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# Ionic Liquids in Multiphase Systems

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Additional information is available at the end of the chapter

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## Abstract

Ionic liquids (ILs) can be used to replace one or more phases in conventional oil/water emulsions including Pickering emulsions—surfactant-free emulsions which utilize nano- or micron-sized particles to stabilize the immiscible liquid-liquid interface. Due to the extreme tunability of both the ILs and particles used, the study of IL-based Pickering emulsions yields novel emulsion morphologies and insights into the ionic liquid-liquid-particle interactions present. This work discusses extensive experimental work on IL-based Pickering emulsions and IL/liquid interfaces, emphasizing unique phenomena—such as “bridging” between emulsion droplets and spontaneous particle transport across the interface—never observed in more conventional Pickering emulsions. Molecular dynamics (MD) simulations of particles at the IL/liquid interface are also discussed, and fundamental insights from these simulations are used to enhance understanding of the unique interface behavior revealed by experiment.

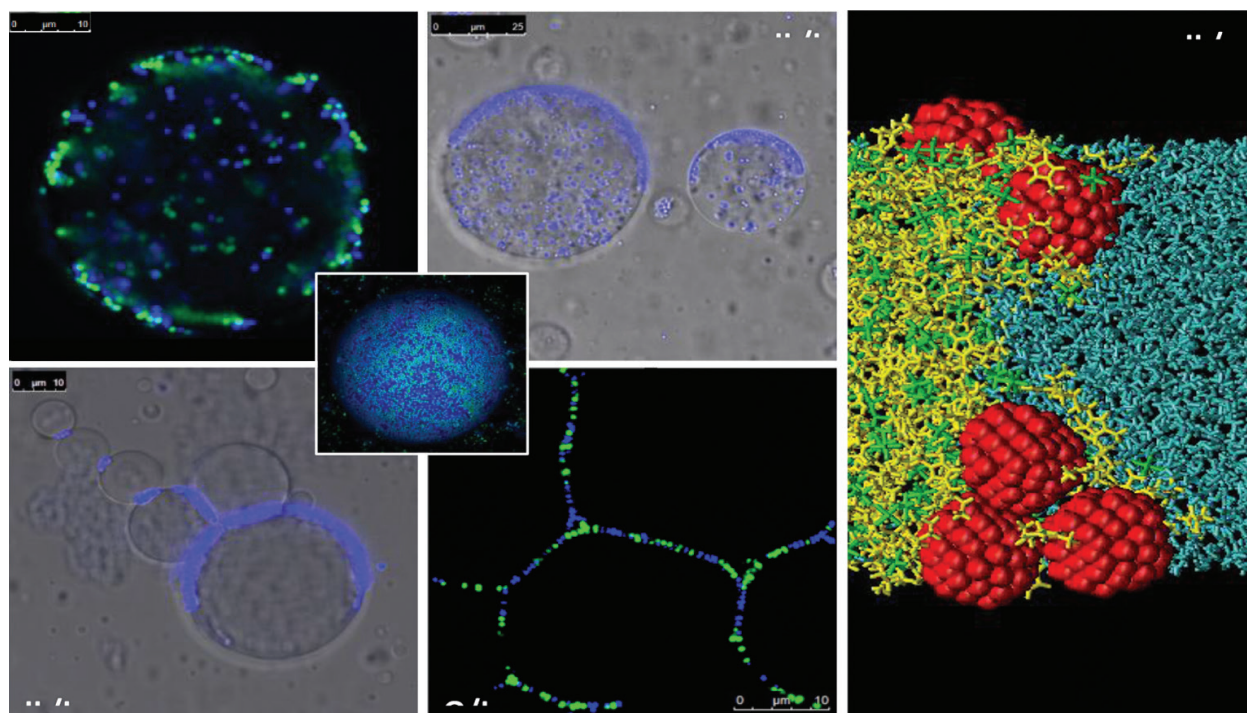
**Keywords:** ionic liquids, emulsions, Pickering emulsions, particles, colloids, interfaces

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## 1. Introduction

The unique properties and rich variety of ionic liquids (ILs) make them promising for a wide range of applications and the potential of pure ILs is multiplied by introducing them to multicomponent systems. Ionic liquids’ complex interactions with other materials enable multiphase systems that are both theoretically fascinating and potentially useful. This work focuses in particular on systems involving solid particles and immiscible liquid phases. It explores ionic liquid-liquid interfaces and their role in ionic liquid Pickering emulsions through both experimental and simulation approaches, including several unique and fascinating interface phenomena. **Figure 1** illustrates some of these phenomena—particle self-assembly on an emulsion surface, particle “bridging” between emulsion droplets, and spontaneous transport

across the liquid-liquid interface—as well as an example of the molecular dynamics (MD) simulations used to further explore the fundamentals of IL interactions with other phases. There continues to be active research in Pickering emulsions [1, 2], immiscible phases [3, 4], and ILs [5–9], and one particularly relevant application is employing ionic liquid-in-water emulsions as “a new class of fluorescent sensors for metal ions” [9].



**Figure 1.** Upper left: confocal microscopy image of an IL-in-water emulsion droplet. Upper-middle: confocal microscopy image of IL-in-IL emulsion droplets. Lower left and lower-middle: particle bridging between emulsion droplets. Right: MD simulation of nanoparticles at IL/water interface.

Given the complex and unusual molecular-scale interactions at ionic liquid/liquid interfaces, it is reasonable to suspect that they might behave differently than conventional aqueous/organic interfaces. Accepting this, the challenge becomes identifying those unique behaviors and developing applications based on them. It is equally important to develop fundamental theories of these interfaces and their interactions with, for example, solid particles. This work outlines the progress made toward these goals.

## 2. Ionic liquid-liquid interfaces and particle interactions

### 2.1. Unique morphologies of aqueous and nonaqueous ionic liquid Pickering emulsions

The extremely high tunability of the material properties of ionic liquids (ILs), caused by the virtually endless combinations of anions and cations, allows ILs to be unique candidates for the study of liquid-liquid interfaces. Additionally, by incorporating particles into these IL-liquid systems, novel and varied behaviors can be achieved. These suggest unique

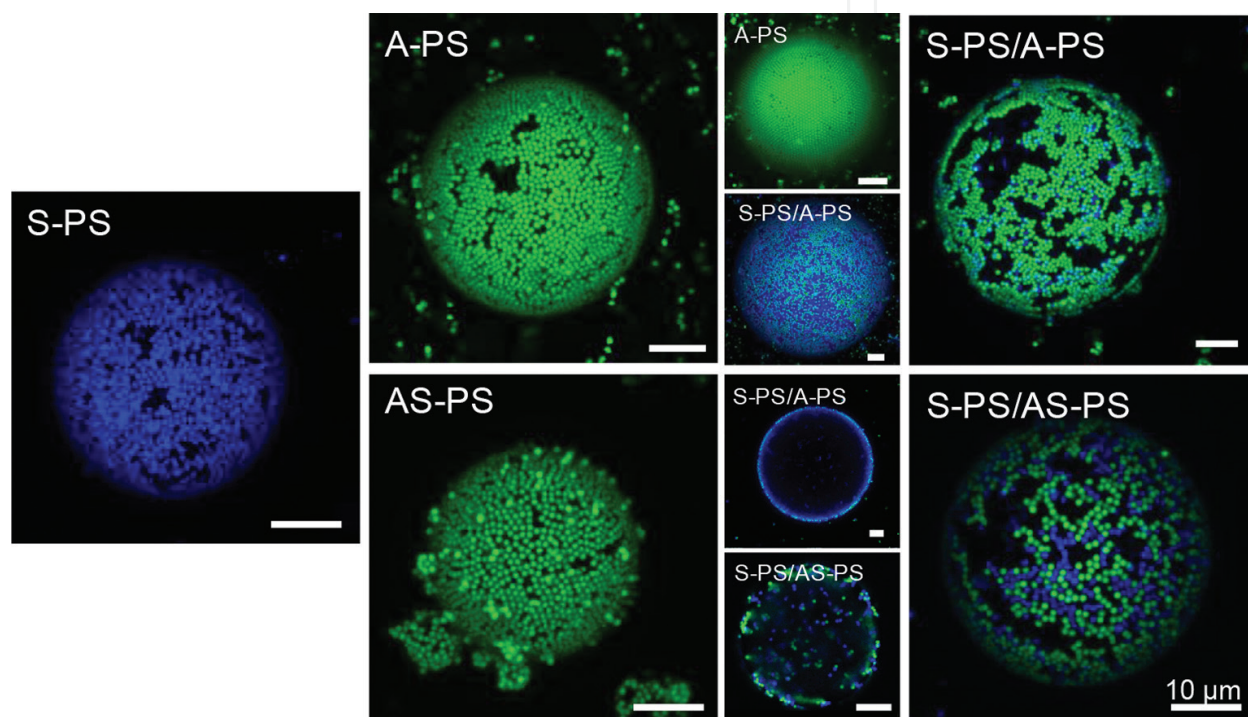
applications in extraction, catalysis, reaction schemes, etc., and provide even more extensive tunability through the complex interactions of differing choices of particles and ionic liquids. Surfactant-free, solid-stabilized Pickering emulsions can act as templates for these studies in which the ionic liquid subsists as the droplet phase, continuous phase, or both phases in the emulsion. Deviating from the conventional oil-in-water emulsion systems, employing ILs allows for interesting interfacial phenomena due to the charged nature of the IL and other factors intrinsic to the liquid including ion ordering, interfacial tension, etc.

Our first foray into ionic liquid-based Pickering emulsions was to simply replace the droplet phase in a conventional oil-in-water emulsion with an IL to create an IL-in-water Pickering emulsion [10]. While IL-in-water Pickering emulsions had been created previously, their use of silica nanoparticles prevented easy observation of the resulting particle morphology [11, 12], and thus, fluorescent micron-sized particles were used in this work. The hydrophobic IL 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF<sub>6</sub>]), which is immiscible with water, was chosen for the droplet phase. In order to observe the effect of particle hydrophobicity and surface charge and learn the resultant particle morphology on the droplets and the partition preference of the particles, 1  $\mu$ m fluorescent surface-treated polystyrene (PS) particles were employed in conjunction with a confocal laser-scanning microscope. For this work, the various surface chemistries of the PS were sulfate (–SO<sub>3</sub>H, S-PS, blue color), aldehyde sulfate (–CHO and –SO<sub>3</sub>H, AS-PS, green color), or amine (–NH<sub>2</sub>, A-PS, green color). The S-PS and AS-PS particles were relatively hydrophobic and negatively charged, while the A-PS particles were relatively hydrophilic and positively charged.

**Figure 2** shows the resulting droplet morphologies and partition preferences of the particles, each image showing a [BMIM][PF<sub>6</sub>] IL emulsion droplet suspended in water. The three images on the left of the figure show the resulting surface coverage of the droplet when a single particle type is used, while the two large images on the right, with additional smaller representative images of selected systems in the middle, show the morphology when two differing particle types are mixed in the emulsion at equal concentrations. All of the larger images, whether a single or binary particle type was used, show the aggregated domain morphology in which the IL droplet is nearly fully covered by the particles. In the binary systems, there is no significant partitioning of the particles on the droplet interface, that is to say, the particles are well mixed. For the A-PS and S-PS/A-PS particle systems, some fully covered droplets were observed in addition to the aggregated domain morphology. Full covered droplets were never seen in the S-PS, AS-PS, or S-PS/AS-PS systems, likely suggesting that the hydrophobicity or contact angle plays a role, as the A-PS particles were the only hydrophilic particles used. This contact angle difference could thus allow for closer packing on the IL droplet. This hypothesis is further confirmed by the partition preference of the particles for either the water phase or the ionic liquid phase. For the S-PS, A-PS, and S-PS/A-PS systems, many A-PS particles remain in the water phase, while the S-PS particles prefer the IL phase, even being extracted into the IL droplets (as seen for the cross section of the S-PS/A-PS droplet in the middle of **Figure 2**). The AS-PS particles also show a higher affinity for the IL-water interface, and the S-PS/AS-PS system further shows this behavior with a large amount of both S-PS and AS-PS particles being extracted into the IL phase, as seen in the cross section droplet



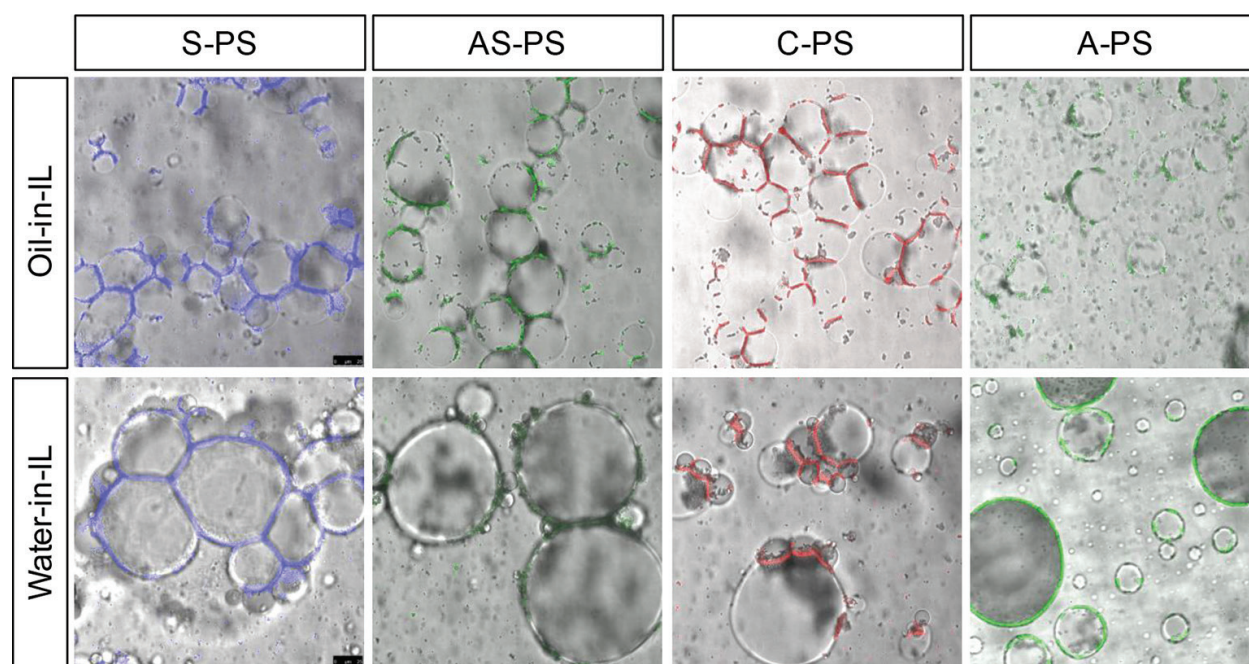
for the S-PS/AS-PS system. As the Gibbs free energy of adhesion to the interface is very high for microparticles, and the particles were originally dispersed in the water phase, this extraction phenomenon is quite interesting as it defies the general thermodynamic thinking. This is likely due to the fact that the S-PS and AS-PS particles are hydrophobic, and thus prefer the hydrophobic IL phase, rather than the aqueous. Thus the surface chemistry of the particles was found to have a significant effect on the resultant droplet morphologies and extraction characteristic of the IL, with the resultant emulsion scheme being tuned by the hydrophobicity of the particle type or types chosen. However, it is important to that such extraction has never been reported in systems involving oil-water interfaces thus the uniqueness of ILs plays a critical role.



**Figure 2.** Various observed particle morphologies on [BMIM][PF<sub>6</sub>] IL droplets in water for a variety of PS particle surface chemistries with 1 μm particle diameters in all images. All scale bars are 10 μm.

After studying the effect of having an ionic liquid as the droplet phase of a Pickering emulsion, we then turned to using the IL as the continuous phase, to form oil-in- or water-in-ionic liquid Pickering emulsions [13, 14]. Polydimethylsiloxane (PDMS) oil was used, and the same [BMIM][PF<sub>6</sub>] IL was used for either oil-in- or water-in-IL emulsions, as this IL is immiscible with both water and the PDMS oil used. For the particle types, 1 μm fluorescent surface-treated polystyrene particles were again employed with the same surface chemistries as the IL-in-water Pickering emulsion work, including sulfate (–SO<sub>3</sub>H, S-PS, blue color), aldehyde sulfate (–CHO and –SO<sub>3</sub>H, AS-PS, green color), and amine (–NH<sub>2</sub>, A-PS, green color), adding the carboxylate (–COOH, C-PS, red color) for this work. It is worthwhile to note that the S-PS and AS-PS are relatively hydrophobic while the C-PS and A-PS are relatively hydrophilic, with all particles exhibiting a negative surface charge in water, except for A-PS, which is positively charged.

The simple inversion of the droplet phase/continuous phase identities in these IL-based Pickering emulsions lead to a very interesting and novel particle morphology not seen in the conventional oil-in-water or IL-in-water emulsions, that of particle bridging. **Figure 3** outlines this phenomenon for both the oil-in-IL and water-in-IL Pickering emulsions studied, focusing on emulsions of S-PS, AS-PS, C-PS, and A-PS particles. In the oil-in-IL emulsions, for the negatively charged particles used (S-PS, AS-PS, and C-PS), a clear bridged morphology was observed in which the particles preferred inter-oil droplet bridges rather than the oil-IL interface, with this liquid-liquid interface being nearly completely devoid of particles. For the A-PS (positively charged) system, some bridges were observed, but the main morphology consisted of the particles sparsely covering the visible oil droplets, with more particles simply dispersed in the continuous IL phase. As both C-PS and A-PS are hydrophilic, this shows that for these systems, particle surface charge rather than hydrophobicity plays a more important role in terms of the bridge formation. Additionally, the bridges formed were monolayers between connected droplets, and the bridges prevented droplet coalescence by hindering drainage of the inter-droplet film. Also, there was no particle transport into the oil droplet phase, which was expected, as there is no particle extraction with conventional oil-in-water Pickering emulsions [15, 16].



**Figure 3.** Various observed particle morphologies on (upper row) PDMS droplets and (bottom row) water droplets in a [BMIM][PF<sub>6</sub>] IL continuous phase for a variety of PS particle surface chemistries with 1  $\mu\text{m}$  particle diameters in all images. The 25  $\mu\text{m}$  scale bar is valid for all images.

For the water-in-IL Pickering emulsions, a similar trend was observed in which the negatively charged S-PS, AS-PS, and C-PS showed bridging, while the positively charged A-PS did not, with no particle extraction seen in any of the cases. It is interesting that the bridging phenomenon occurs in these systems, as the particles were originally dispersed in water, thus it was first hypothesized that the water droplets would reabsorb the particles, making bridge

formation impossible. However, the bridging did similarly occur, with more compact structures seen rather than the long chains of droplets observed in the oil-in-IL systems. This occurrence provides an interesting look at the importance of contact angle, as the same particles stabilize the aqueous/nonaqueous emulsions to yield similar bridged morphologies. We may want to add the practical significance—instead of particle stabilization, the bridging caused a creamy layer and made the emulsions less stable.

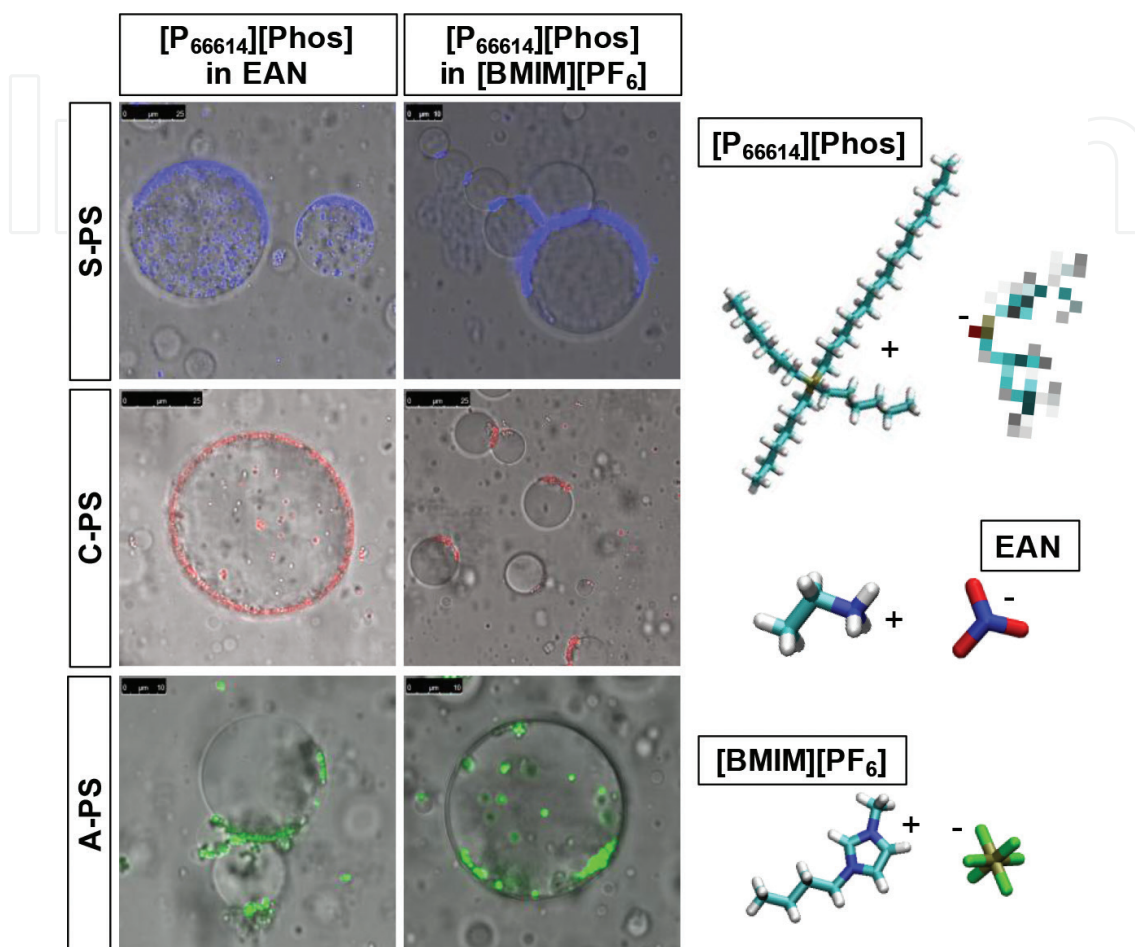
## 2.2. Ionic liquid-in-ionic liquid Pickering emulsions

Prior to our work on the subject, ionic liquid-in-ionic liquid Pickering emulsions had not been studied [17]. While many IL systems are miscible due to ion exchange, immiscible ionic liquid pairs do exist, and we chose two systems to study: (1) trihexyltetradecylphosphonium *bis*-(2,2,4-trimethylphentyl)-phosphinate ( $[P_{66614}][Phos]$ ) and ethylammonium nitrate (EAN) and (2)  $[P_{66614}][Phos]$  and [BMIM][PF<sub>6</sub>]. Imidazolium- and phosphonium-based ILs are known to form an immiscible pair, which is thought to be caused by strong hydrogen bonds formed when the imidazolium ions diffuse into the phosphonium IL, increasing the degree of order within the phosphonium IL, resulting in a negative entropy of mixing. However, while it was observed that the [BMIM][PF<sub>6</sub>] IL slowly gelled the  $[P_{66614}][Phos]$  IL over time, the diffusion between the two ILs was slow enough to allow for droplets to remain stable for hours, and thus their subsequent droplet morphology study. For the  $[P_{66614}][Phos]$ /EAN system, it was quite stable against mixing as long as EAN was the continuous phase of the emulsion.

The chemical structures of the ILs used can be seen in the right schematic of **Figure 4**. As far as droplet morphologies are concerned, the  $[P_{66614}][Phos]$ /EAN system showed very similar results as the [BMIM][PF<sub>6</sub>]-in-water Pickering emulsions we studied previously, as seen in the leftmost column of images in **Figure 4**. The S-PS and C-PS systems showed aggregated domains of particles at the interface with particle absorption into the droplet. The A-PS system interestingly showed a different morphology, that of droplet bridging, as seen in the oil/water-in-IL emulsions, with no particle absorption, as typical of the bridged systems. Previously, A-PS particles were the only particles that did not form bridges in either water/IL or oil/IL systems, so the presence of bridging in the IL-in-IL system was unexpected. This allows for the overarching hypothesis describing the modulation of particle morphology in these IL-based Pickering emulsion systems that an active surface chemistry is required in order for particles to exclusively form bridges. For a further explanation, the major difference between this system and the bridging systems reported previously is that the continuous phase here is protic. This is significant as in order for A-PS particles to assume a surface charge, the amine groups needed to accept a proton and can do so from the protic EAN. This is further illuminated by observing the  $[P_{66614}][Phos]$ -in-[BMIM][PF<sub>6</sub>] system in which the S-PS and C-PS particle types form bridges, while the A-PS does not. It is hypothesized that the anion [BMIM][PF<sub>6</sub>] can remove the acidic hydrogens of the sulfate and carboxylate surface chemistries, activating them, and thus allowing for bridging to occur. This driving force does not exist in the  $[P_{66614}][Phos]$ /EAN system, and thus bridging does not occur there for S-PS and C-PS. For the A-PS in  $[P_{66614}][Phos]$ /[BMIM][PF<sub>6</sub>], again there are no protons to activate the surface chemistry, and thus bridging does not occur. Overall, it is clear that the particle self-assembly phenomena is a strong function of the continuous phase/IL type and that phenomena generally unique to IL-based Pickering emulsions, including exclusive bridging and particle absorption, can also



occur when both phases are ILs. These results additionally show that these morphologies can be tuned by the constituent ILs, not only the particles, and can have important implications for various IL-based applications.



**Figure 4.** Confocal laser-scanning fluorescent images of IL-in-IL Pickering emulsions, including  $[P_{66614}][Phos]$ -in-EAN and  $[P_{66614}][Phos]$ -in- $[BMIM][PF_6]$ , stabilized by 1  $\mu m$  particle diameter PS particles. The right schematic shows generated chemical structures of the IL molecules for visualization purposes.

Further research in this area includes ionic liquid emulsions stabilized by more exotic particles—microgel particles, for example. Work by Monteillet et al., for example, finds that microgels self-assemble on the surface of IL emulsion droplets in a similar manner to the solid particles discussed above. These microgel particles, however, are responsive to various stimuli such as pH and temperature, making the emulsion system itself responsive and opening up still further potential applications [5].

### 2.3. Spontaneous particle transport across the ionic liquid interface

During our extensive study of ionic liquid-based Pickering emulsions, we noticed the separate and unique phenomenon of microparticle extraction across the liquid-liquid interface [18]. Spontaneous particle transport defies traditional understanding of the thermodynamics of particle-interface interactions and suggests intriguing and novel physics taking place at the



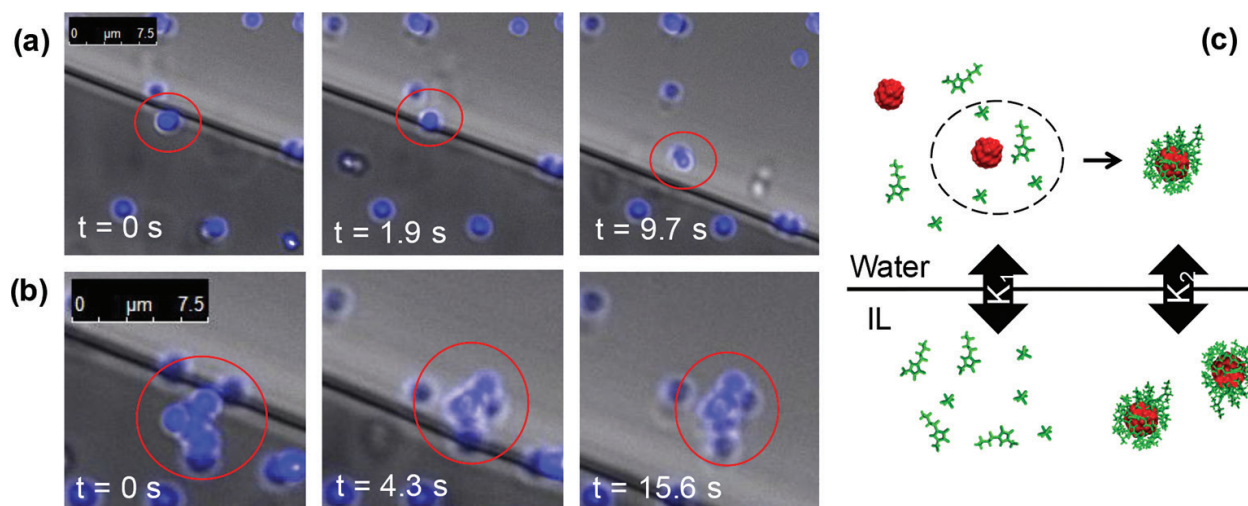
molecular scale. For this work, 1  $\mu\text{m}$  fluorescent sulfate-treated polystyrene particles were again employed ( $-\text{SO}_3\text{H}$ , S-PS, blue color) and dispersed in the water phase. The water phase was then carefully brought into contact with the particle free IL  $[\text{P}_{66614}][\text{Phos}]$ , by placing droplets in contact with one another on a glass slide. The interface was then observed over time with a confocal laser-scanning microscope to observe the resulting particle motion.

**Figure 5** shows the spontaneous microparticle transport for both (a) a single particle and (b) a cluster of particles from the water phase to the IL phase. The adhesive Gibbs energy for a microparticle at the liquid-liquid interface is in the order of  $10^7$  kT, thus prior to this work, spontaneous particle transport was not observed, instead propelling the particles by shear forces or functionalizing them with surfactants was required to see this phenomenon. The single particle moved through the interface onto the IL side at  $t = 0.8$  s, and moving past the interface and into the IL, the particle remained attached to the IL/water interface for a time before finally detaching. For the particle cluster, it moved through the interface at  $t = 0.4$  s, followed by two more particles at  $t = 4.3$  s. The latter event forced the first cluster to detach from the interface, with only one particle of the cluster remaining attached until complete absorption at  $t = 15.6$  s.

**Figure 5(c)** shows the proposed mechanism for the microparticle transport across the liquid-liquid interface, from the water phase to the IL phase, showing spontaneous particle extraction by the IL. This is due to the association of the ions with the particle surfaces that can be thought of as multiple equilibrium constants driving this association and the subsequent particle motion. Because the ILs removed particles from the continuous phase, we hypothesized that the dissolved IL ions in this phase played a role in the absorption process, as it is known that IL solubility in water depends on both the hydrophobicities of the cation and anion. A series of equilibrium relationships were used to describe the mechanism, as seen in **Figure 5(c)**.  $K_1$  represents the equilibrium between IL ions in the IL phase and those IL ions dissolved in the aqueous or solvent phase. The dissolved ions can then interact with and cover the particles dispersed in the aqueous phase. This is likely given the previous observations of the particle extraction for S-PS particles in the studied IL-based Pickering emulsions. Similarly,  $K_2$  represents the equilibrium between ion-covered particles dispersed in the aqueous phase and the particles extracted into the IL phase. This explanation allows for identification of IL-particle-solvent systems that may be adequate to experience particle absorption. For example,  $[\text{P}_{66614}][\text{Phos}]$  is minimally soluble in water, thus exhibiting a low  $K_1$ , but the constituent ions would exhibit strong binding to the particles, exhibiting a high  $K_2$ . This supports the fact that  $[\text{P}_{66614}][\text{Phos}]$  was one of the most efficient ILs for particle absorption and fits with the results seen for extraction with a myriad of other ILs in our work on the subject [18].

Thus, the study of ionic liquids and their interfaces with other liquids and solid particles reveal many interesting phenomena, including fully covered emulsion droplets, droplet/particle bridging, particle transport into the IL during emulsification and spontaneously, and a combination of these phenomena for the same emulsion system depending on the particle type. These phenomena are unique to IL-based emulsions, not seen in their traditional oil/water emulsion counterparts, and were likely due to the charged nature of the ionic liquid and additionally due to the behavior of their substituent cations and anions at the particle-IL

and liquid-IL interfaces. Additionally, the discovery of spontaneous transport of microparticles through a liquid-liquid interface was highlighted to show the intrinsic, powerful particle extraction capability of ionic liquids.



**Figure 5.** Images showing the microparticle transport phenomenon across the IL-water interface for (a) a single 1  $\mu\text{m}$  S-PS particle and (b) a cluster of S-PS particles over time. (c) Schematic of the proposed mechanism for the observed spontaneous particle transport. Adapted from Ref. [18].

### 3. Insights from molecular dynamic simulations

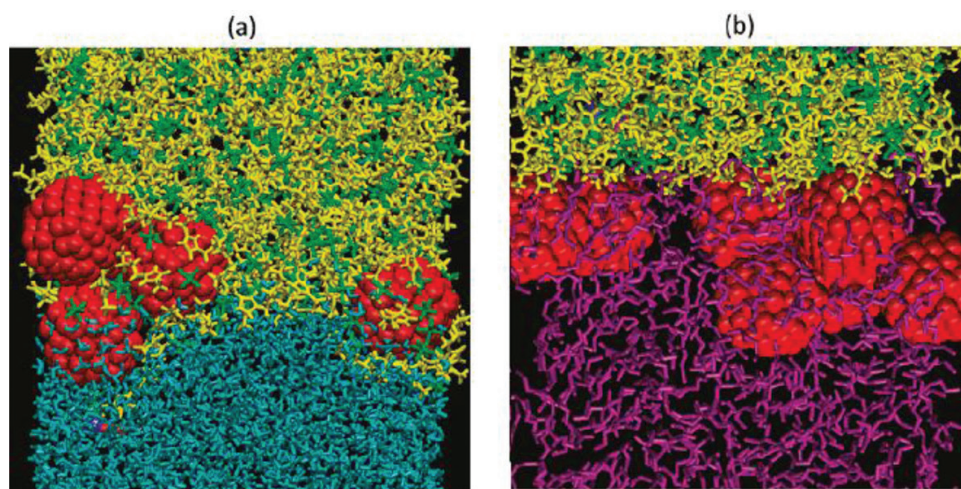
The unique nature of ionic liquids is largely due to molecular-scale effects—bulky, asymmetric organic molecules that resist steric packing, ionic charges distributed across each IL molecule, and the endless tunability provided by the ability to mix and match cation/anion pairs. Given the importance of the molecular scale to ILs and their behaviors, it is vital to study IL systems at the level of individual molecules and atoms. Molecular dynamics (MD) simulations provide a valuable tool in this effort. By modeling the forces between atoms and predicting the behavior of molecules, we can gain insight into the fundamental physics of ILs in multiphase systems and are able to form solid theories on the phenomena explored in our experimental work.

#### 3.1. Particle self-assembly at ionic liquid interfaces at the molecular-scale

Our first molecular dynamics study of ionic liquids in multiphase systems used a model IL and a model nanoparticle to examine the behavior of particles at IL/water and IL/oil interfaces [19]. The IL was chosen as 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF<sub>6</sub>]), perhaps the most commonly studied IL, and because it is immiscible with both water and hexane (our model oil). Furthermore, a force field model had been developed for it specifically tuned to surface properties [20]. For the nanoparticle, we took a diamond lattice, cut it off in a roughly spherical shape, and saturated the surface with hydrogen. This model was taken to represent hydrophobic nanoparticles as a class. Two interfaces were simulated—IL/water and

IL/hexane—both with and without nanoparticles. The systems simulated with nanoparticles are shown in **Figure 6**.

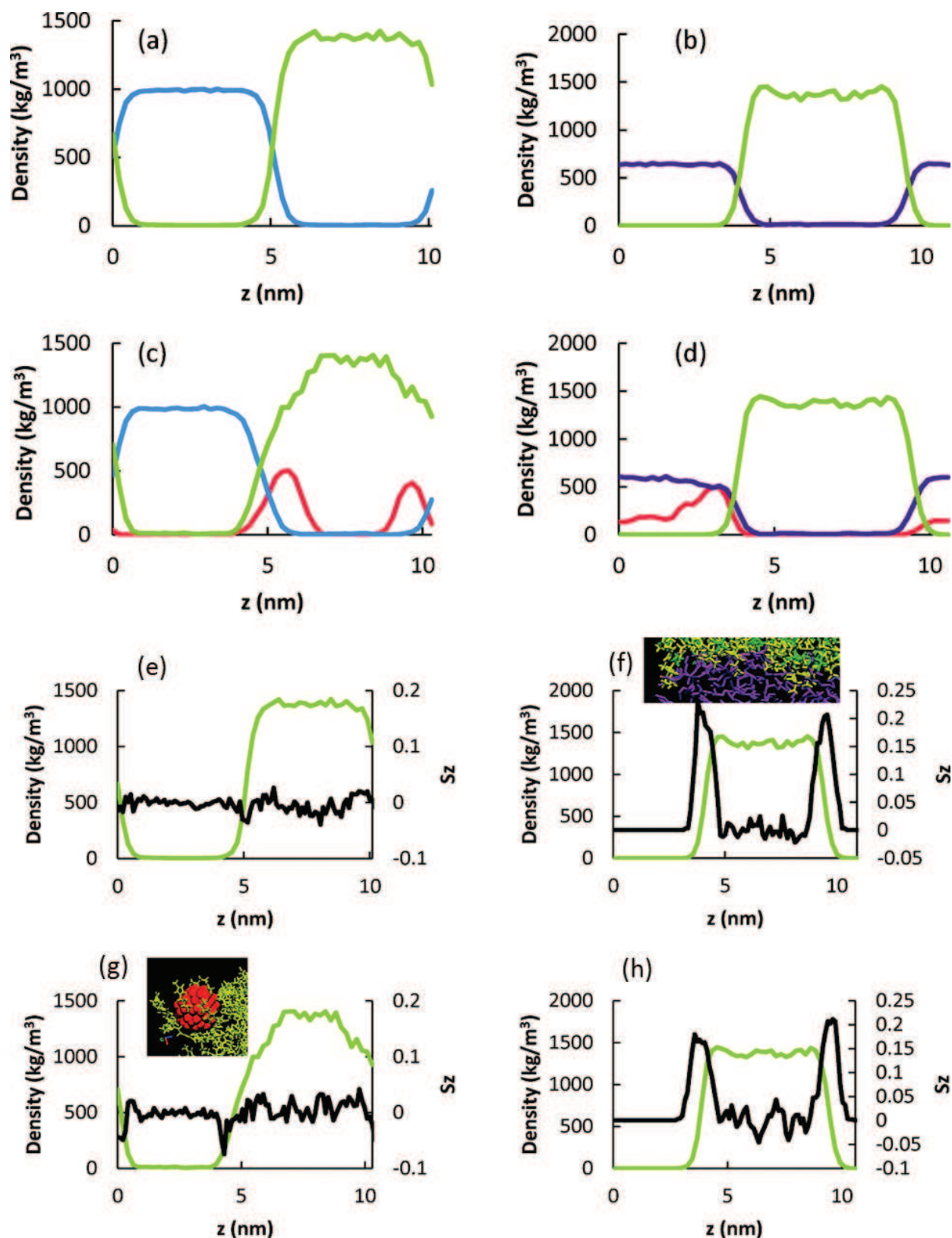
As shown in that figure, the second immiscible liquid phase makes a dramatic difference to the self-assembly of nanoparticles at the liquid-liquid interface. When the second phase is water, the hydrophobic nanoparticles are partially absorbed into the IL phase. However, when the second phase is hydrophobic oil, the particles prefer to remain on the hexane-side of the interface. This has obvious implications for several potential applications of these systems, including particle extraction from an oil or water phase or the formation of microscale structure from particles adhered to emulsion droplets.



**Figure 6.** Snapshots from MD simulations of particles at the (a) IL/water and (b) IL/hexane interface. [BMIM] is yellow, [PF<sub>6</sub>] is green, particles are red, water is blue, and hexane is purple. Adapted from Ref. [19].

While the molecules of the liquid phases influence particle behavior, the opposite is equally true. By comparing the simulations of the systems with nanoparticles to those without, we were able to examine the effect of nanoparticles on the interface through various analytical techniques. **Figure 7** illustrates two of those techniques—calculating density profiles and ordering parameters. Mass density profiles are a simple way to illustrate the physical distribution of molecules across the system. The ordering parameter  $S_z$  is a measure of how flat the carbon chain on the IL cation (the butyl in 1-butyl-3-methylimidazolium) lies against the plane of the interface. When  $S_z$  is zero, there is no particular ordering of ionic liquid atoms—they are oriented in all directions.  $S_z$  rising indicates that the IL cation is orienting itself flat against the plane of the interface, creating an ordered pattern of molecules. This ordering is similar to that widely observed in molecular dynamics studies of other ionic liquid interfaces including the IL/oil [21], IL/graphite [22], IL/gold [23], and IL/vapor interfaces [24, 25]. Drawing from this wide range of studies, it can confidently be said that ordering of ionic liquid molecules is a fundamental trait of IL interfaces, and it is no surprise that it affects and is affected by particles at the interface. Such ordering has also been confirmed experimentally through spectroscopy [26].





**Figure 7.** Density profiles and ordering parameters for IL/water (a, c, e, g) and IL/hexane (b, d, f, h) systems without (a, b, e, f) and with (c, d, g, h) particles. The four figures above (a, b, c, d) show density profiles for water (blue), IL (green), and particles (red). The four figures below (e, f, g, h) compare the IL density profile to the ordering parameter  $S_z$ , a measure of how flat the IL cation molecules lay against the interface. Adapted from Ref. [19].

**Figure 7** illustrates the impact of the particles on the IL/water interface. In the case of the IL/water system, the addition of particles broadens the interface, with potential relevance to interface properties such as surface tension. However, this does not occur in the IL/hexane system, likely because the hydrophobic oil is especially repulsive to [BMIM][PF<sub>6</sub>] molecules. Instead, the density of the IL features a slight bump at the IL/hexane interface. Examining the ordering parameter *S<sub>z</sub>* explains this oddity—*S<sub>z</sub>* spikes up at the interface as [BMIM] molecules lie laterally against the surface. This ordering likely explains, in part, why particles equilibrate on the hexane side of the interface—absorption into the IL would disrupt this ordering.

This study gave an important insight into the effect of the second, non-IL, liquid phase on the self-assembly of particles at the interface. It also demonstrated that the particles influence the interface as well. These effects occur at the molecular scale because of the interactions between atoms in the IL and other phases, and are vital to fully understanding corresponding behavior at the macroscale.

### 3.2. Particle effects: particle hydrophobicity and charge

The initial MD study described in Section 3.1 was inherently limited. It only examined one type of ionic liquid and one type of particle. Two further studies allowed us to examine the effect of changing particle properties on self-assembly. This is an extremely important variable to study if we are to derive conclusions about real-world phenomena. In particular, one of the most promising applications for ILs in multiphase systems is the extraction of sand particles from water or oil, and sand is made up of hydrophilic silica that cannot be expected to behave like our model hydrophobic carbon particle. Another important factor is particle charge. Many particles of interest have some charge, which would obviously have an effect on the ions making up ionic liquids. Therefore, we completed two studies. Both simulated the same [BMIM][PF<sub>6</sub>]/water and [BMIM][PF<sub>6</sub>]/hexane interfaces as the original study. The first compared two types of particles—the same hydrophobic carbon particle as before, and a new, hydrophilic silica particle meant to behave similarly to, for example, a grain of sand [26]. The second utilized the carbon particle but arbitrarily varied the charge [27].

These systems were analyzed using the same techniques utilized in the first study. Some results were as expected. For example, the hydrophilic silica particle equilibrated on the opposite side of the interface from the hydrophobic carbon particle—on the water side in the IL/water system, and on the IL side in the IL/hexane system. Though this result was predictable, it is highly encouraging to one of the most exciting potential applications of these systems—oil spill clean-up. If silica particles are naturally absorbed into the ionic liquid phase when it is placed alongside oil, ionic liquids may be able to passively clean oil by absorbing grains of sand.

Somewhat more interestingly, the silica particle did not adhere as strongly to the IL/water interface as the carbon particle did to the IL/hexane interface. In fact, many of the silica particles remained in the water phase throughout the simulation. This indicates that a silica particle, or particles with similar properties, would be less effective at stabilizing Pickering emulsions than more hydrophobic particles. The silica particles also had the fascinating effect of eliminating the “ordering” of cation molecules at the IL/hexane interface. This suggests that the particle intermediates the repulsive forces between the two liquid phases. (This observation in part inspired aspects of another study described in Section 3.3 below.)

In Section 3.1, it was concluded that the presence of the particle at the interface affected properties of that interface. In particle, a hydrophobic particle broadened and softened the IL/water interface, leading to a region of relatively intermingled water and IL molecules. Particle charge was found to have a significant influence on this effect. In the IL/water system, a neutral particle widened the interface significantly more than either negatively or positively charged particles, and the interface tended to narrow as the charge grew strongly positive. The effect on the IL/hexane system showed the opposite trend, with a neutral particle resulting in a narrower interface than either a negative or positive charge. This indicates that particle charge contributes to a complex system of balanced coulombic forces affecting the interactions of all elements within the interfaces.

Another technique that was utilized in the first study (though that data was not described in this work) was the potential of mean force (PMF). A PMF diagram allows researchers to compare the energy effects of physical configurations with a simulation system. In the case of these particle/interface studies, a particle was forcibly dragged from midway in the water or hexane phase to midway within the IL phase. Snapshots were saved of the system with the particles at intervals of 0.2 nm. Then, each of these snapshots were taken as the starting point of a new simulation. This time, however, the particle was frozen in place. The system energies were then recorded as the system moved around the frozen particle and plotted against the distance of the particle from the interface. The result is shown in **Figure 7**.

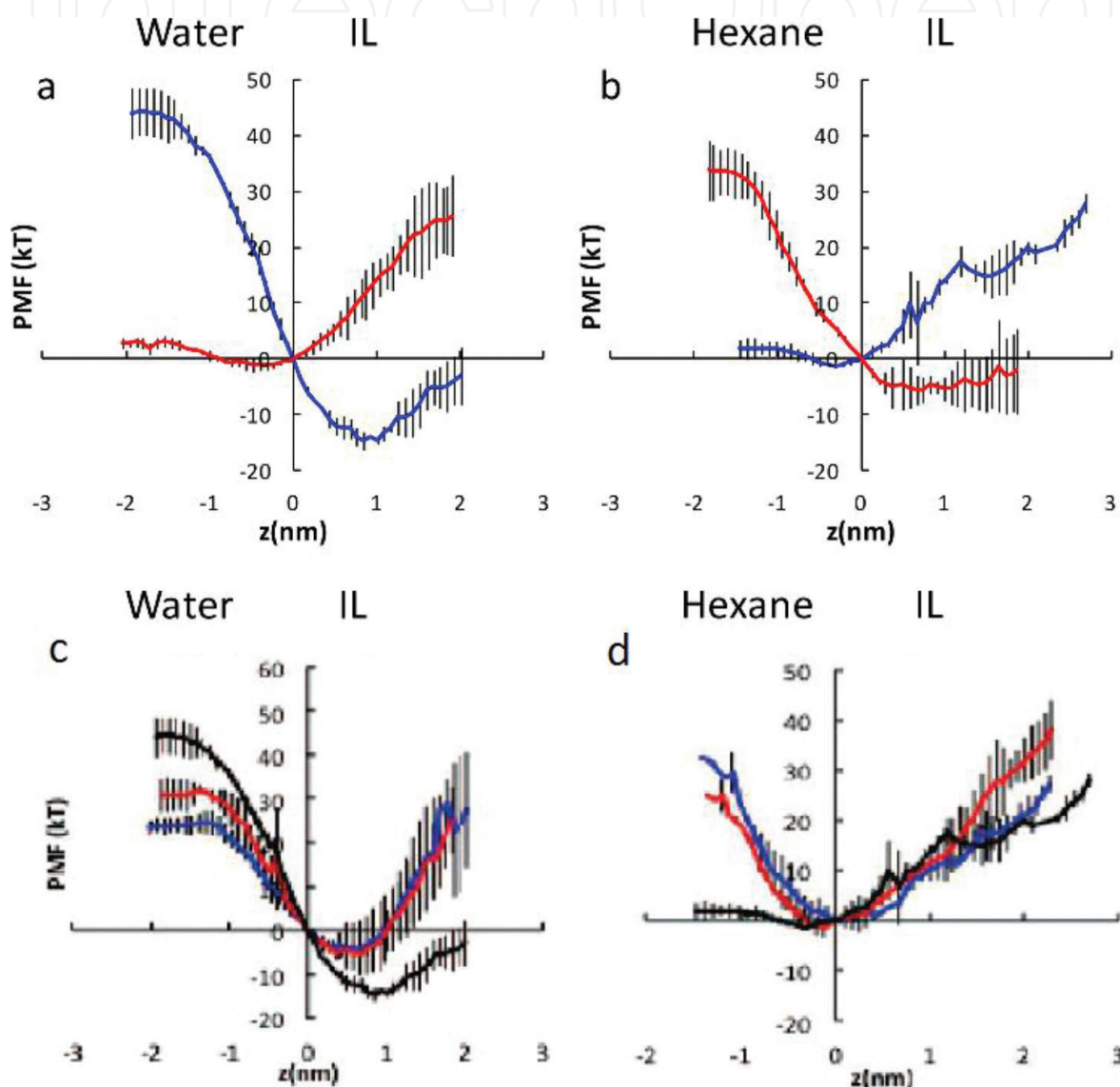
Graphs (a) and (b) in **Figure 8** compare carbon and silica particles. Graphs (c) and (d) compare carbon particles with  $-4$ , neutral, and  $+4$  charges. The equilibrium state of each system is at the lowest point of the energy. This allows us to confirm some things that we already know — that carbon particles equilibrate just inside the IL phase in the IL/water system and just inside the hexane phase in the IL/hexane system, that the hydrophilic and hydrophobic particles exhibit roughly opposing trends. From (c) we determine that [BMIM][PF<sub>6</sub>] has stronger, more attractive interactions with a neutral particle than either a negative or positively charged one. We also see that in the hexane system, the particle tends to equilibrate at the interface regardless of charge. This again shows the powerful influence of the second liquid phase. In a multiphase system, all elements affect all others in profound ways. When one of those phases is an ionic liquid with its complex constituent ions, the interactions become even more elaborate, allowing for the unusual behavior and intriguing phenomena revealed by experiment.

### 3.3. Ionic liquid effects: IL cation and anion influence on interface/particle interactions

The previous studies all utilized the ionic liquid [BMIM][PF<sub>6</sub>]. This is a solid choice for a model IL since it is widely studied, and a well-tested model is available. However, one of the greatest assets of ionic liquids is their near endless variety, tunability, and adaptability. Different ionic liquids differ from each other in profound ways, and we are inherently unable to make definitive statements on the nature of IL interfaces after only studying one IL. The final study described here aims to address that issue. It compares four ionic liquids: 1-ethyl-3-methylimidazolium hexafluorophosphate ([EMIM][PF<sub>6</sub>]), 1-butyl-3-methyl-imidazolium hexafluorophosphate ([BMIM][PF<sub>6</sub>]), 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIM][PF<sub>6</sub>]), and 1-butyl-3-methyl bis(trifluoromethylsulfonyl)imide ([BMIM][Tf<sub>2</sub>N]). The length of the carbon chain on the cation is directly correlated to the hydrophobicity



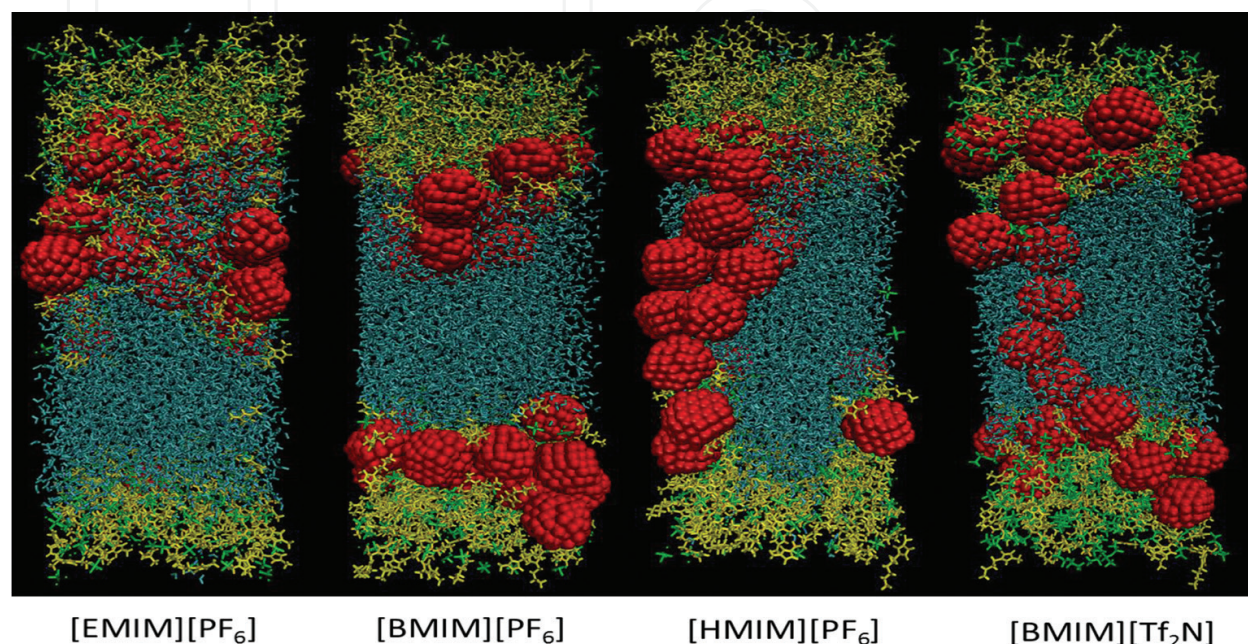
of the IL, so adjusting the length makes for a convenient comparison.  $\text{Tf}_2\text{N}$  is both more hydrophobic than  $\text{PF}_6$  and allows us to study an IL with an anion of a different shape. We are particularly interested in any insight this might give to the phenomenon of spontaneous particle transport across the interface as described in Section 2.3, which varies widely with different ILs. This study also varied the number of particles, simulating systems of zero, eight, and thirty-two particles. This was done to allow a further study of particle effects on the rest of the system.



**Figure 8.** Potential of mean force (PMF) diagrams. (a) and (b) compare carbon (blue) and silica (red) particles. (c) and (d) compare carbon particles with -4 (red), neutral (black), and +4 (blue) charges. Adapted from Refs. [26, 27].

Adding particles to these systems reveals how these interface properties affect particle/interface interactions. **Figure 9** shows snapshots from the 32-particle simulations of each interface system. To some extent all four interfaces behave similarly, equilibrating with the particles aggregated at the surface and a thin layer of IL molecules wrapping around, insulating the

hydrophobic nanoparticles from the water phase. However, the [EMIM][PF<sub>6</sub>] also seems to have drawn water molecules into the ionic liquid phase with them. [BMIM][PF<sub>6</sub>] and [HMIM][PF<sub>6</sub>] also seem to be doing this to different extents. The [BMIM][Tf<sub>2</sub>N] system, however, shows a sharp interface with very little uptake into the IL. Density profiles confirm these suspicions.



**Figure 9.** Snapshots from simulations of four IL interfaces with 32 particles.

Given these observations, it would seem that differences in hydrophobicity do not entirely explain the differing behavior of the IL interfaces. Hydrophobicity is certainly a factor—after all, relatively hydrophilic EMIM experiences more interface-broadening than hydrophobic HMIM. However, HMIM does not experience the same IL-crowding at the interface. The difference is not hydrophobicity but the shape of the anion, with Tf<sub>2</sub>N being linear and capable of lying flat on the interface, while PF<sub>6</sub> is round. Applying these observations to the particle transport exhibited in **Figure 5**, it becomes clear that a major relevant difference between [BMIM][Tf<sub>2</sub>N] (no transport) and [P<sub>66614</sub>][Phos] (strong transport), both highly hydrophobic ILs, may be the shape of the anion, with Tf<sub>2</sub>N much more linear and much more rigid than phosphinate with its branching chains.

The results of the thirty-two particle simulations are intriguing for another reason. [EMIM][PF<sub>6</sub>], water, and particles form a broad, intermingled interface, with the particles quickly aggregating into a single cluster (this behavior was also observed in the parallel simulation runs). Hydrophobic [HMIM][PF<sub>6</sub>] and [BMIM][Tf<sub>2</sub>N], on the other hand, maintain relatively distinct interfaces, and the nanoparticles are not quickly drawn into a large cluster. In the [HMIM][PF<sub>6</sub>] snapshot, the particles can be seen drawing ions out into the water phase. This confirms prior suspicions that nanoparticles intermediate the repulsive interactions between water and the ionic liquid molecules. This creates a unique energy-favorable region with

water, ionic liquid, and particles commingling. This observation was further confirmed by calculating interaction energies between the ILs and water for system with varying numbers of particles. It was found that changing the number of particles had a profound effect on the repulsive and attractive forces between ionic liquids and water. This may explain phenomena such as spontaneous transport of particles across the IL-water interface—the particles themselves distort and broaden the interface, changing their fundamental nature and the energetic physics which typically cause particles to adhere strongly to the interface.

#### 4. Summary and discussion

The unique properties of ionic liquids lend themselves to a multitude of applications relying on various diverse and intriguing systems. This work has focused on multiphasic systems where IL undergo complex interactions with other materials. In particular, this work explored ionic-liquid-based Pickering emulsions (stabilized by solid particles) and the behavior of particles at ionic liquid/liquid interfaces. These systems exhibit several remarkable phenomena including “bridging” of particles in between emulsion droplets and, perhaps most intriguingly, spontaneous transport of particles across the liquid/liquid interface. The unique behavior and properties of ionic liquids in these systems make them potentially relevant to a variety of applications including oil spill cleanup, drug delivery, and the creation of novel materials. What is more, the unusual nature of ionic liquids makes their study a vital tool in fully understanding the fundamental nature of physical systems such as liquid/liquid interfaces and Pickering emulsions. Molecular dynamics simulations, in particular, reveal how the properties of ionic liquids at the molecular level influence the behaviors of the systems. Further work in this field may take a variety of directions including developing practical extraction techniques based on ionic liquids, developing novel materials utilizing or based on ionic liquid Pickering emulsions, or environmentally responsive emulsions. Regardless, ionic liquids in multiphase systems promise continued relevance to both scientific advancement and practical application in the years to come.

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