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HAL Id: hal-01287384
https://hal.sorbonne-universite.fr/hal-01287384v1

Submitted on 12 Mar 2016

THE JOURNAL OF
PHYSICAL CHEMISTRY
Letters

Structural Transitions at Ionic Liquid Interfaces

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ABSTRACT: Recent advances in experimental and computational techniques have allowed for an accurate description of the adsorption of ionic liquids on metallic electrodes. It is now well-established that they adopt a multilayered structure and that the composition of the layers changes with the potential of the electrode. In some cases, potential-driven ordering transitions in the first adsorbed layer have been observed in experiments probing the interface on the molecular scale or by molecular simulations. This perspective gives an overview of the current understanding of such transitions and of their potential impact on the physical and (electro)chemical processes at the interface. In particular, peaks in the differential capacitance, slow dynamics at the interface, and changes in the reactivity have been reported in electrochemical studies. Interfaces between ionic liquids and metallic electrodes are also highly relevant for their friction properties, the voltage-dependence of which opens the way to exciting applications.
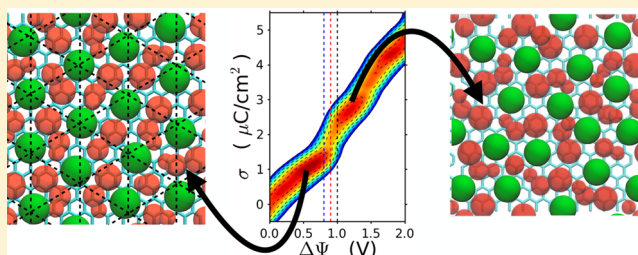
Solid−liquid interfaces play a key role in many processes, such as catalysis or electrochemical reactions, to mention only chemistry and energy related applications. Despite their importance, our understanding of the molecular-scale structure of such interfaces, where all the essential (electro)chemical processes occur, has long remained limited compared to the case of the corresponding pure solid and liquid phases. Probing directly the interface in experiments is particularly challenging, and computer simulations are also more involved because of the symmetry breaking in the direction perpendicular to the interface, which hinders the efficient use of periodic boundary conditions. Indeed, although simulating a few tens of water molecules may be sufficient to investigate the bulk properties of the liquid,[1] a similar number of molecules results in finite-size effects different from the physically relevant effects induced by the presence of the interface.

The past 10 years have witnessed the development of many experimental techniques which are sensitive to molecular arrangements at the interface, such as scanning tunneling microscopy (STM), sum-frequency generation (SFG), atomic force microscopy (AFM), high-energy X-ray reflectivity (XR), or surface force apparatus (SFA). They probe the structure of the liquid via different observables (vibrations, electron density, resistance to shear, etc.), thus providing complementary views of the interface. For example, the SFG signal is dominated by the innermost adsorbed layer,[2−4] whereas AFM or XR studies probe several layers of fluid.[5−8] In parallel, the access to high-performance computers and the development of new algorithms[9,10] also allowed the more accurate simulation of solid−liquid interfaces, shedding new light on interfacial processes such as adsorption. For example, the combination of STM and density functional theory (DFT) calculations demonstrated that water molecules adsorbed at metal surfaces exhibit a surprisingly rich variety of structures.[11] Their arrangement depends on the interplay between the geometry and energetics of the water−metal interaction and of the hydrogen bonding between the water molecules, which varies strongly from one metal to another (and even from one crystal plane of a given metal to another) and with the water coverage of the surface. This structuring impacts the dynamics at the interface[12] and ultimately the kinetics of electrochemical processes. Due to the range of length and time scales involved, from the electron transfer event to the local rearrangements of the interfacial fluid, a full understanding of the water-splitting mechanisms from computer simulations will therefore require bridging the gap between ab initio[13,14] and classical[15] approaches.

Here we will focus on a particular class of electrolytes, namely, room-temperature ionic liquids (RTILs). They are increasingly used in electrochemistry, with applications ranging from energy storage (batteries, supercapacitors) to electrodeposition.[16] Because they are made of ions, their interfacial properties have long been interpreted following the Gouy−Chapman−Stern theory. However, many of the underlying assumptions are not valid due the very high density of ions, an extreme case considering the absence of solvent in these liquids.[17−19] A significant number of experiments and molecular simulations have thus been devoted to the study of

the interfaces of ionic liquids with a solid.[6,20] The main conclusion arising from XR, AFM, SFA, and molecular dynamics (MD) is that the structure perpendicular to the interface is characterized by a strong layering of the liquid,[6,7,21,22] as expected for a molecular liquid, which extends up to a few nanometers. The local composition of the layers mostly depends on the surface charge of the solid[23] and displays strong local correlations due to charge-ordering.

> At electrochemical interfaces, the contact between RTILs and an electrified metal opens the way to voltage-induced ordering transitions within the adsorbed liquid.

Many recent studies on interfaces of RTILs reported intriguing results, highlighting the role of the molecular structure within the adsorbed layers. As pointed out in an editorial by Kornyshev and Qiao, it is indeed necessary to account for the three-dimensionality of the interface.[24] In particular, the formation of an ordered layer of ions has been reported at the interfaces of 1-butyl-3-methylimidazolium-hexafluorophosphate ($[C_4mim^+][PF_6^-]$) with mica[25] or with vapor.[26] At electrochemical interfaces, the contact between RTILs and an electrified metal opens the way to voltage-induced ordering transitions within the adsorbed liquid. The universality of such transitions is far from being established, in particular the extent of concerned RTILs—substrate combinations should be clarified. A first objective of this perspective article is therefore to summarize the studies, both experimental and theoretical, in which such transitions have been observed. We then discuss the impact of this finding on the physicochemical properties of the interface. In particular, the following questions will be addressed: How can we detect structural transitions in experiments and in simulations? Is there a templating action from the solid? What is the main electrochemical signature of these transitions? Is there an impact on the friction properties of the interface? Some of these questions remain open and call for further studies.

Evidence for Structural Transitions at Ionic Liquid Interfaces. Experimental Studies. To our knowledge, the first studies dealing with interfacial phase transitions in Coulomb fluids were conducted by Freyland.[27] His in situ STM study of the interface between the $[C_4mim^+][PF_6^-]$ and the (111) face of gold reported the formation of Moiré-like patterns at potentials greater than −0.2 V with respect to a platinum reference electrode. These were attributed to the formation of an ordered adlayer of PF_6^-. At negative potentials, the STM images were consistent with the formation of a layer of anions with the ($\sqrt{3} \times \sqrt{3}$) structure, indicating a two-dimensional ordering transition at this interface. It is worth noting that these observations closely follow a previous work performed on the adsorption of iodine from aqueous solutions on similar gold surfaces.[28] A further study on the electrodeposition of Cd on Au(111) in a chloroaluminate ionic liquid has also revealed the formation of an ordered $AlCl_4^-$ adlayer.[29]

When changing both the nature of the anion (from PF_6^- to BF_4^-) and of the surface of gold in contact with the RTIL (from (111) to (100)), Su et al. have also evidenced the existence of potential-driven ordering transitions.[31] When the potential is increased from −0.3 V, an ordered layer of anions is

formed between −0.1 and 0.4 V. In contrast, when scanning in the negative potentials direction, they first observed a loose film-like layer which was attributed to a disordered adsorption of C_4mim^+ cations. Then, for potentials lower than −0.95 V, perpendicularly oriented double-row strips were observed. These strips were assigned to the formation of micelle-like arrangements of aligned C_4mim^+ cations. These structures also formed with PF_6^- and $SO_3CF_3^-$ anions, but not on (111) surfaces of gold,[31] which shows that in this case a structural commensurability of the adsorbed layer and the metal surface is necessary for the formation of ordered structures.

This conclusion was confirmed in a study using in situ video-STM to probe the (111) Au interface with a RTIL composed of a different cation, namely 1-butyl-1-methylpyrrolidinium (BMP$^+$) associated with the bis(trifluoromethylsulfonyl)imide anion (TFSI$^-$).[30] Stable images could be obtained only for negative potentials below −1 V. For such potentials the images showed the formation of ordered structures. Several distinct arrangements of cations were proposed in order to interpret the observations at various potentials; one of them is shown in Figure 1. In both structures proposed by Wen et al., the cation
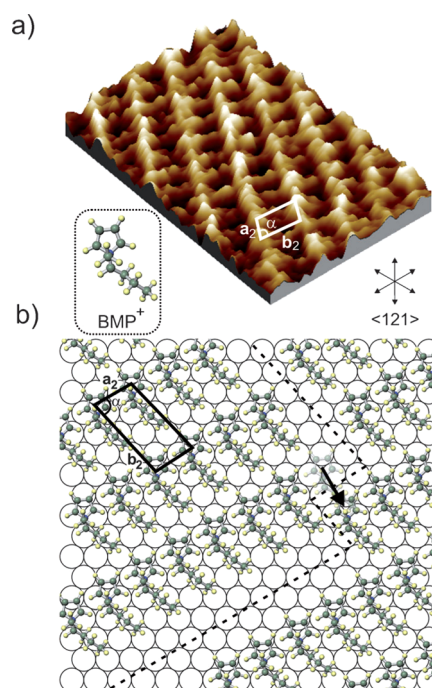

Figure 1. (a) High-resolution STM image (5.4 nm × 7.5 nm) of the BMP$^+$ adlayer on Au(111) at −1.4 and (b) proposed structural model, showing two domains of the ($\sqrt{3} \times \sqrt{13}$) BMP$^+$ adlayer separated by a translational domain boundary (indicated by dashed line). Reprinted with permission from ref 30. Copyright 2015 Wiley.

rings are adsorbed on the surface; in contrast, the alkyl chains lie flat on the surface only for the lower charge density (hence lateral cation density in the adsorbed fluid) and extend into the perpendicular direction for the higher density. The lattice parameters for the adlayer superstructure decrease accordingly and may change symmetry, resulting for the densest packing in a square lattice which differs from the hexagonal substrate. Finally, the video-STM furter allowed the first direct observation of the dynamical evolution of the adsorbed liquid. In particular, it was found that the fluctuations occur mainly at the boundaries between ordered domains.

All the structural transitions observed with STM have so far involved Au electrodes because this metal can be produced as single crystals with well-defined surfaces. Elbourne et al. have recently used another technique, in situ amplitude-modulated AFM, to study interfaces of highly ordered pyrolytic graphite (HOPG) instead.[32] This substrate presents the advantage of having flat surfaces with high area and avoids the surface reconstructions or etching which can occur in the case of gold.[31] These authors studied the effect of applied potential on the adsorbed layer structure for a $[C_4mim^+][TFSI^-]$ ionic liquid. At the open-circuit potential, well-defined rows are present on the surface. Unlike previous works, in which the ordered structures were apparently formed of only one type of ions, the unit cell is composed of an anion−cation−cation−anion arrangement.[32] This structure changes markedly with surface potential or when relatively low concentrations of lithium or chloride ions are present in the RTIL.

The variety of systems in which transitions are observed clearly show that it is a common feature of metal−ionic liquids interfaces. However, the few works reported so far raise very interesting questions. In particular, all the ordered structures proposed to interpret the STM data are composed of a single species only. Nevertheless, the relatively small applied potentials which are used ($\sim \pm 1$ V) may not be sufficient to fully separate cations from anions. In the case of the AFM study, the anion−cation−cation−anion rows result in an overall neutral layer, but there is a strong charge imbalance on the nanometer scale. A few hypotheses can thus be proposed to explain the observations: (i) there may be a specific adsorption of the ions on gold with the formation of partially covalent bonds;[33] (ii) on top of the observed layer, there could be an oppositely charged layer of ions which is not observed by the experiment; and (iii) it remains possible that the proposed structures, which are based on only the relative size of the ions (keeping the possibility of some kind of conformational ordering, for example only the imidazolium rings of the cations would lie parallel to the surface), are not the correct ones. Using additional techniques such as SFG, which is sensitive to the orientation of the ions,[4] could possibly shed a complementary light on this issue. Another open question is whether commensurability between the adsorbed layer and the metal substrate is necessary to observe a transition. Here also, the recent study performed with HOPG electrodes[32] suggests that it is not the case, and that the electric fluctuations at a homogeneous and flat metallic surface are sufficient to trigger ordering transitions in the interfacial layer of RTIL. In addition, the use of carbon electrodes in this study demonstrates that a perfect metallic behavior is not necessary to induce such transitions.

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In order to simulate electrochemical systems, it is necessary to fix the potential of the electrode. In classical molecular dynamics or Monte Carlo simulations, this can be done by various methods.[22] Our approach consists in treating the partial charges carried by the electrode atoms as additional degrees of freedom which fluctuate during the simulation. Their values are determined at each time step from a self-consistent calculation.[10,37,38] In such simulations, the electrochemical cell consists in a wide slab of electrolyte held between two electrodes with different voltages. As in experiments, the potentials are not absolute. The only fixed quantity is the potential difference between the two electrodes, $\Delta\Psi = \Psi^+ - \Psi^-$, although it is also possible to calculate the potential of each electrode with respect to the bulk liquid in the case of flat electrodes; we will note this potential as $\Psi^{elec/bulk}$. In the following, we will assimilate an ordering transition to an abrupt change in the structure observed when changing the potential. However, it is worth noting that first-order transitions are associated with a discontinuity in an order parameter and a corresponding singularity in a partition function, which are not easy to prove in simulations.[39] This point will be further discussed in the next section.

Using this simulation approach, a first example of voltage-driven transition was reported for a rather exotic system, formed with a high-temperature molten salt (LiCl) and an aluminum electrode with its (100) surface in contact with the liquid.[34,40] An advantage of this system is that a polarizable force field could be built directly from accurate DFT calculations using a generalized force-matching approach.[40] For potential drops $\Psi^{elec/bulk}$ across the interface more negative than −1.76 V, which corresponds to the point of zero charge (PZC), the molten salt adopted a disordered structure at the interface, while for larger potentials an ordered structure was obtained.[40] This structure, which is shown in the top panel of Figure 2, was commensurate with the aluminum substrate, and
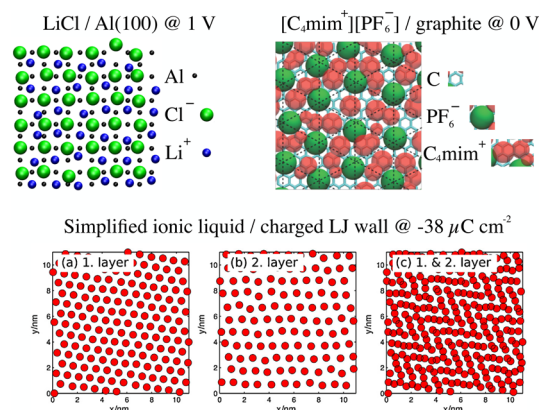

Figure 2. Snapshots of typical ordered structures observed in computer simulations. Top left: First adsorbed layer of a LiCl molten salt electrolyte on the (100) surface of an aluminum electrode at a negative potential. Adapted from ref 34. Copyright 2010 American Chemical Society. Top right: First adsorbed layer of a $[C_4mim^+]$-$[PF_6^-]$ RTIL on a graphite electrode at a neutral potential. Adapted from ref 35. Copyright 2014 American Chemical Society. Bottom: First two adsorbed layers of a simplified RTIL on a charged Lennard-Jones wall with a large negative surface charge density. Reprinted with permission from ref 36. Copyright 2013 Elsevier.

a strong alignment of the dipole components of the chloride anion and the normal of the surface was observed for large potentials.[34] Interestingly, no transition was observed when the plane of the metal was changed to (110) instead of (100), but a different ordered structure was then obtained showing that an

epitaxial mechanism is at play, whereby the molten salt adapts it structure to that of the electrode surface.

In a recent work, Kirchner et al. studied interfaces between primitive models of ionic liquids and solid surfaces with various net charges (i.e., the electric potential was not controlled).[36] At certain charge densities ($\sim$−16 μC cm^{-2}) the structure of the adsorbed layer of cations undergoes a structural transition to a surface-frozen monolayer of densely packed counterions with a Moiré-like structure. At lower surface charge densities (i.e., lower than −30 μC cm^{-2}), they even observed the formation of a herringbone structure arising from the superposition of two ordered monolayers of ions (see the bottom panel of Figure 2). These findings provide an interesting support for the STM studies discussed above, but it is worth noting that the charge densities employed are somewhat larger than the experimental charge densities; they would correspond to potentials which are above the electrochemical window of typical RTILs.

Going toward more realistic models, an ordering transition was reported from molecular simulations for the interface between $[\text{C}_4\text{mim}^+][\text{PF}_6^-]$ (for which a coarse-grained force field was used) and an electrified surface of graphite.[35] The presence of the ordered structure could be monitored by computing the in-plane structure factor in the first layer of the adsorbed liquid. This structure factor was liquid-like on a wide range of potentials, but it showed some strong Bragg-like peaks suggesting a two-dimensional lattice-like organization for both the anions and cations, which is shown in the top-right panel of Figure 2. This ordered structure contained on average as many anions as cations, and it was also observed by Kislenko et al. in simulations of the same RTIL (with an all-atom model) adsorbed on an uncharged surface of graphite.[41] By using importance sampling techniques, it was shown by Merlet et al. that this structure was the most stable one for small positive potentials ($\sim$0 < $\Psi^{\text{elec/bulk}}$ < $\sim$0.5 V) and metastable for small negative electrode potentials. It is worth noting that similarly to the experimental work of Elbourne et al. involving HOPG electrodes, no commensurability with the electrode surface seems necessary to observe such ordered structures.

So far, no ordering transitions have been observed using more elaborate, all-atom models of RTILs in contact with electrodes at fixed potential. In particular, the adsorption of $[\text{C}_4\text{mim}^+][\text{PF}_6^-]$ and $[\text{C}_4\text{mim}^+][\text{BF}_4^-]$ on electrified surfaces of gold was studied by Hu et al.,[42] but they did not report any ordering transition similar to the experimental observations by STM.

These simulation results, while confirming the possibility of transitions in the adsorbed layer of the fluid, also raise their share of questions. Future works will need to address the issue of finite-size effects because there must be a commensurability between the formed ordered structure and the simulation cell. Time scales are important too, because metastable states may be much longer-lived than the typical simulation times, which are on the order of the nanosecond only because of the computational cost. There is therefore a possibility that the reported transitions are artifacts of the simulation setups, but the similarities with experimental findings seem to weaken this hypothesis. The question of specific interactions with surfaces such as gold will also have to be treated. This requires in turn the development of accurate force fields for this purpose. First steps in this direction have recently been made in the case of carbon materials.[43]

Impact of the Transitions on Physicochemical Properties. We now turn to the consequences of structural transitions within the adsorbed fluid on the physicochemical properties of the interface. Specifically, we discuss the impact of voltage-induced transitions on the electrochemical response of the electrode–RTIL interface in terms of differential capacitance, cyclic voltammograms, and electrochemical reaction, as well as on the mechanical response (solid–liquid friction).

Peaks in the Differential Capacitance. The differential capacitance, C_{diff}, measures the response of the average surface charge density, $\langle\sigma\rangle$, to changes in the voltage, $\Delta\Psi$:

$$C_{\text{diff}} = \frac{\partial\langle\sigma\rangle}{\partial\Delta\Psi} \tag{1}$$

By definition, a capacitor corresponds to a voltage-independent differential capacitance. However, the charge of the electrode reflects the composition and the charge distribution within the interfacial liquid. As a result, one should expect a signature of abrupt structural changes at voltages corresponding to putative phase transitions in the electrode charge, hence peaks in the corresponding differential capacitance. While experimentally such peaks have indeed been observed,[31,44,45] their possible link with changes in the structure or the interface has been difficult to demonstrate until recently because of the experimental challenges of in situ imaging and the occurrence of other processes such as surface reconstruction of the electrode.

Indeed, in their STM study of $[\text{C}_4\text{mim}^+][\text{BF}_4^-]$ on a (100) gold electrode, Su et al. have also measured the capacitance of the interface.[31] They observed a 5-fold increase in this quantity in the potential region of transition from anion adsorption to cation adsorption. In the case of the in situ video-STM study of the $[\text{BMP}^+][\text{TFSA}^-]$ on a (111) gold electrode,[30] thanks to the high temporal resolution or the video-STM technique, the authors were able to visualize the evolution of the interfacial fluid during cyclic voltammetry (CV) experiments. The cyclic voltammogram displays two current peaks associated with two surface transitions which could also be linked to the formation of the ordered cationic structures, such as the one shown in Figure 1, upon increasingly negative surface charge density.

In computer simulations, it is relatively straightforward to calculate the capacitance of the interface in constant potential simulations. The generic method consists in simulating an electrochemical cell at various voltages and extracting the average surface charge. Then the $\langle\sigma\rangle = f(\Delta\Psi)$ plot is differentiated, which provides the differential capacitance through eq 1. However, close to a transition, a large peak in the capacitance is expected, so that many voltages should in principle be sampled in this region. An alternative was recently proposed, which consists of using importance sampling methods.[35,46] In short, by using the whole distribution of surface charges during the simulations, it is possible to sample the probability distributions of any variable as continuous functions of the applied potential. There is in principle no need to acquire more data close to the transition, the only requisite is to have a good overlap between the histograms of surface charges from the various voltages.

The probability distribution of the charge density, σ, of graphite electrodes in contact with the $[\text{C}_4\text{mim}^+][\text{PF}_6^-]$ ionic liquid[35] obtained with this approach is shown in Figure 3a. The figure shows the probability distribution on a logarithmic scale. It is clear that there are three branches along which the distribution of the surface charge distribution shifts almost linearly upon increasing the potential. These branches are separated by more complex changes in the distribution around particular voltages. We will focus on the one occurring at $\Delta\Psi$ =
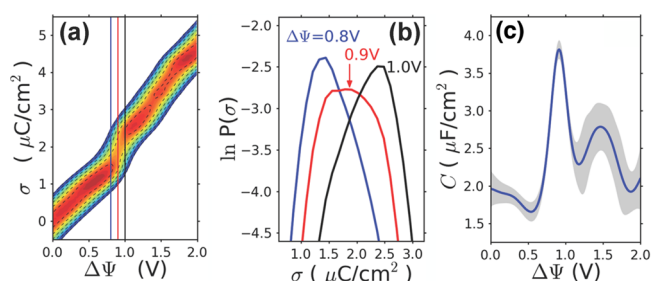
Figure 3. (a) Calculated probability distribution of the charge density σ of graphite electrodes in contact with the $[C_4mim^+][PF_6^-]$ ionic liquid with respect to the applied potential $\Delta\Psi$. The two-dimensional graph of the distribution employs a logarithmic scale with lines separated by a difference of 0.5 and is plotted as a function of σ in panel b. Note the fat tails in the distribution, $P(\sigma)$, and the markedly nonlinear shifts with changing voltage. (c) Differential capacitance, C, as a function of $\Delta\Psi$. Adapted from ref 35. Copyright 2014 American Chemical Society.

0.9 V because this is the potential for which the order−disorder transition discussed above occurs. Figure 3b shows the distribution, $P(\sigma)$, at three applied voltages (0.8, 0.9, and 1.0 V). They are characteristic of a first-order phase transition. Away from phase coexistence (at 0.8 and 1.0 V), they show the presence of "fat tails", which are due to the small probability of sampling the metastable phase. At the transition the distribution displays hints of bimodality, which is expected if the two phases are equiprobable. However, it would be necessary to simulate larger systems to fully conclude on this point.

The differential capacitance computed from these simulations is shown in Figure 3c. Note that much better statistics could again be obtained compared to the usual method involving eq 1 by using the Johnson−Nyquist relation

$$C = \frac{S}{k_B T}\langle(\delta\sigma)^2\rangle \tag{2}$$

where S is the surface of the electrode and $\delta\sigma = \sigma - \langle\sigma\rangle$ are the fluctuations in the electrode surface charge density. A large peak in the differential capacitance is observed at the applied voltage where the transition occurs, which is consistent with the experimental findings of Su et al.[31] Note that again, larger systems should lead to a singular charge-density transition in a macroscopic limit.[39] Our simulations therefore confirm that the presence of large peaks in experimental measures of the capacitance of an interface can indeed be the signature that a potential-driven transition is occurring.

Hysteresis and Slow Dynamics. The above-mentioned domain boundaries between phases also have important implications by themselves, due to the entailed free-energy cost. In three dimensions, this would be a surface free energy. In the present case the topology of the boundary between interfacial domains at the surface of the electrode remains to be clarified.[24] As a result, annealing these boundaries, either between grains of otherwise identical domains, or between different domains, requires overcoming the corresponding free-energy barrier. In practice, the consequences of these barriers are observable as long time scales in the dynamics of the interface or as hysteresis in cyclic voltammetry.

Uysal et al. reported a potential-dependent hysteresis at an electrified graphene−RTIL interface.[47,48] X-ray reflectivity measurements during cyclic voltammetry and potential step

measurements are used to probe the electronic density in the direction perpendicular to an epitaxial graphene surface, within the adsorbed $[C_9mim^+][TFSI^-]$ ionic liquid. The resulting profiles were consistent with that obtained from MD simulations, by assuming a combination of two limiting structures, with weights varying as a function of applied voltage. The structure evolves very slowly after a potential step, with processes occurring over time scales exceeding 10 s. In addition, the CV scans exhibit significant (scan rate dependent) hysteresis. While in this work the authors safely indicated that the nature of the apparent barrier and the associated mechanism require further investigation, these observations clearly point to the crucial role of structural transitions and the associated domain boundaries in the observed hysteresis and slow dynamics. Another manifestation of slow processes occurring at the ionic liquid−electrode interface was reported by Roling et al., who have carefully analyzed the capacitance spectra on a broad range of frequencies.[49,50] Although no particular ordering transition was observed by STM, these authors concluded that the slower capacitive process could be related to structural reorganizations of the gold surface or to strong rearrangements in the first adsorbed layer of ions.

Recently, Limmer proposed a detailed study of these effects using a coarse-grained model capturing strong interionic correlations.[51] Its limited computational cost compared to molecular simulations allowed for a systematic finite-size scaling analysis, which demonstrated the first-order nature of the fluctuation-induced transition and spontaneous charge density ordering at the interface, in the presence of an otherwise disordered bulk solution, already observed in molecular simulations.[35] A crucial step in this demonstration is the extensive growth of the free-energy barrier between phases analogous to the ones observed in ref 47, which indeed implies hysteresis and long time scales.

Impact on Reactivity. Structural changes in the ionic liquid at the interface also have implications on the local environment of other species in the liquid, in particular electro-active species. This in turn may result in changes in their reactivity. A direct observation of this feature has recently been reported by García Rey and Dlott, who studied CO_2 reduction on a polycrystalline Ag electrode, with 1-ethyl-3-methylimidazolium tetrafluoroborate $[C_2mim^+][BF_4^-]$ containing 0.3 mol % water as electrolyte.[52] Such systems have been shown to reduce the overpotential for CO_2 reduction. SFG and IR were used to probe the surface field experienced by the adsorbed CO molecules produced by the electrochemical reduction of CO_2. From the CO Stark shift, a sudden increase of the field at the electrode surface was observed at the threshold potential for CO_2 reduction, which could be traced back to a structural transition within the RTIL, even though no information could be obtained on the nature of these structural changes. Nevertheless, this study illustrates the potential benefit of exploiting the peculiar structure of ionic liquid interfaces and the voltage-driven changes thereof (with potentially much greater diversity than in solvent-based electrolytes) for electrochemical reactions.

Voltage-Dependent Friction. Finally, voltage-driven changes in the structure and composition of the interfacial fluid also have implications from the dynamical point of view. Sweeney et al. conducted nanotribology experiments to probe the lubrication properties of 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl) trifluorophosphate ($[BMP^+][FAP^-]$) confined between silica colloid probes or sharp silica tips and a Au(111) substrate,

using AFM.[53] As the composition of the adsorbed layers is tuned by the electrode potential, from cation-enriched to anion-enriched, the friction also evolves. Figure 4 illustrates that these
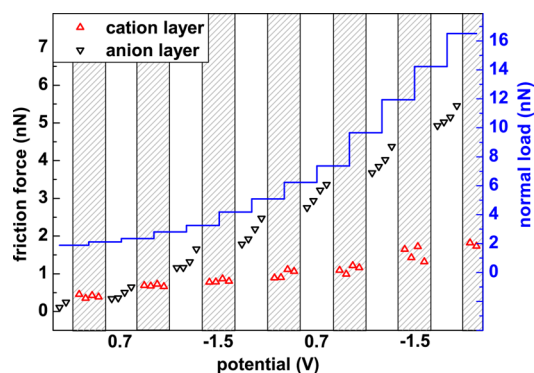

Figure 4. Friction forces as functions of load and applied potential recorded for a sharp AFM tip sliding on Au(111) in $[BMP^+][FAP^-]$. Each data point represents the average over a full scan frame of 14 nm side length. The potential is switched between -1.5 and 0.7 V for each value of the applied normal load. Reprinted with permission from ref 53. Copyright 2012 American Physical Society.

variations are directly linked to the nature of the sliding plane, which may correspond to cation or anion layers, depending on the electrode potential and on the normal load exerted on the confined fluid. While the voltage-driven structural changes on the microscopic interfacial structures remain to be investigated, such studies open the way to a new tuning of frictional forces at the molecular scale without changing the substrate.

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More detailed information on the role of key microscopic and macroscopic factors can be obtained using molecular simulations, such as load, shear velocity, surface topology, and length of alkyl side chains in the ionic liquid.[54] Simulations with fixed surface charge density (instead of potential) have further evidenced two mechanisms underlying friction changes in such systems, namely, charge effects on normal and in-plane ordering in the film, as well as swapping between anion and cation layers at the surface.[55]

Summary and Outlook. There is now a large body of experiments pointing toward the existence of potential-driven transitions at the interface between ionic liquids and metallic electrodes. However, as discussed above, the exact structure and composition of the ordered phases remain open questions. Computer simulations bring some theoretical support on the question, but they are still scarce because of the technical difficulty associated with the use of constant applied potential ensemble. They also suffer from sampling issues (both in size and time) which render the observation and the characterization of the transitions difficult. The current works, in which

the interactions are determined using classical force fields, may also be limited if particular bonding occurs at the interface. The recent inclusion of constant voltage methods in DFT-based molecular dynamics packages[56] may open new opportunities for tackling this difficult problem, as it was shown recently in the context of nanotribology.[57,58]

In addition, the role of many parameters remains to be established. For example, how do the composition of RTIL and the possible presence of impurities affect the occurrence of ordering transitions? What is the impact of the temperature? Also, many applications of RTILs use them in the presence of a solvent, which will also impact the whole structure of the electric double layer. Finally, although it is clear that the nature of the substrate plays a strong role, it is not certain that there is always a commensurability between the ordered structure of the liquid and the metal. Topological defects at the surface of the metal may also play a predominant role,[59] and it is likely that corrugation effects can modify the formation and/or the detection of ordered layers. Recent simulations have shown that the heterogeneous nucleation of ice at a surface depended markedly on the morphology of the latter.[60] Additional works with varying metal electrodes will allow better understanding of these issues.

Whether these transitions will have practical applications remains an open question, but they clearly impact many of the physicochemical properties: peaks in the differential capacitances, slow dynamics at the interface, varying reactivity, and voltage-dependent friction properties have already been reported. Overall, such transitions reinforce the view of RTILs as solvents with multifaceted properties, with a composition that can be specifically tailored to a given task.

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