

Three-Dimensional Double Layers

Electrical double layers are ubiquitous; they will inevitably emerge, given mobile charge carriers and an interface. They play a decisive role in well-known problems such as electrochemical reactions, electrokinetics, and colloidal stability and thus have been studied extensively since the very concept of the double layer was postulated by Helmholtz. Some classical textbooks relate those issues in the title: “Double layer and electrode kinetics”.¹ The recent renaissance of research on double layers is driven by the development of new materials and technologies. In particular, the development of room-temperature ionic liquids (RTILs) and their applications in electrochemical energy storage, electrode kinetics, and controlled friction have triggered a new wave of research on double layers at electrified interfaces and in nanoconfinement.²

The development of the theory has refined and diversified pictures of the double layers: from the compact ionic layer originally postulated by Helmholtz, to the compact plus diffuse layer structure of Gouy–Chapman taught in textbooks with discreteness of charge modifications,³ and finally to the alternating counterion and co-ion layers in highly concentrated ionic systems, revealed most recently. However, if not counting the lateral two-dimensional (2D) structure of the first layer of specifically adsorbed ions or counterions condensed on highly charged surfaces,^{4–6} both of which might break the translational invariance in lateral directions and thus endow 2D features to the double layers, the theory mainly focused on one-dimensional (1D) ion distributions resolved in the direction normal to the interface. Such a picture, though, is currently being revised on several fronts. In particular, for double layers in concentrated systems such as room temperature ionic liquids (RTILs), the transitions between different lateral arrangements of ions adsorbed on open electrodes have been reported experimentally and revealed in simulations. Furthermore, the transition between different lateral arrangements of counter- and co-ions during electrification of narrow pores has been observed in simulations and shown to greatly affect both the capacitance and dynamics of the double layers. These relatively new issues and developments all point to new challenges in understanding the three-dimensional (3D) structures of the double layers controlled by the electrification of surfaces.

The article by Merlet et al.⁷ comprises an important step in this direction. Although it did not come out of the blue (cf. Figure 1), it moves the story of the double layer to the next round, and it has triggered us to write these notes.

■ SINCE WHEN DOES THE DOUBLE LAYER GO 3D?

Speaking about ionic liquids, for a while experimentalists have been interested not only in the distribution of ions and charge density perpendicular to the interface but also in lateral direction.^{8–14} However, theorists got interested in it only recently.^{15–18,14} The voltage-driven structural transition of ionic layers adjacent to electrode surfaces has been observed on single-crystalline gold and bismuth electrodes,^{9,19–22} but at least in the case of gold it was not clear how much those transitions are coupled to the possible field-induced surface reconstruction

of the electrode as well as to the adsorption–desorption and restructuring of specifically adsorbed ions.

However, in ordinarily diluted electrolytes, voltage-controlled phase transitions at electrode–electrolyte interfaces were a hot topic in electrochemistry in the 1980s–1990s; for review see a feature article²³ and a book chapter.⁴ Two types of transitions have been considered then: (i) structural transitions in the so-called specifically adsorbed layers of ions with commensurate or incommensurate arrangement with respect to the substrate and (ii) structural transitions in the surface layer of the electrode, such as surface reconstruction of single-crystal gold electrodes. This was made possible at that time because new in situ methods of characterization of surface structures became available for interfacial electrochemistry, such as AFM and STM, and synchrotron X-ray diffraction from the interface. Extensive literature on the subject has been reviewed in refs 23 and 4. The studies of the structure of adsorbed layers was not only empirical, but also theories of different level of sophistication were developed and compared with experiments by many groups in the past (see, e.g., the works of Blum,²⁴ Rikvold,²⁵ Vorotyntsev,^{26,27} and many others, which we cannot list all here, referring the reader to a detailed review of ref 23).

Generally, the culture of studies of phase transitions at the electrochemical interfaces goes back to the story of the first-order adsorption–desorption of organic molecules; for a review see a classical comprehensive monograph of Damaskin et al.⁵ or a brief overview of Damaskin and Petrii,²⁸ although ordinarily those works did not focus on lateral resolution of adsorbed structures, operating with average values and appealing to mean-field descriptions. Along that path, the first attempts to describe the electric-field-induced desorption of organic molecules from the electrodes gave rise to the famous Frumkin isotherm^{5,28} and to its sophisticated follow up studies (for review see ref 29).

Phase transitions at the electrochemical interface usually affect the double-layer properties, including its electrical capacitance, giving it singular features. These are jumps or peaks, depending on whether these transitions were in the change of the population of the interfacial layer through adsorption–desorption (of first-order kind) or related with the lateral rearrangement of atoms and molecules along the interface (which are typically of second or infinite order).

Note that in the ordinary electrochemistry of relatively diluted solutions only the structures composed of the species “belonging to the interface” (adsorbed species or/and atoms of the frontier layer of the electrode) could undergo transitions in their lateral organization; the double layer in such systems was clearly “2 + 1D” but not 3D. The new feature of the double layer in ionic liquids is that structural transitions can take place in the adjacent layer to the electrode, even when its ions may not be specifically adsorbed on the electrode. Generally, they may quite likely extend in the third dimension. Indeed, the density of ions in ionic liquids is so high that the overscreening

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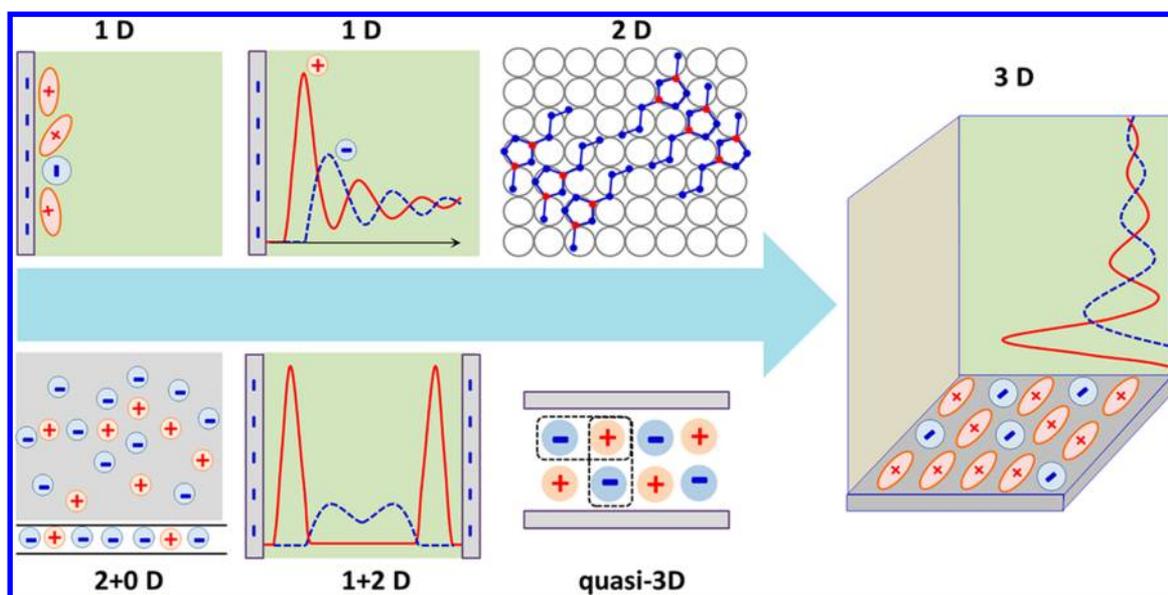


Figure 1. New focus: double layers in ionic liquids as 3D entities. The double layers near open electrodes (left top panels) were first perceived as 1D Helmholtz layers homogeneous in the lateral plane.⁵⁴ This “1D” picture of the double layer was later refined as alternating layers of counterions and co-ions in the direction normal to the electrode surface.² The discovery that ions adsorbed on the electrode surface form a well-defined pattern in a certain voltage window indicates that double layers can have distinct structures in the lateral plane, at least in the first layer adjacent to the electrode—call it “2D features”.¹⁹ The double layers in nanopores (left bottom panels) are 2D entities in nanopores accommodating only one layer of ions but exhibit 1 + 2D and quasi-3D features in wider pores.^{39,40,48–50} From these diverse pictures of the double layers and the latest analysis by Merlet et al.⁷ and Kirchner et al.³⁵ emerges a new paradigm that the 3D nature of double layers in RTILs should be taken seriously.

phenomenon, related with alternation of the net charge in the neighboring layers, could, in principle, affect the transitions in the first layer. Such coupling, although not examined in the study of Merlet et al.,⁷ should exist because overscreening has been observed in similar systems.³⁰

Reference 7 has clearly shown that the discovered structural transitions correlate with the maxima in the differential capacitance of the interface. This was one of the important findings of that paper. Indeed, the main focus in theoretical, simulation, and experimental studies (with, perhaps, an exception of the work of Mao’s group¹⁹) of capacitance was how the latter was affected by the distribution of ions perpendicular to the interface. But that new result was not unexpected. If with voltage variation the structural transition in the double layer abruptly changes the overall accumulated charge in it, there must be a peak in its derivative over voltage, i.e., in the differential capacitance. This was already known in ordinary electrochemistry with structural transitions in the layers of adsorbed ions on single-crystal electrodes,⁴ as well as upon surface reconstruction.²³

Merlet et al.⁷ have further found that there is a half-of-a-volt potential window within which the first layer of ions looks ordered, whereas it becomes disordered at low and high voltages. Note that the overscreening effect is the strongest at low voltages, and it gradually disappears at large voltages.^{31,32} The narrow intermediate interval of potentials may likely be associated with the following factors:

- (i) freezing of fluctuations at the lower voltage border of this region;
- (ii) an excess of ions of one sign typical for overscreening (which never favors the order) below that border;
- (iii) re-entrant increase of the population of one kind of ions above the border, without building yet Wigner crystals due to small charge of and relatively complicated shape of the ions.

Due to the novelty, depth, and breadth of analysis, ref 7 comprises a milestone in the theory of the double layer of ionic liquids, but it is, nevertheless, not the first one to predict voltage-induced structural transitions in it.

Not for RTILs, but for molten salts, using molecular dynamic simulations a group of authors, including two of ref 7, obtained clear signatures of structural ordering in the double layer.³³ This was shown for a model molten salt LiCl on Al(100) electrode. Crystallization was also voltage induced and occurred in the first ionic layer adjacent to the electrode surface. The same study predicted, however, that for (110) the two first layers got crystallized by the corresponding voltage, but they have a completely different, nonstoichiometric structure. Thus, the effect of the 2D surface structure of the underlying metal was found to be important for the 3D double-layer structure. Reference 33 has also established the critical importance of electronic polarizability of the metal electrode (image forces) and of the ions. Without any of the two effects the adjacent layers remained liquid-like! (Note that the importance of image forces on the correlations of ions at the interface has been independently emphasized and explored by the group of Shklovskii³⁴.)

For RTILs, a year ago (if counted from the publication on the Web), Kirchner et al.³⁵ have reported molecular dynamic simulations in which ordering of ions in the double layer has been observed, as a function of both voltage and temperature (the temperature effects appeared to be, however, minor). As in the previous work³⁶ as well as many other earlier papers (for review see ref 2), Kirchner et al.³⁵ have found that the double layer has a multilayered structure with multiple alternating layers of counter- and co-ions at the electrode–RTIL interface. The new feature that they have obtained was that at certain electrode polarization within the alternating multilayer structure of the electrical double layer a structural transition takes place, which gives rise to a surface-frozen monolayer

adjacent to the electrode, characteristic of densely packed counterions. The authors refer to those structures as “Moire-like”. They have found that at this point a densely ordered monolayer of counterions close to the electrode surface coexists with apparently laterally nonstructured RTIL further from the electrode. This conclusion was qualitatively similar to the findings of Merlet et al.⁷ Note that the force field in ref 35 was not polarizable (i.e., image forces were not taken into account), but the effect of structural ordering was there!

To rationalize the criteria of formation of different structures at the interface Kirchner et al.³⁵ introduced a so-called surface charge compensation parameter κ . This dimensionless parameter is the ratio between the actual charge density on the electrode σ and the maximum charge density of a densely packed monolayer of the RTIL ions θ_{\max} , i.e., $\kappa = \sigma/\theta_{\max}$, the parameter implicitly used already in ref 31. It has been suggested and demonstrated in ref 35 and further stressed in a later critical review by Ivaniššev and Fedorov³⁷ that the charge compensation parameter κ may be used for qualitative description of structural transitions in the double layer upon charging the interface in *different* RTILs. These findings give hope that with a proper theoretical ansatz one can reveal general trends in the seemingly complex picture of structural transitions in the double layer in RTIL systems. However, more work is required to prove that this hope is not illusive.

The emergence of Moire-like structures agrees with experimental STM patterns observed at the interface between Au(111) and 1-butyl-3-methylimidazoliumhexafluorophosphate.⁹ However, it was never clear in those pioneering experiments whether this was not in some way associated with the field-induced surface reconstruction of gold. In the simulations by Kirchner et al.,³⁵ as well as in Merlet et al.,⁷ the electrode does not reconstruct, so that the electric-field-induced transitions that both groups observed are the features of the double layer in RTILs.

Kirchner et al.³⁵ also reported the formation of herringbone interfacial structures at higher surface charge densities. These appear as a result of superposition of two ordered monolayers of RTIL ions at the electrode–RTIL interface. Merlet et al.,⁷ however, do not observe such structures, which can be due to several reasons. When simulating electrode polarization Kirchner et al. conducted constant charge simulations, whereas Merlet et al. performed more realistic and self-consistent constant voltage simulations in which the charge on the electrode atoms responds dynamically to the ions around them. Furthermore, the atomistic force fields used by the two groups to model their “RTILs” were different. One of the lessening signatures presented by Merlet et al. was the lateral correlation function (the Fourier transform of the in-plane correlation function), an objective characteristic of the degree of lateral ordering of the layer. The paper shows and discusses the evolution of that structure factor $S(k)$. The method of histogram reweighting introduced in ref 7 allows predicting the evolution of this structure factor as a function of voltage in a much more accurate manner than previously possible. Some interesting lateral structures of cations and anions have also been observed in the MD-simulations of Paek et al.³⁸ on graphene, but they have not been characterized in detail.

Lateral ordering of the first layer, of course, does not mean that the double layer becomes “2D”. The quantification of the sharp transition of lateral arrangements of ions during the electrification of electrodes, along with the information on the distribution of ions in the direction normal to the electrode,

provides unequivocal evidence of the 3D nature of the double layers in RTILs and under some conditions presumably also in molten salts.

As we stressed above, the particular feature of both simulations^{7,35} is that the field-induced surface reconstruction is excluded, so that the transitions are solely due to the nontrivial *response of the liquid* to the external electric field. Electrochemistry has encountered such situations in the past. Water in the compact layer was often considered liquid at low fields, but it becomes “frozen” and ordered at larger fields that suppress the translational and orientational freedom of the molecules, giving them a chance to build more stable 2D-like networks of hydrogen bonds. However, with the further increase of the voltage, those structures get destroyed by strong electric fields, when all molecules in the layer are oriented in the field and bonding between them is impeded. Signatures of such transitions were much less clear,²³ and generally such analogies are interesting but in no way direct.

■ FROM 2D TO “2 + 1D” IN NARROW GAPS: THE REALITY OF NANOSTRUCTURED SUPERCAPACITORS AND NANOTRIBOLOGY

The trend to look at double layers in ionic liquids as 3D entities, with structures in both lateral and vertical directions, is also emerging from the studies of double layers in narrow gaps. These studies probed the double layers from two different angles, one from the charge storage/transport perspective and one from the tribology perspective. Studies of the double layers in narrow gaps from the charge storage/transport perspective are motivated by the development of supercapacitors based on nanostructured electrodes. They were initially focused on the lateral packing of ions inside nanopores (i.e., double layers’ 2D aspects). In such systems, the pores are often only slightly wider than the ion diameter, and charge storage is controlled mostly by the lateral packing and interionic interactions. Because the lateral ion–ion interactions are screened strongly by the metallic walls and such screening is stronger in narrower pores, narrower pores store charge more effectively.^{39–42} This helps explain the anomalous enhancement of capacitance in subnanometer pores,⁴³ which has puzzled both experimental and theoretical communities for quite a while. More interestingly, the relative abundance and lateral packing of counterions and co-ions in these pores can be tuned by varying electrode voltage. For example, a first-order phase transition separating co-ion rich and co-ion deficient phases has been predicted in mean-field theories,³⁹ and counterion and co-ion demixing has been observed in MD simulations.^{44,45} As in the case of open electrodes, the variation of these 2D characteristics of the double layers also greatly affects their thermodynamic and dynamic properties. For example, the counterion and co-ion demixing leads to a peak in the capacitance–voltage curve⁴⁴ and, perhaps more importantly, a sharp increase of the self-diffusion coefficient of ions inside very narrow pores.⁴⁶ The latter effect originates from the disruption of interlocked counter/co-ion lattice and plays a fundamental role in the unexpected fast charging dynamics in narrow pores.⁴⁷

Once the width of the nanopore exceeds twice that of the ion diameter, the double layers inside the pores are no longer quasi-2D entities, and the distribution of ions in the direction normal to the pore wall may start to affect double layers’ macroscopic properties. In a trio of papers published practically at the same time, it was revealed that the capacitance of nanopores oscillates when pore width increases from one to several ion

diameters.^{48–50} Jiang et al. and Feng and Cummings both attributed such an oscillation to the interference of the double layers adjacent to the opposing walls of the same nanopore.^{49,50} Such a view clearly goes beyond the 2D lateral packing picture of double layers and highlights that the distribution of ions across the pore must be examined. A 2D + 1D picture of the double layers in narrow gaps is pushed somewhat further in Wu et al.'s work.⁴⁸ There, it was observed that when the pore accommodates just one contact pair of counterion and co-ion in the cross-pore direction at the potential of zero charge (PZC) conditions the capacitance–pore width curve exhibits a distinct peak. Their analysis indicated that this capacitance peak originates from the perfect pairing of cations and anions in *both* lateral and cross-pore directions at the PZC condition and the disruption of such 3D ion pairing (termed ionic solvation in that work) upon electrification of the pore. Their analysis thus attempted to treat double layers as quasi-3D entities and addressed how the response of the quasi-3D structures to electrification governs the capacitance of the nanopore.

Yet another way to appreciate the 3D nature of double layers is to probe the tribology of double layers confined in narrow gaps. Surface force measurements can probe directly the layering of counterions and co-ions inside the narrow gap and indirectly the organization of ions in the lateral and perpendicular directions. Such measurements are thus useful for inferring the 3D double-layer organization in narrow gaps and their response to external stimuli (e.g., pressure across film and shearing speed). Perkin et al. reported the first study of shearing ionic liquid films confined between mica surfaces.⁵¹ Their measurement of normal force provides clear evidence for the formation of distinct ion layers inside the narrow gaps. More importantly, measurement of the shearing force indicated that the yield stress for shearing is relatively low and sliding is smooth (rather than stick–slip) when sheared. These observations suggest that the ordering of ions in the lateral direction is not crystalline-like but likely features disorder of ions. More recently, the Perkin group has further demonstrated quantized frictions between two microspheres filled with up to nine ionic layers.⁵² Since the friction between two sliding surfaces depends on the ordering of ions between them and the latter in turn depends on the surface charge, one should be able to manipulate the friction force by directly controlling the surface charge. While such an idea was not examined in the experiments by the Perkin group, it has been demonstrated recently. Specifically, Li et al. showed that the friction behavior can be controlled by varying the electrical potential of the sliding surfaces.⁵³ Clearly, the organization of interfacial ions in both lateral and normal directions, their response to the surface potential, and their commensurability with structure of the underlying surface are crucial for understanding the observed challenging effects.

The insights on the 3D nature of double layers near open electrodes, in particular the phase transition in lateral directions and its correlation with the divergence of differential capacitance,⁷ help, although not always directly, the understanding of double layers in nanopores and nanogaps. Most importantly, those insights call for in-depth characterization of the structure of double layers in the lateral direction with pore/gap width and operating conditions such as electrode voltage and sliding velocities. Such characterization will benefit from the quantitative structural characterization reported in ref 7 and can lead to better understanding of effects such as “interference of the double layers”. In turn, the ideas from prior studies of

double layers in nanopores influence the study of 3D double layers near open electrodes. In prior analysis of the double layers in nanopores, the importance of clarifying how the quasi-3D or 1D + 2D structure of the double layers (in particular, the local coordination of counterions and co-ions^{48,46}) *varies in response to* the electrification of the pore walls was highlighted, and a theoretical framework was developed to connect the structural variation to the double-layer capacitance.⁴⁸ Analysis of these aspects should provide further insights into possible singularities (sharp peaks) of the of double-layer capacitance near open electrodes when structural transitions in the lateral plane occur.

■ NEW CHALLENGES AND OPPORTUNITIES

Pioneering experimental investigations^{18–20} and mechanistic computer simulation studies^{7,16,35} trigger a “change of the angle of attack” in the theory of the double layers in ionic liquids at open interfaces, refocusing it from perpendicular to lateral distributions. Meanwhile, studies of double layers confined in narrow gaps, which initially focused on the lateral distributions of ions, have led to the conclusion that the packing of ions in both lateral and perpendicular directions exhibits rich behavior.^{39,40,44,48} All in all, these findings point to double layers in concentrated systems such as ionic liquids being entities with rich 3D structures that can be tailored by a variety of means, e.g., electrode voltage, confinement, and shearing, to name just a few.

Although not counterintuitive, a turn from the simpler 1D or 2D pictures of double layers in ionic liquids also shows that the structure of the double layer in RTILs, which just a year ago seemed to be majorly understood, still raises new puzzles and challenges for the theory. Perhaps one of the most essential issues to address is how the lateral arrangement of ions is coupled with their distribution in the perpendicular directions; namely, how is it affected by overscreening? Generally, how is coupling between lateral and perpendicular distribution of ions controlled by the electrode potential, the molecular structure of the ions, and the solid substrate, as well as the mechanical factors such as shear and normal stress? While prior studies have already provided some hints on these issues, deeper and systematic exploration is needed.

It is, of course, legitimate to ask, why should we care about the emergence of 3D structures in double layers, apart from the fact that order–disorder transitions are curious physical phenomena. Near open interfaces, the formation of a crystalline-like layer may have rich consequences in electrode kinetics. RTILs are considered to be promising solvents for various electrode reactions of solutes dissolved in them that are supposed to take place at the interface at voltages lower than the electrochemical decomposition of the constituent ions. Therefore, the emergence of a “solid-like” layer at the interface may affect the penetration of the solute across this layer to the immediate vicinity of the electrode. Since the solute reactant will have the same charge as the ions of RTILs dominating the first layer, the history of the reactant's presence in the layer could cause strong hysteresis of the current–voltage characteristics. It may look different, whether the reactants have reached the surface of the electrode before or after the first surface layer gets frozen. Developing measures to avoid hysteresis, or utilize it, will require understanding of the emerging structures both in lateral and perpendicular directions. In narrow gaps, the 3D packing of ions and their response to external stimuli such as electrification and shearing have already been shown to affect

the thermodynamics and dynamics of the charge storage in nanopores,^{39,40,44,48–50} and the friction between solid surfaces.^{51–53} Further understanding of these effects may open doors for manipulation of the 3D packing of ions inside narrow pores or gaps to achieve more efficient energy storage or lubrication.

The 3D structure of double layers and their response to external stimuli, the importance of which became obvious in ionic liquids, will seemingly occupy theorists and experimentalists in the next few years, driven first, as usual, by curiosity, but the interest in them will be further boosted by applications in energy storage, voltage-controlled tribology, and electrocatalysis. With no doubt, there will be exciting discoveries ahead!

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Notes

Views expressed in this editorial are those of the authors and not necessarily the views of the ACS.

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