Double Layer in Ionic Liquids: Overscreening versus Crowding

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We develop a simple Landau-Ginzburg-type continuum theory of solvent-free ionic liquids and use it to predict the structure of the electrical double layer. The model captures overscreening from short-range correlations, dominant at small voltages, and steric constraints of finite ion sizes, which prevail at large voltages. Increasing the voltage gradually suppresses overscreening in favor of the crowding of counterions in a condensed inner layer near the electrode. This prediction, the ion profiles, and the capacitance-voltage dependence are consistent with recent computer simulations and experiments on room-temperature ionic liquids, using a correlation length of order the ion size.

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Introduction.—The rediscovery of room-temperature ionic liquids (RTILs) as designer solvents promised a revolution in synthetic chemistry [1]. Thousands of RTILs have been synthesized with large organic cations and similar organic or smaller inorganic anions. Nonvolatile and capable of withstanding up to ±4–6 V without decomposition, RTILs also hold promise as solvent-free electrolytes for supercapacitors, solar cells, batteries, and electroactuators [2–10].

For such applications, it is crucial to understand the structure of the RTIL-electrode double layer. The classical Gouy-Chapman-Stern model for dilute electrolytes was used to interpret RTIL capacitance data until recently, when a mean-field theory for the *crowding* of finite-sized ions [11] suggested bell or camel shapes of the differential capacitance versus voltage, decaying as $C \sim V^{-1/2}$. These were basically confirmed in subsequent experimental [12–16], theoretical [17,18], and computational [19–23] studies. Similar theories have also been developed for highly concentrated electrolytic solutions [24–26], but none of these models accounts for short-range Coulomb correlations [27], which could be very strong in RTIL [28,29]. As first revealed by linear response theories of molten salts [30], correlations generally lead to *overscreening* [27], where the first layer at the electrode delivers more countercharge than is on the surface, the next layer then sees a smaller net charge of the opposite sign, which it again overscreens, and so on, until electroneutrality is reached. Recent computer simulations of a model RTIL-electrode interface have demonstrated overscreening structures at low voltage, similar to experiments [28], which are gradually overcome by the formation of a condensed layer of counterions at high voltage [19], as shown in Fig. 1.

In this Letter, we suggest a phenomenological theory to describe the interplay between overscreening and crowding. Compared to more involved models of statistical mechanics, the theory only crudely approximates discrete interactions near a surface, but it is simple enough to be applied to dynamical problems in nanotribology, electroactuation, and porous supercapacitors.

Theory.—We propose a Landau-Ginzburg-like functional for the total free energy [31]:

$$G = \int_V d\mathbf{r}\left\{g + \rho\phi - \frac{\varepsilon}{2}[|\nabla\phi|^2 + \ell_c^2(\nabla^2\phi)^2]\right\} + \oint_S d\mathbf{r} q_s \phi \quad (1)$$

where $g(c_+, c_-)$ is the enthalpy density, depending on the ionic concentrations $c_\pm$, as described below; $\rho = e(z_+c_+ - z_-c_-)$ is the mean charge density in the liquid volume V; q_s is the surface charge density on a bounding

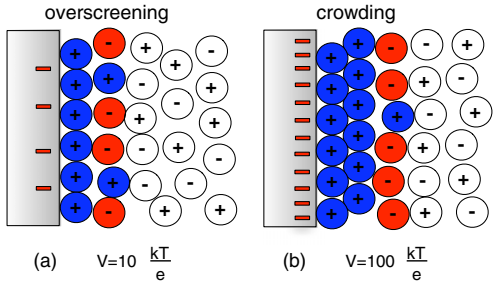

FIG. 1 (color online). Structure of the ionic-liquid double layer (in color) predicted by our theory and molecular dynamics simulations [19] [Figs. 2 and 3]. (a) At a moderate voltage, $V = 10k_BT/e$ (0.26 V), the surface charge is overscreened by a monolayer of counterions, which is corrected by an excess of coions in the second monolayer. (b) At a high voltage, $V = 100k_BT/e$ (2.6 V), the crowding of counterions extends across two monolayers and dominates overscreening, which now leads to a coion excess in the third monolayer. Because of electrostriction, the diffuse double layer (colored ions) is more dense than the quasineutral bulk liquid (white ions).

metal surface S; ϕ is the mean electrostatic potential, and we subtract the self energy of the electric field $-\frac{\varepsilon}{2}|\nabla\phi|^2$, assuming a constant permittivity ε to describe the polarizability of the ions. The first three terms in brackets are those used in mean-field theories of ionic liquids [11], ionic crystals [32], and electrolytes [24,33]. To go beyond that approximation, we introduce the next allowable potential gradient term, $-\frac{\varepsilon}{2}\ell_c^2(\nabla^2\phi)^2$, similar to Cahn-Hilliard concentration-gradient expansions [34,35], where ℓ_c is an electrostatic correlation length [31].

The sign of the correlation term is negative to describe *overscreening* in strongly correlated liquids: The energy is lowered by *enhancing* the curvature of ϕ, a measure of the "mean-field charge density," $\bar{\rho} \equiv -\varepsilon\nabla^2\phi$. For point charges, ℓ_c is on the order of the Bjerrum length $\ell_B = (ze)^2/4\pi\varepsilon kT$ (in SI units). For RTILs with $\varepsilon \approx 10\varepsilon_0$, the Bjerrum length, $\ell_B \approx 5.5$ nm, is much larger than the ion diameter, $a \approx 1$ nm [1], so the correlation length $\ell_c \approx a$ is typically at the molecular scale [28].

Setting $\delta G/\delta\phi = 0$ for bulk and surface variations [31], we obtain a modified Poisson equation [36,37] and modified electrostatic boundary condition, respectively,

$$\varepsilon(\ell_c^2\nabla^2 - 1)\nabla^2\phi = \rho = \nabla\cdot\mathbf{D}, \tag{2}$$

$$\hat{n}\cdot\varepsilon(\ell_c^2\nabla^2 - 1)\nabla\phi = q_s = \hat{n}\cdot\mathbf{D}, \tag{3}$$

where $\mathbf{D}$ is the displacement field. Because of correlations, the medium permittivity $\hat{\varepsilon}$, defined by $\mathbf{D} = -\hat{\varepsilon}\nabla\phi$, is a linear differential operator, $\hat{\varepsilon} = \varepsilon(1 - \ell_c^2\nabla^2)$, whose Fourier transform (valid for wave number $|k| \ll \ell_c^{-1}$), $\hat{\varepsilon}_k \sim \varepsilon(1 + \ell_c^2k^2)$, increases with k, as is typical for molten salts [38]. It is important to note that our $\hat{\varepsilon}$ is not the complete dielectric function of the ionic liquid, which should diverge at small k, as for any conducting medium [38]. This divergence is subtracted since translational degrees of freedom are treated explicitly via $\rho(\phi)$, which also takes into account the nonlinear response in the rearrangement of ions. In our model, $\hat{\varepsilon}$ approximates the linear dielectric response of the liquid of correlated ion pairs (zwitterions), which are considered to be bound by stronger forces, independent of the mean electric field.

Since Poisson's Eq. (2) is now fourth order, we need additional boundary conditions, similar to electrodynamics with spatial dispersion [39]. Consistent with our bulk gradient expansion, we neglect correlations at the surface and apply the standard boundary condition, $-\varepsilon\hat{n}\cdot\nabla\phi = q_s$. Equation (3) then implies $\hat{n}\cdot\nabla(\nabla^2\phi) = 0$, which requires that the mean-field charge density is "flat" at the surface, $\hat{n}\cdot\nabla\bar{\rho} = 0$, consistent with a continuum model of finite-sized ions.

Following Ref. [11], we describe crowding effects via the classical model [40]

$$g = \frac{k_BT}{\upsilon}\{\upsilon c_+\ln(\upsilon c_+) + \upsilon c_-\ln(\upsilon c_-) + [1 - \upsilon(c_+ + c_-)]\ln[1 - \upsilon(c_+ + c_-)]\} \tag{4}$$

which is the entropy density $g = -TS/\upsilon$ of an ideal solution of cations, anions, and holes, respectively, of minimum volume υ. We set $\upsilon = (\pi/6)a^3/\Phi_{\max} = 0.83a^3$ for random close packing of spheres at volume fraction $\Phi_{\max} = 0.63$. More accurate expressions for g are available for uniform hard-sphere mixtures [24], but, due to the breakdown of the local-density approximation [27], they overestimate steric repulsion in the double layer [42]. The weaker repulsion in (4) actually provides a better first approximation for the packing entropy.

The electrochemical potentials of the ions are then

$$\mu_\pm = \frac{\delta G}{\delta c_\pm} = k_BT\ln\left[\frac{c_\pm}{1 - \upsilon(c_+ + c_-)}\right] \pm z_\pm e\phi, \tag{5}$$

and their gradients $\nabla\mu_\pm$ produce ionic fluxes [24]. In equilibrium with a reference solution with $\phi = 0$ and volume fraction, $\gamma = 2\upsilon c_+^{\text{ref}} = 2\upsilon c_-^{\text{ref}}$, the conditions $\mu_\pm = \text{const}$ determine the Fermi-like charge density distribution, $\rho(\phi)$. In electrolytes, γ is the volume fraction of solvated ions in the bulk [24,25,33,41]. In ionic liquids γ (≤ 1) is the ratio of the bulk ion density to the maximum possible density, which characterizes their ability to compress [11]. In equilibrium, we obtain a (dimensionless) modified Poisson-Fermi equation,

$$(1 - \delta_c^2\tilde{\nabla}^2)\tilde{\nabla}^2\tilde{\phi} = \frac{\sinh\tilde{\phi}}{1 + 2\gamma\sinh^2(\tilde{\phi}/2)} = -\tilde{\rho}(\tilde{\phi}) \tag{6}$$

where $\tilde{x} = x/\lambda_D$, $\tilde{\nabla} = \lambda_D\nabla$, $\tilde{\phi} = ze\phi/k_BT$. Here, $\lambda_D = \sqrt{\varepsilon k_BT\upsilon}/ze$ is the Debye screening length, and $\delta_c = \ell_c/\lambda_D$ is the dimensionless correlation length, which controls deviations from the mean-field theory. For $\varepsilon = 10\varepsilon_0$ and $a = 10$ Å, the Debye length is very small, $\lambda_D = 1.1$ Å, so the ion size a becomes the relevant length scale [43]. If we chose $\delta_c = 10$ to reproduce double-layer properties from simulations [19] (below), then correlations are indeed at the molecular scale, $\ell_c \approx a$.

Results.—Let us apply our model to a half space by solving $\delta_c^2\tilde{\phi}'''' - \tilde{\phi}'' = \tilde{\rho}(\tilde{\phi})$ for $\tilde{x} > 0$ subject to $\tilde{\phi}'''(0) = 0$, and $\tilde{\phi}(0) = \tilde{V} = zeV/k_BT$, where V is the surface potential relative to the bulk. We solve the model analytically for small, moderate, and large voltages [31] and compare with numerical solutions.

1. Structure of the double layer.—In Fig. 2 we show the calculated charge density (a), mass density, and ion concentrations (b) for $\gamma = 1/2$ and $\delta_c = 10$. For $a = 10$ Å, $T = 450$ K and $\varepsilon = 5\varepsilon_0$, which imply $\ell_c = 0.95a$, the model predicts molecular-scale charge-density oscillations, similar to experiments [28] and in good agreement with simulations [19], as shown in Fig. 3. At small potentials, the oscillation period and damping length are $\tilde{\lambda}_o \sim 2\pi\sqrt{2\delta_c}$ for $\delta_c \gg 1$ [31], or with units restored, $\lambda_o \sim 2\pi\sqrt{\lambda_D\ell_c} = 20$ Å $= 2.0a$. With increasing voltage, a condensed layer of counterions forms and expands into the bulk, as predicted by the mean-field theory [11], but with the important difference that this layer overscreens the

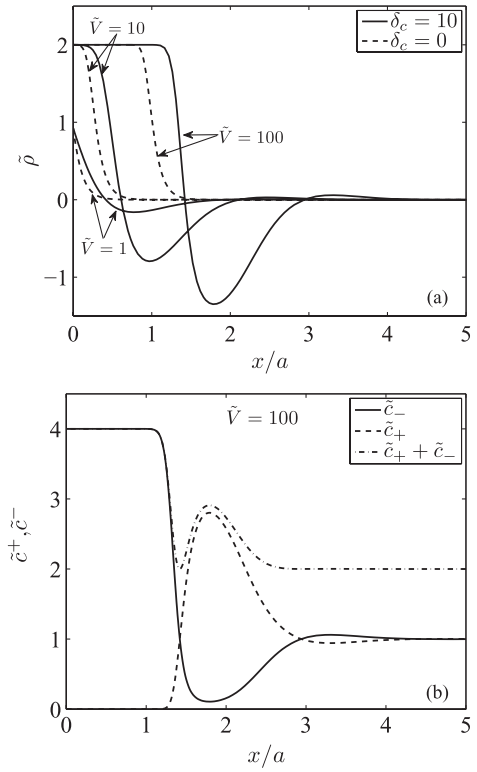

FIG. 2. Voltage-dependent double-layer structure predicted by our model. (a) Dimensionless charge density versus x/a for $\tilde{V} = eV/k_BT = 1,\ 10,\ 100$ (solid curves), compared to the mean-field theory [11] which corresponds to $\delta_c = 0$ (dashed curves). (b) Dimensionless cation (solid curve) and anion (dashed curve) concentrations and mass density (dash-dotted curve) at high voltage, $\tilde{V} = 100$. Position x is measured from the distance of closest approach and scaled to the ion diameter $a = 10$ Å. Model parameters $\gamma = 0.5$, $\delta_c = 10$, and $\varepsilon = 5\varepsilon_0$ are those fitting ion profiles in simulations [19] [Fig. 3].

surface charge, leading to a second layer of excess coions, which again (slightly) overscreens and triggers the same low-voltage damped charge-density oscillations. The model also predicts nonuniform electrostriction at high voltage [Fig. 2(b)] consistent with simulations [19] [Fig. 3]: The first counterion layer attains the maximum density, while the next co-ion-rich layer has a lower density, but still larger than the bulk.

2. Double-layer capacitance.—An important property of the double layer is its voltage-dependent capacitance $C(V)$. It has been found that excluded volume effects explain trends in the experimental data, but the mean-field theory overestimates C, unless an empirical Stern-layer correction is added [19,20]. In Fig. 4 we show the double-layer capacitance versus voltage in our model, which is in very close agreement with simulations of Ref. [19] without fitting any additional parameters. We only account for the extra capacitance, $C_s = 2\varepsilon/a$, in series with the diffuse double layer, due to the distance of closest approach of ion centers, $a/2$. The value of C_s relative to the mean-field Debye value, $C_D = \varepsilon/\lambda_D$, is $\tilde{C}_s = C_s/C_D = 2\lambda_D/a \approx 2/\delta_c$.

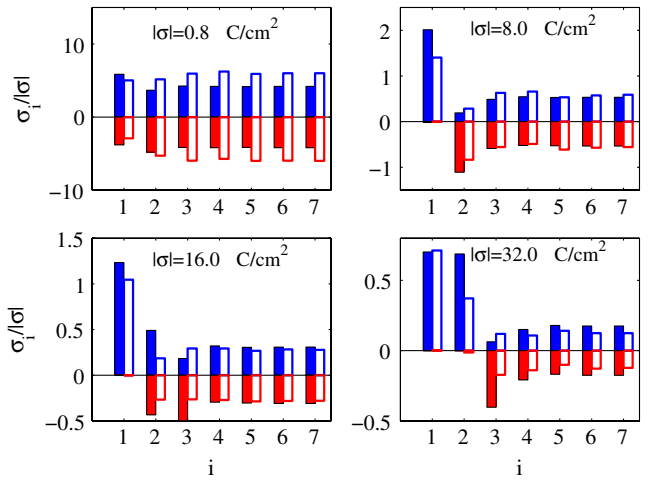

FIG. 3 (color online). Distributions of cations (top panels) and anions (bottom panels) sorted into monolayer bins $i = 1, 2, \ldots$ for different surface charges σ, as predicted by our model (solid bars) in qualitative agreement with simulations [Fig. 2 of Ref. [19], open bars].

At low voltage, the model can be linearized and solved to find the diffuse layer capacitance, C_d [31],

$$\tilde{C}_d = \frac{C_d \lambda_D}{\varepsilon} \sim \frac{\sqrt{2\delta_c + 1}}{\delta_c + 1} \quad \text{for } |\tilde{V}| \ll 1. \tag{7}$$

By extending the composite diffuse layer model of Ref. [25] we can also approximate C_d at moderate voltages, once the condensed counterion layer forms and $\delta_c \gg 1$;

$$\tilde{C}_d \sim \frac{8^{3/4}}{3(\delta_c^2 \gamma \tilde{V})^{1/4}} \quad \text{for } \frac{128}{81\gamma} \ll |\tilde{V}| \ll \frac{81\delta_c^2}{128\gamma}. \tag{8}$$

This scaling breaks down at very large voltages when the condensed layer of charge grows enough to dominate the capacitance, yielding $\tilde{C}_d \sim \sqrt{2/\gamma\tilde{V}}$ as in the mean-field theory [11,25]. These scalings compare well with numerical solutions for $\delta_c \gg 1$ [31] and explain why our model is

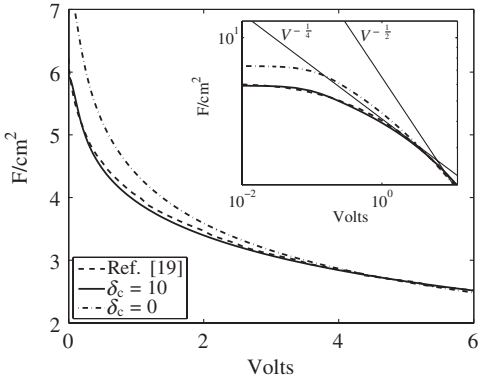

FIG. 4. Double-layer differential capacitance C_d from our model (solid curve), simulations [19] (dashed curve), mean-field theory [11] (dash-dotted curve), and our asymptotic scalings (inset) as a function of voltage across the double layer.

closer to simulations than the mean-field theory without correlations [Fig. 4].

Conclusion.—In this Letter we have made a first attempt to describe both overscreening and crowding in dense Coulomb liquids, such as RTILs and molten salts. Our simple phenomenological theory predicts that overscreening is pronounced at small voltages and gradually replaced by the formation of a condensed layer of counterions, followed by complete lattice saturation at very large voltages. Each of these three regimes is characterized by its own capacitance-voltage dependence. Our findings are in line with simulations and experiments, and they give a more complete picture of the nonlinear polarization of ionic liquids.

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