

Mean-Field Theory of the Electrical Double Layer in Ionic Liquids



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Introduction

Ionic liquids (ILs) are superconcentrated electrolytes of great interest in energy storage devices. The lack of electrolysable solvents, since ILs are solely composed of cations and anions, means the voltages that ILs can withstand (~ 3 V) are roughly twice that of conventional aqueous electrolytes [1]. As the energy stored increases with the voltage, ILs are promising candidates as electrolytes for electrical double layer supercapacitors.

In such a capacitor, electrodes are in contact with an electrolyte. The ions in the electrolyte redistribute such that they reside in energetically

favorable electrostatic environments, forming a layer rich in countercharges that screens the electrostatic fields arising from the charged electrodes. This structure is commonly referred to as the electrical double layer (EDL). The work done separating charges in the EDL is stored as energy in EDL capacitors.

The intensive study of EDL capacitors with ILs has burgeoned theories for the EDL. The theory one develops for the EDL sensitively depends on the geometry of the interface: In highly porous electrodes with nanoconfined, overlapping EDLs, the structure differs from isolated planar electrodes. Here we focus on the equilibrium EDL structure in ILs at planar interfaces (note we do not review specific surface interactions with the ions but only focus on the space-charge of the IL). Importantly, the equilibrium theory serves as a starting point for describing ionic transport out-of-equilibrium [2, 3]. The case of nanoconfinement exhibits very different physics, which depends both on the charge screening of the electrode material as well as the electrolyte. For a review of possible and observed effects in nanoconfinement, see Ref. [1].

In pure ILs, the concentration of the electrolyte is approximately determined by the size of the composing ions. As the cations are typically large organic molecules and the anions are often bulky inorganic molecules, the concentration of ions is in the range of 1–10 M [1, 4]. Since there is no solvent present in *pure* ILs, there are strong electrostatic and steric interactions between the

ions. Furthermore, the structures and chemistries of the ions can be vastly different, which means that despite two ILs having a similar concentration, their properties can be quite distinct. Therefore, one requires a general theory of the EDL in ILs which not only includes strong electrostatic and steric interactions, but also retains at least some elements of chemical specificity.

These three requirements clearly manifest themselves in the EDL of ILs, where there are mainly two regimes of behavior. At small voltages, there is the overscreening regime [1, 5, 6]. This is where the charge density exhibits decaying oscillations from the interface, with a period of the order of an ion diameter, that propagates many ion diameters into the liquid [1, 5, 6]. The overscreening structure is a direct consequence of electrostatic interactions between densely packed ions [7]. At larger voltages, the overscreening structure gives way to a crowding regime, where layers of counterions line up before the overscreening structure appears at distances further from the electrode, where the majority of the electrode charge is already screened [1, 5–7]. The crowding regime is dominated by the steric interactions [7–9]. Depending on the chemistry of the ions, the electrochemical signatures of overscreening and overcrowding are quite sensitive [1]. For example, when the cation has a long alkyl chain, the overscreening regime is further complicated by the orientation of the cations: The charged part of the cation prefers to be closer to the interface, causing a peak in the capacitance at moderate voltages from the compression (“electrostriction”) of the EDL [10].

These features (electrostatic, steric, and specific interactions) can be captured by simple mean-field theories of the EDL with varying levels of complexity. We first outline the general formalism used for such theories of the EDL. We shall summarize theories of the EDL of neat ILs within the local density approximation, and then move onto more accurate theories. We also briefly review some advancements of solvent impurities and mixtures of ILs. Finally, we summarize the underscreening paradox, and other directions of research.

General Formalism

Here theories based on classical density functional theory (cDFT) for the EDL in ILs near planar interfaces are reviewed. The free energy, \mathcal{F} , of ILs in proximity to electrified interfaces can be separated into two components

$$\mathcal{F} = \mathcal{F}_{\text{el}} + \mathcal{F}_{\text{chem}}, \quad (1)$$

(i) the electrostatic contribution, \mathcal{F}_{el} , which describes the energetics of the electrostatic fields and the electrostatic interactions between the ions, and also (ii) the chemical contribution, $\mathcal{F}_{\text{chem}}$, which accounts for energy and entropic contributions from excluded volume effects and specific interactions. These contributions can be further subdivided into ideal contributions – those which apply for dilute solutions – and excess contributions – which are required for concentrated solutions.

In a mean-field theory, assuming that the effective dielectric response (in the way that it counts for degrees of freedom not explicitly accounted for in the theory) of the IL is a constant, the ideal electrostatic contribution, $\mathcal{F}_{\text{el}}^{\text{id}}$, to the free energy is given by

$$\mathcal{F}_{\text{el}}^{\text{id}}[\phi, \rho] = \int d\mathbf{r} \left\{ -\frac{\epsilon}{2} [\nabla\phi(\mathbf{r})]^2 + \rho(\mathbf{r})\phi(\mathbf{r}) \right\}, \quad (2)$$

where ∇ is the differential operator and ρ and ϕ are the mean-field charge density and electrostatic potential of the IL, respectively. Within this mean-field approximation, the electrostatic potential is $\phi(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{4\pi\epsilon|\mathbf{r}-\mathbf{r}'|}$. Here the dielectric constant ϵ of the IL includes the contributions to system polarizability not explicitly accounted for in the rest of the theory. There can be internal contributions from the electronic polarizability of ions and dipolar contributions, if present. In addition, there can be contributions from the effective dipolar moments of ionic pairs and clusters. These all contribute to the, so-called, high frequency dielectric constant that is measured to be 10–20 [4]. In the EDL, this value can actually change due to

effects that we will discuss later. For now, let us consider ε to be constant.

Taking the functional derivative of the free energy with respect to the electrostatic potential, $\delta\mathcal{F}/\delta\phi = 0$ yields

$$\varepsilon\nabla^2\phi(\mathbf{r}) = -\rho(\mathbf{r}). \quad (3)$$

This is the Poisson equation, with further knowledge of the charge density being required. The charge density is $\rho(\mathbf{r}) = q[c_+(\mathbf{r}) - c_-(\mathbf{r})]$, where q is the charge of an ion (note that when one is considering systems more complex than neat ILs, the expression for the charge density must be generalized), and $c_+(\mathbf{r})$ and $c_-(\mathbf{r})$ are the concentrations of cations and anions, respectively. There can be additional electrostatic contributions to the free energy, $\mathcal{F}_{\text{el}}^{\text{ex}}$, which either include electrostatic correlations or dielectric responses, that modify the Poisson equation. These excess electrostatic contributions shall be discussed later.

The ideal contribution to the chemical free energy, accounts for the entropy of ions that can move without any restrictions. Here k_B is Boltzmann's constant, T is temperature, and Λ is the thermal de Broglie wavelength. This ideal term is the basis of the classical Gouy-Chapman theory of the EDL of dilute electrolytes [1, 2].

$$\mathcal{F}_{\text{chem}}^{\text{id}}[c_+, c_-] = k_B T \sum_{i=\pm} \int d\mathbf{r} \{c_i(\mathbf{r}) [\ln\{\Lambda^3 c_i(\mathbf{r})\} - 1]\}, \quad (4)$$

The (electro)chemical potential of cations (anions), μ_+ (μ_-), is determined from minimizing the free energy with respect to the concentration of cations (anions). At equilibrium, the chemical potential of the cations (anions) in the bulk must equal the electrochemical potential of the cations (anions) in the EDL. Therefore, the equations for the concentration of ions are given by

$$c_{\pm} = \bar{c} \exp\{\beta[\mp q\phi + \Delta\mu_{\pm}^{\text{ex}}]\}, \quad (5)$$

where $\beta = 1/k_B T$, \bar{c} is the bulk concentration of salt, and $\Delta\mu_{\pm}^{\text{ex}}$ is the change in excess chemical potential (between the excess chemical potential

in the bulk and the excess electrochemical potential in the EDL), which can be both chemical and electrostatic in origin. Inserting these equations for concentration into the charge density yields a general Poisson-Boltzmann (PB) equation

$$\varepsilon\nabla^2\phi = -q\bar{c}(\exp\{\beta[-q\phi + \Delta\mu_+^{\text{ex}}]\} - \exp\{\beta[+q\phi + \Delta\mu_-^{\text{ex}}]\}). \quad (6)$$

It is by specifying $\Delta\mu_{\pm}^{\text{ex}}$ and solving such modified PB equations that we can describe the EDL of ILs. By linearizing this PB equation in the electrostatic potential for the case $\Delta\mu_+^{\text{ex}} = \Delta\mu_-^{\text{ex}}$, we obtain the Helmholtz equation

$$\nabla^2\phi = \kappa^2\phi, \quad (7)$$

where $\kappa = \sqrt{2q^2\bar{c}/k_B T\varepsilon}$ is the inverse Debye length, which is a key length scale that describes the ability of a dilute electrolyte to screen charge.

There are two physical observables of the EDL that we shall discuss: ionic density profiles and differential capacitance. The signatures of ionic density profiles are accessible through surface force measurements, but also molecular simulations can provide a great wealth of information on the interfacial arrangement of ions [1]. The differential capacitance is readily obtained from impedance experiments or from molecular simulations [1]. The differential capacitance describes the differential charge accumulated at the interface per change in electrode potential, as defined by

$$C = \frac{d\sigma}{d\phi_0}, \quad (8)$$

where $\sigma = -n \cdot \varepsilon \nabla \phi|_0$ is the surface charge density, with n denoting the vector normal to the planar interface, $|_0$ signifying evaluation at the interface, and ϕ_0 is the voltage drop across the entire EDL.

Neat Ionic Liquids

The “local density approximation” shall be reviewed first, where excluded volume effects, specific interactions, and electrostatics are only described with local, mean-field variables, after which the developments beyond the simplest theories of the EDL in ILs shall be discussed.

Local Density Approximation

To have qualitative agreement between theory and experiments/simulations for the differential capacitance, one must include excluded volume effects [1]. Before ILs, there were pioneering theories for excluded volume effects of ions in the EDL [2]. These approaches came ahead of their time, having not attracted the attention they deserved by those who worked with diluted electrolytic solutions. These approaches were independently “rediscovered” [1, 11], triggered by the study of the importance of these effects in ILs.

One of the first and simplest theories for excluded volume effects in ILs was an ideal lattice-gas model [8]. The multiplicity of ions distributed on the lattice, in the thermodynamic limit, gives an excess term which logarithmically diverges as the concentration of ions approaches the maximum concentration

$$\mu_{\pm}^{\text{ex}} = -k_{\text{B}}T \ln \{1 - \nu c_{+} - \nu c_{-}\}, \quad (9)$$

where ν is the volume of the ions/lattice sites, which is equal to the inverse of the maximum concentration of ions (assumed to be the same for cations and anions). For ILs, this was first proposed by Kornyshev [8], leading to a paradigm shift in the field, although an equivalent formulation had been introduced by Bikerman [12] and since rediscovered by several others [2, 11, 13] in the context of moderately concentrated electrolytes. As such, this term is often referred to as the Bikerman excess chemical potential, which takes the form $\mu^{\text{ex}} = -k_{\text{B}}T \ln \{1 - 2\nu\bar{c}\}$ in the bulk. The $\gamma = 2\nu\bar{c}$ term is referred to as the compacity of the IL [8], as it is a measure of how much the electrolyte can be compressed. In dilute electrolytes, $2\nu\bar{c} \approx 0$, such that this excess term is negligible (unless one is at large voltages

[11, 13]). For ILs however, $2\nu\bar{c} \approx 1$, as the size of ions/lattice sites determines the bulk concentration, meaning that excluded volume effects are extremely important.

Including this excess term results in the following modified PB equation

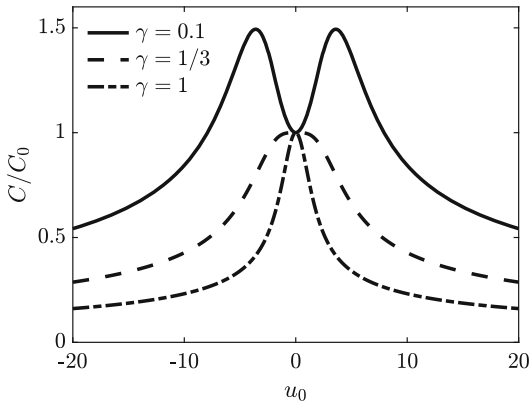
$$\nabla^2\phi = \frac{2q\bar{c}}{\varepsilon} \frac{\sinh(\beta q\phi)}{1 - 2\nu\bar{c} + 2\nu\bar{c} \cosh(\beta q\phi)}. \quad (10)$$

The excluded volume effects of the lattice model are naturally present in the Fermi-like functions for the concentration of ions. At very large positive (negative) voltages, the concentration of anions (cations) reaches the maximum concentration, $1/\nu$, and the concentration of cations (anions) tends toward 0. When the concentration reaches the maximum value, the system is said to be in the crowding regime. An advantage of the approach of Kornyshev [8] is that a closed-form analytical solution of the differential capacitance can be obtained

$$C = C_0 \frac{\cosh(u_0/2)}{1 + 4\nu\bar{c} \sinh^2(u_0/2)} \sqrt{\frac{4\nu\bar{c} \sinh^2(u_0/2)}{\ln \{1 + 4\nu\bar{c} \sinh^2(u_0/2)\}}}, \quad (11)$$

where $C_0 = \varepsilon\kappa$ is the Debye capacitance and $u_0 = \beta q\phi_0$ is the voltage drop across the EDL in units of thermal volts. It is interesting to note that this formula was also obtained by Kilic, Bazant, and Ajdari at the same time [11], but in the context of moderately concentrated electrolytes. In fact, as reviewed in Refs. [1, 2], this equation was first derived by Freise [14] based on Bikerman’s model [12].

The capacitance-voltage response predicted by Eq. (11) is qualitatively different depending on the compacity [8]. When the compacity tends to zero, the U-shape Gouy-Chapman differential capacitance curve [$C = C_0 \cosh(u_0/2)$] of dilute electrolytes is recovered [8]. For values of compacity that are not vanishingly small and satisfy $2\nu\bar{c} < 1/3$, the differential capacitance curve has a characteristic “camel”-shape [8]. That being, the differential



Mean-Field Theory of the Electrical Double Layer in Ionic Liquids, Fig. 1 Differential capacitance [calculated from Eq. (11) following Ref. [8] in units of Debye capacitance as a function of applied voltage in units of thermal volts. Differential capacitance curves are plotted for three values of the compacity, demonstrating the qualitatively different capacitance-voltage responses. The shape of the differential capacitance curve goes from a “camel” to a “bell” shape for $\gamma > 1/3$

capacitance initially increases with applied voltage, as the electrolyte can compress, but then the electrolyte reaches the crowding regime and the differential capacitance decreases with further applied voltage. This can be seen in Fig. 1 for $\gamma = 0.1$. While, for values of $2v\bar{c} \geq 1/3$, the differential capacitance monotonically decreases in a “bell”-shape [8]. At very large voltages, the differential capacitance follows $C \approx C_0/\sqrt{4v\bar{c}u_0}$, which is a law that describes how the effective length of the EDL grows with voltage in the crowding regime [8], which is model independent up to a numerical factor (for a discussion, see Ref. [1]).

In ILs, “bell”- or “camel”-shaped differential capacitance curves are often found [1], which was a major success of the theory [8]. However, the volume used for an ion had to typically be larger than the intrinsic volume of an ion, as the Bikerman term underestimates steric repulsion [2]. As such, the compacity has been used as an effective fitting parameter. Moreover, the value of the Debye capacitance was predicted to be of the order of $100 \mu\text{Fcm}^{-2}$ (at room temperature with the effective dielectric constant of ILs in the range of $10\text{--}20\epsilon_0$ [4]) and to sharply vary over a voltage range of 0.1 V . Experiments and simulations measured values of the Debye capacitance which were

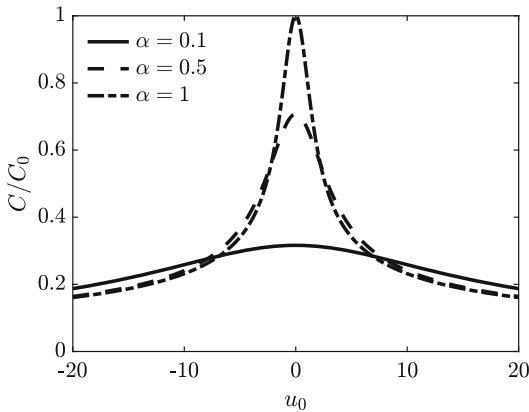
of the order of $10 \mu\text{Fcm}^{-2}$ and varying on the scale of 1 V [1].

To correct the differential capacitance, a Stern layer was typically added to suppress the capacitance at zero charge [1]. A Stern layer arises because the ions can only approach within an ion radius of the interface, meaning that there is a linear potential drop until the charges are reached. The capacitance of the Stern layer, given by $C_s = \epsilon/R$ where R is the radius of an ion, and EDL occur in series, which results in the smallest contribution dominating. At small voltages, the Stern layer capacitance is of the order of $10 \mu\text{Fcm}^{-2}$, but at large voltages the capacitance of the crowding regime can be much lower.

Later, Goodwin, Feng, and Kornyshev [15] introduced regular-solution terms to the free energy (also investigated earlier by di Caprio et al. [16]). These virial-coefficient terms represented additional short-range interactions beyond the Bikerman excess chemical potential, such as additional steric interactions or favorable interactions between cations and anions [2]. Generally, introducing regular-solution terms results in a transcendental equation which can only be numerically solved. Using a perturbative approach, Goodwin et al. [15] showed that a contribution to the excess chemical potential could be approximated as

$$\begin{aligned} \Delta\mu_{\pm}^{\text{ex}} &= Av(c_{\pm} - \bar{c}) + Bv(c_{\mp} - \bar{c}) \\ &\approx \mp(\alpha - 1)q\phi_0, \end{aligned} \quad (12)$$

where $\alpha = [1 + v\bar{c}\beta(A - B)]^{-1}$ with A and B representing the short-range interactions between ions of the same sign and between cations and anions, respectively [15]. When A is positive and B is negative, the value of α is less than 1, which makes it harder to form the EDL [15]. It was assumed that Eq. (12) worked for all applied voltages, and the resulting equation for differential capacitance recovered the same form of Eq. (11), but where the Debye capacitance was multiplied by a factor of $\sqrt{\alpha}$, and the voltage dependence was multiplied by a factor of α [15]. This causes a suppression of the Debye capacitance and its variation with applied voltage to be significantly smoothed [17]. Moreover, at



Mean-Field Theory of the Electrical Double Layer in Ionic Liquids, Fig. 2 Differential capacitance [calculated using a modified version of Eq. (11) in Ref. [15] in units of Debye capacitance as a function of potential drop in units of thermal volts. Several values of the short-range interaction parameter α are displayed for a fixed compacity of $\gamma = 1$. As α decreases, a suppression and smoothing of the capacitance-voltage response is observed

large voltages, the universal law ($C \approx C_0/\sqrt{4v\bar{c}u_0}$) is recovered. These features can all be seen in Fig. 2, where the capacitance-voltage response is shown for several values of α . This approach allowed differential capacitance curves to be fitted at the expense of an additional parameter in the theory, α .

The regular solution type modification of the mean-field theory proposed in Ref. [15] introduces a new cumulative parameter to the theory. Although it has a clear physical origin, its value is not known, so that, strictly speaking, it comes out as a fitting parameter of the theory. Note that, earlier, in order to improve the correspondence with Monte Carlo simulations, Fawcett and Ryan [18] introduced a number of fitting parameters intended to correct for finite size and correlation effects beyond the Bikerman excess term. In their approach, the values of those parameters were determined by comparison of the theory with restricted primitive model Monte Carlo simulations of electrolytes at charged interfaces up to 2 M in concentration.

The differential capacitance curves of ILs are typically quite asymmetric, however, while Eq. (11) is an even function of the applied voltage. One reason why there are asymmetric differential capacitance curves is because the sizes of ions in

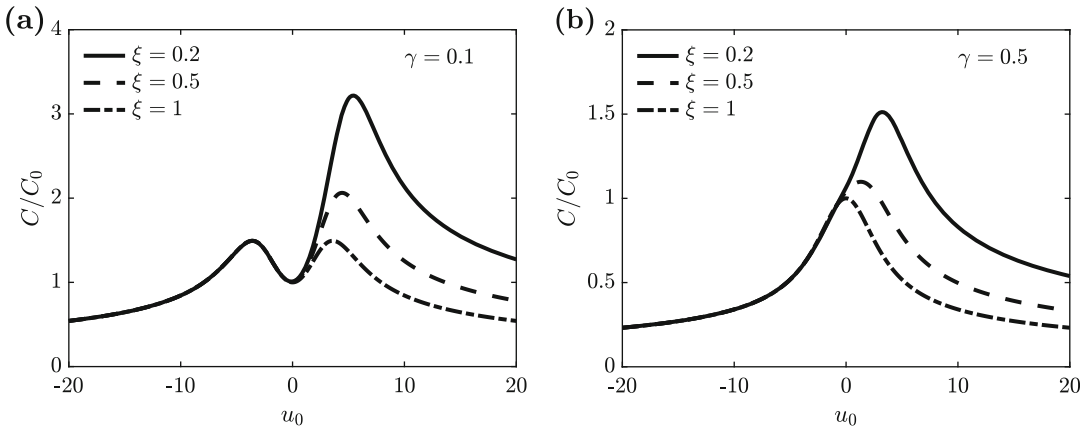
ILs can often be quite different. For example, a prototypical IL is [Emim]Cl. The Emim⁺ cation is a large, organic molecule, while the anion is an inorganic Cl⁻ ion that is much smaller. To introduce this, Kornyshev phenomenologically parameterized the value of compacity to depend on voltage, such that the lattice volume tends to that of cations (anions) in the limit of large negative (positive) voltages [8].

Similar results have been obtained by Han, Huang, and Yan [19] in a more rigorous asymmetric version of the lattice-gas model, while only introducing a single additional parameter which is the ratio of the volume of (the lattice sites of) anions to cations $\xi = v_-/v_+$. An advantage of the approach of Han et al. [19] is that analytical solutions for the differential capacitance can be obtained, curves of which can be seen in Fig. 3. At large negative voltages, the capacitance is approximately $C \approx C_0/\sqrt{4v_+\bar{c}u_0}$, but at large positive voltages it reduces to $C \approx C_0/\sqrt{4v_-\bar{c}u_0}$, which is a reflection of the EDL being larger for bulkier ions. The asymmetric ion approaches with different lattice-gas types have been investigated by Gongadze and Iglič [20], Maggs and Podgornik [21], and M. Popović and A. Šiber [22], and also Yin et al. [23] incorporated short-range interactions with asymmetric steric interactions into one theory.

The Bikerman style excess chemical potential is quite a crude approximation, however. The Carnahan-Starling equation of state is significantly more accurate than the Bikerman one, and generalizations to multicomponent, asymmetric fluids are possible [2]. With this equation of state in the local density approximation, however, one requires a numerical solution for the differential capacitance, and the interfacial layering and overscreening structure are not described. Therefore, one needs to go beyond local variables to achieve more accurate descriptions of the EDL.

Beyond the Local Density Approximation

In the previous section, advancements in the understanding of the capacitance-voltage response of ILs was reviewed. In those works, the charge density profiles always monotonically decayed. The strong charge-charge correlations in



Mean-Field Theory of the Electrical Double Layer in Ionic Liquids, Fig. 3 Differential capacitance [calculated from a generalized form of Eq. (11) in Ref. [19]] in units of Debye capacitance as a function of voltage drop across the EDL in units of thermal voltage. We display the

curve for a value of compactness as $\gamma = 0.1$ (a) and $\gamma = 0.5$ (b) for a range of values of the ion asymmetry ratio, ξ . The capacitance profile becomes asymmetric when $\xi \neq 1$, since the smaller ions experience less crowding and more easily populate the EDL

ILs cannot be accurately described by those mean-field theories, however, as they excessively smear out the detailed structure of the IL. Furthermore, the treatment of steric interactions with local densities cannot describe the layered structure of crowded ions at interfaces. Both electrostatic and steric interactions are inherently nonlocal interactions. Therefore, to obtain more accurate descriptions of the system, covering, in particular, overscreening, one needs to develop a theory that includes effects beyond a local description, either in terms of higher-order derivatives or integrals of the electrostatic potential and/or ionic densities.

To go beyond the limitations of mean-field electrostatics, Bazant, Storey, and Kornyshev (BSK) [7] introduced an additional term in the electrostatic energy

$$\mathcal{F}_{\text{el}}^{\text{ex}}[\phi] = - \int d\mathbf{r} \frac{\epsilon l_c^2}{2} [\nabla^2 \phi(\mathbf{r})]^2, \quad (13)$$

where l_c is the phenomenological correlation length, of the order of an ion diameter in ILs [7]. The term lowers the free energy when there is curvature in the electrostatic potential, and therefore, it favors oscillations in the electrostatic potential. Taking the functional derivative of the

free energy with respect to the electrostatic potential yields the modified PB equation

$$\epsilon(1 - l_c^2 \nabla^2) \nabla^2 \phi(\mathbf{r}) = -\rho(\mathbf{r}), \quad (14)$$

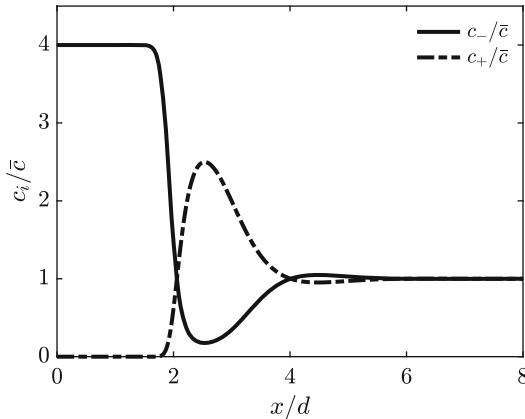
which has fourth-order derivatives too. This means additional boundary conditions are required to obtain a solution. In the bulk, the potential and its derivative should go to zero, and at the interface one boundary condition is fixed by the voltage of the electrode. While numerous other boundary conditions have been applied to close the system [7], a final boundary condition arises naturally from the mechanical equilibrium constraint at a charged interface [24]. The boundary condition implicitly accounts for the short-ranged part of the electrostatic interactions within a correlation length.

In the charge density of Eq. (14), the chemical part of the free energy from the previous sections can be utilized. At small voltages, one can linearize the charge density, which practically becomes independent of the equation of state which is used to account for excluded volume effects. Solving the resulting modified Helmholtz equation for a planar surface yields for the electrostatic potential, in the linear response approximation

$$\phi = \phi_0 \exp(-k_1 x) [\cos(k_2 x) + A \sin(k_2 x)], \quad (15)$$

where $k_1 = \sqrt{2\delta_c + 1/2\delta_c}$, $k_2 = \sqrt{2\delta_c - 1/2\delta_c}$, and $A = (1 - \delta_c k_1)/(\delta_c k_2)$ with $\delta_c = l_c/\lambda_D > 0.5$. Clearly, the electrostatic interactions accounted for by the square of the Laplacian of the potential results in overscreening at small voltages, which gives way to crowding at higher voltages [7], as seen in Fig. 4. This extension of the mean-field theory was a major advancement toward understanding the EDL of ILs, as it included all of the qualitative features observed in molecular simulations and experiments, while retaining the simplicity of the PB equation with one phenomenological parameter, l_c .

However, as seen in Fig. 4, the overscreening structure from the BSK theory is actually quite weak. There is perhaps only one oscillation in the electrostatic potential (equivalently the charge density) before it is exponentially suppressed



Mean-Field Theory of the Electrical Double Layer in Ionic Liquids, Fig. 4 BSK theory [7] predictions [calculated from combining Eqs. (10) and (14) as shown in Ref. [7]] for the concentration profiles of ions as a function of distance from the electrode in units of ion diameter, d . Here, the compacity is $\gamma = 0.5$ and the correlation length is $\kappa l_c = 10$. This corresponds to an ion diameter of $d = 1$ nm, a permittivity of $\epsilon = 5\epsilon_0$, a temperature of $T = 450$ K, and a concentration of $\bar{c} = 0.5$ M, implying $l_c = 1.33d$ [7]. The electrode potential in units of thermal volts is $u_0 = 100$. At such large voltages, the counterion density saturates to its maximal value, and the dense “layers” of counterions are followed by an overscreening layer of opposite charge

[7]. In surface force measurements and molecular simulations, it is typical to observe many oscillations in the ionic density near an interface. Moreover, one needs to introduce either short-range interactions or a Stern layer to obtain reasonable values of the differential capacitance [7].

To achieve more pronounced charge density oscillations, Gavish and Yochelis [25] developed a phase-field type model of ILs. This model relies on the Cahn-Hilliard regular solution terms in the free energy functional, which are postulated to describe nonelectrostatic like-charge attraction that leads to cation-anion phase separation. Similarly, Limmer developed a Landau-Ginzburg theory of the EDL which relies on the assumption that cations and anions phase separate [26]. These sorts of models predict snake-like patterns of ionic phase separation in the bulk, reminiscent of spinodal decomposition, but a microscopic theory of the underlying like-charge attraction has yet to be developed.

In the outlined approaches above, the crowding regime is described by a continuously extending region where the concentration is that of the macroscopic maximal concentration, as seen in Fig. 4 for the BSK theory. In atomic-force measurements and atomic simulations, however, discrete layers of countercharge clearly form in the crowding regime. In these layers, there is a coherence in where the center of the ions resides, which causes a much larger concentration of ions (than the macroscopic maximum allowed) in a small region separated by regions where ions do not reside. Upon integrating the ion profiles, the maximal macroscopic concentration is recovered.

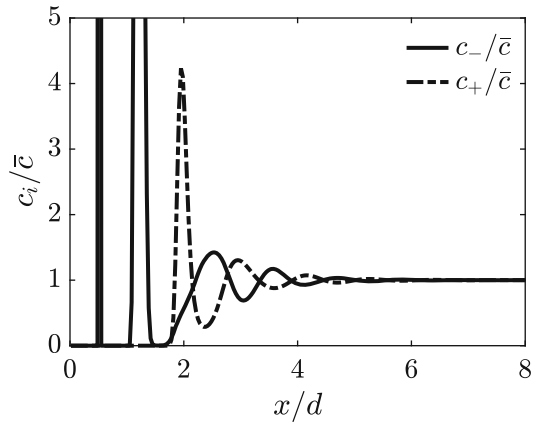
To describe the layered structure of the crowding regime, a very accurate description of the steric interactions is required. Commonly, the reference system of hard sphere ions with an implicit solvent, known as the primitive model, is used to describe these structures mathematically within the framework of classical Density Functional Theory (cDFT). In cDFT, the excess free energy, and thus the excess chemical potential, is represented in a nonlocal manner by various approximations. While no exact equation of state is known for inhomogeneous hard-sphere fluids, the most accurate functional is based on

Fundamental Measure Theory, which represents the excess free energy density in terms of various weighted densities of the ions [26, 27]. The Fundamental Measure Theory approach can accurately describe the layering for a hard-sphere fluid at an interface [27, 28].

Along with describing the excess free energy due to crowding, cDFT approaches also provide corrections for the finite size of the ions in terms of electrostatics, as well as the correlations between ions. One common approach is to include a contribution to the chemical potential from convolutions of ionic densities with direct correlation functions [28, 29], which is itself supplied as an input from the Mean Spherical Approximation. This approach, and other related approaches, can give overscreening and charge ordering at an interface that is characteristic of concentrated electrolytes and ILs [29, 30].

The nonlinear integro-differential equations that result from the cDFT theories are far less computationally expensive than Monte Carlo or Molecular Dynamics simulations. Even so, they do not have the same analytical simplicity and physical transparency of the simple modified PB approaches described above that they seek to replace. For example, due to the complexity of the functionals, it can be significantly more difficult to implement the functional numerically than the simple PB theories [28]. Furthermore, the functionals do not output simple formulas for important quantities such as decay lengths from an interface or differential capacitance, in contrast to the modified PB theories. While the predictive power of cDFT functionals for the microscopic structure of the EDL is strong, the application of less accurate local density approximation approaches as described in previous sections can be more practical.

Recently, de Souza et al. [9] took inspiration from integral theories of the EDL and developed a simplified version for ILs. In the model, the electrostatic part of the free energy is expressed in terms of the weighted ionic densities, homogenized over the size of a single ion. The approach is similar to preceding theories including intramolecular ionic charge distributions and also to the charged-shell functionals derived from the Mean



Mean-Field Theory of the Electrical Double Layer in Ionic Liquids, Fig. 5 Ionic concentration profile as predicted by the weighted-density functional in Ref. [9] as a function of distance from the electrode in units of ion diameter. Here, the parameters are $T = 300$ K, $\epsilon = 2\epsilon_0$, $\bar{c} = 5$ M, $d = 0.5$ nm, and $\sigma = 1.2$ C/m². Due to the use of weighted densities, the theory predicts sharp overcrowding peaks and a long tail of decaying oscillations in charge density further from the interface

Spherical Approximation [53–59]. When applied to the highly concentrated limit of ILs, the theory reproduces the layered structure at interfaces, as seen in Fig. 5. At high concentrations, the effective screening length for the decay of oscillations scales inversely with the Debye length, as qualitatively observed in experiments and simulations. The resulting theory is successful in quantitatively reproducing the charge density distributions and differential capacitance observed in molecular simulations as well as experimentally observed EDL structures involving crowding of large cations [30]. Interestingly, Adar et al. [32] also modified the electrostatic term and obtained a similar decay length.

Practically all of these theories neglect internal degrees of freedom of the ILs. Many ILs ions are actually quite large organic molecules, sometimes with lengthy alkyl chains [1, 10]. To include these effects, approaches have either coarse grained [29] the ions into a few representative spheres or developed approaches from polymer physics and applied them to ILs [33, 34]. These theories for the EDL of ILs can account for internal rearrangement of ions in applied field, which is often observed in molecular simulations.

Solvents and Mixtures

The EDL of ILs in their pure form is perhaps a simplified picture. Some ILs are hygroscopic, meaning that they sorb water from the environment, but actually ILs in their pure form are possibly not the most interesting for applications [1]. Introducing organic solvents in ILs increases the ionic conductivity of these electrolytes dramatically [1]. It is, therefore, practically even more interesting to have a picture of the EDL in ILs with added solvent. Alternatively, several ILs can be mixed to tune the exact physiochemical properties that are desired, or more conventional inorganic salts can be dissolved in ILs [1], and EDLs in such cases would also be worthy of description.

As has been typical in theories of dilute electrolytes, the solvent has often been modeled as dielectric continuum in which the ions reside [1, 2]. This simply means one alters the salt concentration and dielectric constant in the above theories. Such an approach can often capture the qualitative changes to the differential capacitance which occurs upon dilution of ILs [1, 2]. However, this approach misses the competition which occurs between the ions and solvent in the EDL or in an adsorbed state at the electrode, which manifests itself in differential capacitance measurements, for example [17]. Therefore, one requires theories of the EDL which are generalizable to more than two components, with the responses to electrostatic fields possibly being different for each component [20].

The competition between solvent and ions in ILs, or even different types of ions in mixtures of ILs, is a balance between the steric, specific, and electrostatic interactions. For excluded volume effects, generalizations of the above equations of state exist to any number of components with different sizes [35]. One quickly loses analytical tractability when the number of components is more than 3–4, which means it is favorable to opt for more accurate equations of state, such as multicomponent generalizations of the CS, Eq. (2).

Specific interactions can also become quite important when solvent or water is present

[36]. The cations of ILs are often hydrophobic, but the anions are usually not (an example of which is [Bmim][PF₆]), which leads to large asymmetry in the response of water in the EDL depending on the polarity of the interface [37]. Interestingly in Ref. [38], it was shown that hydrophilic ILs may have less water at the electrodes, the signatures of which were experimentally confirmed through cyclic voltammetry. Alternatively, if lithium salts are dissolved, the water will coordinate to the lithium cations, drastically changing the response [35].

It is also essential to include how the species respond to electrostatic potentials. For mixtures of ILs, the charge of the ions is typically the dominant effect, but for solvent the responses can be quite different. If the solvent has a large dipole moment, such as water, one can include a Langevin term [36] to describe the response of the dipole to external fields (note, this approach has limitations, and one often needs to use effective dipole moments to recover bulk properties of the solvents). In the absence of significant dipole moments, the polarizability of the solvent could be accounted for [39].

As an example of these competitions, Budkov et al. [36] investigated a theory of a small amount of water in an IL. The dipolar response of the water and its affinity for anions caused an enrichment of water in the EDL at moderate positive voltages, but a depletion at moderate negative voltages took place owing to unfavorable specific interactions with cations [37]. This caused a peak to occur in the differential capacitance at moderate positive voltages, which is often seen in experiments [17]. At large (negative and positive) applied voltages, there is always enrichment of water in the EDL as it is favorable for water to reside in regions of large electric fields.

Underscreening and Beyond

As previously mentioned, surface force measurements can reveal the layered structure of ILs at interfaces [40], which the more involved EDL theories can capture [28]. These theories predict that the charge density has decaying oscillations

until the bulk is reached. However, past the layered structure, these measurements actually find monotonically decaying interactions that extend far beyond what one expects. This was first reported by Gebbie et al. [41], where the effect was interpreted as ILs behaving as a dilute electrolyte with 99.997% of the ions being bound up in ion pairs. This observation was further confirmed by a number of groups, with Smith et al. [40] demonstrating that moderately concentrated electrolytes (1 M) exhibit this monotonic tail, referred to as underscreening [42], that would extend further into the electrolyte with increasing concentration.

This motivated the investigation of ion pairing effects in the EDL of ILs. If ILs are actually dilute electrolytes, with the concentration of free charge carriers of the order of 0.003%, then one can reinterpret the compacity parameter as the concentration of “free” ions (not bound up into ion pairs or aggregates) over the maximal concentration of “free” ions [1, 15]. Upon doing so with 0.003% of “free” ions, the values of Debye capacitance are significantly smaller than what is found in experiments. Moreover, for a “dilute electrolyte,” there should be a strong U-shaped differential capacitance curve consistent with Gouy-Chapman, but a bell shape is often found in experiments of ILs. This was further investigated by Ma et al. [43] in a cDFT theory, where it was found that the Debye capacitance when 99.997% of the ions were paired was not consistent with experimental observations.

The extent of ion pairing is still an open question in ILs [44–47]. Aside from mean-field theories [43, 44], the balance between ions in a “clustered state” and in “free” state has been explored using molecular dynamics simulations, such as Refs. [46, 48]. The former study showed that for typical ILs, the percentage of free ions (which is equivalent to the revised meaning of compacity) is of the order of 10–20%, depending on temperature – the larger percentage for higher temperatures following the Arrhenius-like law with very small free energy difference between the states of the order of $1 k_B T$.

Importantly, one could expect that the extent of ion pairing and clustering will “effectively

change” in the EDL, due to changed balance between the two states (paired vs. free). Indeed, with ions clustered, and majorly into neutral clusters, they contribute less or no charge into the EDL, increasing the effective (high-frequency) dielectric constant. The effect expected here is the electric field-induced destruction of clusters – “dipoles” – in the EDL in favor of free ions – “monopoles” (the physics of this effect is analogous to the Frumkin effect of electric field-induced desorption of organic molecules from electrodes in favor of electroadsorption of ions of electrolyte [49]). In Ref. [50], a simple mean-field theory was constructed to describe this effect. The main new prediction was, in spite of the low value of compacity in the bulk of IL, it effectively increases in the EDL and gives rise to the “bell” shape of differential capacitance rather than the “camel” shape that a simpler theory would suggest for low values of compacity.

In such concentrated electrolytes as ILs, aggregates larger than ion pairs can exist, motivating theories of ionic aggregation and clustering [51]. Recently, McEldrew et al. [52] applied polymer theories to superconcentrated electrolytes, where aggregates of arbitrarily large size can be systematically accounted for in a general framework. It was predicted there that an infinite, percolating network of ions can form, which is referred to as the gel phase. The existence and properties of the gel phase in ILs, and its relation to the fragile glass phase, are open questions.

Beyond underscreening, there are still many other interesting avenues of research. For example, the dynamics of charging the EDL in supercapacitors (electrokinetic phenomena at interfaces) and surface chemistry of any defects are all areas of great importance in improving the performance of EDL supercapacitors which have ILs as electrolytes.

Cross-References

- ▶ [All-Atom Models of Ionic Liquids](#)
- ▶ [Capacitance with Different Electrode Topology](#)
- ▶ [Interfacial Microstructure of Ionic Liquids](#)
- ▶ [Ion Pairing in Ionic Liquids](#)

- ▶ Mixture of Ionic Liquids/Water
- ▶ Monte Carlo Simulation of Ionic Liquids
- ▶ Nanopore-confined Ionic Liquids
- ▶ Property Prediction of Ionic Liquids by Molecular Dynamics
- ▶ Structure Heterogeneity in Ionic Liquids

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