

## SUPPLEMENTARY INFORMATION

### Double layer in ionic liquids: Overscreening vs. crowding

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#### I. PHENOMENOLOGICAL THEORY OF ELECTROSTATIC CORRELATIONS

Let  $G = G_{el} + G_{chem}$ , where  $G_{el}$  is the electrostatic energy and  $G_{chem} = \int_V d\mathbf{r} g$  is the chemical (non-electrostatic) part of the free energy. Suppose that  $G_{chem}$  is known, and focus on electrostatic correlation effects in  $G_{el}$ .

The electrostatic potential,  $\phi$ , is the free energy per ion (free charge). The electrostatic energy cost for adding a charge  $\delta\rho$  in the bulk liquid volume  $V$  or  $\delta q_s$  on the metal surface  $S$  is,

$$\delta G_{el} = \int_V d\mathbf{r} \phi \delta\rho + \int_S d\mathbf{r} \phi \delta q_s. \quad (1)$$

The charge is related to the displacement field  $\mathbf{D}$  via Maxwell's "first" equation,

$$\nabla \cdot \mathbf{D} = \rho \Rightarrow \delta\rho = \nabla \cdot \delta\mathbf{D}. \quad (2)$$

The corresponding boundary condition for an ideal metal surface (where  $\mathbf{D} = 0$ ) is,

$$[\hat{n} \cdot \mathbf{D}] = \hat{n} \cdot \mathbf{D} = -q_s \Rightarrow \delta q_s = -\hat{n} \cdot \delta\mathbf{D}. \quad (3)$$

Substituting these expressions into (1) and using Gauss' theorem, along with the definition of the electric field,  $\mathbf{E} = -\nabla\phi$ , we recover the standard electrostatic free energy equation [1],

$$\delta G_{el} = \int_V d\mathbf{r} \mathbf{E} \cdot \delta\mathbf{D}. \quad (4)$$

In the linear response regime (for small external electric fields), we have

$$\mathbf{D} = \hat{\varepsilon} \mathbf{E}, \quad (5)$$

where  $\hat{\varepsilon}$  is a linear operator, whose Fourier transform  $\hat{\varepsilon}(k)$  encodes how *the permittivity depends on the wavelength*  $2\pi/k$  of the  $k$ -Fourier component of the field, due to discrete ion-ion correlations, as well as any non-local dielectric response of the ions, such as exponentially decaying Debye correlations in ionic plasma, as well as correlations in polarization fluctuations due to any other molecules if

they are present in the liquid. We can then integrate (4) over  $\delta\mathbf{D}$  through a charging process that creates all the charges in the bulk and surface from zero to obtain

$$G_{el} = \frac{1}{2} \int_V d\mathbf{r} \mathbf{E} \cdot \mathbf{D}. \quad (6)$$

For a given distribution of charges  $\rho$  and  $q_s$ , with associated displacement field  $\mathbf{D}$ , the physical electric field  $\mathbf{E}$  is the one that minimizes  $G_{el}$ , subject to the constraint of satisfying Maxwell's equations (2)-(3). Since  $\mathbf{E} = -\nabla\phi$  to enforce  $\nabla \times \mathbf{E} = 0$ , we can minimize  $G_{el}$  with respect to variations in  $\phi$ , using Lagrange multipliers  $\lambda_1$  and  $\lambda_2$  to enforce the constraints,

$$G_{el}[\phi] = \int_V d\mathbf{r} \left[ \frac{1}{2} \mathbf{E} \cdot \mathbf{D} + \lambda_1 (\rho - \nabla \cdot \mathbf{D}) \right] + \oint_S d\mathbf{r}_s \lambda_2 (q_s + \hat{n} \cdot \mathbf{D}). \quad (7)$$

To calculate the extremum, we use the Fréchet functional derivative:

$$\frac{\delta G_{el}}{\delta\phi} = \lim_{\epsilon \rightarrow 0} \frac{G_{el}[\phi + \epsilon\phi_0\delta\epsilon] - G_{el}[\phi]}{\epsilon\phi_0} \quad (8)$$

where  $\delta\phi_\epsilon = \phi_0\delta\epsilon(\mathbf{r}, \mathbf{r}')$  is a localized perturbation of the potential (with compact support), which tends either to a 3D delta function in the liquid ( $\mathbf{r} \in V$ ) or to a 2D delta function on the surface ( $\mathbf{r} \in S$ ) as  $\epsilon \rightarrow 0$ , and  $\phi_0$  is an arbitrary potential scale for dimensional consistency. By setting  $\delta G_{el}/\delta\phi = 0$  for both surface and bulk variations, we find  $\lambda_1 = \lambda_2 = \phi$ . Finally, using vector identities, we arrive at a general functional for the electrostatic energy,

$$G_{el}[\phi] = \int_V d\mathbf{r} \left( \rho\phi + \frac{1}{2} \nabla\phi \cdot \mathbf{D} \right) + \oint_S d\mathbf{r}_s q_s\phi \quad (9)$$

to be minimized with respect to  $\phi$ , once we know the relationship between  $\mathbf{D}$  and  $\mathbf{E} = -\nabla\phi$ .

To model the field energy in an ionic liquid, we assume *linear dielectric response of the molecules with constant permittivity  $\varepsilon$  plus a non-local contribution for ion-ion correlations*. Here, the permittivity  $\varepsilon$  describes the electronic polarizability of the ions.

$$g_{field} = -\frac{1}{2} \nabla\phi \cdot \mathbf{D} = \frac{\varepsilon}{2} \left( \mathbf{E}(\mathbf{r})^2 + \int_V d\mathbf{r}' K(\mathbf{r}, \mathbf{r}') \bar{\rho}(\mathbf{r}) \bar{\rho}(\mathbf{r}') \right) \quad (10)$$

where

$$\bar{\rho} = \varepsilon \nabla \cdot \mathbf{E} = -\varepsilon \nabla^2 \phi, \quad (11)$$

is the “mean-field charge density”, which would produce the electric field in the dielectric medium without accounting for ion-ion correlations. Suppose that the non-local kernel  $K(\mathbf{r}, \mathbf{r}')$  decays over a length scale  $\ell_c$ , bounded below by the finite ion size  $a$  and above by the Bjerrum length  $\ell_B$ , which sets the scale for electrostatic correlations among point charges. For charge variations over scales larger than  $\ell_c$  (corresponding to small perturbation wavenumbers,  $\ell_c |k| \ll 1$ ), we obtain a gradient expansion for the non-local term

$$g_{field} \sim \frac{\varepsilon}{2} \left[ |\nabla \phi|^2 + \sum_{n=0}^{\infty} \alpha_n \left( \frac{\ell_c^{n-1}}{\varepsilon} \nabla^n \bar{\rho} \right)^2 \right] \quad (12)$$

where  $\alpha_n$  are dimensionless coefficients, which implies

$$G_{el}[\phi] \sim \int_V d\mathbf{r} \left\{ \rho \phi - \frac{\varepsilon}{2} \left[ |\nabla \phi|^2 + \sum_{n=2}^{\infty} \alpha_{n-2} (\ell_c^{n-1} \nabla^n \phi)^2 \right] \right\} + \int_S d\mathbf{r}_s q_s \phi \quad (13)$$

Equation (1) in the main text results from the first term in the gradient expansion of the non-local electrostatic energy with the choice  $\alpha_0 = 1$  (after suitably rescaling  $\ell_c$ ), where the overall negative sign of this term is chosen to promote over-screening.

By setting  $\delta G_{el}/\delta\phi = 0$  for bulk and surface perturbations in (13), we recover Maxwell’s equations (2)-(3), with  $\mathbf{D} = \hat{\varepsilon} \mathbf{E}$ , where the permittivity operator has the following gradient expansion,

$$\hat{\varepsilon} = \varepsilon \left( 1 - \sum_{n=1}^{\infty} \alpha_{n-1} \ell_c^{2n} \nabla^{2n} \right) \quad (14)$$

and corresponding small- $k$  expansion of the Fourier transform,

$$\hat{\varepsilon}(k) = \varepsilon \left[ 1 + \sum_{n=1}^{\infty} \alpha_{n-1} (-1)^{n-1} (\ell_c k)^{2n} \right] \quad (15)$$

$$\sim \varepsilon [1 + \alpha_0 (\ell_c k)^2] \quad (16)$$

which grows with  $k$  at small wavenumbers in the case where correlations promote overscreening,  $\alpha_0 > 0$ . Note that it is well known that such an expansion only holds at small  $k$ . At larger  $k$ ,  $\hat{\varepsilon}(k)$  diverges, becomes negative on the other side of the singularity, then diverges again to  $-\infty$  at another point, and becomes positive after the second divergence; see Refs. [2, 3].

## II. CHARGE PROFILES AND VERIFICATION OF OVER-SCREENING

In the main text we show charge density profiles for a specific set of parameters. The charge density profiles

in the text are presented in spatial coordinates scaled by the ion size. However, the natural length scale for the dimensionless problem is the Debye length. The solutions to the equation in dimensionless form depend upon the applied voltage, the correlation length scale  $\delta_c$ , and the volume fraction  $\gamma$ . In Fig. 1 we show the charge density as a function of distance (normalized by the Debye length) for increasing values of  $\delta_c$ . To convert these ion profiles to dimensional form, the  $x$ -axis need only be scaled by the value of  $\lambda_D/a$  as given by the physical parameters of the problem. Fig. 1 shows that the strength of the over-screening is a strong function of  $\delta_c$ .

To prove that our simple continuum model predicts over-screening by the first, condensed layer of counterions, in Fig. 2 we plot the integrated charge density up to position  $x$  from the surface versus  $x$ . The integrated charge is then normalized by the total charge in the double layer, as in Ref. [4]. This graph provides a quantitative characterization of the strength of over-screening in the first layer.

## III. LOW-VOLTAGE ANALYTICAL SOLUTION

The solution to the equations must be calculated numerically. However, at low voltage we can obtain an analytical solution. At low voltage, we have the approximation that,

$$\left( \delta_c^2 \frac{d^4 \tilde{\phi}}{d\tilde{x}^4} - \frac{d^2 \tilde{\phi}}{d\tilde{x}^2} \right) = -\tilde{\phi}. \quad (17)$$

The analytical solution to this equation depends on whether  $\delta_c$  is greater than, equal to, or less than  $\frac{1}{2}$ . Since  $\delta_c$  is presumed large in case of ionic liquids, we present the analytical solution for  $\delta_c > \frac{1}{2}$ ,

$$\tilde{\phi}(x) = \tilde{V} e^{-k_1 x} (\cos(k_2 x) + A \sin(k_2 x)), \quad (18)$$

where

$$k_1 = \frac{\sqrt{2\delta_c + 1}}{2\delta_c}, \quad k_2 = \frac{\sqrt{2\delta_c - 1}}{2\delta_c}, \quad A = -\frac{\sqrt{2\delta_c + 1}(\delta_c - 1)}{\sqrt{2\delta_c - 1}(\delta_c + 1)}.$$

The total charge in the diffuse double layer can be evaluated from

$$q = - \int_0^{\infty} \tilde{\phi} d\tilde{x} = \delta_c^2 \frac{\partial^3 \tilde{\phi}}{\partial \tilde{x}^3} \bigg|_{\tilde{x}=0} - \frac{\partial \tilde{\phi}}{\partial \tilde{x}} \bigg|_{\tilde{x}=0} = -\tilde{V} \frac{\sqrt{2\delta_c + 1}}{\delta_c + 1}.$$

The diffuse layer capacitance in the limit when  $\delta_c$  is large is approximately  $\tilde{C}_d = \sqrt{2/\delta_c}$ . The diffuse layer capacitance is less than the classical theory without correlations and decreases with the square root of  $\delta_c$ .

## IV. HIGH-VOLTAGE COMPOSITE APPROXIMATION

In ionic liquids, the parameter  $\gamma$  is on the order of unity and excluded volume effects are significant. At voltages

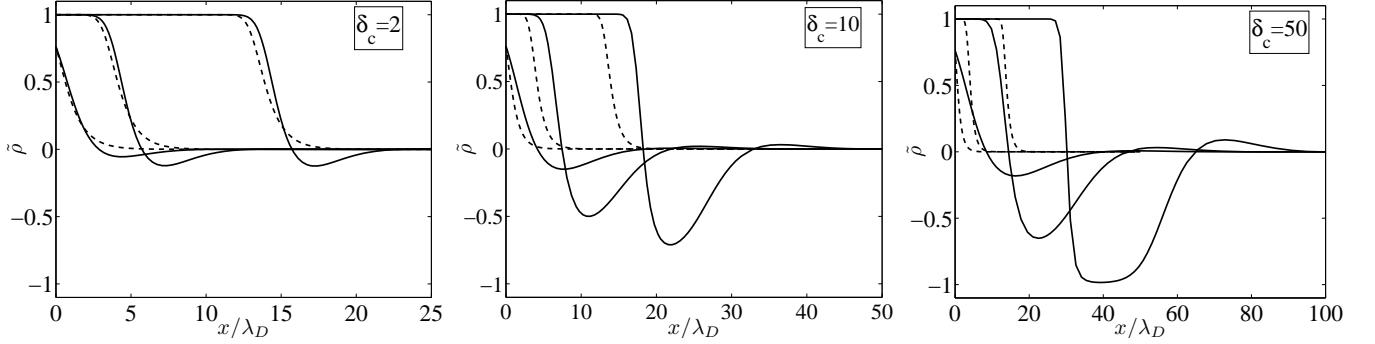


FIG. 1: Charge density profiles for  $\gamma = 1$  and  $\delta_c = 2, 10$ , and  $50$ , as indicated. The solid curves are calculated from our model while the dashed curves are calculated for the case where  $\delta_c = 0$  and there are no correlations. Solutions are shown for applied voltages of  $\tilde{V} = 1, 10$  and  $100$  measured in units of  $k_B T/e \approx 25$  mV. Similar results are obtained for different values of the volume fraction,  $\gamma$ .

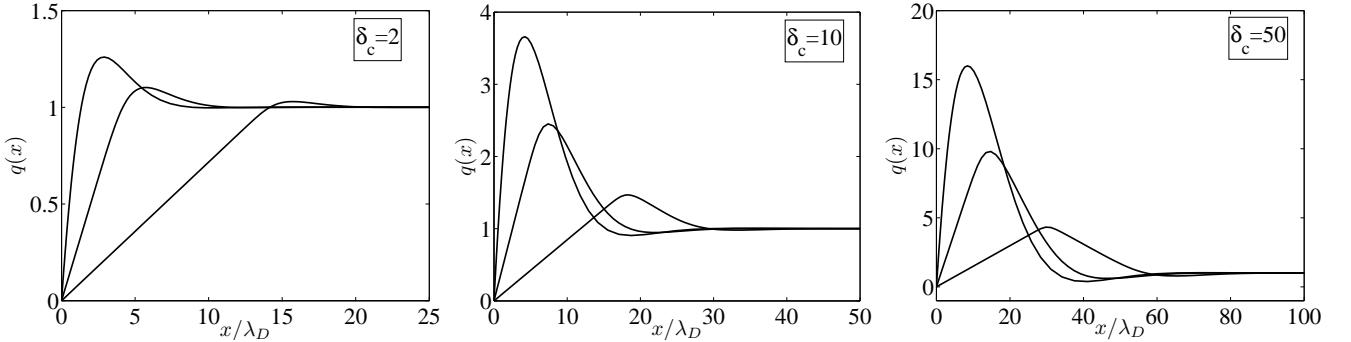


FIG. 2: Cumulative charge density profiles as a function of distance from the electrode. The charge is integrated cumulatively in space and normalized by the total double layer charge; namely  $q(x) = \int_0^x \rho(\hat{x}) d\hat{x} / \int_0^\infty \rho(\hat{x}) d\hat{x}$ . Solutions are shown for  $\gamma = 1$  and  $\delta_c = 2, 10$  and  $50$ , as indicated. Applied voltages are  $\tilde{V} = 1, 10$  and  $100$  measured in units of  $k_B T/e \approx 25$  mV. These cumulative profiles clearly show over-screening.

beyond the linear response we find that a condensed layer of counter-ions forms near the wall. In this condensed region close the wall we could solve,

$$\left( \delta_c^2 \frac{d^4 \tilde{\phi}}{d\tilde{x}^4} - \frac{d^2 \tilde{\phi}}{d\tilde{x}^2} \right) = \tilde{\rho}_{\max}$$

where we assume that the charge density is a constant,  $\tilde{\rho}_{\max}$ , and has reached the maximum value defined by the value of  $\gamma$ ; i.e.  $\tilde{\rho}_{\max} = 1/\gamma$  if we apply a negative voltage. In order to further simplify the approximation, we can assume that in ionic liquids,  $\delta_c$  is typically large and we solve as an approximation,

$$\delta_c^2 \frac{d^4 \tilde{\phi}}{d\tilde{x}^4} = \tilde{\rho}_{\max}, \quad (19)$$

in the wall region.

The general solution for the potential in the wall region becomes a fourth order polynomial. Using the boundary conditions that we have fixed voltage  $\tilde{V}$  at  $x = 0$ , along with  $\partial^3 \tilde{\phi} / \partial \tilde{x}^3 = 0$  at the wall, our solution for the po-

tential has a simple form,

$$\tilde{\phi}(x) = \frac{\tilde{\rho}_{\max}}{24\delta_c^2} \tilde{x}^4 + B\tilde{x}^2 + C\tilde{x} + \tilde{V}$$

This polynomial solution which is valid near the wall can be matched to the low voltage solution provided in the previous section. Ensuring continuity of the potential, the charge density, and all the derivatives allows us to solve for the unknown constants of integration. The resulting analysis yields a quartic equation for the size of the condensed layer. Once the size of the condensed layer is known, all the constants for the matching are easy to obtain. The approximate composite model was found to match the full numerical simulation as long as the voltage was low enough that a second condensed layer of opposite charge did not begin to form (see Fig. 1c at  $\tilde{V} = 100$ ).

While this analysis may be useful, the resulting quartic equation does not provide a simple form for the double layer capacitance. A much simpler form of this composite solution emerges if we make the additional approximation that all of the voltage drop occurs across the condensed layer and, after the condensed layer, the potential and all its derivatives go to zero. While this is not

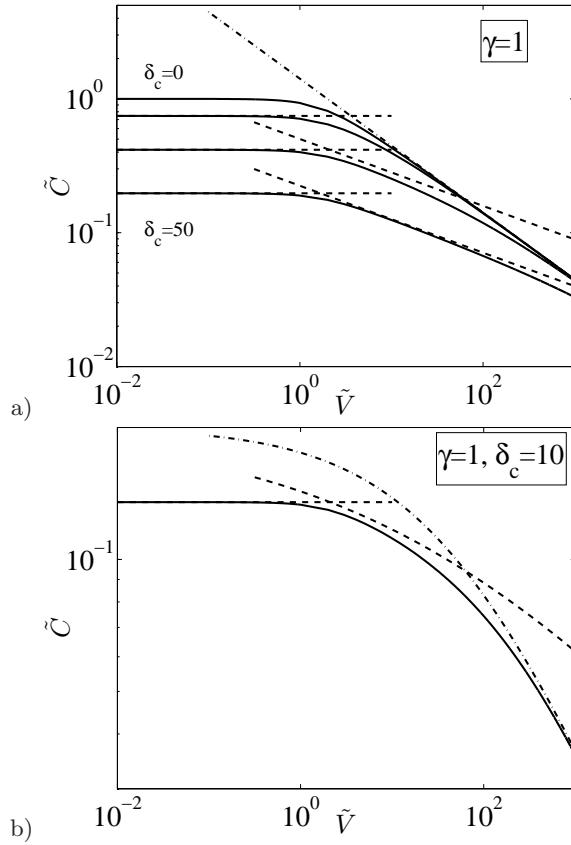


FIG. 3: (a) Capacitance of the diffuse double layer, normalized by the Debye value, as a function of voltage for  $\delta_c = 0, 2, 10$ , and  $50$  while holding  $\gamma = 1$ . Numerical solutions (solid curve) are compared with the low-voltage and moderate voltage approximations in Eqs. (7) and (8) of the main text (dashed lines) and the high-voltage scaling,  $\tilde{C}_d \sim \sqrt{2/\gamma\tilde{V}}$  (dash-dot line). We show only the diffuse layer capacitance to highlight the different scaling laws. (b) Total capacitance of the double layer for  $\delta_c = 10$  and  $\gamma = 1$ ; the inner layer is included in series with diffuse layer.

true, it is found from the numerical solutions to provide a reasonable prediction of the capacitance at "intermediate voltages", where a condensed layer forms, but not so high that a second condensed layer of opposite charge forms due to over-screening. While this assumption does not yield complete charge density profiles, it does provide a useful approximation for the potential in the condensed layer and thus the capacitance.

Returning to the general solution and using the simplified boundary conditions,  $\tilde{\phi}(\tilde{x} = L) = 0$  and

$\partial\tilde{\phi}/\partial\tilde{x}\bigg|_{\tilde{x}=L} = 0$ , we find,

$$\tilde{\phi}(\tilde{x}) = \frac{-1}{24\gamma\delta_c^2}(\tilde{x}^4 - L^3\tilde{x}) + \left(\frac{\tilde{V}}{L^2} + \frac{L^2}{8\gamma\delta_c^2}\right)(\tilde{x}^2 - L\tilde{x}) + \tilde{V}\left(1 - \frac{\tilde{x}}{L}\right).$$

Setting the second derivative to zero at  $\tilde{x} = L$  yields the size of the condensed layer,

$$L = (\tilde{V}\gamma\delta_c^2 8)^{\frac{1}{4}}.$$

Solving for the total charge  $q = \frac{\partial\tilde{\phi}}{\partial\tilde{x}}\bigg|_{\tilde{x}=0}$ , we obtain a simple approximation for the diffuse layer differential capacitance ( $\tilde{C}_d = d\tilde{Q}/d\tilde{V}$ ),

$$\tilde{C}_d \sim \frac{8/3}{(8\delta_c^2\gamma\tilde{V})^{\frac{1}{4}}} \quad (20)$$

The scaling presented above is essentially valid at large  $\delta_c$  and moderately large voltages. At high voltage, correlations become irrelevant, since "crowding beats over-screening", and the capacitance is determined by the excluded volume effects only and has a scaling  $C_d \sim \sqrt{2/\gamma\tilde{V}}$  as previously discovered.

The transitions between these three regimes are evident in Fig. 3 where we compare the numerical solution for the capacitance to the simple scaling laws derived above. The range of validity of the intermediate voltage expression simply comes from the intersection of the three regimes. In Fig. 3a we show the diffuse layer capacitance only to clearly show the results of the simple scaling laws. At  $\delta_c = 10$  we find a short transition regime where the  $V^{-1/4}$  scaling appears, and for  $\delta_c > 50$  the scaling is valid over a wide range. All the capacitance curves appear to converge to the  $\delta_c = 0$  solution at high voltages, as expected from our analysis. When  $\delta_c$  is large, however, the voltages where the capacitance curves converge are quite extreme, so this limiting behavior may have limited applicability. Perhaps it could be used to validate simulations.

In Fig. 3b we show the total capacitance (inner layer and diffuse layer in series) for  $\delta_c = 10$  and  $\gamma = 1$ . Here we find that the simple scaling laws are useful for understanding the capacitance computed from the numerical solution of our model.

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