Continuum theory of electrostatic correlations at charged surfaces

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(Dated: February 15, 2019)

The standard model for diffuse charge phenomena in colloid science, electrokinetics and biology is the Poisson-Boltzmann mean-field theory, which breaks down for multivalent ions and large surface charge densities due to electrostatic correlations. In this Letter, we formulate a predictive continuum theory of correlated electrolytes based on two extensions of the Bazant-Storey-Kornyshev (BSK) framework: (i) a physical boundary condition enforcing continuity of the Maxwell stress at a charged interface, which upholds the contact theorem for dilute primitive-model electrolytes, and (ii) scaling relationships for the correlation length, for a one-component plasma at a charged plane and around a cylinder, as well as a dilute z:1 electrolyte screening a planar surface. In these cases, the theory accurately reproduces Monte Carlo simulation results from weak to strong coupling, and extensions are possible for more complex models of electrolytes and ionic liquids.

Introduction.—Electrostatic correlations can significantly affect the structure and thermodynamic properties of the electrical double layer [1, 2], resulting in qualitative differences from mean-field Poisson-Boltzmann (PB) theory, such as like-charge attraction or over-screening of surface charge. Bazant, Storey and Kornyshev (BSK) proposed a continuum framework to account for the non-local dielectric permittivity of ionic liquids resulting from ion-ion correlations [3], which leads to a higher-order Poisson equation, building on intermediate coupling approximations of Santangelo [4] and Hatlo and Lue [5] for the one-component plasma. The BSK theory provides a simple framework to predict charge density oscillations and over-screening phenomena in a variety of electrokinetic [6, 7], electrochemical [8, 9], biophysical [10], and colloidal [11] phenomena in electrolytes and ionic liquids. Even so, fundamental questions remain about the proper boundary conditions and correlation length required to complete the BSK theory.

In this Letter, we show that the appropriate boundary constraint for the higher-order Poisson equation is based on an interfacial stress balance. With corrected boundary conditions, the BSK theory becomes exact in the strong and weak coupling limits for one-component plasma, and agrees with Monte Carlo (MC) simulations in intermediate coupling. We also suggest scalings for the correlation length without steric constraints in one-component plasma and in multivalent electrolytes, for all the scenarios in Fig. 1. Although generalizations are possible, we restrict the analysis to a primitive electrolyte with hard, spherical ions in a constant permittivity, $\epsilon$, medium and smeared out surface charge density, $q_s$, and neglect all concentrated-solution effects.

Theory.—The BSK free energy functional is given by:

$$G = \int_V dr \left\{ g + \rho \phi - \frac{\epsilon}{2} \left[ (\nabla \phi)^2 + \ell_c^2 (\nabla^2 \phi)^2 + \ldots \right] \right\} + \int_S ds q_s \phi. \quad (1)$$

Here, $g = (H - TS)/V$ is the enthalpy and entropy density, $\rho$ is the charge density, and $\phi$ is the electrostatic potential. While the original authors performed a gradient expansion to arrive at Eq. 1 [3,6], the mathematical procedure is equivalent to modifying the interaction potential between ions from $U_{\alpha\beta}(r) = z_\alpha z_\beta \epsilon_B / r$ to $U_{\alpha\beta}(r) = z_\alpha z_\beta \epsilon_B / r$ for $r < \ell_B$ and $U_{\alpha\beta}(r) = z_\alpha z_\beta \epsilon_B / r - (1 - e^{-r/\ell_c})^4$ [4,12]. The modified interaction potential is solved in the mean-field limit. Thus the BSK theory is a phenomenological correction to PB within the mean-field approximation, by subtracting out interactions with smeared out charges within a correlation length $\ell_c$, which should scale as the size of the correlation hole. The modified Poisson equation results by finding the extremal of the functional $\left( \frac{dG}{d\phi} = 0 \right)$:

$$\epsilon (\ell_c^2 \nabla^2 - 1) \nabla^2 \phi = \rho. \quad (2)$$

FIG. 1. The scenarios considered in the application of the BSK theory.
Eq. 2 is a statement of Maxwell’s equation, \( \nabla \cdot \mathbf{D} = \rho \) where the displacement field is \( \mathbf{D} = \hat{\epsilon} \mathbf{E} \) with a non-local permittivity operator \( \hat{\epsilon} = (\ell_c^2 \nabla^2 - 1) \) applied on the electric field, \( \mathbf{E} = -\nabla \phi \). PB theory is recovered when \( \ell_c = 0 \). The charge density at equilibrium, \( \rho = \sum z_i c_i \), will be determined by the constraint that the electrochemical potential for each ion is a constant at equilibrium. The electrochemical potential can be defined as the variation of the Gibbs free energy with respect to concentration [13], \( \mu_i = \frac{\delta G}{\delta c_i} \), or \( \mu_i = \mu_i^0 + kT \ln(c_i) + z_i e \phi + \mu_i^{\infty} \), where the first term is a reference value, the second term is the ideal entropy contribution, the third term is the electrostatic potential contribution, and the fourth term is the excess electrochemical potential.

The first open question in applying BSK theory is that of additional boundary conditions, beyond Maxwell’s equation \( \hat{n} \cdot \mathbf{D} = q_n \). Presumably, the boundary condition must take care of the unaccounted short-range part of \( U_{\text{gb}} \). In the original BSK formulation and all subsequent works, the boundary condition of \( \hat{n} \cdot \nabla^3 \phi = 0 \) was applied, with the justification that the correlation effects should disappear at the interface [6–9, 12, 14–22]. The theory provided reasonable agreement to simulation and experimental results for ionic liquids and multivalent electrolytes. However, the boundary conditions have not yet been proven or validated systematically.

The second open question is the choice of correlation length, which has been arbitrarily set to the Bjerrum length for electrolytes [3, 7], and the ion diameter for ionic liquids [3]. The theory is ultimately very sensitive to the choice of boundary conditions and correlation length. We analyze the boundary condition in terms of a stress balance at the interface and then validate \( \ell_c \) by comparison to MC simulations.

**Interfacial balance.**—Applying the Gibbs-Duhem equation at constant temperature to the electrolyte and screened surface charges, following [23], and neglecting the external electrostatic work done on the system, gives \( dP = \sum_i c_i d\mu_i \). Taking the gradient in three-dimensional space and applying the definition of the electrochemical potential:

\[
f = \nabla P = kT \sum_i \nabla c_i + \rho \nabla \phi + \sum_i c_i \nabla \mu_i^{\infty}, \tag{3}
\]

where \( f \) is the total thermodynamic force. The first and third terms on the RHS of Eq. 3 correspond to the gradient of osmotic pressure, \( \nabla \). For an ideal gas, \( \mu_i^{\infty} = 0 \). The gradient of the defined thermodynamic pressure is equivalent to the divergence of the total stress tensor of the electrolyte system, \( f = \nabla \cdot \tau \). The total stress tensor is composed of an osmotic pressure component, \( \Pi \) and a Maxwell stress tensor, \( \tau_e \), such that \( \tau = -\Pi + \tau_e \). The component of interest in this analysis, \( \tau_e \), can be defined by:

\[
\nabla \cdot \tau_e = \rho \mathbf{E} = \nabla \cdot (\hat{\epsilon} \mathbf{E}) \mathbf{E} \tag{4}
\]

in a constant \( \epsilon \) medium. Plugging in for the charge density using the BSK Eq. 2 and performing integration by parts, one arrives at an expression for the Maxwell stress tensor for a fluid with a non-local permittivity,

\[
\tau_e = \epsilon \mathbf{E} \mathbf{E} - \frac{1}{2} \epsilon \mathbf{E}^2 \mathbf{I} + \epsilon \ell_c^2 \left[ (\mathbf{E} \cdot \nabla^2 \mathbf{E}) \mathbf{I} - \mathbf{E} (\nabla^2 \mathbf{E}) \right] - \left( \nabla^2 \mathbf{E} \right) \mathbf{E} + \frac{1}{2} (\nabla \cdot \mathbf{E})^2 \mathbf{I} \tag{5}
\]

While the above equation was derived for constant \( \epsilon \) and \( \ell_c \), the expression is identical if these parameters vary. For varying \( \epsilon \) or \( \ell_c \), the Korteweg-Helmholtz force density must be included in the electrostatic stress [24],

\[
\nabla \cdot \tau_e = \rho \mathbf{E} - \frac{1}{2} \epsilon \mathbf{E}^2 \nabla \epsilon + \frac{1}{2} (\nabla \cdot \mathbf{E})^2 \nabla (\ell_c^2). \tag{6}
\]

Within the distance of closest approach of the ions to the surface, correlations cannot affect the value of the Maxwell stress at the surface, \( \tau_{e, \text{surf}} \), generated by the surface charge density. The mechanical equilibrium problem therefore requires continuity in the electrostatic stress tensor evaluated in the solution and at the surface,

\[
\tau_e - \tau_{e, \text{surf}} = 0. \tag{7}
\]

At a uniformly-charged, flat surface without a dielectric jump, the Maxwell stress tensor is simply \( \tau_{e, \text{surf}} = q_n^2 / (2\epsilon) \hat{n} n \), while the Maxwell stress tensor in the electrolyte is given by Eq. 5. Equating these two expressions, and substituting in \( \hat{n} \cdot \mathbf{D} = q_n \), we arrive at a final boundary for a potential varying in one coordinate direction, \( \hat{n} \cdot \ell_c \nabla^3 \phi = \nabla^2 \phi \rvert_S \).

The method amounts to applying the contact value theorem to the correlated electrolyte in the absence of correlations, shown below for \( \mu_i^{\infty} = 0 \) at a flat electrode with constant charge density without a dielectric jump [25]:

\[
P = -\frac{q_n^2}{2\epsilon} + kT \sum_i c_i \rvert_S = -\hat{n} \cdot \tau_e \cdot \hat{n} + kT \sum_i c_i \rvert_S. \tag{8}
\]

The contact theorem is a statement of mechanical equilibrium, where the repulsive osmotic pressure contribution is balanced by the electrostatic attraction from the Maxwell stress. Without the constraint from Eq. 7, the BSK theory does not obey this simple relationship which should be valid even for dilute electrolytes in the primitive model [26–28]. The procedure of ensuring continuity in the Maxwell stress can be repeated for any higher order \( \hat{\epsilon} \) by equating the \( \tau_e \) at successive orders of derivatives. The condition in Eq. 7 is also applicable to any extended electrolyte mean-field theory with arbitrary models of concentrated solution activity and solvent polarizability, including interactions with a soft wall. The approach may even be extended to media with non-local dielectric constant \( \hat{\epsilon} \) driven by solvent polarization [29, 30].

**One-component plasma.**—Considering a system of counterions neutralizing a charged surface, the importance of correlations is governed by a coupling constant
FIG. 2. BSK theory compared to MC simulations from [26] with $\alpha = 0.68$. The solid lines are the predictions of the BSK theory, and the markers are from the MC simulations. Strong coupling limits are plotted as dashed lines. (a) The charge density is plotted as a function of distance from an isolated surface. (b) The pressure is calculated as a function of separation distance between the two plates. As the coupling increases, the pressures between the like-charged surfaces become attractive rather than repulsive. The nondimensional pressure is $\tilde{P} = P e^2/(2\pi \ell_B q_s^2)$. Thus, with boundary conditions of $\mathbf{n} \cdot (\alpha^2 \Xi \tilde{\nabla}^3 \tilde{\phi} - \tilde{\nabla}^2 \tilde{\phi}) = -2$ and $\mathbf{n} \cdot \alpha \sqrt{\Xi} \tilde{\nabla}^3 \tilde{\phi} = \tilde{\nabla}^2 \tilde{\phi}$ at $\tilde{x} = 0$, where $\alpha$ is an order one constant. Therefore, the importance of the higher order derivative is governed by the coupling parameter, $\Xi$. The solution to these equations is compared to the results of MC simulations in Fig. 2a for a one-component plasma screening a plane of charge. The BSK theory reproduces the behavior of the one-component plasma from weak coupling, in intermediate coupling, and matches the strong coupling limit with $\alpha = 0.68$.

We can also consider the one-component plasma between two charged surfaces of equal charge density with the same sign, confining the counterions in a gap of dimensionless distance $\tilde{d}$. In Fig. 2b, the pressure is plotted as a function of separation distances between two charged surfaces with different coupling parameters, using Eq. 7 and using the same value for $\alpha$. The BSK theory again provides good agreement with the results of the MC simulations at all the coupling parameters.

Another critical question is the validity of Eq. 7 at a curved interface. The simplest model system to test is a charged cylinder for $\xi = 4$. The solid lines are the results of applying Eq. 9 and the markers are the MC simulation results. The weak coupling, strong coupling, and re-normalized strong coupling needle limits are plotted [32].

The one-component plasma consists of a single mobile ionic species which neutralizes the charge of a smeared out surface charge density. We can non-dimensionalize lengths with the Gouy-Chapman length, $\ell_{GC} = e/(2\pi \ell_B q_s)$. The potential by the thermal voltage is $\phi_0 = k_B T z e$, and the charge density by $\rho_0 = 2\pi \ell_B q_s^2 e^{-1}$. Here, we assume that the correlation length scales with the size of a correlation hole at the surface, $\delta_c = \ell_c/\ell_{GC} = \alpha \sqrt{\Xi}$.

Using $\Xi = 2\pi z^3 \ell_B^2 q_s/e$, which is a measure of the correlation hole size, $R = (ze/\pi q_s)^{1/2}$, compared to the characteristic ion distance from the surface, $\ell_{GC}$, the Gouy-Chapman length, $\Xi = R^2/2\ell_{GC}^2$. Here, $z$ is the ion valence, $\ell_B$ is the Bjerrum length, and $e$ is an elementary charge. In the weak coupling limit ($\Xi << 1$), PB theory is valid. In the strong coupling limit ($\Xi >> 1$), counterions interact with the electric potential created by the surface since ion-surface interactions dominate [26, 31].

Now we consider applying the mechanical constraint, starting with the one-component plasma of infinitesimally small size with $\mu^e x = 0$. The one-component plasma consists of a single mobile ionic species which neutralizes the charge of a smeared out surface charge density. We can non-dimensionalize lengths with the Gouy-Chapman length, $\ell_{GC} = e/(2\pi \ell_B q_s)$. The potential by the thermal voltage is $\phi_0 = k_B T z e$, and the charge density by $\rho_0 = 2\pi \ell_B q_s^2 e^{-1}$. Here, we assume that the correlation length scales with the size of a correlation hole at the surface, $\delta_c = \ell_c/\ell_{GC} = \alpha \sqrt{\Xi}$. Using $\sim$ to denote non-dimensionalized variables:

$$\alpha^2 \Xi \tilde{\nabla}^4 \tilde{\phi} - \tilde{\nabla}^2 \tilde{\phi} = 2 \tilde{\phi} = 2e^{-\tilde{\phi}}$$

with boundary conditions of $\mathbf{n} \cdot (\alpha^2 \Xi \tilde{\nabla}^3 \tilde{\phi} - \tilde{\nabla}^2 \tilde{\phi}) = -2$ and $\mathbf{n} \cdot \alpha \sqrt{\Xi} \tilde{\nabla}^3 \tilde{\phi} = \tilde{\nabla}^2 \tilde{\phi}$ at $\tilde{x} = 0$, where $\alpha$ is an order one constant. Therefore, the importance of the higher order derivative is governed by the coupling parameter, $\Xi$. The solution to these equations is compared to the results of MC simulations in Fig. 2a for a one-component plasma screening a plane of charge. The BSK theory reproduces the behavior of the one-component plasma from weak coupling, in intermediate coupling, and matches the strong coupling limit with $\alpha = 0.68$.

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the hypothesis is the one-component plasma surrounding a charged cylinder of radius $\xi = R_{\text{cyl}}/\ell_{\text{GC}}$ at infinite dilution, corresponding to a cylindrical cell with outer radius $R_{\text{out}} \to \infty$. The smaller the radius of curvature, the more likely that the configuration of correlated ions is influenced by curvature. In the “needle limit,” where $\sqrt{\Xi/\xi} \gg 1$, ions are distributed in a nearly linear fashion along the cylindrical backbone with spacing scaling as $\hat{a} \sim \Xi/\xi$, which is also the relevant scaling for the correlation length in this regime. As shown in Fig. 3, the BSK equation reproduces the results of the weak and strong coupling limits correctly. However, similar to the strong coupling expansion of [33], the theory does not correctly describe the renormalization of charge arising from Manning condensation in the needle limit, where a fraction $f = 1 - 1/\xi$ of the charge is “condensed” onto cylinder [34]. The charge density must be multiplied by this fraction, $f$, in order to match the strong coupling expansion taking into account the charge renormalization in the needle limit [32, 35].

**Electrolytes.**— A more useful and relevant application of the BSK theory is to describe the distribution of charges in electrolytes and ionic liquids, as was originally proposed. If the BSK equation for a z:1 electrolyte with salt concentration $C_{\text{ref}}$ is non-dimensionalized with the thermal voltage $\phi = (e\phi)/(kT)$ and the Debye length $\lambda_D = \sqrt{\frac{e^2kT}{(z+2)e\epsilon}}$, $\hat{\nabla} = \lambda_D \nabla$ and $\hat{\epsilon}_c = \ell_c/\lambda_D$ the BSK equation becomes:

$$
\delta^2 \nabla^4 \phi - \nabla^2 \phi = \hat{\rho} = \frac{ze^{-z\phi} - ze^\phi}{z^2 + z}.
$$

(10)

The boundary conditions are similarly modified to: $\hat{n} \cdot (\delta^2 \nabla^3 \phi - \nabla \phi) = \hat{q}_n$ and $\hat{n} \cdot \delta_c \nabla^3 \phi = \nabla^2 \phi$. To define the correlation length, we used the Grand Canonical MC data from [36], and fit the correlation length by matching to the charge density profile from an isolated surface with $\epsilon = 78.5\epsilon_0$ for a range of conditions: 1:1, 2:1, 3:1, 1:2, and 1:3 (z:1 electrolyte : electrolyte) electrolytes, $C_{\text{ref}}$ of 0.01 M, 0.1 M, and 1 M, and $q_e$ of 0.02, 0.04, 0.06, 0.08, 0.1, 0.175, 0.25, 0.375, and 0.5 C/m$^2$. The finite size of ions with symmetric 0.3 nm diameter is not taken into account in solving Eq. 10. In some cases, the contact densities for the simulations do not match PB, particularly at higher concentrations and lower charge densities, due to problems with the assumption of $\mu^{\text{CE}} = 0$. In these cases, the profiles cannot be adequately fit by varying the correlation length, and this leads to large errors in the fits. Using only profiles that can be fit with low error, we correlated the fitted correlation length, $\delta_c$, to a power law relationship of dimensionless quantities. The result is given in Fig. 4 and below:

$$
\delta_c = 0.35 \left( \frac{z^2 \ell_B}{\ell_{\text{GC}}} \right)^{-1/8} \left( \frac{z^2 \ell_B}{\lambda_D} \right)^{2/3},
$$

(11)

where $z$ is the counterion valence. This relationship gives the scaling $\ell_c \sim \ell_B^{1/4}(q_e/e)^{-1/8}C_{\text{ref}}^{-1/6}$. The correlation length scaling is thus a combination of the intrinsic lengths in the system, $\ell_B$,$(q_e/e)^{-1/2}$, and $C_{\text{ref}}^{-1/3}$. The agreement of the predicted charge density profiles from Eq. 10 with the GCMC data is very good, as exhibited in Fig. 4 for a 0.1 M 2:1 electrolyte.

One implication of the boundary condition is that the differential capacitance for $\ell_c = 0$ is equivalent to the case of $\ell_c \neq 0$ if $\mu^{\text{CE}} = 0$. Therefore, the differential capacitance for the correlated, dilute electrolyte is given by the traditional Gouy-Chapman equation: $C_D = \frac{e^2}{\lambda_D^2} \cosh(\frac{2\phi}{\lambda_D})$, in stark contrast to the original work in the limit of $\mu^{\text{CE}} = 0$ [3, 6]. It would be interesting to explore the implications of the boundary condition on electrokinetic reversals, electrochemical interfaces, biological channels, or colloidal phenomena [6–9, 12, 14–21]. For example, the DLVO theory of colloidal interactions can be modified to include attractive correlation effects [37].

Note that the Maxwell stress condition (Eq. 5) has only been stated without a dielectric jump. The stress condition may need further validation at a dielectric interface. A more general statement of matching the Maxwell stress with and without correlations might be given by a jump condition between the two media:

$$
\hat{n} \cdot [\tau_{c,1} - \tau_{c,2}] = \hat{n} \cdot [\tau_{c,1} - \tau_{c,2}]_{\ell_c=0}.
$$

(12)

For a uniformly-charged, flat interface without a dielectric jump, $\tau_{c,2} = 0$, so the RHS of the above equation reduces to $\hat{n} \cdot [\tau_{c,1} - \tau_{c,2}]_{\ell_c=0} = \frac{q_e^2}{24\epsilon} \hat{n}$.

The present analysis attempts to isolate the effect of ion correlations in a dilute electrolyte. Ion size effects, particularly for $a/\lambda_D > 1$ will require further validation to properly account for correlations guided by ion size combined with electrostatics. A non-local free energy functional might be necessary to capture the size correlations in concentrated solutions [38, 39], in conjunction with electrostatic correlations. Short-range bulk correlations [40] are not captured in this theory. Furthermore, if surface charges are discrete rather than smeared out, the contact condition may change [41]. For an arbitrary mixture of ions with different valence, the effective correlation length will depend upon correlations between each pair of species.

The phenomenological BSK theory describes non-local, discrete correlation effects with a higher-order, local, continuum description of the free energy quite well. In such a regime, one might not expect continuum models to succeed. The remarkable agreement of the theory with the one-component plasma and primitive model electrolyte suggest that higher-order, continuum equations can properly account for correlation effects, as long as the appropriate constraints are imposed at boundaries. The formalism used here could be extended to the ionic liquid limit, although ion pairing, short-range non-electrostatic correlations, and “spin glass” ordering [42] might preclude a simple continuum description.

This work was supported by an Amar G. Bose Research Grant. JPD is also supported by the National Science Foundation Graduate Research Fellowship under Grant No. 1122374.
FIG. 4. BSK theory compared to MC simulations [36] with the fitted relationship for $\delta_c$ from Eq. 11. (a-b) An example of the charge density profile with correlation length from Eq. 11 for a 2:1 electrolyte at 0.1 M concentration. (c) The agreement of the fitted correlation lengths with the scaling from Eq. 11. The profiles that can be fit with low error are used to determine the correct scaling. Non-ideal effects $\mu_\infty \neq 0$ can lead to the poor fits. The low error fits are defined by the sum of square errors between the best fit BSK charge density profile and the MC data is less than 0.005, in units of the contact charge density.

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Supplemental information: Continuum theory of electrostatic correlations at charged surfaces

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(Dated: February 15, 2019)

I. DERIVATION OF MAXWELL STRESS

Starting from the equation
\[ \nabla \cdot \tau_e = \rho E = \nabla \cdot (\epsilon E), \] \hspace{1cm} (1)

the derivation of the Maxwell stress makes use of two vector identities:
\[ \nabla (A \cdot B) = A \cdot \nabla B + B \cdot \nabla A \]
\[ \nabla \cdot (AB) = (\nabla \cdot A)B + A \cdot \nabla B, \] \hspace{1cm} (2)

for two vectors \( A \) and \( B \), valid when \( \nabla \times A = 0 \) and \( \nabla \times B = 0 \). Using the permittivity operator \( \epsilon = \epsilon(1 - \ell_c^2 \nabla^2) \), the expression can be split into two terms that can be analyzed separately,

\[ \nabla \cdot \tau_e = \nabla \cdot (\epsilon E)E - \nabla \cdot (\ell_c^2 \nabla^2 E)E. \] \hspace{1cm} (3)

With the requirement of \( \nabla \times E = 0 \), the first term can be written as

\[ \nabla \cdot (\epsilon E)E = \nabla \cdot (\epsilon E)E + \frac{1}{2} \epsilon \nabla \cdot \nabla E + \frac{1}{2} E \cdot \nabla (\epsilon E) - \frac{1}{2} (\epsilon E \cdot E) \]
\[ = \nabla \cdot (\epsilon EE) - \frac{1}{2} \epsilon E^2 I + \frac{1}{2} E \cdot \nabla \epsilon \]
\[ = \nabla \cdot (\epsilon EE) - \frac{1}{2} \epsilon E^2 I, \] \hspace{1cm} (4)

with constant \( \epsilon \), where \( I \) is the identity tensor. The second term can be similarly expanded:

\[ -\nabla \cdot (\ell_c^2 \nabla^2 E)E = -\nabla \cdot (\ell_c^2 \nabla^2 E)E - \ell_c^2 \nabla E \cdot \nabla E \]
\[ - E \cdot \nabla (\ell_c^2 \nabla^2 E) + \nabla E \cdot \ell_c^2 \nabla^2 E \]
\[ = -\nabla \cdot (\ell_c^2 \nabla^2 E)E - \ell_c^2 \nabla E \cdot \nabla E - E \cdot \nabla (\ell_c^2 \nabla^2 E) \]
\[ + \nabla (E \cdot \ell_c^2 \nabla^2 E) + E \cdot \nabla (\ell_c^2 \nabla^2 E) + (\nabla \cdot E)\ell_c^2 \nabla^2 E \]
\[ - \nabla \cdot (E \ell_c^2 \nabla^2 E) \]
\[ = \nabla \cdot [-\ell_c^2 (\nabla^2 E)E - \ell_c^2 E (\nabla^2 E) + E \cdot (\ell_c^2 \nabla^2 E)I] \]
\[ + (\nabla \cdot E)\ell_c^2 \nabla^2 E. \] \hspace{1cm} (5)

At this point, another product rule must be used:
\[ a \nabla a = \frac{1}{2} \nabla (a^2), \] \hspace{1cm} (6)

where \( a \) is a scalar. Applying the above identity gives:

\[ -\nabla \cdot (\ell_c^2 \nabla^2 E)E = \]
\[ \nabla \cdot [-\ell_c^2 (\nabla^2 E)E - \ell_c^2 E (\nabla^2 E) + E \cdot (\ell_c^2 \nabla^2 E)I] \]
\[ + \frac{\ell_c^2}{2} \nabla (\nabla \cdot E)^2 \]
\[ = -\nabla \cdot [-\ell_c^2 (\nabla^2 E)E - \ell_c^2 E (\nabla^2 E) + E \cdot (\ell_c^2 \nabla^2 E)I] \]
\[ + \frac{\ell_c^2}{2} \nabla (\nabla \cdot E)^2. \] \hspace{1cm} (7)

with constant \( \epsilon \) and \( \ell_c \). The final expression for the Maxwell stress is therefore:

\[ \tau_e = \epsilon EE - \frac{1}{2} \epsilon E^2 I + \ell_c^2 \left[ (E \cdot \nabla^2 E) I - E (\nabla^2 E) \right. \]
\[ - \left. (\nabla^2 E) E + \frac{1}{2} (\nabla \cdot E)^2 I \right]. \] \hspace{1cm} (8)

II. ONE-COMPONENT PLASMA AROUND A CYLINDER

Additional results for the one-component plasma are exhibited in Fig. S1, showing the occurrence of Manning criticality in MC simulations, which cannot be reproduced by the BSK theory. While the condensation phenomenon should only occur at infinite dilution, a finite system size must be chosen for the numerical solution of the BSK equation. The parameter \( \Delta = \ln(R_{out}/R_{cyl}) \) is varied between 6.2 and 13 to ensure numerical accuracy of the solutions over the large domain, depending on the value of \( \delta_c \).
III. COMPARISON TO FULL ELECTROLYTE DATA SET

The comparisons the data from [2] is explored more extensively in Fig. S2. Given the fitted correlation lengths, the BSK theory can closely match the structure of the charge density for many of the plots. However, at large concentrations, the excess electrochemical potential and ion size effects play a bigger role, leading to inaccuracies of the theory. Even so, the theory is quite adequate up to to provide the correct qualitative corrections up to 1M for the symmetric ions. Note that the MC profiles are shifted by one ion radius, so that the zero $x$ values of the theory and the simulations match.

FIG. S1. BSK theory compared to additional MC simulations from [1] using $\delta_c = \Xi / \xi$ for the counterion density around a charged cylinder for (a) $\xi = 1.2$ and (b) $\xi = 1.4$. The solid lines are the BSK theory and the markers are the MC simulation results.

[1] J. P. Mallarino, G. Tellez, and E. Trizac, The Journal of Physical Chemistry B 117, 12702 (2013).
[2] M. Valiskó, T. Kristóf, D. Gillespie, and D. Boda, AIP Advances 8, 025320 (2018).
FIG. S2. Comprehensive comparison of BSK theory with MC simulations from [2]. Note that the profiles are organized by $z_{\text{counterion}} : z_{\text{coion}}$ in each row and by $C_{\text{ref}}$ in each column.