# Double Layer in Ionic Liquids: Overscreening versus Crowding

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# Double layer in ionic liquids: Overscreening vs. 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. The predicted ion profiles and capacitance-voltage relations are consistent with recent computer simulations and experiments on room-temperature ionic liquids, using a correlation length of order the ion size.

PACS numbers:

*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 super-capacitors, 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 (GCS) 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 [17–19] and computational[20–24] studies. Similar theories have also been developed for highly concentrated electrolytic solutions [25–27], but none of these models accounts for short-range Coulomb correlations [28], which could be very strong in RTIL [29]. As first revealed by linear response theories of molten salts [30], correlations generally lead to *over-screening* [28], where the first layer at the electrode delivers more counter-charge 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 neutrality is reached. Recent computer simulations of a model RTIL/electrode interface have demonstrated overscreening structures at low voltage, similar to experiments [29], which are gradually overcome by the formation of a condensed layer of counter-ions at high voltage [20], as shown in Fig. 1.

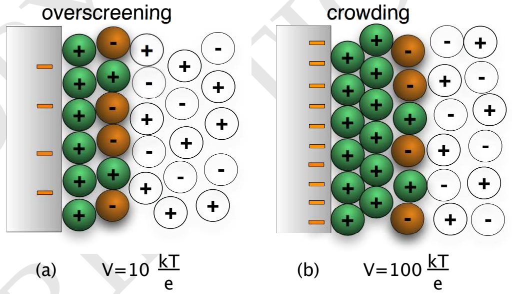

FIG. 1: Structure of the ionic-liquid double layer (in color) predicted by our theory and molecular dynamics simulations [20] (Figs. 2-3 below). (a) At a moderate voltage, $V = 10k_BT/e$ (0.26 V), the surface charge is overscreened by a monolayer of counterions, which is corrected by an excess of co-ions in the second monolayer. (b) At a high voltage, $V = 100k_BT/e$ (2.6 V), the crowding of counter-ions extends across two monolayers and dominates overscreening, which now leads to a co-ion excess in the third monolayer. Due to electrostriction, the diffuse double layer (colored ions) is more dense than the quasi-neutral bulk liquid (white ions).

In this Letter, we suggest a phenomenological theory to describe the interplay between over-screening 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 super-capacitors.

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

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

where $g(c_+, c_-)$ is the enthalpy density, depending on the ionic concentations $c_\pm$, 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 metal surface $S$; $\phi$ 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 $\varepsilon$ 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 [25, 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 $\ell_c$ is an electrostatic correlation length [31].

The sign of the correlation term is negative to describe *over-screening* in strongly correlated liquids: The energy is lowered by *enhancing* the curvature of $\phi$, a measure of the "mean-field charge density", $\bar{\rho} \equiv -\varepsilon\nabla^2\phi$. For point charges, $\ell_c$ 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 [29].

Setting $\delta G/\delta\phi = 0$ for bulk and surface variations [31], we obtain a modified Poisson equation [40] [41] and modified electrostatic boundary condition, respectively:

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

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

where $\mathbf{D}$ is the displacement field. Due to correlations, the medium permittivity $\hat{\varepsilon}$, defined by $\mathbf{D} = -\hat{\varepsilon}\nabla\phi$, is a linear differential operator, $\hat{\varepsilon} = \varepsilon\left(1 - \ell_c^2\nabla^2\right)$, whose Fourier transform (valid for wavenumber $|k| \ll \ell_c^{-1}$), $\hat{\varepsilon}_k \sim \varepsilon(1 + \ell_c^2k^2)$, increases with $k$, as is typical for molten salts [36]. 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 [36]. 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 equation (2) is now fourth-order, we need additional boundary conditions, similar to electrodynamics with spatial dispersion [37]. 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 [42]:

$$\begin{aligned} g \;&=\; \frac{k_BT}{v}\left\{vc_+\ln(vc_+) + vc_-\ln(vc_-)\right. \\ &+\; \left.[1 - v(c_+ + c_-)]\ln[1 - v(c_+ + c_-)]\right\} \qquad (4) \end{aligned}$$

which is the entropy density $g = -TS/v$ of an ideal solution of cations, anions, and holes, respectively, of minimum volume $v$. We set $v = (\pi/6)a^3/\Phi_{max} = 0.83a^3$ 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 [25], but, due to the breakdown of the local-density approximation [28], they over-estimate steric repulsion in the double layer [38]. The weaker repulsion in (4) actually provides a better first approximation for the packing entropy.

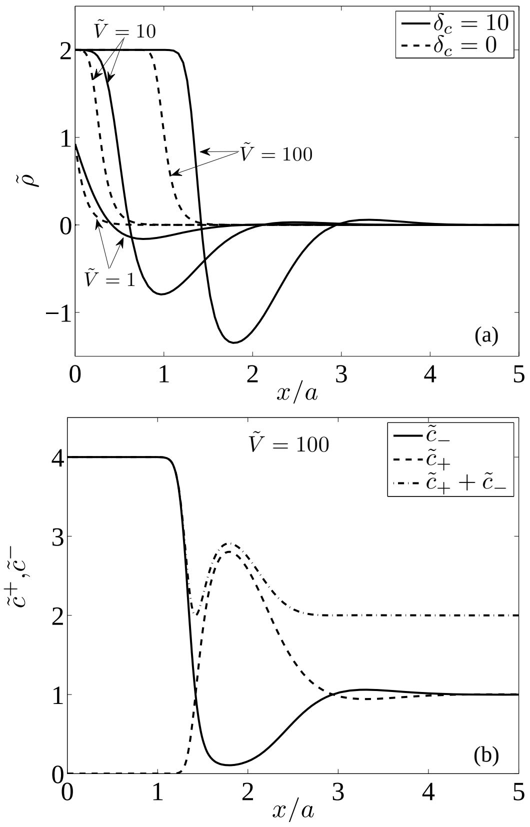

FIG. 2: Voltage-dependent double-layer structure predicted by our model. (a) Dimensionless charge density versus $x/a$ for $\tilde{V} = eV/k_BT = 1, 10, 100$ (solid curves), compared to the mean-field theory [11] with $\delta_c = 0$ (dashed curves). (b) Dimensionless cation (solid) and anion (dashed) concentrations and mass density (dash-dot) 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 $\gamma = 0.5$ (bulk/maximum density), $\delta_c = 10$ (correlation/Debye length), and $\varepsilon = 5\varepsilon_0$ are estimated from ion profiles in simulations [20] (Fig. 3 below).

The electrochemical potentials of the ions are then

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

and their gradients $\nabla\mu_\pm$ produce ionic fluxes [25]. In equilibrium with a reference solution with $\phi = 0$ and volume fraction, $\gamma = 2vc_+^{ref} = 2vc_-^{ref}$, the conditions $\mu_\pm =$constant determine the Fermi-like charge density distribution, $\rho(\phi)$. In electrolytes, $\gamma$ is the volume fraction of solvated ions in the bulk [25, 26, 33, 39]. In ionic liquids $\gamma$ $(\leq 1)$ is the ratio of the bulk ion density to

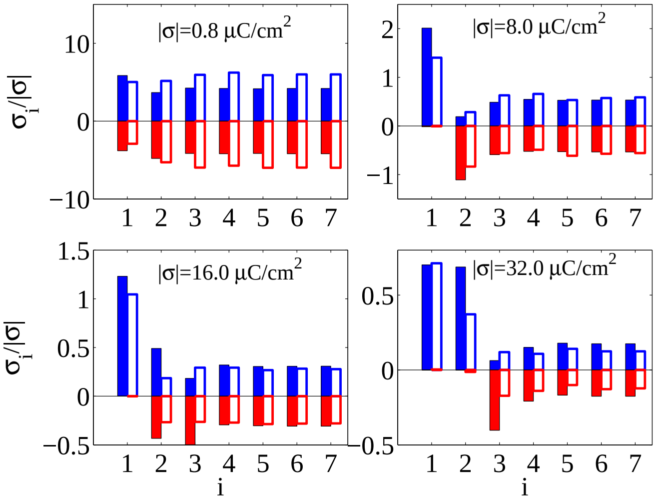

FIG. 3: Distributions of cations (above) and anions (below) sorted into monolayer bins $i = 1, 2, \ldots$ for different surface charges $\sigma$, as predicted by our model (solid bars) in qualitative agreement with simulations (Fig. 2 of Ref. [20], open bars).

the maximum possible density, which characterizes their ability to compress [11]. In equilibrium, we obtain a (dimensionless) modified Poisson-Fermi equation,

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

where $\tilde{x} = x/\lambda_D$, $\tilde{\nabla} = \lambda_D\nabla$, $\tilde{\phi} = ze\phi/k_BT$. Here, $\lambda_D = \sqrt{\varepsilon k_BTv}/ze$ 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 [20] (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, $T = 450K$ and $\varepsilon = 5\varepsilon_0$, which imply $\ell_c = 0.95a$, the model predicts molecular-scale charge-density oscillations, similar to experiments [29] and in good agreement with simulations [20], 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 surface charge, leading to a second layer of excess co-ions, which again (slightly) overscreens and triggers the same low-voltage damped charge-density oscillations. The model also predicts non-uniform electrostriction at high voltage (Fig. 2(b)) consistent with simulations (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.

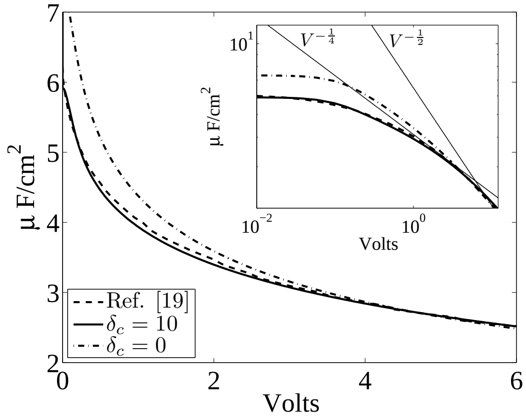

FIG. 4: Double-layer differential capacitance $C_d$ from our model (solid), simulations [20] (dashed), mean-field theory [11] (dash-dot), and our asymptotic scalings (inset).

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 over-estimates $C$, unless an empirical Stern-layer correction is added [20, 21]. In Fig. 4 we show the double-layer capacitance versus voltage in our model, which is in very close agreement with simulations of Ref. [20] 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 $\tilde{C}_s = C_s/C_D = 2\lambda_D/a \approx 2/\delta_c$.

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

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

By extending the Composite Diffuse Layer Model of Ref. [26] we can also approximate $C_d$ at moderate voltages, once the condensed counterion layer forms and $\delta_c \gg 1$;

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

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, 26]. These scalings compare well with numerical solutions for $\delta_c \gg 1$ [31] and explain why our model is closer to simulations than the mean-field theory without correlations (Fig. 4).

*Conclusion.* — In this paper 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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[1] T. Welton, Chem.Rev. **99**, 2071 (1999).
[2] D. Silvester and R. Compton, Z. Phys. Chem. **220**, 1247 (2006).
[3] W. Freyland, Phys. Chem. Chem. Phys. **10**, 923 (2008).
[4] M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, and B. Scrosati, Nat. Mater. **8**, 621 (2009).
[5] S. Ito, S. M. Zakeeruddin, P. Comte, P. Liska, D. Kuang, and M. Gratzel, Nat. Photonics **2**, 693 (2008).
[6] Y. Bai, Y. Cao, J. Zhang, M. Wang, R. Li, P. Wang, S. M. Zakeeruddin, and M. Gratzel, Nat. Mater. **7**, 626 (2008).
[7] M. Buzzeo, R. Evans, and R.G.Compton, Chem. Phys. Chem. **5**, 1106 (2004).
[8] C. Ye, W. Liu, Y. Chen, and L. Yu, Chem. Commun. **2244** (2001).
[9] B. Bhushan, M. Palacio, and B. Kinzig, J. Colloid Interface Sci. **317**, 275 (2008).
[10] P. Simon and Y. Gogotsi, Nat. Mater. **7**, 845 (2008).
[11] A. A. Kornyshev, J. Phys. Chem. B **111**, 5545 (2007).
[12] M. T. Alam, M. M. Islam, T. Okajima, and T. Ohsaka, Phys. Chem. C **111**, 18326 (2007).
[13] M. T. Alam, M. M. Islam, T. Okajima, and T. Ohsaka, Electrochem. Comm. **9**, 2370 (2007).
[14] M. T. Alam, M. M. Islam, T. Okajima, and T. Ohsaka, J.Phys. Chem. C **112**, 16568 (2008).
[15] V. Lockett, R. Sedev, J. Ralston, M. Horne, and T. Rodopoulos, J. Phys. Chem. C **112**, 7486 (2008).
[16] W. Zhou, S. Inoue, and T. Iwahashi, Electrochem. Commun. **12**, 672 (2010).
[17] K. B. Oldham, J. Electroanal. Chem. **613** (2008).
[18] Y. Lauw, M. D. Horne, T. Rodopoulos, and F. A. M. Leermakers, Phys. Rev. Lett. **103**, 117801 (2009).
[19] B. Skinner, M. S. Loth, and B. I. Shklovskii, Phys. Rev. Lett. **104**, 128302 (2010).
[20] M. V. Fedorov and A. A. Kornyshev, Electrochim. Acta **53**, 6835 (2008).
[21] M. V. Fedorov and A. A. Kornyshev, J. Phys. Chem. B **112**, 11868 (2008).
[22] M. V. Fedorov, N. Georgi, and A. A. Kornyshev, Electrochem. Commun. **12**, 296 (2010).
[23] M. Trulsson, J. Algotsson, and J. Forsman, J. Phys. Chem. Lett. **1**, 1191 (2010).
[24] J. Vatamanu, O. Borodin, and G. D. Smith, Phys. Chem. Chem. Phys. **12**, 170 (2010).
[25] M. Z. Bazant, M. S. Kilic, B. D. Storey, and A. Ajdari, Adv. Coll. Interface Sci. **152**, 48 (2009).
[26] M. S. Kilic, M. Z. Bazant, and A. Ajdari, Phys. Rev. E **75**, 021502 (2007).
[27] V. Freise, Z. Elektrochemie **56**, 822 (1952).
[28] Y. Levin, Rep. Prog. Phys. **65**, 1577 (2002).
[29] M. Mezger, H. Schroder, H. Reichert, S. Schramm, J. S. Okasinski, S. Schoder, V. Honkimaki, M. Deutsch, B. M. Ocko, J. Ralston, et al., Science **322**, 424 (2008).
[30] M. Rovere and M. P. Tosi, Rep. Prog. Phys. **49**, 1001 (1986).
[31] See EPAPS Document No. [XXX] for details.
[32] T. B. Grimley and N. F. Mott, Disc. Faraday Soc. **1**, 3 (1947).
[33] I. Borukhov, D. Andelman, and H. Orland, Phys. Rev. Lett. **79**, 435 (1997).
[34] J. W. Cahn and J. W. Hilliard, J. Chem Phys. **28**, 258 (1958).
[35] E. B. Nauman and D. Q. Heb, Chem. Eng. Sci. **56**, 19992018 (2001).
[36] M. P. Tosi, *Condensed Matter Physics Aspects of Electrochemistry* (World Scientific, 1991), p. p. 68.
[37] V. M. Agranovich and V. L. Ginzburg, *Crystal Optics with Spatial Dispersion* (Springer, New York, 1984).
[38] D. Antypov, M. C. Barbosa, and C. Holm, Phys. Rev. E **71**, 061106 (2005).
[39] J. J. Bikerman, Phil. Mag. **33**, 384 (1942).
[40] Similar equations have been derived for the equilibrium profile of point-like counterions near a charged wall; C. Santangelo [Phys. Rev. E **73**, 041512 (2006)] showed that (2) is exact for both weak and strong coupling and a good approximation at intermediate coupling with $\ell_c = \ell_B$; M. M. Hatlo and L. Lue [Europhys. Lett. **89**, 25002 (2010)] developed a systematic approximation for $\ell_c$.
[41] A. Hildebrandt, R. Blossey, S. Rjasanow, O. Kohlbacher, and H.-P. Lenhof [Phys. Rev. Lett. **93**, 108104 (2004)] derived a similar gradient approximation for nonlocal solvent dielectric response [A. Kornyshev, A. I. Rubinstein, and M. A. Vorotyntsev, J. Phys. C **11**, 3307 (1978)].
[42] This model was originally developed for concentrated electrolytes [39] and ionic solids [32], as reviewed in [25].
[43] Due to the local-density approximation, our model cannot resolve discrete layers of ions [25], but more accurate weighted-density approximations [28] require solving nonlinear integro-differential equations.