

Molecular Structure and Dynamics of Novel Polymer Electrolytes Featuring Coulombic Liquids

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ABSTRACT

Polymer electrolytes are indispensable in numerous electrochemical systems. Existing polymer electrolytes rarely meet all technical demands by their applications (e.g., high ionic conductivity and good mechanical strength), and new types of polymer electrolytes continue to be developed. In this dissertation, the molecular structure and dynamics of three emerging types of polymer electrolytes featuring Coulombic liquids, i.e., polymerized ionic liquids (polyILs), nanoscale ionic materials (NIMs), and polymeric ion gels, were investigated using molecular dynamics (MD) simulations to help guide their rational design.

First, the molecular structure and dynamics of a prototypical polyILs, i.e., poly(1-butyl-3-vinylimidazolium hexafluorophosphate), supported on neutral and charged quartz substrates were investigated. It was found that the structure of the interfacial polyILs is affected by the surface charge on the substrate and deviates greatly from that in bulk. The mobile anions at the polyIL-substrate interfaces diffuse mainly by intra-chain hopping, similar to that in bulk polyILs. However, the diffusion rate of the interfacial mobile anions is much slower than that in bulk due to the slower decay of their association with neighboring polymerized cations.

Second, the structure and dynamics of polymeric canopies in the modeling NIMs where the canopy thickness is much smaller than their host nanoparticle were studied. Without added electrolyte ions, the polymeric canopies are strongly adsorbed on the solid substrate but maintain modest in-plane mobility. When electrolyte ion pairs are added, the added counter-ions exchange with the polymeric canopies adsorbed on the charged substrate. However, the number of the

adsorbed electrolyte counter-ions exceeds the number of desorbed polymeric canopies, which leads to an overscreening of the substrate's charge. The desorbed polymers can rapidly exchange with the polymers grafted electrostatically on the substrate.

Finally, the molecular structure and dynamics of an ion gel consisting of PBDT polyanions and room-temperature ionic liquids (RTIL) were studied. First, a semi-coarse-grained model was developed to investigate the packing and dynamics of the ions in this ion gel. Ions in the interstitial space between polyanions exhibit distinct ordering, which suggests the formation of a long-range “electrostatic network” in the ion gel. The dynamics of ions slow down compared to that in bulk due to the association of the counter-ions with the polyanions' sulfonate groups. Next, the RTIL-mediated interactions between charged nanorods were studied. It was discovered that effective rod-rod interaction energy oscillates with rod-rod spacing due to the interference between the space charge near each rod as the two rods approach each other. To separate two rods initially positioned at the principal free energy minimum, a significant energy barrier ($\sim$ several $k_B T$ per nanometer of the nanorod) must be overcome, which helps explain the large mechanical modulus of the PBDT ion gel reported experimentally.

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GENERAL AUDIENCE ABSTRACT

Polymer electrolytes are an indispensable component in numerous electrochemical devices. However, despite decades of research and development, few existing polymer electrolytes can offer the electrochemical, transport, mechanical, and thermal properties demanded by practical devices and new polymer electrolytes are continuously being developed to address this issue. In this dissertation, the molecular structure and dynamics of three emerging novel polymer electrolytes, i.e., polymerized ionic liquids (polyILs), nanoscale ionic materials (NIMs), and polymeric ion gels, are investigated to understand how their transport and mechanical properties are affected by their molecular design.

The study of polyILs focused on the interfacial behavior of a prototypical polyILs supported on neutral and charged quartz substrates. It was shown that the structure and diffusion mechanism of the interfacial polyILs are sensitive to the surface charges of the substrate and can deviate strongly from that in bulk polyILs. The study of NIMs focused on how the transport properties of the dynamically grafted polymers are affected by electrolyte ion pairs. It was discovered that the contaminated ions can affect the conformation the polymeric canopies and the exchange between the “free” and “grafted” polymers. The study of polymeric ion gels focused on the molecular and mesoscopic structure of the ionic liquids in the gel and the mechanisms of ion transport in these gels. It was discovered that the ions exhibit distinct structure at the intermolecular and the inter-rod scales, suggesting the formation of extensive electrostatic networks in the gel. The dynamics of ions captured in simulations is qualitatively consistent with experimental observations.

Dedication

To my family and friends

Acknowledgments

The past three and a half years is a period of intense learning for me, not only in the scientific arena but also on a personal level. There are many people that have earned my gratitude for their contribution to my time in graduate school. This dissertation would not have been possible without their help.

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CHAPTER 1 Introduction

1.1 Electrolytes for Electrochemical Storage and Conversion

Electrochemical storage and conversion devices such as batteries, fuel cells, and supercapacitor have many appealing features, e.g., high round-trip efficiency, flexible power, low maintenance, and environmental friendliness.¹ In the past decades, these devices play an increasingly important role in our society, e.g., batteries and fuel cells are increasingly used in automobiles and full electric vehicles are likely to enter the mainstream market in the coming decade. These and other applications call for electrochemical storage and conversion devices with higher energy density, higher power density, better reliability, etc. Driven by these demands, research on electrochemical storage and conversion has become one of the most exciting frontiers in scientific and engineering research.

One of the most active research direction in electrochemical storage and conversion is the development of new electrolytes. Electrolytes are an essential component in any electrochemical device. Even though electrolytes function differently in different electrochemical devices, they generally work as an ionic conductor to enable ion transport and serve as an electronic insulator to prevent short-circuiting. Electrolytes often determine the power density, stability, and reliability of an electrochemical device.¹

Generally, an ideal electrolyte should meet the following requirements simultaneously: (1) It should have a wide electrochemical window to guarantee that electrolyte degradation would not occur within the range of the working potentials of the electrodes; (2) It should have a high ionic conductivity to ensure facile ion transport and thus low Ohmic loss; (3) It should have a high

chemical and electrochemical inertness to other component of the electrochemical devices such as electrodes, current collectors and casing; (4) It should have a high thermal and chemical stability (i.e., a low volatility and flammability) to ensure that their physicochemical properties remain stable within the interval of the device's operating temperature; (5) It should have no or low toxicity and be environmentally friendly; (6) It should be based on sustainable chemistries, i.e., it can be prepared from abundant materials through inexpensive synthesis processes.¹⁻² In addition, in applications such as Li-metal batteries, high mechanical modulus is desired as it helps retard the growth of the dangerous dendrites.

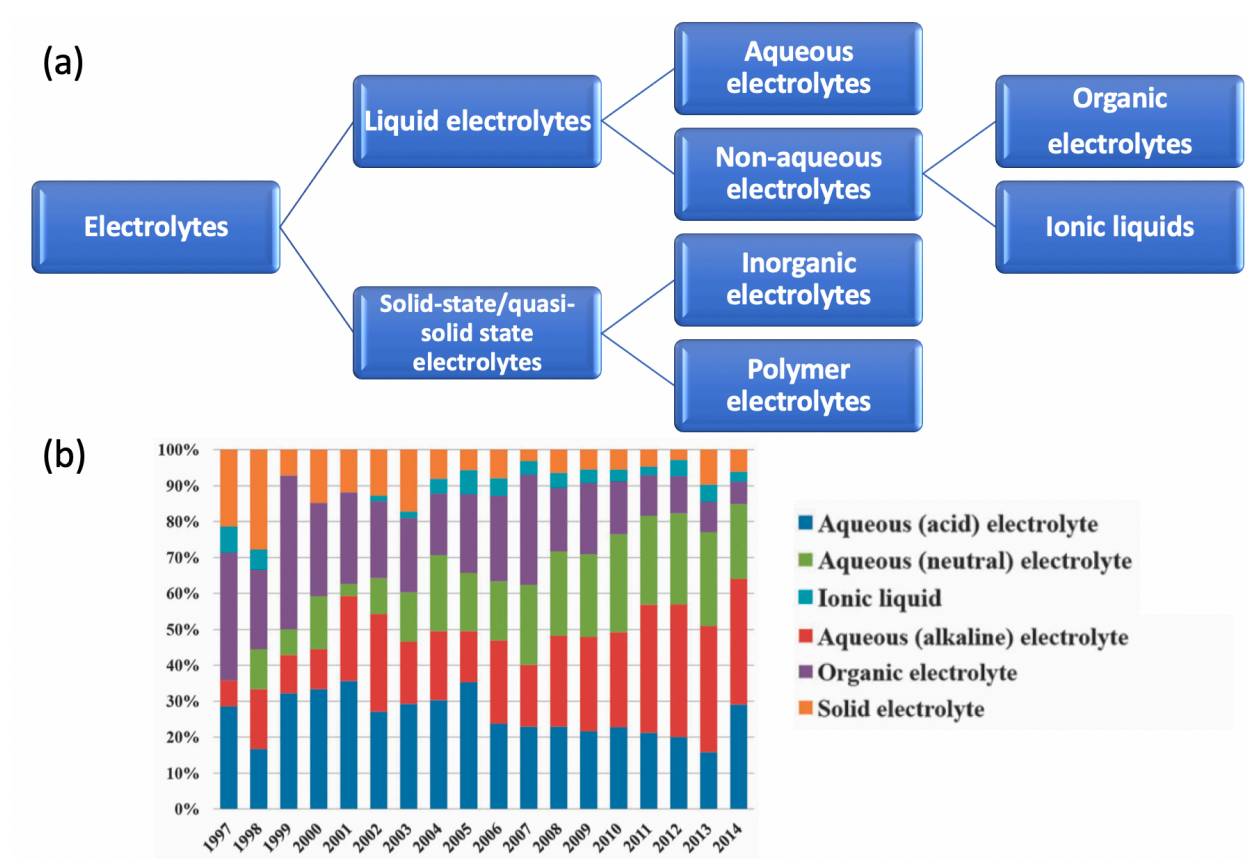


Figure 1-1. (a) Classification of electrolytes for electrochemical devices. (b) Percentage of reported literatures on different electrolytes from 1997 to 2014. (b) is reproduced based on Ref. 2.

Figure 1-1a shows various types of electrolytes developed for electrochemical conversion and storage devices. Broadly speaking, these electrolytes can be classified as liquid electrolytes and

solid-state/quasi-solid-state electrolytes. The liquid electrolytes can be further divided into aqueous electrolytes, organic electrolytes, and ionic liquids, depending on the type of solvents (if present) used. The solid/quasi-solid-state electrolytes can be grouped into inorganic electrolytes and organic polymer electrolytes. Below I briefly review the application and development of the various electrolytes for application in batteries, fuel cells, and supercapacitors because they are among the most widely encountered electrochemical energy storage and conversion devices. The advantages and limitations of each electrolyte for these applications are highlighted.

1.1.1 Liquid Electrolytes

Electrolytes are substances that can conduct ions. If an electrolyte is in the liquid state at its operating condition, it is typically referred to as liquid electrolyte. While liquid electrolytes often feature ions dissolved in a solvent (e.g., an aqueous NaCl solution), they can also be free of any solvent (e.g., room-temperature ionic liquids or RTILs). Liquid electrolytes often offer high ionic conductivity and do not experience significant volume change due to changes in the composition of the electrode materials as they are charged and discharged.³ The most common types of liquid electrolytes are aqueous electrolytes, organic electrolytes, and RTILs. Table 1-1 summarizes the properties of these electrolytes, their applications, and their stage of developments. Below we briefly review the development history, advantages, and limitations of each of these electrolytes.

Aqueous electrolytes. Aqueous electrolytes typically consist of inorganic salts dissolved in water. Aqueous electrolytes have been extensively investigated in the literature (see Figure 1-1b). In the mid-1990s, the lithium nitrate (LiNO_3) aqueous electrolyte was first used in a rechargeable Li-ion battery by the Dahn group.⁴ The early rechargeable Li-ion batteries with LiNO_3 aqueous electrolytes showed poor cycling performances. Since then, different aqueous electrolytes (e.g.,

Table 1-1. Applications of liquid electrolytes

Type	Application	Example	Ion concentration	Typical working temperature	Conductivity	Stage of development	Ref.
Aqueous electrolytes	Battery	LiNO ₃ + water	5 M	25°C	0.170 S cm ⁻¹	Research	5
		Li ₂ SO ₄ + water	2 M	25°C	0.090 S cm ⁻¹		6
	Fuel cell	KOH + water	6 M	25°C	0.600 S cm ⁻¹	Commercial/Research	2
	Supercapacitor	H ₂ SO ₄ + water	1 M	25°C	0.800 S cm ⁻¹	Research	7
		KOH + water	6 M	25°C	0.600 S cm ⁻¹		2
		Na ₂ SO ₄ + water	0.5 M	25°C	0.065 S cm ⁻¹		8
		NaNO ₃ + water	5 M	25°C	0.200 S cm ⁻¹		8
Organic electrolytes	Battery	LiPF ₆ /EC-EMC	1 M (LiPF ₆), EC:EMC=1	30°C	0.012 S cm ⁻¹	Commercial/Research	9
		LiPF ₆ /PC	1.1 M (LiPF ₆)	25°C	0.006 S cm ⁻¹		10
	Supercapacitor	[TEA][BF ₄]/PC	0.65 M ([TEA][BF ₄])	25°C	0.011 S cm ⁻¹	Commercial/Research	11
		[TEA][BF ₄]/ACN	0.65 M ([TEA][BF ₄])	25°C	0.050 S cm ⁻¹		11
Ionic liquids	Battery	LiTf ₂ N/[Pyr ₁₄][FSI]	0.2 M (LiTf ₂ N)	30°C	0.006 S cm ⁻¹	Research	12
		LiTf ₂ N/[Pyr ₁₄][Tf ₂ N]	0.2 M (LiTf ₂ N)	30°C	0.003 S cm ⁻¹		12
	Fuel cell	HTf ₂ N/Bim	HTf ₂ N:Bim=1	140°C	0.008 S cm ⁻¹	Research	13
	Supercapacitor	[EMIM][BF ₄]	~6.5 M (pure)	45°C	0.003 S cm ⁻¹	Research	14
		[BMIM][BF ₄]	~5.2 M (pure)	45°C	0.001 S cm ⁻¹		14

Li₂SO₄) with matching electrodes have been explored to improve the cycling performance of rechargeable Li-ion batteries.¹⁵⁻¹⁶ Aqueous electrolytes (e.g., NaOH solution) have also been used in the alkaline fuel cell for NASA's space mission since the mid-1960s. Although alkaline fuel cells are among the most efficient fuel cell with potential to reach 70% efficiency, their commercial applications are still at the early stage because alkaline aqueous electrolytes can become "poisoned" through the conversion of OH⁻ to CO₃²⁻.¹⁷

Aqueous electrolytes have been broadly employed in the electrochemical supercapacitor. H₂SO₄ and KOH solutions are the most commonly used acid/alkaline aqueous electrolytes due to their high ionic conductivity. Since ionic conductivity depends strongly on the concentration of the electrolytes, most research has been devoted to find the optimum concentrations to achieve the maximum ionic conductivities.¹⁸ The maximum ionic conductivity of H₂SO₄ solution is achieved at 1.0 M concentration at 25 °C.² Neutral aqueous electrolytes (e.g., Li, Na, K, Ca, and Mg salts) have also been widely investigated for supercapacitors due to their reduced propensity to less corrosion and greater safety.²

Aqueous electrolytes have a voltage window of ~1.2 V due to the electrolysis of water, which limits their applications. However, compared to other liquid electrolytes, aqueous electrolytes typically exhibit higher ionic conductivity and less processing cost.

Organic electrolytes. Organic electrolytes consist of a salt dissolved in an organic solvent. Most of the electrolytes used in commercial Li-ion batteries are organic electrolytes, in which lithium hexafluorophosphate (LiPF₆) salts are dissolved in ethylene carbonate (EC), dimethyl carbonate (DMC), propylene carbonate (PC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), or their mixtures.¹⁹ The electrochemical stability of conventional carbonate solvents (usually less than 3 V) impedes the development of Li-ion batteries with higher energy and power

density. Therefore, it's critical to explore new organic solvents and lithium salts. Organic fluoro-compounds are the promising solvents for high voltage operations due to the high oxidation potentials of fluorinated molecules.²⁰ Recent research showed that substituting conventional organic solvents with fluoro-compounds can improve the voltage window of organic electrolytes to 6.8 V.²¹

Organic electrolytes dominate over other liquid electrolytes in commercial supercapacitors. Typical organic electrolytes for supercapacitors include tetraethylammonium tetrafluoroborate [TEA][BF₄] dissolved in acetonitrile (ACN) or PC. Considerable efforts have been devoted to understand the relationship between the ion size and pore size for the applications of organic electrolytes in supercapacitors.²²⁻²⁴ This is because that small pores can increase the surface area of carbon materials. However, large organic electrolyte ions cannot access to small pores, leading to a negative effect on the specific capacitance.

Compared with the aqueous electrolytes, organic electrolytes have a high operation potential window typically in the range of 2.5 to 2.8 V. Meanwhile, these electrolytes often have a high chemical and electrochemical inertness. Cheap materials (e.g., Al) can be used as current collectors and casing of electrochemical devices with many organic electrolytes. However, organic electrolytes often have a higher cost than aqueous electrolyte due to the complicated purification and fabrication processes. Meanwhile, there are also some safety concerns including flammability, volatility, and toxicity. Furthermore, the ion conductivity of organic electrolytes is usually much lower than that of aqueous electrolytes (see Table 1-1).

Ionic liquids. RTILs are composed entirely of ions but remain in the liquid state at a relatively low temperature (e.g., < 100 °C).²⁵ Many RTILs exhibit decent ionic conductivity, great electrochemical stability, low vapor pressure, and nonflammability, which are appealing in many

electrochemical applications.²⁶ Typical cations in RTILs include imidazolium, pyridinium, and pyrrolidinium ring. Tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), bis(trifluoromethane)-sulfonimide (Tf_2N^-), and trifluoromethanesulfonate (TfO^-) are the common anions (see Figure 1-2).²⁶ In the past few years, several important works explore the applications of RTILs in Li-ion, Li-S, and Li-Air batteries. RTILs-based electrolytes (e.g., $[\text{Pyr}_{14}][\text{Tf}_2\text{N}]$, $[\text{Pyr}_{14}][\text{FSI}]$, $[\text{Pyr}_{1201}][\text{Tf}_2\text{N}]$, etc.) show promise for applications in Li-ion battery.¹² Byon et al. found that organic electrolytes doped with RTILs, N-methyl-N-propylpiperidinium bis-(tri-fluoromethane-sulfonyl) imide ($[\text{PP}_{13}][\text{Tf}_2\text{N}]$), can improve the discharge capacity of Li-S batteries.²⁷ Recently, a Li-air battery using RTILs was reported with an apparently improved energy efficiency.²⁸

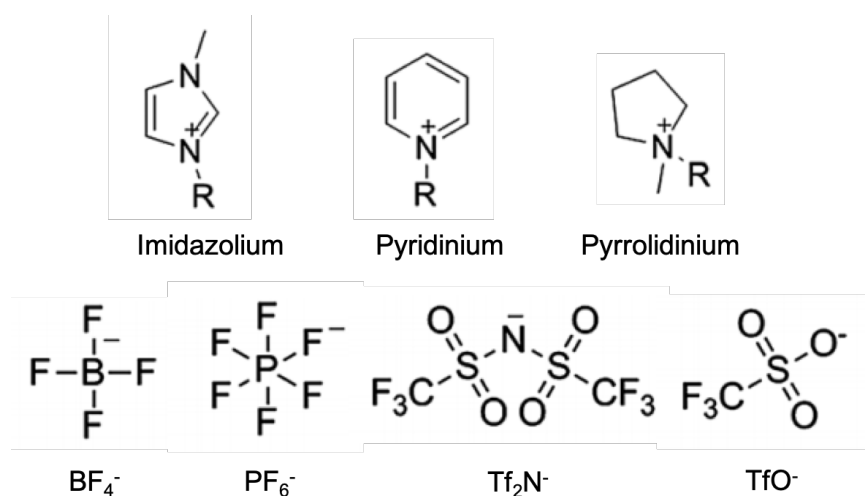


Figure 1-2. Some common cations and anions used in RTILs.

Many research groups have studied RTILs as Proton Exchange Membrane electrolytes in fuel cells. The protic neutral salt formed by a mixture at the equivalent molar ratio of bis(trifluoromethanesulphonyl)imide (HTf_2N) and benzimidazole (Bim) is thermal stable up to 350 °C and has a proton conductivity of $8.3 \times 10^{-3} \text{ S cm}^{-1}$ at 140 °C. Open circuit voltages are lower compared to a phosphoric acid fuel cell under the same condition.¹³ Other investigations reported the use of 3-(1-butyl-1H-imidazol-3-ium-3-yl)propane-1-sulphonate mixed with different acids

(HTf₂N, CH₃SO₃H, and CF₃SO₃H) as proton transport electrolytes. RTILs can affect the conductivity and glass transition temperature of proton transport electrolytes significantly.²⁹

The application of RTILs in supercapacitor has been explored for more than 10 years. The key advantage of RTILs in these applications is that the operating voltage of RTILs (up to 6 V) is much higher than conventional organic electrolytes (usually <3 V), which helps improve the energy density of supercapacitors.^{2, 30} A rather comprehensive review of the applications of RTILs in supercapacitor and related fundamental issues have been provided by Fedorov and Kornyshev.³⁰

Compared with organic electrolytes, RTILs exhibit appealing properties such as higher thermal, chemical, and electrochemical stability, negligible volatility, and nonflammability. Furthermore, RTILs' physical and chemical properties can be tuned relatively easily to meet various requirements due to their large variety of combinations of cations and anions.³¹ However, most RTILs are more expensive than common organic solvents. Meanwhile, the ionic conductivity of RTILs is usually lower than that of the organic electrolytes due to the high viscosity of RTILs, which can negatively affect the rate and power performance of electrochemical devices such as supercapacitors.²

1.1.2 Solid-state/Quasi-solid-state Electrolytes

Solid-state electrolytes often refer to solids with highly mobile ions. Due to the presence of a liquid phase in gel polymer electrolytes, some studies called them quasi-solid-state electrolytes.³²⁻³³ Although the ionic conductivity of solid-state/quasi-solid-state electrolytes is usually much lower than that of liquid electrolytes, they offer many benefits including higher energy density, increased cycle life, no leakage risk, and wider operating temperature/potential window.³⁴ From Figure 1-3 we can see there is still a huge gap between the objectives and current status of solid-

state electrolytes on some key technical parameters, which promote the further development of these materials.

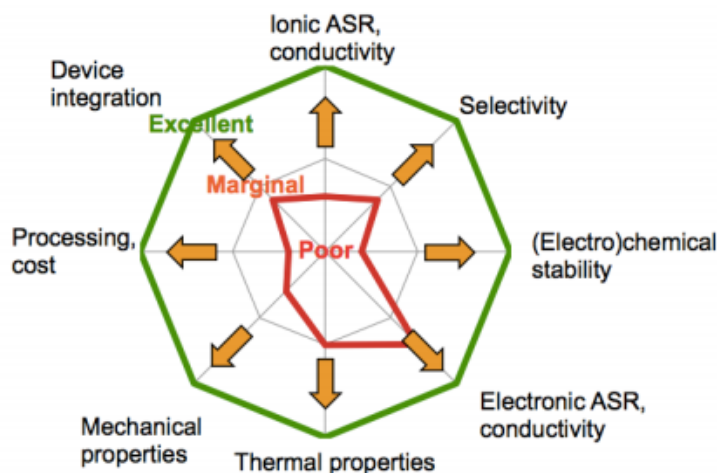


Figure 1-3. A radar diagram showing the overall objectives of solid-state electrolytes. Red lines denote the current status of solid-state electrolytes. Green lines denote the objective for ideal solid-state electrolytes. Partial axis labels: the ionic area-specific resistance (ASR) helps determine the power capability. Selectivity is the ability of a material to transport ions and neutral molecules at different rates. Processing refers to the method used to create electrolytes in the electrochemical devices. Device integration refers to the ability to integrate electrolytes with other device components. This figure is reproduced based on Ref. 35.

Inorganic electrolytes. Solid-state inorganic electrolytes continue to attract great interest, especially for application in Li-ion batteries. Much research has focused on a number of crystal structures including perovskite-type Lithium Lanthanum Titanates, NASICON-type, LiSICON- and Thio-LiSICON-type Li-ion conductors, and garnet-type Li-ion conducting oxides.³⁶ Recently, the ionic conductivities of some solid-state inorganic electrolytes (e.g. silver- and sodium-ion conductors) have approached that of liquid electrolytes.³⁷ For solid oxide fuel cells, the electrolyte is a dense ceramic layer made of zirconia-, ceria-, and lanthanum gallate-based materials that conducts oxygen ions.³⁸ The key requirements for the development and fabrication of the solid electrolyte in a solid oxide fuel cell are (1) to increase ionic conductivity and thus to reduce cell impedance; (2) to limit electronic conduction to reduce leakage currents.³⁸ For supercapacitors, there is very limited work on inorganic solid materials (i.e., ceramic electrolytes).³⁹⁻⁴⁰

Compared with the aprotic solvent electrolytes used in the current Li-ion batteries, inorganic solid-state electrolytes have higher lithium transference number (i.e., ~ 1), enhanced thermal stability, greater electrochemical stability voltage window, and diminished flammability. Furthermore, using the solid-state electrolyte can simplify the packaging and fabrication of electrochemical devices and reduces the liquid leakage risk in them. Although many inorganic solid-state electrolytes have wide electrochemical windows, there are still numerous fast ion conductors that are unstable at low potentials against negative electrodes (e.g., graphite and metallic lithium).³⁷

Polymer electrolytes. Polymer electrolytes have attracted great interest in recent years due to the possibility of overcoming the low mechanical strength and safety issue of liquid electrolytes. The ideal polymer electrolytes should meet the following requirements: (1) high conductivity, (2) high ionic transference number (i.e., ~ 1), (3) sufficient mechanical strength, and (4) high chemical, electrochemical, and thermal stability. Generally, polymer electrolytes can be roughly classified into solid polymer electrolytes, gel polymer electrolytes, and polyelectrolytes based on the ion transport mechanism and the material state. Solid polymer electrolytes are prepared by dissolving ionic salts into polymer hosts (e.g., poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), etc.) without any solvents. The diffusion of ions depends on the polymers in the electrolytes. Gel polymer electrolytes are usually fabricated by incorporating a large number of aqueous electrolytes or conducting salts dissolved in organic liquid solvents into the polymer matrix to form a stable gel with a polymer host structure. The ions diffuse in the solvent instead of in the polymer phase in these electrolytes. The systems including repeating charged groups along the backbone are known as polyelectrolytes. The ionic conductivity is contributed by the charged polymer chains and ions in polyelectrolytes.²

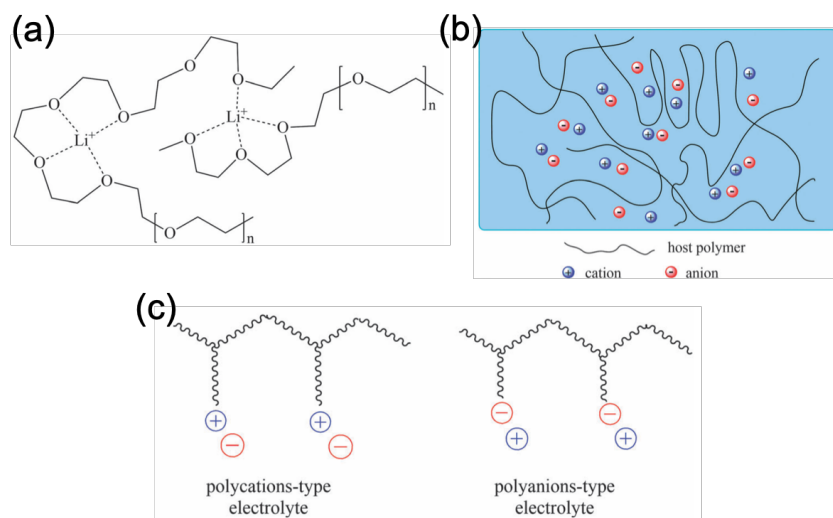


Figure 1-4. The schematic diagrams of (a) solid polymer electrolytes (e.g., PEO/ Li^+), (b) gel polymer electrolytes, and (c) polyelectrolytes. This figure is reproduced based on Ref. 2.

Solid polymer electrolyte was first fabricated in 1973 as a mixture of PEO and alkali metal salts.⁴¹ The first solid-state Li-ion battery was assembled using a mixture of PEO and Li^+ ion salt as the solid polymer electrolyte in 1979.⁴² Since then solid polymer electrolytes have been advanced tremendously. The major challenge of the application of solid polymer electrolytes in Li-ion battery is their limited ionic conductivity. Many polymer-salt complexes have been investigated. The conductivity is usually below $1 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature.^{1, 43} Fenullade and Perche first fabricated gel polymer electrolytes with the organic solution of the alkali metal salt trapped within the matrix of polymers.⁴⁴ Since then many polymer hosts have been investigated (e.g., PEO, poly(vinylidene fluoride) (PVdF), poly(acrylonitrile)(PAN), poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride-hexafluoropropylene) (PVdF-co-HFP)).² The conductivity values have largely stayed in the range of $10^{-4} \sim 10^{-3} \text{ S cm}^{-1}$ at room temperature.⁴³ The applications of polyelectrolytes in batteries have also been extensively investigated, e.g., polymers with anions (e.g., $-\text{COO}^-$, SO_3^- , and PhO^-) attached as pendant groups and with the anions (e.g., BO_4^- , AlO_4^- , AlS_4^- , and $(\text{SiO}_4)\text{Al}^-$) along the main chain have been explored.⁴⁵ Ohno et al. has

investigated the ionic conductivity of various polyelectrolytes for Li-ion batteries and reported conductivities ranging from 10^{-6} to 10^{-4} S cm⁻¹ at 50 °C.⁴⁵⁻⁴⁶

For proton-exchange membrane fuel cells, the current membranes are mostly based on the perfluorosulfonic acids, which belongs to the category of polyelectrolytes. The most prominent example is Nafion[®], which was first developed by the DuPont Company in the 1960s.⁴⁷ The backbone structure of polytetrafluoroethylene and pendant sulfonate groups in Nafion[®] provide mechanical strength and charge sites for proton transport, respectively.⁴⁷ Additionally, other perfluorinated polymer materials such as Neosepta-F[™] (Tokuyama), Gore-Select[™] (W.L. Gore and Associates, Inc.), Flemion[™] (Asahi Glass Company), Asiplex[™] (Asahi Chemical Industry) have also been adopted for proton-exchange membrane fuel cell applications.⁴⁸

Gel polymer electrolytes are most extensively studied polymer electrolytes for supercapacitors because they have the highest ionic conductivity in solid-state electrolytes. Poly(vinyl alcohol) (PVA) is a prominent representative host polymer in the hydrogel polymer electrolytes, which is the gel polymer electrolytes with water as the plasticizer. PVA offers many great properties such as high hydrophilicity, good film-forming properties, non-toxicity, and inexpensive.⁴⁹ Generally, PVA is mixed with various aqueous solutions (e.g., H₂SO₄, H₃PO₃, KOH, and LiCl) to fabricate hydrogels.² To increase the working voltage window, organic solvents (plasticizers) have been used to fabricate gel polymer electrolytes, which is called as organogel electrolytes. Copolymers with different constituent units have been regarded as promising polymeric hosts in organogel electrolytes-based supercapacitors.⁵⁰ A maximal ionic conductivity of 1.1×10^{-2} S cm⁻¹ was obtained in organogel electrolytes with copolymers as hosts.⁵¹

Overall, polymer electrolytes have reasonable mechanical properties. Meanwhile, solid-state electrolytes allow the development of diverse and bendable structures and tunable shapes for various desired applications. The ionic conductivity in polymer electrolytes is usually lower than that in the aqueous electrolytes. However, the development of gel polymer electrolyte has the potential to make up this gap.

1.2 Emerging Polymer Electrolytes and Outstanding Issues

During the past decades, polymer electrolytes have attracted more attention in the numerous potential applications due to their many great properties mentioned above. These applications often demand the electrolytes to meet multiple characteristics (e.g., high ionic conductivity and good mechanical rigidity) simultaneously. In this dissertation, the molecular structure and dynamics properties of three emerging polymer electrolytes including polymerized ionic liquids, nanoscale ionic materials, and polymeric ion gels have been investigated using molecular dynamics (MD) simulations to elucidate the physics behind their transport and/or mechanical properties.

1.2.1 Polymerized Ionic Liquids

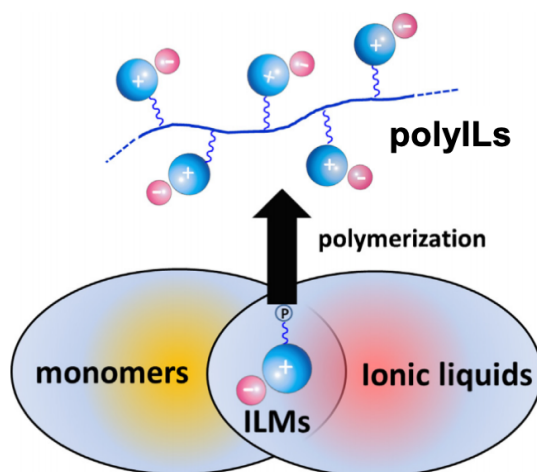


Figure 1-5. Illustration of the relationship between ILs and polyILs. ILMs: ionic liquid monomers. “P”: polymerizable group. This figure is reproduced based on Ref. 52.

Polymerized ionic liquids (polyILs), also called polymeric ionic liquids or simply poly(ionic liquid)s, are the polymeric form of RTILs (see Figure 1-5). They represent a new class of functional polymers that combine the unique properties of conventional RTILs, including good ionic conductivity, electrochemical stability, and thermal stability, with the outstanding mechanical properties of polymers. The polyILs are promising electrolytes for a variety of potential applications, such as energy conversion and storage, catalysis, separation, and adsorption.⁵²

To meet the need of such a broad range of applications, the structure and dynamics of polyILs in various systems have been intensively studied. The charge transport and structural dynamics in polyILs have been investigated experimentally using broadband dielectric spectroscopy, dynamic mechanical spectroscopy, and differential scanning calorimetry.⁵³⁻⁵⁸ By analyzing the relationship between the relaxation rate of the dynamic glass transition and the charge carrier hopping rate, it was suggested that the nature of the charge transport in these polyILs is the glass transition assisted hopping.⁵⁶ MD simulations have also been used to investigate the impact of the chemical structure on ion transport, nanoscale morphology, and dynamics in polyILs.⁵⁹⁻⁶³ The seminal work by Mogurampelly *et al.* suggested that the transport of mobile anions in bulk polyILs proceeds by intra- and intermolecular ion hopping, which occurred through the formation and breaking of ion-association between the pendant cation and the mobile anion.⁶⁴

These prior studies on the structure and dynamics of polyILs have greatly advanced our understanding of the bulk properties of polyILs. Since in many applications, polyILs are confined near extended surfaces or in narrow pores, the fundamental understanding of the structure and dynamics of polyILs near solid surfaces is often more relevant than in bulk. However, research on interfacial polyILs is still at an early stage. Many questions remain open. For example, how do the properties of a solid substrate such as surface charge affect the nanostructures of polyILs near the

substrate? How do the properties of a solid substrate affect the diffusion mechanism of the mobile ions? Which kind of mechanism, e.g., intra- or inter- chain hopping, dominates the diffusion of the interfacial mobile anions at different scales? Answering these questions are essential for the rational design of polyIL to optimize their performance in electrochemical energy storage and conversion systems.

1.2.2 Nanoscale Ionic Materials

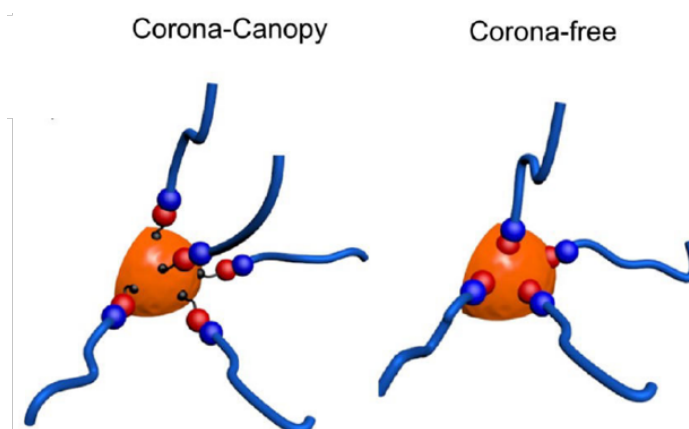


Figure 1-6. The schematic diagrams of two nanoscale ionic materials. This figure is reproduced based on Ref. 65.

Nanoscale ionic materials (NIMs) are an emerging class of materials made of nanoparticles and charged polymeric canopies.⁶⁵⁻⁶⁸ Each nanoparticle carries a net charge, either due to its surface groups or covalently-attached corona featuring ionic functional groups. The canopies, essentially oligomeric counterions, are attached to individual nanoparticles *dynamically* through electrostatic interactions. NIMs have been used as plasmonic materials, battery electrolytes, luminescent materials, and porous liquids for gas separation.⁶⁹⁻⁷³

To fully exploit NIMs' potential for a given target application, their properties must be optimized. Many existing studies focused on NIMs made of nanoparticles with moderate/high surface charge density and polymers with relatively long chains.^{65, 69, 74} As charged polymers are

attracted toward the nanoparticle, polymer crowding occurs. An “onion-like” model has been proposed for the canopy in such situations.^{65, 67} polymers in the canopy form layers around the particle, with those in the inner (outer) layer strongly (weakly) associated with the particle. In neat NIMs, the mobility of the polymers strongly associated with the nanoparticle can be more than ten times less mobile than bulk polymers. The exchange between these populations of polymers is slow.⁶⁷ When electrolyte ions are presented in NIMs, they screen nanoparticle’s charge. This decreases (increases) the number of the strongly (weakly) associated polymers and facilitates the exchange between polymers in these two populations.⁶⁷ These seminal works greatly improved our understanding of polymeric canopies, but some important practical questions and conceptual issues remain to be addressed.

From a practical perspective, while the existence of multiple layers (populations) of polymers across canopies is established, many key questions on the quantitative aspects of canopy remain unanswered. Specifically, how are polymers distributed across the canopy – do they form two or more layers? What is the relative population of the polymers in different layers and how does it respond to the addition of electrolyte ions? What conformation do polymers in different layers adopt? Since polymers strongly associated with nanoparticles experiences crowding, their conformation should differ from that of the bulk polymers. However, the conformation of these polymers is not yet known. Hence, the radius of gyration of bulk polymers is often used to infer the packing and thus the population of polymers near nanoparticles. The accuracy of this approach is yet to be clarified.

1.2.3 Polymeric Ion Gels

Ion gels, polymeric networks swollen by RTILs, are another class of polymer electrolytes that has attracted much attention recently.⁷⁵ When RTILs are combined with suitable polymers, the resulting ion gels can provide many of the electrical, thermal, and mechanical properties desired for polymer electrolytes.⁷⁶⁻⁸¹ A recent breakthrough in this field is the synthesis of liquid crystalline gels containing a rigid-rod polyanionic aramid poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide (abbreviated PBDT) and a RTIL 1-ethyl-3-methyl imidazolium trifluoromethane-sulfonate ([C₂mim][TfO]).⁸² Figure 1-7 shows that this ion gel is formed through the ion exchange between a water-miscible ionic liquids and an aqueous polyelectrolyte seed solution containing polyanions PBDT and Na⁺ counterions. The as-formed gel is then heated under vacuum to remove the water inside it. These gels exhibit high ionic conductivity, widely tunable modulus, excellent thermal stability, and transport anisotropy.

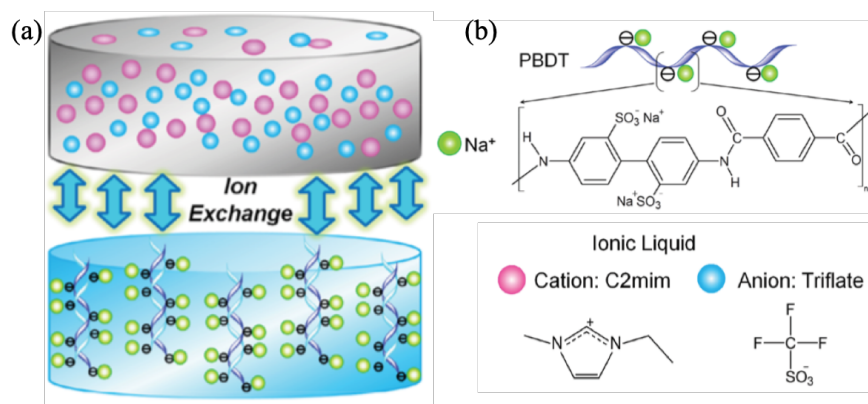


Figure 1-7. (a) Preparation of the anisotropic PBDT ion gels through ion exchange between a top RTIL layer and a bottom PBDT aqueous seed solution. (b) The chemical structure of the PBDT polyanion and RTIL ion pair. This figure is reproduced from Ref. 82.

At present, the structure of this ion gel is not yet well understood. XRD measurement suggests that the PBDT nanorods are well aligned and the spacing between the neighboring nanorods is less than a few nanometers.⁸² The distribution and diffusion of RTILs in the ion gel, which control the gel's ion transport and mechanical properties, is largely unknown. Nevertheless, prior research on

bulk and interfacial RTILs⁸³⁻⁹⁶ can serve as a foundation for understanding the RTILs in ion gels. In bulk RTILs, cation-anion interactions are strong and thus each ion effectively resides in a cage formed by its neighbor ions. The diffusion of an ion is strongly affected by the cage surrounding it.⁹⁶⁻⁹⁹ When RTILs are confined near charged surface or within cylindrical nanopores, alternating layers of counter-ions and co-ions form and charge overscreening often occurs near the charged walls.^{30, 87, 100} The diffusion of ions adjacent to charged pores wall is usually slowed down compared to the bulk ions.^{96, 101} When RTILs are confined in polymer membranes such as PEO, the local structure of ion pairing exhibits similar pattern as in bulk RTILs although the imidazolium cations are also found to be partly solvated by polymer chains.¹⁰² The dynamics of the imidazolium cations is notably slowed down by the polymers.¹⁰³ It would be useful to explore to what extent the distribution and dynamics of RTILs in ion gel differ from the above more widely explored systems.

Beside the structure and dynamics of RTILs in this material, the superior mechanical property of the ion gels is little understood. One anticipates that the structure of interfacial RTILs and the surface forces mediated by RTILs play an essential role in the mechanical behavior of ion gels. In this regard, the interfacial interactions between charged objects separated by RTILs have recently gained significant attention, e.g., systematic experimental studies using various surfaces (e.g., mica and silica) and RTILs (e.g., 1-ethyl-3-methylimidazolium ethylsulfate and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide) have been reported recently.¹⁰⁴⁻¹⁰⁸ These studies revealed that, for small surface separations of typically less than 10 ion diameters, the surface force resembles the classical short-range structural force. While a growing body of experiments shows that such surface force can also be long-range, especially when aprotic RTILs are involved.¹⁰⁸⁻¹¹¹

It has been established that the structure of RTILs confined between charged surfaces are essential for understanding these interactions.

The insight from the existing research on interfacial RTILs and the inter-surface interactions mediated by them can serve as a useful starting point for understanding the structure and dynamics of RTILs and the interaction between PBDT nanorods in ion gels. Nevertheless, the RTILs in these new gels exist in a rather different environment compared to those examined in the prior studies (e.g., bulk liquids, nanopores, and neutral polymer membranes). Meanwhile, few simulations have been performed to delineate the surface forces and interfacial RTIL structure between two nanorods with a critical dimension comparable to the ion size. It is hard to extrapolate the data from prior studies to the ion gels and many questions remain open. For example, how do cations and anions organize around the polyanions? What are their dynamics? How are these dynamics related to the ion distribution near the polyanions, and ultimately the mass fraction of polyanions and the presence of metal ion impurities in the ion gel? How does the surface charge affect the interactions between the polyanion nanorods? What is the range of these interactions? How do the distributions of ions around the objects determine these interactions? Before these questions are answered, the transport and mechanical properties of ion gels cannot be understood fundamentally.

1.3 Outline of the Dissertation Work

In this dissertation, I explore the molecular structure and dynamics of three novel polymer electrolytes, polyILs, NIMs, and polymeric ion gels using molecular dynamics simulations. These

three types of polymer materials share the commonalities that they all feature Coulombic liquids^{*} and their properties are controlled by the Coulombic interactions between the charged polymers and the liquids, between the liquids, and between the charged polymers. The central line of the dissertation is to understand the molecular mechanisms underlying the structural and transport properties of these systems, with a focus on answering the questions raised at the end of Sections 1.2.1, 1.2.2, and 1.2.3. By understanding these mechanisms and answering those questions, I hope to provide theoretical guidance on how to tailor the properties of these materials through rational material design. The rest of the dissertation is organized as follows.

In Chapter 2, the structure and dynamics of a representative polyILs (poly(1-butyl-3-vinylimidazolium hexafluorophosphate)) near neutral and charged quartz substrates were investigated. It was shown that solid substrates can affect the nanostructure of the interfacial polyILs (e.g., out-of-plane layering, in-plane clustering, and coordination of the interfacial anions) and the diffusion mechanism of the interfacial mobile ions (e.g., intra- or inter-chain hopping).

In Chapter 3, the structure and dynamics of the canopies of a model NIM with long polymer chains, high surface charge density, and large nanoparticle diameter were studied. It was showed that the contaminated ions can affect the conformation of the polymeric canopies (e.g., the end-to-end distance and the radius of gyration) and the dynamics of canopies (e.g., attached/detached time scale and diffusion coefficients). Meanwhile, the electrical double layers formed by the canopies exhibit both commonalities with those in RTILs and new features unique to NIMs.

^{*} Coulombic liquids are liquids whose structure and dynamics are controlled primarily by the Coulombic interactions between its constituent molecules. Typical examples of Coulombic liquids include RTILs and highly concentrated organic electrolytes.

In Chapter 4, the structure and dynamics of C_2mim^+ and TfO^- ions in the PBDT- $[\text{C}_2\text{mim}][\text{TfO}]$ ion gel were investigated. It was discovered that the ions exhibit distinct structure at intermolecular scale and inter-rod scales. The effects of the loading of PBDT polyanion and the residual Na^+ ions in the ion gel on the dynamics of ions were clarified.

In Chapter 5, the interactions between two aligned nanorods mediated by RTILs were studied. It was found that the rod-rod interaction energy oscillates with rod-rod spacing. To separate two rods initially positioned at the principal energy minimum, a significant energy barrier must be overcome. The molecular mechanisms behind these observations and their technical implications were discussed.

In Chapter 6, the major contributions of this dissertation are summarized.

CHAPTER 2 Molecular Structure and Dynamics of Interfacial Polymerized Ionic Liquids

Disclosure

This work has been published by the American Chemical Society: Z. Yu, C. Fang, J. Huang, B.G. Sumpter, and R. Qiao, "Molecular Structure and Dynamics of Interfacial Polymerized Ionic Liquids". J. Phys. Chem. C, 122, 22494, 2018

2.1 Introduction

Polymerized ionic liquids (polyILs), also called polymeric ionic liquids or simply poly(ionic liquid)s, are the polymeric form of ionic liquid units. They represent a new class of functional polymers that combine the unique properties of conventional room-temperature ionic liquids (RTILs) including high ionic conductivity, electrochemical stability, and thermal stability, with the outstanding mechanical properties of polymers.^{52, 112-113} Through polymerization of RTIL monomers or chemical modification of existing polymers, polyILs can be synthesized with polymeric repeating units consisting of cations/anions of RTILs.¹¹⁴⁻¹¹⁵ The common IL cations include the imidazolium, pyridinium, alkylammonium, pyrrolidinium, and guanidinium ions. The anions can be selected from a broad range of inorganic (e.g., PF_6^- , BF_4^-) and organic (e.g., TFSI⁻) ions.¹¹² The polyILs are promising electrolytes for a variety of potential applications such as energy conversion and storage, thermoresponsive materials, catalysts, separation, and adsorption.⁵²

To meet the need of such a broad range of applications, the structure and dynamics of polyILs in various systems have been intensively studied in recent years. The charge transport and structural dynamics in polyILs have been investigated experimentally using broadband dielectric

spectroscopy, dynamic mechanical spectroscopy, and differential scanning calorimetry.⁵³⁻⁵⁸ Although a decoupling between ion transport and structural dynamics was observed for polyILs in some studies, implying a failure of the classical theories in describing RTILs,^{53-54, 116} the conductivity of polyILs could still be quantitatively described using an effective-medium approximation reflecting their microphase-separated character.⁵⁵ More recently, Kremer and co-workers examined the glassy dynamics and charge transport in a group of polyILs that exhibit the highest dc-conductivity at temperature lower than 100°C so far.⁵⁶ By analyzing the relation between the relaxation rate of the dynamic glass transition and the charge carrier hopping rate, it was suggested that the nature of the charge transport in these polyILs is the glass transition assisted hopping. Intriguingly, for the first time, the dc-conductivity of these polyILs increases with the degree of polymerization (DP).⁵⁶ The hopping rate also increases with DP, suggesting that transport along the polymer chains is facilitated as the chains grow longer.

Molecular dynamics (MD) simulations have also been used to study the structure and dynamics of polyILs. Excellent agreement was found on the structure factors obtained from X-ray scattering and MD simulations.¹¹⁷ This demonstrates the power of MD simulations in providing a fundamental understanding of the molecular structure of polyILs. MD simulations have been further used to investigate the impact of the chemical structure on ion transport, nanoscale morphology, and dynamics in polyILs.⁵⁹⁻⁶³ These works were corroborated by experiments,⁶² highlighting that polyILs with small mobile counterions and short alkyl side chain usually have higher ionic conductivity. The seminal work by Mogurampelly *et al.* suggested that the transport of mobile anions in bulk polyILs proceeds by intra- and intermolecular ion hopping, which occurred through the formation and breaking of ion-associations between the pendant cation and

the mobile anion.⁶⁴ As a result, anions' mobility in polyILs was correlated to the average lifetime of ion-associations.⁶⁴

These prior studies on the structure and dynamics of polyILs have greatly advanced our understanding of the bulk properties of polyILs. Since in many applications, polyILs are confined near extended surfaces or in narrow pores, the fundamental understanding of the structure and dynamics of polyILs near solid surfaces is more relevant than in bulk. There have been extensive studies of polymers at solid interfaces, which generally reveal a wall-bound polymer layer with distinct structures.¹¹⁸⁻¹¹⁹ However, research on interfacial polyILs is still at an early stage. To our best knowledge, only one experimental work exists about the dynamics of polyILs film on silica substrates.¹²⁰ This study showed that, above the glass transition temperature, ion dynamics slowed down with a decrease of the film thickness, which could be attributed to the increasing influence of the polyILs/substrate interactions.¹²⁰ Due to limited studies, many questions remain open. For example, how do the properties of a solid substrate such as surface charge affect the nanostructures of polyILs near the substrate? How do the properties of a solid substrate affect the diffusion mechanism of the mobile ions? Which kind of mechanism, e.g., intra- or inter- chain hopping, dominates the diffusion of the interfacial mobile anions at different scales? In this work, we aim to address these questions by carrying out MD simulations of the structure and dynamics for polyILs supported on charged and neutral quartz substrates.

2.2 Simulation Systems and Methods

MD systems and molecular models. The MD system consisted of a polyIL film supported on an quartz substrate (see Figure 2-1). The system, periodic in all three directions, measured 6.880, 5.897, and 30 nm in the x , y , z directions, respectively. The system size in the x and y directions

was determined by the lateral dimensions of the substrate. The large size of 30 nm in the z direction was adopted to ensure a vacuum space to be created above the polyIL film. As a reference, a bulk polyIL was also simulated. Poly(1-butyl-3-vinylimidazolium hexafluorophosphate) was used as the polyIL in all simulations. Each polymer chain consisted of 32 monomer units. The structure of the monomer and the anion are shown in the inset of Figure 2-1. The polyIL film had 16 polyIL chains, giving a film thickness of ~ 5.0 nm (see Figure A-1). This thickness is chosen because (1) it is close to the regime that can be explored experimentally (e.g., the thinnest polyIL films studied by the Sangoro group is 7.5 nm)¹²⁰ and (2) exploring thicker films is computationally demanding because an all-atom description is adopted for the polymers in this work (see below). In each simulation, the number of anions (PF_6^-) was adjusted to maintain the electrical neutrality of the system. The polyILs were modeled using the force fields developed by Mogurampelly *et al.*⁶⁴

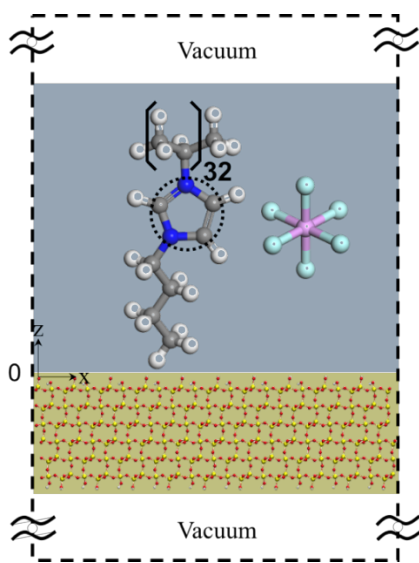


Figure 2-1. A schematic of the simulation system. The quartz substrate (yellow region) is covered by a slab of polyILs (blue region). The upmost layer of oxygen atom of the substrate is defined as $z = 0$. The inset shows the chemical structure of the polyIL that consists of 32 units (not to scale with the substrate). The grey, blue, white, magenta, and cyan spheres denote the carbon, nitrogen, hydrogen, phosphorus, and fluorine atoms, respectively. The dashed black lines denote the simulation box.

The substrate of ~ 2 nm in thickness was cleaved from the (101) plane of an α -quartz crystal. Both of the top and bottom surfaces were covered by silanol groups, with a surface density of 5.92 nm^{-2} . The outmost layer of oxygen atom in the silanol groups on the top surface is defined as $z = 0$. Both neutral and charged quartz surfaces were simulated. The termination of silanol groups made the substrate neutral. For the system with a charged substrate, randomly selected silanol groups on the top surface were deprotonated to produce a surface charge density of -0.24 C/m^2 . We note that, although the mechanisms for electrifying solid surfaces in RTILs are generally not well understood, recent experimental works suggest that silica surfaces in contact with ionic liquids are often negatively charged.¹²¹⁻¹²³ Because we are mainly interested in how the net surface charge affects the structure and dynamics of the interfacial ions, we selected two charge densities (0 and -0.24 C/m^2) that correspond to the relatively low and high surface charge limits. We hope the effects of surface charge on interfacial polyIL structure revealed here will stimulate new experimental and theoretical studies on the electrification of solid surfaces (and silica surface in particular) in ionic liquids in the future. The neutral and deprotonated quartz substrates were constructed and modeled following the procedure and force fields in the work of Krouti *et al.*¹²⁴ The structures of the neutral and charged quartz substrates are shown in Figure A-1.

MD methods. All-atom simulations were performed using the GROMACS code¹²⁵ with a 2 fs time step. The non-electrostatic interactions were computed by direct summation with a cutoff length of 1.2 nm. The electrostatic interactions were computed using the Particle Mesh Ewald (PME) method. The real space cutoff and FFT spacing were set to 1.2 and 0.12 nm, respectively. All bonded interactions were computed except that the length of bonds involving hydrogen atoms were constrained using the LINCS algorithm.¹²⁶ The oxygen and silicon atoms of the substrate are fixed, while the movement of the hydrogen atoms of the silanol groups is allowed by taking into

account the bond-angle and dihedral-angle variations. To remove the periodicity in the direction normal to the wall, the slab correction to the PME method was applied.¹²⁷

To enable a realistic simulation of polyILs, after the polyILs were packed into a system, the system was heated and then annealed to surmount the local energy barriers in the polymer chain's conformation. In the heating stage, the temperature of polyILs was increased from 300 K to 1200 K over 30 ns. The system was then equilibrated for 20 ns at $T=1200$ K. In the annealing stage, the system was cooled down to 540 K at a rate of 10 K/ns. After the annealing step, each system was further equilibrated for 80 ns, followed by 240 ns production run at 540 K, which is ~ 1.2 times of the glass transition temperature (T_g) of the bulk polyIL.⁶⁴ The temperature of the system was maintained using the velocity rescaling thermostat.¹²⁸ The heating and annealing processes of the bulk polyIL system were executed in the NPT ensemble. All other simulations were performed in the NVT ensemble. For each of the systems considered, three different configurations were extracted during the equilibration at 1200 K. Subsequent annealing and equilibration of these configurations led to three independent initial configurations of each system at 540 K. The data reported here are averaged results from the simulations of the three initial configurations.

2.3 Results and Discussion

2.3.1 Structure of Interfacial PolyILs

It is known that near extended surfaces, conventional RTILs often exhibit structures distinctly different from their bulk structures.³⁰ Since polyILs share many similar properties with RTILs, interesting structures should develop in polyILs near extended surfaces. Understanding these structures and their responses to external stimuli, e.g., the electrification of the extended surfaces, can help understand the transport properties of polyILs. In this section, we examine the structure

of polyILs near neutral and charged substrates, i.e., the out-of-plane layering of polyILs, the in-plane clustering of interfacial cations, and the coordination of interfacial anions by cations.

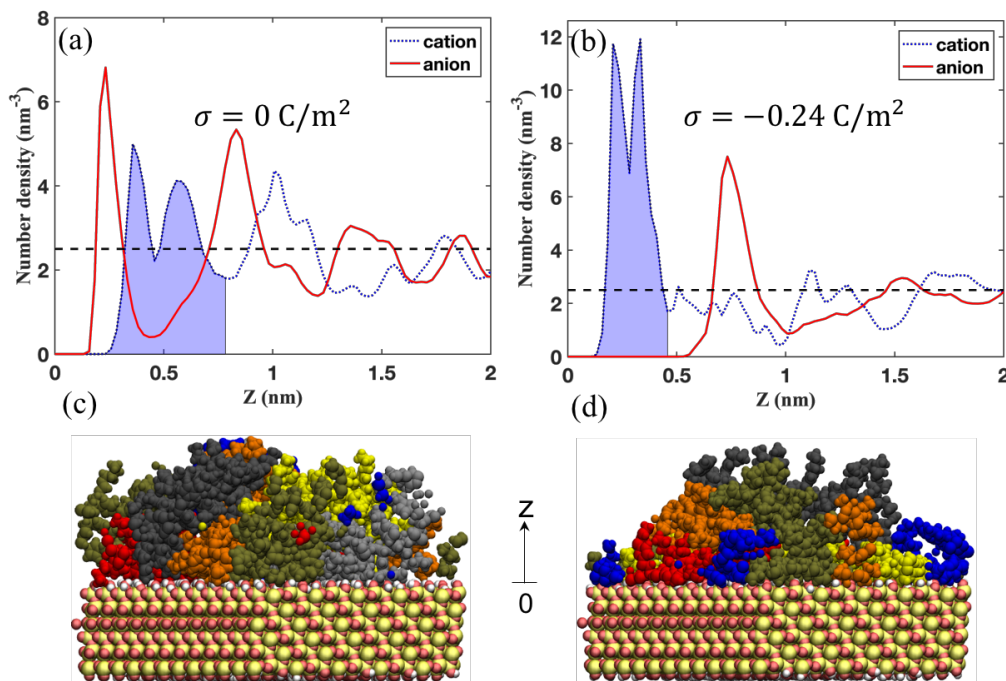


Figure 2-2. Distribution of polyILs near quartz substrates. (a-b) The number density profiles of anions and cations near the neutral (a) and charged (b) quartz surfaces. The dashed lines indicate the average bulk ion density. (c-d) Snapshots of representative frames of the polymer chains with at least one of its pendant cations in the first cation layer near the quartz surfaces (i.e., in the shaded region in panels a and b). Polymers in different chains are shown in different colors.

Out-of-plane layering. We start by examining the out-of-plane layering of polyILs near the neutral and charged substrates. Figure 2-2a and 2-2b show the number density profiles of the PF_6^- and polymerized cations (i.e., BMIM^+ ions) in the direction normal to the neutral and charged quartz substrates, respectively. The position of the cations is based on the center of mass (COM) of their imidazolium rings (labeled by a dashed circle in Figure 2-1; for brevity, the imidazolium rings of the polymerized BMIM^+ ions are hereafter referred to as the cations). Regardless of the surface charge, layering of ions can be clearly observed in the region $0 < z < \sim 1.5\text{-}2.0$ nm, which is expected for liquids near solid substrates. The first few layers of ions near the substrates are termed as interfacial ions and will be studied in detail below. In addition, in the middle portion of

the polyIL films ($z = 2.5\text{-}4\text{ nm}$), the ion density is relatively flat (see Figure A-1), e.g., the average PF_6^- ion density in this middle portion is 2.37 and 2.40 nm^{-3} for the polyIL films on the neutral and charged substrates, respectively. These densities are close to the PF_6^- ion density in the reference bulk polyIL system we modeled separately (2.50 nm^{-3}), thus making it reasonable to link the polyIL films studied here to the reference bulk polyILs.

Near the neutral quartz surface, visualization of the trajectory shows that the cations in the first density peak ($0.21\text{ nm} < z < 0.81\text{ nm}$ in Figure 2-2a) are adsorbed on the quartz surface. This cation layer is flanked by two layers of PF_6^- ions residing in the first and second anion density peaks ($0.13\text{ nm} < z < 0.43\text{ nm}$ and $0.43\text{ nm} < z < 1.21\text{ nm}$). While the concurrent accumulation of cations and anions on neutral quartz surfaces is similar to that observed when conventional $[\text{BMIM}][\text{PF}_6]$ liquids are brought into contact with the same surfaces, subtle differences are also noted. For conventional RTILs, the layers of cation ring and the PF_6^- ions are located at roughly the same distance from the quartz surface.¹²⁹ For polyILs, the first anion layer is closer to the quartz surface than the cation rings by $\sim 0.2\text{ nm}$. Such a difference can be attributed to the combined steric and entropic effects of the cations and, to a lesser extent, to the local interactions between the PF_6^- ions and quartz surfaces. Specifically, unlike the BMIM^+ ions in RTILs, the cations in polyILs are branches of polymer chains. Therefore, bringing these cations closely to the quartz surface incurs higher entropic cost (as the chains' conformation is constrained by the solid substrate) and stronger steric hindrance (as the space near the substrate is partially occupied by polymer backbones) than in $[\text{BMIM}][\text{PF}_6]$ liquids. Furthermore, the electrostatic attraction between the PF_6^- ions and atoms of the quartz surface protruding into the polyILs with positive partial charges (e.g., the silanol groups' hydrogen atoms, see Figure A-2) favors the accumulation of PF_6^- ions near the surface.

The situation changes significantly when the quartz substrate carries a surface charge density of -0.24 C/m^2 . As shown in Figure 2-2b, a more distinct and compact cation layer appears in $0.10 \text{ nm} < z < 0.46 \text{ nm}$ from the quartz surface. PF_6^- ions are no longer contact adsorbed on the quartz surface because of their electrostatic repulsion with the negatively charged quartz surface. Instead, the first layer of anions appears in the range $0.50 \text{ nm} < z < 1.01 \text{ nm}$. The layering of ions is more pronounced near the charged quartz surface: alternating layering of cations and anions, a key signature of interfacial structure of RTILs near electrified surfaces, is observed even at $\sim 2.0 \text{ nm}$ from the quartz surface. The different layering of cations and anions near neutral and negatively charged substrates leads to interesting features of ions and polymers in the interfacial zone.

First, while formation of distinct cation and anion layers near both types of substrates leads to charge separation near the quartz surface, the extent and nature of charge separation is different. Very close to the neutral quartz surface ($z < 1.2 \text{ nm}$), the space charge in the electrolyte phase is mainly negative (cf. Figure A-3) because the first cation layer is flanked by two PF_6^- ion layers with higher peak intensities (cf. Figure 2-2a). Charge separation is very weak at $z > 1.2 \text{ nm}$. On the other hand, very close to the charged quartz surface ($z < 0.6 \text{ nm}$), the space charge is positive to balance the surface charge on the substrate. Similar to the situation in simple RTILs,³⁰ at larger distance, the space charge density oscillates and the surface charge can become overscreened in some region (e.g., $0.6 \text{ nm} < z < 1 \text{ nm}$, see Figure A-3).

Second, the more significant and compact accumulation of cations near the negatively charged quartz substrate implies that polymers are packed more densely than near neutral substrates, which can lead to different polymer conformations near the substrate. Indeed, as shown in the snapshots of the polymers chains with at least one of their pendant cations in the first cation layer near neutral (Figure 2-2c) and charged substrates (Figure 2-2d), polymers whose cations are adsorbed on the

negatively charged substrates are less stretched in the z -direction compared to those adsorbed on the neutral substrates. As will be shown below, the different conformations of polymers near these substrates can also lead to significant difference in the lateral organization of interfacial cations.

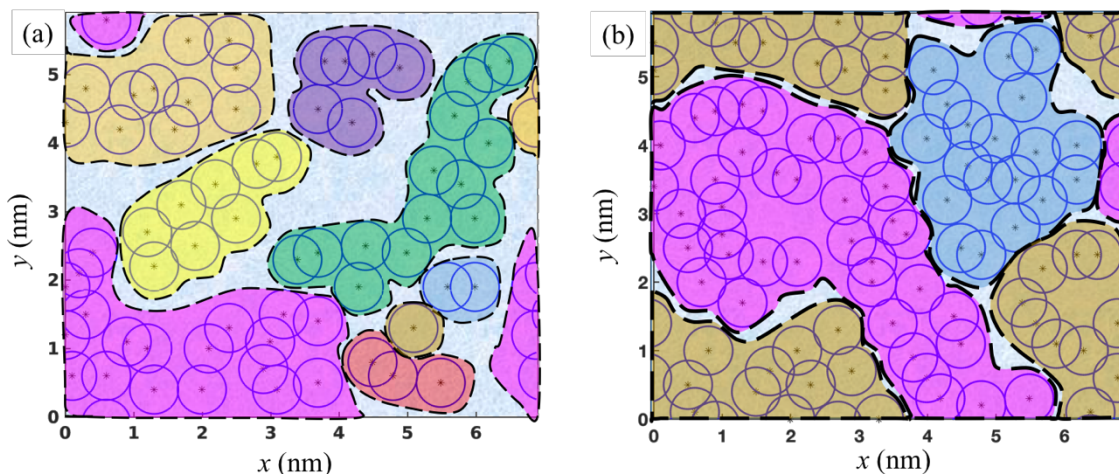


Figure 2-3. Representative lateral distribution of the first layer of cations near (a) neutral and (b) charged substrates. Each circle represents one contact-adsorbed cation. Areas with different colors denote different clusters of cations.

In-plane clustering. We next examine the lateral organization of interfacial cations. Such lateral organization is potentially important for two reasons. First, prior work on simple RTILs near solid substrates shows that the lateral organization of interfacial ions can affect their dynamics.¹³⁰⁻¹³¹ Second, the organization of cations in polyILs is known to affect the inter- and intra- chain hopping of the mobile anions and thus their dynamic properties.⁶⁴ Here we focus on the clustering of cations in the first cation layer near quartz surfaces. By examining MD trajectories, we identify the representative configuration of these cations near neutral and charged quartz surfaces. In Figure 2-3a, a representative frame of the trajectory is presented, where each cation in the first cation layer near the neutral quartz surface, i.e., the cations in the shaded region in Figure 2-2a, is projected onto the xy plane and denoted using a circle with a diameter of 0.71 nm. Note that 0.71 nm corresponds to the location of the first valley of the cation-anion and cation-cation

radial distribution functions (RDFs) in bulk polyILs and can be roughly taken as the effective diameter of the cation (see Figure A-4). Some partial overlap between the circles representing the cations is observed because not all cations are in the same height from the surface and their rings are not necessarily parallel to the surface. The space not covered by the circles is not empty but occupied by the cations' tails (see inset of Figure 2-1) or the mobile anions. The cations shown in Figure 2-3 are divided into clusters under the condition that the circles representing all ions in a cluster are in direct contact or indirect contact through circles representing other ions in the same cluster. It is evident that ions in the first cation layer near the neutral quartz substrate form several small clusters (marked by different colors Figure 2-3a), whereas those near the charged quartz substrate aggregate into larger clusters (marked by different colors in Figure 2-3b). A comprehensive analysis of the MD trajectories further shows that, in the systems studied here, the first cation layer near the neutral quartz surface on average has 10.5 clusters each with an average of 6.25 cations. In comparison, the first cation layer near the charged quartz surface on average has only 3.0 clusters each consisting of 29.92 cations. These results thus indicate that, the interfacial cations near neutral quartz substrates can form a greater number of smaller clusters in the horizontal plane, while the interfacial cations near charged quartz substrate tend to form a smaller number of more extensive clusters.

Coordination of interfacial PF_6^- ions. We then consider the coordination of interfacial anions by cations because ion coordination in bulk polyILs is known to play a critical role in controlling the transport of bulk anions.¹³²⁻¹³³ We focus on three types of interfacial anions: those in the first and second anion layers near the neutral quartz substrate ($0.13 < z < 0.43$ nm; 0.43 nm $< z < 1.21$ nm) and those in the first anion layer near the charged quartz substrate (0.50 nm $< z < 1.01$ nm).

An anion is coordinated by a cation if its distance to the cation is less than 0.71 nm, which corresponds to the first valley of the cation-anion RDF in bulk polyILs (see Figure A-4).

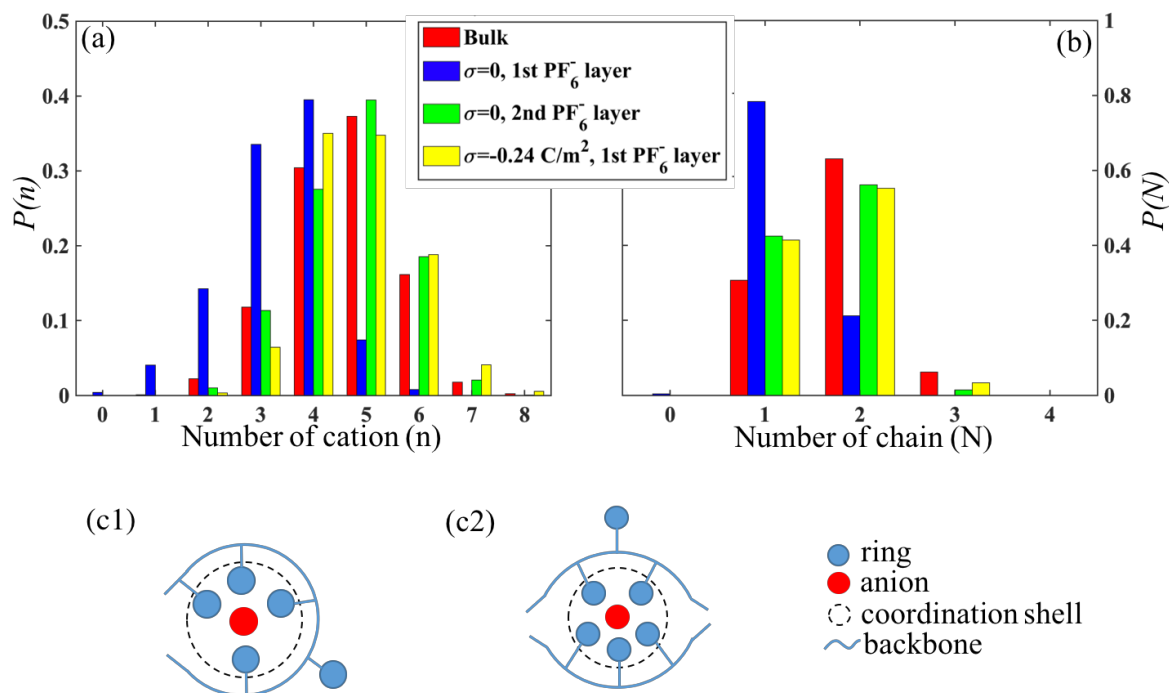


Figure 2-4. (a-b) The probability that a given anion is simultaneously coordinated with n cations ($P(n)$, panel a) and N polymer chains ($P(N)$, panel b). (c) Schematics of the representative coordination of the anions in the first anion layer near the neutral substrate (c1) and in bulk, second anion layer near neutral quartz surfaces, or the first anion layer near charged quartz surfaces (c2).

For each of the three types of interfacial anions, the probability of finding different number of cations in their coordination shell is shown in Figure 2-4a and their average number of coordination cations is summarized in Table 2-1. Near neutral quartz surfaces, the coordination of the first layer of anions by cations deviates strongly from that in bulk polyILs. Figure 2-4a shows that the probability distribution shifts toward a smaller number of coordination cations, and a majority of the anions in this region are associated with three to four cations, compared to four to five cations for the bulk anions. The average number of cations coordinating these anions is reduced to 3.33, compared to 4.59 in bulk polyILs (see Table 2-1). Such a reduced coordination number is mostly caused by the geometrical confinement. The coordination of the second layer of anions, however,

is rather similar to that of the bulk anions: these anions are most likely coordinated by five cations and the probabilities of an anion being associated with four or six cations are also more than 10%.

Near negatively charged quartz surfaces, the coordination of the first layer of anions also resemble that of bulk anions. A small difference is that the probability of an anion associating with 4, 6, and 7 cations is slightly higher than the bulk anions. As a result, the average number of cations coordinating these anions is ~5% higher than that in bulk polyILs (see Table 2-1). Two factors contribute to the slightly enhanced coordination of the interfacial anions by cations. First, the first interfacial anion layer is located at a distance >0.5 nm from the surface. Thus, the reduction of cation coordination due to geometrical confinement, which is significant for the first anion layer near neutral quartz surfaces, is minor. Second, the significant accumulation of cations near the negatively charged quartz surface (e.g., Figure 2-2b shows that the first cation density peak is ~5 times of the bulk cation density) provides a cation-rich micro-environment for the interfacial anions.

Table 2-1. The average number of cations and chains coordinating interfacial anions and bulk anions.

	Anions in bulk polyILs	1 st anion layer near neutral quartz surfaces (0 nm $< z < 0.43$ nm)	2 nd anion layer near neutral quartz surfaces (0.43 nm $< z < 1.21$ nm)	1 st anion layer near charged quartz surfaces (0.50 nm $< z < 1.01$ nm)
Number of coordination cations	4.59	3.33	4.69	4.80
Number of coordination chains	1.76	1.21	1.59	1.62

In addition to the number of coordination cations, the number of polymer chains that contribute cations to the coordination of a mobile anion is also critical to examine. This has a profound effect on the transport and dynamics of mobile anions in polyILs because intra-chain and inter-chain hoppings contribute differently to the transport of mobile anions, at least in bulk polyILs.⁶⁴ For each of the three types of interfacial anions, the probability of an anion being coordinated by

cations belonging to different number of polymer chains is shown in Figure 2-4b and their average number of coordination polymers is summarized in Table 2-1. As shown in Figure 2-4b, similar to bulk anions, the second anion layer near the neutral quartz surface and the first anion layer near the negatively charged surfaces are mainly associated with two polymer chains simultaneously, and the average number of coordination chain for both types of interfacial anions are only marginally smaller than that in bulk polyILs (cf. Table 2-1). In comparison, anions in the first anion layer near the neutral quartz surface are mostly coordinated by just one polymer chain, suggesting that the confinement by neutral quartz surface greatly perturbs the coordination environment of these anions. Based on these results, the prevailing coordination structure of the interfacial anions can be constructed as shown in Figure 2-4(c1-c2): the ions in the first anion layer near neutral quartz surfaces are associated with four cations belonging to a single polymer chain while the ions in the second anion layer near neutral quartz surfaces and in the first anion layer near negatively charged quartz surfaces are associated with five cations coming from two different polymer chains.

2.3.2 Transport to Interfacial polyILs

The prior work on transport of mobile ions in bulk polyILs highlighted the key role of anion-cation association in controlling the ion diffusion.⁶⁴ Because anions at quartz-polyIL interfaces are coordinated by interfacial cations that show heterogeneous distributions in terms of out-of-plane layering and in-plane clustering (cf. Figure 2-2 and 2-3), their transport could be more complicated than that of bulk anions. To delineate the transport of the interfacial anions, we first characterize several different aspects of their movement and then examine their diffusion behavior.

Ion hopping. In bulk polyILs, mobile anions diffuse by hopping between the relatively stationary cations on polymer chains.⁶⁴ For the interfacial anions, this diffusion mechanism should also prevail because the dynamics of the pendant cations and polymer chains in the solid-polyIL interfacial zone are more sluggish than their bulk counterparts. To clarify how interfacial anions diffuse along/between the polymer chains, we define a hopping event as the movement of an anion in which its association with the cations changes (e.g., the number *or* the identity of its coordination cation(s) changes), and distinguish two types of ion hopping events. If an anion remains coordinated by the cation(s) of the same polymer chain(s) after hopping, such a hopping is defined as the type A hopping, i.e., an intra-chain hopping. Otherwise, the hopping is defined as the type B hopping, i.e., an inter-chain hopping. For the polyIL and temperature considered here, ion hoppings occur at picoseconds time scale.⁶⁴ Thus we examined the movement of anions at 1 ps time interval and categorized their hopping (using time intervals such as 10 ps does not notably change the results, similar to that reported for bulk polyILs⁶⁴).

Figure 2-5 shows the probability of the two types of hoppings for different interfacial anions in comparison with bulk anions. The statistics of the hopping events of the interfacial anions are similar to that of bulk anions: the type A intra-chain hopping is the dominant hopping mode for the anions near both neutral and charged quartz surfaces and the type B inter-chain hopping accounts for less than 10% of the hopping events. Therefore, similar to that of the bulk anions, the diffusion of interfacial anions is dominated by intra-chain hopping, even though the distribution of the pendant cations and polymer chains in the interfacial zone is heterogeneous and deviates from that in bulk polyILs (cf. Figure 2-2 and 2-3).

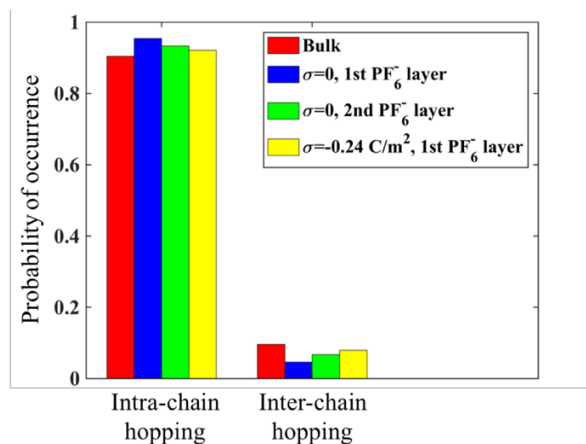


Figure 2-5. Statistics of the hopping events by bulk anions and anions near the quartz substrates.

The interfacial ions hop in an environment that is strongly heterogeneous in the z direction due to the layering of polyILs near the quartz surfaces. Therefore, we further decomposed the hopping events into intra-layer and inter-layer hoppings: after an intra-layer hopping, an anion remains in the same interfacial layer (e.g., an ion initially in the first anion layer near the charged quartz surface is still in the same layer); after an inter-layer hopping, an anion escapes the original layer. Table 2-2 shows that, for each type of interfacial anions considered, after an intra-chain hopping, the anion predominately stays within the original interfacial layer (>96% chance). After an inter-chain hopping, the chance an interfacial anion leaves its original layer increases by a factor of 1.7-2.7 compared to that for the intra-chain hopping, suggesting that the inter-chain hopping causes more inter-layer movements. Overall, the hopping of the first layer of anions near charged surfaces involves lower percentage of inter-layer movements than those in the first and second anion layers near neutral quartz surfaces. This is likely caused by the fact that near charged surfaces, more polymers align their chains parallel to the quartz surface (see Figure 2-2), which tends to prompt intra-layer movements and thus reduce the percentage of inter-layer movements.

Inter-layer movement of anions. Because diffusion of interfacial anions likely depends on their relative position with respect to the solid substrate, we next examine how interfacial anions escape

from their original layer for different interfacial anions. We computed the residence correlation function for interfacial anions: $ACF_l(t) = \langle l(0)l(t) \rangle$, where $l(t)$ is an indicator of the anions' position. $l(t)$ is defined as 1.0 if an anion in a certain interfacial layer at time $t=0$ resides continuously in this layer by time t . A faster decay of $ACF_l(t)$ indicates that an anion escapes a particular interfacial layer more readily.

Table 2-2. Decomposition of the hopping events of interfacial anions near neutral and charged quartz surfaces.

	1 st anion layer near neutral quartz surfaces		2 nd anion layer near neutral quartz surfaces		1 st anion layer near charged quartz surfaces	
	Type A	Type B	Type A	Type B	Type A	Type B
Inter-layer	2.9%	7.9%	3.9%	6.6%	1.4%	3.0%
Intra-layer	97.1%	92.1%	96.1%	93.4%	98.6%	97.0%

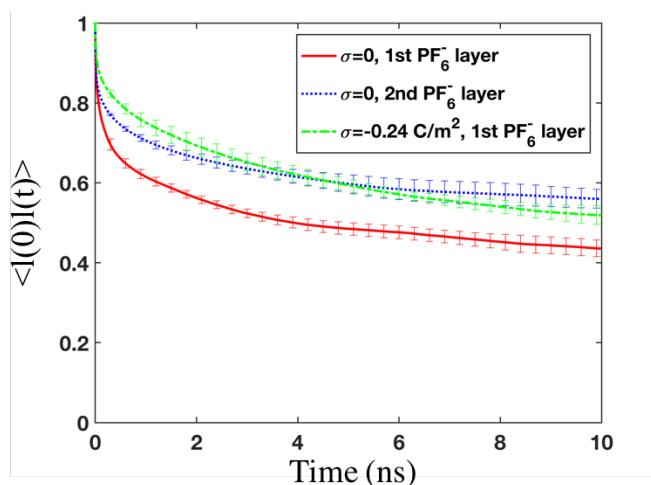


Figure 2-6. Residence correlation function for interfacial anions near neutral and charged quartz surfaces. Error bar is marked every 300 ps for clarity.

Figure 2-6 compares the $ACF_l(t)$ for different interfacial anions. At short time ($t \lesssim 1$ ns), more ions in the first and second anion layers near the neutral surfaces escape their original layer than those in the first anion layer near the charged surfaces. This is in line with the observation that, for ion hopping events examined at 1 ps time interval, inter-layer hopping is more prevalent for anions

near neutral surfaces than near charged surfaces (see Table 2-2) due to the more stretched polymer chains near neutral surfaces. At long time ($t \gtrsim 3$ ns), anions near the charged surface escape their original layer faster than those near the neutral surfaces. To understand this, we note that the first and second anion layers near the neutral surface are either flanked by the wall and a distinct cation layer or by two distinct cation layers (see Figure 2-2a). Because the wall is stationary, and cations are largely immobile, it is quite difficult for these interfacial anions to escape from their original layer. On the other hand, there is no distinct cation layer above the first anion layer near the charged surface (see Figure 2-2b). Therefore, the anions in this layer experience less hindrance moving away from this layer and thus escape relatively easily. Although the anions in different interfacial layers escape their original layers at different rates, Figure 2-6 shows that a significant fraction of these anions stay within their original layer for more than 10 ns, i.e., the inter-layer exchange of anions is sluggish.

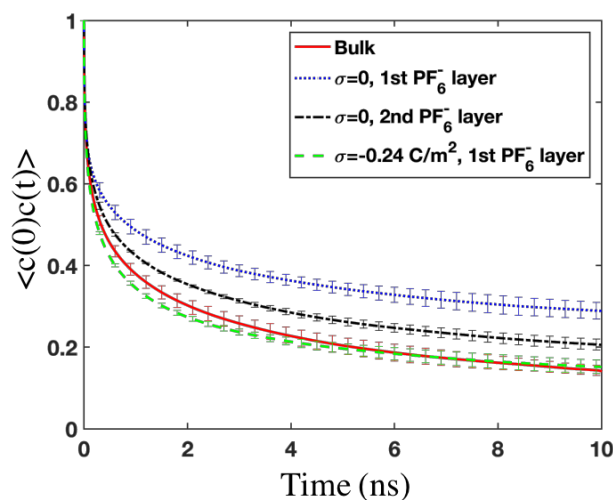


Figure 2-7. Time correlation function for the association of interfacial and bulk anions with their neighboring cations. The correlation functions are fitted to the stretched exponential function $ACF(t) = a_0 \exp(-(t/a_1)^{a_2})$, where a_0 , a_1 , and a_2 are fitting constants. The relaxation time constant of $ACF(t)$, τ_s , is computed using $\tau_s = a_0 a_1 \Gamma(1 + 1/a_2)$, where Γ is the gamma function. Error bar is marked every 300 ps for clarity.

Ion-ion association dynamics. The mode of anion movements in polyILs (intra-chain vs. inter-chain hoppings; inter-layer vs. intra-layer movements) control their pathway of diffusion, but the rate of diffusion depends more directly on how readily an anion hops. The hopping of an anion is directly tied to the change of its coordination by (or association with) cations. To characterize how the association of anions with cations breaks, we defined an ion-ion association correlation function as $ACF_c(t) = \langle c(0)c(t) \rangle$, where $c(t)$ is an indicator of the anion-cation association. $c(t)$ is 1.0 if an anion coordinated by a certain cation at time 0 is continuously coordinated by this cation at by time t . A faster decay of $ACF_c(t)$ to zero indicates that an anion breaks from its association by cations faster.

Figure 2-7 shows the $ACF_c(t)$ for anions initially residing in the interfacial layers near neutral and charged quartz surfaces. We observe that an anion can escape from its association with a cation, a necessary step for the ion diffusion, at a time scale on the order of tens of nanoseconds. The breakage of the association of an interfacial anion with neighboring cations is slower than that of a bulk anion. Fitting the correlation functions to the stretched exponential function, we extracted the time constants for interfacial anions to escape their association with coordinating cations to be 205.1 ns, 39.0 ns, 27.5 ns, for the anions initially residing in the first and second anion layer near the neutral quartz surface and the first anion layer near the charged quartz surface, respectively. The time constant for bulk anions was determined to be 10.6 ns. The slower dynamics of interfacial anions to break away from their association with coordination cations is closely related to their coordination environment near the surfaces. The first layer of anions near neutral quartz surfaces are coordinated by the first interfacial cation layer. As shown in Figure 2-3a, these cations form small and disconnected clusters near the surface, which make the hopping of an anion between cations rather difficult, thus slowing down the breakage of their association with cations. This

effect is much weaker for anions in the second anion layer near neutral quartz surface and in the first anion layer near the charged quartz surface, e.g., the cations near the charged quartz surface form a connected network (see Figure 2-3b), and thus the time constant for these anions to escape their association with cations is much smaller. Nevertheless, these anions have a larger number of cations coordinating to them compared to that of bulk anion (see Table 2-1), and such a tighter coordination slows down the escape of an anion from its association with neighboring cations.

Ion diffusion. We studied the diffusion of anions in the horizontal plane by computing the lateral component of their mean-square-displacement (MSD): $\text{MSD}_{xy}(t) = \langle (x_i(t) - x_i(0))^2 + (y_i(t) - y_i(0))^2 \rangle$, where x_i (y_i) is the x - (y -) position of an anion i and $\langle \dots \rangle$ denotes the ensemble average. Figure 2-8 shows the MSDs of anions *initially* located in different interfacial layers near the neutral and charged quartz surfaces in comparison with bulk. Because anions can diffuse out of their original layer (see Figure 2-6), these MSDs do not strictly measure the diffusion behavior of ions in each interfacial layer. At the time scale simulated here, the random movement of anions has not reached the diffusive regime (i.e., $\text{MSD}_{xy}(t) \sim t$, see the thin black solid line in Figure 2-8) and thus a diffusion coefficient cannot be computed. Nevertheless, it is clear that the MSDs of the ions initially residing in the interfacial layers are 3-8 times smaller than that of bulk anions at 100 ns. Given that some interfacial ions leave the interfacial region within tens of nanoseconds, it is clear that the diffusion of interfacial anions is significantly slower than that of the bulk anions, which is similar to that inferred from broadband dielectric spectroscopy measurement of polyIL thin films supported on silica substrates. The slower diffusion of interfacial anions is consistent with the observation that the interfacial anions break away from their association with the neighboring cations by a slower rate than the bulk anions (see Figure 2-7). Furthermore, Figure 2-8 suggests that the diffusion of the first layer of anions near the neutral quartz surfaces is the

slowest among all interfacial anions. The slowest diffusion of these anions can be traced back to the fact that these anions must diffuse in an environment where they are associated with cations from small and disconnected clusters (see Figure 2-3a) and confined by the stationary wall, both of which hinder their hopping along and between polymer chains.

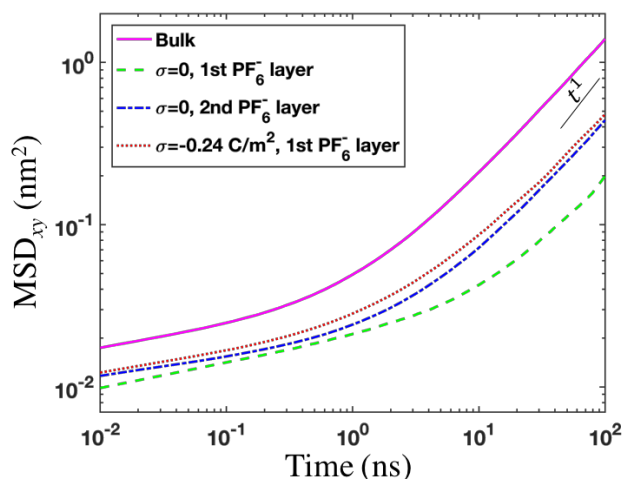


Figure 2-8. The xy component of the mean-square-displacement (MSD) curves for anions in bulk polyILs and initially residing in different interfacial layers.

The diffusion of anions becomes more bulk like at distance several ion layers away from the substrate. For example, near the negatively charged electrode, the lateral MSD of anions initially located more than 3.28 nm away from the substrate shows little difference compared to that of bulk anions (see Figure A-5a) at time scale up to ~ 100 ps. However, because anions in the thin film can eventually diffuse to position very close to the substrate, the diffusion of the ions initially far away from the substrate still shows lateral MSD smaller than that of bulk anions at large time scale (e.g., at ~ 100 ns time scale, see Figure A-5a) and the average diffusion of the anions in the film studied here is still slower than that in bulk (see Figure A-5b). The latter observation is in good agreement with the dielectric spectroscopy measurement of thin polyIL films.¹²⁰

2.3.3 Relevance to Other Interfacial polyILs and Polyelectrolytes

In the above study, we focused on a polyIL film deposited on solid substrates and the top surface of the polyIL film is exposed to a vacuum. Replacing the vacuum layer with a solid wall will likely change the anion dynamics near the existing wall, but not dramatically. From the density profiles shown in Figure 2-2, the packing of polymers' backbone and pendant cations near a solid wall is perturbed greatly up to a distance of ~ 2 nm from the wall. Since our liquid film is ~ 5 nm thick, replacing the vacuum layer by a solid wall should lead to some, but not significant, change of polymers' packing near the existing wall. Because our study shows that the dynamics of interfacial free anions is largely governed by the structure of interfacial polymers (especially their cations), it is expected that the dynamics of the anions near the existing wall will be changed, but not dramatically, by introduction of solid walls.

The behavior of polyILs near charged substrates revealed in our study exhibits both similarities and differences from that of the extensively studied polyelectrolytes near charged substrates in water (see Refs. 134-136 and the references therein). Near negatively charged substrates, the pendant cations of polyILs adsorb on the substrate to form molecularly continuous clusters while their host polymer chains are packed densely near the substrate. Polyelectrolytes can also adsorb onto oppositely charged substrates to form a thin layer. However, because polyelectrolytes can retain their hydration by water, their charged motifs may not become contact-adsorbed on the substrate to form molecularly continuous clusters on the substrate like the polyILs. For the polyILs adsorbed on negatively charged substrates, the dynamics of their free PF_6^- anions is slowed down greatly compared to that in bulk polyILs. A similar slowdown of the counterions of the polyelectrolytes adsorbed on substrates in contact with water should be weaker. This is because

the polyelectrolytes' counterions can diffuse in the aqueous solution rather than having to rely on intra- and inter-chain hoppings.

2.4 Conclusions

In summary, we have studied the structure and dynamics of poly(1-butyl-3-vinylimidazolium hexafluorophosphate) near neutral and charged quartz substrates using MD simulations. The quartz surface induces unique structure of interfacial polyILs beyond the simple layering of ions near solid substrates observed for conventional RTILs. Near neutral surfaces, the PF_6^- ions, which are similar in size with the cations, approach the surface closer than the cations due to the entropic and steric effects. The polymer chains of the first layer of cations are stretched in the direction normal to the surface and their cations form small clusters on the quartz surface. For charged substrates, the contact-adsorbed cations form larger clusters on their surfaces and the polymer chains of these cations are packed more densely and are less stretched than near neutral surfaces. The different out-of-plane layering, in-plane clustering, and packing of polymer chains near neutral and charged surfaces lead to different coordination environment for the interfacial anions. The first layer of anions near neutral surfaces are mostly coordinated by four cations from one polymer chain, while the first layer of anions near charged surfaces and the second layer of anions near neutral surfaces are typically coordinated by five cations from two chains.

For the dynamics of the polyILs near quartz substrates, regardless of the surface charge of the substrates, the diffusion of the interfacial anions is still dominated by the intra-chain hopping as in bulk polyILs. Interfacial ions can escape their original layer by inter-layer hopping, but the escape process is sluggish, and a majority of the ions remains trapped in their original layer for at least a few tens of nanoseconds. The interfacial anions break their association with neighboring cations

by a much slower rate than in bulk polyILs, and this is especially pronounced for the first layer of anions near the neutral quartz surfaces because the hopping of anions between cations is hindered by the separation of small cation clusters adsorbed on the surface. Because of the slower breakage of interfacial anions from the association with neighboring cations, the interfacial anions diffuse much slower than the bulk anions, especially for the first layer of anions near the neutral surfaces.

Based on our study, we have found that confinement by solid substrates changes the structure and consequently the dynamics of the first few layers of polyILs near them. While the dynamics of anions is only greatly perturbed at position within ~ 3 nm from the substrate on a time scale of ~ 100 ps, the diffusion of anions in the thin film on average is suppressed at longer time scales because the anions will eventually sample the entire film thickness. Although we only focused on how such change depends on the surface charge of a substrate, we can expect other properties of the substrate, e.g., its surface roughness and curvature, should also affect the structure and dynamics of the interfacial ions. Exploring these effects can potentially open new avenues for engineering polyILs toward target applications and merits further studies in the future.

Supporting Information

All supporting information cited in this chapter is located in Appendix A.

CHAPTER 3 Structure and Dynamics of Polymeric Canopies in Nanoscale Ionic Materials: An Electrical Double Layer Perspective

Disclosure

This work has been published by a nature research journal: Z. Yu, F. Yang, S. Dai, and R. Qiao, "Structure and Dynamics of Polymeric Canopies in Nanoscale Ionic Materials: An Electrical Double Layer Perspective", Sci. Rep, 8:5191, 2018

3.1 Introduction

Nanoscale ionic materials (NIMs) are a new class of hybrid materials made of nanoparticles and charged polymeric canopies.⁶⁵⁻⁶⁸ Each nanoparticle carries a net charge, either due to its surface groups or covalently-attached corona featuring ionic functional groups. The canopies, essentially oligomeric counterions, are attached to individual nanoparticles *dynamically* through electrostatic interactions. NIMs are multi-faceted materials: they can be considered as ionic liquids, colloidal dispersions, or composites based on hairy nanoparticles. NIMs have received much attention recently because they exhibit many appealing properties. First, despite that nanoparticles can be tens of nanometers in size and no solvents are used, NIMs are often liquids at room temperature.⁶⁵ Second, depending on nanoparticles' size, shape and composition, NIMs can exhibit a wide spectrum of chemical, optical, and electrical properties. Such an unusual combination of liquid state with the tunable properties of nanoparticles makes NIMs a versatile material platform for diverse applications. Indeed, NIMs have been used as plasmonic material, battery electrolytes, luminescent material, and porous liquids for gas separation.⁶⁹⁻⁷³

To fully exploit NIMs' potential for a given target application, their properties must be optimized. Such optimization is not straightforward. Despite their conceptual simplicity, NIMs have vast design parameter space, e.g., the density/charge of nanoparticle's surface groups/corona, the composition and chain length of the canopy, and the size/shape of the nanoparticles can all be varied. Clearly, optimization guided by knowledge on how design parameters and processing conditions control the structure/dynamics of NIMs and how they in turn determine NIMs' macroscopic properties, is needed. In particular, a fundamental understanding of the structure and dynamics of NIMs' canopies is essential. Although research in this area is rather limited, a general picture is emerging.

Many existing studies focused on NIMs made of nanoparticles with moderate/high surface charge density and polymers with relatively long chains.^{65, 69, 74} In these NIMs, the spacing between the charge sites on nanoparticle's surface (or ionic terminal functional groups of its corona), is smaller than the radius of gyration of *bulk* polymers. As charged polymers are attracted toward the nanoparticle, polymer crowding occurs. An "onion-like" model has been proposed for the canopy in such situations:^{65, 67} polymers in the canopy form layers around the particle, with those in the inner (outer) layer strongly (weakly) associated with the particle. In neat NIMs, mobility of the polymers strongly associated with the nanoparticle can be more than ten times less mobile than bulk polymers; mobility of the polymers weakly coupled with the nanoparticle, however, is only moderately smaller than that of bulk polymers. The exchange between these populations of polymers is slow.⁶⁷ When electrolyte ions are presented in NIMs (either introduced intentionally or exist as contaminants), they screen nanoparticle's charge. This decreases (increases) the number of the strongly (weakly) associated polymers and facilitates the exchange between polymers in these two populations. When enough electrolyte ions are introduced, the population of the strongly

associated polymers diminishes and all polymers exhibit mobility similar to that in bulk.⁶⁷ These seminal works greatly improved our understanding of the polymeric canopies, but some important practical questions and conceptual issues remain to be addressed.

From a practical perspective, while the existence of multiple layers (populations) of polymers across canopies is established, many key questions on the quantitative aspects of canopy remain unanswered. Specifically, how are polymers distributed across the canopy – do they form two or more layers? What is the relative population of the polymers in different layers and how does it respond to the addition of electrolyte ions? What conformation do polymers in different layers adopt? Since polymers strongly associated with nanoparticles experiences crowding, their conformation should differ from that of the bulk polymers. However, the conformation of these polymers is not yet known. Hence, the radius of gyration of bulk polymers is often used to infer the packing and thus population of polymers near nanoparticles. The accuracy of this approach is yet to be clarified.

On a more conceptual front, the interactions between the charged terminal group of polymers and nanoparticles were treated or discussed in the framework of “ionic bonds” in most prior studies, which emphasizes the electrostatic “association” between the *individual* charged sites of oligomeric counterions and the *individual* charged sites on the nanoparticles. While this framework has its merit and advantage, the long-ranged nature and global effect of electrostatic interactions is not fully taken into account. Since the charged polymeric canopy and the nanoparticle’s surface charges form an electrical double layer (EDL),⁶⁵ and long-range electrostatic forces play a crucial role in determining the structure of EDLs, the long-range nature of electrostatic interactions warrants attention in studies of canopies. In particular, how long-range electrostatic interactions

and polymeric interactions jointly control the structure and dynamics of canopies should be examined.

The above open questions and issues can be addressed using molecular dynamics (MD) simulations. A few such simulations have been reported.¹³⁷⁻¹⁴⁰ A common feature of these simulations is that the radius of the nanoparticles is small (~ 1 nm), the chain length of the polymers is short and comparable to the nanoparticle's radius (e.g., the linear polymers used in Ref. 138 have ~ 14 monomers), and the nanoparticles carry moderate surface charge density (e.g., $-2e/\text{nm}^2$). Study of these systems revealed that the charged layer of the nanoparticles approaches each other closely and the charged site of polymers can bridge neighboring nanoparticles.¹³⁸ The charged site of most polymers are dynamically attached to the charged sites of nanoparticles: a polymer can detach from its original attachment point on a nanoparticle over tens of nanoseconds and become attached to another charged surface site on the same nanoparticle; a polymer can “hop” to another nanoparticle over hundreds of nanoseconds because its charged site can bridge the two nanoparticles. These studies offered useful insights into the structure and dynamics of NIMs. Nevertheless, some important parts of NIM's parameter space were not explored and the structure and dynamics of the polymeric canopy can exhibit new physics not studied in these studies.

In many NIMs, the nanoparticles have a diameter of a few tens of nanometers and the polymeric canopies are several nanometers thick.^{66-67, 69, 141-144} The surface charge density of nanoparticles can reach $\sim -4e/\text{nm}^2$ in many systems.⁶⁹ The thickness of the polymeric canopies and the radius of nanoparticles in these NIMs are thus much larger than those in prior simulations. These have several implications. First, the surface charge layers of adjacent nanoparticles cannot approach each other closely as in the prior simulations and bridging of adjacent nanoparticles by the charged site of the polymers is unlikely. Second, the packing of the polymers dynamically

“grafted” to the nanoparticle faces more entropic and steric costs because each “grafted” chain occupies more volume (due to the longer chain length) and space for packing a polymer grafted to the surface of a sphere decreases as its radius increases. Third, the collective, long-range electrostatic interactions become more important not only because the surface charge density of nanoparticles is higher, but also because the collectively screening of a nanoparticle’s surface charge by ions near it becomes less effective as the nanoparticle’s radius increases (This can be seen qualitatively from decay of electrical potential near a charged, isolated sphere in an 1:1 electrolyte $\phi(r) = \phi_0 a(\kappa r)^{-1} e^{-(r-a)\kappa}$, where ϕ_0 is the potential on the sphere’s surface, a is the sphere’s radius, and κ^{-1} is the Debye length of the electrolyte, and r is the distance from the sphere’s center). Because of these factors, the competition between the electrostatic attraction of charged site of the polymers to the nanoparticles’ surface and the steric and entropic penalties of packing polymers near the nanoparticles can differ from that studied in prior simulations. Consequently, the structure and dynamics of the polymeric canopies in these NIMs can differ from those revealed in prior simulations. Furthermore, in practical NIMs, there are inevitably some contaminant ions, but how such impurity affects the structure and dynamics of the polymeric canopies has not been studied in prior simulations.

In this work, we use MD simulations to study the structure and dynamics of the canopies of model NIMs with relatively long polymer chains, relatively high surface charge density, and in the limit of large nanoparticle diameter. We also investigate how ion contamination affects the properties of canopy. We show that, while the canopy exhibits the onion-like structure proposed earlier, the conformation of polymers strongly associated with the charged walls and the distribution of weakly associated polymers exhibit new features. The EDLs formed by canopies exhibit commonalities with those in room-temperature ionic liquids (RTILs) but also new features

unique to NIMs. We show that these observations originate from the interplay of electrostatic and entropic effects in the canopies.

3.2 Simulation System and Methods

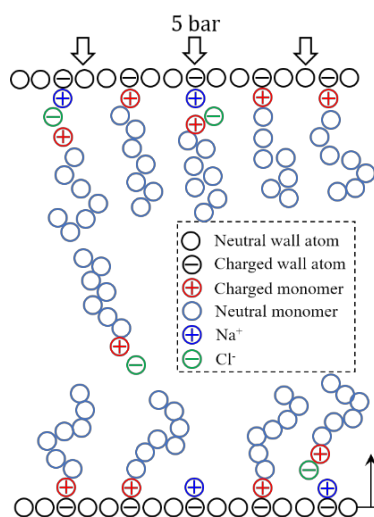


Figure 3-1. A schematic of the molecular system for studying canopies in corona-free nanoscale ionic materials.

Model systems. Ideally, a large number of nanoparticles and their polymeric canopies should be included in molecular systems for studying NIMs. While this approach is viable for NIMs with very small nanoparticles (e.g., 1 nm in radius), it is impractical when the nanoparticle diameter is large (e.g., tens of nanometers). Since our focus is the polymeric canopy in NIMs with large nanoparticles, we adopt the model shown in Figure 3-1. The system consists of two planar walls with negative surface charge densities, polymers with one of their end monomers carrying a positive charge $+e$, and optionally, pairs of electrolyte ions (to model the electrolyte ions presented in NIMs). The system used here effectively models the canopies between two very large nanoparticles, with the two planar walls representing the surface of each nanoparticle. Hence our model is appropriate only when the curvature of the nanoparticles in NIMs can be neglected, i.e., if the canopy thickness is much smaller than the radius of the nanoparticles. Since the canopy

thickness is often a few to tens of nanometers in practical NIMs, our results are relevant to NIMs with nanoparticles measuring tens to hundreds of nanometers in diameter.

We study the canopies in two systems. In the first system, the number of polymers in the canopy is chosen such that their charge exactly balances the charge on the solid wall. The second system has the same number of polymers as in the first system, but electrolyte ion pairs (counterions and co-ions) are added into the canopy. The number of counterions is chosen such that their charge balances 75% of the wall charge. The second system is experimentally relevant since electrolyte ions are inevitably presented in NIMs and sometimes even intentionally introduced to tune NIMs' properties.⁶⁷ Hereinafter, the first and second system will be referred to as neat canopy and doped canopy, respectively. We also simulate a bulk polymer melt that contains the same polymers as in the above two systems except that the charge on each polymer's end monomer is removed. Table 3-1 summarizes the setup of the three systems examined in this work.

Table 3-1. Setup of the simulation systems studied in this work

System	Surface charge density of wall (e/nm^2)	Number of polymers	Degree of polymerization	Number of Na^+/Cl^- pairs
1 (neat canopy)	-3.5	448	25	0
2 (doped canopy)	-3.5	448	25	336
3 (bulk polymer melts)	-	100	25	-

Molecular models. The solid wall is modeled as a square lattice of Lennard-Jones (LJ) atoms, and measures $8 \times 8 \text{ nm}^2$ in the lateral direction. The lower solid wall is fixed during the simulation. The top wall is modeled as a rigid body. Randomly selected wall atoms are each given a charge of $-e$ to produce a net surface charge density of $-3.5 e/\text{nm}^2$ ($1 e = 1.6 \times 10^{-19} \text{ C}$), which is within the range of surface charge densities reported experimentally.^{67, 69, 145} A modest external pressure (5 bar) is applied on the top wall to mimic the dispersive interactions between neighboring

nanoparticles (see Figure 3-1), and we verified that the results changes little if a different pressure (e.g., 10bar) is applied. Each polymer is modeled as a linear chain of 25 beads bonded by harmonic springs. Each bead approximately represents one ethoxy repeat unit ($-\text{CH}_2\text{OCH}_2-$) and the chain length is approximately determined based on the real chemical structure.⁶⁹ The details on the chemical structure and the coarse-grained force field are introduced in the Appendix B. One of its end beads is given a charge of $+e$, and is hereinafter termed “charged end monomer”. The chain length of the polymers is within the range found in prior experiments.^{67, 69, 142} The force field parameters of the polymer beads are taken from Ref. 138. Briefly, for the bead-bead LJ potential, the depth of its energy minimum is $\epsilon_{ij}/k_B = 377\text{K}$ (k_B is the Boltzmann constant) and the bead-bead separation at which potential energy is zero is $\sigma_{lj} = 0.4\text{ nm}$.¹³⁸ Each bead has a mass of 44 g/mol. To account for polymers’ polarizability, a dielectric constant of $\epsilon_r = 10$ is used in the calculation of electrostatic interactions. This value is on the high end of the dielectric constant for polymers and is adopted so that the desorption of polymer’s charged end monomer from the charged wall can be probed at the time scale accessible in simulations. Without losing generality, Na^+ and Cl^- ions are used to mimic the electrolyte ions presented in NIMs. No solvents are explicitly included because, even in NIMs spiked intentionally by electrolytes, solvents are usually removed by intensive drying.⁶⁷ Force fields for the wall atoms and the electrolyte ions are taken from the Optimized Potentials for Liquid Simulations-All Atom (OPLS-AA) force fields,¹⁴⁶ and are summarized in the Supplementary Information.

MD methods. Simulations are performed using the Gromacs code.¹²⁵ The neat and doped canopies (systems 1 and 2 in Table 3-1) are simulated in the NVT ensemble. The box length in the direction normal to the wall is 50 nm. The position of the upper wall is *not* fixed. The separation between the two walls depends on the canopy’s conformation and is $\sim 10\text{-}15\text{ nm}$ for the canopies

studied here (see below). The large vacuum space above the upper wall allows the periodicity in the direction normal to the wall to be removed. The polymer melts (system 3) are simulated in the NPT ensemble ($P=1\text{atm}$). In all simulations, the temperature is maintained at 400 K using the velocity rescaling thermostat.¹²⁸ The elevated temperature chosen here helps to achieve good statistics of polymer displacement. The Parrinello-Rahman pressure coupling scheme is used in the NPT simulations. A time step size of 2 fs is used. The non-electrostatic interactions are computed using direct summation with a 1.0 nm cutoff length. Electrostatic interactions are computed using the PME method (real space cutoff: 1.0 nm; FFT spacing: 0.12 nm). To remove the periodicity in the direction normal to the wall, the slab correction to the PME method is applied.¹²⁷ Periodical boundary conditions are applied in the lateral (xy -) directions.

To set up systems 1 and 2, 448 polymers and appropriate number of Na^+/Cl^- ion pairs are packed between the two charged walls randomly using Packmol package.¹⁴⁷ Note that the initial chain conformation of the packed polymers is taken from equilibrium runs of polymer melts and thus is not stretched. Systems 1 and 2 are equilibrated for 100 ns and followed by a production run of 400 ns. The evolution of the conformation of representative polymer chains in system 1 is shown in Figure B-1 in the Supplementary Information. To set up system 3, 100 polymers with random chain conformation are packed into a cubic box. The system is equilibrated for 30ns and followed by a production run of 100 ns. Each of the above systems is simulated twice with different initial polymer configurations and the difference in the results is small.

3.3 Results and Discussion

3.3.1 Canopy Structure

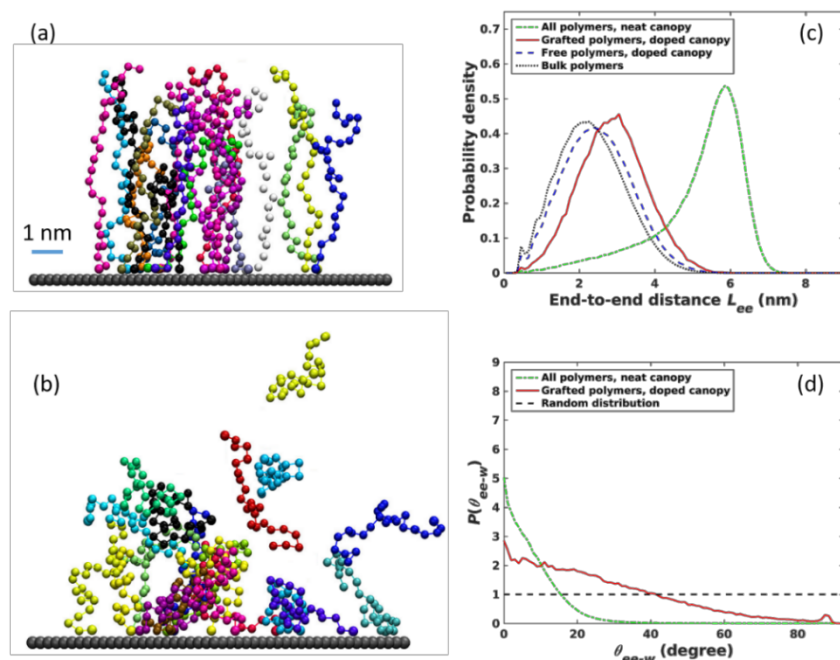


Figure 3-2. Structure of neat and doped canopies near the lower wall. (a-b) Snapshots of some representative polymers in the neat (a) and doped canopies (b). (c-d) Probability density distribution of the end-to-end distance (c) and the angle between end-to-end vector and the normal vector of the charged solid surface (d) in neat and doped canopies near the lower charged wall. In (d), the probability density is normalized such that a random distribution gives unity at all angles.

Neat canopies. We first focus on the conformation of *individual* polymers in the canopies. Here, the positively charged end monomers of nearly all polymers are adsorbed on the negatively charged walls after 10 ns, thereby “grafting” these polymers to the wall. Because of the symmetry of the system with respect to the middle plane between the two walls, hereinafter we focus on the polymers near the lower wall. Figure 3-2a shows that, at such a high “grafting” density, polymers are highly stretched. Table 3-2 further shows that, compared to bulk polymers, the mean radius of gyration (R_g) and end-to-end distance (L_{ee}) of the polymers in the canopy increases by $\sim 75\%$ and $\sim 110\%$, respectively. The distribution of the polymers’ L_{ee} shifts toward their full contour length

(see Figure 3-2b) and exhibits a sharp peak at $L_{ee}=5.85$ nm. The population of polymers with L_{ee} smaller than 2.48 nm (the mean L_{ee} of bulk polymers, see Table 3-2) nearly vanishes. Hence, the neutral end monomer of these polymers can hardly access the space within ~ 2 -3 nm from the wall. Indeed, Figure 3-2d shows that angle formed by the polymers' end-to-end vector and the wall's normal vector (θ_{ee-w}) is restricted to $\theta_{ee-w} < 30^\circ$.

The stretched conformation of the polymers shown in Figure 3-2 are in contrast to the more random-coil like chain conformation revealed in the prior simulations.¹³⁸ We note that, in both the prior and the present simulations, all the charged monomers are grafted to the charged solid surfaces. However, in the present case, where the surface charge density is $\sim 90\%$ higher than that in Ref. 138, the grafting density of the polymer is much larger. The higher grafting density is compounded by the fact that our polymer chains are $\sim 80\%$ longer than those in Ref. 138. Furthermore, even at the same grafting density (i.e., the number of polymers grafted per unit area of solid surfaces), the packing of polymers grafted on a planar wall (or the surface of a large sphere) is more susceptible to crowding than those grafted on a small sphere because of the smaller curvature of the surface. Because of these factors, polymers are much more stretched in our system than in earlier simulations. This difference highlights the fact that the polymeric canopies in NIMs can exhibit rich structure depending on the choice of material parameters including the particle size and surface charge density.

Table 3-2. Conformation characteristics of individual polymers in canopies and bulk polymer melts.

	Polymers in the neat canopy	Wall-associated polymers in the doped canopy	Detached polymers in the doped canopy	Bulk polymer melts
Radius of gyration (nm)	1.75 $\pm$ 0.00	1.11 $\pm$ 0.02	1.01 $\pm$ 0.01	1.00 $\pm$ 0.02
End-to-end distance (nm)	5.31 $\pm$ 0.02	2.99 $\pm$ 0.07	2.50 $\pm$ 0.06	2.47 $\pm$ 0.09

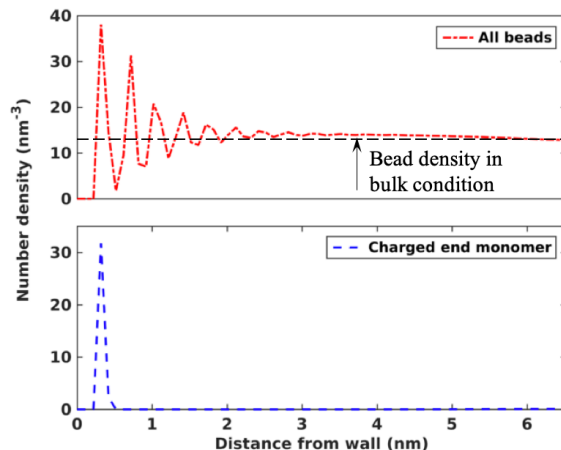


Figure 3-3. Structure of the neat canopy near the lower wall. Density profiles of all polymer beads (a) and charged end monomers (b) across the canopy.

We next examine the distribution of polymer beads, in particular the polymer's charged end monomers, across the canopy. Figure 3-3a shows that the density profile of polymer beads exhibits key signatures of liquid films adsorbed on solid substrates: the bead density oscillates significantly near the wall and decays gradually as we move far away the wall. The oscillation of the density of polymer beads as we move away from the solid substrate is ultimately caused by the strong interactions between the polymer bead and the substrate and the solid nature of the substrate. Driven by the van der Waals attractions, a layer of polymer beads tends to adsorb on the substrate. Because the solid atoms in the substrate only vibrate around their lattice, the layer of polymer beads tend to adopt a structure commensurate to the solid surface and has a low mobility. Therefore, the solid surface induces a well-defined first polymer atom layer with a sharp density peak. Just like the solid layer, the first polymer bead layer can induce a polymer bead layer next to it. This second layer is much less well-defined, but still discernable because the first layer of polymer atoms has much less distinct structure compared to the solid substrate. The second layer of polymer atoms can further induce the layering of another polymer atoms near it, and this cycle repeats itself, ultimately leading to the oscillation of the bead density.

Inspection of the MD trajectories indicated that the mild interpenetration of the polymers grafted on the two walls occurs in the middle portion of the system, as anticipated based on prior simulations.¹³⁸ A key observation of the density profile shown in Figure 3-3a is that, the bead density within 6nm from the wall is slightly higher than that in bulk polymers. Such a dense packing of polymers, along with the extended-chain conformation of individual polymers revealed in Figure 3-2, highlights that steep entropic cost originating from inter- and intra-polymer interactions must be overcome for the neat canopy to adopt its present structure. In our system, the only mechanism that can overcome this cost is the electrostatic attractions between the polymers' charged end monomers and the charged wall. The number of polymers grafted to the substrate and their conformation is governed by the interplay among the above electrostatic effect, the entropic effects, and the steric effects. While the electrostatic effect tends to graft each polymer to the substrate, the steric effects dictate that the number of polymer atoms near the wall cannot exceed the close packing limit. The latter forces the grafted polymers to adopt a stretched conformation near the substrate because one cannot pack many polymers with the globous conformation near the substrate. The stretched conformation of the polymers lowers the entropy of the polymers (because many polymer chain arrangements are now forbidden) and incurs an entropic penalty. In prior studies of NIMs, the electrostatic attractions were often conceptualized as “ionic bonds” between the polymers' charged terminal groups and the nanoparticles' charge sites although the long-range electrostatic interactions were computed in prior MD simulations. The interaction energy between a polymer's charged terminal group and a charged site of a nanoparticle at contact, E_{ionic} , is used to gauge the strength of the ionic bonds. With the force fields for monomers and wall atoms adopted here, the closest separation between a charged end monomer and a charged wall atom is $\sim 0.32\text{nm}$, and thus an E_{ionic} of $13.1k_B T$ is obtained. This E_{ionic} signifies a rather

modest bonding between *a single pair* of charged end monomer and charged wall atom in contact. Such an ionic “bond”, even in absence of the entropic penalty associated with inserting a polymer chain into a densely packed canopy and stretching it greatly, can be broken over a few tens of nanoseconds, thereby freeing its host polymer from the wall and allowing it to adopt random coil-like configurations. These, however, are in contrast with the canopy structure revealed in Figure 3-2a and the fact that charged end monomers rarely desorb from the wall (see Section 3.2).

The original insight of our MD simulation is that, in neat NIMs, the electrostatic effects are so strong that all polymers are grafted onto the substrate despite the great entropic penalty associated with the stretched conformation these polymers must adopt due to the steric effect. We suggest that the strong adsorption of the charged end monomers on the wall can be attributed to the long-range, collective electrostatic interactions between *all* charged end monomers and wall charges. This is a different perspective compared to the ionic bond concept, which emphasizes the strong electrostatic attraction between pairs of charged end monomers and wall charge site at close separation. Such a perspective is better understood by noting that the charged end monomers and the charges on wall together form an EDL, in which the long-range electrostatic interactions control the distribution of the charged end monomers (counterions). Figure 3-3b shows that, in the neat canopy, the charged end monomers of polymers adsorb on the wall in a single layer. The EDL formed by these monomers closely resembles the classical Helmholtz model of EDLs, in which a counterion layer condenses on the wall to screen its charge. If just 10% of these charged end monomers desorb from the wall and migrate to the canopy’s edge (say, 6nm from the wall) to relieve their host polymers from crowding near the wall, then an electric field of $\sim 0.6\text{V/nm}$ is setup between the wall and the new position of the desorbed charged end monomers. In a neat NIM, the number of charged polymer monomers (i.e., the counterions) for each nanoparticle is equal to its

net surface charge. Unless some charged monomers are shared by neighboring particles, which can occur only when the nanoparticles are small and the canopy is thin (e.g., the situation examined in Ref. 138), no extra ions are available to screen the hypothetical electric field created above. Therefore, moving each of these charged end monomers from the wall to their hypothetical positions 6nm from the wall must overcome an electrostatic energy penalty of $\sim 100k_B T$. This significant electrostatic penalty thus overwhelms the entropic penalty due to polymer interactions. It explains why nearly all charged end monomers adsorb on the wall, which forces the neat canopy to adopt the structure revealed in Figure 3-2 and 3-3.

The adsorption of charged end monomers on the oppositely charged wall as a single layer rather than as a more diffusive space charge layer can also be understood using classical EDL theories. In neat canopies, the charges on the wall are screened *solely* by the charged end monomers (which serve as counterions) and there is no co-ion in the system. Such counterion-only EDLs have been studied using the classical Poisson-Boltzmann equation, and analytical solution of the ion density near walls is available. In particular, the counterion density on the surface of an isolated planar wall, ρ_s , is given by¹⁴⁸

$$\rho_s = \sigma_e^2 / 2\epsilon_0\epsilon_r k_B T \quad (3-1)$$

where σ_e is the surface charge density on the wall and ϵ_0 is the vacuum permittivity. In presence of additional charged walls, ρ_s near individual walls increases. Using parameters relevant to our system ($\sigma_e = -3.5e/\text{nm}^2$, $\epsilon_r = 10$, $T = 400\text{K}$), a ρ_s of 322nm^{-3} is obtained. Such a ρ_s exceeds the close packing density of the charged end monomers, and is caused by the fact that the finite ion size is not taken into account in the Poisson-Boltzmann equation. Nevertheless, it indicates that there is a strong tendency for all charged end monomers to adsorb on the wall. To see this

more quantitatively, let's assume that 90% of the surface charge of the wall is neutralized by end monomers contact-adsorbed on the wall, and consider how the rest of the charged end monomers distribute in the EDL. Here the wall's effective surface charge density is reduced to $-0.35e/\text{nm}^2$, and Eq. 3-1 predicts a density of $\rho_s = 3.2\text{nm}^{-3}$ for the charged end monomers on the wall. If we assume that these monomers occupy a layer thickness of 0.1nm , the surface density of these monomers is $0.32 e/\text{nm}^2$, which is about the same as the effective surface charge density of the wall. Therefore, these monomers will be localized within a few angstroms from the wall.

A key premise of the above discussions leading to the idea that charged end monomers form a compact, rather than diffusive, layer near wall, is that co-ions are absent from the system. If co-ions exist in the system, then the thickness of an EDL is characterized by the Debye length $\lambda_D = (\epsilon_0 \epsilon_r k_B T / 2e^2 \rho_\infty)^{1/2}$ in 1:1 dilute electrolytes, where ρ_∞ is the counter/co-ion density in the bulk solution, i.e., outside of the EDL (in electrolytes such as RTILs, λ_D is not a good indicator of the EDL thickness, and theories^{87, 149} that can take into account the ion-ion correlations are needed). As ion contamination is difficult to completely remove in NIM, co-ions likely exist in NIMs and affect the EDL thickness (or more specifically, how the charged end monomers distribute near the wall). It is safe to expect that the charged monomers of some polymers will be “exchanged” off the charged walls by the added counterions and thus their host polymers are no longer “grafted” on the walls. Nevertheless, a quantitative picture is not yet available and some questions remain open. For example, is amount of polymers desorbed from the wall equal to the number of added counterions? How do the added counterions and co-ions distribute in the canopy? What conformation do the desorbed polymers adopt? To answer these questions, we next study canopies doped with electrolyte ions.

Doped canopies. We again first focus on the conformation of individual polymers. When pairs of Na^+ and Cl^- ions are introduced into the canopy, the counterions (Na^+ ions) adsorb on the wall. They adsorb on the wall more easily and strongly than the charged end monomers of the polymers because, unlike the charged end monomers, their adsorption does not incur entropic penalty associated with the stretching of polymer chains. Since these Na^+ ions screen part of the wall charges, they displace some of the charged end monomers originally adsorbed on the wall, causing their host polymers to become “free” polymers (see Figure 3-2b). Trying to avoid the entropic penalty due to polymer crowding near the wall, these “free” polymers migrate away from the wall and adopt conformation close to those of bulk polymers. For example, as shown in Table 3-2 and Figure 3-2c, their mean R_g and L_{ee} as well as the distribution of their L_{ee} are all nearly indistinguishable from those of bulk polymers.

In the doped canopy, the charged end monomers of many polymers are still associated with the charged wall (though more dynamic than that in the neat canopy, see Section 3.2), thus attaching them to the wall. On average, ~ 90 charged end monomers are associated with each wall, which gives an effective “grafting” density of $\sigma \approx 1.41 \text{ nm}^{-2}$. The much lower effective grafting density compared to that in neat canopy means that the crowding of polymers near the wall is greatly relieved in the doped canopy. Figure 3-2b suggests that, while these wall-associated polymers are still stretched, the stretching is no longer significant. In fact, their R_g and L_{ee} are only $\sim 10\%$ and 20% larger than those of bulk polymers, respectively (see Table 3-2); the peak position of the distribution of their L_{ee} is only shifted by 1 nm from that in bulk polymers (see Figure 3-2c). Using the σ and R_g obtained above, the reduced “grafting” density is found to be $\Sigma = \sigma \pi R_g^2 \approx 5.45$. Because this Σ is larger than 5, the typical cutoff for wall-grafted polymers to be considered as polymer brushes,¹⁵⁰ the wall-associated polymers may be considered as polymer brushes.

However, we emphasize that these wall-associated polymers are not statically grafted to the wall as in conventional polymer brushes, and they can explore a rather large configurational space. For example, Figure 3-2d shows that the distribution of their θ_{ee-w} is not narrowly focused near 0° as in the neat canopy and a weak peak even appears at $\theta_{ee-w} \approx 90^\circ$. The latter indicates that both the charged and neutral end monomers of a polymer can adsorb on the wall simultaneously, which rarely occurs in the neat canopy.

Overall, doping a canopy with electrolyte ion pairs causes some polymers originally “grafted” to the wall by electrostatic interactions to detach and become “free” polymers. This greatly relieves the crowding of polymers near the wall, and allows both the free and grafted polymers in the canopy to adopt more random coil-like conformations, which should change the average structure of the canopy. To assess such change, we next compute the polymer density profile across the doped canopy. Figure 3-4a shows that the polymer bead density in doped canopy is lower than that in neat canopy. Meanwhile, the distance between the two walls increases. Since the space between these walls is shared by the two canopies near them, we define the canopy thickness as half of the equilibrium separation between the top and bottom walls. The thickness of the neat and doped canopies is found to be $6.47 \pm 0.01 \text{ nm}$ and $7.10 \pm 0.01 \text{ nm}$, respectively. Hence, doping leads to a dilation of the canopy by $\sim 10\%$.

The above discussion shows that the response of a neat canopy to doping by Na^+/Cl^- ion pairs depends strongly on the adsorption (desorption) of Na^+ ions (charged end monomers) from the wall, or more generally the change of the EDL structure in the canopy. To quantitatively assess the change of the EDL structure caused by electrolyte ion doping and to gain more insight into the structure of doped canopies, we examine the EDL structure in the doped canopy.

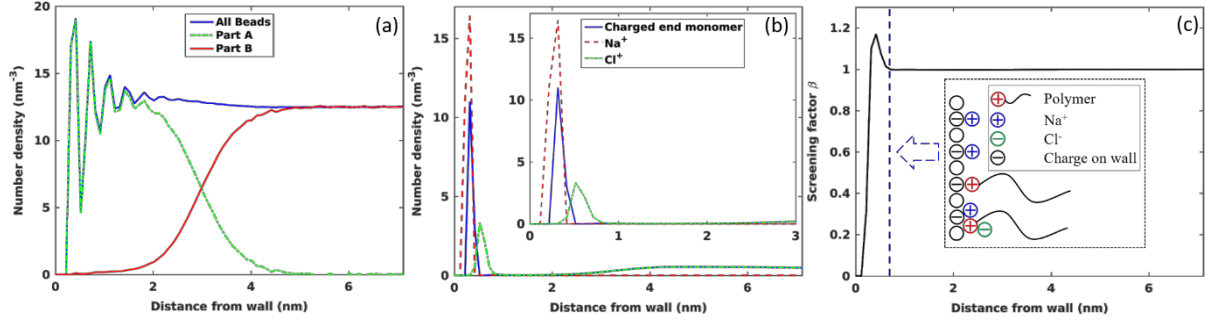


Figure 3-4. Structure of the doped canopy in direction normal to the solid wall. (a) Density profile of the polymer beads near the charged solid wall and its contribution by polymers whose charged end monomer resides in different regions (Part A: $z=0-0.6$ nm; Part B: $z>0.6$ nm). (b) Density profiles of the charged end monomers, Na⁺, and Cl⁻ ions. (c) Variation of the screening factor β near the charged solid wall. Inset shows the arrangement of polymer and electrolyte ions near the wall.

Figure 3-4b shows the density profiles of the Na⁺ ion, Cl⁻ ion, and the charged end monomer across the canopy. The Na⁺ ions form a single layer near the wall. Some charged end monomers, having a size larger than the Na⁺ ions, adsorb on the wall to form another distinct layer. These counterion layers are followed by a co-ion (Cl⁻ ion) layer. The arrangement of these ion layers are shown schematically in the inset of Figure 3-4c. To explore how these ion layers screen the charge on the wall, we compute the charge screening factor β as a function of distance from the wall¹⁵¹

$$\beta(z) = -1/\sigma_e \int_0^z \rho_e(s) ds \quad (3-2)$$

where $\rho_e(s)$ is space charge density due to ions and charged end monomers at a distance s from the wall, and σ_e is the surface charge density on the wall (-3.5 e/nm²). At positions with $\beta>1.0$, the surface charge on the wall is over-screened. Figure 3-4c shows that overscreening occurs in the region $0.3 \text{ nm} < z < 0.75 \text{ nm}$, and disappears at $z > 0.75 \text{ nm}$. Examining ρ_e and its components due to various species shows that the adsorption of Na⁺ ions on the wall screens $\sim 75\%$ of its charge. However, these Na⁺ ions displaces 59.8% (rather than 75%) of the charged end

monomers *originally* adsorbed on the wall, i.e., Na^+ ions do not simply execute an ion exchange with the charged end monomers adsorbed on the wall. Consequently, more counterions adsorb on the wall than that is needed to fully screen its charge, and overscreening occurs. Such an overscreening brings Cl^- ions toward the wall (see the Cl^- peak at $z \approx 0.52\text{nm}$) to neutralize the excessive charges due to Na^+ ions and charged end monomers adsorbed on the wall. Hence overscreening disappears at $z = 0.75\text{ nm}$. Overscreening originates from the strong ion-ion correlations in electrolytes⁸⁷ and is a generic feature of EDLs in RTILs.^{30, 87, 151} NIMs can be viewed as unique member of RTILs,⁶⁵ with the nanoparticles, charged polymers, and the introduced ion pairs as ions. As such, overscreening is rather expected. In molecular RTILs, overscreening affects the capacitance-voltage curve of the EDLs in them.⁸⁷ Here, by reducing the electrolyte doping-induced desorption of charged end monomers, overscreening enhances polymer crowding in the interfacial region.

At $z > 0.75\text{ nm}$, the wall charge is fully screened. For EDLs in conventional electrolytes, the densities of counterions and co-ions are equal *and* uniform beyond this position. Here, the densities of the charged end monomers (counterions) and Cl^- ions (co-ions) are indeed close to each other at $z > 0.75\text{ nm}$. However, their distributions are highly non-uniform: they are depleted in the regions centering $z \sim 1.5\text{ nm}$ and accumulate preferentially in the regions $z > 4\text{ nm}$. Such non-uniform distribution is mainly caused by the entropic interactions between polymers. For example, the region centering at $z \sim 1.5\text{ nm}$ is populated by polymers whose charged end monomers adsorb on the wall (see Figure 3-4a, in which the density of the beads of these polymers are shown as green dashed line). Inserting a charged end monomer (and hence its host polymer) here incurs a large entropic penalty. Hence few charged end monomer appears here. Since local electro-neutrality is maintained at $z > 0.75\text{ nm}$, Cl^- ions are also depleted here.

Discussion. The canopy structure revealed above is obtained from a system that best resembles polymeric canopies in NIMs with large nanoparticles, moderately long polymer chains, and moderate to high surface densities on the particle surface. The canopy structure revealed here agrees broadly with the onion-like model derived from prior experimental data. In particular, the observation that, in doped canopies, there can be two populations of polymers, some anchored to the nanoparticle's surface/corona and the rest interacting weakly with nanoparticles, is captured in our simulations. In addition, the fact that doping using electrolyte ions increases the population of polymers interacting weakly with nanoparticles is also reproduced. Our simulations further suggest that these polymers form more than one layers near the charged solid surface and there is notable energy barrier (as implied by the valleys between the density peaks of the charged end monomers in Figure 3-4b). Therefore, the structure of polymeric canopy truly resembles that of an onion in that there are many layers of polymers in the canopy. The energy barrier for polymers in different layers should affect the exchange of the polymers between these layers and thus can impact the transport properties (e.g., electrical conductivity) of NIMs.

Some difference between the simulation results and experimental observations does exist. In neat canopies, the existence of polymers that are not “grafted” to charged walls cannot be established with certainty in our simulations. This is in contrast to the suggestion by prior NMR measurements that some polymers in NIMs are not “grafted” to nanoparticles even in absence of intentionally added electrolyte ions.⁶⁷ The difference is likely caused by two reasons. First, the molecular model adopted here may have underestimated the strength of the entropic penalty of stretching the polymers. For example, since polymers are modeled as flexible chains, our model may underestimate the energy penalty of stretching a non-flexible polymer chain. Second, the nominally neat canopies probed experimentally may contain electrolyte ion pairs. NIMs are often

prepared by concentrating dilute solutions, and thus impurities presented in nominally pure solutions are extremely difficult to remove. Indeed, some studies showed that even fully neutralized NIMs contain $\sim 0.1 \text{ Na}^+$ ions per charged site on the nanoparticle's surface.^{66-67, 142}

3.3.2 Canopy Dynamics

Polymer exchange dynamics. To assess how fast a polymer grafted electrostatically to the charged walls desorb and exchange with other “free” polymers (if exist) in the canopy, we compute the time correlation function for the association of a charged end monomer with the charged wall

$$ACF_c(t) = \langle c(0)c(t) \rangle \quad (3-3)$$

where $c(t)$ is defined as 1.0 if a charged end monomer is within 0.6nm from the wall (see Figure 3-4b), and $\langle \dots \rangle$ denotes ensemble average. Figure 3-5 shows that, in neat canopies, the adsorbed charged end monomers do not desorb over the sub-microsecond time scale probed in our simulations. This is consistent with the very high free energy penalty for a counterion (charged end monomer here) to move away from the wall in absence of co-ions. This result is different from that obtained from simulation of NIMs with particle diameter of 1nm in Ref. 138, where it was found that a polymer can hop from one nanoparticle to another nanoparticle over hundreds of nanoseconds. This difference is in fact anticipated because the hopping of polymer from one particles to another in the prior study was enabled by the bridging of two charged nanoparticles by the charged monomers in the polymers. Because such bridging does not occur in our systems, once a polymer is “grafted” to one of the charged walls, it rarely leaves that wall. Interestingly, we find that the charged monomer attached to one the charged walls can diffuse from one charged site on the wall to other sites (this is also evident from the modest lateral diffusion coefficient of the attached polymers on the wall, see Figure 3-6). This is consistent with the finding from previous

simulations that the charged monomer of a polymer grafted dynamically to a nanoparticle can move between different charged sites of the same nanoparticle.¹³⁸

Figure 3-6 shows that, in doped canopies, desorption of the charged end monomers from wall occurs at a time scale of one hundred nanoseconds. This is consistent with the experimental observation that, in NIMs, the exchange between the free and bound polymers in canopies is greatly accelerated by doping the NIMs using electrolyte ions.⁶⁷

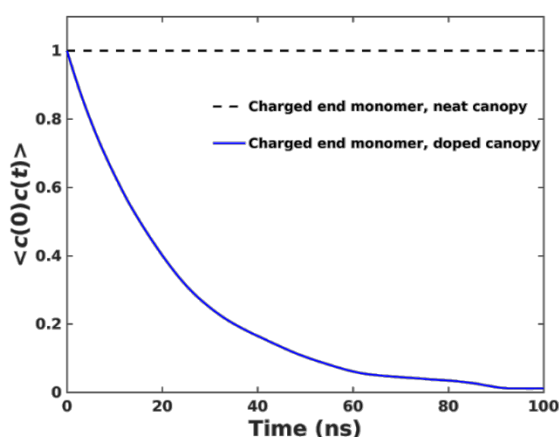


Figure 3-5. Time correlation function for the adsorption of a charged end monomer on the solid wall. A charged end monomer is considered to be associated with the wall if it is within 0.6 nm from the wall (i.e., in the first density peak of the charged end monomer in Figure 3-4b).

Single polymer dynamics. We examine the diffusion of polymers in directions parallel to the wall by computing their mean-square displacement (MSD) in the xy -plane. Figure 3-6a shows that, in neat canopies, despite that the charged end monomers of each polymer is adsorbed strongly on the wall and do not desorb over sub-microsecond time scale, these monomers exhibit modest in-plane mobility. Such a phenomenon can be attributed to the hopping of the charged end monomers between the charged sites on the same solid surface, which has also been reported in a prior MD study of NIMs consisting of 1nm-radius nanoparticles and charged polymers.¹³⁸ Figure 3-6a shows that, at short time scale (<20 ns), the MSD of the center-of-mass (COM) of polymers is distinctly smaller than that of the charged end monomers. This is expected. At short time, the movement of

the charged end monomers is hindered mostly by electrostatic interactions with charged wall atoms in contact with them. The movement of a polymer's COM, however, is the net result of the movement of all its beads, and is thus additionally hindered by other factors such as entanglement of polymer chains. At short time, the MSDs of both the charged end monomer and the COM exhibits sub-diffusive behavior as can be expected for diffusion in a crowded environment. The sub-diffusive movement of the charged end monomer persists to a longer time than the COM, likely because the movement of these monomers is strongly arrested by the attractions by the charged wall atoms. From the MSD shown in Figure 3-6a, the average lateral diffusion coefficient of polymers' COM is determined to be $3.60 \pm 0.01 \times 10^{-11} \text{ m}^2/\text{s}$, which is about an order of magnitude slower than that of the bulk polymers ($D_{\text{bulk}} = 3.16 \times 10^{-10} \text{ m}^2/\text{s}$).

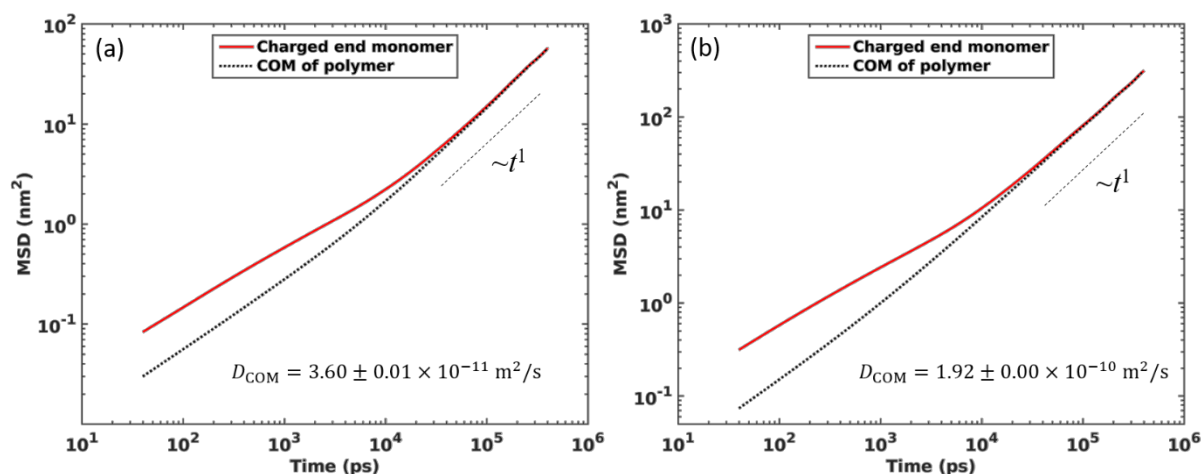


Figure 3-6. Diffusion of polymers in neat and doped canopies. The lateral mean-square-displacement (MSD) of the charged end monomer and center-of-mass (COM) of polymers in (a) the neat canopy and (b) the doped canopy.

Figure 3-6b shows the MSDs of the charged end monomers and the COM of the polymers in doped canopies. Over the same time period, these MSDs are much larger than their counterparts in the neat canopies. This is caused by two reasons. First, there are many “free” polymers in the doped canopies and these polymers exist in an environment rather similar to that in bulk polymers,

which allows fast diffusion. Second, there is relatively fast exchange between the “free” polymers and the polymers “grafted” to the charged wall. Using the MSD shown in Figure 3-6b, the average lateral diffusion coefficient of polymers’ COM is determined to be $1.92 \pm 0.00 \times 10^{-10} \text{ m}^2/\text{s}$, which is moderately smaller than bulk polymers but ~ 5 times faster than the polymers in neat canopies. This result is in good agreement with the observation that doping canopies using electrolyte ions greatly accelerates the diffusion of the polymers in them.⁶⁷

3.4 Conclusions

In summary, we study the polymeric canopies in model NIMs with moderate polymer chain length, relatively high surface charge density, and in the limit of large nanoparticle diameter. In neat canopies, charged end monomers form a Helmholtz layer near the charged surface, thereby “grafting” practically all polymers to the wall. These polymers are highly stretched. While hardly desorbing from the wall, they maintain modest lateral mobility. Doping the canopy with electrolyte ions causes some of the polymers to migrate away from the wall and become “free” polymers. The remaining “grafted” polymers are no longer highly stretched and the “free” polymers adopt configuration similar to bulk polymers. Therefore, the canopy is dilated. The “free” polymers move in an environment similar to that in bulk polymers. This, along with the rather rapid exchange between the “grafted” and “free” polymers, means that polymer dynamics in the canopy is greatly accelerated by electrolyte doping.

The canopy structure and dynamics revealed in our simulations are consistent with those inferred from prior experimental studies. However, some subtle features not yet widely recognized are also noted. For example, while the desorption of the charged end monomers from the wall is driven by the adsorption of electrolyte counterions introduced into the canopy, the number of the

desorbed monomers is less than that of adsorbed electrolyte counterions due to the overscreening phenomenon.

The structure and dynamics of polymeric canopies as well as their response to electrolyte doping are controlled primarily by the interplay of electrostatic and entropic effects. Adjacent to the charged wall, electrostatic effects dominate over the entropic effects, and polymers are “grafted” to the wall despite significant entropic penalty associated with polymer crowding. Beyond this interfacial layer, entropic effects play a more important role, which leads to the formation of multiple polymer layers. While the importance of electrostatic interactions is long recognized, until now attention has been focused on interactions between *individual* charged monomers and charged wall atoms. However, we show that the long-range, *collective* electrostatic interactions are important in deciding the canopy structure when the wall’s surface charge density is high. In this regard, it is instructive to consider the canopy as a special electrical double layer screening the charges on the wall. While entropic effects due to polymer crowding undoubtedly give new characteristics to these double layers compared to those in RTILs, some key features of double layers in RTILs such as overscreening are preserved. Such a perspective of the canopies in NIMs complements the “ionic bond” concept adopted in prior models for NIMs, and may help develop improved theories for NIMs.

Supporting Information

All supporting information cited in this chapter is located in Appendix B.

CHAPTER 4 Molecular Structure and Dynamics of Ionic Liquids in a Rigid-Rod Polyanion-Based Ion Gel

Disclosure

This work has been published by the American Chemical Society: Z. Yu, Y. He, Y. Wang, L.A. Madsen, and R. Qiao, "Molecular Structure and Dynamics of Ionic Liquids in a Rigid-Rod Polyanion-Based Ion Gel", *Langmuir*, 33, 322, 2017

4.1 Introduction

Polymer electrolyte materials play a critical role in numerous applications including fuel cells, solar cells, and rechargeable batteries.¹⁵²⁻¹⁵³ These applications often demand high ionic conductivity, mechanical strength and stiffness, and excellent thermal stability.¹⁵⁴⁻¹⁵⁵ However, despite intensive research in the past decades, few existing materials can meet these demands simultaneously. In recent years, ion gels, polymeric networks swollen by room-temperature ionic liquids (RTILs), have shown great promise in meeting these demands.⁷⁵ RTILs are electrolytes that are composed entirely of ions but remain in the liquid state at relatively low temperature (e.g., $<100^{\circ}\text{C}$).¹⁵⁶ Many RTILs exhibit excellent ionic conductivity, electrochemical stability, and thermal stability.^{30, 157-158} Therefore, when RTILs are combined with suitable polymers, the resulting ion gels can provide many of the electrical, thermal, and mechanical properties desired for polymer electrolyte materials.⁷⁶⁻⁸¹ A recent breakthrough in this field is the synthesis of liquid crystalline gels containing a rigid-rod polyanionic aramid poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide (abbreviated PBDT) and a RTIL 1-ethyl-3-methyl imidazolium trifluoromethanesulfonate ([C₂mim][TfO]).⁸² These gels exhibit high ionic conductivity (up to $8\text{ mS}\cdot\text{cm}^{-1}$ at room-

temperature), widely tunable modulus (0.003 - 3 GPa), excellent thermal stability (up to 300°C), and transport anisotropy (up to 3.5×). The fabrication of this ion gel opens up exciting new avenues for engineering polymer electrolyte materials. Given the flexibility of the molecular design of RTILs and ionic polymers, one can expect to even further improve both the ionic transport and mechanical properties of this type of ion gels through judicious selection of RTILs and polymers. Such rational design, however, demands a fundamental understanding of the structure and dynamics properties of the RTILs in the gel.

The structure and dynamics of RTILs in various systems have been studied intensely in recent years. First, in bulk RTILs, cation-anion interactions are strong and thus each ion effectively resides in a cage formed by its neighbor ions. The hydrophobic tails of cations can aggregate to form spatially heterogeneous domains.^{102, 159} The dynamics of ions also exhibit heterogeneity, with some ions diffusing considerably faster than other ions.^{99, 160} The diffusion of an ion in RTILs is strongly affected by the cage surrounding it: at short time when the ion has not yet escaped from its cage, ion diffusion is in the ballistic and then sub-diffusive regime; at large time scale when the cage is broken due to cleavage by other ions, ion diffusion reaches the diffusive regime.⁹⁶⁻⁹⁹ Secondly, for RTILs confined in planar or cylindrical nanopores, similar to most liquids, significant layering of RTILs occurs near the pore walls.³⁰ When the pore walls are charged, counterions and co-ions form alternating layers near the wall. Except when the wall is very highly charged, the wall charge is over-screened by the first ionic layer near the pore wall.^{30, 87, 100} The dynamic properties of ions vary notably across the pore, with the diffusion of the ions adjacent to pores wall typically being slowest.^{96, 101} While the dynamics of ions are usually slowed down by confinement, sometimes the diffusion of ions inside the pore can be much faster than in the bulk,¹⁶¹⁻¹⁶² e.g., when ion density inside sub-nanometer pores becomes notably smaller than that of bulk

RTILs.¹⁶² Finally, for RTILs in polymer membranes, most work focused on the situation when RTILs are mixed with disordered polymers such as poly(ethylene oxide), and usually lithium salts such as lithium-bis(trifluoro-methane)-sulfonimide were also included.^{102-103, 163-165} The local structure of ion pairing in polymer membranes exhibits similar pattern as in bulk RTILs, though the imidazolium cations are also found to be partly solvated by polymer chains.¹⁰² The dynamics of the imidazolium cations is notably slowed down by the polymers.¹⁰³ The RTILs can modify the conformation of the polymers and enhance their segmental dynamics compared to that in polymer lithium salt mixtures.¹⁶⁴

These above prior studies of RTILs are a useful starting point for understanding the structure and dynamics of the RTILs in the ion gels developed in Ref. 82. Nevertheless, the RTILs in these new gels exist in rather different environment compared to those examined in the prior studies. Importantly, unlike those in bulk liquids, nanopores, or neutral polymer membranes, the RTILs in these gels are confined between rod-like, mobile but largely ordered polyanions with discrete charge moieties. Furthermore, the polyanion has a hydrophobic backbone and a radius that is comparable to the ion size. The structure and dynamics of RTILs in such a heterogeneous, confined environment cannot be simply extrapolated from the results obtained in other systems, and many questions about these properties remain open. For example, how do cations and anions organize around the polyanions? What are their dynamics? How are these dynamics related to the ion distribution near the polyanions, and ultimately the mass fraction of polyanions and the presence of metal ion impurities in the gel? In this work, we address these questions through MD simulations using the PBDT-[C₂mim][TfO] ion gels as a model system. Given that the study this type of gel is still at the earliest stage, we focus on revealing the essential features of RTIL structure and dynamics in the gel rather than quantitatively reproducing experimental measurables such as the

ion diffusion coefficients. The rest of the manuscript is organized as follows. The simulation system, model and methods are presented in Section 2; results on the structure and dynamics of the ions between PBDT rods are presented in Section 3. Finally, conclusions are presented in Section 4.

4.2 Simulation System, Molecular Models and Methods

Since these sulfonated aramid-based ion gels are new,⁸² we first outline the method for fabricating them before describing how they are simulated in this work. PBDT is a rigid-rod polyelectrolyte with high ion density along its backbone. PBDT forms a lyotropic liquid crystalline (LC) phase above a critical mass concentration of 1.2 wt%.¹⁶⁶ To make ion gels, an aqueous seed solution containing the polyanion PBDT and Na⁺ counterions is placed inside a test tube and subjected to a magnetic field applied along the tube axis.⁸² [C₂mim][TfO] liquids are then placed above the seed solution. Driven by processes including the ion and water exchange between the seed solution and the RTILs, ion gels form at the bottom of the test tube. The as-formed gel is then heated to high temperature to remove the water inside it. X-ray diffraction shows that the PBDT⁻ polyanions are highly ordered in the dried gel and RTILs are dispersed within the aligned PBDT matrix. Experimental nuclear magnetic resonance (NMR) measurements show that approximately half of the Na⁺ ions in the seed solution remain in the dried ion gel when using the fabrication procedure of Ref. 82. The amount of residual Na⁺ ions further depends on parameters that include the mass fraction of PBDT in the seed solution and the relative volume of the seed solution and the RTIL. Supporting Information section 9 describes NMR measurements to quantify Na⁺ content in the ion gels.

MD system. Based on the ion gel structure measured experimentally, a molecular simulation system was developed. Figure 4-1 shows that the system consists of four rigid rods representing PBDT polyanions and the accompanying RTILs (in some cases, residual Na^+ ions were also added, see Table 4-1). In reality, each PBDT rod is tens of nanometers in length, too long to be modeled in MD simulations. Here each rod is 6.72 nm long. Initially, all rods are perfectly aligned in the z -direction. The simulation system is periodic in all three directions. These rods, together with their periodic images, form a hexagonal lattice in the xy -plane (see Figure C-1 in supporting information). The spacing between adjacent rods is denoted as S_{r-r} . The number of C_2mim^+ and TfO^- ions was chosen to ensure the overall electroneutrality of the system. Initially, two slabs of RTILs were placed in contact with the two ends of the rods and a vacuum space was placed between the RTIL slabs (see Figure 4-1b). To obtain an ion gel, we fixed the rods and performed an NVT run for the RTILs to enter the space between the rods. This pre-equilibration process ends when the rods become fully wetted by RTILs and the number of RTIL molecules between the PBDT rods no longer changes (This typically takes less than 20 ns. See Figure C-2 for the evolution of the number of RTIL molecules between PBDT rods when S_{r-r} is 2.2 nm). The PBDT rods and the RTILs between them obtained at the end of the equilibration process are considered as a model ion gel (see Figure 4-1b). We verified that the ion gel thus formed is electrically neutral. Ion gels with different mass fraction of PBDT were obtained by using different initial rod-rod spacing S_{r-r} during the above pre-equilibration process. Table 4-1 summarizes the various ion gels studied in the present work.

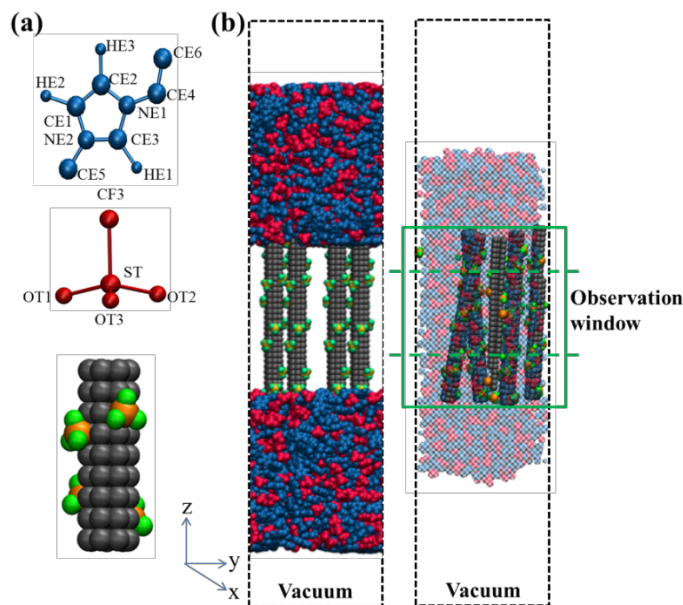


Figure 4-1. Molecular models of the PBDT-RTIL gel. (a) Structure of the C_2mim^+ , TfO^- , and the semi-coarse-grained PBDT rod. Each rod consists of four chemical repeat units of PBDT. The orange (green) balls denote the sulfur (oxygen) atoms of PBDT sulfonate groups. (b) Snapshots of the system at the beginning and the end of the pre-equilibration process. The thin black dashed lines denote the simulation box, which is periodic in all three directions. The solid green lines enclose the model ion gel. The space between the two dashed green lines denotes the “observation window” in which the structure and dynamics of the RTILs were analyzed.

Molecular models. C_2mim^+ and TfO^- ions were modeled using united-atom force fields,¹⁶⁷ in which the net charge of each ion was scaled to $0.8|e|$. These force fields were chosen as a compromise between computational cost and accuracy. Specifically, while these force fields are less rigorous compared to the polarizable force fields,¹⁶⁸⁻¹⁶⁹ they enable the structure and dynamics of RTILs to be simulated relatively accurately with greatly reduced computational cost. For example, based on these force fields, our simulations of bulk $[C_2mim][TfO]$ at 353 K and 1 atm predict a diffusion coefficient of $22.0 \times 10^{-11} \text{ m}^2/\text{s}$ for the C_2mim^+ and $12.1 \times 10^{-11} \text{ m}^2/\text{s}$ for the TfO^- ions, which agree quite well with those measured using NMR ($17.5 \times 10^{-11} \text{ m}^2/\text{s}$ for the C_2mim^+ ion and $12.5 \times 10^{-11} \text{ m}^2/\text{s}$ for the TfO^- ions). In addition, prior studies indicated that simulations based on this type of force fields can capture the structure of interfacial RTILs (e.g., those near electrode

surfaces) quite well.¹⁷⁰ The force fields of the sodium ion was taken from the OPLS-AA force field.¹⁷¹

The precise structure of the PBDT rods in the ion gel has not yet been fully clarified. Prior studies suggested that PBDT molecules self-assemble into rigid-rod building blocks in the form of double helix,^{82, 166} and such structure should persist in the ion gel. With the dimensions of the PBDT building block and the distribution of sulfonate groups on the rod inferred from X-ray diffraction data,⁸² we built a semi-coarse grained model for the PBDT polyanions. These polyanions were modeled as rigid rods decorated with explicitly resolved sulfonate groups (see Figure 4-1b). Each rod is 6.72 nm long and consists of four 1.68 nm-long repeating units. Each repeating unit (see Figure 4-1a) is further made of 9 layers of carbon atoms arranged into a regular heptagon (side length: 0.173 nm), and the spacing between adjacent carbon layers is 0.21 nm. Each repeating unit has four sulfonate groups anchored on the carbon atoms in different layers, and these units were stacked onto each other in a way that produced a helical pattern of the sulfonate groups on the PBDT rod (see Figure 4-1b and Figure C-3). The force field parameters for the carbon atoms and the sulfonate groups were taken from the OPLS-AA force fields, and are summarized in the Table A-1. Because the objective of the present study is to delineate the essential features of the structure and dynamics of RTILs in ion gels and the precise structure of PBDT is not fully elucidated yet, the above molecular model is deemed a reasonable choice for several reasons. First, it captures the key chemical features of the PBDT rod including its semi-rigid structure, the hydrophobic nature of its backbone, and the discrete distribution of charge groups on the rod. By resolving the sulfonate groups explicitly, it also allows the strong interactions between the sulfonate groups and RTILs, which can greatly affect the structure and dynamics RTILs, to be modeled in detail. Second, by adopting a simple model for the PBDT rods with well-defined

geometry, it facilitates the parametric study of how gel design parameters such as the PBDT mass fraction affects the properties of RTILs in the gel. Finally, the semi-coarse grained model allows large system to be simulated for relatively long time period, which is necessary in the study of RTIL dynamics.

Simulation and analysis methods. Simulations were performed using the Gromacs code.¹²⁵ All simulations were executed in the NVT ensemble. The temperature of the RTILs was maintained at 353.15K using the velocity rescaling thermostat.¹²⁸ The elevated temperature chosen here helps to achieve good statistics of ion displacement. After the pre-equilibration process described above, each system was further equilibrated for another 20 ns (except for a few selected cases, the PBDT rods were allowed to move during this equilibration step). This was followed by a production run of 80 ns. Table 4-1 lists the composition of the equilibrated ion gel systems studied in this work. A detailed list of the number of ions in each system (including those outside of the observation window shown in Figure 4-1b) is shown in Table C-2 in Supporting Information.

Table 4-1. Properties of the equilibrated ion gel systems studied in this work.

System	Nominal rod-rod spacing*	PBDT mass fraction	C_2mim^+/SO_3^- ratio	TfO^-/SO_3^- ratio	Na^+/SO_3^- ratio	Lateral size $L_x \times L_y$
1	2.0 nm	19.6%	4.45	3.21	0.0	$3.46 \times 4.00 \text{ nm}^2$
2	2.2 nm	16.3%	5.39	4.18	0.0	$3.81 \times 4.40 \text{ nm}^2$
3	2.2 nm	16.1%	5.05	4.47	0.5	$3.81 \times 4.40 \text{ nm}^2$
4	2.4 nm	13.8%	6.41	5.21	0.0	$4.16 \times 4.80 \text{ nm}^2$
5	2.8 nm	10.1%	8.74	7.65	0.0	$4.85 \times 5.60 \text{ nm}^2$

* This is taken as the rod-rod spacing during the pre-equilibration process, when perfectly aligned PBDT rods were fixed and formed a hexagonal lattice in the xy -plane.

In the MD simulations, the non-electrostatic interactions were computed by direct summation with a cut-off length of 1.2 nm. The electrostatic interactions were computed using the Particle

Mesh Ewald (PME) method. The real space cutoff and FFT spacing were 1.2 and 0.12 nm, respectively. All bonded interactions were computed except that the length of the C-H bonds were constrained using the LINCS algorithm.¹²⁶ Note that to ensure the rigidity of the PBDT rod, strong harmonic bonds (bond constant: 5×10^6 kJ/(mol·nm²)) were imposed between carbon atoms in different carbon layers and repeating units.

The trajectories of the system were saved during the production run. To avoid edge effects, only the RTILs in the middle portion of the ion gel (marked out as the “observation window” in Figure 4-1b) were considered in the analysis of the structure and dynamics of the RTILs. Since most PBDT rods were found to be aligned very well along the z -axis even when they were allowed to move, the ion diffusion coefficient in the perpendicular-to-rod direction was computed using $D_{\perp} = \lim_{t \rightarrow \infty} \text{MSD}_{xy}(t)/4t$. $\text{MSD}_{xy}(t)$ is the ion mean-square displacement in the xy -plane given by $\text{MSD}_{xy}(t) = \langle (x_i(t) - x_i(0))^2 + (y_i(t) - y_i(0))^2 \rangle$, where x_i and y_i are the x - and y -position of ion i , respectively. $\langle \dots \rangle$ denotes the ensemble average. The diffusion coefficient in the direction along the PBDT rods was computed using $D_{\parallel} = \lim_{t \rightarrow \infty} \text{MSD}_z(t)/2t$. $\text{MSD}_z(t)$ is the ion mean-square displacement in the z -direction given by $\text{MSD}_z(t) = \langle (z_i(t) - z_i(0))^2 \rangle$, where z_i is the z -position of ion i . To determine the error bars for $D_{\parallel}$ and $D_{\perp}$ (denoted using $\varepsilon_{D_{\perp}}$ and $\varepsilon_{D_{\parallel}}$), we first computed the MSDs for five different time periods of the ion trajectory. $\varepsilon_{D_{\perp}}$ and $\varepsilon_{D_{\parallel}}$ were then calculated as the standard deviation of the diffusion coefficients obtained from MSDs. The error bar of $D_{\parallel}/D_{\perp}$ was obtained using $\varepsilon(D_{\parallel}/D_{\perp}) \approx |D_{\parallel}|/|D_{\perp}|^2 \varepsilon_{D_{\perp}} + |D_{\perp}|^{-1} \varepsilon_{D_{\parallel}}$. We note that the finite size of simulation box can potentially affect the value of computed diffusion coefficient.¹⁷² Such a finite size effect is expected to be small in the system we are studying here. This is because the hydrodynamic interactions, which are responsible for finite size effects in the calculation of

dynamic properties (e.g., diffusion coefficient) in MD simulations, are strongly screened by the PBDT rods in our system.

4.3 Results and Discussion

4.3.1 Structure of Ionic Liquids in Ion Gels

Near extended surfaces, RTILs exhibit distinct structures at intermolecular and larger (e.g., inter-surface) scales.^{30, 95, 100} These structures and their response to external stimuli (e.g., a change of the distance between extended surfaces) often control macroscale observables such as the interactions between extended surfaces. In our ion gels,⁸² distinct structures of RTILs should also develop, both at inter-rod and intermolecular scales. The structure of RTILs at the inter-rod scale likely plays a key role in controlling the interactions between the polyanions and thus ultimately the mechanical and transport properties of the ion gel. Quantifying the structure of RTILs at this scale is complicated: although PBDT polyanions are highly ordered, there exist small variations in their orientation and their separation from other PBDT polyanions, and hence the RTIL structure must in principle be quantified between all PBDT polyanions simultaneously. To circumvent this complexity, we first consider the RTIL structure in a special case, in which perfectly aligned PBDT polyanions were arranged into a hexagonal lattice and fixed throughout the simulation. Figure 4-2 shows the distribution of C_2mim^+ and TfO^- ions in the interstitial space between PBDT rods when the rod-rod distance is 2.2 nm. A layer of C_2mim^+ ions adsorb on the surface of the negatively charged PBDT rods. The adsorption of these ions is not uniform along the rod's circumference because the sulfonate groups are distributed discretely on the PBDT rod. Some TfO^- ions are also found on the rod's surface. Visualization of the trajectories revealed that these anions are in contact with the PBDT rod's hydrophobic backbone, and they are partially shielded from the sulfonate

groups by the C_2mim^+ ions solvating these groups. The first cation layer around the PBDT rod is further surrounded by a layer of TfO^- ions. These TfO^- ions form a hexagonal pattern, reflecting the pattern for the arrangement of PBDT rods. Hence, at a rod-rod separation of 2.2 nm (or equivalently, a PBDT mass fraction of $\sim 16\%$ in the gel), the distribution of ions not immediately adjacent to the PBDT rods are already heavily affected by the packing of the PBDT rods. Finally, Figure 4-2 also shows that very few ion can reach a distance ≤ 0.5 nm from the rod's axis. Using the surface area of a cylinder with a radius of 0.5 nm and the charge on the PBDT rod ($-2.38 e/nm$), the effective surface charge density of the PBDT rod is determined as $-0.12 C/m^2$.

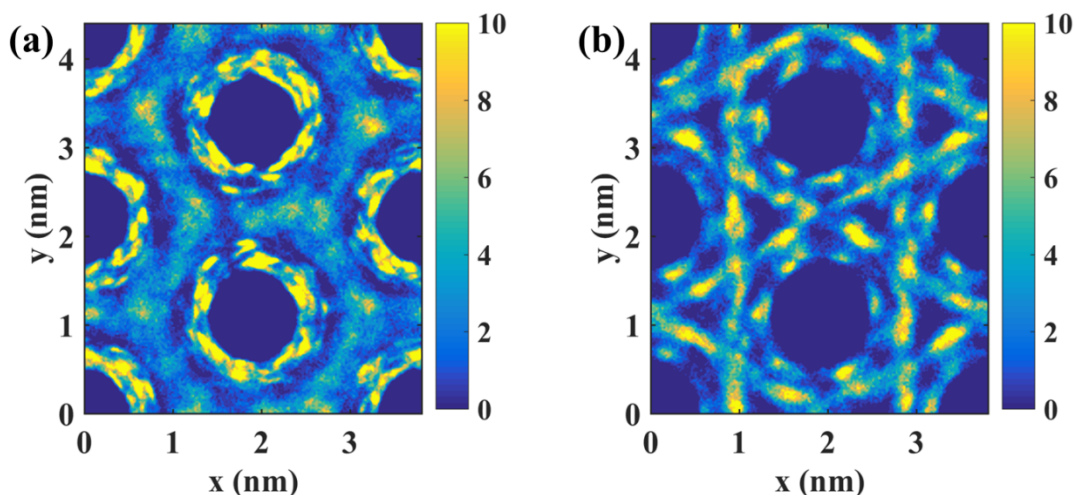


Figure 4-2. Density distribution of C_2mim^+ (a) and TfO^- ions (b) in the interstitial space between the PBDT polyanions in an ion gel. PBDT rods are fixed into a hexagonal lattice in the simulation and the rod spacing is 2.2 nm. The ion density is color-coded, and the unit of the colorbar is nm^{-3} .

The inter-rod structure of RTILs shown in Figure 4-2 also exists when the PBDT rods are mobile (hereafter all results were obtained from simulations with mobile PBDT rods). Figure 4-3a shows the average ion density as a function of distance from the PBDT rod axis. The RTIL structures revealed here are similar to those shown in Figure 4-2: C_2mim^+ ions and TfO^- ions form alternating layers near the rod and some TfO^- ions appear at positions next to the PBDT rods' surface. The former is a hallmark of the distribution of RTILs near charged surfaces.^{30, 101, 162} The

latter is consistent with the anion concentration distribution shown in Figure 4-2 but rarely reported in studies of RTILs near solid surfaces with similar charge densities.¹⁷³ The notable adsorption of anions on surfaces occurs because, unlike in prior studies where charges are distributed uniformly on surfaces, here charges are distributed discretely along the PBDT rod in the form of sulfonate groups and there is space between these groups. This space is occupied primarily by the cations. However, some anions can also access this inter-cation area since their repulsive electrostatic interactions with the sulfonate groups are partially compensated by their attractive interactions with the cations adsorbed on the rod's surface.

To explore how RTILs screen the charge of the PBDT rods, we computed the charge screening factor β as a function of radial distance r from the rod axis¹⁷³

$$\beta(r) = -\frac{1}{q_L} \int_0^r 2\pi r \rho_e(s) ds \quad (4-1)$$

where $\rho_e(s)$ is space charge density due to ions at a radial distance s and q_L is the charge on the PBDT rod per unit length (-2.38 e/nm). At positions with $\beta > 1.0$, the surface charge on the rod is over-screened. Charge overscreening is a universal feature of the electrical double layers at the interfaces of RTILs and surfaces with low to moderate charge densities.^{30, 87} Figure 4-3b confirms that charge overscreening also occurs near PBDT rods. Since charge overscreening often leads to attractions between like-charged surfaces or polyelectrolytes,¹⁷⁴ the results shown in Figure 4-3b may help explain the mechanical strength of the ion gel studied here. Exploring the relation between charge overscreening (or more broadly, the RTIL structure in ion gels) and collective ionic interactions between charged rods and RTILs will form the basis of future studies.

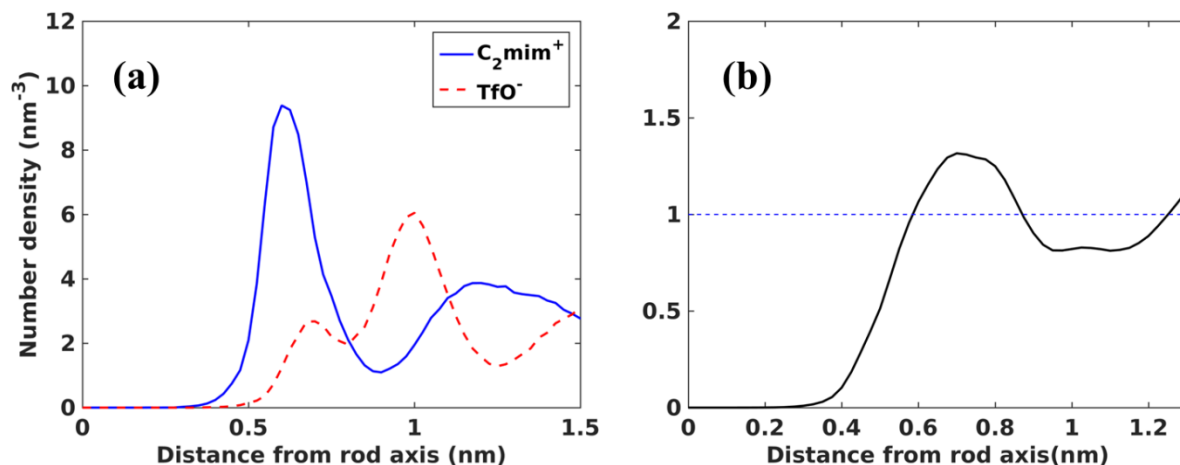


Figure 4-3. Ion density (a) and screening factor β (b) as a function of the radial distance from the PBDT rod axis in an ion gel. The positions of the C₂mim⁺ and TfO⁻ ions are taken as atoms NE1 and ST in Figure 4-1a, respectively. The nominal rod spacing in the ion gel is 2.2 nm.

The structures of RTILs in ion gels with different nominal PBDT rod spacing are similar to those revealed in Figure 4-2 and 4-3a. In particular, as the rod spacing decreases from 2.8 to 2.0 nm, the amount of the C₂mim⁺ and TfO⁻ ions in the first two ion layers near the PBDT rod only changes slightly (see Figure C-7). To understand this, we note that the contact adsorption of C₂mim⁺ ions on a PBDT rod is governed mostly by short range electrostatic interactions with the sulfonate groups on this rod. Since these interactions are not greatly affected by the change of rod spacing (at least in the range explored here), the number of C₂mim⁺ ions in contact with the sulfonate groups (and thus the PBDT rod) does not depend sensitively on the rod spacing. To see this quantitatively, we analyzed the density distribution of ions around the sulfonate groups in ion gels with different rod spacing and the results are shown in Figure 4-4. The sharp C₂mim⁺ peak at $r = 0.49$ nm indicates that each sulfonate group is coordinated (or “solvated”) by several C₂mim⁺ ions, and this coordination (or “solvation”) changes weakly as the rod spacing varies.

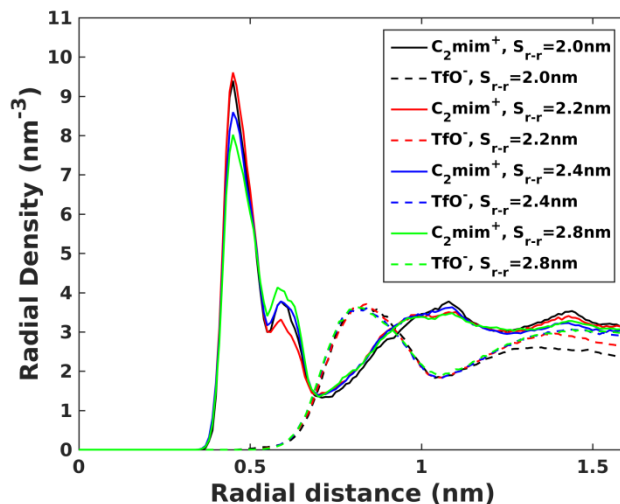


Figure 4-4. Radial density profiles of C_2mim^+ and TfO^- ions as a function of the ion distance to the sulfonate groups of the PBDT rod. The sulfur atom of the sulfonate group is taken as the origin.

Overall, the above results revealed that RTIL ions confined between PBDT rods are strongly heterogeneous and exhibit distinct structures at both inter-rod and smaller intermolecular scales. The structures at the inter-rod scale share key features of the RTIL structure near extended surfaces or within nanopores, but the chemical heterogeneity of individual rod and the packing of PBDT rods also introduce new features in these structures. These correlated ion localizations form what we might call an “electrostatic network” that spans the entire ion gel, and which may give rise to the mechanical cohesion in this new class of ion gel materials.

4.3.2 Dynamics of Ionic Liquids in Ion Gels

Basic features. Figure 4-5a shows the mean square displacement (MSD) curves of C_2mim^+ ions in bulk and in ion gels with a nominal rod spacing of 2.2 nm. The MSDs for ions in bulk liquids and in ion gels share some common features: all MSD curves exhibit three distinct regimes: the ballistic, sub-diffusive, and diffusive regimes.⁹⁸ At the sub-picosecond time scale, a C_2mim^+ ion does not yet interact with its neighbors. It thus moves nearly ballistically and the MSD increases sharply with time. At a time scale of roughly 1 ps, the ion interacts with the ions

surrounding it and its movement is hindered by the cage formed by neighboring molecules. Hence the MSD increases sublinearly, and the ion dynamics is sub-diffusive. At a longer time scale (100-1000 ps and longer), the C_2mim^+ ion escapes the cage formed by its neighbors, and its MSD increases linearly with time as the ion dynamics reaches the diffusive regime.

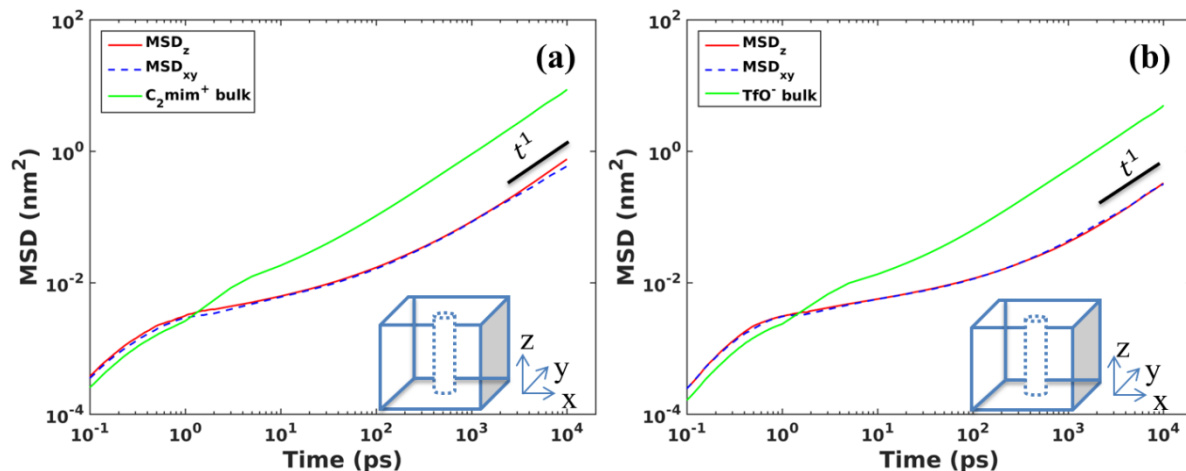


Figure 4-5. Mean-square-displacement (MSD) curves of C_2mim^+ (a) and TfO^- (b) ions in bulk and in ion gel with a nominal rod spacing of 2.2 nm. The xy -component of the MSD curves was divided by a factor of two to facilitate its comparison with the z -component of the MSD curves. In (a), the differences between the MSDs in the xy - and z -directions are not easily discerned in the log-scale plot. The differences between these MSDs are more easily observed in the linear scale plot shown in Figure C-8.

Ion dynamics in these ion gels also show important differences from those in bulk liquids. First, the transition to the diffusive regime occurs at ~ 2 ns in ion gels, much later than the ~ 200 ps in bulk liquids. Second, ion diffusion is slower (a factor of 2 – 10) than in bulk liquids. Third, in line with experimental observations, the diffusion coefficient of C_2mim^+ ion in the direction along the rod ($D_{\parallel} = 3.6 \times 10^{-11} \text{ m}^2/\text{s}$) is larger than in the direction across the rod ($D_{\perp} = 2.3 \times 10^{-11} \text{ m}^2/\text{s}$). The first two observations originate from the association of C_2mim^+ ions with the sulfonate groups on the PBDT rod. As shown in Figure 4-4, several C_2mim^+ ions are in close contact with each sulfonate group. Since these C_2mim^+ ions are attracted to the sulfonate group quite strongly, they

are hereafter called “sulfonate-associated ions”. However, we note that any given associated cation will have a lifetime of approximately 5 ns on any given polymer-fixed SO_3^- anion (See Figure 4-6 below). This means that these associated cations are diffusing and exchanging with “free” cations on this relatively fast time scale.

To understand how the sulfonate-associated ions contribute to the first two observations, we note that any ion in RTILs exists in the cage formed by its neighboring counterions.^{97, 175-176} The dynamics of an ion depends strongly on how easy the ion can escape its cage. For the sulfonate-associated C_2mim^+ ions, escaping their cage usually necessitates leaving the first coordinate shell of the sulfonate group. This is more difficult than C_2mim^+ ions escaping the coordination shell of their neighboring TfO^- ions in bulk liquids because the sulfonate group is nearly stationary while TfO^- ions in bulk liquids themselves diffuse randomly. Consequently, the transition of the MSD to diffusive regime is delayed and the diffusion is slower than in bulk liquids. To see how fast a sulfonate-associated C_2mim^+ ion escapes the coordination shell of its host sulfonate group, we computed the time correlation function for sulfonate- C_2mim^+ coordination

$$ACF_c(t) = \langle c(0)c(t) \rangle \quad (4-2)$$

where $c(t)$ is an indicator of the sulfonate- C_2mim^+ coordination. $c(t)$ is defined as 1.0 if a C_2mim^+ ion in the coordination shell of a sulfonate group (i.e., the first density peak in Figure 4-4) at time $t = 0$ is continuously coordinated to the sulfonate group by time t . Figure 4-6 shows that $ACF_c(t)$ decays to 0.1 in a few nanoseconds, which is similar to the time scale at which the MSD of C_2mim^+ ions in ion gels transition to the diffusive regime (see Figure 4-5a).

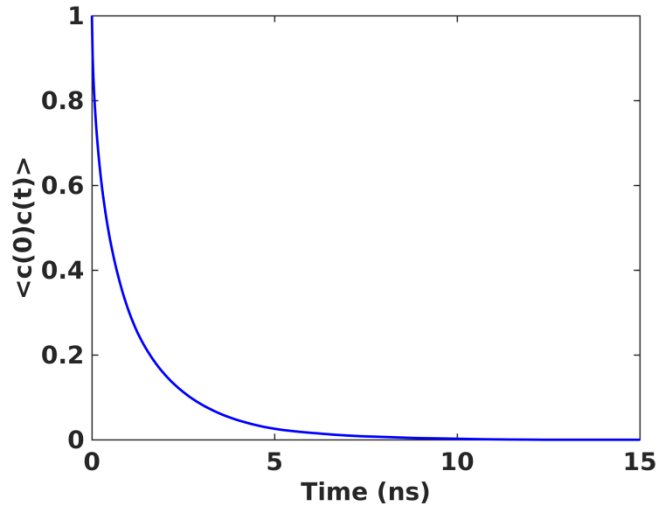


Figure 4-6. Time correlation function for the sulfonate- C_2mim^+ ion coordination in an ion gel with a nominal rod spacing of 2.2 nm.

To confirm that sulfonate-associated C_2mim^+ ions contribute most significantly to the overall slow diffusion of the C_2mim^+ ions in the ion gel, we term the C_2mim^+ ions not in the coordination shell of any sulfonate group to be “free” ions. We then computed the self-part of the van Hove correlation function $G_s(r, t)$ for the sulfonate-associated ions and “free” C_2mim^+ ions using

$$G_s(r, t) = \frac{1}{N} \sum_{i=1}^N \langle \delta[\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_i(t)] \rangle \quad (4-3)$$

where $\delta(\cdot)$ is the Delta function, $\mathbf{r}_i$ is the position of ion i . The function $4\pi r^2 G_s(r, t)$ measures the probability that a particle has moved to a distance r away from its position at time $t = 0$. Figure 4-7 shows the function $4\pi r^2 G_s(r, t)$ for the sulfonate-associated and free C_2mim^+ ions in the ion gel at several time instants. Compared to those of the free ions, the peaks of $4\pi r^2 G_s(r, t)$ for the sulfonate-associated ions are narrower and shift systematically toward smaller distance r , thus confirming that these ions diffuse slower than the “free” ions.

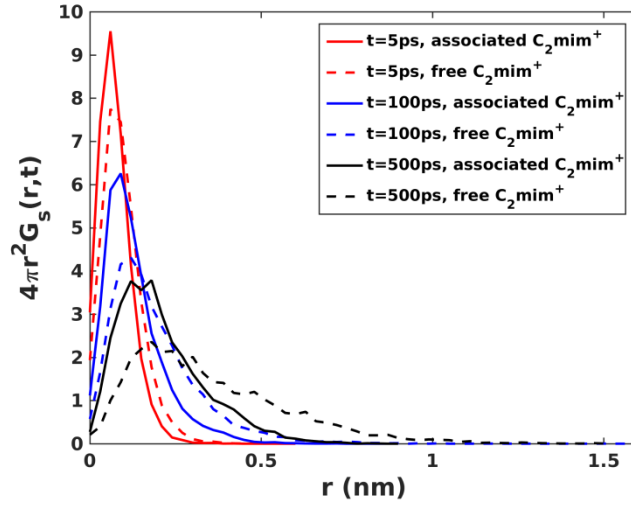


Figure 4-7. Self-part of the van Hove correlation function $4\pi r^2 G_s(r, t)$ for the sulfonate-associated and free C_2mim^+ ions in an ion gel with nominal rod spacing of 2.2 nm.

We also observe anisotropy of ion diffusion in the gel, which arises from several factors. First, due to hydrodynamic interactions, the hydrodynamic self-mobility of a particle adjacent to a planar surface is reduced compared to that in bulk fluids, and the reduction is more significant in the direction normal to the surface than parallel to the surface.¹⁷⁷ Such an effect, although expected to be weaker near PBDT rods due to their small radius, should still lead to a faster diffusion of ions parallel to the PBDT rod axis than normal to the PBDT rod. Second, the different pathways for ion transport along and across the rods also contribute to the anisotropy of the ion diffusion coefficient. Since the PBDT rods are well aligned, the movement of ions across the rods involves much more torturous pathways compared to that along the rods, leading to a smaller ion diffusion coefficient in the rod-perpendicular direction. This geometrical effect is further amplified by the presence of sulfonate-associated C_2mim^+ ions, which can associate with the sulfonate groups for a prolonged time period. As shown in Figure 4-8, these low-mobility ions create significant restrictions to ion diffusion perpendicular to the rods, thus enhancing diffusion anisotropy.

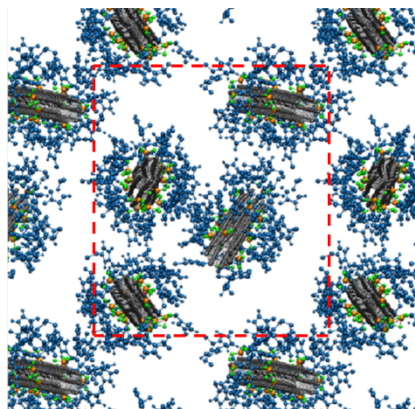


Figure 4-8. A top view snapshot of the ion gel with a nominal rod-rod spacing of 2.2 nm. The C_2mim^+ ions within the first coordination shell of the PBDT rod sulfonate groups are also shown. The red dashed lines denote the boundary of the simulation box.

Thus far, we have examined only the dynamics of the C_2mim^+ ions in the ion gel. Figure 4-5b shows that the dynamics of the TfO^- ions exhibits similar features as the C_2mim^+ ions. That is, compared to those in bulk RTILs, the transition of the MSDs to the diffusive regime is delayed and the diffusion of the TfO^- ions is slower. These features are likely caused by the strong association of many TfO^- ions with the sulfonate-associated C_2mim^+ ions: Since the dynamics of the sulfonate-associated C_2mim^+ ions is sluggish, the TfO^- ions in their first coordinate shells will also be sluggish. In other words, cations and anions in the ion gel form an expansive, dynamic network due to the ion-ion electrostatic interactions. This “electrostatic network”, already visible in the ion distribution shown in Figure 4-2, presumably contributes to the strong cohesion of the ion gel while also playing a fundamental role in the dynamics of ions. Importantly, many cations in this electrostatic network can become temporarily associated (~ 5 ns) with the stationary sulfonate groups of the PBDT rods, which tends to both anchor the electrostatic network and also slow down the dynamics of both cation and anions in the ion gel.

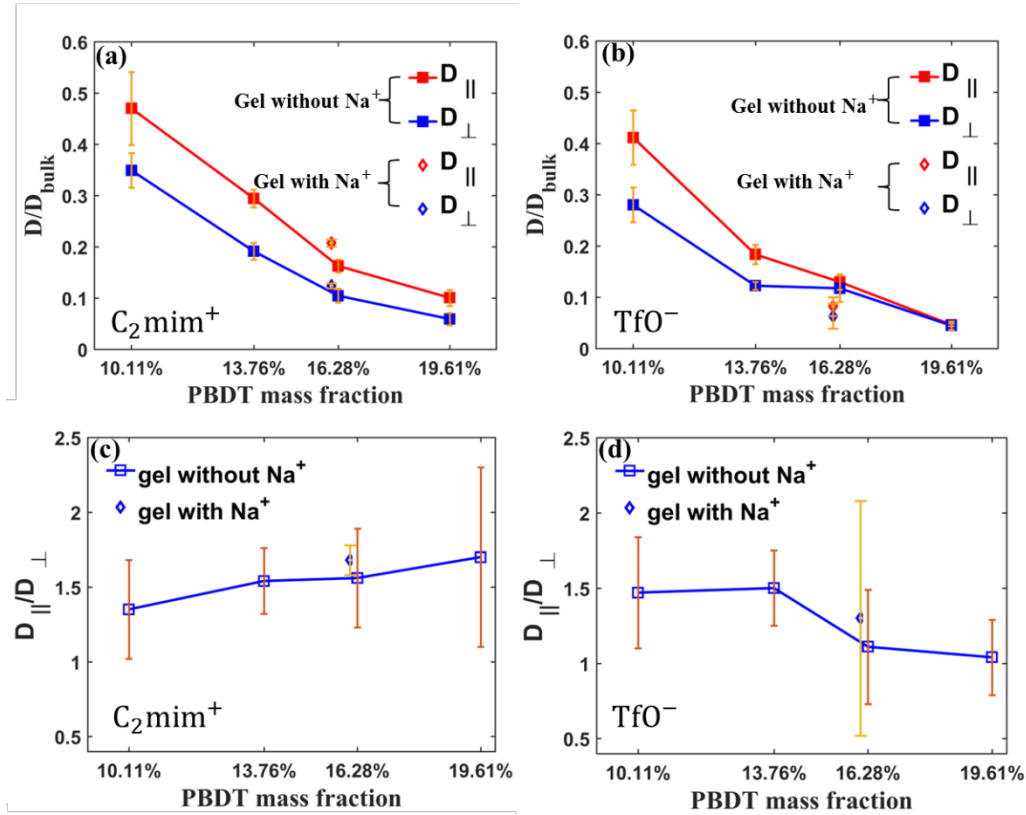


Figure 4-9. Diffusion coefficients of C_2mim^+ (a, c) and TfO^- (b, d) ions in ion gels with different PBDT mass fraction and residual Na^+ ions. Table 4-1 lists the nominal rod-rod spacing corresponding to the various PBDT mass fractions. The diffusion coefficients of the C_2mim^+ and TfO^- ions are 22.0×10^{-11} and $12.1 \times 10^{-11} \text{ m}^2/\text{s}$ in bulk $[C_2mim][TfO]$, respectively. Error bars are generated as described in methods.

Effects of PBDT loading. Figure 4-9 shows the effects of PBDT mass fraction (or equivalently, the nominal rod-rod spacing) on the diffusion coefficients of C_2mim^+ and TfO^- ions. The diffusion coefficients of C_2mim^+ and TfO^- ions are normalized using their respective bulk liquid values to better illustrate how rod-rod spacing affects the dynamics of these ions. Figure 4-9a shows that, $D_{||}$ and $D_{\perp}$ of the C_2mim^+ ions decrease as the rod spacing decreases. We attribute this to the fact that, although the number of sulfonate-associated C_2mim^+ ions in the ion gel does not change greatly as the rod spacing decreases (cf. Figure 4-4), the fraction of sulfonate-associated C_2mim^+ ions increases. Since the sulfonate-associated C_2mim^+ ions diffuse slower than the “free” C_2mim^+ ions in the gel, the average diffusion coefficient of C_2mim^+ ions decreases. A similar decrease of

diffusion coefficient is observed for the TfO^- ions (see Figure 4-9b). This is likely caused by the following factors. In the electrostatic network formed by C_2mim^+ and TfO^- ions that spans the entire ion gel, the dynamics of TfO^- ions are strongly correlated with that of the C_2mim^+ ions. Hence a slowdown of the dynamics of the C_2mim^+ ions at higher PBDT loading is accompanied by a slowdown of the dynamics of the TfO^- ions. Figure 4-9c and 4-9d show that the anisotropy of ion diffusion in the gel is maintained in most of the gels studied here. However, a definite trend cannot yet be established due to the large statistical uncertainty of the data.

These MD simulations have captured the overall trends of the ion dynamics in ion gels, e.g., the decrease of ion diffusion coefficients as the PBDT loading increases and the notable diffusion anisotropy. However, some differences between simulations and experiment⁸² do exist. The predicted slowdown of ion diffusion at increased PBDT loading is more significant than that measured experimentally. The predicted transport anisotropy is similar for C_2mim^+ and TfO^- ions, while experiments indicate a more distinct anisotropy for the TfO^- ions. These differences can originate from several sources. First, the force fields adopted here are parametrized for bulk liquids, and thus they may not capture the dynamics of RTILs confined in the highly heterogeneous environment in the ion gels. Second, the model adopted for the PBDT rods is relatively crude, although it captures some key features of the rods. Finally, experimentally, there are residual Na^+ ions in the ion gel, which are not taken into account in the above calculations. As shown below, these ions can significantly affect RTIL dynamics in the ion gel.

4.3.3 Structure and Dynamics of Ionic Liquids in Ion Gels with Residual Na^+ Ions

As discussed in Section 2, some of the Na^+ ions in the aqueous PBDT seed solution used to prepare the ion gels remain in the dried gel.^{82, 166} To study how these Na^+ ions affect the structure

and dynamics of RTILs in the gel, we built an ion gel with Na^+ ions. In the pre-equilibration step, PBDT rods were fixed into a hexagonal lattice with a rod-rod spacing of 2.2 nm. Na^+ ions were first inserted between the PBDT rods to balance 50% of the charges on the PBDT rods, which is in line with the experimental observation that $\sim 50\%$ of the Na^+ ions in the original seed solution are found to remain in the dried ion gels (see Supporting Information section 9). Next RTIL layers were placed at the two ends of the PBDT rods, and the pre-equilibration step proceeded as in the case for ion gels without Na^+ ions. This step was then followed by further equilibrium and production runs as described in Section 2, during which the PBDT rods were allowed to move. Within the time scale (~ 100 ns) examined here, all Na^+ ions stayed in the ion gel zone (denoted using a green box in Figure 4-1b), consistent with the counterion condensation effect found for PBDT solutions.¹⁶⁶ Therefore Na^+ ions balance 50% of the negative charge on the PBDT rod, which is within the range found experimentally.

Figure 4-10 shows the ion distribution near the PBDT rods. We observe that Na^+ ions are concentrated near the surface of the PBDT rods. Compared to those in ion gels free of Na^+ ions, the height of the first C_2mim^+ peak decreases while that of the first TfO^- peak increases. Here we postulate that, because Na^+ ions are small, they are attracted toward the sulfonate groups of the PBDT rods more strongly than the bulky C_2mim^+ ions, thus displacing C_2mim^+ ions from the rod. The Na^+ ions adsorbed on the sulfonate groups in turn attract TfO^- toward the rod, leading to an enrichment of TfO^- near the rod. These postulations are corroborated by the calculations of the radial density distribution around the sulfonate groups. As shown in Figure C-9, when Na^+ ions are introduced into the ion gel, they approach the sulfonate groups more closely than the C_2mim^+ ions. These Na^+ ions screen the electrostatic interactions between sulfonate groups and C_2mim^+

and TfO⁻ ions, which leads to a reduced coordination of the sulfonate groups by the C₂mim⁺ ions and closer approach of the TfO⁻ ions toward the sulfonate group.

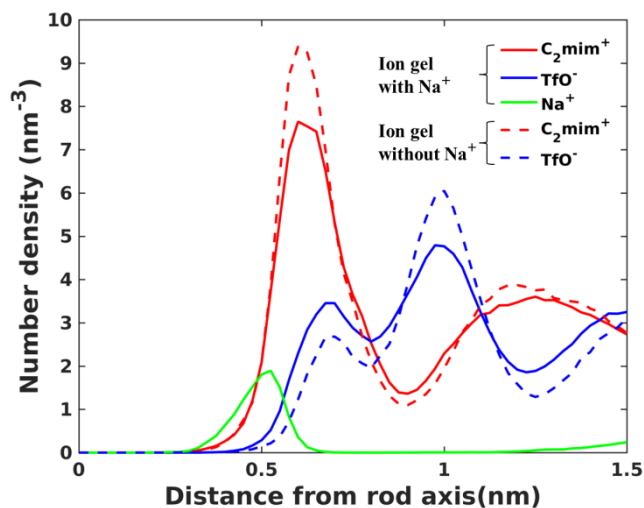


Figure 4-10. Ion density as a function of the radial distance from the axis of a PBDT rod in ion gels with and without residual Na⁺ ions. The nominal rod spacing is 2.2 nm.

The change of RTIL structure in the gels induced by residual Na⁺ ions leads to changes in RTIL dynamics (see Figure 4-9). Na⁺ ions speed up the diffusion of the C₂mim⁺ ions, which is consistent with the weakened association of C₂mim⁺ ions with the PBDT rods (see Figure C-9). Na⁺ ions, however, slow down the diffusion of TfO⁻ ions in the gel. This is likely because TfO⁻ ions in the gel are more strongly coordinated with the less mobile Na⁺ ions adsorbed on the PBDT rods. We propose to systematically test the effect of Na⁺ concentration on the diffusion of C₂mim⁺ and TfO⁻ ions in future experiments.

4.4 Conclusions

In summary, we have studied the structure and dynamics of [C₂mim][TfO] in sulfonated aramid-based ion gels using MD simulations. This type of gel differs greatly from other polymer-based ion gels in that RTILs are dispersed between rigid, highly aligned, rod-like polyanions. The

structure of RTILs in the ion gel exhibits features that are both unique to this ion gel as well as similar to ionic ordering near extended surfaces. For example, because of the discrete distribution of sulfonate groups and presence of hydrophobic domains on the PBDT rods, association of C_2mim^+ ions with the sulfonate groups of the PBDT rods and notable presence of anions on the surface of the negatively charged rods are observed. These RTIL structures can be modified to different extents by factors such as PBDT mass fraction (i.e., rod-rod spacing) and presence of smaller inorganic ions in the gel. On the other hand, alternating layering of C_2mim^+ and TfO^- ions and charge over-screening, the hallmark of RTIL structure near charged surfaces, are also observed near the PBDT rods.

The RTIL dynamics predicted by our MD simulations agree qualitatively with that measured experimentally but some important differences exist. These differences may originate from the relatively simple models adopted in the present simulations. For example, the RTIL force fields are based on charge rescaling, which may not function well in the heterogeneous environment found in these ion gels. Likewise, the semi-coarse-grained rod model for the PBDT polyanions may not resolve important chemical details of these polyanions. In the future, RTIL force fields developed from first principles¹⁷⁸ and all-atom models for PBDT polyanions need to be adopted to obtain a more accurate understanding of the structure and dynamics of RTILs in ion gels.

Since the distinct ordering of cations and anions both near the sulfonate groups and in the interstitial space between the PBDT rods are driven primarily by the electrostatic ion-ion interactions, we may view the heterogeneous structure formed by the ions as an “electrostatic network” that spans the entire gel. Such an electrostatic network, while far from being static, can impact greatly both the mechanical and transport properties of the ion gel. For example, the charge over screening underlying such a network likely contributes to the attraction between PBDT rods

and thus to the mechanical cohesion and high modulus of the gel. Likewise, since some of the cations in the network are associated with the sulfonate groups of the PBDT rods, these associated ions tend to slow down the dynamics of the ions in the entire network. Even so, the ions on average diffuse quite fast ($D \sim 10^{-11} \text{ m}^2/\text{s}$) in these high modulus gels, showing promise for these materials to enable, e.g., high density Li-metal batteries.

Finally, we expect that specific molecular interactions, which vary substantially with IL chemical structure and are driven by, e.g., charge distribution and hydrophobicity, will strongly affect the final gel properties. RTIL correlations (nm-scale structuring) will influence both conductivity and modulus in these gels. For example, we expect that ILs with stronger correlations in time and space (as reflected in radial distribution functions and velocity autocorrelation functions) will drive the formation of higher modulus gels.

Supporting Information

All supporting information cited in this chapter is located in Appendix C.

CHAPTER 5 Ionic Liquids-Mediated Interactions between Nanorods

Disclosure

This work has been published by the AIP Publishing: Z. Yu, F. Zhang, J. Huang, B.G. Sumpter, and R. Qiao, "Ionic Liquids-Mediated Interactions between Nanorods". J. Chem. Phys., 147, 134704, 2017

5.1 Introduction

The past decades have witnessed extensive interest and attention to room-temperature ionic liquids (RTILs) due to their unique combination of various properties such as low volatility, wide electrochemical windows, and excellent thermal stability.^{30, 156, 179} Because of these properties, RTILs have found many potential and even practical applications in diverse areas including electrochemical energy storage, green solvents, and drug delivery, to name a few.^{156, 180-182} In many of these applications, RTILs are confined in nanostructures or between extended surfaces, e.g., they are confined between nanorods in macromolecular ionic composites and ion gels,⁸² or in nanopores in porous electrodes of supercapacitors,^{30, 180, 183} or between extended surfaces when used as lubricants.^{104, 184-187} Because the structure of the interfacial RTILs and the surface forces mediated by RTILs play an essential role in the aforementioned applications, they have been intensively investigated in recent years.

The interactions between surfaces mediated by RTILs are often investigated experimentally using surface forces apparatus (SFA) and atomic force microscopy (AFM).^{148, 188} The forces between two negatively charged mica surfaces separated by ethylammonium nitrate were

measured using SFA as early as 1988.¹⁸⁹ Systematic experimental studies using various surfaces (e.g., mica and silica) and RTILs (e.g., 1-ethyl-3-methylimidazolium ethylsulfate, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, *etc.*) have been reported recently.¹⁰⁴⁻¹⁰⁸ These studies revealed that, for small surface separations of typically less than 10 ion diameters, the surface force resembles the classical structural force, i.e., the force is oscillatory with its period commensurate with the estimated diameter of an ion pair and it decays rapidly as the surface separation increases. While some experiments suggest that surface forces mediated by some RTILs, especially protic ones, are short-range, a growing body of experiments shows that such surface force can also be long-range, especially when aprotic RTILs are involved.¹⁰⁸⁻¹¹¹ Specifically, the surface force decays exponentially as the surface separation increases and decay lengths of 5-10 nm have been reported.¹⁸⁸ Such long-range interactions are not anticipated from the classical DLVO theory. Although their physical origins are not fully understood, it has been suggested that they are electrostatic in nature based on the observation that they depend greatly on the ion density and the dielectric constant of the RTILs.^{109, 188, 190}

Since the inter-surface forces, especially their short-range oscillations, are closely related to the organization and distribution of RTILs confined between surfaces, the structure of RTILs can be inferred from the force-distance curves measured experimentally. For instance, based on the oscillation of the interaction force, it has been suggested that eight to nine ordered layers of ions form in the RTILs that are confined between mica surfaces,¹⁸⁹ although a more elaborate assignment of the RTIL structure is also possible.¹⁹¹ The layered structure of RTILs near solid surfaces has been confirmed experimentally using high-energy x-ray reflectivity studies.¹⁹² However, the direct measurement of the RTIL structure, especially in confined space, is usually challenging. This limitation, however, can be addressed partially using theoretical or simulation

studies in which the structure of RTILs is resolved explicitly at molecular scales. Indeed, the structure of RTILs confined between surfaces (usually planar walls) has been investigated extensively in the past decade using analytical theories, molecular simulations, and classical DFT calculations.⁸³⁻⁹⁶ The findings of these studies are largely in reasonable agreement with those derived from experimental studies, and interested readers are referred to two recent reviews for further details.^{30, 179}

While the theoretical and computational studies of the structure of confined RTILs are fairly advanced by now, similar studies of the surface forces mediated by RTILs are still at a relatively early stage. The classical DLVO theory is not expected to describe the interactions between charged surfaces separated by RTILs because the excluded volume effects associated with the finite size of ions and the correlations between ions, both important for RTILs, are not taken into account in this theory.¹⁸⁵ In addition, the Debye length, the characteristics length scale for the electrostatic inter-surface interactions in the DLVO theory, is usually smaller than the ion size in RTILs. This suggests that other length scales, e.g., the ion-ion correlation length,^{87, 149} are involved in the long-range electrostatic interactions revealed in recent experiments. The limitations of the classical DLVO theory can be addressed using more advanced theories or molecular simulations, which have been successful in predicting the structure of simple liquids, aqueous electrolytes, and polymers confined between surfaces and inter-surface interactions.¹⁹³⁻¹⁹⁶ Nevertheless, only a limited number of analytical theories and simulations have been reported for inter-surface interactions mediated by RTILs. Using the Coulomb gas model, Lee et al. showed that inter-surface force between two planar walls separated by RTILs decays in an oscillatory manner as the inter-surface separation increases and the force maxima correspond to the insertion of new ion layers into the gap formed between the planar walls, which agree qualitatively with available

experimental data.¹⁹⁷ A key insight from the model is that the inter-surface force is controlled strongly by the fugacity of bulk RTILs. More recently, using models built upon the Ginzburg-Landau theory and molecular simulations, Vaikuntanathan, Talapin, and their colleagues studied the interactions of planar surfaces and nanocrystals separated by a high-temperature molten inorganic salt KCl.¹⁹⁸ Their analytical model and simulations captured the oscillatory nature of the inter-surface forces well. A key insight from their study is that the interference between the charge density oscillations near opposing surfaces greatly affects the sign and magnitude of the inter-surface interactions.¹⁹⁸ The fact that theories and simulations can capture key aspects of the inter-surface forces mediated by ionic liquids revealed in the experiments suggests that theories and simulations are promising tools for studying these forces.

The prior studies on the interfacial structure of RTILs and surface forces mediated by RTILs have greatly advanced our understanding of these problems. Nevertheless, some important knowledge gaps still remain. For instance, few simulations have been performed to delineate the surface forces and interfacial RTIL structure concurrently to provide insight into their correlation. Furthermore, most of the available studies deal with extended surfaces like planar walls. Situations in which the critical dimension of the objects is comparable to the ion size, which are often encountered in molecular self-assembly, are rarely explored. It is not yet clear to what extent the interactions between these objects resemble the interactions between extended surfaces and therefore many questions remain open. For example, how does surface charge affect the interactions between these objects? What is the range of these interactions? How do the distributions of ions around the objects determine these interactions? In this work, we investigate the interactions between nanorods mediated by RTILs using MD simulations to address these questions. We focus on the situation in which nanorods are fully aligned because of its relevance

to the recently synthesized macromolecular ionic composites, in which polyanion rods are highly aligned.⁸² The insight gained here will help lay a foundation for understanding the interactions between tilted rods and surfaces.¹⁹⁸⁻¹⁹⁹ The rest of the manuscript is organized as follows. The simulation system, molecular model and methods are presented in Section II. The simulation results on the interactions between neutral or charged nanorods and their relation with the underlying RTILs structure near the nanorods are presented in Section III. Finally, conclusions are drawn in Section IV.

5.2 Simulation System, Molecular Models, and Methods

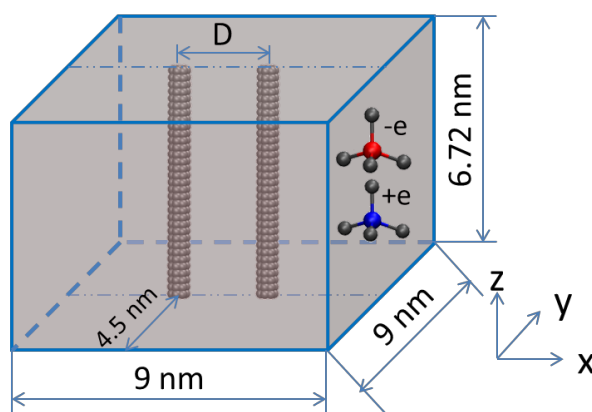


Figure 5-1. A schematic of the simulation system. Two aligned nanorods are immersed in model ionic liquids. The system is periodic in all three directions. The cations and anions have geometry identical to the BF_4^- ions but only their central atoms carry a unit charge.

Figure 5-1 shows a schematic of the simulation system, which features two aligned nanorods immersed in model RTILs. The rod-rod distance D is defined as the distance measured between the axes of the two rods. We performed two sets of studies, one with neutral nanorods and the other with charge nanorods. For each set of study, the distance D was varied systematically to study the rod-rod interactions mediated by the RTILs. The number of ions inside the system was fixed in all simulations. Due to the large size of the simulation box (see Figure 5-1 for the

dimension of the simulation system), the nanorods occupy less than 0.9% of its total volume. Consequently, a bulk like behavior is recovered at positions away from the rods and ions in the system have approximately the same chemical potential in systems with different rod-rod spacings.

In the spirit of the coarse-grained models used in many prior studies of RTILs, which have been successful in capturing key features of the structure and dynamics of bulk and interfacial ions,^{88-89, 92, 200} herein we adopted similar coarse-grained models for both the nanorod and model RTILs. Each rigid nanorod consists of 33 layers of carbon atoms distributed evenly in the rod length direction. Each layer includes seven carbon atoms arranged as a regular heptagon with a side length of 0.17 nm. For charged nanorods, small partial charges are assigned equally to each atom in the nanorod to give a line charge density of $-2.38\ e/\text{nm}$. The structure and charge of the rod thus constructed are relevant to the rigid-rod polyanion poly(2,2'-disulfonyl-4,4'-benzidine terephtha-lamide), or PBDT, used in the synthesis of some macromolecular ionic composites.⁸² Cations and anions in our model RTILs, both rigid, have geometries identical to the BF_4^- ions (see Figure 5-1) and only their central atoms carry a unit positive/negative charge. To account for ions' electronic polarizability, a background dielectric constant of $\epsilon_r = 2.5$ was used in the calculation of electrostatic interactions. All atoms in the nanorod have Lennard-Jones (LJ) parameters of $\sigma_{LJ} = 0.355\ \text{nm}$ and $\epsilon_{LJ} = 0.293\ \text{kJ/mol}$. Atoms in the cation and anion have LJ parameters of $\sigma_{LJ} = 0.336\ \text{nm}$ and $\epsilon_{LJ} = 0.360\ \text{kJ/mol}$, and more details of the force field for RTILs can be found in Table D-1 in the supplementary material.

With the above force fields, the bulk density of the RTILs is $\rho_+ = \rho_- = 4.11\ \text{nm}^{-3}$ (P=1 atm; T=400 K). The radius of the cation/anion is $\sim 0.22\ \text{nm}$ based on the radial distribution function of bulk RTILs (see Figure D-1 in the supplementary material). The effective radius of each nanorod

is ~ 0.35 nm based on the ion density profile around isolated nanorods (see Figure D-2 in the supplementary material). The coarse-grained models adopted here do not take into account many of the subtle details of real polyanions and RTILs, e.g., the discreteness of polyanions' surface charge groups and the complex shape of the ions. With these simplifications, we seek to reveal the most essential features of the interactions between nanorods mediated by RTILs, unobscured by the chemical complexity of RTILs and nanorods. The potential limitations of the coarse-grained model are discussed in Section IV.

Simulations were performed using the Gromacs code.¹²⁵ All simulations were executed in the NVT ensemble ($T=400$ K). Similar to many prior studies on RTILs, an elevated temperature was used to ensure that the phase space is explored effectively within the time scale accessible to our simulations (~ 50 ns). The temperature of the system was maintained using the velocity rescaling thermostat.¹²⁸ The non-electrostatic interactions were computed by direct summation with a cut-off length of 1.5 nm. The electrostatic interactions were computed using the Particle Mesh Ewald (PME) method. The real space cutoff and FFT spacing were 1.5 and 0.13 nm, respectively. For each system, an equilibrium run of 20 ns was performed, followed by a 30 ns production run.

During the production run, the force acting on each atom of the rod was recorded and summed to give the total force acting on each rod. The free energy (potential of mean force, or PMF) for rod-rod interactions was calculated using $E(D) = - \int_{D_0}^D f(x) dx$, where $f(x)$ is the force at a rod-rod separation of x , $D_0 = 4$ nm is the largest rod-rod separation explored in our simulations, and the free energy at rod-rod separation of D_0 is taken as zero. Hereafter, energy is measured in $k_B T$ with $T=400$ K for convenience, where k_B is the Boltzmann constant.

5.3 Results and Discussion

5.3.1 Interactions between Neutral Nanorods

Figure 5-2a shows the rod-rod interaction force as a function of the distance between two neutral nanorods. As the two rods initially in physical contact are separated from each other, they first attract each other ($0.7 \text{ nm} < D < 1.0 \text{ nm}$). As the separation further increases, their interaction force exhibits strongly damped oscillations, which nearly vanish at separations larger than $\sim 2.0 \text{ nm}$. The force profile $f(D)$ at $D > 0.9 \text{ nm}$ can be fitted to a damped sine wave function

$$f(D) = ae^{-D/L_d^f} \sin\left(\frac{2\pi}{L_p^f}(D - b)\right) \quad (5-1)$$

where L_d^f is the decay length, L_p^f is the oscillation period, and a and b are fitting constants. Using the data shown in Figure 5-2a, L_d^f and L_p^f are determined to be 0.50 nm and 0.48 nm , respectively.

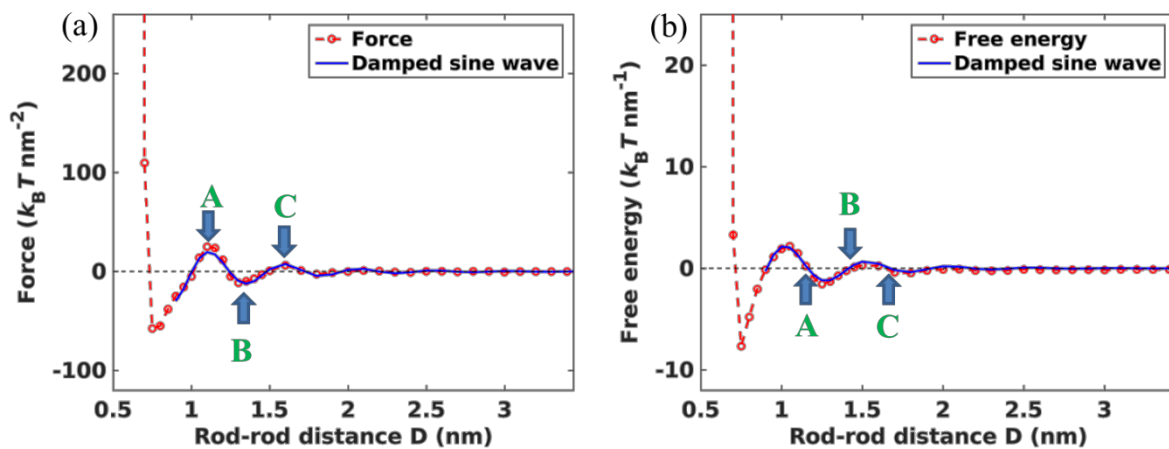


Figure 5-2. Interactions between two neutral nanorods immersed in ionic liquids. (a) Interaction force. (b) Interaction energy.

The integration of the force shown in Figure 5-2a leads to the interaction free energy $E(D)$ between the nanorods presented in Figure 5-2b. $E(D)$ is also oscillatory and decays with D rapidly.

Its decay length ($L_d^E = 0.44$ nm) and oscillation period ($L_p^E = 0.51$ nm) are determined by fitting $E(D)$ to the form of Eq. 5-1, and they are found to be comparable to those of the interaction force. It can be seen that separating two nanorods initially in contact must overcome an energy barrier of $\sim 10 k_B T/\text{nm}$. Such a large energy barrier is attributed mostly to the attractive rod-rod interactions at separations of 0.7-1.0 nm, which are caused by the van der Waals attractions between the two rods and the capillary effects. For $D \leq 1.0$ nm, one cannot even fit one ion between the closest surface points of the two rods (see Figure D-3 in the supplementary material). As such, a vacuum is developed between the two rods and a vacuum-RTIL interface is formed. To lower the free energy associated with the vacuum-RTIL interface, an attractive force between the rods, which pulls the rods closer to reduce the area of the vacuum-RTIL interface, is developed.

The short-range, oscillatory forces between two neutral rods observed here resemble the structural forces between extended surfaces separated by simple fluids. The latter is usually understood using the contact value theorem and the superposition approximation method.^{148, 185} Following the contact value theorem, the interaction force P between two planar walls separated by a distance D is given by $P(D) = k_B T [\rho_D(0) - \rho_\infty(0)]$, where $\rho_D(0)$ is the contact fluid density (i.e., fluid density on a wall's surface) when the walls are separated by a distance D . Therefore, repulsive (attractive) forces are accompanied by the highly (weakly) ordered fluid structure between the walls and accordingly the high (low) fluid contact density on the walls.¹⁴⁸ The fluid structure between the two walls, embodied in the contact fluid density and affected by the geometrical constraints imposed by the two walls, can be qualitatively inferred from the fluid structure near isolated walls by superposition:²⁰¹ the fluid density between two walls separated by a distance of h varies as $\rho_h(z) \sim \rho_\infty(z) + \rho_\infty(h - z)$, where z is the distance from one wall and ρ_∞ is the fluid density near an isolated wall. It follows that $P(D) \sim k_B T [\rho_\infty(D) - \rho_b] \sim k_B T \rho_\infty^{ex}(D)$,

where ρ_b is the density of bulk fluids and $\rho_\infty^{ex}(D) = \rho_\infty(D) - \rho_b$ is the excess fluid density at a distance of D from the wall. This relation has been used successfully to understand structural forces.^{194, 202} Importantly, it suggests that the oscillation period of structural forces between two planar walls is close to the oscillation period of the fluid density near an isolated planar wall, which in turn is comparable to the size of the fluid molecules. The structural forces between curved surfaces are often understood from those between planar walls with the help of the Derjaguin approximation, and it can be shown that key characteristics of structural forces, e.g., their oscillation period, are not affected by the curvature of the surfaces.¹⁴⁸

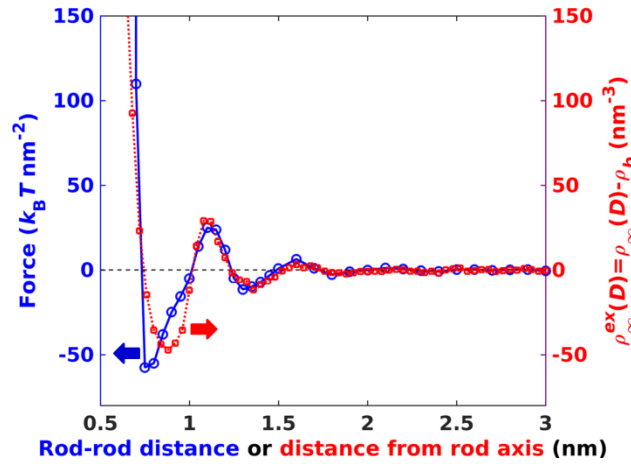


Figure 5-3. Correlation between the rod-rod interaction force $f(D)$ with the excess fluid density near an isolated, neutral nanorod $\rho_\infty^{ex}(D)$.

For the interactions between molecularly thin, neutral nanorods in RTILs considered here, the Derjaguin approximation is no longer rigorous since the radius of nanorods, the size of ions, and rod-rod separations are all comparable. Nevertheless, we shall examine to what extent the rod-rod interactions can be understood using the above framework established for the structural forces between extended surfaces. Assuming that the rod-rod interaction is controlled primarily by the structure of RTILs along the centerline connecting the two rods' axes, we have $f(D) \sim (\rho_\infty(D) - \rho_b)$. Because the cations and anions are symmetric in our RTILs and the nanorods are neutral, the

fluid densities $\rho_{\infty}(D)$ and ρ_b are taken as the summation of cation and anion density. Figure 5-3 compares the rod-rod interaction force $f(D)$ and the excess fluid density $\rho_{\infty}^{ex}(D)$. Excellent commensuration between $f(D)$ and $\rho_{\infty}^{ex}(D)$ is observed. Importantly, the oscillation period of the rod-rod interactions (0.48 nm) agrees with that of the fluid density near isolated rods (0.48 nm), and both oscillation periods are close to the ion diameter (~ 0.44 nm). These results indicate that the structural forces between molecularly thin nanorods immersed in RTILs can be understood qualitatively using the established method for the structural forces between planar walls mediated by simple fluids.

The above discussion suggests that the liquid structure around nanorods, which is controlled by the geometrical constraints imposed by the nanorods, greatly affects the rod-rod interactions. Nevertheless, the superposition method for inferring the liquid structure near the rods does not take into account the rods' small radius and thus cannot provide a full picture of the liquid structure near them. To address this limitation, next we examine the distribution of RTILs around the nanorods at rod-rod separations corresponding to the three extrema of $f(D)$ in Figure 5-2a. The left column of Figure 5-4 shows the fluid density distribution ($\rho_f = \rho_+ + \rho_-$) near the two nanorods corresponding to points A, B, and C in Figure 5-2a. Clearly, each nanorod affects the fluid structure near the other rod, especially in the gap between them. The schematics in the right column of Figure 5-4 highlight the evolution of the fluid structure as the rods are gradually separated from each other and the areas in which strong interference of fluid structure near neighboring nanorods is enclosed by the red dashed lines. At a rod-rod separation of 1.10 nm, the strong interference of the first ion density peaks centering on the two rods leads to greatly enhanced ion density along portion of the rod surface (see the high density spots in Figure 5-4a1 and the magenta lines in Figure 5-4a2), and consequently a strong repulsion between the rods Figure 5-

4b2 shows that as the rod-rod separation is increased to 1.30 nm, two kinds of interferences set in: a constructive interference between the first ion density peak centering on each rod and a destructive interference between the first ion density peak centering on one rod and the first ion

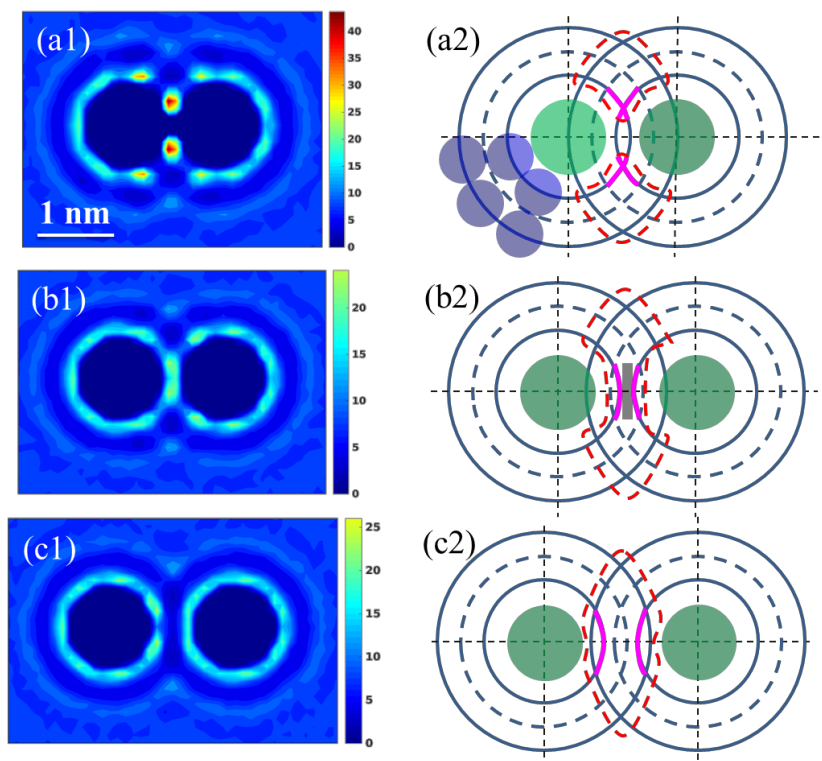


Figure 5-4. Distribution of ionic liquids near neutral nanorods. The three rows are for three rod-rod separations corresponding to the force extrema in Figure 5-2a ((a1, a2) $\rightarrow$ point A; (b1, b2) $\rightarrow$ point B; (c1, c2) $\rightarrow$ point C). Fluid density is computed as the summation of cation and anion densities. Fluid density is color-coded in panels (a1, b1, and c1) (unit: nm^{-3}) and illustrated schematically in panels (a2, b2, and c2) to highlight the interference between fluid distributions near the two rods (the schematics are drawn to scale). The inner solid circle, the dashed circle, and the outer solid circle around each rod denote the first peak, first valley, and second peak of the fluid density around a rod if it is isolated in ionic liquids (see Figure D-2 in the supplementary material). The filled green and blue circles denote the nanorods and ions, respectively. Notable interference of fluid distribution occurs in areas enclosed by red dashed lines. Positions of the rod surface where ion density is modified by the interference between ion distributions around the two rods are marked using magenta lines.

density valley centering on the other rod. The constructive interference enhances the ion density in the space between the two rods (see Figure 5-4b1 and the grey patch between the two rods in Figure 5-4b2) but the destructive interference decreases the ion density along a portion of each rod's surface (see the magenta lines in Figure 5-4b2). Following the contact value theorem, the latter interference reduces the repulsion between the rods, which is consistent with the force valley at point B in Figure 5-2a. As the rods move further apart to a rod-rod separation of 1.6 nm, the geometrical constraints provided by one rod to the ions near the other rod become quite weak. However, a weak constructive interference between the first ion density peak centering on one rod and the second ion density peak centering on the other rod leads to a slight enhancement of the ion density along a portion of each rod's surface (see the magenta lines in Figure 5-4c2), and consequently a peak in the rod-rod repulsion force in Figure 5-2a.

5.3.2 Interactions between Charged Nanorods

Next we turn to the rod-rod interactions when both rods are negatively charged. Here, the double layer forces are expected to become important. Figure 5-5a shows the rod-rod interaction force as a function of the distance between two charged nanorods. The interaction force between charged rods shows damped oscillations similar to those between neutral rods. However, some differences are also notable. First, compared to that between neutral rods, the interactions between charged rods have a longer range (~ 3 nm) and the period of force oscillation is larger. Indeed, fitting the force curve in Figure 5-5a to Eq. 5-1 gives a period of $L_p^f = 0.58$ nm and a decay length of $L_d^f = 0.80$ nm, compared to $L_p^f = 0.48$ nm and $L_d^f = 0.50$ nm for the neutral rods. Second, the first valley of the force curve appears at a rod-rod separation ~ 0.30 nm farther compared to that for neutral rods and it is shallower than the first valley in the force curve for neutral rods. This

observation is caused by the electrostatic repulsion between the two negative charged rods. Finally, a kink is observed in the force curve at a rod-rod separation of 1.15 nm (point A in Figure 5-5). This observation can be attributed to the structural force. At a rod-rod separation of ~ 1.15 nm, the first counter-ion layer around both rods merges in the gap between them to enhance the ion density there (see Figure D-4 in the supplementary material). The high density of this counter-ion layer helps reduce the electrostatic repulsion between the rods. Meanwhile, since these ions also serve as the liquid medium for the two interacting rods, their high local density in the gap between the rods contributes to a repulsive force peak. This force peak is similar to the repulsive, structural (entropic) force peak for the interactions between two neutral rods (cf. the force peak at point A in Figure 5-2), which occurs at essentially the same rod-rod separation.

Figure 5-5b shows the interaction free energy between the two charged rods as a function of the rod-rod separation. The free energy curve shows oscillation period ($L_p^E = 0.59$ nm) and decay length ($L_d^E = 0.87$ nm) similar to those for the force curve in Figure 5-5a. Despite that both rods carry the same charge, a primary free energy minimum occurs at a rod-rod separation of 1.00 nm. Separating two rods initially positioned at this separation must overcome an energy barrier of $\sim 4.6 k_B T/\text{nm}$. Such a barrier can help stabilize nanorods in RTILs and may contribute to the mechanical strength of the polyanion nanorod-based ionic composites developed recently.⁸²

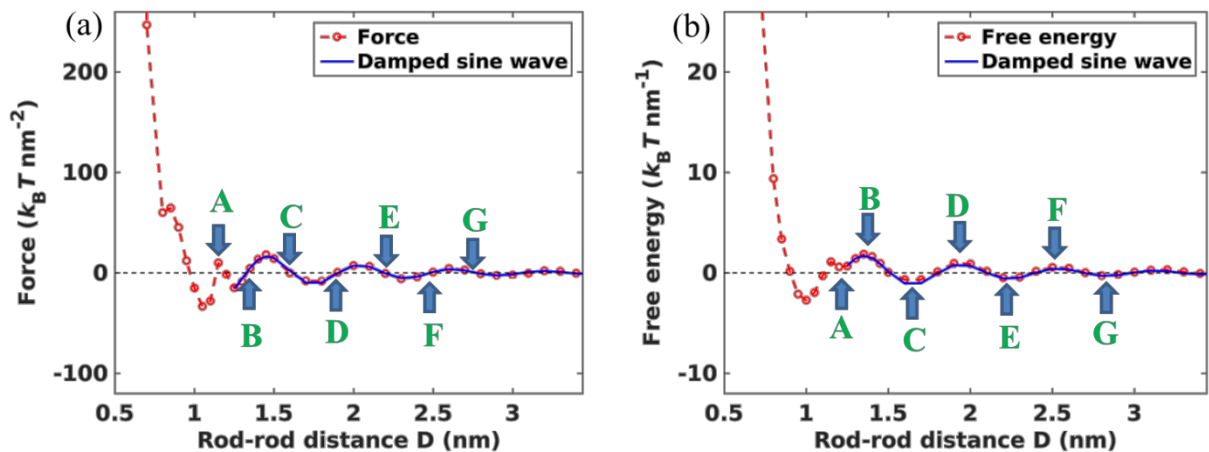


Figure 5-5. Interactions between two charged nanorods immersed in ionic liquids. (a) Interaction force. (b) Interaction energy.

Since the current understanding of the interactions between charged rods mediated by RTILs is quite limited, hereafter we focus on understanding how the interactions oscillate and decay with the rod-rod separation. Because the decay length and oscillation period are similar for the interaction force and free energy and it is customary to focus on the free energy in the analysis of colloidal interactions,¹⁴⁸ below we examined the interaction free energy between charged rods. In particular, we focused on how the structure of RTILs near two rods evolves as their separation changes and how the structure change affects the oscillation and decay of the free energy with rod separation. Given that the interactions between charged colloids is most closely tied to the distribution of the space charge around the objects, the structure of the RTILs near the rods will be characterized using the local space charge $\rho_e = e(\rho_+ - \rho_-)$, where $\rho_{\pm}$ is the local cation/anion number density.

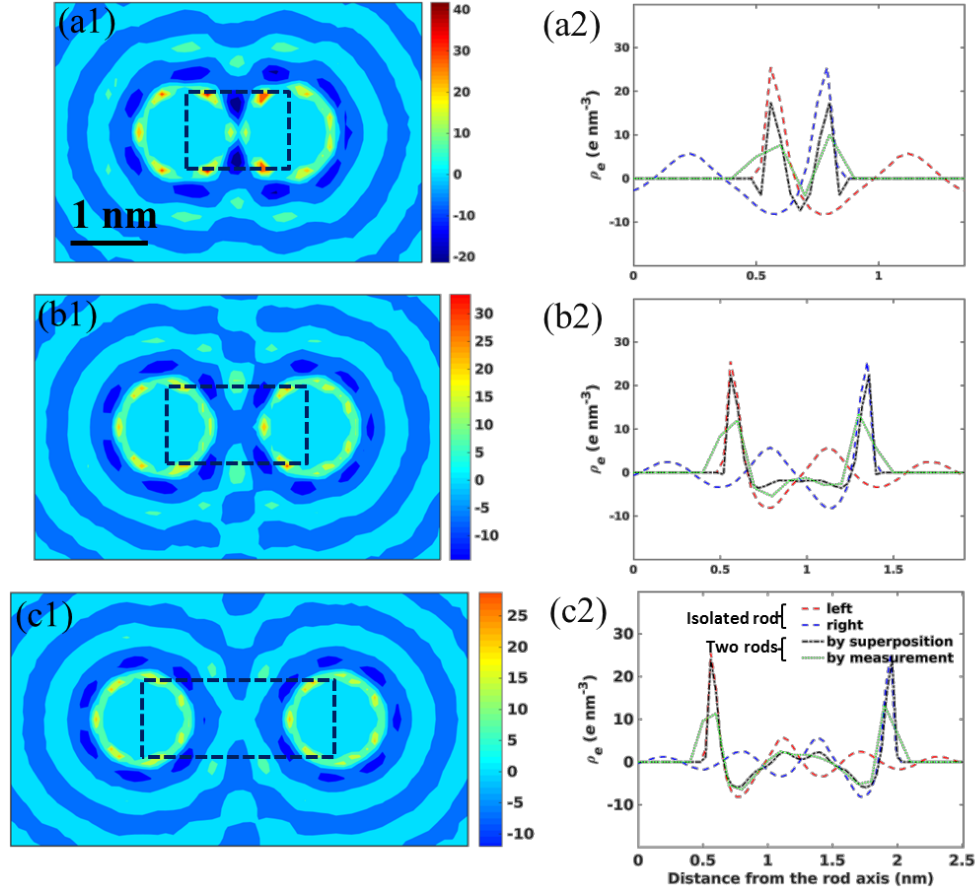


Figure 5-6. Interference between ion distributions near two nanorods. The three rows are for three rod-rod separations corresponding to the three energy extrema in Figure 5-5b ((a1, a2) $\rightarrow$ point B; (b1, b2) $\rightarrow$ point D; (c1, c2) $\rightarrow$ point F). The local space charge density is color-coded in panels (a1, b1, and c1) (unit: $e \text{ nm}^{-3}$). The charge density profiles measured along the rod-rod centerline are compared with that computed by simple superposition of charge density profiles near isolated rods in panels (a2, b2, and c2).

The left column of Figure 5-6 shows the space charge distribution near the two rods at three rod-rod separations corresponding to the three local free energy maxima in Figure 5-5b (points B, D and F). The interference of the space charge distribution near the two rods is evident in the gap between the two rods. Prior researches have shown that, for space charges enclosed between two charged planes, their distribution can be understood from the simple superposition of the space charge near an isolated plane.¹⁹⁸ Here we check whether this simple superposition is also reasonable for the space charge near rods whose radius and separation from each other are both

comparable to the ion size. To this end, we computed the space charge along the centerline connecting the axes of the two rods by superposing the space charge near isolated nanorods and the results are compared to that measured directly from MD simulations in the right column of Figure 5-6. For all three rod-rod separations, the space charge along the rod-rod centerline is captured quite well by the superposition method. A key observation of Figure 5-6a2, 5-6b2, and 5-6c2 is that the interference of the space charge from the opposing rods is “destructive” in nature, i.e., a space charge peak (valley) associated with one rod is cancelled by a space charge valley (peak) associated with the other rod. Such a destructive interference of the space charges near two rods reduces the positive space charge along the centerline of the two negatively charged rods, thus causing less effective screening of the rods’ negative surface charges by the counter-charges in the gap between them. The weakened screening of the electrostatic repulsion between the like-charged rods drives up the overall interaction energy between them energetically, which helps to explain why free energy is maximized locally at points B, D and F in Figure 5-5b.

The interference of the space charge near two rods with separations corresponding to the local minima of the free energy (points C, E and G in Figure 5-5b) is shown in Figure 5-7. A key difference from the interference shown in Figure 5-6 is that the interference is “constructive” in nature here, i.e., a space charge peak (valley) associated with one rod is enhanced by another space charge peak (valley) near the other rod. Such a constructive interference tends to increase the positive space density in the gap between the two rods and thus leads to more effective screening of the surface charge of the rods. Consequently, the free energy is minimized locally at points C, E and G in Figure 5-5b.

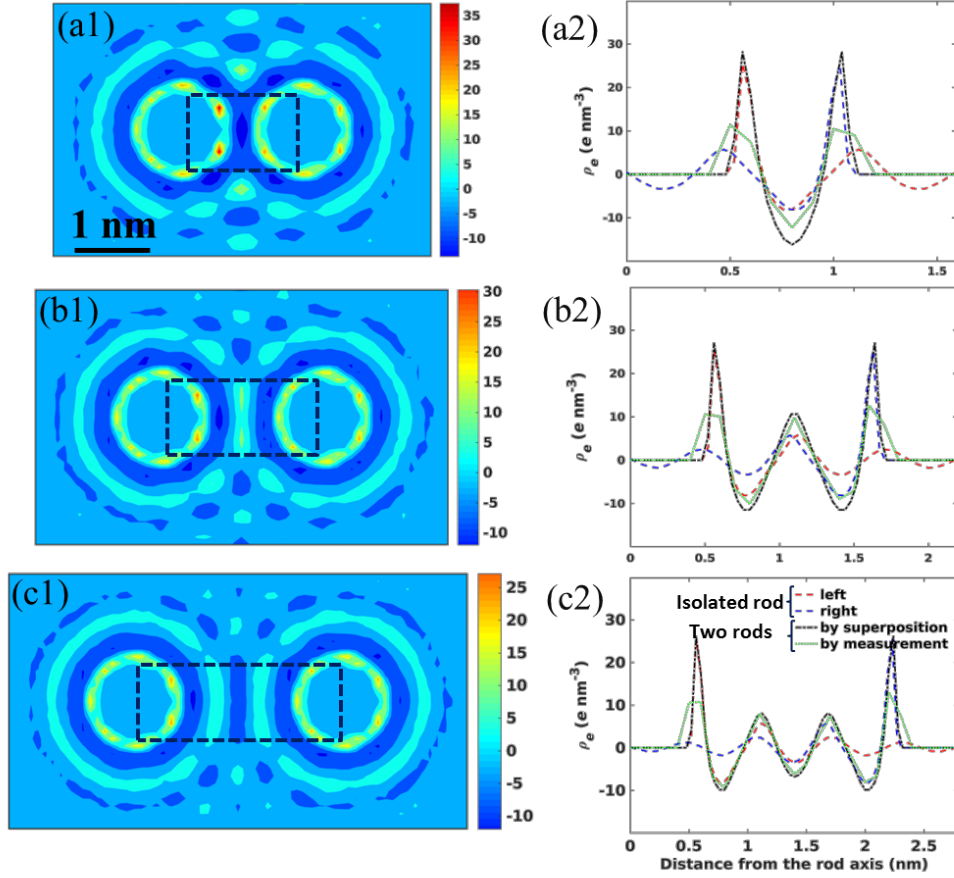


Figure 5-7. Interference between ion distributions near two nanorods. The three rows are for three rod-rod separations corresponding to the three energy extrema in Figure 5-5b ((a1, a2) → point C; (b1, b2) → point E; (c1, c2) → point G). The local space charge density is color-coded in panels (a1, b1, and c1) (unit: $e \text{ nm}^{-3}$). The charge density profiles measured along the rod-rod centerline are compared with that computed by simple superposition of charge density profiles near isolated rods in panels (a2, b2, and c2).

In the above discussion (in particular the right columns of Figure 5-6 and 5-7), only the interference of the space charge along the centerline of the two rods is explicitly addressed. Consequently, the effect of the finite radius of the rods on space charge interference is not considered. To examine the interference more accurately, we computed the net space charge in the gap between the two rods for rod-rod separations corresponding to points B to G in Figure 5-5. The gap is defined as a rectangle box with a height of 1.0 nm and its two sides are bounded by the axes of the two rods (see Figure 5-6 and 5-7). Table 5-1 shows that the net space charge in the gap

at points B, D and F is much smaller than at points C, E and G. This is in good agreement with the difference expected from the destructive interference and constructive interference for these two sets of points.

Table 5-1. The net charges confined between two charged nanorods, measured in a 1.0 nm-wide box between the two rods (cf. dashed boxes in Figure 5-6 and 5-7).

Maximal free energy positions			Minimal free energy positions		
Point B	Point D	Point F	Point C	Point E	Point G
+1.24 e/nm	+1.37 e/nm	+1.71 e/nm	+2.61 e/nm	+2.29 e/nm	+2.12 e/nm

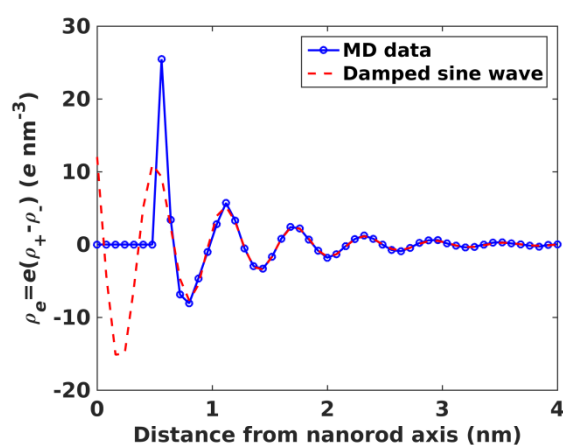


Figure 5-8. The space charge density profile near an isolated, charged nanorod.

The above results suggest that the interference of space charge near molecularly thin rods can be understood reasonably well by superposition of the space charge near isolated rods. Together with the understanding that the destructive (constructive) interference of the space charge around two neighboring rods tends to increase (decrease) their interaction free energy, it is reasonable to conclude that the interactions between thin rods in RTILs can be qualitatively understood from the superposition of the space charge around isolated rods. In a recent study of the interactions between planar surfaces mediated by molten salts, it has been analytically shown that using the superposition method for evaluating the space charge between surfaces, the oscillation period and decay length of the interactions between two surfaces are the same as those for the space charge

profile near the isolated surfaces.¹⁹⁸ Here we checked whether the same would be true for the thin rods considered in this work. Figure 5-8 shows the space charge density profile near an isolated rod, where the damped oscillation of the space charge is evident. Fitting the space charge curve to the form given by Eq. 5-1 gives an oscillation period of $L_p^e = 0.61$ nm and a decay length of $L_d^e = 0.80$ nm. The computed L_p^e agrees with the free energy oscillation period of $L_p^E = 0.59$ nm extracted from Figure 5-5b. Physically, the oscillation period of the space charge profile near an isolated rod is similar to the thickness of a counter-ion and co-ion layer positioned next to each other shown in Figure D-5 in the supplementary material. Since earlier experiments showed that each period of interaction force (and consequently interaction energy) oscillation corresponds to a neighboring pair of counter- and co-ion layer being removed between two interacting surfaces,¹⁸⁵ the agreement of L_p^e with L_p^E is physically sound. The computed decay length of the space charge near isolated rods L_d^e agrees with the rod-rod free energy decay length of $L_d^E = 0.87$ nm extracted from Figure 5-5b. These results thus support the method of inferring rod-rod interactions from the space charge profiles near isolated rods.

The results in Figure 5-2 and 5-5 show that the wavelength (L_p) and decay length (L_d) of the damped, oscillatory rod-rod interactions mediated by RTILs depend apparently on the surface charge of the rods. Fundamentally, however, L_p and L_d are mainly the properties of the RTILs,^{188,}²⁰³ and to a lesser extent, they are also affected by the geometry of the interacting surfaces. Two important types of length scales exist in RTILs. One is the size of the ions and the other is the L_p and L_d of the space charge density wave within them (for bulk RTILs, a charge density wave is observed near individual ions; for RTILs near electrified surfaces, a charge density wave is also observed as one moves from the surfaces toward bulk liquids). L_p and L_d depend on the size and

the interactions between ions, and are thus primarily the properties of the RTILs. For RTILs near electrified surfaces, L_p and L_d are also affected by the geometry of the interacting surfaces to some extent because the distribution of space charge near an electrified surface is known to be affected somewhat by its curvature.¹⁷³ For example, L_d is 1.25 nm in our bulk RTILs, but it is reduced by ~20% in the same RTILs near planar walls (surface charge density: 0.75 e/nm^2) and is reduced further by ~15% in the same RTILs near the charged rods considered in this work.

The principal role of surface charge is to control which length scales in RTILs are manifested more prominently in rod-rod interactions. The interactions between neutral rods are dominated by structural forces, which are mainly controlled by the packing of ions in the gaps between the rods. Consequently, the wavelength and decay length of these interactions are controlled mostly by the ion size. In comparison, the interactions between highly charged rods are dominated by double layer forces, which depend strongly on the interferences of the space charge near individual rods. As such, the wavelength and decay length of these interactions are controlled primarily by L_p and L_d of the space charge density waves within RTILs. One can expect the wavelength and decay length of the rod-rod interaction force/energy to evolve continuously as the surface charge on the rods deviates from zero. A systematic investigation of such an evolution is beyond the scope of the present work but is worth pursuing in the future.

The rod-rod interactions revealed in our simulations are rather short-range. This seems to be in agreement with the range of protic RTIL-mediated surface forces measured experimentally,^{186, 188} but different from the long-range interactions reported in many other experiments (e.g., decay length of ~5-10 nm has been reported).^{188, 203} The absence of long-range rod-rod interactions in our simulations can potentially be caused by the limitations of the MD simulations and may also

be related to the nature of the model RTILs and the nanorods used here. First, in our simulations, the periodic boundary conditions are used. Therefore, long-range rod-rod interactions may be smeared out because of the interactions between the rods and their images. Second, since only very strong forces can be reliably measured in MD simulations, it is possible that the weak long-range interactions are simply buried in statistical noises. Finally, some recent theoretical and experimental studies suggested that the decay length of the inter-surface interactions in RTILs is likely a property of bulk RTILs.²⁰³ Given that the model RTILs adopted here have a small ion diameter (~ 0.44 nm) and the nanorods are molecularly narrow, it is possible that inter-surface interactions mediated by our model RTILs are truly short-range. In light of the uncertainties associated with these considerations, we caution that the present study of rod-rod interactions mediated by RTILs does not provide a definitive answer on the decay length scale of RTIL-mediated interactions. Instead, it mainly provides insight into the interactions at short-range when both structural and double layer forces are strong, which are important in applications such as synthesis of macromolecular ionic composites using polyanions and RTILs.⁸²

5.4 Conclusions

Using molecular simulations, we have studied the interactions between nanorods mediated by RTILs when both structural and double layer forces are important. When the rods are neutral, the force between them shows damped oscillation as a function of increasing separation, and both the oscillation period and decay length of the interaction force are close to the ion diameter. Such oscillatory force is essentially the classical structural force and is controlled by the packing constraints imposed by the rods to their neighboring RTILs. When the rods are charged, the force between them still shows damped oscillation as their separation increases. However, both the

oscillation period and the decay length are larger than those for the interactions between neutral rods. In addition, the first valley of their interaction force becomes shallower and shifts to a larger rod-rod separation. Nevertheless, separating two rods initially positioned at the first force valley must overcome an energy barrier of $\sim 5 k_B T/\text{nm}$.

We have shown that, using the simple superposition method for estimating the ion density profile between rods and the classical contact value theorem, the oscillation pattern and decay length for interactions between neutral rods can be estimated using the ion density profile despite the diameter of the rod being comparable to the ion size. Likewise, the interactions between charged rods can be interpreted qualitatively by considering the interference of the space charge around different rods. It is found that, even for molecularly thin rods, the interference of space charge can be estimated from the space charge near isolated rods using the simple superposition method. The destructive (constructive) interference of the space charge near neighboring rods leads to the reduced (enhanced) screening of the surface charge of the rods and thus higher (lower) rod-rod interaction energy. Because of such interferences, the oscillation period of the rod-rod interaction energy is close to the thickness of a pair of counter- and co-ion layers, in good agreement with that found experimentally. The rod-rod interactions revealed by our simulations are short-range. However, for reasons such as the nature of the model RTILs used and noise in the measurement of interaction forces, we caution that this result does not preclude the existence of long-range force between charged surfaces separated by RTILs.

We note that the insight gained in this work is derived from simulations based on RTILs featuring cations and anions with identical size. In practice, many RTILs have cations and anions with different sizes (e.g., [BMIM][Cl]). Nevertheless, the basic features of the rod-rod interactions mediated by these asymmetric RTILs can be inferred from the present study. Specifically, the

periodicity and decay length (L_p and L_d) of the interactions between neutral rods should be determined primarily by the size of the larger ions. This is because the distribution of ions near the rods, which governs the structural force between them, is constrained mostly by the packing of the larger ions. On the other hand, L_p and L_d of the interactions between highly charged rods should still depend mostly on L_p and L_d of the charge density wave in RTILs. Since L_p and L_d of the charge density wave in RTILs are affected greatly by both the small and the large ions, we expect the small ions to have a stronger effect on L_p and L_d of the interactions between highly charged rods than between neutral rods. A systematic study of how asymmetric ions affect RTIL-mediated interactions between nanorods will be pursued in the future.

Supporting Information

All supporting information cited in this chapter is located in Appendix D.

CHAPTER 6 Summary of Contributions

Because of their many appealing properties such as high conductivity, high ionic transference number, good mechanical strength, and excellent chemical, electrochemical, and thermal stability, polymer electrolytes and their derivatives are considered as promising candidates for use in a wide array of electrochemical devices. Nevertheless, few existing polymer electrolytes can offer all the desired properties simultaneously, and new polymer electrolytes are continuously being developed to address this issue. In this dissertation, three emerging polymer electrolytes including polyILs, NIMs, and polymeric ion gels were investigated using MD simulations to elucidate their molecular structure and ion dynamics and thus to facilitate their rational design and optimization.

The study of polyILs focused on understanding their behaviors near solid surfaces since such behaviors often control their performance in electrochemical devices but are little understood. Simulations of poly(1-butyl-3-vinylimidazolium hexafluorophosphate) supported on neutral and negatively charged quartz substrates showed that the structure and dynamics of interfacial polyILs deviates greatly from that of bulk polyILs and are affected by the distance from the substrate and the surface charge on the substrate. Specifically,

1. Near neutral surfaces, the PF_6^- ions, which are similar in size with the cations, approach the surface closer than the cations due to the entropic and steric effects. The polymer chains of the first cation layer are stretched in the direction normal to the surface and the cations in the first layer form small clusters on the quartz surface. For charged substrates, the contact-adsorbed cations form larger clusters on their surfaces and the polymer chains of these cations are packed more compactly and are less stretched than near neutral surfaces.
2. The different out-of-plane layering, in-plane clustering, and packing of polymer chains near neutral and charged surfaces lead to different coordination environment for the interfacial

anions. The first layer of anions near neutral surfaces are mostly coordinated by four cations from one polymer chain, while the first layer of anions near charged surfaces and the second layer of anions near neutral surfaces are typically coordinated by five cations from two chains.

3. The diffusion of the interfacial anions is dominated by the intra-chain hopping, which is similar to that in bulk polyILs. Because of the slower breakage of interfacial anions from their association with neighboring cations, the interfacial anions diffuse much slower than the bulk anions, especially for the first layer of anions near the neutral substrates.

The study of NIMs focused on the structure and dynamics of the polymeric canopies in NIMs where the canopy thickness is much smaller than the nanoparticle diameter and the nanoparticles are highly charged. The parameter space explored here is practically relevant but has not been explored in prior computational researches. Both neat canopies free of electrolyte ions and canopies doped with electrolyte ion pairs have been examined. The key findings of the simulations are as follows:

1. In neat canopies, the polymers are highly stretched and their charged end monomers form a Helmholtz layer near the charged solid surfaces. The polymeric canopies maintain modest lateral mobility, while they can hardly desorb from the charged solid surfaces.
2. Doping a canopy with electrolyte ions causes some of its polymers to migrate away from the solid surface and become “free” polymers. The remaining “grafted” polymers are no longer highly stretched and the “free” polymers adopt configuration similar to the bulk polymers. The dynamics of the “free” polymers in the doped system is similar to that in the bulk polymers. This, along with the rather rapid exchange between the “grafted” and “free” polymers, means that polymer dynamics in the canopy is greatly accelerated by electrolyte doping.

3. The polymeric canopies in NIMs can be taken as special electrical double layers as their structure and dynamics are controlled primarily by the interplay of electrostatic and entropic effects. While entropic effects due to polymer crowding undoubtedly give new characteristics to these double layers compared to those in Coulombic liquids, some key features of double layers in Coulombic liquids such as overscreening are preserved. Taking the polymeric canopies as electrical double layers emphasizes the importance of the long-range, *collective* electrostatic interactions in these systems, which, although treated correctly in some previous simulations of NIMs, are little appreciated in the interpretation of the simulation results.

The study of polymeric ion gels focused on the structure and dynamics of the RTILs in ion gels featuring rigid-rod PBDT polyanions and RTILs and the origins of the mechanical cohesiveness of these gels. The key findings of this study are as follows:

1. The ion distribution in the interstitial space between PBDT nanorods exhibits the hallmarks of the RTIL structure near extended charged surfaces, e.g., cations and anions form alternating layers around the PBDT and the charge on PBDT is overscreened by the ionic layer around it. The distinct ordering of ions suggests the formation of a long-range “electrostatic network” in the ion gel, which may contribute to its mechanical cohesiveness.
2. Because of the discrete distribution of sulfonate groups and presence of hydrophobic domains on the PBDT polyanion, the association of cations with the sulfonate groups of the PBDT rods and the notable presence of anions on the surface of the negatively charged rods are observed. These inter-molecular scale structures can be modified to different extents by factors such as PBDT mass fraction and the presence of smaller inorganic ions in the gel.

3. The RTIL dynamics predicted by the MD simulations agree qualitatively with that measured experimentally. Although the associated cations tend to slow down the dynamics of the ions in the gel, the ions on average diffuse quite fast ($D \sim 10^{-11} \text{ m}^2/\text{s}$).
4. The force and interaction energy between two charged nanorods immersed in RTILs oscillate as their distance increases. The RTIL-mediated interactions between the charged nanorods can be interpreted qualitatively by considering the interference of the space charge around different rods. The destructive (constructive) interference of the space charge near neighboring rods leads to the reduced (enhanced) screening of the surface charge of the rods and thus higher (lower) rod-rod interaction energy.
5. Separating two rods initially positioned at the first free energy valley must overcome an energy barrier of $\sim 5 k_B T/\text{nm}$. Because the length of PBDT nanorods can reach tens of nanometers, separating a pair of these nanorods in an ion gel is likely very difficult, which helps explain the mechanical cohesiveness of the ion gels reported experimentally.

The three types of polymer electrolytes investigated in this dissertation are vastly different at first sight. Nevertheless, at a fundamental level, they have significant similarity, i.e., their structure and dynamics are controlled primarily by the electrostatic interactions between charged polymers and free mobile ions and these interactions can be tuned by manipulating the Coulombic liquids in them. The computational studies in this dissertation represent the initial work exploring the physics of such interactions in these electrolytes. The insights from this dissertation and further research in similar directions will help provide theoretical guidance for the rational design and engineering of these electrolytes to meet the need for next-generation electrochemical energy storage and conversion systems.

Appendix

Appendix A Supporting Information for Chapter 2

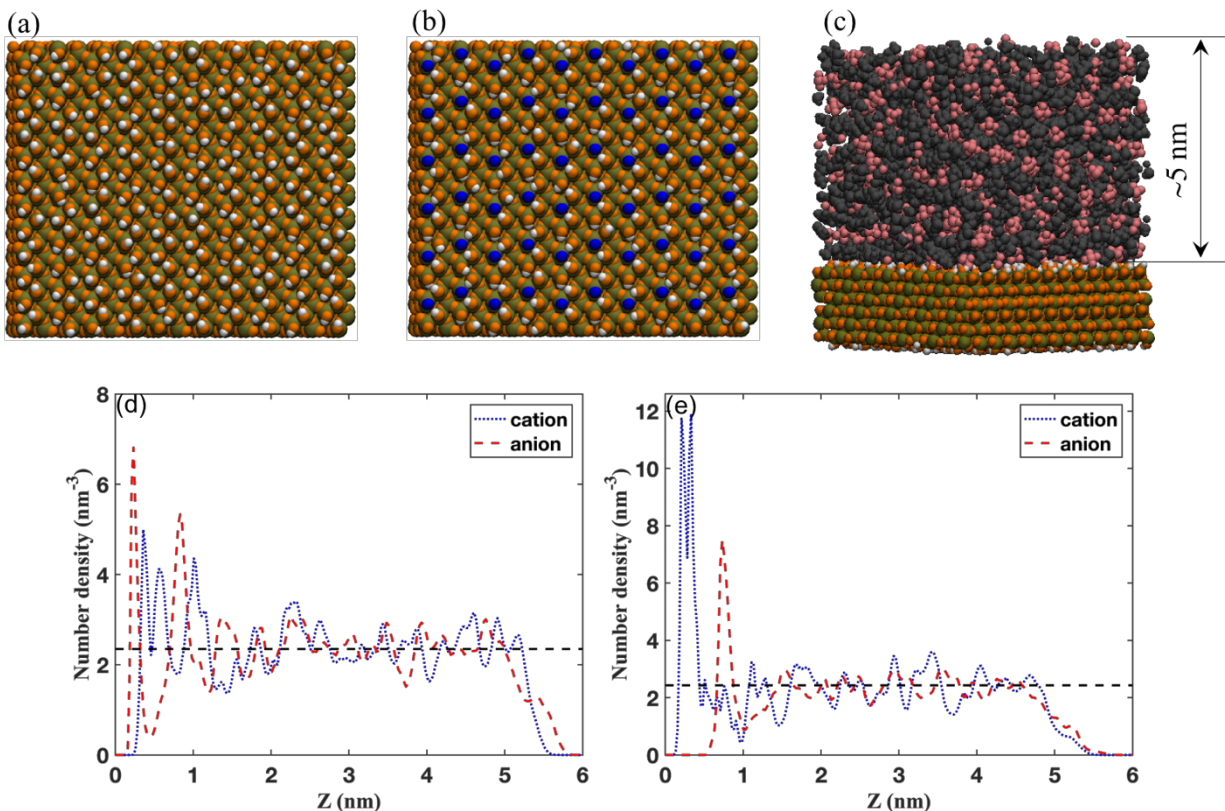


Figure A-1. (a-c) Snapshots of the MD system. (a-b) A top view of the neutral (a) and charged (b) substrates. The tan, orange, white, and blue spheres denote silicon, oxygen, hydrogen, and deprotonated oxygen atoms. (c) A side view of the polyIL film supported on a neutral quartz substrate. The gray and pink spheres denote the atoms on the polymer chains and anions. (d-e) The density profile of the pendant cation and free anion across the polyIL films on the neutral (d) and charged (e) quartz substrates. The black dashed lines denote the average anion density in the region $z=2.5-4.0$ nm, in which the anion density profile is relatively flat.

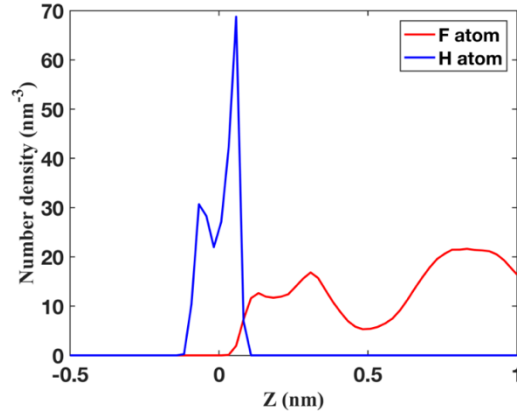


Figure A-2. Number density profiles of the fluorine atoms in the anions and hydrogen atoms of the silanol groups on the neutral quartz substrate.

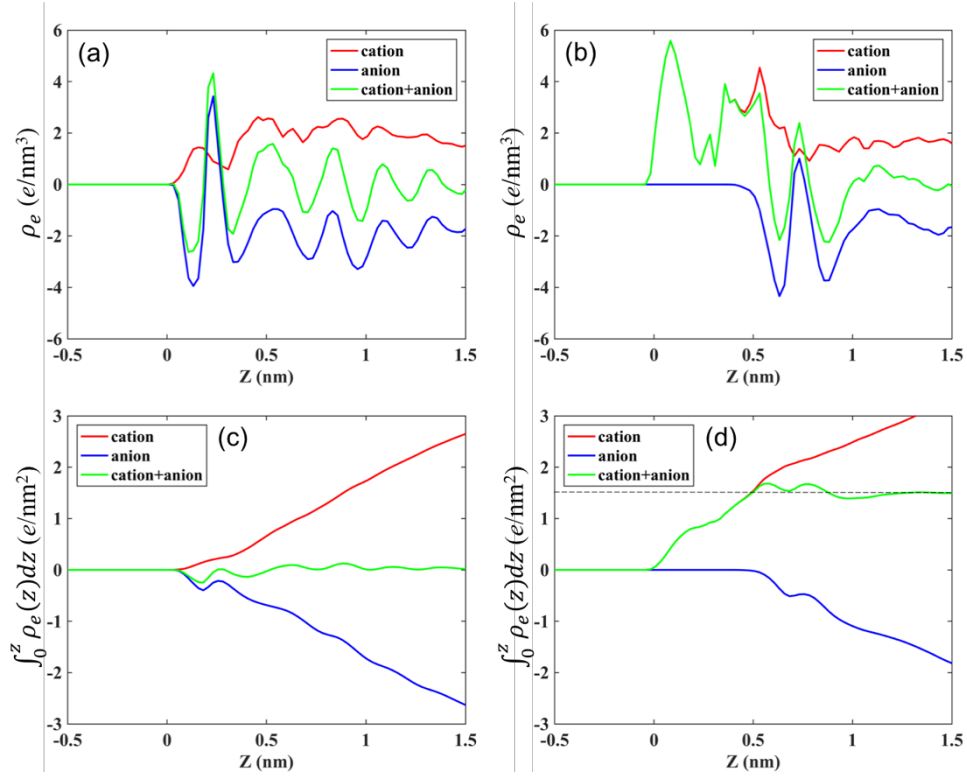


Figure A-3. Space charge distribution near neutral and charged quartz surfaces. (a-b) Ionic charge density profiles as a function of distance from the neutral (a) and charged substrates (b). (c-d) Integration of the space charge density profiles as function distance from the neutral (c) and charged (d) substrates. In (d), the horizontal dashed line denotes the surface charge density of the quartz substrate.

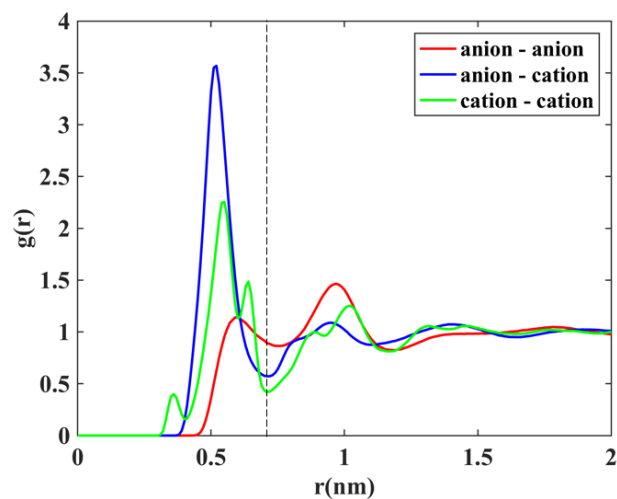


Figure A-4. Radial distribution function of cation and anion in bulk polyILs. The vertical dashed line marks the radial distance of 0.71 nm. The position of the cation and anion is based on the center of mass of the cation's imidazolium ring and the whole anion, respectively.

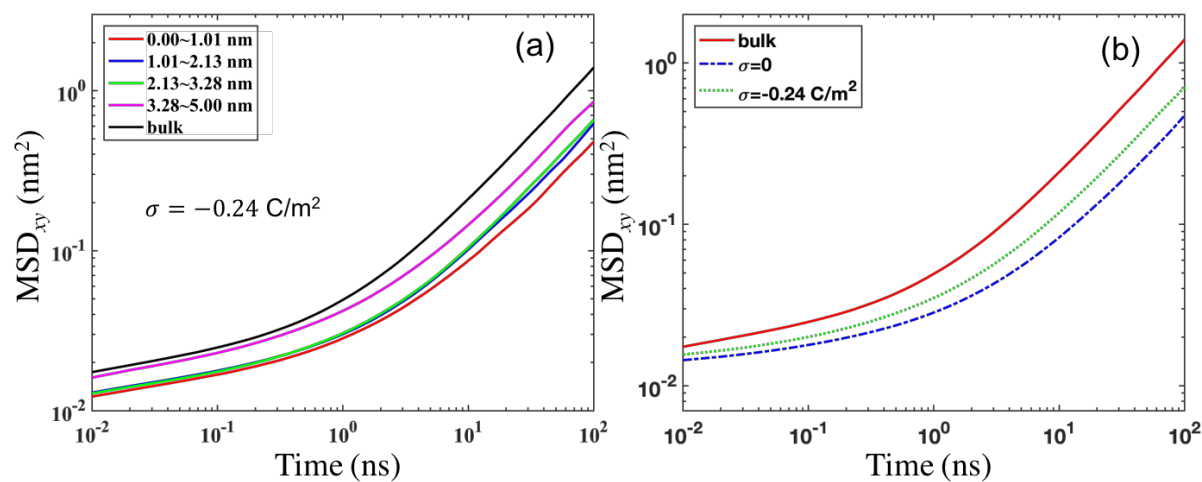


Figure A-5. (a) Lateral MSD for anions initially located in different distances from the charged substrate. (b) Average lateral MSD for all anions in the polyIL film supported on neutral and charged substrate studied in this work.

1. Validation of the force field

The force fields were developed by Prof. Ganesan's group in UT-Austin (see ref. 64). In this force field, the non-bonded and improper parameters were adopted from OPLS-AA set for pure ionic liquids. Partial charges were refined based on quantum MD simulations using density functional theory (DFT) with B3LYP/6-311g** basis set. The geometry of polyBMIM⁺ dimer was optimized for the equilibrium bond and angle values. These potentials were also optimized at atomistic level to reproduce the gas phase reference energy obtained from the quantum mechanical calculations. Apart from validation against quantum calculations, the authors did not provide further validation against experimental data. After obtaining the above force fields, we performed many NPT simulations of bulk polyILs. In these simulations, we computed the molecular structure, dynamics, and macroscopic properties of the polyILs and validate our results against those published in the literature.

First, we computed the molecular structure of the polyILs. For example, we calculated the radial distribution functions (RDFs) between the NA1 atoms and P atoms (see Figure A-6(a)) in bulk polyILs at 600 K. We are able to quantitatively reproduce their results reported by the Ganesan group (see figure below), thus lending confidence to our MD simulation method and protocol.

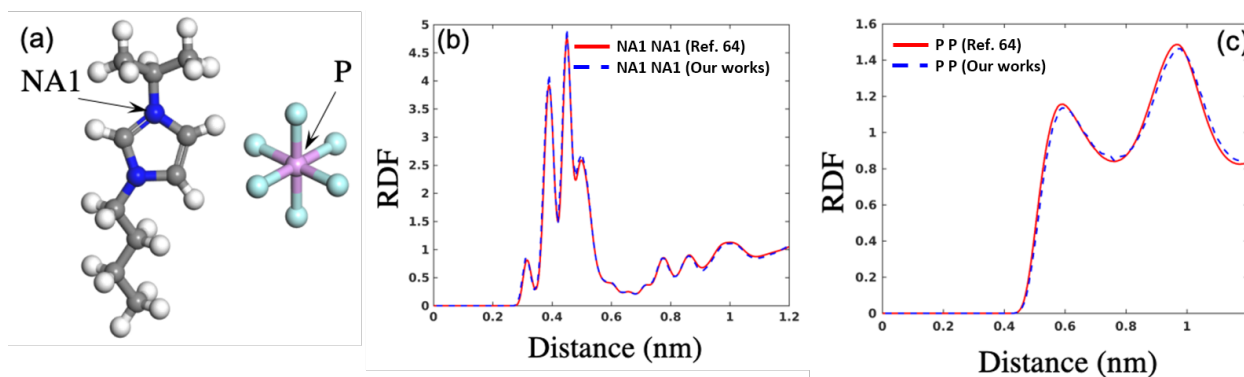


Figure A-6. (a) Chemical structure of one repeat unit of poly-cations and anion. (b-c) The radial distribution functions between the NA1 atoms and P atoms in bulk polyILs obtained from our simulations and by the Ganesan group in their paper (ref. 64 in the dissertation).

Second, we computed the dynamics properties of the polyILs. Specifically, we calculated the intermittent and continuous correlation function for ion-ion associations. Intermittent correlation function is defined as $C(t) = \langle h(t)h(0) \rangle / \langle h \rangle$, where $h(t)$ is an indicator of the anion-cation association. $h(t)$ is 1.0 if anion coordinated by a certain cation at time 0 remains intact at a given time t . Continuous correlation function is defined as $S(t) = \langle H(t)H(0) \rangle / \langle H \rangle$, where $H(t)$ is also an indicator of the anion-cation association. $H(t)$ is 1.0 if an anion coordinated by a certain cation at time 0 is continuously coordinated by this cation by time t . Then two structural relaxation time τ_C and τ_S can be calculated using $\tau_C = \int_0^\infty C(t)dt$ and $\tau_S = \int_0^\infty S(t)dt$. In our simulations, the scaled temperature (i.e., T/T_g) of the MD system is set as 1.2 and we computed τ_C and τ_S for the same polyILs studied in Ref. 64. The two structural relaxation time we computed are marked using filled blue and green circles in Figure A-7. The good agreement of our results with the published data lends support to our ability in simulating the ion dynamics in polyILs.

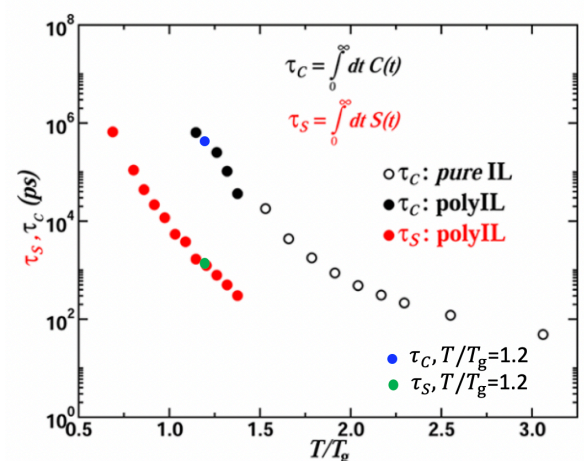


Figure A-7. A comparison of τ_C and τ_S of polyILs computed in our simulations and reported in Ref. 64. The red filled circles are data reproduced from Ref. 64, and the filled blue and green circles are extracted from our MD simulations at a scaled temperature of 1.2. The figure is partially adapted from ref. 64.

Third, we computed the density of bulk polyILs at 600 K. The figure below shows the evolution of the density as a function of time. The average density reported by Prof. Ganesan's group and our current work is 1.253 ± 0.009 and 1.255 ± 0.008 g/cm³, respectively. The difference is less than 0.2 %, which lends further support to the validity of our implementation of their force fields in our simulations.

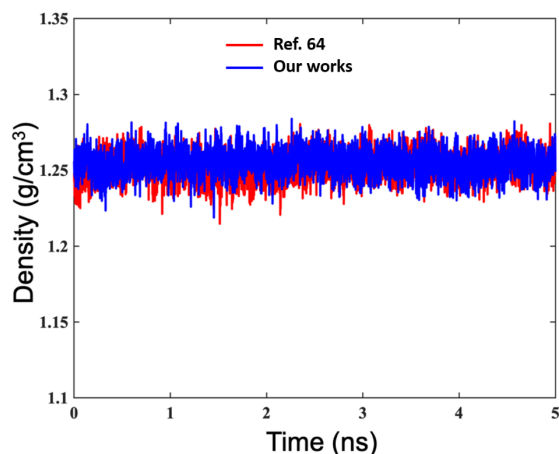


Figure A-8. Comparison of the evolution of the density of polyILs reported in Ref. 64 and obtained in our simulations during the last 5 ns period of a 240 ns-long simulation.

Finally, although the structural and dynamics of interfacial polyILs have not been measured with the resolution we studied in our simulations, the averaged dynamics of the free anions in thin films of polyILs spin-coated on silicon wafer (which always have a native oxide layer) have been shown to be slower than that in bulk polyILs at temperature above the glass transition temperature (see Ref. 120). Our results are consistent with this experimental report.

2. The force fields for polymerized ionic liquids used in Gromacs

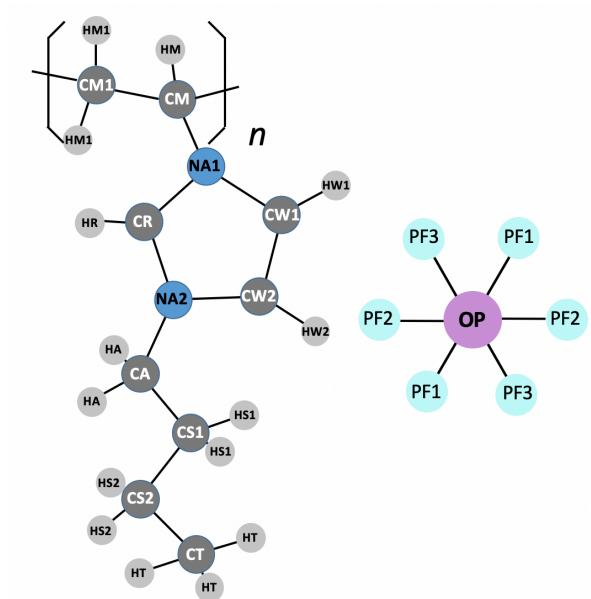


Figure A-9: Atom type name for polymerized $[\text{BMIM}]^+$ cation and $[\text{PF}_6]^-$ anion.

[atomtypes]

; name atom_number mass charge ptype sigma (nm) epsilon (kJ mol ⁻¹)						
CA	6	12.0107	-0.0575328	A	0.3500	2.76144e-01
CM	6	12.0107	-0.1530248	A	0.3500	2.76144e-01
CM1	6	12.0107	-0.2292472	A	0.3500	2.76144e-01
CM2	6	12.0107	-0.1146236	A	0.3500	2.76144e-01
CR	6	12.0107	-0.0653120	A	0.3550	2.92880e-01
CS1	6	12.0107	-0.0898512	A	0.3500	2.76144e-01
CS2	6	12.0107	0.0470392	A	0.3500	2.76144e-01
CT	6	12.0107	-0.1344248	A	0.3500	2.76144e-01
CW1	6	12.0107	-0.1627056	A	0.3550	2.92880e-01
CW2	6	12.0107	-0.1326112	A	0.3550	2.92880e-01
HA	1	1.00794	0.0826304	A	0.1920	1.25520e-01
HM	1	1.00794	0.1604424	A	0.1920	1.25520e-01
HM1	1	1.00794	0.1589736	A	0.2500	1.25520e-01
HM2	1	1.00794	0.0529912	A	0.2500	1.25520e-01
HR	1	1.00794	0.1721744	A	0.1720	1.25520e-01
HS1	1	1.00794	0.0506960	A	0.2500	1.25520e-01
HS2	1	1.00794	0.0259472	A	0.2500	1.25520e-01
HT	1	1.00794	0.0448336	A	0.2500	1.25520e-01
HW1	1	1.00794	0.1904320	A	0.1720	1.25520e-01
HW2	1	1.00794	0.1958048	A	0.1720	1.25520e-01
NA1	7	14.0067	0.2213776	A	0.3250	7.11280e-01

NA2	7	14.0067	0.0664440	A	0.3250	7.11280e-01
OP	15	30.9738	1.0720000	A	0.3940	8.36800e-01
PF1	9	18.9980	-0.3120000	A	0.3118	2.55224e-01
PF2	9	18.9980	-0.3120000	A	0.3118	2.55224e-01
PF3	9	18.9980	-0.3120000	A	0.3118	2.55224e-01

[bondtypes]

; i	j	func	b0 (nm)	kb (kJ mol ⁻¹ nm ⁻²)
CA	CS1	1	0.1534	2.34440e+05
CA	HA	1	0.1092	2.99340e+05
CA	NA2	1	0.1478	2.40420e+05
CS1	HS1	1	0.1091	2.90780e+05
CS1	CS2	1	0.1536	2.35570e+05
CS2	HS2	1	0.1095	2.92130e+05
CS2	CT	1	0.1532	2.40680e+05
CT	HT	1	0.1093	2.94370e+05
NA2	CR	1	0.1335	4.62240e+05
NA2	CW2	1	0.1384	3.41780e+05
CR	HR	1	0.1074	3.35730e+05
CR	NA1	1	0.1385	3.88620e+05
NA1	CW1	1	0.1386	3.43370e+05
NA1	CM	1	0.1486	2.29440e+05
CW1	CW2	1	0.1352	4.44780e+05
CW1	HW1	1	0.1081	3.31700e+05
CW2	HW2	1	0.1079	3.30920e+05
CM	HM	1	0.1083	3.04300e+05
CM	CM1	1	0.1532	2.31040e+05
CM	CM2	1	0.1532	2.31040e+05
CM1	HM1	1	0.1095	2.91940e+05
CM2	HM2	1	0.1095	2.91940e+05
OP	PF1	1	0.1596	4.18400e+05
OP	PF2	1	0.1596	4.18400e+05
OP	PF3	1	0.1596	4.18400e+05

[angletypes]

; i	j	k	func	theta (deg)	kth (kJ mol ⁻¹ rad ⁻²)
HA	CA	CS1	1	111.966000	527.468512
CS1	CA	NA2	1	112.124000	659.641072
HA	CA	NA2	1	106.307000	600.897712
HA	CA	HA	1	107.853000	527.292784
CA	CS1	HS1	1	109.146000	562.396544
CA	CS1	CS2	1	112.443000	677.297552

HS1	CS1	CS2	1	108.941000	462.072592
HS1	CS1	HS1	1	107.458000	473.319184
CS1	CS2	HS2	1	107.908000	497.569648
CS1	CS2	CT	1	114.212000	672.787200
HS2	CS2	HS2	1	106.005000	686.970960
HS2	CS2	CT	1	109.477000	492.741312
CS2	CT	HT	1	111.352000	535.351168
HT	CT	HT	1	108.358000	571.827280
CA	NA2	CR	1	126.178000	707.882592
CA	NA2	CW2	1	126.334000	739.622416
CR	NA2	CW2	1	108.165000	813.746160
NA2	CR	HR	1	125.132000	552.974176
NA2	CR	NA1	1	109.164000	2114.961792
HR	CR	NA1	1	125.669000	540.715056
CR	NA1	CW1	1	107.813000	2231.954800
CR	NA1	CM	1	126.384000	758.852080
CW1	NA1	CM	1	125.886000	814.825632
NA1	CW1	CW2	1	106.709000	2135.270928
NA1	CW1	HW1	1	122.790000	571.584608
HW1	CW1	CW2	1	130.162000	490.590736
NA2	CW2	CW1	1	107.291000	2245.159504
NA2	CW2	HW2	1	122.991000	517.293024
CW1	CW2	HW2	1	130.027000	541.585328
NA1	CM	HM	1	104.182000	684.293200
NA1	CM	CM1	1	109.948000	843.009056
NA1	CM	CM2	1	109.948000	843.009056
CM1	CM	HM	1	109.018000	521.828480
CM2	CM	HM	1	109.018000	521.828480
CM1	CM	CM1	1	113.354000	724.710640
CM1	CM	CM2	1	113.354000	724.710640
CM	CM1	CM	1	116.755000	781.378736
CM	CM1	HM1	1	109.352000	551.141584
CM	CM2	HM2	1	109.352000	551.141584
HM1	CM1	HM1	1	108.068000	453.821744
HM2	CM2	HM2	1	108.068000	453.821744
PF1	OP	PF1	1	180.000000	627.600000
PF2	OP	PF2	1	180.000000	627.600000
PF3	OP	PF3	1	180.000000	627.600000
PF1	OP	PF2	1	90.000000	627.600000
PF1	OP	PF3	1	90.000000	627.600000
PF2	OP	PF3	1	90.000000	627.600000

[dihedraltypes]

; i	j	k	h	func	V0 (kJ mol ⁻¹)	V1 (kJ mol ⁻¹)	V2 (kJ mol ⁻¹)	V3 (kJ mol ⁻¹)	
NA2	CR	NA1	CW1	5	0.000000	19.459784	0.000000	0.000000	
HM	CM	NA1	CR	5	0.000000	0.000000	0.000000	0.000000	
HS1	CS1	CS2	CT	5	0.000000	0.000000	1.531344	0.000000	
CM2	CM	CM1	HM1	5	0.000000	0.000000	11.203790	0.000000	
CM1	CM	CM1	HM1	5	0.000000	0.000000	11.203790	0.000000	
CM1	CM	CM2	HM2	5	0.000000	0.000000	11.203790	0.000000	
HM	CM	CM1	CM	5	0.000000	0.000000	11.203790	0.000000	
HA	CA	NA2	CW2	5	-5.857600	-11.087600	0.732200	0.000000	
HA	CA	NA2	CR	5	0.000000	0.000000	0.000000	0.000000	
CW1	CW2	NA2	CA	5	0.000000	12.552000	0.000000	0.000000	
HA	CA	CS1	CS2	5	0.000000	0.000000	1.531344	0.000000	
NA2	CA	CS1	CS2	5	-7.480992	3.163104	-1.204992	0.000000	
CW1	CW2	NA2	CR	5	0.000000	12.552000	0.000000	0.000000	
CM1	CM	NA1	CW1	5	0.000000	0.000000	9.953903	0.000000	
CM2	CM	NA1	CW1	5	0.000000	0.000000	9.953903	0.000000	
CM1	CM	NA1	CR	5	10.264356	-2.340007	-3.403981	6.394449	
CM2	CM	NA1	CR	5	10.264356	-2.340007	-3.403981	6.394449	
CW2	CW1	NA1	CM	5	0.000000	12.552000	0.000000	0.000000	
HW1	CW1	CW2	HW2	5	0.000000	44.978000	0.000000	0.000000	
HM	CM	CM2	HM2	5	0.000000	0.000000	11.638800	0.000000	
HM	CM	CM1	HM1	5	0.000000	0.000000	11.638800	0.000000	
HW1	CW1	CW2	NA2	5	0.000000	44.978000	0.000000	0.000000	
NA1	CW1	CW2	HW2	5	0.000000	44.978000	0.000000	0.000000	
NA1	CM	CM1	HM1	5	-3.511435	-1.299170	19.582710	3.541216	
NA1	CM	CM2	HM2	5	-3.511435	-1.299170	19.582710	3.541216	
NA1	CW1	CW2	NA2	5	0.000000	44.978000	0.000000	0.000000	
HM	CM	NA1	CW1	5	0.000000	0.000000	0.518816	0.000000	
HS1	CS1	CS2	HS2	5	0.000000	0.000000	1.330512	0.000000	
HA	CA	CS1	HS1	5	0.000000	0.000000	1.330512	0.000000	
NA2	CA	CS1	HS1	5	0.000000	0.000000	0.000000	0.000000	
CS1	CA	NA2	CW2	5	-7.991440	-6.276000	1.213360	0.000000	
CS1	CA	NA2	CR	5	-6.941256	-2.322120	-1.569000	0.000000	
HR	CR	NA1	CW1	5	0.000000	19.459784	0.000000	0.000000	
NA1	CR	NA2	CW2	5	0.000000	19.459784	0.000000	0.000000	
NA1	CR	NA2	CA	5	0.000000	19.459784	0.000000	0.000000	
NA1	CM	CM1	CM	5	0.000000	0.000000	18.585830	0.000000	
HW2	CW2	NA2	CA	5	0.000000	12.552000	0.000000	0.000000	
CS1	CS2	CT	HT	5	0.000000	0.000000	1.531344	0.000000	
CA	CS1	CS2	CT	5	5.439200	-0.209200	0.836800	0.000000	
CM1	CM	CM1	CM	5	-3.245960	1.310634	19.632918	1.297333	

CM2	CM	CM1	CM	5	-3.245960	1.310634	19.632918	1.297333
HW1	CW1	NA1	CM	5	0.000000	12.552000	0.000000	0.000000
HW2	CW2	NA2	CR	5	0.000000	12.552000	0.000000	0.000000
CW2	CW1	NA1	CR	5	0.000000	12.552000	0.000000	0.000000
HR	CR	NA2	CW2	5	0.000000	19.459784	0.000000	0.000000
HR	CR	NA2	CA	5	0.000000	19.459784	0.000000	0.000000
NA2	CR	NA1	CM	5	0.000000	19.459784	0.000000	0.000000
HR	CR	NA1	CM	5	0.000000	19.459784	0.000000	0.000000
HW1	CW1	NA1	CR	5	0.000000	12.552000	0.000000	0.000000
HS2	CS2	CT	HT	5	0.000000	0.000000	1.330512	0.000000
CA	CS1	CS2	HS2	5	0.000000	0.000000	1.531344	0.000000

; i j k h func theta (degree), K(kJ mol⁻¹) n

NA1	CM	CR	CW1	4	180.0	4.1840	2
NA2	CA	CW2	CR	4	180.0	4.1840	2
CW1	HW1	NA1	CW2	4	180.0	4.6024	2
CW2	HW2	CW1	NA2	4	180.0	4.6024	2
CR	HR	NA2	NA1	4	180.0	4.6024	2

3. Gromacs input file for the production run

```

integrator          = md
nsteps              = 40000000
dt                  = 0.002
nstcalcenergy       = 10
; Output control
nstxtcout           = 5000
nstxout              = 1000000
nstvout              = 1000000
nstenergy           = 2000
nstlog               = 10000
; Bond parameters
constraint_algorithm = lincs
constraints          = h-bonds
lincs_iter           = 1
lincs_order          = 4
; Neighborsearching
cutoff-scheme        = group
ns_type              = grid
nstlist              = 5
vdw-type              = Cut-off
rlist                = 1.2

```

```

coulombtype      = PME
rcoulomb         = 1.2
rvdw            = 1.2
pme_order       = 5
ewald_rtol       = 1e-05
ewald_geometry   = 3dc
; Temperature coupling is on
tcoupl          = v-rescale ;
tc-grps         = w_fix HH BMIM PF6
tau_t           = -1 0.2 0.2 0.2
ref_t           = 0 540 540 540
; Periodic boundary conditions
pbc             = xyz
gen_vel         = yes
; Freeze
freezegrps      = w_fix
freezedim       = Y Y Y
energygrps      = w_fix HH PF6 BMIM
energygrp_excl  = w_fix w_fix

```

4. The MATLAB codes used to calculate the continuous time correlation function for Figure 2-6 and Figure 2-7

```

clear all
close all
num=256; %%number of anion;
frame=10000; %%%time frame number-1
step=1;
parfor i=1:num;
    filename=['mask2_' num2str(i) '.xvg'];
    X{i}=dlmread(filename,',16,1);
    sprintf('%d',i)
end
sprintf('finish feeding data')
final=0;
parfor i=1:num
    S=correlation_c(X{i},frame,i);
    final=final+S;
end
time=0:step:(step*frame);
plot(time/1000,final/256,'linewidth',2);
ylabel('<c(0)c(t)>');

```

```

xlabel('Time (ns)');
legend('polymer','location','north');
set(gca,'fontsize',15,'fontweight','bold');
set(gca,'linewidth',1);
set(get(gca,'xlabel'),'FontSize', 15, 'FontWeight', 'Bold','Fontname','Times New Roman');
set(get(gca,'ylabel'),'FontSize', 15, 'FontWeight', 'Bold','Fontname','Times New Roman');
print('-dpng','-r300','correlation_c_1ps2.png');
save correlation_c_1ps2.dat final -ascii

```

```

function corr=correlation(A,frame,time)
a=zeros(1,frame);
count=zeros(1,frame);
for i=1:frame
    B{i}=find(A(i,:)==1); %%%%save the index of A into B
end
for i=1:1:frame
    %%%%B{i} is empty, a=0
    if isempty(B{i})
        sprintf('!!%d!!\t',i)
        continue
    end %%%%if B{i} is empty, it can not be as a reference
    clear temp1;
    temp1 = A(i,B{i});
    for j=1:1:frame-i
        temp1 = temp1.*A(i+j,B{i});%%%continus attached
        %temp1 = A(i,B{i}).*A(i+j,B{i});%%%only consider the first and last
        a(j) = a(j) + length(find(temp1==1))/length(B{i});
        count(j) = count(j)+1;
    end
    %sprintf('%d',i)
end
a = a./count;
sprintf('finish_ "%d" _anion',time)
final=[1,a];
corr=final;

```

Disclosure

This work has been published by the American Chemical Society (see Ref. 204).

Appendix B Supporting Information for Chapter 3

1. The evolution of polymer chain's conformation in neat canopy system

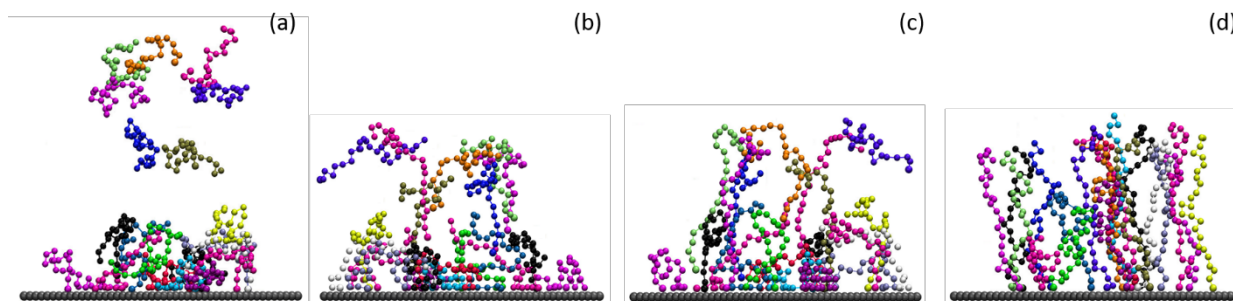


Figure B-1. Evolution of polymer chains' conformation in the neat canopy system during the equilibration process. Initially, polymers with random, coil-like conformation are packed between the two charged walls. The snapshots of 20 representative polymers near the lower wall are shown at time 0 ps, 400 ps, 800 ps, and 10 ns in panels (a), (b), (c), and (d), respectively.

2. Chemical structure and coarse-grained model

The chemical structure of the materials reported in that paper is shown in the figure below. The polymers in the canopy is made of ~ 20 ethoxy repeat units, one benzene ring, and a hydrocarbon tail. Since our focus is the general behavior of polymers in canopy and there is no structure characterization data of the polymers in Ref. 69, we model the polymer as 25 identical beads, with each bead representing on ethoxy repeat unit. We note that that the molecular weight of one benzene ring and a hydrocarbon tail is close to 5 ethoxy repeat units.

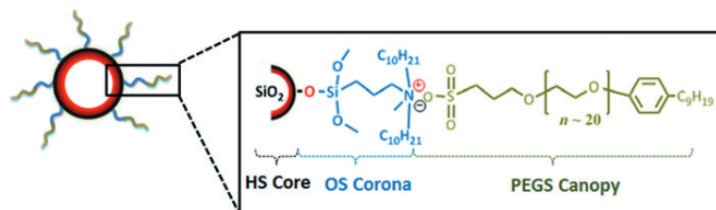


Figure B-2. The chemical structure of the nanoscale ionic material. The zoom-in view of the canopy shows the chemical structure of the polymers in the canopy. This figure is reproduced based on ref. 69 in the dissertation.

3. Validation of force fields

The coarse-grained force field used for the polymer chains were extracted from the work by Prof. Panagiotopoulos' group (see ref.138). The validation of the force fields includes the following two aspects.

First, I clarified how the previous work determined the size and energy parameter for each bead in the polymer chains. The interactions between neutral beads are described by a shifted Lennard-Jones potential with the cutoff distance $r_c = 2.5\sigma$:

$$V(r) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] - V_c & r \leq r_c \\ 0 & r > r_c \end{cases}$$

The size and energy parameters of the chain beads were obtained to approximately represent an ethoxy repeat unit. Although the ethoxy repeat unit does not exist as a single molecule, Prof. Panagiotopoulos' group estimated the critical temperature and critical volume is 409 K and 0.124 L mol⁻¹ based on the group contribution method, which is close to the parameters for dimethyl ether measured experimentally. Previous work determined the reduced critical parameters of the shifted Lennard-Jones fluid as $k_B T_c / \varepsilon = 1.085$ and $\sigma^3 / V_c = 0.317$. Then they obtained the energy parameter for the bead-bead interactions and the size parameter as $\varepsilon / k_B = 377$ K and $\sigma = 0.40$ nm.

Second, simulation results on the canopy structure based on this force field qualitatively captured several experimental observations reported in the literature. For example, the polymeric canopy indeed exhibits several layers (cf. Fig. 3-4 in the dissertation), the polymers in the different layers exchange rather rapidly (cf. Fig. 3-5 in the dissertation), and the polymers grafted on the substrate dynamically exhibit smaller mobility (cf. Fig. 3-6 in the dissertation). For the coarse-grained force fields adopted here, this level of consistency with experimental reports is deemed satisfactory.

4. Force field parameters for polymers, ions and wall atoms

```
[ atomtypes ]
; name at.num mass charge ptype sigma (nm) epsilon (kJ mol-1)
SC 7 28.08000 -1.0000 A 3.38550e-01 2.44704e+00 ; charged wall atom
SI 6 28.08000 0.0000 A 3.38550e-01 2.44704e+00 ; neutral wall atom
OT 10 44.00000 0.0000 A 4.00000e-01 3.13200e+00 ; charged polymer bead
CT 10 44.00000 1.0000 A 4.00000e-01 3.13200e+00 ; neutral polymer bead
NA 13 22.98977 1.0000 A 2.87600e-01 0.52160e+00 ; Na+
CL 15 35.45000 -1.0000 A 3.78500e-01 0.52160e+00 ; Cl-
```

```
[ bondtypes ]
; i j func b0 (nm) kb (kJ mol-1 nm-2)
OT OT 1 4.0000000e-01 3.9150000e+04
CT OT 1 4.0000000e-01 3.9150000e+04
```

5. The input file for Gromacs is similar to that for the polymerized ionic liquids project except that a mild pressure is applied on the top surface.

```
acc_grps = wat
accelerate = 0.0 0.0 -0.0006
```

6. The main body of C codes used to calculate the end-to-end vector and distance for Figure 3-2(c-d)

```

pos1 = CreateMatrix_3d(nm1,295,3);
pos = CreateMatrix(nm1,3);
pos_C1=CreateMatrix(nm1,3);
pos_O1=CreateMatrix(nm1,3);
costheta1 = CreateMatrix(endframe-preframe,nm1);
distance = CreateMatrix(endframe-preframe,nm1);
// initialize
for(k=0;k<endframe-preframe;k++){
    for(i=0;i<nm1;i++){
        costheta1[k][i] = 10.0; //tantheta=10.0
        distance[k][i] = 0.0;
    }
}
for(k=0;k<3;k++){
    center_f[k]=0;
}
// read position (make molecule whole), then get molecule mass center
frame_index = 0;
do{
    index = 0;
    frame_index ++;
    Lbox[0] = trj->fr->box[XX][XX];
    Lbox[1] = trj->fr->box[YY][YY];
    Lbox[2] = trj->fr->box[ZZ][ZZ];
//get the position of O1
    for(j=0;j<nm1;j++){
        for(k=0;k<3;k++){
            pos_O1[j][k] = trj->fr->x[be_o1+j*25][k];
        }
    }
//get the position of C1
    for(i=0;i<nm1;i++){
        for(k=0;k<3;k++){
            pos_C1[i][k] = trj->fr->x[be_c1+25*i][k];
        }
    }
//FI=1 attach
    if(FI==1){
        for(i=0;i<nm1;i++){
            if(pos_C1[i][2]<0.9){

```

```

xx=pos_O1[i][0]-pos_C1[i][0];
yy=pos_O1[i][1]-pos_C1[i][1];
zz=pos_O1[i][2]-pos_C1[i][2];
costheta1[frame_index-1][i]=zz/sqrt(xx*xx+yy*yy);
distance[frame_index-1][i]=sqrt(xx*xx+yy*yy+zz*zz);
}
}
}
//FI=2 all
if(FI==2){
for(i=0;i<nm1;i++){
//if(pos_C1[i][2]<1.0){
xx=pos_O1[i][0]-pos_C1[i][0];
yy=pos_O1[i][1]-pos_C1[i][1];
zz=pos_O1[i][2]-pos_C1[i][2];
costheta1[frame_index-1][i]=zz/sqrt(xx*xx+yy*yy);
distance[frame_index-1][i]=sqrt(xx*xx+yy*yy+zz*zz);
//}
}
}
step++;
if(step==endframe) break;
}while (read_next_frame(trj->oenv, trj->status, trj->fr));
if(step<preframe+10){printf("\nInput trajectory file only has few frames!\n"); };

```

Disclosure

This work has been published by a nature research journal (see Ref. 205).

Appendix C Supporting Information for Chapter 4

1. Arrangement of PBDT rods in horizontal plane

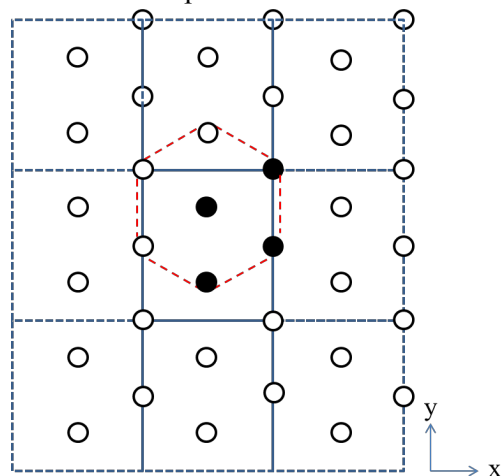


Figure C-1. A schematic of the PBDT rod arrangement during the pre-equilibration run. The PBDT rods (filled circle) and their periodical images (empty circles) in the xy-plane form a hexagonal lattice.

2. The evolution of the number of RTIL molecules

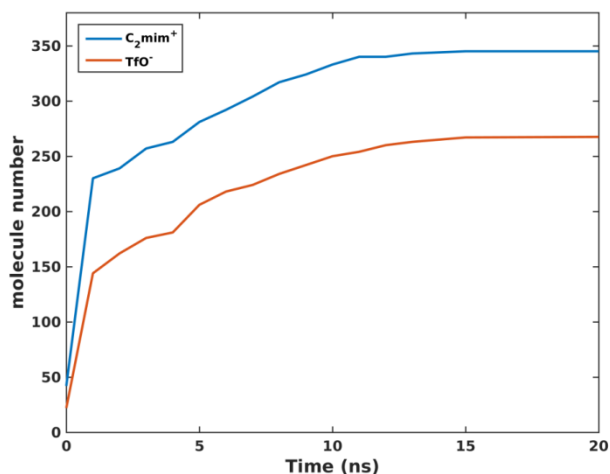


Figure C-2. The evolution of the number of RTIL molecules between PBDT rods when $S_{r-r} = 2.2$ nm.

3. Molecular model of the PBDT rods

Each PBDT rod is made of four repeating units. As discussed in the main text, each repeating unit is made of 9 layers of carbon atoms arranged into a regular heptagon (side length: 0.173 nm) and the spacing between adjacent carbon layers is 0.21 nm. Each repeating unit has four sulfonate groups, each two of which represent those from one PBDT molecule and are anchored on the carbon atoms in

adjacent layers. When projected onto the horizontal (xy -) plane, the two vectors pointing from the center of the heptagon toward the two anchoring atoms form an angle of 103° . To build a PBDT rod, four repeating units were stacked onto each other. For the SO_3^- groups on the PBDT rod to form a helical pattern, each repeating unit is rotated around the rod axis by 51.4° with respect to the unit below it. Figure C-3 shows a snapshot of a single PBDT rod.

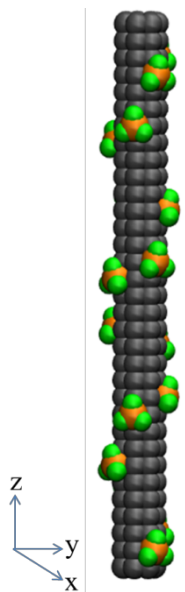


Figure C-3. A snapshot of a single PBDT rod. The black spheres denote the carbon atoms used to mimic PBDT's hydrophobic backbone. The orange and green balls denote the sulfur and oxygen atoms of the sulfonate groups, respectively.

4. Validation of force fields

In this work, the force fields of the ionic liquids are taken from Ref. 167. Prior to using this force field in the simulations of ion gels, we performed NPT simulations of bulk [EMIM][TfO] liquids using this force field. From the mean square displacement of the ions (see Figure 4-5), the diffusion coefficients of cations and anions at 353 K and 1 atm are determined to be $22 \times 10^{-11} \text{ m}^2/\text{s}$ and $12.1 \times 10^{-11} \text{ m}^2/\text{s}$, respectively. These diffusion coefficients agree quite well with experimental data measured using NMR ($17.5 \times 10^{-11} \text{ m}^2/\text{s}$ and $12.5 \times 10^{-11} \text{ m}^2/\text{s}$ for cations and anions, respectively).

The semi-coarse grained force fields for the polyanions are developed by me. Since the materials studied here has been fabricated recently and the structure of polyanions are poorly characterized at present, the goal of our simulations is not to quantitatively capture the structure and dynamics of the polymer and ions. Rather, we seek to capture the essential physics of the ion distribution within this material to help understand the transport and mechanical properties of this material. Below I explain the rationale behind the force field I developed for the polyanion and its validation.

First, the polyanion is modeled as a rigid rod decorated with sulfonate groups distributed on the rod in a helical pattern (see Fig. 4-1 in the dissertation). The interaction parameters are taken from the

OPLS-AA force fields. Modeling the polyanion as rigid rod is consistent with the experimental observation that the polyanions has a double-helix structure and is very rigid (its persistent length is $\sim 1 \mu\text{m}$ according to Professor Madsen). The radius of the polyanion and the distribution of the sulfonate groups along its backbone are consistent with the X-ray diffraction (XRD) experiments (see ref. 82 and figure below).

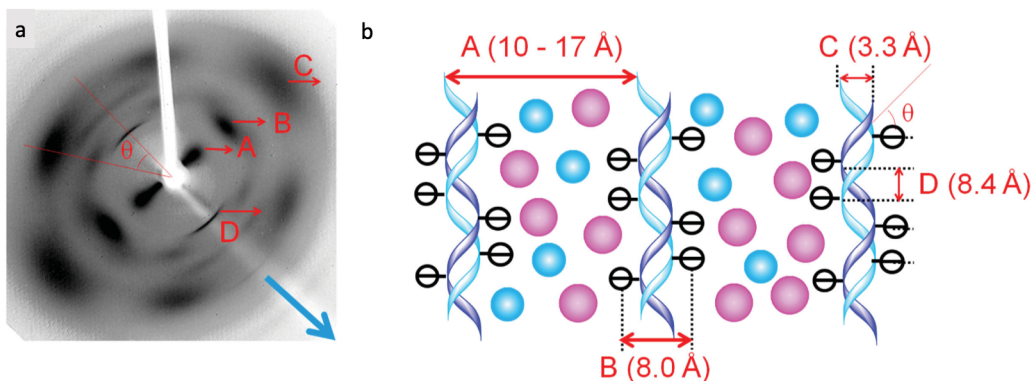


Figure C-4. (a) The difference image of X-ray diffraction patterns between 5% and 21 % PBDT IL gel. (b) A schematic of the polyanions in the ion gel derived from the scattering pattern. This figure is reproduced based on Ref. 82.

Second, simulations based on the force fields used here predict diffusion coefficient in qualitative agreement with the experimental data. For example, the anisotropy of the diffusion coefficient of cations in the gel reported in the experiment is captured relatively well by our simulations (see figure below).

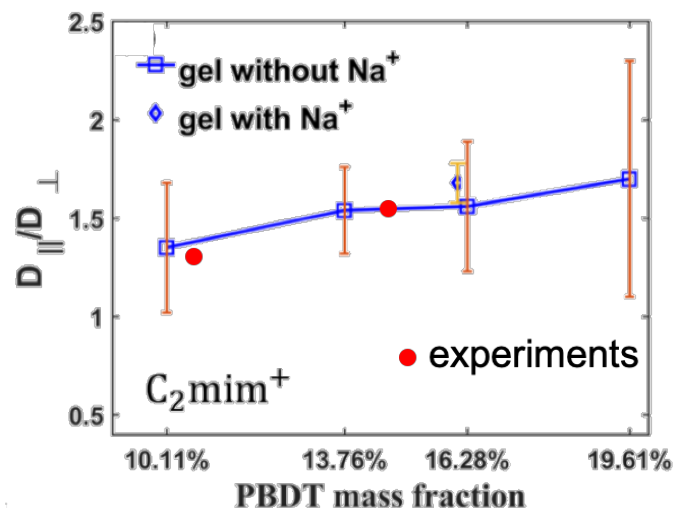


Figure C-5. Comparison of the anisotropy of the diffusion coefficient of cations inside the ion gel as predicted by the MD simulation (squares and diamonds) and reported experimentally (filled red circles, taken from Ref. 82).

4. Force field parameters

4.1. PBDT rods

Table C-1. The Lennard-Jones parameters and atom charge for PBDT atoms.

atom pair	σ (nm)	ϵ (kJ/mol)	charge (e)
S	0.374177	1.966480	1.451
O	0.302905	0.502080	-0.817
C	0.355000	0.292880	0.000

The Lennard-Jones parameters for atom pairs consisting of different atoms were obtained using the Lorentz-Berthelot rule. Each S-O pair in the sulfonate group forms a harmonic bond (bond length: 0.145 nm, bond constant: 647258.9 kJ mol⁻¹nm⁻²). Each O-S-O group in the sulfonate group forms a harmonic angle bond (bond angle: 120.924°, bond angle constant: 944.86 kJ mol⁻¹rad⁻²).

4.2. Ionic liquids

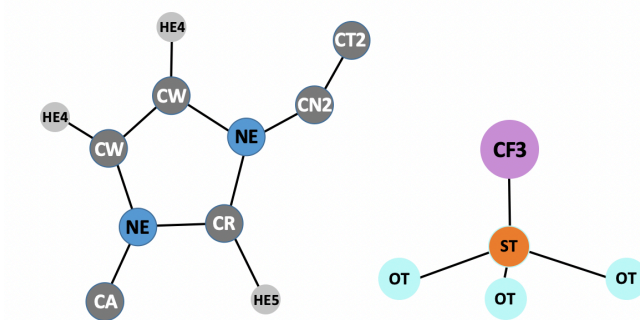


Figure C-6: Atom type name for polymerized C₂mim⁺ cation and TfO⁻ anion.

[atomtypes]							
; name	at.num	mass	charge	ptype	sigma	epsilon	
NE	7	14.0067			0.0150	A	3.2500000e-01 7.1128000e-01
CR	6	12.011			0.0000	A	3.4000000e-01 3.5982400e-01
CW	6	12.011	-0.1600			A	3.4000000e-01 3.5982400e-01
HE5	1	1.008			0.1500	A	1.2470000e-01 1.2552000e-01
HE4	1	1.008			0.2000	A	1.6040000e-01 1.2552000e-01
CN3	12	15.035			0.2600	A	3.6600000e-01 7.9496000e-01
CN2	12	14.027			0.2300	A	3.8200000e-01 3.8074400e-01
CT2	12	15.035			0.0500	A	3.9500000e-01 3.8074400e-01
CF3	6	69.0062	-0.138			A	4.4720000e-01 6.6944000e-01
ST	16	32.0664			0.6940	A	3.5640000e-01 1.0460000
OT	8	15.9994	-0.4520			A	2.9600000e-01 8.7864000e-01

[bondtypes]

; i	j	func	b0	kb
NE	CR	1	1.3250000e-01	3.4400848e+05
CW	NE	1	1.3780000e-01	3.4400848e+05
CW	CW	1	1.3430000e-01	4.0032512e+05
CW	HE4	1	1.0700000e-01	2.8811024e+05
CR	HE5	1	1.0700000e-01	2.8811024e+05
NE	CN3	1	1.5000000e-01	2.1631280e+05
NE	CN2	1	1.4900000e-01	2.1631280e+05
CT2	CN2	1	1.6100000e-01	1.6284128e+05
CF3	ST	1	2.4000000e-01	1.3162864e+05
ST	OT	1	1.4500000e-01	4.5279248e+05

[angletypes]

; i	j	k	func	th0	kth
CW	NE	CR	1	1.0800000e+02	5.6735040e+02
NE	CR	NE	1	1.0990000e+02	6.1672160e+02
NE	CR	HE5	1	1.2570000e+02	4.2844160e+02
HE4	CW	NE	1	1.2210000e+02	4.2844160e+02
HE4	CW	CW	1	1.3070000e+02	4.1840000e+02
NE	CW	CW	1	1.0710000e+02	5.8408640e+02
NE	CN2	CT2	1	1.1220000e+02	6.6944000e+02
CW	NE	CN2	1	1.2570000e+02	5.3722560e+02
CR	NE	CN2	1	1.2630000e+02	5.3722560e+02
CN3	NE	CW	1	1.2570000e+02	5.3722560e+02
CN3	NE	CR	1	1.2630000e+02	5.3722560e+02
CF3	ST	OT	1	1.0320000e+02	6.4015200e+02
OT	ST	OT	1	1.1460000e+02	6.2425280e+02

[dihedraltypes]

; i	j	k	l	func	phi	k	n
HE4	CW	NE	CN2	9	1.8000000e+02	6.2760000e+00	2
HE4	CW	NE	CN3	9	1.8000000e+02	6.2760000e+00	2
HE4	CW	NE	CR	9	1.8000000e+02	8.3680000e+00	2
CW	CW	NE	CR	9	1.8000000e+02	5.0208000e+01	2
CW	CW	NE	CN2	9	1.8000000e+02	8.3680000e+00	2
CW	CW	NE	CN3	9	1.8000000e+02	8.3680000e+00	2
NE	CW	CW	HE4	9	1.8000000e+02	6.2760000e+00	2
HE4	CW	CW	HE4	9	1.8000000e+02	6.2760000e+00	2
NE	CW	CW	NE	9	1.8000000e+02	5.0208000e+01	2
CN2	NE	CR	NE	9	1.8000000e+02	8.3680000e+00	2
CN3	NE	CR	NE	9	1.8000000e+02	8.3680000e+00	2

CN2	NE	CR	HE5	9	1.8000000e+02	6.2760000e+00	2
CN3	NE	CR	HE5	9	1.8000000e+02	6.2760000e+00	2
CW	NE	CR	NE	9	1.8000000e+02	5.0208000e+01	2
CW	NE	CR	HE5	9	1.8000000e+02	6.2760000e+00	2
CW	NE	CN2	CT2	9	0.0000000e+00	8.0751200e-01	1
CW	NE	CN2	CT2	9	1.8000000e+02	9.2048000e-01	2
CW	NE	CN2	CT2	9	0.0000000e+00	3.7656000e-02	3
CR	NE	CN2	CT2	9	0.0000000e+00	7.1128000e-02	1
CR	NE	CN2	CT2	9	1.8000000e+02	6.2760000e-02	2
CR	NE	CN2	CT2	9	0.0000000e+00	-8.8700800e-01	3

6. The composition of each simulation system

Table C-2. Number of molecules in the five systems studied in the main text.[†]

System	Nominal rod-rod spacing	C ₂ mim ⁺	TfO ⁻	Na ⁺
1	2.0 nm	536	456	0
2	2.2 nm	648	568	0
3	2.2 nm	618	578	32
4	2.4 nm	720	640	0
5	2.8 nm	932	852	0

[†] The number of ions shown here include the ions within and outside of the observation window shown in Figure 4-1b. The number of ions shown in Table 4-1 includes *only* the ions within the observation window.

7. Distribution of ions around PBDT rods in ion gels

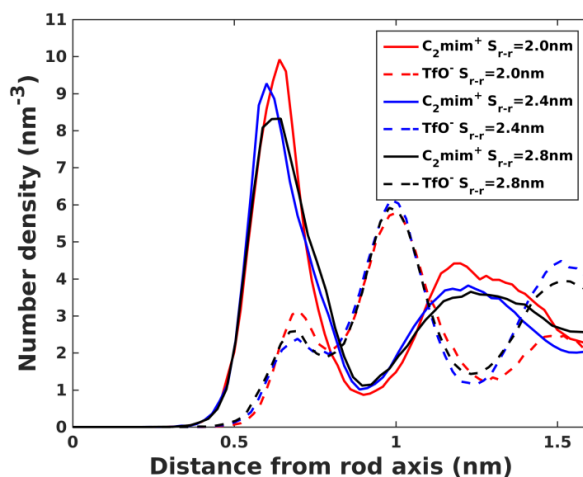


Figure C-7. The ion density as a function of the radial distance from the axis of a PBDT rod in ion gels. The nominal rod spacing is 2.0, 2.4, and 2.8 nm.

7. Comparison of the MSDs for the cation on a log scale and on a linear scale

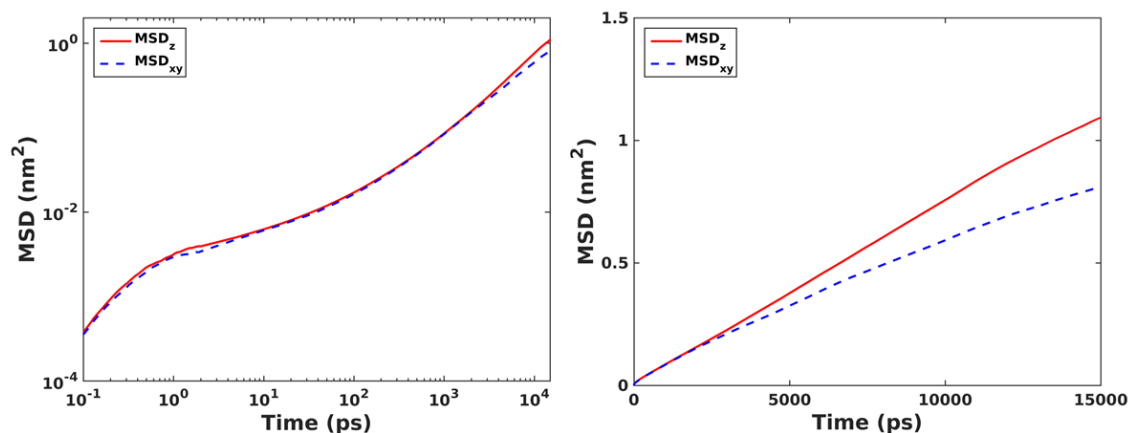


Figure C-8. (a) The MSDs of C_2mim^+ ions in log-log scale. (b) The MSDs in panel (a) plotted in linear scale. The nominal rod spacing is 2.2 nm.

8. Distribution of ions around sulfonate groups in ion gels

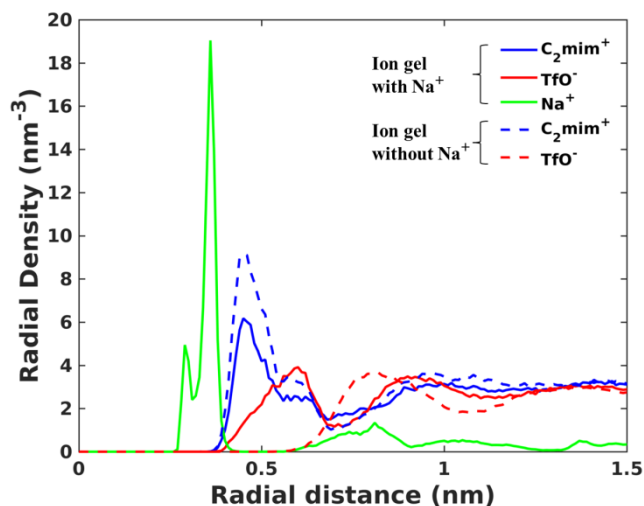


Figure C-9. Radial density profiles of various ions around the sulfonate groups of the PBDT rods in ion gels with and without Na^+ ions. The nominal rod spacing is 2.2 nm.

9. Quantitative ^{23}Na NMR study of Na^+ concentration in PBDT-IL ion gels

Figure C-10 briefly illustrates fabrication of the PBDT ion gel (see also reference 82 in the main text). The ion gel can be obtained by an ion exchange process between the ionic liquid $[C_2mim][TfO]$ and the 4wt% PBDT aqueous seed solution (with 100% Na^+ counterions). This process yields a dried ion gel with 15 wt% PBDT, in the middle of the range explored computationally in this paper.

To quantify the relative concentration of Na^+ (C_{Na^+}) in the as-fabricated ion gels, we employ a simple and robust pulse-acquire sequence of ^{23}Na NMR to measure abundance of Na^+ in the PBDT ion gel (Green region in Figure C-10) as compared to that in the PBDT seed solution (Blue region in Figure C-10).

Additionally, we also use a predetermined NaCl aqueous reference solution (0.036 mol/kg) to quantify the absolute concentration of Na^+ in the ion gels to inform the corresponding molecular dynamics simulations. The acquisition parameters are maintained constant for all the NMR experiments, and the NMR spectra and peak integrals are shown in Figure C-11. We also measure the 90° pulse time for the three samples to ensure the experimental accuracy in determining spin concentration without the effect of differential probe coil sensitivity.

Table C-3 shows detailed sample information and calculated results for Na^+ concentration. C_{Na^+} (0.056 mol/kg) in the as-formed ion gel is nearly half that in the PBDT seed solution (0.12 mol/kg). We have repeated this experiment for gels with lower PBDT content (down to 5 wt% in the dried gel) with similar C_{Na^+} results.

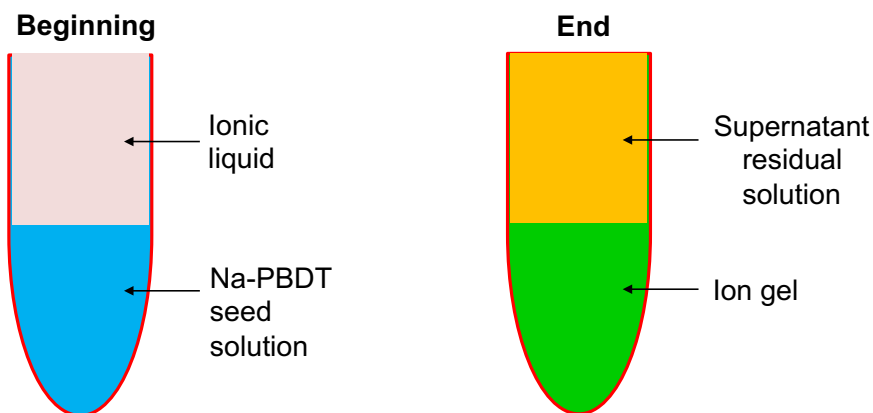


Figure C-10. The fabrication process for the ion gel sample. At the beginning, we slowly pipette the pure IL $[\text{C}_2\text{mim}][\text{TfO}]$ on top of the 4 wt% Na-PBDT seed solution. At the end, the system has ion gel formed in the bottom phase and the supernatant residual solution on the top phase.

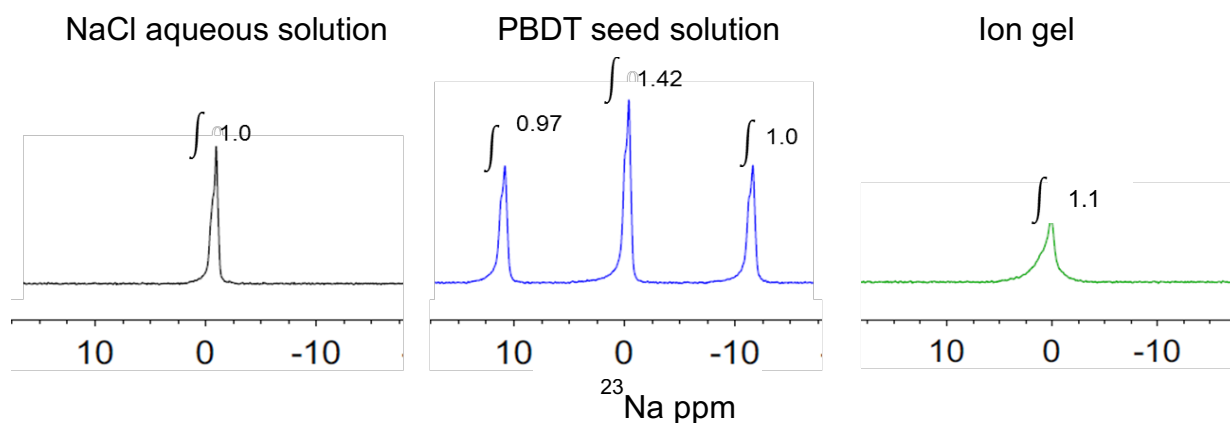


Figure C-11. ^{23}Na spectra for NaCl aqueous solution, PBDT seed solution and hydrated PBDT ion gel, respectively (left to right). Note the presence of the 3 peaks in the PBDT seed solution are due to the nuclear quadrupole splitting of the ^{23}Na ions, which are partially ordered by the aligned polymer chains in the spectrometer magnetic field (see reference 82 in main text).

Table C-3. Detailed sample information, measured 90° pulse times and calculated concentrations. The concentration of NaCl aqueous solution is a predetermined reference to which the others are compared to determine unknown Na^+ concentrations. NMR peak integrals (relative areas) are shown in Figure C-11. Error in concentration is $\leq \pm 10\%$.

Sample	90° pulse time (μs)	Weight (mg)	Peak area (relative)	Concentration (mol/kg)
NaCl Aqueous sol	8.5	100	1.0	0.036
PBDT seed sol	8.5	100	3.4	0.12
Ion gel	8.5	71.3	1.1	0.056

Experimental section:

NaCl aqueous and PBDT seed solutions. NaCl aqueous solution was prepared by loading the predetermined amount of NaCl and H_2O into a 5mm NMR tube (see Table C-3). Aqueous solution with a PBDT weight percentage of 4% was prepared by loading the prescribed amount of PBDT and H_2O into a 5 mm NMR tube.

Ion gel: Ion gel sample was obtained as shown in Figure C-10 by combining the IL [C2mim][TfO] and the 4 wt% PBDT seed solution. The final composition of the dried gel was 15 wt% PBDT relative to IL.

^{23}Na NMR quantitation: A Bruker Avance III NB 600 MHz (14.1 T) NMR was equipped with a 5 mm BBO (broadband observe) solution probe. A simple 90° RF pulse was applied for all measurements at room temperature (22°C). The 90° pulse was measured to be the same (8.5 μs) for all samples, without retuning the probe or changing the transmitter power, in order to ensure that the SNR per spin

was equal for all samples (see D. I. Hoult and R. E. Richards, *Journal of Magnetic Resonance*, 24, 71-85, 1976).

10. The input file for Gromacs is similar to that for the polymerized ionic liquids project. The diffusion coefficient in the bulk condition is calculated based on the NPT ensemble. The input file on the temperature coupling part is listed in the following.

```
pcoupl          = Parrinello-Rahman
pcoupltype      = isotropic
tau_p           = 2.0
compressibility = 4.5e-5
ref_p           = 1.0135
```

11. The main body of C codes used to calculate the density distribution of C2mim⁺ and TfO⁻ for Figure 4-2.

```
pos1 = CreateMatrix_3d(nm1,atoms1,3);
pos  = CreateMatrix_3d(endframe-preframe,nm1,3);
density = CreateMatrix(nx+1,ny+1);

// initialize
for(i=0;i<nx+1;i++)
    for(j=0;j<ny+1;j++)
        density[i][j] = 0.0;
// read position (make molecule whole), then get molecule mass center
frame_index = 0;
do{
    index = 0;
    frame_index ++;
    Lbox[0] = trj->fr->box[XX][XX];
    Lbox[1] = trj->fr->box[YY][YY];
    Lbox[2] = trj->fr->box[ZZ][ZZ];
    load_position(trj->fr,nm1,atoms1,nStart1,pos1,Lbox);
    for(i=0;i<nm1;i++){
        // get the center of the first type of molecules
        for(k=0;k<3;k++){
            center_f[k] = 0;
            for(m=0;m<atoms1;m++){
                center_f[k] += pos1[i][m][k]*atNCM[n_NCM][tN1][m];
            }
            center_f[k] /= mol_NCM[n_NCM][tN1];
        }
        pos[frame_index-1][i][0] = center_f[0];
```

```

    pos[frame_index-1][i][1] = center_f[1];
    pos[frame_index-1][i][2] = center_f[2];
    //printf("%f %f %f\n",center_f[0],center_f[1],center_f[2]);
}
step++;
if(step==endframe) break;
}while (read_next_frame(trj->oenv, trj->status, trj->fr));
if(step<preframe+10){printf("\nInput trajectory file only has few frames!\n"); };

// get density
int indexx,indexy;
double dx = Lbox[0]/(double)(nx);
double dy = Lbox[1]/(double)(ny);

for(k=0;k<endframe-preframe;k++){
    for(i=0;i<nm1;i++){
        //printf("k = %d i = %d\n",k,i);
        if(pos[k][i][2] > z1 && pos[k][i][2] < z2){
            if(pos[k][i][0]>Lbox[0])
                pos[k][i][0] -= Lbox[0];
            if(pos[k][i][0]<0)
                pos[k][i][0] += Lbox[0];
            if(pos[k][i][1]>Lbox[1])
                pos[k][i][1] -= Lbox[1];
            if(pos[k][i][1]<0)
                pos[k][i][1] += Lbox[1];
            indexx = (pos[k][i][0]+dx/2.0)/dx;
            indexy = (pos[k][i][1]+dx/2.0)/dy;
            density[indexx][indexy] += 1.0;
        }
    }
}
printf("here 2\n");
for(i=0;i<nx+1;i++)
    for(j=0;j<ny+1;j++)
        density[i][j] /= (double)(endframe-preframe)*(dx*dy*(z2-z1));

```

Disclosure

This work has been published by the American Chemical Society (see Ref. 206).

Appendix D Supporting Information for Chapter 5

1. Force fields for the model ionic liquids and nanorods

The cation and anions are identical to each other except that they carry opposite charge. Both are made of five atoms arranged into a geometry of T_d symmetry identical to that of a BF_4^- ion. The center atom (C1) is connected to each of the four other atoms (C2) by a harmonic bond with a bond length of 0.139 nm and a bond constant of $242680 \text{ kJ mol}^{-1} \text{ nm}^{-2}$. Every C2-C1-C2 group in each ion forms a harmonic bond angle of 109.5° with a bond angle constant of $418.4 \text{ kJ mol}^{-1} \text{ rad}^{-2}$.

Table D-1 shows the Lennard-Jones (LJ) parameters and atom charges for all atoms. The LJ parameters for atom pairs consisting of different types of atoms were obtained using the Lorentz-Berthelot rule.

Table D-1. The Lennard-Jones parameters and atomic charges for the nanorod and model RTILs.

atom	σ_{LJ} (nm)	ϵ_{LJ} (kJ/mol)	charge (e)	
			neutral	charged
C (nanorod)	0.3550	0.2929	0.000	-0.069264
C1 (center in ion)	0.3360	0.3599	--	+1.0 (cation) / -1.0 (anion)
C2 (others in ion)	0.3360	0.3599	--	0.000

2. Properties of the model ionic liquids and the nanorods

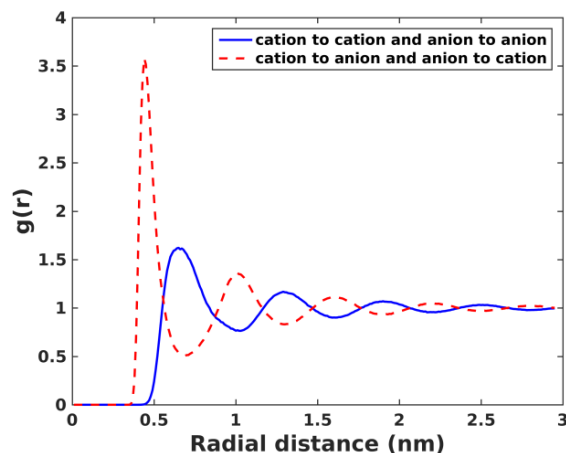


Figure D-1. The radial distribution function $g(r)$ of the cations and anions in the bulk model RTILs ($T=400$ K, $P=1$ atm). The first peak of $g(r)$ is located at $r = 0.44$ nm. It follows that the radius of the cation and anion of the model RTILs is 0.22 nm.

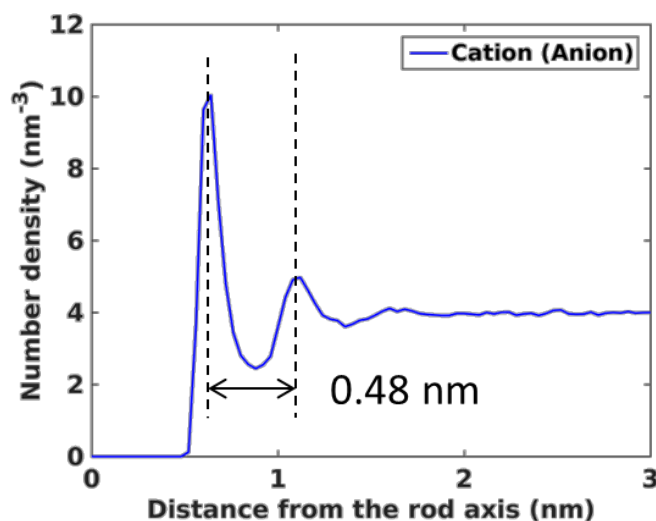


Figure D-2. Density profiles of cations and anions around a neutral nanorod. Near neutral rods, the cation and anion density profiles are the same because these ions are identical except with opposite charge. The first ion density peak is located at 0.57 nm. Because the radius of the ion is 0.22 nm (see Figure D-1's caption), the effective radius of the nanorod is determined as 0.35 nm.

3. Structure of model ionic liquids near the nanorods

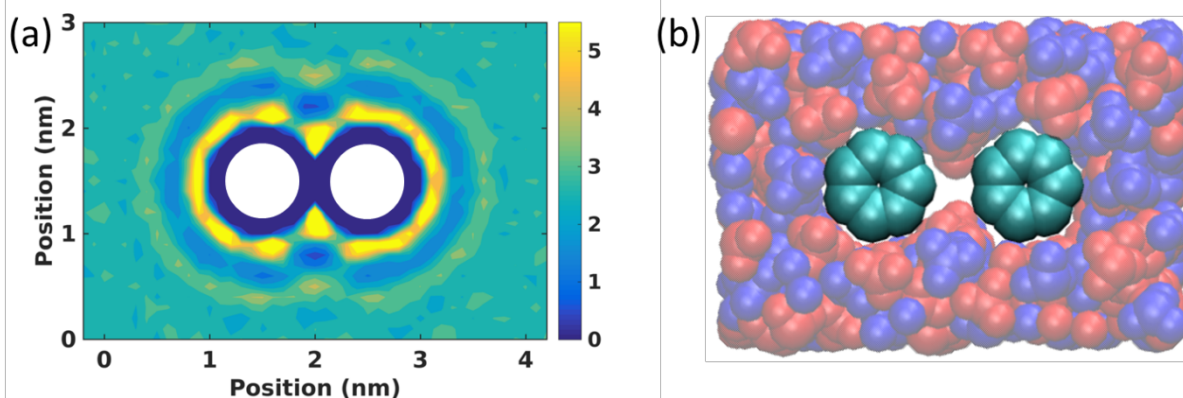


Figure D-3. Ion distribution near two neutral nanorods with a rod-rod separation of 1.0 nm. (a) The density distribution of cations and anions. The ion density (unit: nm^{-3}) is color-coded. (b) A snapshot of the rods and the ions around them. The red, blue, and cyan balls denote anions, cations, and carbon atoms, respectively. The white space between the rods is vacuum.

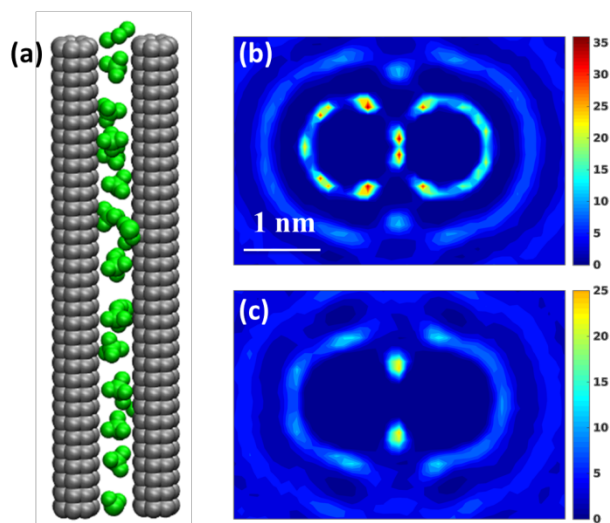


Figure D-4. Ion distribution at point A in Figure 5-5 of the main text. (a) A snapshot of cations intercalated between two charged nanorods (line charge density: $-2.38 e/\text{nm}$). Distribution of cations (b) and anions (c) near the two nanorods. The ion density is color-coded and the unit of the color bar is nm^{-3} .

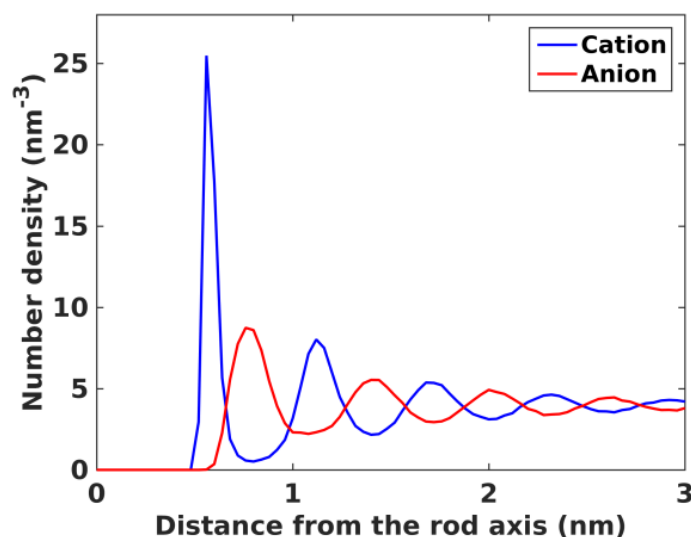


Figure D-5. Ion density as a function of the radial distance from the axis of an isolated nanorod.

4. The input file for Gromacs is similar to that for the polymerized ionic liquids project except that a parameter file is added to conduct the on-fly calculation. The parameter is attached.

```
File_index: 10
number_of_chosen_atom: 231
start_index_of_chosen_molecule: 0
output_frequency: 500
sample_frequency: 10
```

5. In this work, the force on each atom in the rods were reported and accumulated on the fly. The code segment is attached in the following.

```
int output(long step, t_state *state_global, long nsteps)
{
    //-----define variables-----
    static int nmole;          //number of all atom -- 231
    static int startIndex;     //number of the first rod atom in .gro file -- 0
    static int outFreq;        //the frequency to record onfly data
    static int accumFreq;      //the frequency to accumulate the dat
    static int FI;             //output file index
    static int frameCount;     //frame count
    int i,j;
    static double forceAtom_X
    static double forceAtom_Y
    static double forceAtom_Z
    static char name0[60];
    static char name1[60];
```

```

static char name2[60];
char readpara[100];
FILE *fp,*fread,*fp1,*fp2;

//-----read parameter values-----
if(step == 0){ //READ ONLY ONCE
    fread = fopen("Parameter.dat","r");
    if(fread == NULL) {
        printf("input file cannot be opened!\n");
        exit(0);
    }
    fscanf(fread,"%s %d \n",readpara,&FI);
    printf("\n%s %d\n",readpara,FI);
    fscanf(fread,"%s %d \n",readpara,&nmole);
    printf("%s %d\n",readpara,nmole);
    fscanf(fread,"%s %d \n",readpara,&startIndex);
    printf("%s %d\n",readpara,startIndex);
    fscanf(fread,"%s %d \n",readpara,&outFreq);
    printf("%s %d\n",readpara,outFreq);
    fscanf(fread,"%s %d \n",readpara,&accumFreq);
    printf("%s %d\n",readpara,accumFreq);
    frameCount = 1;
    sprintf(name0, "SumF_X_%d.dat",FI);
    sprintf(name1, "SumF_Y_%d.dat",FI);
    sprintf(name2, "SumF_Z_%d.dat",FI);
    forceAtom_X = 0.0;
    forceAtom_Y = 0.0;
    forceAtom_Z = 0.0;

    printf("Subfunction Initialization Finished!\n");
    fclose(fread);
}

//-----accumulate positions and velocities-----
if(step > 0 && do_per_step(step,accumFreq)){
    for(i=0; i<nmole; i++){
        forceAtom_X += f_global[startIndex+i][0];
        forceAtom_Y += f_global[startIndex+i][1];
        forceAtom_Z += f_global[startIndex+i][2];
    }
}

```

```

//-----judge-whether-output-or-not-----
if(step > 0 && do_per_step(step,outFreq)){
    //printf("Why not out put?? step = %d, outFreq = %d\n");
    if(step == outFreq){
        fp = fopen(name0,"w");
        fp1 = fopen(name1,"w");
        fp2 = fopen(name2,"w");
    }
    else{
        fp = fopen(name0,"a");
        fp1 = fopen(name1,"a");
        fp2 = fopen(name2,"a");
    }
    forceAtom_X=forceAtom_X/(outFreq/accumFreq);
    forceAtom_Y=forceAtom_Y/(outFreq/accumFreq);
    forceAtom_Z=forceAtom_Z/(outFreq/accumFreq);
    fprintf(fp,"%d %12.5f\n",frameCount, forceAtom_X);
    fprintf(fp1,"%d %12.5f\n",frameCount, forceAtom_Y);
    fprintf(fp2,"%d %12.5f\n",frameCount, forceAtom_Z);
    frameCount++;
    fflush(fp);fflush(fp1);fflush(fp2);
    fclose(fp);fclose(fp1);fflush(fp2);

    // initialize for the following accumulations
    forceAtom_X = 0;
    forceAtom_Y = 0;
    forceAtom_Z = 0;
}
//-----free the memory-----
if(step == nsteps){
    printf("\nSimulation end. The onfly codes cleaned.\n");
}
return accumFreq;
}

//-----Force communication-----
static int accFreq;
if(step == 0){
    // We will force communication at 1st step in case of accFreq = 1;
    accFreq = output(step,state_global,ir->nsteps);
}
mdof_flags = 0;

```

```

if(step>1 && do_per_step(step,accFreq)) {
    mdof_flags |= MDOF_X;
    mdof_flags |= MDOF_V;
    mdof_flags |= MDOF_F;
}
if (mdof_flags != 0){
    wallcycle_start(wcycle,ewcTRAJ);
    forced_commu(fplog,cr,outf,mdof_flags,top_global,step,t,state,state_global,f,f_global,&n_xtc,&x
_xtc);
    wallcycle_stop(wcycle,ewcTRAJ);
}
//-----call subfunction to accumulate data and/or output-----
if(step > 0 && do_per_step(step,accFreq) && MASTER(cr)){
    printf("Will go to subfunction, step = %d\n",step);
    accFreq = output(step,state_global,ir->nsteps);
}

```

Disclosure

This work has been published by the AIP Publishing (see Ref. 207).

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