Molecular Structure and Dynamics of Interfacial Polymerized Ionic Liquids

Zhou Yu,† Chao Fang,† Jingsong Huang,‡ Bobby G. Sumpter,‡ and Rui Qiao*†

†Department of Mechanical Engineering, Virginia Tech, Blacksburg, Virginia 24061, United States
‡Center for Nanophase Materials Sciences and Computational Sciences & Engineering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

ABSTRACT: Polymerized ionic liquids (polyILs) hold great promise for applications in energy conversion and storage. Many of these applications are underpinned by the structures and processes at the interface between polyILs and solid surfaces; however, the interfacial behavior of polyILs remains largely unexplored. We herein report the molecular simulation results of poly((1-butyl-3-vinylimidazolium hexafluorophosphate) supported on neutral and charged quartz substrates. It is found that the structure of interfacial polyILs deviates greatly from that of bulk polyILs, affected by the distance from the substrate and the surface charge on the substrate. Particularly, the coordination of interfacial anions by the cations differs from that in the bulk since their coordination environment, e.g., conformation and clustering of polymer chains and their pendant cations, is greatly modified by the confinement at the substrate and the electrostatic polyIL–substrate interactions. Similar to the bulk anions, the interfacial anions diffuse mainly by intrachain hopping, but at a rate much slower than in the bulk due to the slow decay of the association between interfacial anions and their neighboring cations, which can be traced to the unique structure of polymer chains and cations near the quartz surfaces.

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.1–3 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.4,5 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., PF6 −, BF4 −) and organic (e.g., TFSI −) ions.1

The polyILs are promising electrolytes for a variety of potential applications, such as energy conversion and storage, thermoresponsive materials, catalysts, separation, and adsorption.2 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.6–11 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,12,13 the conductivity of polyILs could still be quantitatively described using an effective-medium approximation reflecting their microphase-separated character.12 More recently, Kremer and co-workers examined the glassy dynamics and charge transport in a group of polyILs that exhibit the highest direct current (dc)-conductivity at temperature lower than 100 °C so far.12 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 a glass-transition-assisted hopping. Intriguingly, for the first time, the dc-conductivity of these polyILs increases with the degree of polymerization (DP).12 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.13 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. These works were corroborated by experiments, 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. As a result, anions’ mobility in polyILs was correlated to the average lifetime of ion-associations.

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. 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. 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. 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-chain or interchain 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. SIMULATION SYSTEMS AND METHODS

2.1. MD Systems and Molecular Models. The MD system consisted of a polyIL film supported on an α-quartz substrate (see Figure 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 separately. Poly(1-butyl-3-vinylimidazolium hexafluorophosphate) was used as the polyIL in all simulations. Each polymer chain consisted of 32 monomer units. The structures of the monomer and the anion are shown in the inset of Figure 1. The polyIL film had 16 polyIL chains, giving a film thickness of ~5.0 nm (see Figure S1). 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) 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.

![Figure 1](image)

The substrate of ~2 nm in thickness was cleaved from the (101) plane of an α-quartz crystal. Both 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. The inset shows the chemical structure of the polyIL that consists of 32 units (not to scale with the substrate). The gray, blue, white, magenta, and cyan spheres denote the carbon, nitrogen, hydrogen, phosphorus, and fluorine atoms, respectively. The dashed black lines denote the simulation box.

2.2. MD Methods. All-atom simulations were performed using the GROMACS code with a 2 fs time step. The nonelectrostatic 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 fast Fourier transform 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 was constrained using the LINCS algorithm. The oxygen and silicon atoms of the substrate are fixed, whereas 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.\(^{29}\)

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 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 \(\sim 1.2\) times of the glass-transition temperature \(T_g\) of the bulk polyIL.\(^{19}\) The temperature of the system was maintained using the velocity rescaling thermostat.\(^{30}\) The heating and annealing processes of the bulk polyIL system were executed in the NVT ensemble. All other simulations were performed in the NPT ensemble. All other simulations 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.

3. RESULTS AND DISCUSSION

3.1. Structure of Interfacial PolyILs. It is known that near extended surfaces, conventional RTILs often exhibit structures distinctly different from their bulk structures.\(^{31}\) Since polyILs share many similar properties with RTILs, interesting structures should also 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.

3.1.1. Out-of-Plane Layering. We start by examining the out-of-plane layering of polyILs near the neutral and charged substrates. Figure 2a, b shows 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 of their imidazolium rings (labeled by the dashed circle in Figure 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 nm < \(z\) < \(\sim 1.5\)–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 (\(z = 2.5\)–4 nm), the ion density is relatively flat (see Figure S1), 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 nm < \(z\) < 0.81 nm in Figure 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 nm < \(z\) < 0.43 nm and 0.43 nm < \(z\) < 1.21 nm). Although the concurrent accumulation of cations and anions on neutral quartz surfaces is similar to that observed when conventional [BMIM][PF\(_6^−\)] liquids are bought into contact...
with the same surfaces, subtle differences are also noted. For conventional RTILs, the layers of cation rings and the PF$_6^-$ ions are located at roughly the same distance from the quartz surface.\textsuperscript{32} For polyILs, the first anion layer is closer to the quartz surface than the cation rings by \(0.2\) 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 [BMIM][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 S2) 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 2b, a more distinct and compact cation layer appears in \(0.10\) nm \(< z < 0.46\) 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 \(0.50\) nm \(< z < 1.01\) 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 \(\sim 2.0\) 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, although 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 are different. Very close to the neutral quartz surface \((z < 1.2\) nm), the space charge in the electrolyte phase is mainly negative (cf. Figure S3) because the first cation layer is flanked by two PF$_6^-$ ion layers with higher peak intensities (cf. Figure 2a). Charge separation is very weak at \(z > 1.2\) nm. On the other hand, very close to the charged quartz surface \((z < 0.6\) nm), the space charge is positive to balance the surface charge on the substrate. Similar to the situation in simple RTILs,\textsuperscript{51} at larger distance, the space charge density oscillates and the surface charge can become overscreened in some regions (e.g., \(0.6\) nm \(< z < 1\) nm, see Figure S3).

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 2c) and charged substrates (Figure 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.

### 3.1.2. 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.\textsuperscript{33,34} Second, the organization of cations in polyILs is known to affect the inter- and intrachain hopping of the mobile anions and thus their dynamic properties.\textsuperscript{59} 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 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 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 S4). Some partial overlaps between the circles representing the cations are 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 1) or the
mobile anions. The cations shown in Figure 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 3a), whereas those near the charged quartz substrate aggregate into larger clusters (marked by different colors in Figure 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, whereas the interfacial cations near charged quartz substrate tend to form a smaller number of more extensive clusters.

3.1.3. 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. 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 S4). For each of the three types of interfacial anions, the probability of finding different numbers of cations in their coordination shell is shown in Figure 4a, and their average number of coordination cations is summarized in Table 1. Near neutral quartz surfaces, the coordination of the first layer of anions by cations deviates strongly from that in bulk polyILs. Figure 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 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%.

![Figure 4](image_url)

**Figure 4.** (a, b) 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).

**Table 1. Average Number of Cations and Chains Coordinating Interfacial Anions and Bulk Anions**

<table>
<thead>
<tr>
<th></th>
<th>In bulk polyILs</th>
<th>1st anion layer near neutral quartz surfaces (0 nm &lt; $z$ &lt; 0.43 nm)</th>
<th>2nd anion layer near neutral quartz surfaces (0.43 nm &lt; $z$ &lt; 1.21 nm)</th>
<th>1st anion layer near charged quartz surfaces (0.50 nm &lt; $z$ &lt; 1.01 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of coordination cations</td>
<td>4.59</td>
<td>3.33</td>
<td>4.69</td>
<td>4.80</td>
</tr>
<tr>
<td>number of coordination chains</td>
<td>1.76</td>
<td>1.21</td>
<td>1.59</td>
<td>1.62</td>
</tr>
</tbody>
</table>
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 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 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.

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 intrachain and interchain hoppings contribute differently to the transport of mobile anions, at least in bulk polyILs. For each of the three types of interfacial anions, the probability of an anion being coordinated by cations belonging to different numbers of polymer chains is shown in Figure 4b, and their average number of coordination polymers is summarized in Table 1. As shown in Figure 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 to two polymer chains simultaneously, and the average number of coordination chain for both types of interfacial anions is only marginally smaller than that in bulk polyILs (cf. Table 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. On the basis of these results, the prevailing coordination structure of the interfacial anions can be constructed, as shown in Figure 4c1,c2: the ions in the first anion layer near neutral quartz surfaces are associated with four cations belonging to a single polymer chain, whereas 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.

3.2. Transport of 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. 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. Figures 2 and 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.

3.2.1. Ion Hopping. In bulk polyILs, mobile anions diffuse by hopping between the relatively stationary cations on polymer chains. 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 distinguishes 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 type A hopping, i.e., an intrachain hopping. Otherwise, the hopping is defined as type B hopping, i.e., an interchain hopping. For the polyIL and temperature considered here, ion hoppings occur at picoseconds time scale. 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 polyILs).

Figure 5 shows the probability of the two types of hoppings for different interfacial anions in comparison with bulk anions.

![Figure 5](image)

The statistics of the hopping events of the interfacial anions are similar to that of bulk anions: the type A intrachain hopping is the dominant hopping mode for the anions near both neutral and charged quartz surfaces and the type B interchain 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 intrachain 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. Figures 2 and 3).

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 intralayer and interlayer hoppings: after an intralayer 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 interlayer hopping, an anion escapes the original layer. Table 2 shows that for each type of interfacial anions considered, after

**Table 2. Decomposition of the Hopping Events of Interfacial Anions Near Neutral and Charged Quartz Surfaces**

<table>
<thead>
<tr>
<th></th>
<th>1st anion layer near neutral quartz surfaces (%)</th>
<th>2nd anion layer near neutral quartz surfaces (%)</th>
<th>1st anion layer near charged quartz surfaces (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>type A</td>
<td>type B</td>
<td>type A</td>
</tr>
<tr>
<td>interlayer</td>
<td>2.9</td>
<td>7.9</td>
<td>3.9</td>
</tr>
<tr>
<td>intralayer</td>
<td>97.1</td>
<td>92.1</td>
<td>96.1</td>
</tr>
</tbody>
</table>
an intrachain hopping, the anion predominately stays within the original interfacial layer (>96% chance). After an interchain hopping, the chance an interfacial anion leaves its original layer increases by a factor of 1.7−2.7 compared to that for the intrachain hopping, suggesting that the interchain hopping causes more interlayer movements. Overall, the hopping of the first layer of anions near charged surfaces involves lower percentage of interlayer 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), which tends to prompt intralayer movements and thus reduce the percentage of interlayer movements.

3.2.2. Interlayer 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: 

$$\text{ACF}_l(t) = \langle l(0) l(t) \rangle$$

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 \(\text{ACF}_l(t)\) indicates that an anion escapes a particular interfacial layer more readily.

Figure 6 compares the \(\text{ACF}_l(t)\) for different interfacial anions. At short time \((t \lesssim 1 \text{ ns})\), 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, interlayer hopping is more prevalent for anions near neutral surfaces than near charged surfaces (see Table 2) due to the more stretched polymer chains near neutral surfaces. At long time \((t \gtrsim 3 \text{ ns})\), 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 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 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 6 shows that a significant fraction of these anions stay within their original layer for more than 10 ns, i.e., the interlayer exchange of anions is sluggish.

3.2.3. Ion–Ion Association Dynamics. The mode of anion movements in polyILs (intrachain vs interchain hoppings; interlayer vs intralayer movements) controls 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 \(\text{ACF}_c(t) = \langle c(0) c(t) \rangle\), where \(c(t)\) is an indicator of the anion–cation association. \(c(t) = 1.0\) 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 \(\text{ACF}_c(t)\) to zero indicates that an anion breaks from its association by cations faster.

Figure 7 shows the \(\text{ACF}_c(t)\) 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, 39.0, 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 is coordinated by the first

![Figure 6](Image 282x210 to 308x288)

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

![Figure 7](Image 380x261 to 406x312)

**Figure 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 \(\text{ACF}_c(t) = a_0 \exp(-t/\tau_0)^\alpha\), where \(a_0\), \(\alpha\), and \(\tau_0\) are fitting constants. The relaxation time constant of \(\text{ACF}_c(t)\), \(\tau_0\), is computed using \(\tau_0 = a_0 \Gamma(1 + 1/\alpha)\), where \(\Gamma\) is the gamma function. Error bar is marked every 300 ps for clarity.
interfacial cation layer. As shown in Figure 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 breaking 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 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 1), and such a tighter coordination slows down the escape of an anion from its association with neighboring cations.

3.2.4. 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 \( \langle \cdots \rangle \) denotes the ensemble average. Figure 8 shows the MSDs of anions initially located in different interfacial layers near the neutral and charged quartz surfaces in comparison to bulk. Because anions can diffuse out of their original layer (see Figure 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., MSD\(_{xy}\)(t) \( \sim t \), see the thin black solid line in Figure 8), 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 7). Furthermore, Figure 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 3a) and confined by the stationary wall, both of which hinder their hopping along and between polymer chains.

The diffusion of anions becomes more bulk like at distances 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 S5a) at time scale up to \( \sim 10^2 \) 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 \( \sim 100 \) ns time scale, see Figure S5a), and the average diffusion of the anions in the film studied here is still slower than that in bulk (see Figure S5b).

The latter observation is in good agreement with the dielectric spectroscopy measurement of thin polyIL films.22

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, the packing of polymers’ backbone and pendant cations near a solid wall is perturbed greatly up to a distance of \( \sim 2 \) nm from the wall. Since our liquid film is \( \sim 5 \) 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 37–39 and the references therein). Near negatively charged substrates, the pendant cations of polyILs adsorb on the substrate and 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 PF6− 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 interchain hopings.

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
PF6− 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 a different coordination environment for the interfacial anions. The first layer of anions near neutral surfaces is mostly coordinated by four cations from one polymer chain, whereas 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 intrachain hopping as in bulk polyILs. Interfacial ions can escape their original layer by interlayer hopping, but the escape process is sluggish, and a majority of the ions remain 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.

On the basis of 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. Although the dynamics of anions is only greatly perturbed at positions 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.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b06065.

Top view of the substrate and side view of the polyIL films supported on neutral quartz substrates; density profiles of the hydrogen atoms of the silanol group of the neutral quartz surface and the fluorine atoms in the anions near the neutral quartz surface; space charge distribution near neutral and charged quartz surfaces; radial distribution of cation and anions in bulk polyILs; lateral MSD for anions (PDF)

**REFERENCES**


