in the center of a pore for an uncharged system; increases in the surface charge density lead to formation of distinct layers of cations and anions, where the local maxima in $\rho(z)$ of the cations coincide with the local minima in $\rho(z)$ of the anions and vice versa (Fig. 3.2c). These out-of-phase oscillations in the density profiles indicate strong cation-anion correlations. At a given value of $\sigma$, the density profile of the cations reaches its absolute maximum near the negatively charged surfaces, and this maximum in density becomes larger as $\sigma$ increases (Fig. 3.2a). This increase in the local density of the cation layer near the negatively charged surface as $\sigma$ becomes larger, leads to a more modest increase in $\rho(z)$ in the layer of anions contiguous to that layer of cations (Fig. 3.2b). For the anions, as $\sigma$ becomes larger we observe increases in $\rho(z)$ of the anion layer near the positively charged surface, but these increases are very small when compared to the trends noted for the layer of cations near the negatively charged surface. For example, for $\sigma = 16.0$ $\mu$C/cm$^2$, the local density of cations near the negatively charged surface increases in about 120% with respect to the value observed for the same layer of cations near an uncharged surface. In contrast, for the anions near the positively charged surface the increase in local density is only about 22%. These trends suggest that the adsorption of anions at the positively charged surface is weaker than the adsorption of cations at the negatively charged surface. This observation can be rationalized as a combination of different factors. First, the carbon atoms in the graphitic walls will have stronger dispersion interactions
with the cation as compared to the anions, because of the larger number of carbon atoms present in the cation. Furthermore, the cation-anion interactions are weaker than those observed in other ionic liquids, mainly because the anion has its negative charge delocalized along its S-N-S core (Figure 3.1a); the charge is also partially shielded by the sulfonyl oxygen atoms and trifluoromethane groups, which do not carry significant charges.\[150, 151\] These features in the anion, which cause [emim]$^+$[NTf$_2^-$] to have low melting points and low viscosities, should also lead to weaker interactions of the anion with the pore walls. This behavior of adsorption of ions cannot be generalized for all ILs; for example, in a previous study\[102\] larger adsorption of [PF$_6^-$] near positively charged walls was observed as compared to [bmim]$^+$ near negatively charged walls.

The peak value of $\rho(z)$ for the cations near the positively charged surface becomes smaller with increasing surface charge density; however, the density of cations near the positively charged surface is still significant even at $\sigma = 16.0 \, \mu\text{C/cm}^2$ (Fig. 3.2c). Similar trends are observed for the anions near the negatively charged surface, although the peak density of anions near this surface is significantly smaller than that of the cations near the positive surface. We also observed that the layer of cations near the negatively charged surface becomes thinner as the surface charge density increases; in contrast, the width of the layer of anions closest to the positively charged surface remains almost unchanged with variations in $\sigma$. The trends described above are also observed when both the top and bottom walls of the nanopore have charges of the same sign. In Figure C-1 (Appendix C) we show the density profiles observed in the cases where both walls are negatively charged with a surface charge density $\sigma = -7.2 \, \mu\text{C/cm}^2$ (Fig. C-1a), and when both walls are positively charged, $\sigma = +7.2 \, \mu\text{C/cm}^2$ (Fig. C-1c); these results are contrasted with those observed when the bottom walls have negative charge and the top walls have positive
charges, \( \sigma = \pm 5.3 \ \mu\text{C/cm}^2 \) (Fig. C-1b). Large increases in the local density of cations are observed near the two negatively charged walls (Fig. C-1a), in analogy to what was observed for \( \rho(z) \) of the cations near the negatively charged wall (Figs. C-1b, 3.2a and 3.2c). Likewise, significant but more modest increases are also observed for \( \rho(z) \) of the anions near the two positively charged walls (Fig. C-1b), in analogy to what was observed before for anions near the positively charged wall (Figs. C-1b, 3.2b and 3.2c). Furthermore, out-of-phase oscillations in the density profiles of cations and anions are also observed in the cases where the two walls have charges of the same sign; however, these oscillations are more pronounced in the case where the bottom and top walls have charges of opposite signs (Figs. C-1a, C-1b and C-1c). All these trends agree with similar results reported in recent simulation studies.[102-105]

**Figure 3.2.** Number density of (a) cations and (b) anions confined inside a pore size of 5.2 nm with surface charge density \( \sigma \) of 0, 5.3, 8.9, 12.4, 16.0 \( \mu\text{C/cm}^2 \). The vertical dashed lines indicate how the confined ions were divided into layers/regions for further study. In (c), the number density of cations (blue) and anions (red) are shown in the same plot for \( \sigma = 16.0 \ \mu\text{C/cm}^2 \).

In Figure 3.3 we show orientational order parameters for \([\text{emim}^+]\) and \([\text{NTf}_2^-]\) as a function of the \( z \)-coordinate for different surface charge densities. The orientation order parameter is defined as the ensemble average of the second Legendre polynomial \(<P_1[\cos(\theta)]> = <\cos(\theta)>\), where \( \theta \) is the angle formed between a direction vector in an ion and the vector normal to the graphitic surfaces. The direction vectors considered in this work are (1) a vector normal to the imidazolium ring of \([\text{emim}^+]\), and (2) a vector connecting the two carbon atoms in \([\text{NTf}_2^-]\)
(labeled CJ in Fig. 3.1a). We have cut the curves of the orientational order parameters in Figure 3.3 at the values of $z$ at which the density profiles (Figure 3.2) reach a value of zero. Increases in surface charge density $\sigma$ leads to small changes in the orientation of the cations near the negatively charged surface, which remain mostly parallel to the graphitic surface ($<\cos(\theta)>$ close to 1). The order parameter of the cations near the positively charged surface drop from ~0.83 to ~0.4 as $\sigma$ changes from 0 to 16.0 $\mu$C/cm$^2$, indicating that the cations tend to lose their orientation parallel to the graphitic surfaces as the surface exhibits increasingly positive charges. Nevertheless, these observations only apply to the relatively small number of cations that are close to the positively charged surface (Figure 3.2). Regarding the anions, the small value of the order parameter for anions near the positively charged surface indicates that the anions lie flat close to that wall. Near the negatively charged surface, increasing values of $\sigma$ make the anions to align perpendicular to this surface, as signaled by increasing values of $<\cos(\theta)>$; however, this observation again only apply to the small number of anions that are near the negative walls. Increasing values of $\sigma$ also lead to larger oscillations in the values of the order parameters in the center regions of the pore. Similar trends were observed in the cases where both walls have charges of the same sign.

To further investigate the local structure of IL, the ions were divided into three layers/regions as per the number density profiles (see dashed lines in Fig. 3.2): a layer of ions close to the negatively charged surface, ions in the center regions and a layer of ions near the positively charged surface.
Figure 3.3. Orientational order parameter, $P(\cos \theta)$ of $[\text{emim}^+]$ (CR-CR atoms) and $[\text{NTf}_2^-]$ (CJ-CJ atoms) confined inside a pore size of 5.2 nm at different values of surface charge density $\sigma$.

Cation-cation, cation-anion and anion-anion radial distribution functions for the ions in these layers/regions are depicted in Figure 3.4 at different values of surface charge density $\sigma$. Increasing values of $\sigma$ causes increases in the height of the first and the second peaks in the cation-cation $g(r)$ (Fig. 3.4a, right) near the positively charged surface, and in the anion-anion $g(r)$ (Fig. 3.4c, left) near the negatively charged surface. Increases in the value of $\sigma$ also lead to increases in the heights of the peaks in the cation-cation $g(r)$ near the negatively charged surface (Fig. 3.4a, left), and in the anion-anion $g(r)$ near the positively charged surface (Fig. 3.4c, right).
However, in the layer of ions near the negative surface, the first and second peaks of the cation-cation $g(r)$ are displaced to smaller values of $r$ as $\sigma$ increases (Fig. 3.4a, left). Increasing values of $\sigma$ causes increases in the heights of the peaks in the cation-anion $g(r)$ (Fig. 3.4b, left) near the negative surface; these peaks are also slightly displaced to smaller values of $r$. An additional peak at smaller values of $r$ develops in the anion-anion $g(r)$ near the positively charged surface as the value of $\sigma$ is raised (Fig. 3.4c, right). Furthermore, in this same layer of ions, increasing values of $\sigma$ makes the first peak in the cation-anion $g(r)$ to vanish (Fig. 3.4b, right). These trends observed for the layer of ions near the positive surface suggest a reduction in the importance of the cation-anion interactions, and an increase in the strength of the anion-anion interactions in this layer of ions. Therefore, the presence of charges in the pore walls lead to significant changes in the liquid structure of the layer of ions near the charged pore walls. A different scenario is observed for the ions in the center of the pore. Going from uncharged pore walls to a surface charge density $\sigma = 5.3 \, \mu C/cm^2$ causes a reduction in the height of the peaks in all the $g(r)$ curves (center panels of Figs. 3.4a, 3.4b and 3.4c); further increases in $\sigma$ causes negligible changes in the liquid structure of the ions in the center of the pore. Similar qualitative trends are observed in the cases where both walls have charges of the same sign (see Figure C-2, Appendix C).

Previous simulation[152-154] and experimental[154-156] studies for bulk dialkylimidazolium ILs have shown that their polar and nonpolar groups would cluster together and form nanodomains. In the case of [emim$^+$][NTf$_2^-$], the imidazolium ring (including the methyl group) of the cation, as well as the whole anion, were considered as polar groups; and the aliphatic (ethyl) chain of the cation were considered as the nonpolar group. Lopes and Pádua[153] studied dialkylimidazolium cations with aliphatic chains of different lengths, and found that nonpolar nanodomains would form in bulk ILs when the cations have relatively long
aliphatic chains (i.e., 1-butyl-3-methylimidazolium and longer). However, in our simulation study we observed formation of nonpolar nanodomains for [emim$^+$][NTf$_2$] in the layer of ions near the negatively-charged pore wall when the surface charge density increases.

**Figure 3.4.** Radial distribution functions of (a) cation-cation, (b) cation-anion and (c) anion-anion for the ions at the layer near the negatively charged surface (left panel), in the center region (center panel) and at the layer near the positively charged surface (right panel), for different values of surface charge density $\sigma$.

In Figure 3.5(a) we show snapshots of the polar (red) and non-polar (green) regions for the layers of ions near the negative surface and near the positive surface, for uncharged walls and for charged walls with $\sigma = 16.0$ µC/cm$^2$. Near the negatively charged pore wall, the ethyl groups of the cation cluster together and form small nanodomains; these are not observed near the
positively charged pore wall, or when the pore walls are not electrically charged. These results are associated with the increase in the density of cations near the negatively charged pore wall (Fig. 3.2), and with the flat orientation of the cations near this pore wall (Fig. 3.3). In contrast, the layer of ions close to the positively charged surface is mainly occupied with anions, with a lower density of cations that does not allow formation of non-polar regions. These trends suggest that electrical charges can induce the formation of nonpolar nanodomains even for dialkylimidazolium cations with small chain lengths such as [emim$^+$]. In Figure 3.5b we show the $g(r)$ functions between the CE atoms of the ethyl group of the cation, and between the CR atoms in the imidazolium ring of the cation (Fig. 3.1a), for the layers of ions close to the negatively charged pore wall, in the center of the pore, and near the positive wall, at two values of surface charge density, $\sigma = 0$ and 16.0 $\mu$C/cm$^2$. Formation of non-polar domains near the negatively charged surface is indicated again by a very high first peak for the CE-CE $g(r)$ in the layer close to the negative surface for $\sigma = 16$ $\mu$C/cm$^2$, as compared to that observed for the CE-CE $g(r)$ in the same layer for $\sigma = 0$ $\mu$C/cm$^2$. The CR-CR $g(r)$ near the negative surface also has a first peak with very high value that is displaced to lower values of $r$, and a significant second peak when $\sigma = 16$ $\mu$C/cm$^2$. These trends reflect the fact that, as $\sigma$ is increased, the cations get closer together as the density of cations near the negative surface becomes larger. The low values of the peaks in the CE-CE $g(r)$ near the positive surface and in the center of the pore also suggests that non-polar nanodomains do not form in these regions. The results shown in Figs. 3.4 and 3.5 indicate the presence of structural heterogeneities in charged systems, which could also play a role in the dynamics of the ions (see below).
3.3.2. Dynamical Properties

Previous simulation studies on ILs inside electrically-charged nanopores have mostly focused on the structure of the IL, however the dynamics of the IL inside charged nanopores have not been studied in detail before. The mobility of the confined ions in different directions is one of the factors in determining the internal resistance in EDLC, which ultimately affects its specific power. The translational dynamics of the confined IL is first studied by measuring their mean square displacement (MSD). ILs exhibit complex and slower dynamics as compared to inorganic molten salts because of their bulky nature and high viscosity. The parallel (x and y directions) and the z-components of the MSD of the different layers/regions of $[\text{emim}^+][\text{NTf}_2^-]$ inside a graphitic slit pore of $H = 5.2$ nm with surface charge density $\sigma = 16.0$ $\mu$C/cm$^2$ (bottom
wall negatively charged, top wall positively charged, Fig. 3.1b) is shown in Figure 3.6. As found in our previous studies considering uncharged pore walls,[60, 112, 141] (1) the dynamics of the confined ions is a strong function of their distance to the pore walls, (2) cations move faster than anions in all regions of the pore, a finding already reported in bulk imidazolium ILs[130, 154] that was rationalized by pointing out at a preferential displacement of the cation ring along the direction of the CR carbon in between the two nitrogen atoms (Figure 3.1a);[130, 154] (3) within the same layer/region, the dynamics in the parallel direction are faster than those in the z-direction for all ions, and (4) the fastest dynamics are observed for the ions in the center of the pore in the directions parallel to the pore walls. For the cations, the slowest dynamics are observed in the z-direction in the first layer (closest to the negatively charged pore wall); similarly, the anions in the third layer (closest to the positively charged pore wall) exhibit the lowest values of MSD in the z-direction. These results indicate that the strong interactions between the cations and the negative surface, and those between anions and the positive surface, cause the dynamics in the z-direction to slow down in addition of inducing changes in the structure (see Figs. 3.2 and 3.4). The results shown in Fig. 3.6 also indicate that the cations in the first layer (closest to the negative surface) move faster in the parallel direction than the cations in the third layer (closest to the positive surface). In contrast, the layer of anions closest to the positive surface moves slower in the parallel direction than the layer of anions closest to the negative surface. Moreover, that layer of anions closest to the positive surface has a parallel MSD that is even lower than the z-component of the MSD of the anions in the center regions. These trends suggest that the presence of charges in the pore walls seems to affect the dynamics of cations and anions in a different way. When the dynamics of the different layers/regions of [emim$^+$][NTf$_2^-$] inside the charged pore are compared with the dynamics of the bulk IL, it is
observed that the parallel component of the MSD of cations and anions in the center of the pore is larger than the MSD of the bulk IL, which suggest that these confined ions have dynamics in the x and y directions that are faster than those of the bulk IL. In our previous paper for the same IL inside an uncharged slit graphitic nanopore, we also observed that the dynamics of the confined IL were faster than those of the bulk IL, when the density of the confined IL was such that $\rho = 0.8\rho_{\text{bulk}}$.\[141\] Furthermore, recent quasielastic neutron scattering experiments for $[\text{bmim}^+][\text{NTf}_2^-]$ inside a mesoporous carbon matrix suggest that the cations that are in the center of the pore exhibit enhanced (rather than suppressed) diffusivity, when compared to the diffusivity of the cation in the bulk IL.\[157\] The results shown in Fig. 3.6 also indicate that the MSD of the bulk ions is comparable to the parallel MSD of the cations and anions near the negatively charged pore wall, and to the parallel MSD of the cations near the positively charged wall (Fig. 3.6). The motion of the confined ions in the z-direction and the dynamics of the anions in the x-y plane near the positively charged walls, are slower than the dynamics of the bulk ions. We have also calculated the conductivity in the different regions in the pores. For $\sigma = 16.0 \mu\text{C/cm}^2$, the conductivities in the first layer (close to the negative surface), center of the pore, and third layer (close to the positive surface) were found to be 12.6 mS/cm, 18.5 mS/cm and 6.09 mS/cm. The reported value for the bulk IL is 22 mS/cm.\[158\] These values indicate that the conductivity is lowest near the surface close to the positive electrode, followed by the value near the negative electrode, and is highest in the center of the pore. This finding corroborates that the collective dynamics are faster in the center of the pore.
Figure 3.6. Log-log scale plot of the MSD in z-direction (solid lines) and parallel direction (dashed lines) for [emim\textsuperscript{+}][NTf\textsubscript{2}\textsuperscript{-}] inside a slit graphitic nanopore of $H = 5.2$ nm with $\sigma = 16.0 \mu$C/cm\textsuperscript{2}. Data are presented for the ions based on their distance to the pore walls (see Fig. 3.2). The first layer of ions is close to the negatively charged pore wall, whereas the third layer of ions is near the positively charged pore wall (Fig. 3.2).

Figure 3.7 shows a log-log plot of the MSDs (z- and parallel components) of the different layers/regions of [emim\textsuperscript{+}][NTf\textsubscript{2}\textsuperscript{-}] inside the slit graphitic pore for different values of surface charge density, $\sigma = 0, 5.3, 8.9, 12.4$ and $16.0 \mu$C/cm\textsuperscript{2}. As expected, three regimes are observed in the MSDs reported in Fig. 3.7: ballistic at early times when the ions have not interacted much with their neighbors (MSD $\propto t^2$); sub-diffusive at intermediate times where ions rattle inside a cage formed by their neighbors (MSD $\propto t^{1/2}$); and when the ions escape from these cages, they reach the diffusive or Fickian regime at larger times (MSD $\propto t$). These results suggest that varying $\sigma$ seems to have small effects on the parallel and z-components of the MSD of the cations in the center of the pore and in the layer closest to the positively charged pore wall, and in the MSD of the anions in the center of the pore. For the cations near the negatively charged surface (Fig. 3.7, top left), variations in $\sigma$ also seem to have small effects on the parallel component of the MSD, but it strongly affects the MSD in the z-direction. Small reductions in the magnitude of this component of the MSD of the cations in this layer are observed when $\sigma$ changes from 0 to 8.9 $\mu$C/cm\textsuperscript{2}, but further increases in $\sigma$ lead to a drastic reduction in the z-
component of the MSD (a change of about two orders of magnitude between the $z$-MSD at $\sigma = 0$ and that at $\sigma = 16.0 \ \mu$C/cm$^2$). Similar trends are observed for the anions in the third layer (near the positively charged surface; Fig. 3.7, bottom right); however, larger variations with $\sigma$ are observed for the parallel MSD of the anions in this layer, as compared to the parallel MSD of the cations near the negative surface. In contrast to what was observed for the cations near the negative surface, the anions near the positive surface experience a significant reduction in their mobility in the $z$-direction when $\sigma$ changes from 0 to 8.9 $\mu$C/cm$^2$. The dynamics of the layer of anions near the negatively charged surface (Fig. 3.7, bottom left) also seem to be significantly affected by variations in $\sigma$, but those effects are not as large as those observed in the $z$-component of the MSD of the cations near the negative surface and of the anions near the positive surface. The results shown in Fig. 3.7 also suggest that, with the exception of the layer of anions near the positively charged pore walls, going from electrically uncharged to charged pore walls leads to a small but appreciable increase in the parallel component of the MSD of the ions. These results indicate that increases in surface charge density results in two tightly-adsorbed layers of ions near walls with electrical charges of the opposite sign, and the $z$-component of the MSD of this layer of ions has very small values. These trends agree with what was observed in a previous simulation study by Sha et al., who also noted decrease in diffusion of ions close to a negatively charged surface.[99] However, these important reductions in the dynamics are not transferred to the ions that are farther away from the charged surfaces.

The trends described above in the dynamics of confined ILs in a slit graphitic pore where one wall has negative charges and the other wall has positive charges, are similar to those observed in situations where both pore walls have charges of the same sign. Results for the $z$-component of the MSD of the layers of ions near the pore walls are shown in Figure C-3.
(Appendix C) for situations where both walls have charges of the same sign to the scenario where one wall is charged negatively and the other has positive electric charges.

Figure 3.7. MSD in z direction (solid lines) and parallel direction (dashed lines) of cations and anions confined in a pore size of 5.2 nm in three different layers for surface charge densities $\sigma = 0, 5.3, 8.9, 12.4$ and $16.0 \mu$C/cm$^2$. The first layer of ions is close to the negatively charged pore wall, whereas the third layer of ions is near the positively charged pore wall (Fig. 3.2).

Four different systems were studied with surface charge density of $\sigma = -2.8, -7.2, +2.8$ and $+7.2 \mu$C/cm$^2$. Results are compared to those observed in a system where one wall is charged negatively ($\sigma = -5.4 \mu$C/cm$^2$) and the other has positive charges ($\sigma = +5.4 \mu$C/cm$^2$). The trends are similar to those discussed above in Figure 3.7.

Single particle dynamics were further studied by monitoring the time dependence of the self-part of the van Hove self-correlation function $G_s(r, t)$:[159]

$$G_s (r, t) = \frac{1}{N} \sum_{i=1}^{N} < \delta[ r + r_i(t) - r_i(0) ] >$$

(1)

$G_s(r, t)$ gives the probability of finding a particle $i$ in a region $dr$ around a point $r$ at time $t$, provided that the particle $i$ was at the origin at $t = 0$ at a particular temperature.[159] $G_s(r, t)$ for
the ions in the first layer (close to the negatively charged pore wall), center of the pore and the third layer (near the positive surface) is shown at three different times, \( t = 0.2 \) ps, \( t = 100 \) ps and \( t = 25000 \) ps, and at surface charge densities of \( \sigma = 0, 5.3, 8.9, 12.4, 16.0 \) \( \mu \)C/cm\(^2\) in Figures C-4 (cations) and C-5 (anions) (Appendix C). For brevity, a short discussion of these figures is included in the Appendix C of this chapter. The space Fourier transform of \( G_s(r,t) \) gives the incoherent intermediate scattering function \( F_s(q,t) \), which can be measured from light scattering experiments:[159, 160]

\[
F_s(q, t) = \left\langle \frac{1}{N} \sum_{i=1}^{N} \exp(iq[r_i(t) - r_i(0)]) \right\rangle
\]  

(2)

In Figure 3.8a we show \( F_s(q,t) \) for the ions in the first layer (near the negatively charged walls), center region and the third layer (close to the positively charged walls) at the wave vector \( q = 15.0 \) nm\(^{-1}\) (maximum in structure factor for the bulk IL), and \( \sigma = 16.0 \) \( \mu \)C/cm\(^2\). For the cations in the different regions, no significant differences are observed at times \( t < 20 \) ps; afterwards, \( F_s(q,t) \) for the cations in the center of the pore and near the positive surface have faster relaxation (i.e., decay to zero faster) than \( F_s(q,t) \) for the cations near the negative surface. Similar trends are observed for the anions, but the anions in the center of the pore and near the negatively charged pore wall relax significantly faster than the anions near the positively charged wall, which show the slowest relaxation behavior among all ions inside the pore. In Figure 3.8b we show the effect of surface charge density on \( F_s(q,t) \) of the first layer of cations (near the negatively charged wall) and on \( F_s(q,t) \) of the third layer of anions (close to the positively charged wall, Fig. 3.8c) at a wave vector \( q = 15.0 \) nm\(^{-1}\) for different values of \( \sigma \). These results show that surface charge density has a somewhat larger effect on the relaxation dynamics of anions near positive surfaces, as compared to the cations near the negative surface. The relaxation dynamics seem to vary nonmonotonically with increases in the value of \( \sigma \).
Figure 3.8. Incoherent scattering function $F_s(q,t)$ for [emim$^+$][NTf$_2^-$] inside a slit graphitic nanopore of $H = 5.2$ nm. (a) Cations (solid lines) and anions (dotted lines) in the different regions of the pore, $\sigma = 16.0$ µC/cm$^2$. (b) First layer of cations, and (c) third layer of anions at different surface charge densities $\sigma = 0, 5.3, 8.9, 12.4$ and 16.0 µC/cm$^2$. In all figures, the first layer of ions is close to the negatively charged pore wall, and the third layer of ions is close to the positively charged wall. In all cases $q = 15$ nm$^{-1}$.

3.4. Conclusions

Molecular dynamics simulations were performed to study the effect of electrical charges on the structure and dynamics of the IL [emim$^+$][NTf$_2^-$] confined in a slit graphitic nanopore of
width $H = 5.2$ nm. We studied systems in which one of the pore walls had negative charges and the other was positively charged, as well as systems where both pore walls had charges of the same sign. We observed that the qualitative trend remains the same in these two types of systems. Our results indicate that surface charge density $\sigma$ affects the structure and dynamics of the confined IL, especially in the layers of ions close to the electrically charged walls. The local density of cations in the layer of fluid near the negatively charged pore wall increases as $\sigma$ increases; a much smaller increase in the local density of anions is also observed in the layer of fluid near the positively charged wall as $\sigma$ increases. The cations near the negatively charged walls orient with their imidazolium ring parallel to the pore wall; similarly, the anions lie flat close to the positively charged walls. The presence of charges in the pore walls lead to significant changes in the liquid structure of the ions, particularly in the layers close to the charged pore walls. The radial distribution functions show differences in the height of the peaks, some peaks are displaced to smaller values of $r$, additional peaks arise or some peaks disappear as $\sigma$ increases. Similarly, increases in surface charge density also lead to the formation of nonpolar domains formed by the ethyl groups of $[\text{emim}^+]$, in the layer of ions near the negatively charged walls; similar nonpolar domains were observed in bulk systems only for imidazolium cations with larger alkyl chains (i.e., 1-butyl-3-methylimidazolium and longer). Increases in surface charge density also induces important reductions in the dynamics of the cations near the negatively charged walls, and of the anions close to the positively charged walls. In particular, the ions in those two layers exhibit important reductions in the $z$-component of their MSDs and slower relaxation times as $\sigma$ is increased. Increases in surface charge density also cause variations in the parallel component of the MSD of the ions in those two layers of ions, although these variations are smaller in magnitude. As expected, in general the dynamics of the ions in the
different layers/regions of the pore are slower than those of the ions in the bulk IL. However, at larger surface charge densities, the magnitude of the parallel component of the MSDs of the ions near the charged pore walls is comparable to the MSDs of the bulk ions; furthermore, the parallel component of the MSDs of the ions in the center of the pore is larger than the MSDs of the ions in the bulk IL. Variations in $\sigma$ seem to have a small effect in the dynamics of the ions in the center of the pore. Analysis of the self-part of the van Hove correlation functions indicates that the dynamics of the ions near electrically charged walls deviate significantly from Gaussian behavior.
CHAPTER 4 INFLUENCE OF PORE GEOMETRY ON THE STRUCTURAL AND DYNAMICAL PROPERTIES OF CONFINED IONIC LIQUIDS

4.1. Introduction

It has been reported that Ionic liquids with their unique properties have the potential to replace the conventional electrolytes in electrochemical double-layer capacitors (EDLCs) [3, 39, 46, 65, 81-84, 139] and DSSCs [65, 86, 87]. Low volatility, non-toxicity, excellent thermal stability and wide electrochemical window of ILs make them better and safer than traditional organic electrolytes. Recent studies have shown that when ILs are confined inside nanoporous materials, they show varied physical properties from the non-confined IL.[161-166] Researchers have studied ILs confined inside nanopores of different materials such as graphite, silica, mica, quartz, sapphire and rutile [14, 47-60, 111, 113, 117, 167]. Experimental and computational studies confirm a drastic change in the structure and dynamics of the ions under confinement. Although different pore materials have been considered in such studies, the effect of the pore morphology is still unexplored. The main objective of this research is to study the effect of the pore morphology on the structural and dynamics of the ILs [BMIM⁺][PF₆⁻] and give a comprehensive overview. We considered three different pore geometries in this study: graphitic slit-like pore, carbon nanotube (CNT) and the hexagonally arranged CMK-3 model. The rest of this paper is structured as follows. Section 4.2 contains a description of our computational models and methods. In Section 4.3 we present analysis of the structural arrangement and mobility of the ionic liquid [BMIM⁺][PF₆⁻] confined inside three carbon models, and in Section 4.4 we summarize our main findings.
4.2. Computational Details

Classical molecular dynamic (MD) simulations have been conducted with the NVT ensemble using GROMACS MD package[61] to study the structural and dynamical properties of the ionic liquid [BMIM$^+$][PF$_6^-$] confined inside multiple nanopore models. Three different pore morphologies were considered in this work (namely slit-like graphitic pore, carbon nanotubes and CMK-3) with two different pore sizes (H) of 2.5 and 3.7 nm. The schematic representation of the IL used is shown in Figure 4.1. In Figure 4.2, the ionic liquid is shown in each of the three carbon models. The neutral carbon atoms that make up the carbon surfaces were modeled as LJ spheres with $\sigma_c = 0.340$ nm and $\epsilon_c/k = 28.0$ K.

The IL [BMIM$^+$][PF$_6^-$] was modeled using the non-polarizable force field developed by Bhargava and Balasubramanian.[168] In this model, charges on the cations and anions are chosen to be 0.8e and -0.8e respectively (see refs. [168] and [154] for a discussion of the reasons behind this choice of net charges for the ions). Bhargava and Balasubramanian have reported simulated density values within 1.4% of the experimental values, and diffusion coefficients that are within 20% of experimental values in the temperature range between 300 K and 500 K. Prior to studying confined system, we carried out preliminary MD simulations of bulk [BMIM$^+$][PF$_6^-$] in the NVT and NPT ensembles. From these simulations we obtained a value of 1.38 g/cm$^3$ for the bulk liquid density at 25 °C; diffusion coefficients for the cations and anions were found to be $9.2\times10^{-12}$ m$^2$/s and $6.7\times10^{-12}$ m$^2$/s respectively. Our simulated values are comparable to results from previous simulations and reported experimental values.[139, 168]

In every simulation, the Lennard-Jones interactions were cut off at 1.2 nm and the long range coulomb interactions were handled by the particle-mesh Ewald (PME) method[127] with a cutoff of 1.0 nm and a grid spacing of 0.1 nm. Periodic boundary conditions were applied in the
x, y, and z directions. Each pore morphology was kept in the center of an orthorhombic box and for the slit pore and CNT models enough vacuum was introduced in the confined directions to remove any interaction between the periodic mirrored ions. Detailed descriptions of these systems can be found in our previous publications.[38-40] The improved velocity-rescaling algorithm recently proposed by Parrinello et al.[125, 126] was used to mimic weak coupling at different temperatures with a coupling constant of 0.1 ps.

![Figure 4.1](image1.png)

**Figure 4.1.** Schematic representation of the IL [BMIM][PF$_6^-$]. Vectors N-N and N-H are shown for the calculation of the correlation functions along these vectors.

![Figure 4.2](image2.png)

**Figure 4.2.** Representative simulation snapshot of the IL [BMIM][PF$_6^-$] confined inside nanopores of different morphologies of a pore size of 2.5 nm at 300 K. Left panel: slit-like graphitic pore, center panel: multi-walled carbon nanotubes, right panel: CMK-3. Cations and anions are depicted in purple and green. The density of the confined IL is similar to that of the bulk IL at the same temperature.

We first minimized the energy of our initial configurations using the steepest descent method. Afterwards, we ran MD simulation using a time step of 0.5 fs. The systems were then melted at
800 K for 2 ns, and annealed from 800 to 300 K in three stages each 1 ns long. Afterwards, our systems were equilibrated and the properties of interest were sampled for 20 ns at 300 K.

4.3. Structural Properties

In Figure 4.3, we present the mass density profiles of the ions (in g/cm³) confined in different pore morphologies of width 3.7 nm at 300 K. In all cases the density of the confined IL is \( \rho \approx \rho_{bulk} = 1.38 \text{ g/cm}^3 \). Significant ion layering behavior was observed for both cations and anions confined in different pore morphologies, which suggests that the ions prefer to cluster together, creating some regions where the local density is higher than \( \rho_{bulk} \) and some regions where the local density is lower than \( \rho_{bulk} \). The mass density profiles of the confined IL are found to be oscillatory with a local maximum in the density close to the pore walls due to the stacking of the ions near the wall surface. The reason the cations are found closest to the surface is due to the strong Van der Waals interaction of the imidazolium rings and the carbon surface. The IL has a density similar to the bulk density in the center of the pore. However, the oscillation patterns observed in the density profiles greatly depend on the pore morphologies. The IL confined in CMK-3 has broader and fewer layers than the IL confined inside the CNT and slit pore models. Reduced layering near the center of the pore is observed for the slit pore and CMK-3 systems. Similar results are observed for the density profiles of different pore morphologies of pore size 2.5 nm. It was also observed that the number of layers of IL decreases as the pore size decreases to 2.5 nm (not shown). Slit pore and CNT models have more significant layering in the center of the pore than the CMK-3 models when the pore size is 2.5 nm. These results indicate that the number and height of layers for ions are dependent on the pore morphologies and the pore size. Among the three models the ions in CNT have the most significant layers.
Insights on the structure of the confined IL can be obtained from analysis of relevant radial distribution function g(r). In Figure 4.4 we have depicted the g(r) for cation-cation, anion-anion and cation-anion for the different layers of the [BMIM][PF$_6$] confined in the different pore morphologies at 300 K.

![Graph showing mass density profiles of ion [BMIM$^+$] (top panel) and [PF$_6^-$] (bottom panel) confined inside nanopores of different pore morphologies of a pore size 3.7 nm at 300 K. In all cases, the confined IL has a density similar to $\rho_{\text{bulk}}$. The dotted lines represent the density profiles of the ions in a bulk system.](image)

**Figure 4.3.** Mass density profiles of ion [BMIM$^+$] (top panel) and [PF$_6^-$] (bottom panel) confined inside nanopores of different pore morphologies of a pore size 3.7 nm at 300 K. In all cases, the confined IL has a density similar to $\rho_{\text{bulk}}$. The dotted lines represent the density profiles of the ions in a bulk system.

To obtain these g(r), we used the carbon atom bonded to the two Nitrogen atoms in the cation and the Phosphorus atom in the anion. All radial distribution functions were calculated in 3-D. Similar results are observed for the pore size 2.5 nm in this study. From this figure it is apparent that the cation-cation, cation-anion and anion-anion g(r)s for the confined ions in the
center of the pore and for the bulk ions are very similar, suggesting that the ions in the center of the pore have a structure that closely resembles that of the bulk IL.

**Figure 4.4.** Radial distribution function $g(r)$ of cation-cation, cation-anion and anion-anion for the ions in different regions of the three pore morphologies at $T = 300$ K. In all cases, $\rho = \rho_{\text{bulk}}$, pore size $H=3.7$ nm. Each confined $g(r)$ was vertically displaced to help visualize the difference from the bulk system.

However, the $g(r)$ for the ions near the surface exhibits some difference with respect to their counterparts for the bulk IL. The figures indicate that the heights of the different peaks of $g(r)$ for the ions near the surface increase significantly. We can also observe that the first peaks of the cation-cation and anion-anion $g(r)$ for the ions confined in CMK-3 are at slightly shorter distances in the region near the surface as compared with the bulk IL; the first peaks of cation-
cation g(r) for the ions confined in slit pore and anion-anion g(r) for the ions confined in slit pore and CNT show another extra shoulder as compared with the bulk IL. The results suggest that the arrangement of the cations and anions do not represent a purely liquid system, but rather have a short range order near the pore walls. [58, 161, 169]

4.4. Dynamical Properties

In EDLC systems, the specific power is affected by the internal resistance, which in turn is influenced by the mobility of the individual ions. This section presents analysis on the dynamics of the confined IL as a function of pore size and pore morphology. In Figure 4.5 we plot the mean squared displacement (MSD) of ions for different regions in the non-confined direction at 300 K. In this figure all the models have the pore size $H=3.7$ and $\rho = \rho_{bulk}$. For each system the cations are moving slightly faster than anions independent of their distance from the pore walls, but this effect decreases with increasing pore size. The density and dynamics of the ions in the center of the pore are very similar to those observed for the ions in the bulk IL, resulting in faster dynamics than the ions around the surface of the wall pores. Decreasing dynamics are observed for both cations and anions near the surface due to the strong Van der Waals forces between the cations and the carbon surface, and the coulomb forces between the cations and anions. However it is important to note that the atomic level roughness of the amorphous carbon nanorods in the CMK-3 models reduce the attraction between the imidazolium rings and the carbon surface, thus allowing for less layering effects and more mobility. These results agree with the structural results in Figure 4.3 and Figure 4.4. Although not shown, the dynamics are faster as the pore size increases for every carbon model; this is due to the increased ratio of “center ions” to “surface ions”.
It can be observed from Figure 4.2 that the ions are confined in two dimensions in the CNT model and one dimension in the slit pore model; however in the CMK-3 material, the hexagonal arrangement of the carbon rods and their surface curvature results in non-uniform confinement effects.

![Figure 4.5](image)

**Figure 4.5.** Mean squared displacement of the cations and anions confined in different pore morphologies for different regions, as a function of their distance from the pore walls. Results for the bulk system at the same temperature are compared. In all cases, $\rho = \rho_{\text{bulk}}$, pore size $H=3.7$ nm, $T=300$ K, all MSDs are calculated in the non-confined direction.

It is clear in Figure 4.5 that the dynamics of the ions inside the CMK-3 systems are greater than those of the CNT or slit pore models. This large increase in mobility can be explained by the lack of layering as a result of the reduced confinement effects and a higher ratio
of “center ions” due to the geometry of the carbon nanorods. As a whole, these results indicate that the variation in pore morphologies plays an important role in influencing the dynamics of the ionic liquid. In Figure 4.6, we also present multiple single-particle time autocorrection functions (ACF) for the rotational motion of cations, namely, (1) the reorientation of the cation around an axis in the plane of the imidazolium ring, in the direction of a vector joining the N-N atoms, and (2) similar to N-N but now the rotation is in the direction of a vector joining the N-H atoms in the cations. The N-N and N-H vectors are defined in Figure 4.1. The ACF for the velocity of the center of mass of the cation is not included, as previous studies in bulk and confined systems suggest that the translational motion of the cation is orders of magnitude faster than its rotational motion. From Figure 4.6 we observe that in every model the rotational motion of cations requires more time to decorrelate in the N-N direction than the N-H direction; also the rotational motion in the center of the pore needs less time to decorrelate than near the surface of the pore walls. From the discussion above we know that the properties in the center of the pore are less influenced by the pore walls so their properties are more like the properties of the bulk ions. These results also indicate that the decorrelating time is dependent on the pore morphologies. Compared to the CNT and slit pore models, the rotation of cations confined in CMK-3 requires the least amount of time to decorrelate. These observations support the results from Figure 4.5 that fewer ions in the CMK-3 material are affected by the confinement effects found in the CNT and slit pore systems. Therefore, the ACFs of ions in CMK-3 are the most like the bulk ions, which need very short times to decorrelate. The ACF results for the 2.5 nm pore size systems are not shown, but longer decorrelation times are required for every carbon model.
Figure 4.6. Single-particle time correlation functions for the rotational motion of the cations confined in different regions. All the pore morphologies have the same pore size $H=3.7$ nm. The correlation functions depicted are the following: N-N: reorientation of the cation around an axis in the plane of the imidazolium ring, in the direction of a vector joining the N-N atoms, and N-H: similar to N-N but now the rotation is in the direction of a vector joining the N-H atoms in the cation.

4.5. Concluding Remarks

We performed MD simulation of IL $[\text{BMIM}^+][\text{PF}_6^-]$ confined in different nanoporous carbon materials such as CMK-3, multi-walled graphitic slit pores and multi-walled carbon nanotubes of different pore sizes. The structural and dynamical properties of the confined IL
systems were compared to the non-confined system. Our results indicate that varying the pore size and pore morphologies have a profound influence on the structural and dynamical properties of the confined IL. The mass density profiles of the ions show evidence of significant layering, with the number of layers and the relative positions of the density peaks for [BMIM\(^+\)] and [PF\(_6\)\(^-\)] varying with pore morphologies and pore sizes. Larger heterogeneities in the density of confined IL in the CNT model are observed, suggesting that the ions tend to cluster together leaving other regions with lower densities than the bulk density. Furthermore, variations in pore size can cause some changes to the number of layers. The radial distribution functions for the ions in the center regions exhibit the same features as the bulk ions for different pore morphologies and pore sizes; however, some variation in the height and position of the peaks are observed in the region near the pore walls. Regarding the dynamical properties, our results for the MSD and single-particle time correlation functions for the rotational motion of cations indicate that the dynamics of the confined [BMIM\(^+\)][PF\(_6\)\(^-\)] have some common characteristics. The [BMIM\(^+\)] ions have faster dynamics than the [PF\(_6\)\(^-\)] ions and ions near the carbon surfaces exhibit slower dynamics and reduced mobility than the ions near the center of the pore. However there is also evidence that some characteristics are influenced by the pore morphologies. Our results indicate that the ions in the CMK-3 model decorrelates in the least amount of time and also has the fastest dynamics when compared to the ions confined in the CNT and slit pore models. These differences are related to the number of ions in each model that are influenced by the confinement effects such as layering and preferential orientation. A decrease in the pore size is found to decrease the ratio of “central ions” to “surface ions”. When the pore size or ratio is small enough, layering propagates throughout the whole system and the characteristics of the system resembles the surface ions observed in this study.
5.1. Introduction

Ionic liquids (ILs) are molten salts typically composed of bulky organic cations with smaller organic or inorganic anions, and usually are in liquid phase near room temperatures. The properties of ILs are highly tunable; as many as $10^9$ to $10^{18}$ ILs could be formed by combining different cations and anions.\cite{62} Properties such as low vapor pressure, nonflammability, high conductivity, thermal and chemical stability, among others, have made ILs to attract interest for applications as ‘green solvents’ for chemical synthesis and catalysis,\cite{29, 63, 170} CO$_2$ sequestration,\cite{171-176} and as alternative electrolytes in electrochemical double layer capacitors (EDLCs)\cite{65, 66, 75, 76, 177, 178} and dye-sensitized solar cells (DSSCs).\cite{10, 11, 179-189} In EDLCs and DSSCs, the IL is in contact with a nanoporous electrode, and therefore a fundamental understanding of the properties of ILs inside nm-sized pores is crucial to rationally design EDLCs and DSSCs, and significantly advance those technologies. Molecular simulations are well positioned to make important contributions towards achieving a fundamental understanding of the interfacial properties of ILs near nanoporous electrodes.

A number of studies have focused on IL and ions near solid surfaces;\cite{27, 47, 56, 94-98, 101, 190-204} likewise, a number of simulation reports have been published on ILs confined inside nanopores with slit-like,\cite{14, 47-56, 102-115, 142, 205-208} cylindrical\cite{56-60, 114-116, 209} and other complex\cite{117, 144} pore geometries. Previous simulation studies from our group\cite{60, 112, 117, 205, 206} focused on understanding the structure and dynamics of ILs inside carbons with pores of different geometries. In direct relation to our previous studies, the main objective of this work is to study in detail the structural and dynamical properties of the IL [EMIM$^+$][TFMSI]$^-$.
(Figure 5.1) confined inside a slit-like nanopore formed by two parallel (110) rutile TiO₂ walls. TiO₂ is one of the semiconductor materials that have been used extensively in DSSCs, [10, 11, 42-45, 210-219] and a few simulation studies have been published on ILs near a TiO₂ surface. [27, 220] However, these studies focused mainly on understanding the structure and orientation of the ILs [BMIM⁺][PF₆⁻] and [BMIM⁺][NO₃⁻] near the rutile wall. Here we have also focused on the dynamics of the confined IL, which is one of the factors that determine the macroscopic electrical resistance in devices such as EDLCs and DSSCs. Furthermore, we have also explored the effect of variations in pore loading (i.e., the amount of IL inside the nanopores as compared with the density of the IL in the bulk at the same temperature) on these structural and dynamical heterogeneities. For example, in an experimental setup, the amount of IL inside a nanoporous material could vary depending on variables such as temperature, pressure, and nature of the porous material (tortuous pores might be difficult to fill completely; also, the strength of interactions between the pore walls and the IL could affect the amount of IL inside the nanopores). The rest of this paper is structured as follows. Section 5.2 contains a description of our computational models and methods. In section 5.3 we present results and a discussion of the structural and dynamic properties of the confined ILs, and in section 5.4 we summarize our main findings.

5.2. Computational Details

In this work we studied the structural and dynamical properties of the ionic liquid [EMIM⁺][TFMSI⁻] (Figure 5.1) confined inside two parallel (110) rutile TiO₂ walls with a pore size of $H = 5.2$ nm. We considered two types of models in this work; details of our systems are shown in Table 5.1. In model A (Figure 5.2a), the slit rutile pore is directly connected to two IL reservoirs at both sides (Fig. 5.2a).
Initially, the ions are arranged in an arbitrary lattice out of the pore, with dummy walls closing the entrance to the pore. When the simulation starts (see below), the dummy walls are removed and the ions enter the pore. Such a setup has been used in several previous studies of ILs inside nanopores,\cite{103,109} and could (in principle) be used to determine the ‘equilibrium’ amount of IL inside the nanopore (in theory, a grand canonical Monte Carlo simulation could be performed to determine the amount of IL inside the pore that is in equilibrium with an IL reservoir at relevant conditions of chemical potential and temperature; however, such a simulation would be very difficult due to the high density of the IL and the strong interactions between the ions, which would hinder successful insertion and removal of ions). Nevertheless, in setup A, the properties of the confined IL can be affected by the significant amount of IL that is at the interfaces with the two reservoirs. In contrast, in model B (Figure 5.2b) the slit rutile pore is not directly connected to any IL reservoir; the ions are initially placed in a lattice inside the pore, and various pore loadings ($0.6\rho_{\text{bulk}}$, $0.8\rho_{\text{bulk}}$ and $\rho_{\text{bulk}}$, where $\rho_{\text{bulk}} \sim 1.5$ g/cm$^3$) were considered by changing the number of IL pairs inside the volume of the pore (218, 290, and 363 ion pairs, respectively; see Figure 5.3). The setup used in model B was used in our previous simulation studies,\cite{60,112,117,206} and can allow us to explore the effect of varying amounts
of IL inside the pores; however, the main drawback is that one does not know the ‘equilibrium’ amount of IL that should be inside the pore. Periodic boundary conditions were applied in all directions. All our IL/rutile systems were placed in the center of an orthorhombic box; the total length of this box in the z direction was 12 nm, which was large enough to avoid any interaction between the adsorbed ions and its nearest periodic image in that direction. In model A, the total length of the simulation box in the x direction was 30 nm (Table 5.1), and the length of the rutile walls in this direction was 5.6 nm (Figure 5.2). In model B, the total length of the rutile walls in the x and y directions are equal to the dimensions of the simulation box in those directions (Table 5.1, Figure 5.2).

Classical molecular dynamic (MD) simulations in the NVT ensemble were performed using the GROMACS MD package [61] at $T = 333$ K; this temperature is higher than the melting point of [EMIM$^+$][TFMSI$^-$], $T_m = 258.15$ K. The two pore walls are formed by repeating the rutile unit cell along the [100], [010], and [001] and then cutting the box along the (110) plane to form a slab of dimensions 5.60 nm $\times$ 5.10 nm. The oxygen and titanium atoms in the rutile surface were modeled as LJ spheres with $\sigma_o = 0.303$, $\sigma_{Ti} = 0.392$, nm, $\epsilon_o = 0.12$ kcal/mol, and $\epsilon_{Ti} = 0.041$ kcal/mole [221, 222]. The partial charges on oxygen and titanium atoms are -1.098e and 2.196e respectively [223].

The force field parameters for the cations [EMIM$^+$] and anions [TFMSI$^-$] were taken from Kelkar and Maginn;[224] these parameters can adequately reproduce the experimental density, heat of vaporization and diffusion coefficient of the bulk IL. For model B, the densities of the confined IL were calculated using a volume $V_{min} = xy (z-e_c)$. Our results for the mass density profiles (Figure 5.4 and 5.5) indicate that the densities of the confined ions reach a value of zero at $z \sim \sigma_c / 2$. In all our simulations, the Lennard-Jones interactions were cut off at 1.2
nm, and the long range coulomb interactions were handled by the particle-mesh Ewald (PME) method [127] with a cutoff of 1.0 nm and a grid spacing of 0.1 nm. The improved velocity-rescaling algorithm recently proposed by Parrinello et al. [125, 126] was used to mimic weak coupling at different temperatures with a coupling constant of 0.1 ps.

We first minimized the energy of our initial configuration using the steepest descent method. Afterwards, we ran MD simulation using a time step of 1.0 fs. The systems were melted at 600 K for 1 ns, and then annealed from 600 to 333 K in stages: 400 ps at 550 K, 400 ps at 500 K, 200 ps at 450 K, 200 ps at 400 K, 200 ps at 350 K, and 200 ps at 333 K. For model A we removed the dummy walls after annealing the system at the desired temperature of 333 K and let the ions fill the pore. All our systems were equilibrated and the properties of interest were sampled for 20.0 ns at 333 K. Finally, we repeated the above steps (melting, annealing, equilibration and averaging) at least one additional time starting from a different initial configuration; our reported results are averaged over at least two independent realizations of the same system. Such a procedure is adopted in an attempt to overcome the difficulties posed by the slow dynamics of ILs, which are likely to be exacerbated when these compounds are confined inside a nm-sized slit pore. Representative simulation snapshots of the ILs confined inside a rutile(110) pore at 333 K and different pore loadings (model B) are depicted in Figure 5.3.

**Table 5.1. System details**

<table>
<thead>
<tr>
<th>Model system</th>
<th>Number of IL pairs</th>
<th>Dimensions (x, y, z)</th>
<th>Amount of IL inside pore (% of ρ_{bulk})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1056</td>
<td>30.0 × 5.1 × 12.0</td>
<td>111.4</td>
</tr>
<tr>
<td>B</td>
<td>363</td>
<td>5.6 × 5.1 × 12.0</td>
<td>100.0</td>
</tr>
<tr>
<td>B</td>
<td>290</td>
<td>5.6 × 5.1 × 12.0</td>
<td>80.0</td>
</tr>
<tr>
<td>B</td>
<td>218</td>
<td>5.6 × 5.1 × 12.0</td>
<td>60.0</td>
</tr>
</tbody>
</table>
Figure 5.2. Final configurations of the model systems studied, $H = 5.2$ nm and $T = 333$ K. The oxygen and titanium atoms in the rutile (110) surface are depicted in red and white; cations and anions are depicted in purple and green.

Figure 5.3. Representative simulation snapshots of the IL $[\text{EMIM}^+][\text{TFSI}^-]$ confined inside a rutile (110) slit pore of width $H = 5.2$ nm at 333 K and different pore loadings (model B): (a) $\rho = 0.6 \rho_{\text{bulk}}$, (b) $\rho = 0.8 \rho_{\text{bulk}}$, (c) $\rho = \rho_{\text{bulk}}$. Cations and anions are depicted in purple and green.
5.3. Results and Discussion

5.3.1 Structural Properties

In Figure 5.4 we show density profiles in the $z$ direction for the ions inside our rutile pores (models A and B, Fig. 5.2). The results shown in Fig. 5.4 for model B were obtained at a pore loading $\rho = \rho_{\text{bulk}}$. In model A, the IL within the slit rutile nanopore is in contact with two IL reservoirs, and therefore the density of the IL within the slit rutile nanopore evolves during the simulation and equilibrates around a value of $\rho = 1.114\rho_{\text{bulk}}$. For both models A and B, cations and anions have the highest density near the pore surfaces, with noticeable layering behavior observed throughout the system. The oscillations in density reduce in amplitude as we move away from the pore walls towards the center of the pore. The density profiles observed for models A and B are very similar, with the first layer of ions located at about the same distance from the pore walls (0.4 nm) and having about the same thickness (0.7 nm) for both models. We observe small differences in the positions of the peaks for both models A and B as we move farther away from the pore walls, and the density of ions near the center of the pore seems to be larger for model A. These differences can be due to the different amounts of IL inside models A and B (Table 5.1), and due to the fact that model B is a ‘closed’ system where we fixed the density to be $\rho = \rho_{\text{bulk}}$ over the whole simulation. In contrast, model A is an ‘open’ system where the IL within the slit rutile nanopore is in contact with two IL reservoirs, and the density of the confined IL equilibrates around $\rho = 1.114\rho_{\text{bulk}}$. In particular, the results shown in Fig. 5.4 are very similar to those observed by us for the same IL at the same temperature ($T = 333$ K) inside a slit graphitic pore with the same pore size ($H = 5.2$ nm).[205] The layering effects observed for $\text{[EMIM]}^+[\text{TFMSI}^-]$ near the center of a slit graphitic pore (Fig. 5.2 in ref.[205]) were weaker than those observed for the same IL in the center of a rutile slit nanopore (Figure 5.4 here);
furthermore, two peaks in the density are observed for the ions near the graphitic pore walls (Fig. 5.2 in ref.[205]), whereas only one density peak is observed for the ions near the rutile pore walls (Figure 5.4 here). These observations might be explained by looking at the strength of the interactions between [EMIM$^+$][TFMSI$^-$] and the atoms in the pore walls. Electrostatic and dispersion interactions are present between [EMIM$^+$][TFMSI$^-$] and the Ti and O atoms in the rutile walls, whereas only weaker van der Waals interactions were present between the ions and the C atoms in the graphitic walls.

In Figure 5.5 we present the number density profiles for model B, where the confined IL has a density ranging from $0.6\rho_{\text{bulk}}$ to $\rho_{\text{bulk}}$ at 333 K; snapshots of these systems are depicted in Figure 5.3. For $\rho = 0.6\rho_{\text{bulk}}$, the IL is mostly adsorbed near the pore walls, with the center regions of the pore partially depleted of IL (Figs. 5.3, 5.5). Increases in pore loading lead to increases in the density of IL in the center of the rutile pore, but cause negligible changes in the density of ions near the pore walls (Fig. 5.5). This observation contrast to what we observed for the same IL within a slit graphitic nanopore of the same width ($H = 5.2$ nm),[205] where increases in the density of IL within the pore lead to increases in the local density of ions in the center of the pore and near the pore walls. These differences might be caused by differences in the wall-IL interactions discussed above, where the IL-rutile interactions are stronger than the IL-graphite interactions.

Following our previous study,[205] from the density profiles (Figs. 5.4 and 5.5) we divided the confined ions into two different layers/regions: the first layers (closest to the pore walls) and the center region (see dashed lines in Figure 5.5). This separation into layers/regions is slightly different from the one we used in our previous study of the same IL in slit-like
graphitic nanopores,[205] where we had the ions separated into first and second layers and a center region.

![Graph showing number density profiles along the z-direction](image)

**Figure 5.4.** Number density profiles along the z-direction of [EMIM][TFMSI] inside rutile nanopores with \(H = 5.2\) nm, model A (dashed lines) and model B (solid lines). Results for model B were obtained at a pore loading \(\rho = \rho_{\text{bulk}}\).

![Graph showing number density profiles of confined ions](image)

**Figure 5.5.** Number density profiles of the confined ions along the z-direction at different pore loadings (model B). The vertical dotted lines indicate how the confined ions were divided into different layers/regions for further study.

However, direct comparison between the results of that study and this one is still possible, as the first layers in both studies had approximately the same thickness. Furthermore, the second layers...
and the center regions had similar structural properties in our previous study.[205] To further understand the structure of the ions in the different regions of the pore and at different pore loadings, we studied the radial distribution function \( g(r) \) of the ions inside the pore models A and B. These \( g(r) \) functions are calculated using the CR atom of the cation and the NJ atom of the anion (Figure 5.1). Figure 5.6 represents the site-site intermolecular \( g(r) \) for cation-cation, anion-anion and anion-cation confined inside a rutile (110) pore of \( H = 5.2 \) nm at \( T = 333 \) K. The left and right panels of Fig. 5.6 show results for the ions in the first layers and in the center regions (see dashed lines in Figure 5.5) at different pore loadings. For the ions in the center of the pore, the \( g(r) \) functions observed for model A are very similar to those obtained for model B at \( \rho = \rho_{\text{bulk}} \). For model B at decreasing pore loadings, we observe small increases in the height of the \( g(r) \) peaks, but the positions of these peaks remain unchanged with pore loading. These results indicate that variations in the pore loading do not affect the liquid structure of the IL in the center of the pore, which is very similar to the structure observed for the IL in a bulk system (Fig. 5.6).

These results for the IL in the center of the pore are similar to those observed in our previous study[205] of the same IL, \([\text{EMIM}^+][\text{TFMSI}^-]\), inside a graphitic slit like pore of the same size, \( H = 5.2 \) nm; however, larger variations in the height of the peaks were observed for the ions in the center of the graphitic pore. The ions near the rutile pore walls, in contrast, have a liquid structure that is different from that of bulk \([\text{EMIM}^+][\text{TFMSI}^-]\) (Fig. 5.6, left panel). The peaks in the cation-anion \( g(r) \) for the first layers of ions and for the bulk ions are observed at similar values of \( r \), but new peaks are observed for the cation-cation and anion-anion \( g(r) \) at \( r = 0.4 \), which were not present in their bulk counterparts. Therefore, these results suggest that the rutile walls seem to induce changes in the liquid structure of \([\text{EMIM}^+][\text{TFMSI}^-]\) near the pore walls. This observation contrasts with what we observed for the first layers of the same IL within a slit.
graphitic nanopore,[205] which exhibited a liquid structure similar to that of the bulk IL. From the results shown in the left panel of Fig. 5.6, we observe that variations in the amount of IL inside the rutile pore lead to changes in the liquid structure of the ions near the pore walls, with some of the peaks in $g(r)$ moving to slightly different values of $r$, varying their height or disappearing.

The orientation of the ions near the rutile surfaces was determined by calculating $\cos(\theta)$, where $\theta$ is the angle between the vector normal to the rutile surface and (1) the vector normal to the imidazolium ring of the cations, or (2) the vector formed by joining both CJ atoms in the anions (Fig. 5.1). Figure 5.7 (left panel) shows the center of mass of the ions in the first layer, where orange and green circles depict cations and anions lying parallel to the surface ($\theta < 25^\circ$), and blue and purple represent cations and anions lying tilted with respect to the surface ($\theta > 25^\circ$). Results for the cations and anions suggest that they can adopt multiple orientations near the rutile walls; in contrast, the same ions tend to align parallel to carbon walls.[205] Three typical orientations of the cations near rutile walls are shown in the right panel of Figure 5.7. These orientations might be caused by interactions between the O atoms in the rutile walls and the C and H atoms in the imidazolium ring of the cation (CR, CW and HA, Fig. 5.1).

For the anions, the snapshots depicted in the right panel of Fig. 5.7 suggest that their orientations might be caused by interactions between the O atoms in the anions (OJ in Fig. 5.1) and the Ti atoms in the rutile surfaces. In the center region of the pore, the cations and anions do not exhibit any preferential orientations (results not shown for brevity).
Figure 5.6. Radial distribution functions $g(r)$ of (a) cation–cation, (b) cation–anion, and (c) anion–anion for the different regions of [EMIM$^+$][TFMSI$^-$] confined inside a slit pore of $H = 5.2$ nm for model A and at different pore loadings of model B at 333 K. Left panel shows the results for the first layers and right panel for the center region.
Figure 5.7. (Left) Positions of the center of mass of cations and anions in the first layer, when $\rho = \rho_{\text{bulk}}$; different colors are used to show different orientation. Orange and green depict $[\text{EMIM}^+]$ and $[\text{TFMSI}^-]$ lying parallel to surface ($\theta < 25^\circ$), whereas blue and purple depict $[\text{EMIM}^+]$ and $[\text{TFMSI}^-]$ lying tilted with respect to the surface ($\theta > 25^\circ$). Right panel shows multiple preferential orientations of the cations (top) and anions (bottom) at the rutile surface (O = red, Ti = white).

5.3.2 Dynamical Properties

Our previous studies [107, 225-228] suggest that the dynamics of ILs confined inside carbons with pores of different morphologies are complex and heterogeneous. The confined ions have different mobilities depending on how far they are from the pore walls, and their dynamics are significantly affected by properties such as pore size and shape, amount of IL inside the pores, and presence of electrical charges. In Figure 5.8 we present the single-particle time autocorrelation functions for the reorientation of $[\text{EMIM}^+][\text{TFMSI}^-]$ inside rutile slit pores, following the work of Urahata and Ribeiro.[229] The autocorrelation functions of the ions in the center of the pore (Fig. 5.8, bottom panel) reach a value close to zero in about 2 ns; in contrast, the ions near the pore walls still show important correlation effects in their rotational motion after 8 ns, possibly due to the strong interactions of the rutile walls with the ions, which in turn
lead to high densities of IL near the walls. Varying the amount of IL inside the rutile pores does not significantly affect the reorientation dynamics of the confined ions, although the autocorrelation function for the cations near the walls at \( \rho = 0.8 \rho_{\text{bulk}} \) exhibits a slightly faster decay.

**Figure 5.8.** Single-particle time correlation functions for the reorientation of cations (left panel) and anions (right panel) in the different layers/regions (Fig. 5.5) inside a slit rutile pore. The correlation functions depicted are the reorientation of cations around an axis perpendicular to their imidazolium ring, and the reorientation of anions around the vector joining both CJ atoms (Fig. 5.1).

In Figure 5.9 we show the MSD of the ions in the directions parallel to the rutile walls (x and y directions). Results are reported for the cations and anions near the rutile walls (first layers) and in the center of the pore, for models A and B (and in the latter setup, at different pore
loadings). In all cases, the ions in the center of the pore have faster dynamics than the ions near the pore walls. Among the systems studied, the slowest dynamics were observed for both types of ions in model A irrespective of their distance to the pore walls, mainly due to the high density of the confined ions in this setup ($\rho = 1.114\rho_{\text{bulk}}$). For model B, the dynamics of the cations in all regions of the pore, and of the anions in the center of the pore decrease monotonically with a reduction in pore loading; the fastest dynamics are observed for $\rho = \rho_{\text{bulk}}$. The anions near the rutile walls do not follow these trends, exhibiting the fastest dynamics at a pore loading of $\rho = 0.8\rho_{\text{bulk}}$. The slower dynamics observed when we reduce the amounts of IL inside the pore might be due to the formation of regions with low and high density of IL inside the pore (Fig. 5.3). These trends agree with those observed for ILs inside a carbon nanotube,[60] a slit graphitic nanopore[205] and a CMK-3 carbon material[117], in which reducing the amount of IL inside the pore beyond a certain percentage of $\rho_{\text{bulk}}$ could lead to a slowdown in the dynamics of the confined ions. The heterogeneity in the dynamics of the ions inside a rutile nanopore at different pore loadings is depicted in Figure 5.10, where we have color-coded the ions according to their total displacement during 10 ns. Results from this figure indicate that the ions near the pore walls have slow dynamics, as observed in the MSD results (Fig. 5.9). Results from Figure 5.10 also suggest the presence of dynamical heterogeneities for the ions in the center of the pore at both pore loadings. These trends agree with our results for [EMIM]$^+$][TFMSI$^-$] inside a slit graphitic pore of the same size, $H = 5.2$ nm.[205] In that study, for $\rho = 0.6\rho_{\text{bulk}}$, we further divided the ions in the center regions of the pore into two regions, a ‘liquid’ side and a ‘vacuum’ side, and we found that the cations in the ‘liquid’ side have a somewhat reduced mobility, but the anions have fast dynamics (even faster than in a bulk system). These features suggest that the dependence of dynamic properties on pore loading may arise from the separation of ions into a
liquid side and a vacuum side, and possibly from the local heterogeneity introduced by the additional vacuum-liquid interface.

![Figure 5.9](image)

**Figure 5.9.** Mean square displacements (MSDs) of cations (left panel) and anions (right panel) inside a slit rutile pore of $H = 5.2$ nm. The MSDs reported are in the direction parallel to the rutile walls ($x$ and $y$ directions), for the ions in the first layers (close to the pore walls, top panel) and center region of the pore (bottom panel). The parallel component of the MSD of all confined ions (dashed lines) at different pore loadings is also shown.

The dynamics of $[\text{EMIM}^+][\text{TFMSI}]$ inside a slit rutile pore are significantly slower than those observed for the same IL inside a slit graphitic pore of the same size, $H = 5.2$ nm.[205] The dynamics of ions closest to the rutile walls are about an order of magnitude slower than those of ions closest to graphitic walls. The ions in the center of a rutile pore exhibit a slightly enhanced mobility, but their dynamics are about 2-4 times slower than those of ions in the center.
of a graphitic pore. These results suggest that the interactions of the pore walls with the IL ions can significantly affect the dynamics of the confined IL.

Figure 5.10. Total displacement of cations (top panel) and anions (bottom panel) inside a rutile slit pore, $\rho = \rho_{\text{bulk}}$ (a and c) and $\rho = 0.6 \rho_{\text{bulk}}$ (b and d). Displacements were computed over a time of 10 ns.

5.4. Concluding Remarks

The structure and dynamics of the ionic liquid (IL) $[\text{EMIM}^+][\text{TFMSI}^-]$ inside a rutile (110) slit nanopore of width $H = 5.2$ nm at $T = 333$ K were studied using classical molecular dynamics (MD) simulations. The effect of different amounts of IL ($\rho = 60\%$, $80\%$ and $100\%$ of
ρ_{bulk}) inside the rutile nanopore on the structure and dynamics of the confined IL was studied. We also analyzed a situation in which the IL inside the rutile nanopore was in direct contact with two IL reservoirs at both sides (Fig. 5.2a), in which the density of the confined IL equilibrated around ρ = 1.114ρ_{bulk}. All these results were compared against those obtained in our previous study[205] of the same IL inside a slit graphitic nanopore of the same width and at the same temperature. Layering behavior was observed for [EMIM^+][TFMSI^-] inside the slit rutile nanopore; formation of layers was also observed for the same IL inside a slit graphitic pore,[205] but in the latter case layering effects were weaker in the center of the pore and two density peaks were observed near the pore walls. Reductions in the amount of IL inside a slit rutile nanopore lead to a reduction in the density of IL in the center of the pore, with negligible variations in the density of IL near the rutile walls; in a graphitic nanopore, in contrast, reductions in the density of the IL near the walls and in the center of the pore were observed. Changes in the amount of IL inside a rutile nanopore lead to important changes in the liquid structure of the ions near the pore walls, which departed significantly from the g(r) functions observed for a bulk IL; the ions in the center of the rutile pore had a liquid structure similar to that of the bulk IL. These observations contrast to our previous results for the same IL inside a graphitic slit pore,[205] for which the liquid structure near the graphite walls and in the center of the pore was always similar to that of the bulk IL at all the pore loadings considered. Cations and anions adopted multiple orientations near the rutile walls, which contrast with the parallel orientations that were uniformly observed for the same ions near graphitic walls.[205] The dynamics of [EMIM^+][TFMSI^-] inside a slit rutile pore are significantly slower than those observed for the same IL inside a slit graphitic pore of the same size, H = 5.2 nm.[205] The dynamics of ions closest to the rutile walls are about an order of magnitude slower than those of
ions closest to graphitic walls. The ions in the center of a rutile pore exhibit a slightly enhanced mobility, but their dynamics are about 2-4 times slower than those of ions in the center of a graphitic pore. The effects of variations in the amount of IL inside a rutile pore on the dynamics were very marked, with reductions of up to 4 times in the mean squared displacements (MSDs) of the ions in the different regions of the pore; in contrast, pore loading seem to lead to smaller variations in the dynamics of ILs inside a graphitic slit nanopore.[205] All these observations might be explained by looking at the strength of the interactions between [EMIM$^+$][TFMSI$^-$] and the atoms in the pore walls. Electrostatic and dispersion interactions are present between [EMIM$^+$][TFMSI$^-$] and the Ti and O atoms in the rutile walls, whereas only weaker van der Waals interactions were present between the ions and the C atoms in the graphitic walls. These results suggest that the strength of the interactions between the pore walls and the IL can significantly affect the structure and dynamics of the confined IL.
CHAPTER 6 IONIC LIQUIDS CONFINED INSIDE COCONUT SHELL ACTIVATED CARBON ELECTRODES: A MOLECULAR SIMULATION STUDY

6.1. Introduction

A fundamental understanding of the properties of IL electrolytes inside carbon nanopores is relevant for their applications in energy storage in electrochemical double layer capacitors (EDLCs); [3, 39, 46, 65, 79, 82, 85, 230, 231] several groups [20, 26, 65, 66, 68, 70-72, 75, 76] have attempted to use ILs and their mixtures with solvents as alternative electrolytes in EDLCs, motivated by their excellent thermal stability, non-volatility, high ion density and wide electrochemical window. The macroscopic performance of IL-based EDLCs is determined by the structural, dynamical and electrical properties of the IL confined inside the nanopores. Molecular simulations, in close interplay with experiments, are well positioned to provide such fundamental understanding. Recent simulation and theoretical studies have focused on ILs and molten salts confined inside ‘ideal’ nanopores of simple geometry, i.e., slit-like [14, 47-56, 102-115, 141, 142, 206-208] and cylindrical. [56-60, 114-116, 209] Although these studies have provided important insights about the properties of the electrical double layer in confined ILs, ideal pore models typically neglect effects of heterogeneities in pore shape and size and pore surface roughness, which are present in real nanoporous materials. Recent simulation studies [101, 144, 152, 232-235] suggest that the effect of such heterogeneities can be important. For example, we recently found that the structural and dynamical properties of an IL confined in a model CMK-3 carbon (which exhibits regularly interconnected pores with heterogeneous size and morphology, and significant pore surface roughness), are substantially different from the properties of the same IL confined inside slit-like and cylindrical nanopores. [235] Furthermore, the shape of the curve of differential capacitance vs. electrode potential was found to be affected by variations in the
structure of the electrode surface.[101, 232] One fundamental question that remains to be answered is how heterogeneities in pore size, shape and surface roughness, affect the structural and dynamical properties of the IL inside the nanoporous electrodes. These properties ultimately affect macroscopic properties in EDLCs such as the capacitance and electrical resistance.

In this work we performed a systematic study of the structure and dynamics of a typical IL, [emim][NTf₂], confined inside two model carbon porous materials, a slit graphitic nanopore and a realistic model of a coconut shell porous carbon developed by Pikunic et al.[236, 237] This model was generated using a reverse Monte Carlo simulation protocol in a way that the model material matches the experimental radial distribution function $g(r)$ of a coconut shell activated carbon. This model exhibits semi-graphitic carbon sheets with different sizes and shapes, which form irregularly connected pores of roughly rectangular shape. Porous carbons typically used in EDLCs are often derived from coconut shell, wood, coal and other carbon sources that have low cost and are abundant in nature. Results obtained with these two pore models are directly compared here, as slit-shaped graphitic pores are often used as an approximate model for different activated carbon materials. The rest of this paper is structured as follows. Section 6.2 contains a description of our computational models and methods. In section 6.3 we present results and a discussion of the structural and dynamic properties of the ILs confined in both model porous materials, and in section 6.4 we summarize our main findings.

6.2. Computational Details

Classical molecular dynamics (MD) simulations were carried out using GROMACS 4.0.5 software[61] in the $NVT$ ensemble. The IL [emim][NTf₂] (Fig. 6.1) was modeled using parameters from Kelkar and Maginn,[224] which can adequately reproduce the experimental density, heat of vaporization and diffusion coefficient of the bulk IL. Two pore models were
considered in this study (Figure 6.2), a slit graphitic pore similar to the one used in our previous studies,[112, 205, 206] and a realistic model of a coconut shell porous carbon developed by Pikunic et al.[236, 237] This model is very similar to the one developed by Thomson and Gubbins,[238] and was generated using a reverse Monte Carlo simulation protocol in a way that the model material matches the experimental radial distribution function $g(r)$ of a coconut shell activated carbon, subject to several physical constraints typical of graphitic carbons (namely that carbon atoms can only have two or three nearest neighbors, C-C distances are 1.42 Å, and bond angles are 120°). Details of the simulation protocol and the model material are presented in the original references.[236-238] In order to reduce the computational cost of our calculations using this model material, we cut a section of size $L_x = 6.8$ nm, $L_y = 6.3$ nm and $L_z = 1.4$ nm from the original model material to use in our simulations. This section is representative of the original model material and contains all its relevant physical features. The coconut shell porous carbon model used here is composed of semi-graphitic walls of different sizes and shapes and with a minor degree of corrugation, which form pores of roughly rectangular shape that are irregularly interconnected. As in our previous studies, the carbon atoms in our model porous materials were represented as Lennard-Jones spheres with $\frac{\varepsilon_c}{k} = 28$ K and $\sigma_c = 0.340$ nm.

**Figure 6.1.** A schematic representation of the IL [emim$^+$][NTf$_2$]. The labels are the atom notations used in this work.
Figure 6.2. (Top panel) Front views of (a) coconut shell carbon model, average pore size \( H = 0.75 \) nm; and (b) slit graphitic pore, size \( H = 0.75 \) nm. (Bottom panel) Representative simulation snapshots of the model systems studied, \( H = 0.75 \) nm and \( T = 333 \) K. Carbon atoms in the walls are depicted in grey; cations and anions are depicted in red and green.

We considered three pore sizes for our slit graphitic porous carbon, \( H = 0.75, 0.93 \) and \( 1.23 \) nm. These sizes were chosen based on the work of Wu et al.,\cite{103} who reported a U-shaped curve for the capacitance of ILs inside slit-shaped pores, with the minimum in capacitance observed for a pore size of about \( 0.91 \) nm (however, those results were obtained for a coarse-grained model of a different IL, \([\text{dmim}^+][\text{BF}_4^-] \). The original coconut shell porous carbon model had a narrow pore size distribution that peaked at a pore size of about \( 0.4 \) nm.\cite{236, 237} In order to consider model materials with pore sizes comparable to the ones listed above, we took the carbon atoms in the section cut from the original model carbon (see above), and slightly increased the
separation between the carbon layers in the \( z \) direction as to obtain three different model materials with larger pore sizes. Afterwards, we computed the pore size distribution (PSD) of each of these three model materials following the methodology described elsewhere,[148, 238, 239] and ensured that their PSDs peak at the values \( H = 0.75, 0.93 \) and 1.23 nm. These results are shown in Figure 6.3.

In this work we considered a simulation setup in which our model porous carbons were directly connected to two reservoirs of IL at both sides (Figure 6.2). Initially, the ions are arranged in an arbitrary lattice outside of the pore, with dummy walls closing the entrances to the pore. When the simulation starts (see below), the dummy walls are removed and the ions can enter (or exit) the porous material. Such a setup has been used in several previous studies of ILs inside nanopores,[103, 109] and should yield a good estimation of the ‘equilibrium’ amount of IL inside the nanopore. The amount of IL inside the carbon pores at the end of our simulations is reported in Table 6.1 as a percentage of the density of the bulk IL at the same temperature, together with additional details of our model systems. All our systems were placed in the center of an orthorhombic box, with periodic boundary conditions applied in all three directions. For the slit graphitic pores, the total length of the box in the \( y \) direction was equal to 5.8 nm, which is similar to the \( y \)-dimension of the carbon walls. The total length of the box in the \( z \) direction was 8 nm (Table 6.1), and therefore the pore was surrounded on top and bottom by two vacuum regions, which were large enough to avoid any interaction between the adsorbed ions and their nearest periodic image in the \( z \)-direction. These vacuum regions in the \( z \)-direction were not present in our simulations with the coconut shell carbon model (Table 6.1), and therefore the confined IL system was periodic in the \( y \) and \( z \) directions (in the \( x \) direction, the IL inside the pores was surrounded by two IL reservoirs at both sides, Fig. 6.2).
Our initial configurations were relaxed via energy minimizations using the steepest descent scheme. The IL in our systems were then melted at a temperature of 600 K, and then annealed from 600 K to 333 K in 6 stages of 500 ps each. Once the system reached the desired temperature of 333 K, the dummy walls were removed and the ions were allowed to fill the pores during our MD simulation runs. The rest of our simulation details and methods are exactly the same as those described in our previous studies.[112, 205, 206]

Table 6.1. Systems Details

<table>
<thead>
<tr>
<th>Slit graphitic pore size (H) (nm)</th>
<th>Number of IL pairs</th>
<th>Dimensions of simulation box ((x, y, z) in nm)</th>
<th>Amount of IL inside pore ((% \text{ of } \rho_{\text{bulk}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>192</td>
<td>(30.0 \times 5.8 \times 8.0)</td>
<td>122.036</td>
</tr>
<tr>
<td>0.93</td>
<td>288</td>
<td>(30.0 \times 5.8 \times 8.0)</td>
<td>103.934</td>
</tr>
<tr>
<td>1.23</td>
<td>288</td>
<td>(30.0 \times 5.8 \times 8.0)</td>
<td>114.30</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Activated carbon, average pore size ((\text{nm}))</th>
<th>No. of IL pairs</th>
<th>Dimensions of simulation box ((x, y, z) in nm)</th>
<th>Amount of IL inside pore ((% \text{ of } \rho_{\text{bulk}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>416</td>
<td>(20.0 \times 6.3 \times 3.7)</td>
<td>72.891</td>
</tr>
<tr>
<td>0.93</td>
<td>468</td>
<td>(20.0 \times 6.3 \times 4.4)</td>
<td>76.949</td>
</tr>
<tr>
<td>1.23</td>
<td>780</td>
<td>(20.0 \times 6.3 \times 4.7)</td>
<td>81.933</td>
</tr>
</tbody>
</table>

6.3. Results and Discussion

We first examined the structure of cations and anions inside our coconut shell carbon models with three different PSDs peaking at \(H = 0.75, 0.93\) and 1.23 nm, and compared those against results obtained for ILs inside slit-like graphitic pores with the same pore sizes \(H\).
Figure 6.3. Pore size distributions (PSDs) of coconut shell model considered in this work. The PSFs of the model materials peak at (a) $H = 0.75$ nm, (b) $H = 0.93$ nm and (c) $H = 1.23$ nm
These pore widths were chosen based on the work of Wu et al.,[103] who reported a U-shaped curve for the capacitance of ILs inside slit-shaped pores, with the minimum in capacitance observed for a pore size of about 0.91 nm. The capacitance depends on structural properties such as the density of ions inside the nanopores, which is reported in Figures 6.4 and 6.5 for the slit pore and coconut shell carbon systems. In both cases, the density of ions (and of the carbon atoms in the pore walls of the coconut shell carbon) was averaged over the x-y plane at any given value of the z-coordinate, and the carbon walls do not have any electrical charges. The density profiles shown in Fig. 6.3 for the ions inside slit graphitic nanopores show the presence of one layer of cations and anions when the pore size is $H = 0.75$ nm; increasing the pore size to $H = 0.93$ nm makes the layers of cations and anions to become wider, and further increase of the pore size to $H = 1.23$ nm leads to the formation of two distinct layers of cations and three layers of anions (although these three layers are not as well defined as the cations, compare the magnitude of the minima in the density profiles of Fig. 6.4). The density of cations is on average larger than the density of anions. These results agree with those observed in previous studies[103] where the density profiles of ions, particularly in narrow uncharged pores such as the ones considered here, depend strongly on the pore size, geometry and relative size of the ions. However, the equivalent density profiles for the coconut shell carbon model (Fig. 6.5) are more complex due to the irregular nature of the model material (semi-graphitic walls of different sizes and shapes, and with a minor degree of corrugation, which form irregularly connected pores of roughly rectangular shape). In Fig. 6.5, as expected the ions fill the pore space where the density of carbon is low, and the density of cations is always larger than that of anions in all systems. More insights can be obtained from the cross sections ($y$-$z$ plane at four different ranges of $x$) of representative simulation snapshots of the cations and anions inside our
coconut shell carbon models, which are shown in Figure 6.6. Here we only depict the centers of mass of the cations (blue, red spheres) and anions (green, purple spheres), which are color-coded according to their orientation as measured by \( \cos(\theta) \).

**Figure 6.4.** Number density profile of cations and anions confined inside slit graphitic pores for pore widths of (a) \( H = 0.75 \) nm, (b) \( H = 0.93 \) nm and (c) \( H = 1.23 \) nm.

**Figure 6.5.** Number density profile of cations, anions and carbons in the coconut shell carbon model systems with PSDs peaking at (a) \( H = 0.75 \) nm, (b) \( H = 0.93 \) nm and (c) \( H = 1.23 \) nm. Densities were averaged over the x-y plane at any given value of the z-coordinate.

Here, \( \theta \) is the angle between a vector normal to the carbon surfaces, and the vector normal to the imidazolium ring (cations), or the vector joining the two carbon atoms (anions, Fig. 6.1). In Fig. 6.6, blue spheres indicate [emim\(^+\)] lying about parallel to the carbon surfaces (\( \theta < 25^\circ \)), and red beads depict [emim\(^+\)] lying tilted (\( \theta > 25^\circ \)) with respect to the carbon walls; likewise, green beads represent anions lying nearly parallel to the carbon walls (\( \theta < 25^\circ \)), whereas purple spheres depict anions tilted with respect to the carbon surface (\( \theta > 25^\circ \)). Similar
snapshots, but depicting cations and anions separately, are shown in Figures D-1 and D-2 (Appendix D). The majority of the cations confined in the pores have a tilted orientation \( (\theta > 25^\circ) \), red spheres; however, a significant fraction of the cations lie with a parallel orientation \( (\theta < 25^\circ) \), blue beads), especially close to the carbon walls. Regarding the anions, most of them anions adopt an orientation parallel to the carbon walls \( (\theta < 25^\circ) \), green spheres), with a significant fraction lying tilted to the walls \( (\theta > 25^\circ) \), purple spheres). These orientations contrast with those that were obtained for the ions inside the slit carbon model (Figure 6.7). For \( H = 0.75 \) nm, the cations and anions form a single layer inside the slit pore (Fig. 6.4), with most of the cations and all of the anions lie parallel to the carbon walls. As the pore width increases to \( H = 0.93 \) nm, the layer of cations and anions becomes wider (Fig. 6.4) and most of the cations adopt a tilted orientation \( (\theta > 25^\circ) \) whereas the anions still remain parallel to the carbon surfaces. As the pore size increases to \( H = 1.23 \) nm, we observe formation of two layers of cations (Fig. 6.4), with some of the cations lying parallel and some tilted to the carbon surfaces (Fig. 6.7); this increase in pore size also make some of the anions to adopt a tilted orientation. Although the coconut shell and the graphitic slit pore carbon models have similar pore sizes, intrinsic properties of the coconut shell porous carbon model, namely the presence of (1) a distribution of pore sizes, (2) irregularly connected pores formed by the carbon sheets of different sizes and shapes (notice the marked differences in the configuration of the carbon walls and the pores between contiguous rows in Figs. 6.6, D-1 and D-2), cause the important differences in orientation of the ions inside the two pore models (Figs. 6.6 and 6.7). These structural heterogeneities in the coconut shell porous carbon model also make the ions to exhibit more irregular variations in their densities (Figs. 6.5 and 6.6; see also Figs. D-1 and D-2, Appendix D), as opposed to the formation of well-defined layers in the slit pore model (Figs. 6.4 and 6.7).
Figure 6.6. Cross sections (y-z plane at four different ranges of x) of representative simulation snapshots of the cations and anions inside our coconut shell carbon models. Only the centers of mass of the cations (blue, red spheres) and anions (green, purple spheres) are depicted. The ions are color-coded according to their orientation: blue and red spheres indicate [emim+] lying parallel or tilted with respect to the carbon surfaces, whereas green and purple beads represent anions lying parallel or tilted with respect to the carbon walls. Four cross sections of our simulation boxes are shown: 5.5 nm < x < 7.2 nm (first row), 7.2 nm < x < 8.9 nm (second row), 8.9 nm < x < 10.6 nm (third row) and 10.3 nm < x < 12.0 nm (fourth row).

In the coconut shell porous carbon, some formation of layers of ions can still be observed in each particular y-z cross section (those are slightly more evident in Figures D-1 and D-2), but the irregularities in the size and shape of the carbon walls and in the pores make those layers of ions to disappear as we move in the x direction.
Figure 6.7. Side views of representative simulation snapshots of cations (left) and anions (right) inside slit graphitic pore models of widths $H = 0.75$ nm (top), 0.93 nm (center) and 1.23 nm (bottom). Only the centers of mass of the cations and anions are depicted, which are color-coded according to their orientation; for cations, blue and red spheres indicate $[\text{emim}^+]$ at $\theta < 25^\circ$ and $\theta > 25^\circ$ with respect to the carbon surfaces, and in the case of anions, green and purple beads indicate $[\text{NTf}_2^-]$ at $\theta < 25^\circ$ and $\theta > 25^\circ$ with respect to the pore walls.

In Figure 6.8 we show the cation-cation, cation-anion and anion-anion radial distribution functions $g(r)$ for the ions inside the coconut shell porous carbon and slit graphitic pore models. In general, very small differences are observed in the positions of the peaks in all of these $g(r)$ functions between the two pore models at the different pore sizes (with the exception of the slit pore model at $H = 0.75$ nm, see below) and the bulk IL systems, which suggest that the liquid structure of the IL confined inside these two pore models is very similar to that of the bulk IL. In the coconut shell porous carbon model, the cation-cation and anion-anion $g(r)$ at $H = 1.23$ nm...
exhibit minor differences with respect to their $g(r)$ counterparts at the other two pore sizes studied here. Likewise, differences in the heights of the peaks in the cation-anion $g(r)$ are observed as the pore size decreases in the coconut shell porous carbon model. Variations in the pore size in the slit graphitic pore model lead to more noticeable differences in the $g(r)$ functions. In particular, the second peak in the cation-anion $g(r)$ disappeared when the IL is confined inside the narrowest slit pore considered here, $H = 0.75$ nm. This issue was not observed when the IL is inside the coconut shell porous carbon model with the same pore size, mainly because of its distribution of pore sizes (Fig. 6.3) where pores much larger than 0.75 nm are present in this model material. Therefore, the IL inside a slit pore of $H = 0.75$ nm experiences much larger confinement effects as compared to when the IL is inside the coconut shell porous carbon model with the same nominal pore size. Varying the size of the slit pore between 0.93 nm and 1.23 nm leads to variations in the height of the peaks in the $g(r)$ functions, with very small variations in the position of the peaks, in agreement with what we observed in our previous work[205] for the same IL inside slit graphitic pores of larger pore sizes than those considered here.

In Figure 6.9 we show the parallel component ($x$ and $y$ directions) of the mean squared displacement (MSD) of the cations and anions confined inside the coconut shell porous carbon model with three different pore sizes. The cations show faster dynamics than anions, as usually observed for imidazolium ILs in bulk[130, 154] and inside pores.[112, 205, 206, 235, 240] The dynamics of the ions inside the coconut shell porous carbon model are slower than those observed for the bulk IL, in analogy to what we observed in our previous studies for ILs inside porous carbons with regular pore geometries.[205, 235, 240, 241] For the IL inside the coconut shell porous carbon model, the fastest dynamics are observed for the pore size $H = 1.23$ nm,
followed by those of the $H = 0.75$ nm system; the ILs exhibit the slowest dynamics in the $H = 0.93$ nm model material.

Figure 6.8. Cation-cation (top), cation-anion (center), and anion-anion (bottom) radial distribution functions $g(r)$ of the ions inside the coconut shell porous carbon model (left panel) and inside the slit graphitic pore model (right panel).

When $H$ is reduced from 0.93 to 0.75 nm, the dynamics of the cations and anions increase in 32% and 23%, respectively. Likewise, as we increase $H$ from 0.93 to 1.26 nm, the MSD of the cations and anions increase in 70% and 15% respectively. This non-monotonous variation in the dynamics of the confined IL with increases in pore size is similar to what was observed in our
previous study for an IL inside multi-walled carbon nanotubes of different pore sizes.[240] We also observed non-monotonous variations in the MSD of the confined ions as we varied the amount of IL inside carbon pores of different shapes;[205, 235, 240] in those studies, we discussed that varying the amount of IL inside the carbon pores induces the formation of regions with high and low density of IL, which in turn causes complex changes in the dynamics of the confined ions. The snapshots shown in Fig. 6.6 suggest that the complex pore geometry of the coconut shell porous carbon model can also induce the formation of regions with high and low density of ions, which might explain the non-monotonous variations in the MSDs of the ions with increases in pore size.

![Figure 6.9. MSD in parallel direction (x and y) for [emim$^+$] (solid lines) and [NTf2$^-$] (dashed lines) confined inside coconut shell porous carbon model with three different pore sizes (H = 0.75, 0.93 and 1.23 nm)](image)

The parallel component of the MSD of cations and anions confined inside the slit graphitic pore model with different pore sizes is shown in Figure 6.10. In these systems, the dynamics of the cations and anions increases monotonically with increase in pore size from 0.75 to 1.23 nm, in agreement with what we observed in our previous study of the same IL inside slit graphitic pores.
of larger sizes.[205] Surprisingly, the anions show similar mobility as of cations inside the slit pores of width $H = 0.75$ and 1.23 nm. These surprising observations could be caused by the fact that these are very narrow pores, which only allow the formation of 1-2 layers of cations and 1-3 layers of anions; the high degree of confinement could slow down the dynamics to the point where anions can move with similar mobility as of cations in some of these systems. For $H = 0.75$ and 1.23 nm, most of the cations are lying parallel to the graphitic walls, which leads to strong interactions between the imidazolium ring and the carbon atoms; in contrast, for $H = 0.93$ nm the cations are mostly tilted with respect to the graphitic walls and the layer of cations is wider (Fig. 6.4), which could lead to weaker interactions with the carbon atoms in the wall. Although many anions are parallel to the graphitic surfaces, their interactions with the carbon walls are expected to be weaker than in the case of the anions atoms of walls which gives them similar dynamics as cations in pore size of 0.75 and 1.23 nm. The dynamics of the ILs inside the slit graphitic pores are much slower than those observed for the bulk IL, mainly because very narrow pores were considered in this work; in our previous study where larger slit pores were considered,[205] the dynamics of the IL inside a slit graphitic pore of $H = 5.2$ nm were similar to those of the bulk IL. Comparing the dynamics observed for the IL inside both pore models, we observe that in general the ions have faster dynamics inside the coconut shell porous carbon model than inside a slit graphitic pore of the same size. These observations are caused by the distribution of pore sizes and the irregularly connected pores formed by carbon sheets of different sizes and shapes in the coconut shell porous carbon model. These properties result in non-uniform confinement effects that are in general lower than those observed in a slit graphitic
Figure 6.10. MSD in parallel direction (x and y) for [emim+] (solid lines) and [NTf2-] (dashed lines) confined inside slit graphitic pore model with pore widths of H = 0.75, 0.93 and 1.23 nm.

Figure 6.11. Single-particle time correlation function for the reorientation of cations inside coconut shell porous carbon model (left) and slit graphitic pore model (right). The correlation function represents the reorientation of cations around an axis perpendicular to their imidazolium ring.

pore model of the same nominal size, where confinement effects are much larger and lead to a significant reduction in the mobility of the ions. This observation is further illustrated in Figure 6.11, where we present the single-particle time correlation function of the reorientation of the cations around an axis perpendicular to their imidazolium ring cations, when they are confined
inside both carbon models of different pore sizes. These results indicate that the rotational motion of the cations decorrelates (i.e., the correlation function reaches values close to zero) when the cations are inside the coconut shell porous carbon model. In contrast, the rotational motion of cations inside the slit pore model still show significant correlation effects after 10 ns of simulation time.

6.4. Conclusions

In this work we used classical molecular dynamics (MD) simulations to study the structure and dynamics of a typical ionic liquid (IL), [emim$^{+}$][NTf$_2$], confined inside two model carbon porous materials, a slit graphitic nanopore and a model porous carbon developed by Pikunic et al.[236, 237] This model was generated from a reverse Monte Carlo simulation protocol, and matches the experimental radial distribution function $g(r)$ of a coconut shell activated carbon. This model material consists of semi-graphitic carbon sheets with different sizes and shapes, which form irregularly connected pores of roughly rectangular shape. Model materials with three pore sizes were considered here, $H = 0.75, 0.93$ and 1.23 nm. Significant differences in structure and dynamics were found for the IL when confined inside these two model porous materials. The ions form distinct layers when inside a slit graphitic nanopore; the number of layers, as well as the position and width of these layers depend directly on the pore width. Within these layers, the anions align parallel to the pore walls, whereas the cations tend to align parallel to the carbon walls when the layers are narrow and tilted when the layers are wider. In contrast, larger variations in the orientation of cations and anions were observed when they are inside the coconut shell porous carbon material; the cations align parallel to the walls when they are closer to the carbon sheets, and tilted when they are farther away from the walls, whereas the anions adopt both parallel and tilted orientations. Furthermore, irregular variations in the density
profiles of the ions as a function of position were observed within the coconut shell porous carbon material, with tentative formation of layers of ions that quickly diffuse due to the irregularities in the size and shape of the carbon walls and the pores of this material. The radial distribution function of the ions within the coconut shell porous carbon material tend to be very similar to those of the bulk IL; more significant variations from the bulk liquid structure are observed when the IL is within the very narrow slit graphitic nanopores considered here. Regarding the dynamics, in general the ions move slower than their bulk counterparts, and the dynamics of the IL within the coconut shell porous carbon material seem to vary non-monotonically with increases in the pore size. Furthermore, the dynamics of the IL within the coconut shell porous carbon material are significantly faster than within the slit graphitic nanopores of similar sizes, where the high degree of confinement can slow down the dynamics of the ions to the point that anions could move with same mobility as of cations (faster dynamics of cations than anions is usually observed for imidazolium ILs in bulk and inside larger pores).

These significant differences in structure and dynamics of the confined ILs within the two model porous materials studied here, are caused by the heterogeneities in the properties of the model coconut shell porous carbon, namely the presence of a pore size distribution (PSD), and the presence of irregularly connected pores formed by the carbon sheets having different sizes and shapes. We note here that the narrow pore sizes considered here and the somewhat wide PSD of our model coconut shell porous materials may have exacerbated the differences observed in the structure and dynamics of the IL within the two pore models. Nevertheless, the results presented here suggest that the effect of heterogeneities in the properties of the porous materials on the structure and dynamics of confined ILs can be significant, and are not captured by model materials with ideal pore geometries.
CHAPTER 7 ON THE INFLUENCE OF SOLVATION OF IONIC LIQUIDS CONFINED INSIDE COCONUT SHELL ACTIVATED CARBON

7.1. Introduction

Ionic liquids (ILs) and nanoporous materials have promising applications in electrochemical devices such as electrochemical double layer capacitors (EDLCs), Li-ion cells and batteries. ILs are salts composed of an organic cations and organic or inorganic anions with melting temperature below 100 ºC. [30, 159] They encompass extraordinary set of properties such as negligible volatility, chemical, thermal and electrochemical stability, strong charge ordering and a wide liquid range which make them suitable for numerous applications in medical science, electrochemistry, extraction and synthesis. [25, 29, 30, 70, 159] In particular air and moisture stable ILs have been extensively used in electrochemical devices such as electrochemical double layer capacitors (EDLCs), dye sensitized solar cells (DSSCs), fuel cells and batteries as an electrolytes. EDLCs are charge storage devices with structure similar to batteries but it stores electrostatic charge without undergoing faradaic reactions. They have attracted extensive attention in recent years as an attractive technology due to very high specific power and fast charging and discharging ability but they suffer from relatively low energy density as compared to batteries.[3, 242-250] Many experimental and simulation studies have shown that replacing volatile organic electrolytes such as acetonitrile and propylene carbonate by ILs can significantly enhance the energy density of EDLCs. [52-57, 103-107, 110, 111] N,N-dialkylimidazolium, tetralkylammonium and N-alkylpyridinium cations and [BF₄], [PF₆], [(CF₃SO₃)N⁻] anions are often used for electrochemical applications due to their high electrochemical stability window (up to 6 V), low volatility and air and moisture stability. Particularly [(CF₃SO₃)N⁻] based ILs show very good stability and wide electrochemical stability.
However, high viscosity and low ionic conductivity (< 15 mS/cm) of ILs increases the electrical resistance which leads to low power density in EDLCs. Ionic conductivity of ILs can be enhanced by mixing them with molecular organic solvents. Addition of solvents such as water, acetonitrile, ethylene carbonate, propylene carbonate etc. can reduce the viscosity of ILs and make them suitable for low temperature applications in electrochemistry. ACN is a dipolar aprotic solvent with ability to dissolve wide range of ionic and non-polar compounds. It exhibits relatively high dielectric constant, low viscosity (0.34 cp) and high diffusion coefficient (4.3*10^{-9} m^2/s). Previous studies have shown that acetonitrile (ACN) is one of the most successful molecular solvent for improving the dynamics of ILs. In spite of its importance very limited work has been done at molecular level on understanding the effect of concentration of ACN on properties of ILs confined inside realistic nanopores. Hence, in this work we studied the molecular level properties of the binary mixture composed of the IL [EMIM][TFMSI] and ACN molecules confined inside a realistic coconut shell activated carbon model. Nanoporous materials such as activated carbon, carbon nanotubes and carbon nanofibers are commonly used as electrodes in EDLCs. In this work we used coconut shell activated carbon model developed by Jorge Pikunic as electrode. The work is inspired by a recent experimental study by Lin et. al. using 2.0 M solution of the IL [EMIM][TFMSI] in ACN as electrolyte and carbide-derived carbon electrodes at 333 K.

The IL [EMIM][TFMSI] shows very good thermal stability and ion conductivity comparable to organic electrolytes, also it is immiscible with water but miscible with ACN. In this work we studied the effect of molar concentration and surface charge density on the structure and dynamics of the IL [EMIM][TFMSI]/ACN mixture confined inside coconut shell
activated carbon model. The aim of this work is to understand how ACN helps in enhancing the dynamics of ILs confined inside charged surface for its use in electrochemistry.

The remainder of this chapter is organized as follows. Section 7.2 contains description of our computational models and methods. In Section 7.3 we present results and discussions of the structural and dynamical properties of the confined ILs, and in Section 7.4 we summarize our main findings.

7.2. Computational Details

In the present work, we report the structural and dynamical properties of an organic electrolyte formed by the IL [EMIM$^+$][TFMSI$^-$] and molecular organic solvent acetonitrile (ACN). The objective of the present work is to investigate the effect of molar concentration of IL as well as surface charge density of electrodes on the properties of the electrolyte. The simulations were performed using GROMACS MD package [61] version 4.0.5 in the canonical ensemble (constant NVT). A schematic representation of the IL [EMIM$^+$][TFMSI$^-$] and ACN molecule is shown in Figure 7.1

![Figure 7.1](image)

**Figure 7.1.** A schematic representation of IL [EMIM$^+$][TFMSI$^-$] and acetonitrile. The labels are atom notations used throughout in this work.
Non-polarizable OPLS-AA force field parameters for cations and anions were taken from Kelkar and Maginn. [224] and the force field for ACN was taken from Wu et al.[256] Two molar concentrations (1.0 M and 2.0 M) and three surface charge densities ($\sigma = 0, -5.2, \text{ and } +5.2 \mu\text{C/cm}^2$) were considered. The coconut shell activated carbon model considered in this work is developed by Pikunic et al. using reverse monte carlo (RMC) simulations [236-238]. This model exhibits irregularly interconnected rectangular pores with surface corrugation which incorporates true morphology of activated carbon. Details of this model can be found in our previous work. Previous studies have shown anomalous increase in capacitance using organic electrolytes or ILs in subnanometer pores, hence in this work we focus on investigating the properties of electrolyte in system with a pore size distribution (PSD) of 0.75 nm. [103, 249, 259-261] All atoms are considered as separate interaction sites with Lennard-Jones (12,6) parameters and electrostatic charges. In all simulations bond length and angle were held rigid and the Lennard-Jones interactions were cut off at 1.2 nm. Long range coulomb interactions were handled by the particle-mesh Ewald (PME) method with a cutoff of 1.0 nm and a grid spacing of 0.1 nm. The carbon atoms in activated carbon are modeled as Lennard-Jones spheres with $\epsilon_c/k = 28$ K and $\sigma_c = 0.340$ nm. [236, 237] The simulation box of size 30.0 nm*6.4 nm*3.72 nm was made periodic in x, y and z directions to avoid any surface effects. Simulation temperature control was achieved using improved velocity rescaling thermostat developed by Parrinello et al. with a time constant of 0.1 ps. [262, 263] All charged systems were neutralized by removing extra cations from positively charged surface and extra anion from negatively charged surface. The number of cation, anions and acetonitrile in each system is given in Table 7.1. The initial configuration was prepared by placing the bulk IL next to the open ends of activated carbon model (X direction). All the systems were minimized using steepest descent. Systems were first melted at 600 K and
then annealed to 333 K in 6 stages of 500 ps each. Afterwards, productions runs of 20 ns were obtained at the desired temperature of 333 K using a time step of 0.1 fs. All other computational details can be found in our previous work. [205, 206]

![Figure 7.2](image.jpg)

**Figure 7.2.** Representative snapshot of the IL [EMIM][TFMSI] and molecular solvent acetonitrile and coconut shell activated carbon model. The cations, anions, acetonitrile and activated carbon are depicted in red, green, blue and grey colors respectively.

**Table 7.1.** Details of number of ions and molecules at different surface charge densities and molarities (M) considered in this work.

<table>
<thead>
<tr>
<th>Surface charge density (μC/cm²)</th>
<th>M=1</th>
<th>M=2</th>
</tr>
</thead>
<tbody>
<tr>
<td>σ = 0</td>
<td><strong>EMI = 198</strong></td>
<td><strong>TFM=198</strong></td>
</tr>
<tr>
<td></td>
<td><strong>ACN =2794</strong></td>
<td></td>
</tr>
<tr>
<td>σ = +5.2</td>
<td><strong>EMI = 154</strong></td>
<td><strong>TFM=198</strong></td>
</tr>
<tr>
<td></td>
<td><strong>ACN =2794</strong></td>
<td></td>
</tr>
<tr>
<td>σ = -5.2</td>
<td><strong>EMI = 198</strong></td>
<td><strong>TFM=154</strong></td>
</tr>
<tr>
<td></td>
<td><strong>ACN =2794</strong></td>
<td></td>
</tr>
</tbody>
</table>
7.3. Results and Discussions

7.3.1 Structural Properties

The structure of ions in the layers close to the interface affects the formation of electrochemical double layer. It has been shown in many studies that the structure of IL is strongly influenced by the morphology and presence of charges at the interface.[205, 206, 235, 240] We study the effect of concentration of IL and presence of surface charge density on the density and radial distribution function of ions and ACN molecules confined inside the activated carbon model.

![Graph showing number density of cations (red), anions (green) and acetonitrile (blue) at 1.0M (left panel) and 2.0M (right panel) concentration of IL confined inside coconut shell activated carbon with $\sigma = 0 \mu C/cm^2$. Carbon atoms of activated carbon model are shown in gray dotted lines.]

Figure 7.3. Number density of cations (red), anions (green) and acetonitrile (blue) at 1.0M (left panel) and 2.0M (right panel) concentration of IL confined inside coconut shell activated carbon with $\sigma = 0 \mu C/cm^2$. Carbon atoms of activated carbon model are shown in gray dotted lines.

First we studied the effect of molar concentration on structure of ions and ACN molecules. Figure 7.3 shows the number density profile of cations, anions and ACN at 1.0 M and 2.0 M concentrations confined inside coconut shell activated carbon with $\sigma = 0 \mu C/cm^2$. We observed significant layering of cations, anions and ACN molecules near the carbon walls. Due to presence of many rectangular shaped interconnected pores layering of ions and molecules is distributed throughout the model. High density peaks of ions and molecules in the density profile
are observed at places where density of activated carbon is very less. A notable fact is the presence of peaks of all species at the same position indicating complete solvation of IL in ACN molecules. The position of peaks of ions and molecules does not change with change in molar concentration of IL. At 1.0 M concentration of IL, density of ACN molecules inside the pores is higher than that of ions. This is in agreement of previous simulation studies of the IL and ACN confined inside slit graphitic pore model.[1, 37, 250, 264] In previous studies the electrolyte is placed inside the pore in initial configuration however in the current study the pores are allowed to be filled by the bulk electrolyte at specified concentration. This pore filling method is more realistic and gives correct density of electrolyte inside the pores at desired temperature. Even at 2.0 M concentration the average density of ACN molecules is higher than the average density of ions indicating strong Van der Waal interactions of solvent molecules with electrode. Due to highly dipolar characteristic of ACN it’s density is much greater than density of ions irrespective of the molar concentration of IL range considered in this work. Also small pores which are inaccessible by ions are occupied by ACN molecules due to their small size. This indicates that wetting of activated carbon pores is affected primarily by ACN molecules. However non-zero density of ions is observed even in uncharged systems at 1.0 M concentration. This is due to large size and large number of atoms in ions which leads to strong van der Waals interactions between ions and electrode.

This difference in density of ions and ACN molecules decreases with increase in molar concentration of IL. More fluctuations are observed in the density profile of ACN molecules due to their small size and dipolar nature. Fluctuations in density of anions are more than that of cations due to a more dispersed charge on anions as compared to cations. This behavior was also observed in our previous studies of the same IL confined inside slit-graphitic pore.[205, 206] We
observed high density of cations as compared to anions inside the pore and the difference in density of cations and anions increases with increase in molar concentration of IL. This effect is due to strong Van der Walls forces between the imidazolium ring of cations and the carbon atoms of the walls.

Figure 7.4. Number density of cations (top panel), anions (center panel) and acetonitrile (bottom panel) at 1.0 (left panel) and 2.0M (right panel) concentration, $\sigma=0$, -5.2 and +5.2\(\mu\)C/cm\(^2\). Carbon atoms of activated carbon model are shown in gray dotted lines.
We also studied the effect of surface charge density (\( \sigma \)) on the density profile of all the species at 1.0 M and 2.0 M concentrations of IL (Figure 7.4). The results indicate that density of cations confined inside the pores increases with increase in negative value of \( \sigma \) (0 to -5.2) and decreases with increase in positive value of \( \sigma \) (0 to +5.2) at both 1.0 M and 2.0 M concentrations. The difference in density of cations with change in \( \sigma \) is more significant at 1.0 M as compared to 2.0 M concentration. On similar lines the density of anions increases with increase in positive value of \( \sigma \) and decreases with increase in negative value of \( \sigma \). The results indicate that counter ions get adsorbed and co ions get expelled more easily from the pores with increase in concentration of ACN molecules. The difference in density between cations and anions increases with increase in surface charge density. Layering of counter ions near the walls become more pronounced with increase in value of \( \sigma \). The results show that change in density of anions with respect to \( \sigma \) is more pronounced than change in density of cations. This in contrast with our previous study of pure IL confined in charged slit graphitic pore of size 5.2 nm.[206] Being a neutral molecule density of ACN remains unaffected with change in \( \sigma \) at both 1.0 M and 2.0 M concentrations. Previous simulation study using IL and ACN solvent also suggests that density of ACN does not depend on the potential difference of electrodes. [250] We did not observe alternate layers of cations and anions with increase in charge density but we did observe a slight shift in the position of peaks of ions with change in value of \( \sigma \). This may be due to the small PSD of the model considered in this work. Previous studies of ILs and ACN solvent have considered large slit graphitic pores and observed alternating layering of ions of opposite charge which gives rise to over screening of the electrode charge. [1, 37, 250, 253, 264] Due to over screening of charge and alternating layers of ions the structure of EDL cannot be described
by Helmholtz model and Poisson Boltzmann model. As previous experimental studies on mixture of IL and ACN solvent have shown anomalous increase in capacitance in pore size of less than 1 nm, it would be interesting to see the distribution of ions in presence of ACN molecules in sub-nanometer pores of ideal pore morphologies. [76, 260]

![Graph showing the percentage change in density of confined cations, anions and acetonitrile with change in molar concentration from 1.0 M to 2.0 M as a function of surface charge density.](image)

**Figure 7.5.** Percentage change in density of confined cations, anions and acetonitrile with change in molar concentration from 1.0 M to 2.0 M as a function of surface charge density

We also calculated the percentage change in density of cations, anions and ACN with change in molar concentration from 1.0 M to 2.0 M at different values of $\sigma$ (Figure 7.5). The result gives better understanding of quantitative changes in density of ions and molecules with increase in molar concentration and how this variable changes with change in $\sigma$. Overall the density of ions increases and that of ACN molecules decreases inside the pores with increase in molar concentration from 1.0 M to 2.0 M. However this increase in density of ions and decrease in density of ACN varies with change in value of $\sigma$. We observed that increase in density of cations (with increase in molar concentration from 1.0M to 2.0M) at $\sigma = -5.2 \mu\text{C/cm}^2$ is slightly more than the increase in density of anions at $\sigma = +5.2 \mu\text{C/cm}^2$. However the increase in density
of anions at $\sigma = -5.2 \, \mu \text{C/cm}^2$ is very large as compared to increase in density of cations at $\sigma = +5.2 \, \mu \text{C/cm}^2$. The results indicate that as molar concentration of IL increases from 1.0 M to 2.0 M the increase in density of co ions is more than the increase in density of counter ions inside the pores. This effect will be explored further in future studies. The percent decrease in density of ACN with increase in molar concentration does not depend on value of $\sigma$.

To get an insight of the structure of confined ions and molecules radial distribution function (RDF) was computed. Figure 7.6 shows the RDF of cation-cation, anion-anion, ACN-ACN, cation-anion, cation-ACN and anion-ACN at $\sigma = 0 \, \mu \text{C/cm}^2$ for 1.0 M and 2.0 M concentrations. We observed an increase in height of peak of RDF of cation-cation, anion-anion, and ACN-ACN with increase in molar concentration. But the peaks in RDF of cation-cation and anion-anion become broader at 2.0 M concentration indicating weaker ordering of ions. Thus ion-ion correlation becomes weaker with increase in concentration of IL. RDF of cation-cation and anion-anion form only one solvation shell at ca. 0.9 nm and RDF of ACN-ACN has first solvation shell at 0.42 nm followed by a small shoulder. No structural heterogeneity was observed with change in molar concentration of IL. RDF of cross correlations between cation-ACN and anion-ACN shows an increase in height of peak with increase in molar concentration. Very high peaks of ca. 9.7 and 6.0 in RDF of cation-anion at a distance of 0.34 nm and 0.63 nm respectively indicates formation of ion pairs. Apparently increase in concentration of ACN stabilizes the formation of ion aggregates. This formation of ion aggregates with increase in concentration of solvent is in agreement with previous studies by Chaban et. al. [255] This formation of ion-pairs might increases the volatility of [EMIM$^+$][TFMSI$^-$], hence acetonitrile should be added for low temperature applications only. The cation-ACN RDF also indicates two distinguishable peaks and the first peak is sharper as compared to the second peak. This suggests
that the solvation of [EMIM$^+$] cations by ACN introduces a distinct structure of solvation shells often observed when inorganic ions are solvated with aqueous solutions.[1, 265] Two solvation shells (0.35 nm and 0.56 nm) in RDF of cation-ACN as compared to one in anion-ACN distribution (ca. 0.63 nm) indicate stronger ion-dipole interactions between ACN molecules and cations as compared to anions. Recent experimental study by Lin et. al. also suggest that even though [EMIM$^+$] and [TFMSI$^-$] have similar sizes they have different affinity for ACN solvent. [76] Large size and more distributed charges on anions as compared to cations prevent them from forming a dense packing with ACN molecules.

**Figure 7.6.** RDF of cation-cation, anion-anion and ACN-ACN (left panel) and cation-anion, cation-ACN and anion-ACN (right panel) at 1.0 M (solid lines) and 2.0 M (dashed lines) concentration confined inside activated carbon with $\sigma = 0$ µC/cm$^2$.

Figure 7.7 shows the effect of $\sigma$ on structure of IL and ACN molecules. We plotted RDF of cation-cation, anion-anion, ACN-ACN, cation-anion, cation-ACN, anion-ACN at 1.0 M and 2.0 M concentrations with $\sigma = 0$, -5.2, and +5.2 µC/cm$^2$. We observed that position and other features of peaks remains the same in RDF of ions and ACN molecules with change in $\sigma$. The peak of RDF of cation-cation shifts slightly towards the left at negative value of $\sigma$ due to increase in interaction between cations and carbon atoms of walls.[250] Increase in negative $\sigma$
causes increase in height of peak of cation-cation at 2.0 M concentration. On similar lines increase in value of positive $\sigma$ causes increase in height of peak of anion-anion at 2.0 M concentration. Hence strong interactions between electrode and counter ions are more visible at higher concentration of IL. There is no significant change in RDF of ACN-ACN, cation-ACN and anion-ACN with change in $\sigma$. A recent study by Merlet et.al. also suggest that the coordination number of ACN around ions does not change much upon polarization.[250].

![Figure 7.7. RDF of cation-cation, anion-anion, ACN-ACN (top panel) and cation-anion, cation-ACN, anion-ACN (bottom panel) at 1.0 M (solid lines) and 2.0 M (dashed lines) concentrations and $\sigma=0$, -5.2 and +5.2$\mu$C/cm$^2$](image)

7.3.2 Dynamical Properties

ILs possess very high viscosity (more than 50 cp at 300 K) and moderate ionic conductivity (ca. 1 S/m) which limits their use in electrochemical devices.[255, 266] Mobility of the ions inside nanopores is one of the factors that determine the internal resistance in EDLCs, which ultimately affects its specific power [3]. Previous studies have shown that addition of an
organic dipolar solvent such as ACN can enhance the dynamics of ILs. In this work translational
dynamics of the binary mixture of [EMIM$^+$][TFMSI$^-$]/ACN is calculated by plotting mean square
displacement (MSD).

Figure 7.8 shows the effect of molar concentration of IL on the dynamics of cation, anion
and ACN molecules confined inside activated carbon. The MSD of ions and molecules is
calculated in the direction parallel to the activated carbon surface. We observed that dynamics of
cations, anions and ACN increases monotonically with decrease in molar concentration of IL
from 2.0 M to 1.0 M. This indicates that addition of acetonitrile decreases the strong inter-atomic
and intra-atomic interactions between ions hence improving their mobility. Dynamics of ions at
higher concentration of ACN is dominated by ion-molecule interaction.[255] ACN molecules
show fastest mobility followed by dynamics of cations and then anions. Decrease in molar
concentration of IL increases the diffusion coefficients of cations, anions and ACN by 168.42 %,
128.85% and 57.69% respectively. This indicates that increase in concentration of ACN has
maximum effect on dynamics of cations followed by anions and least effect on dynamics of
ACN molecules. The current results in confinement are in good agreement with previous studies
of bulk IL/ACN mixture suggesting that increase in molar concentration of ACN in the bulk ILs
causes exponential increase in dynamics of ions.[255]

Figure 7.9 shows the effect of surface charge density on dynamics of cations, anions and ACN at
1.0 M and 2.0 M concentrations. We observed that change in dynamics of ions with respect to
surface charge density strongly depends on the concentration of ACN. In addition to this factor
surface roughness and heterogeneity of activated carbon model also affects the dynamics of ions.
At 1.0 M concentration dynamics of cations at both positive and negative electrodes is slower as
compared to uncharged electrode.
Figure 7.8. MSD of cations, anions and acetonitrile at 1.0 M, 2.0 M and 3.0 M concentrations confined inside activated carbon with $\sigma=0$ µC/cm$^2$

Dynamics of cations at negatively charged surface is slower than the dynamics at uncharged and positively charged electrodes irrespective of the molar concentration of IL. The slower dynamics of cations with increase in negative $\sigma$ is due to strong interaction of cations for the negatively charged walls. Dynamics of cations at $\sigma=+5.2$ is slower than the dynamics at $\sigma=0$ for 1.0 M concentration but faster for 2.0 M concentration of IL. This can be explained by the fact that at 1.0 M concentration the cation-anion interaction is stronger at $\sigma=+5.2$ as compared to $\sigma=0$ giving slower dynamics to cations at $\sigma=+5.2$. As concentration of IL increases to 2.0 M more anions approach the positively charged electrode hence increasing the dynamics of cations.

Similarly dynamics of anions decreases with increase in positive charge density at both 1.0 M and 2.0 M concentrations due to strong interaction of anions with positively charged electrode. Unlike cations, dynamics of anions at $\sigma=-5.2$ is higher than dynamics at $\sigma=0$ for 1.0 M concentration but at 2.0 M concentration dynamics of anions $\sigma=-5.2$ is slower than dynamics at $\sigma=0$. It is due to the fact that density of anions inside the negatively charged pore at 1.0 M
concentration is very low and no layer formation takes place while at 2.0 M concentration anions show significant layering near carbon walls (Figure 7.3).

![Graphs of MSD for cations, anions, and ACN at 1.0 M and 2.0 M concentrations with various charge densities.](image)

**Figure 7.9.** MSD of cations (top panel) and anions (center panel) and ACN (bottom panel) at 1.0 M (left panel) and 2.0 M (right panel) concentration of IL and $\sigma=0$, -5.2 and +5.2$\mu$C/cm$^2$

Variation in $\sigma$ shows less effect on dynamics of ACN molecules as compared to dynamics of ions. We observed slight increase in dynamics of ACN molecules with increase in positive and negative charge density at 1.0 M as well as 2.0 M concentration. Increase in $\sigma$ reduces the
acetonitrile-electrode interactions (by a small amount) and increases the ion-electrode interactions. Hence there is a slight increase in dynamics of ACN with increase in $\sigma$. In order to understand the quantitative change in dynamics of ions and molecules with change in molar concentration we calculated the diffusion coefficient of cations ($D_{\text{cation}}$), anions ($D_{\text{anions}}$) and ACN ($D_{\text{ACN}}$) in the direction parallel to the surface at different surface charge densities (Figure 7.10). We know from MSD results that the dynamics of ions and ACN molecules increases with decrease in molar concentration of IL from 2.0 M to 1.0 M.

![Graph](image)

**Figure 7.10.** Percent change in diffusion coefficient of the confined cations, anions and CAN molecules with increase in molar concentration from 1.0 M to 2.0 M at $\sigma=0$, -5.2 and +5.2 $\mu$C/cm$^2$

However this increase in dynamics is a strong function of surface charge density. For $\sigma=0$ increase in $D_{\text{cation}}$ is almost double than the increase in $D_{\text{anions}}$ indicating that increasing the concentration of ACN improves the dynamics of cations more than that of anions for an uncharged system. Also in bulk mixture of IL and ACN the increase in $D_{\text{cation}}$ with increase in concentration of ACN is more than increase in $D_{\text{anions}}$. Interestingly at both positively and negatively charged surfaces increase in $D_{\text{anions}}$ is more than the increase in $D_{\text{cation}}$. This difference
increase in $D_{\text{anions}}$ and $D_{\text{cation}}$ is more at positively charged surface ($\sigma = +5.2$) as compared to negatively charged surface ($\sigma = -5.2$). Diffusion coefficient of ACN gets least affected by the change in surface charge density. Increase in $D_{\text{ACN}}$ is maximum at $\sigma = 0$ followed by $\sigma = -5.2$ and is least at $\sigma = +5.2$. The results indicate that even though there is no significant change in dynamics of ACN with change in surface charge density its concentration induces drastic changes in dynamics of ions.

7.4. Conclusions

Organic electrolytes composed of ILs and organic solvents are widely used commercially in EDLCs and in academic research. However molecular level understanding of effect of solvation of ions confined inside realistic carbon nanopores is still in its infancy. In this work we performed MD simulations on the electrolyte composed of binary mixture of the IL [EMIM$^+$$][\text{TFMSI}^-]$ and organic solvent ACN confined inside coconut shell activated carbon. The properties of IL and ACN were studied at different molar concentrations of IL and surface charge densities of electrodes.

Local maxima of cations, anions and ACN is observed at the same position in the activated carbon model irrespective of the molar concentration of IL indicating high degree of solvation of ions. We observed that density of ACN inside the pores is higher as compared to density of cations and anions for all systems studied. Increase in surface charge density increases the density of counter ions and decreases the density of co ions inside the pores. And this effect is more pronounced at 1.0 M as compared to 2.0 M concentration of IL. Density of ACN molecules inside the pores is only weakly affected by change in surface charge density. Quantitative study of change in density of ions and molecules with change in molar
concentration indicates that increase in density of cations at $\sigma = -5.2$ is slightly more as compared to increase in density of anions at $\sigma = +5.2$. However increase in density of anions with change in concentration at $\sigma = -5.2$ is very large as compared to increase in density of cations at $\sigma = +5.2$. This indicates that with increase in molar concentration the increase in density of co ions is more than the increase in density of counter ions inside the pores. No structural heterogeneity was observed in the structure of ions and ACN molecules with change in molar concentration. Height of peak in RDF of cation-cation, anion-anion, ACN-ACN, cation-ACN and anion-ACN increases with increase in molar concentration but the height of peak in RDF of cation-anion decreases suggesting formation of stable ion pairs with increase in concentration of ACN. We also observed that anion-ACN interaction is weaker than cation-ACN interaction. Change in surface charge density does not change the local structure of ions and ACN molecules. However the structure of ions might get affected at higher surface charge density. Height of RDF of cation-cation and anion-anion increases at $\sigma = -5.2$ and $\sigma = +5.2$ respectively. These changes are more significant at 2.0 M as compared to 1.0 M concentration.

Dynamics of ions changes significantly with change in molar concentration and surface charge density. We observed that dynamics of ions and molecules increases monotonically with decrease in molar concentration of IL. However this increase in dynamics of ions and molecules is a strong function of surface charge density. Dynamics of counter ions decreases with increase in surface charge density irrespective of molar concentration. However dynamics of co ions in charged systems strongly depends on the molar concentration. Dynamics of ACN molecules increases by a small amount on charged systems as compared to the uncharged system. With increase in molar concentration the difference in the percent increase in density of cations and
anions is more at negatively charged surface than positively charged surface. However the difference in percent increase in diffusion coefficient of cations and anions is more at positively charged surface as compared to negatively charged surface.

This work gives the fundamental understanding of structure and dynamics of IL and ACN molecules confined inside coconut shell activated carbon model as a function of concentration of IL and surface charge density of electrodes. Such understanding is crucial for the rational design of EDLCs. This work is currently in progress and will be described in detail in an upcoming paper. The factor needed to be considered in future work is the understanding of nanostructural organization of confined ions and molecules and determining the capacitance as a function of molar concentration of electrolyte and surface charge density of electrodes.
CHAPTER 8 CONCLUSION AND FUTURE WORK

8.1. Conclusions

The structural and dynamical properties of ILs inside nanoporous electrodes determine the properties of the electrical double layer at the IL-nanopore interface, which in turn determines macroscopic properties in IL-based devices such as EDLCs and DSScs. In particular, the capacitance in EDLCs depends on the structural properties of the IL inside the nanopores; and the mobility of the confined ions is one of the factors determining the internal resistance in an EDLC, which ultimately affects the specific power in this device.\[38, 267, 268\] Therefore, a fundamental understanding of structure and dynamics of ILs inside nanopores is crucial for the rational design and optimization of EDLCs, DSSCs and other IL-based electrochemical systems. In this work we performed MD simulations of the IL [EMIM\textsuperscript{+}]\[TFMSI\textsuperscript{-}\] confined inside slit-like graphite and rutile (110) pores, and inside a coconut shell activated carbon model. We also studied the IL [BMIM\textsuperscript{+}]\[PF\textsubscript{6}\textsuperscript{-}\] confined inside slit-like graphite pores, CNTs and CMK-3 models. The structural and dynamical properties were studied as a function of pore size, amount of IL inside the pores, surface charge density, material of electrode, pore morphology, pore size distribution, and concentration of organic solvent. Our results indicate that these variables have a profound influence on the structural and dynamical properties of confined ILs, as summarized in the paragraphs below.

In chapter 2, molecular dynamics simulations were performed to investigate the structural and dynamical properties of varying amounts of the ionic liquid (IL) [EMIM\textsuperscript{+}]\[TFMSI\textsuperscript{-}\] confined inside slit-like graphitic pores of different widths \(H\). The ions distributed in layers inside the slit pores, with the number of layers depending on pore size. A reduction in pore loading lead to the formations of regions of high and low density of ions in the center of the pore. Variations in pore
size and pore loading seem to induce only slight changes in the local liquid structure of [EMIM$^+$][TFMSI] in the different layers, as compared to the liquid structure of the bulk IL. This finding, when combined with our previous work for a different IL (Singh, R.; Monk, J.; Hung, F. R., *J. Phys. Chem. C* 2011, 115, 16544-16554), suggest that confinement inside slit-like nanopores may or may not induce changes in the local liquid structure depending on the specific IL. However, pore size and pore loading have a marked effect on the dynamics of confined [EMIM$^+$][TFMSI]. The overall dynamics of the confined ions become faster with increasing pore size. The local dynamics of the IL are heterogeneous, with the ions exhibiting slower dynamics in the layers closer to the walls. For varying amounts of [EMIM$^+$][TFMSI] inside a pore of $H = 5.2$ nm, slight differences in the dynamics of the ions in the first and second layers are observed. In contrast, the dynamics of the ions in the center of the pore change markedly, with the fastest dynamics observed when $\rho = 0.8\,\rho_{\text{bulk}}$ (even faster than those of a bulk system). Marked deviations from Gaussian behavior (e.g., large secondary peaks) arise in the self-part of the van Hove correlation function with reductions in pore loading, which suggest that the local dynamics become more complex as regions of high and low density form in the center of the pore when pore loading is reduced.

In chapter 3, molecular dynamics (MD) simulations were used to study the structure and dynamics of the ionic liquid (IL) [emim$^+$][NTf$_2$] confined inside a slit graphitic nanopore of width $H = 5.2$ nm, where the pore walls have different densities of electrical charges. Previous simulation studies of similar systems have mainly focused on the structural and electrostatic properties of the confined IL, without studying in detail the dynamics of these systems. Our results indicate that the density of electrical charges $\sigma$ affects the structure and the dynamics of the confined IL, especially in the layer of ions close to the electrically charged walls. Increases in
σ in the pore walls lead to increases in the local density of counterions, as well as to important changes in the liquid structure of the ions, especially in the layers close to the pore walls. In particular, important differences in the $g(r)$ functions are observed, and in the layer of ions near negatively charged walls, the ethyl groups of the cation cluster together to form small, nonpolar domains. Increases in σ in the pore walls also induce important changes in the dynamics of the confined ions. In particular, as σ is raised, important reductions in the $z$-component of the mean square displacements (MSDs) of the counterions in the layers near the pore walls are observed. The ions in these layers exhibit slower relaxation times and strong deviations from Gaussian dynamics. In general, the ions inside the pore move slower than the ions in the bulk IL; however, as σ is raised, the parallel component of the MSD of the ions near the pore wall or in the center of the pore becomes comparable and even larger than the MSD of the bulk ions.

In chapter 4, molecular dynamic simulations were performed to investigate the structural and dynamical properties of the ionic liquid (IL) 1-butyl-3-methyl imidazolium hexafluorophosphate, [BMIM$^+$][PF$_6^-$] confined inside different pore morphologies such as the ordered mesoporous carbon CMK3, slit-like graphic pore and multi-walled carbon nanotubes (CNT). Our results indicate that varying the pore morphologies and pore size have a profound influence on the structural and dynamical properties of the confined ILs. Significant ion layering is observed in each system, where ions confined in the 3.7 NM pore-sized CNT system tend to have the most significant layering. The number of layers and the relative positions of the ion’s density peaks vary as a function of both pore morphology and pore size. Analysis of the radial density function and orientation of the imidazolium rings suggest that the ions located near the center of the pore exhibit similar behavior to non-confined or bulk [BMIM$^+$][PF$_6^-$]; whereas ions located near the carbon surfaces show characteristics that differ from the bulk IL. The mean
squared displacement (MSD) profiles indicated that the ions confined within the CMK-3 model have the greatest mobility, which can be attributed to the pseudo-confinement generated by the hexagonal placement of the carbon rods. Our results also indicate that the location and orientation of the ions in each system plays a major role in the dynamics of the system. The preferred orientation of the imidazolium rings, with respect to the carbon surface, greatly diminishes the mobility of the cations near the surface. MSDs and rotational auto-correlation functions were measured for ions at different positions in each model to better understand this characteristic. It was observed that the ions located in the center of the 3.7 nm pore-sized CMK-3 model have the shortest decorrelation time and fastest overall mobility.

The unique properties of ionic liquids (ILs) make them a viable replacement of the conventional electrolytes in Dye Sensitized Solar Cells (DSSCs). Therefore it is desirable to understand the atomic level interactions between the ILs and possible electrode materials such as titanium oxide, zinc oxide and copper oxide used in DSSCs. In chapter 5, The structure and dynamics of the ionic liquid (IL) \([\text{EMIM}^+][\text{TFMSI}^-]\) inside a rutile (110) slit nanopore of width \(H = 5.2\, \text{nm}\) at \(T = 333\, \text{K}\) were studied using classical molecular dynamics (MD) simulations. These results were compared against those obtained in our previous study (N. N. Rajput et al., J. Phys. Chem. C 2012, 116, 14504-14513) of the same IL inside a slit graphitic nanopore of the same width and at the same temperature. Electrostatic and dispersion interactions are present between \([\text{EMIM}^+][\text{TFMSI}^-]\) and the Ti and O atoms in the rutile walls, whereas only weaker van der Waals interactions were present between the ions and the C atoms in the graphitic walls. Our results suggest that the strength of the interactions between the pore walls and the IL can significantly affect the structure and dynamics of the confined IL. Layering effects were more pronounced for the IL inside a rutile pore as compared to inside a graphitic pore. The ions near
the rutile pore walls had a liquid structure that was significantly different from that of the bulk IL; in contrast, the same ions near graphitic pore walls had a liquid structure that was similar to that of the bulk IL. Cations and anions adopted multiple orientations near the rutile walls, which contrast with the parallel orientations that were uniformly observed for the same ions near graphitic walls. The dynamics of \([\text{EMIM}^+][\text{TFMSI}^-]\) inside a slit rutile pore are significantly slower than those observed for the same IL inside a slit graphitic pore of the same size. Near the rutile walls, the dynamics of the ions were about an order of magnitude slower than those of ions near graphitic walls. The ions in the center of a rutile pore exhibit enhanced mobilities, but still about 2-4 times slower than those observed for ions in the center of a graphitic pore. The effects of variations in the amount of IL on the dynamics were very marked inside a rutile pore, with reductions of up to 4 times in the mobilities of the ions in the different regions of the pore; in contrast, pore loading seem to cause smaller variations in the dynamics of ILs inside a graphitic slit nanopore.

In chapter 6 we used classical molecular dynamics (MD) simulations to study the structure and dynamics of the ionic liquid (IL) \([\text{emim}^+][\text{NTf}_2^-]\), confined inside two model carbon porous materials, a slit graphitic nanopore and a model material matching the experimental radial distribution function of a coconut shell activated carbon. This model material consists of semi-graphitic carbon sheets with different sizes and shapes, which form irregularly connected pores that have a distribution of pore sizes of roughly rectangular shape. Three pore sizes were studied, \(H = 0.75, 0.93\) and \(1.23\) nm. We observed significant differences in density, orientation, liquid structure and mean squared displacements for the IL confined inside these two model porous materials. The results presented here suggest that the effect of heterogeneities in the properties of the porous materials (e.g., pore size distribution, interconnected pores of
irregular geometries, variations in size and shape of the pore walls) on the structure and
dynamics of confined ILs can be significant, and are not captured by model materials with ideal
pore geometries.

In chapter 7 we used molecular dynamics simulations to understand the effect of
centrification of an aprotic solvent acetonitrile (ACN) on the structure and dynamics of the ionic
liquid [EMIM][TFMSI+] confined inside coconut shell activated carbon model with pore size
distribution of 0.75 nm, where pore walls have different electrical charge densities (σ). In this
work we considered the effect of different molar concentrations (1.0 M and 2.0 M) of IL and
surface charge densities (0, -5.2, +5.2 µC/cm²) of electrodes. The results indicate significant
layering of cations, anions and ACN molecules near the carbon walls. High density peaks of ions
and molecules are observed at same positions indicating complete solvation of ions in ACN
molecules. We observe that density of counter ions inside the pore increases with increase in σ
but remain less than the density of ACN molecules. RDF results indicate that ACN molecules
have stronger affinity for cations as compared to anions. Increase in concentration of ACN
molecules induces electrostatic intermolecular and ion-molecular interactions causing disruption
to the strong interaction between ions and ions-electrode resulting in faster dynamics. This
increase in dynamics of ions with addition of ACN is a strong function of surface charge density.
However, change in surface charge density does not show any significant change in structure and
dynamics of ACN molecules.
8.2. Proposed and On Going Work

8.2.1. Electroactive Potential

A proposed research in this area could be studying the effect of charged systems by a more complex and realistic model of “electroactive interface” which allows maintaining the nanoporous electrodes at a constant electrical potential. The model considered in the present work is not a completely realistic representation of a charged electrode however it works well for simple pore geometries.[55, 56] Local fluctuations in the structure of the IL near the pore walls can induce a non-uniform distribution of charges among the atoms in the wall. In addition, when using fixed-charge distribution in the nanoporous walls, the electrostatic potential in the simulation cell can vary. This model was proposed by Reed et al.,[55] which was also used by Vatamanu et al. in their recent simulation study.[56] In this method, the charges in the atoms of the electrode can vary based on the imposed electrostatic potential (which is kept fixed in the simulation) and due to variations in the local structure of the electrolyte at the interface. Extensive details of this methodology are given in the original references.[55, 56] Such an approach can be implemented in the proposed study.

8.2.2. Siliceous and Doped Carbonaceous Nanopores

It is important to further investigate physical chemistry of ILs at different electrode surfaces. Not only electrochemical devices but also tribological and catalytic process require the study of physical properties of IL at the interface. The results show that there is a significant change in properties of ILs inside ideal pore models and realistic pore models. Hence it is important to develop and study the properties of ILs in more realistic nanoporous models commonly used as electrochemical devices. The surfaces of carbon models can be doped with
different chemical groups to study their effects on the behavior of confined ILs. Porous carbons used in EDLCs often exhibit oxygenated functional groups (e.g., phenolic, lactonic, carboxylic, etc.); however, other heteroatoms such as nitrogen, sulfur and halogens can also be present.[269, 270] Important functional groups such as oxygenated group (e.g., carboxylic) and nitrogenated group (e.g., amine) can be studied by placing these chemical groups at random positions in the surfaces of the carbons, and model those using standard all-atom force fields such as OPLS-AA.[271] Model materials with different concentrations of surface groups can be studied.

ILs confined inside sol-gels (ionogels) have potential applications as electrolyte membranes and in optics, catalysis and biocatalysis, drug delivery and sensing and biosensing.[89, 91, 272] Fully-atomistic representations of model TMSs developed by Hung et. al. [273-275] that mimic MCM-41 and SBA-15 materials can be studied. These models exhibit either regular cylindrical pores, or roughly cylindrical pores with different degrees of surface roughness (Figure. 8.1). Similar models were also proposed to represent the bicontinuous gyroidal structure of MCM-48 [Fig. 8.1(D)].[276] Furthermore, a variation of the carbon aerogel model [Fig. 8.1(D)] can be used to represent an ionogel, where the spherical particles are made of silica. To represent the interactions between the ILs and the Si, O and H atoms in the (uncharged) pore walls, the parameters can be adopted from Sieffert and Wipff;[277] other options are also available to model these interactions.[278, 279]

Model siliceous materials with different pore sizes can be considered. By comparing the properties of ILs inside these model TMSs, the effect of pore size, pore morphology and surface roughness on the properties of the ILs can be elucidated. Furthermore, by comparing results of ILs confined inside carbonaceous and siliceous pores (e.g., an open-tip MWCNT and a regular
cylindrical silica pore) of similar diameters, the effect of pore chemistry on the properties of confined ILs could be establish.

Figure 8.1. TMS models. Model (A) for SBA-15 exhibits meso- and micro-porosity. Model (B) for MCM-41 has mesopores similar to (A), but has its microporosity removed. Model (C) is a regular cylindrical pore model. All models (A)-(C) have a mean pore diameter of ~ 5.4 nm; silicon, oxygen, and hydrogen atoms are depicted in tan, gray, and black, respectively. (D) Model MCM-48 exhibiting a bicontinuous gyroidal structure. Grey and white spheres represent oxygen and hydrogen atoms; Si atoms were not depicted for clarity. The mean pore size is 3.2 nm.

By fundamentally understanding how the electrical, structural and dynamical properties of ILs are affected by the properties of nanoporous materials (i.e. pore size and shape, surface density of electrical charge, presence of chemical functional groups at the pore surfaces, and various degree of heterogeneities in these properties), a solid platform can be in placed to rationally design EDLCs, DSSCs, ionogels and other IL-based electrochemical systems with optimal properties.
REFERENCES


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APPENDIX A: PERMISSION LETTERS

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APPENDIX B: SUPPORTING INFORMATION (CHAPTER 2)

B.1 Radial Distribution Function

Figure B-1 Cation-cation, cation-anion and anion-anion radial distribution functions of all ions of [EMIM+][TFMSI-] in the bulk (T = 333 K, P = 1 atm) and inside a slit graphitic pore of size H = 5.2 nm (T = 333 K, ρ = ρ_{bulk}).

Figure B-2 Cation-cation radial distribution function of [EMIM+][TFMSI-] in the bulk (T = 333 K, P = 1 atm) and inside slit graphitic pores of different widths (T = 333 K, ρ = ρ_{bulk}).
Figure B-3 Cation-cation (a), cation-anion (b) and anion-anion (c) radial distribution functions for the different layers of [EMIM+]\text{[TFMSI-]} confined inside slit pores of $H = 5.2$ nm and 2.5 nm at 333 K. In all cases $\rho = \rho_{\text{bulk}}$. The same $g(r)$ for the bulk IL are also shown.
B.2 Orientation of Ions

Figure B-4 Orientational order parameter, $P_1(\cos \theta)$ of [TFMSI-] confined in a slit pore of $H = 5.2$ nm at different pore loadings. $\theta$ is the angle between a vector normal to the surface of the pore walls and a vector connecting the two carbon atoms (CJ-CJ) in [TFMSI-].
C.1 Density

Figure C-1 Number density of cations (blue) and anions (red) for the following cases: (a) both walls of the pore are negatively charged, $\sigma = -7.2 \, \text{µC/cm}^2$; (b) bottom walls have negative charge and top walls have positive charge, $\sigma = \pm 5.3 \, \text{µC/cm}^2$; and (c) both walls are positively charged, $\sigma = +7.2 \, \text{µC/cm}^2$. The vertical dashed lines indicate how the confined ions were divided into layers/regions for further study.
C.2 Radial Distribution Function

Figure C-2 Radial distribution functions in systems where both walls have charges of the same sign. Four different systems were studied with both pore walls have surface charge densities of $\sigma = -2.8$, $-7.2$, $+2.8$ and $+7.2$ µC/cm². Results are compared to those observed in a system where one wall is charged negatively ($\sigma = -5.4$ µC/cm²) and the other has positive charges ($\sigma = +5.4$ µC/cm²). Results shown are for (a) cation-cation, (b) cation-anion and (c) anion-anion g(r) functions; left panel are for the layer of ions close to negatively charged walls; right panel are for the layer of ions near positively charged walls, and center panel are for the ions in the center of the pore in all systems.
C.3 Mean Squared Displacement

Figure C-3 MSD in z-direction of the layers of ions near the pore walls, for situations where both walls have charges of the same sign, as compared to the scenario where one wall is charged negatively and the other has positive electric charges. Four different systems were studied with surface charge density of $\sigma = -2.8, -7.2, +2.8$ and $+7.2 \text{ µC/cm}^2$. Results are compared to those observed in a system where one wall is charged negatively ($\sigma = -5.4 \text{ µC/cm}^2$) and the other has positive charges ($\sigma = +5.4 \text{ µC/cm}^2$).
C.4 van Hove Correlation Function

**Figure C-4** $G_s(r, t)$ of cations at the first layer (near negatively charged pore walls, left panel), center region (center panel) and third layer (close to positively charged pore walls, right panel) at (a) $t = 0.2$ ps, (b) $t = 100$ ps, and (c) $t = 25000$ ps (bottom), for surface charge densities of $\sigma = 0$, 5.3, 8.9, 12.4 and 16.0 $\mu$C/cm$^2$. 
Figure C-5 $G_s(r, t)$ of anions at the first layer (near negatively charged pore walls, left panel), center region (center panel) and third layer (close to positively charged pore walls, right panel) at (a) $t = 0.2$ ps, (b) $t = 100$ ps, and (c) $t = 25000$ ps (bottom), for surface charge densities of $\sigma = 0, 5.3, 8.9, 12.4$ and 16.0 $\mu$C/cm$^2$.

C.5. Discussion of Figures C4 and C5

At short time $t = 0.2$ ps, $G_s(r, t)$ of both cations and anions decay rapidly to zero at short values of $r$ in all three layers. Changes in $\sigma$ causes small variations in $G_s(r, t)$ for the cations near the negative surfaces (Fig. C4a, left), and for the anions near the positive surfaces (Fig. C5a, right); the dynamics of the rest of the ions in the rest of the regions of the pore seem to be unaffected by changes in $\sigma$ at this particular time. At $t = 100$ ps, the dynamics of the cations near the negative surface (Fig. C4b, left) experience noticeable reductions as the charge density increases, but the dynamics of cations in the center of the pore and near the positive surface (Fig. C4b, right) maintain their initial behavior. Interestingly, the dynamics of the anions near the positive surface (Fig. C5b, right) show a reduction in $G_s(r, t)$ as well, indicating a significant change in their distribution.
C4b, center and right) experience smaller variations at this particular time as $\sigma$ is changed. At this time, $t = 100$ ps, for $\sigma \neq 0$, two peaks are observed in the $G_s(r, t)$ of anions in the layer close to the positive surface (Fig. C5b, right), the first around $r = 0.05$ nm and the second around $r = 0.16$ nm.

Increases in surface charge density slows down the dynamics of anions near the positive surface, as signaled by an increase in the height of the first peak in $G_s(r, t)$, and a decrease in the height of the second peak (Fig. C5b, right). Changes in $\sigma$ also lead to changes in $G_s(r, t)$ of the anions near the negative surface (Fig. C5b, left), but does not affect the dynamics of the anions in the center of the pore (Fig. C5b, center). The $G_s(r, t)$ for all ions at $t = 100$ ps decay to zero at distances below 0.7 nm, suggesting that at this time ions are still inside the cage formed by neighboring ions and thus are still in the sub-diffusive regime. At longer times ($t = 25$ ns), important differences are observed for $G_s(r, t)$ of the cations near the negative surfaces (Fig. C4c, left) and near the positive walls (Fig. C5c, right) as $\sigma$ is changed; in contrast, variations in $\sigma$ only produces relatively small changes in $G_s(r, t)$ of the cations in the center of the pore (Fig. C4c, center). As found in our previous study,1 small secondary peaks were observed in the $G_s(r,t)$ of the cations in the layers near the negative and the positively charged surfaces (Fig. C4c, left and right) suggesting that the dynamics of cations in these layers are complex and deviate significantly from Gaussian behavior. Variations in $\sigma$ also cause changes in the $G_s(r,t)$ of the anions, especially near the positive walls (Fig. C5c, right) where the dynamics of the anions slow down appreciably as the charge density increases, as signaled by $G_s(r,t)$ curves that are narrower and with higher peaks observed at short distances. Smaller (but still appreciable) changes in $G_s(r,t)$ are observed for the anions near the negative surfaces and in the center of the pore at $t = 25$ ns (Fig. C5c, left and center).
D.1. Orientation of ions

Figure D-1. Cross sections (y-z plane at four different ranges of x) of representative simulation snapshots of the cations inside our coconut shell carbon models. Only the centers of mass of the cations are depicted. The cations are color-coded according to their orientation: blue and red spheres indicate [emim+] lying parallel or tilted with respect to the carbon surfaces. Four cross sections of our simulation boxes are shown: 5.5 nm < x < 7.2 nm (first row), 7.2 nm < x < 8.9 nm (second row), 8.9 nm < x < 10.6 nm (third row) and 10.3 nm < x < 12.0 nm (fourth row).
Figure D-2. Cross sections (y-z plane at four different ranges of x) of representative simulation snapshots of the anions inside our coconut shell carbon models. Only the centers of mass of the anions are depicted. The anions are color-coded according to their orientation: green and purple spheres indicate [NTf2\textsuperscript{-}] lying parallel or tilted with respect to the carbon surfaces. Four cross sections of our simulation boxes are shown: 5.5 nm < x < 7.2 nm (first row), 7.2 nm < x < 8.9 nm (second row), 8.9 nm < x < 10.6 nm (third row) and 10.3 nm < x < 12.0 nm (fourth row).
VITA

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