Transition from non-monotonic to monotonic electrical diffuse layers: impact of confinement on ionic liquids

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Intense investigations of room temperature ionic liquids have revealed not only their advantages in a wide range of technological applications but also triggered scientific debates about charge distribution properties within the bulk and near the solid–liquid interfaces. While many observations report on an alternating charge layering (i.e., spatially extended decaying charge density oscillations), there are recent conjectures that ionic liquids bear similarity to dilute electrolytes. Using a modified Poisson–Nernst–Planck model for ionic liquids (after Bazant et al., Phys. Rev. Lett. 2011, 106, 046102), we show that both behaviors are fundamental properties of ionic liquids. The transition from the non-monotonic (oscillatory) to the monotonic structure of electrical diffuse layers appears to non-trivially depend on ionic density in the bulk, electrostatic correlation length, confinement and surface properties. Consequently, the results not only reconcile the empirical results but also provide a powerful methodology to gain insights into the nonlinear aspects of concentrated electrolytes.

Room temperature ionic liquids (RTILs) have become an increasing subject of investigations due to their unique physicochemical properties and their advantages in numerous technological applications. Fundamental and yet unclear characteristics of RTILs concern the spatial organization of anions and cations in the bulk and at liquid–solid interfaces, both significant to electrochemical applications. While many studies have reported on novel self-assembled charge layering near surfaces, it was recently conjectured that nevertheless RTILs bear similarity to dilute electrolytes, where decrease in conductivity and monotonic decay of the electrical diffuse layer (EDL) was explained by ion association. The latter observation implies fundamental controversy regarding the basic nature of RTILs and thus the subject that we attempt to advance in this study.

The charge layering phenomenon at the liquid–solid interface can be viewed as a non-monotonic (spatially oscillatory) EDL displaying an alternating segregation of cations and anions that decay toward the bulk region. For metal surfaces this layering was attributed to ‘overscreening’ of the electrode potential. However, a similar behavior is also found in experiments employing confined RTILs with surface charge and no applied voltage, suggesting that electrical ordering is a generic meso-scale self-assembly property of RTILs. In general, the physicochemical origin of such phenomena is a combination of many interactions (electrostatic, van der Waals, hydrogen-bonding, etc.) that result between two confined solid surfaces making it difficult to construct an intuitive theoretical framework as the macroscopic Poisson–Nernst–Planck (PNP) type formulation. In this direction, Bazant et al. have proposed a modification for the PNP equations by taking into account both steric effects and electrostatic correlations. The inclusion of the latter showed that the EDL can exhibit spatial oscillations (due to overscreening) under both high and low applied voltages and as such, these oscillations are independent of the condensed layer that forms near the surface at high applied voltages due to steric effects (crowding).

To investigate (and reconcile) the RTIL spatial properties, we implement spatial dynamics methods and show that in confined ionic liquids electrostatic correlations are not the only driving force and that the EDL structure also depends on ionic density in the bulk. The analysis exploits the methodology developed for reaction–diffusion–migration systems, i.e., the selection mechanism of spatial patterns using boundary conditions. Through a semi-phenomenological modified PNP model, we show the existence of spatially extended oscillations already in the bulk even in the absence of any confinement. On infinite domains these oscillations are temporally unstable and being stabilized for example, under applied voltages. In addition, under applied voltages, the charges are attracted and accumulated near the surfaces and thus reduce the ion density within the bulk. Consequently, depletion of ions within the bulk and the extent of electrostatic correlations may lead to monotonic EDL structure.
where \( c(x,t) \) is the local ion density, \( \rho(x,t) \) is the local charge density, \( \phi(x) \) is the electric potential, \( l_c \) is the ratio between the electrostatic length scale and Debye length \( \left( \lambda_D = \sqrt{\varepsilon R T/(2F^2 C_0)} \right) \), \( R \) is the ideal gas constant, \( T \) is the absolute temperature, \( F \) is the Faraday constant, \( \varepsilon \) is the dielectric permittivity and \( \nu \) characterizes the ability of the liquid to compress (we use here \( \nu = 0.5 \)), i.e. molecular packing; for details and physical interpretations of the model, we refer the reader to ref. 49 and the references therein. Eqn (1) were obtained from the original equations by rescaling the spatial scale by \( \lambda_D \), time by \( \lambda_D^2/D \) (where \( D \) is the diffusion coefficient that is taken here to be equal for anions and cations), potential by \( RT/F \) and defining \( c = (c_+ + c_-)/(2C_0), \rho = (c_+ - c_-)/(2C_0), \) where \( C_0 = C_\pm \) is the ion concentration of each in the absence of the electrical field. Eqn (1) is supplemented by boundary conditions (BCs) that correspond to inert (no charge transfer) electrodes and fixed potentials.

Numerical solutions of the above model showed that the spatially oscillatory nature of the EDL is independent of the applied voltages.\(^{36} \) This observation in turn, implies an inherited oscillatory structure that is already ‘hidden’ within the bulk, as has been shown in reaction–diffusion–migration systems, for example.\(^{46,47} \) Thus, the knowledge regarding the spatial bulk structure is an important missing piece in the mechanism behind EDL emergence. To understand the spatial structure of the EDL, we first consider an infinite bulk while the impact of the boundary conditions follows at later stages.

### Spatially oscillatory structure in an infinite bulk

To study the nonuniform spatial properties within the bulk we employ the spatial dynamics methods, i.e., due to flux conservation; we rewrite (after some algebra) eqn (1) as a set of ordinary differential equations:

\[
\begin{align*}
\frac{\partial c}{\partial t} &= \frac{\partial}{\partial x} J^c = \frac{\partial}{\partial x} \left( \frac{\partial c}{\partial x} + \rho \frac{\partial \phi}{\partial x} + \frac{\nu \rho}{1 - \nu \rho} \frac{\partial c}{\partial x} \right), \\
\frac{\partial \rho}{\partial t} &= \frac{\partial}{\partial x} J^\rho = \frac{\partial}{\partial x} \left( \frac{\partial \rho}{\partial x} + \rho \frac{\partial \phi}{\partial x} + \frac{\nu \rho}{1 - \nu \rho} \frac{\partial c}{\partial x} \right), \\
\left( l_c^2 \frac{\partial^2 \phi}{\partial x^2} - 1 \right) \frac{\partial^2 \phi}{\partial x^2} &= \rho,
\end{align*}
\]

where \( c(x,t) \) is the local ion density, \( \rho(x,t) \) is the local charge density, \( \phi(x) \) is the electric potential, \( l_c \) is the ratio between the electrostatic length scale and Debye length \( \left( \lambda_D = \sqrt{\varepsilon R T/(2F^2 C_0)} \right) \), \( R \) is the ideal gas constant, \( T \) is the absolute temperature, \( F \) is the Faraday constant, \( \varepsilon \) is the dielectric permittivity and \( \nu \) characterizes the ability of the liquid to compress (we use here \( \nu = 0.5 \)), i.e. molecular packing; for details and physical interpretations of the model, we refer the reader to ref. 49 and the references therein. Eqn (1) were obtained from the original equations by rescaling the spatial scale by \( \lambda_D \), time by \( \lambda_D^2/D \) (where \( D \) is the diffusion coefficient that is taken here to be equal for anions and cations), potential by \( RT/F \) and defining \( c = (c_+ + c_-)/(2C_0), \rho = (c_+ - c_-)/(2C_0), \) where \( C_0 = C_\pm \) is the ion concentration of each in the absence of the electrical field. Eqn (1) is supplemented by boundary conditions (BCs) that correspond to inert (no charge transfer) electrodes and fixed potentials.

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\[
\begin{align*}
\frac{\partial c}{\partial t} &= (1 - \nu \rho) E \rho, \\
\frac{\partial \rho}{\partial t} &= (c - \nu \rho^2) E, \\
E' &= u, \\
w' &= l_c^{-2}(u - \rho),
\end{align*}
\]

where \( E = -\partial_x \phi \) and primes denote derivatives with respect to the spatial coordinate.

In the absence of applied potential, eqn (1) admit a uniform steady state \((c_*, \rho_*, \phi) = (c^*, 0, 0)\). With this respect, weak spatial
deviations about the uniform state can be viewed as a spatial ‘instability’ that obeys the following form:

\[
\begin{pmatrix}
  c \\
  \rho \\
  E \\
  u \\
  w
\end{pmatrix} - \begin{pmatrix}
  c' \\
  0 \\
  0 \\
  0 \\
  0
\end{pmatrix} \propto \delta e^{-\tilde{x}t} + O(\delta^2),
\]

(3)

where $|\delta| \ll 1$ is an auxiliary parameter. By inserting (3) into (2) and solving for $\lambda$, we obtain five eigenvalues:

\[
\begin{align*}
\lambda_0 &= 0, \\
\lambda_\pm^2 &= \frac{1}{2L^2}(1 \pm \sqrt{1 - 4l_c^2c^*}).
\end{align*}
\]

(4a) \quad (4b)

The trivial eigenvalue corresponds to the translational invariance of the concentration ($c^*$). The other four eigenvalues are either real or complex conjugated, depending on the relation between the electrostatic correlation length and the ionic concentration according to:

\[
l_c^* = \frac{1}{2\sqrt{c^*}}
\]

(5)

Notably, eqn (4b) is identical to an ansatz that was used for low applied voltages ($V < RT/F$) and electro-neutrality $\rho = 0$, $c^* = 1$.\footnote{Under these assumptions the transition between weak and strong electrolytes occurs at $l_c = 1/2$, which is in agreement with (5).}

The distinct configurations of the spatial eigenvalues are presented in Fig. 2. At the onset $l_c = l_c^*$ (right inset), there is a double multiplicity at the real axis, for which $\lambda_+ = -\lambda_-$. For $l_c < l_c^*$ (left inset), the four eigenvalues are real while for $l_c > l_c^*$ (top inset), the eigenvalues become complex conjugated. Under an applied voltage, since $3m_\pm$ corresponds to a wavenumber and the potential is antisymmetric [$\varphi(x) = -\varphi(-x)$], the former case corresponds to a monotonic approach toward $x \to 0^+$ while the latter case corresponds to spatially decaying oscillations.

This behavior can be numerically verified (including the resulting period of the oscillations, $2\pi(3m_\pm)$) by assuming a large domain, $L \gg 1$ (in dimensional units $L \gg l_D$ and $c^* (x \to 0^+) \to 1$), as shown in Fig. 3 for $l_c = l_c^* = 0.5$ and $l_c = 10 > l_c^*$ [the oscillations amplitude $\propto \Re\varphi_{l_c}$ increases with $l_c$, as given by (4b)]. Note that without any applied voltages (as BCs), these deviations decay in time to a uniform state.

The lower limit for electrostatic correlations is of order of the Bjerrum length which due to large ion sizes is of order of $nm$. Now, for fully dissociated ions of RTILs $\lambda_D \sim \Lambda$ for which $l_c > 1$ and thus the criterion (5) is always fulfilled. The latter leads to the emergence of an oscillatory EDL structure, as has been also observed by more refined computations. However, following the recent observations, ions in RTILs may not obey full dissociation.\footnote{Namely, under “dilution” of RTILs $\lambda_D$ increases towards the nm size and thus $l_c$ significantly decreases,\footnote{and, i.e., $l_c \leq 1$, and thus depletion of ion density, contributes significantly to the spatial structure of the EDL. For large separation distances between electrodes, the bulk impact is negligible; however, bulk ion density does become crucial under small confinements, as will be demonstrated next.}

**Diffuse layer emergence under confinement**

Here we consider confinements of moderate separation distances [$L/2 \sim O(10–100)$] (in dimensional units $L/2 \sim O(10–100 \times 10)$) and applied voltages $V \sim O(10)$ (in dimensional units $V \sim O(10 \times V/F)$).

To show that the above analysis also holds under these conditions, we perform numerical integrations and supplement eqn (1) with boundary conditions at $x = \pm L/2$: (6a) \quad (6b)

\[
\begin{align*}
J^c &= J^\rho = 0, \\
\varphi &= \pm V,
\end{align*}
\]

(6c)

which corresponds to inert electrodes (i.e., no charge transfer) and constant potential with no electrostatic correlations at solid surfaces. The initial conditions $c(\pm L/2,\rho(\pm L/2),\varphi(\pm L/2))$ are $(c,\rho,\varphi) = (1.0,2V/L)$.\footnote{This is in agreement with recent observations, ions in RTILs may not obey full dissociation. However, following the recent observations, ions in RTILs may not obey full dissociation. Namely, under “dilution” of RTILs $\lambda_D$ increases towards the nm size and thus $l_c$ significantly decreases,\footnote{and, i.e., $l_c \leq 1$, and thus depletion of ion density, contributes significantly to the spatial structure of the EDL. For large separation distances between electrodes, the bulk impact is negligible; however, bulk ion density does become crucial under small confinements, as will be demonstrated next.}
Asymptotic solutions of eqn (1) show that near the electrodes there is a mass/charge saturation due to steric constraints, a so called ‘crowding’ effect, according to \( \varepsilon = \rho = \nu^{-1} \). Naturally, the larger the applied potential the wider is the saturation plateau since more ions are being attracted towards the surface. On the other hand, widening of the plateau regions (near the electrodes) reduces \( \varepsilon \) in the bulk. This enables the densities and potential that decay toward the bulk to be either monotonic or non-monotonic (oscillatory) depending on the value of \( l_c \), as shown in Fig. 4. The transition from non-monotonic to monotonic EDLs is found to correspond well to the criterion given by (5): there exist \( l_c \) for which the ion density in the bulk becomes lower than the respective critical value, i.e., around \( x = 0: \varepsilon > \varepsilon^*(l_c) \) for non-monotonic and \( \varepsilon < \varepsilon^*(l_c) \) for monotonic.

The behavior described above is rather general and can be also obtained by keeping \( l_c \) constant and varying either domain size, applied voltage or molecular packing (\( \nu \)). Due to our interest in a confined medium, we chose to demonstrate the effect via domain size since in most applications electrolytes are desirably to be confined at meso-scales (10–100 nm). In such a situation, the bulk approaches quasi-electroneutrality and yet, the criterion for the transition from non-monotonic to monotonic diffuse layer can also be efficiently deduced even for large potentials and for relatively small separation distances (as shown in Fig. 5). However, once the separation distance becomes of the order of 1, screening of the electrical field is impossible and electroneutrality cannot be approached.

Existence of spatially extended bulk oscillations also explains charge layering observed in RTILs under equal surfaces, as schematically described in Fig. 1. Importantly, the RTILs in this setup are not subjected to any applied voltage (but rather to a surface charge) and yet exhibit layering (spatial oscillations). This phenomenon is consistent with the analysis discussed here since under symmetric surfaces the solution obeys even symmetry in space (unlike odd symmetry as in the previous case):

\[
\begin{bmatrix}
\varepsilon(x) \\
\rho(x) \\
\varphi(x)
\end{bmatrix} = \begin{bmatrix}
\varepsilon(-x) \\
\rho(-x) \\
\varphi(-x)
\end{bmatrix}.
\]

As such, once the separation distance is increased, additional charge layers are added to the bulk, making the charge at the mid-plane change signs exactly as described by Perkin.

**Dynamical properties of the emergent diffuse layer**

Another significant property of non-monotonic diffuse layers is related to a transient current that is developed under applied constant voltage. Thus, we compare between transient currents that are developed for monotonic and non-monotonic EDLs, as shown in Fig. 6. The current is evaluated via integration of the charge flux over the domain:

\[
I = \frac{1}{L} \left[ \frac{1}{L} \int_{-L/2}^{L/2} \left( \frac{\partial \rho}{\partial x} + \frac{\nu \varepsilon}{1 - \nu \varepsilon} \frac{\partial \varepsilon}{\partial x} \right) dx \right] dx,
\]

where at each time step the profiles are computed numerically from eqn (1), as shown through representative profiles in Fig. 7. For large \( L \gg 1 \) or small \( L \sim O(10) \) domains, the transient currents are expected to be dominated by the formation of the condensed layer near the electrode (i.e., the crowding effect). At moderate distances, \( L \sim O(100) \), spatially extended oscillations occupy a significant portion of the domain and thus their formation contributes significantly to the transient current. The current decay can be qualitatively divided into three temporal stages (Fig. 7):

(A) Initial formation of space charge [representative profiles in Fig. 7 at \( t = 20 \) in (a) and \( t = 50 \) in (b)], which also marks a ‘breaking’ point as shown in the inset of Fig. 6;

(B) Development of the plateau near the electrode [representative profiles in Fig. 7 at \( t = 50 \) in (a) and \( t = 120 \) in (b)]. Note that the profile in (b) already exhibits weak spatial oscillations;

(C) Approach to quasi-electroneutrality (\( I \to 0 \) as \( t \to \infty \)) and enhancement of spatial oscillations [representative profile in Fig. 7 at \( t = 200 \) in (b)] while in (a) there is no significant change.

Although at later times both monotonic and nonmonotonic behaviors exhibit exponential decay (see inset in Fig. 6), spatial oscillations play the role of ‘rate determining step’ since already in stage (B) they dominate the decay rate even though they are just being formed. Moreover, since these oscillations are extended all over the bulk, the system will not reach ultimate

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Fig. 4 Ion density and charge (inset) profiles for distinct values of \( l_c > l^*_c \) (thin line), \( l_c \) slightly above \( l^*_c \) (thick line) and \( l_c < l^*_c \) (dashed line). The critical ion density for \( l_c = 0.6 \) is marked by the dotted line while for all other values of \( l_c \) the critical density is way below the bulk density. Eqn (1) were numerically integrated with \( V = 10 \) and \( L = 22 \).

Fig. 5 Distinct ion density and charge (inset) profiles for \( l_c = 1 \), above (solid line) and below (dashed line) the onset. Eqn (1) were numerically integrated with \( V = 10 \) and \( L = 22 \) (solid line) and \( L = 20 \) (dashed line).
electroneutrality under meso-scale confinement (i.e. a uniform bulk state for which \( \rho = E = 0 \)).

Conclusions

To conclude, studies of RTILs demonstrate not only their advantages in technological applications but also debate about the physicochemical properties of highly concentrated electrolytes, such as spatial distributions of ions near the solid surfaces (the EDL structure). While many studies have reported on alternating layers of opposite ions near the surfaces it was recently conjectured through a revision of empirical methods that RTILs are not much different from dilute electrolytes. Using spatial dynamics methods, we have demonstrated the nature of decaying charge distributions near the surfaces are in fact enslaved by the bulk and thus, EDLs in RTILs can exhibit both ion layering and a standard decaying behavior as in dilute electrolytes. Since the EDL structure is very basic to technological applications, we hope that the approach and results provided here will allow new vistas and advances.

To resolve the emergence of spatiotemporal ion distributions, we have analyzed a modified PNP model which captures semiphenomenologically the critical physicochemical basis of RTILs and it is ‘simple’ enough to allow analytic explorations. Particularly, we showed that non-monotonic (spatially oscillatory charge layering) and monotonic EDL behaviors are both properties of confined RTILs. This unusual emergence of the EDLs stems from the missing puzzle piece that is related to the existence of spatial oscillations already in the bulk. Consequently, the overall EDL behavior (transition from non-monotonic to monotonic) is determined by electrostatic correlations and ion density in the bulk. The decrease in ionic density, however, depends implicitly on applied voltages, molecular packing, domain size and ionic dissociation level (the latter was very recently conjectured by Gebbie et al.). The results appear to be general and apply equally to systems with metal electrodes (under applied voltage) and to confined RTILs under identical surfaces (no applied voltage). In addition, we have performed a temporal analysis (chronoamperometry) and showed that development of spatial oscillations results in an exponential current decay which indeed bears qualitative similarity to dilute electrolytes but with a distinct time scale, as has already been conjectured for low applied voltages (\( V < RT/F \)). Thus, our results should allow conduction and control of specifically targeted experiments toward realization of the basic EDL properties.

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References
