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Journal

Nonlinearity, 26(10)

ISSN

0951-7715

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Publication Date

2013-10-01

DOI

10.1088/0951-7715/26/10/2899

Peer reviewed



Published in final edited form as:

Nonlinearity. 2013 October 1; 26(10): 2899–2922. doi:10.1088/0951-7715/26/10/2899.

Ionic Size Effects: Generalized Boltzmann Distributions, Counterion Stratification, and Modified Debye Length

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Abstract

Near a charged surface, counterions of different valences and sizes cluster; and their concentration profiles stratify. At a distance from such a surface larger than the Debye length, the electric field is screened by counterions. Recent studies by a variational mean-field approach that includes ionic size effects and by Monte Carlo simulations both suggest that the counterion stratification is determined by the ionic valence-to-volume ratios. Central in the mean-field approach is a free-energy functional of ionic concentrations in which the ionic size effects are included through the entropic effect of solvent molecules. The corresponding equilibrium conditions define the generalized Boltzmann distributions relating the ionic concentrations to the electrostatic potential. This paper presents a detailed analysis and numerical calculations of such a free-energy functional to understand the dependence of the ionic charge density on the electrostatic potential through the generalized Boltzmann distributions, the role of ionic valence-to-volume ratios in the counterion stratification, and the modification of Debye length due to the effect of ionic sizes.

1 Introduction

Electrostatic interactions between macromolecules and mobile ions in an aqueous solvent generate strong, long-ranged forces that play a key role in biological processes. In such interactions, ionic sizes or excluded volumes can affect many of the detailed chemical and physical properties of an underlying biological system. For instance, differences in ionic sizes can affect how mobile ions bind to nucleic acids [3,4,32]. The size of monovalent cations can influence the stability of RNA tertiary structures [21]. The ionic size effect is more profound in the ion channel selectivity, see, e.g., [16, 24]. Detailed Monte Carlo simulations and integral equations calculations also confirm some of these experimentally observed properties due to the non-uniformity of ionic sizes [17, 28, 34, and 36].

The classical Poisson–Boltzmann (PB) equation (PBE) is perhaps the most widely used and efficient model of the electrostatics in ionic solutions, particularly in biomolecular systems [2, 10, 12, 14, 27, 30]. Despite of its many successful applications, this mean-field theory is known to fail in capturing the ionic size effects and ion-ion correlations [15, 17, 28, 35, and

36]. Numerical calculations based on the classical PBE often predict unphysically high concentrations of counterions near a charged surface [5, 38].

Recently, there has been a growing interest in studying the ionic size effects within the PB-like mean-field framework [5–7,9,11,18–20,22,23,25,26,31,33,38]. One of the main approaches is to include the additional entropic effect of solvent molecules in the free-energy functional of all local ionic concentrations, $c_1 = c_1(x), \dots, c_M = c_M(x)$ (M being the total number of ionic species), similar to that in the classical PB model. Given the volume v_i of an ion of the i th species ($1 \leq i \leq M$) and the volume v_0 of a solvent molecule, one can define the local solvent concentration $c_0 = c_0(x)$ by

$$c_0(x) = v_0^{-1} \left[1 - \sum_{i=1}^M v_i c_i(x) \right]. \quad (1.1)$$

The size-modified electrostatic free-energy functional is then given by [5, 20, 22, and 26]

$$F[c_1, \dots, c_M] = \int \left[\frac{1}{2} \rho \psi + \beta^{-1} \sum_{i=0}^M c_i [\ln(v_i c_i) - 1] - \sum_{i=1}^M \mu_i c_i \right] dV. \quad (1.2)$$

Here, $\rho = \sum_{i=1}^M q_i c_i$ is the ionic charge density, where $q_i = z_i e$, and z_i is the valence of an ion of the i th species and e is the elementary charge, $\beta = (k_B T)^{-1}$ with k_B the Boltzmann constant and T the temperature, and μ_i is the chemical potential of an ion of the i th species. The electrostatic potential ψ is determined by Poisson's equation $-\nabla \cdot \epsilon \nabla \psi = \rho$, together with some boundary conditions, where ϵ is the dielectric coefficient.

One easily verifies that the equilibrium conditions $\delta_{c_i} F = 0$ ($i = 1, \dots, M$) are given by

$$\frac{v_i}{v_0} \ln(v_0 c_0) - \ln(v_i c_i) = \beta (q_i \psi - \mu_i), \quad i = 1, \dots, M, \quad (1.3)$$

where ψ is the electrostatic potential corresponding to the equilibrium ionic concentrations c_1, \dots, c_M . It is shown in [22] that this system of nonlinear algebraic equations has a unique solution $c_i = B_i(\psi)$ ($i = 1, \dots, M$), defining the generalized Boltzmann distributions. If $v_0 = v_1 = \dots = v_M$, then these distributions are [22,23]

$$c_i = \frac{c_i^\infty e^{-\beta q_i \psi}}{1 + \sum_{j=1}^M v_j c_j^\infty (e^{-\beta q_j \psi} - 1)}, \quad i = 1, \dots, M,$$

where

$$c_i^\infty = \frac{v_i^{-1} e^{\beta \mu_i}}{1 + \sum_{j=1}^M e^{\beta \mu_j}}, \quad i = 1, \dots, M.$$

Note that, for each i , c_i^∞ is the value of c_i when $\psi = 0$. In general, if v_0, v_1, \dots, v_M are not all the same, then explicit formulas for $c_i = B_i(\psi)$ ($i = 1, \dots, M$) seem unavailable.

In studying the ionic size effects in biomolecular reactions, Lu and Zhou [26] minimized the free-energy functional (1.2) by solving for a steady-state solution of a size-modified Poisson–Nernst–Planck system of partial differential equations. In [38], Zhou *et al.* developed a constrained optimization method for numerically minimizing the functional (1.2) with Poisson's equation as a constraint. They found the remarkable stratification of ionic concentrations near a highly charged surface. Moreover, they found that the ionic valence-to-volume ratio is an important parameter that determines the stratification. Specifically, the counterion with the largest valence-to-volume ratio has the highest ionic concentration near the surface, the counterion with the second largest such ratio has also the second highest ionic concentration, and so on. Subsequently, Wen *et al.* [37] performed Monte Carlo simulations that confirm such a phenomenon.

In this work, we further study the size-modified, mean-field free-energy functional (1.2). We begin with a description of two different forms of the electrostatic free-energy functional, one with and the other without the constraint of total number of ions for each ionic species. We show the equivalence of these two forms; cf. Theorem 2.2. We also derive the conditions for the equilibrium concentrations; cf. (1.3).

We then focus on the equilibrium conditions (1.3) to analyze the generalized Boltzmann distributions. In particular, we characterize the behavior of the equilibrium ionic charge

density $\rho_i = \sum_{i=1}^M q_i c_i$ as a function of ψ . Our main results of analysis are as follows:

1. The concentration of ions with the largest and that with smallest valence-to-volume ratios monotonically decreases and monotonically increases, respectively, with respect to the electrostatic potential ψ . As $\psi \rightarrow -\infty$ (or ∞), the concentration of ions with the largest (or smallest) valence-to-volume ratio approaches to the inverse of its corresponding volume, while all other concentrations approach zero.
2. The total ionic charge density $\rho_i = \rho_i(\psi)$ is a monotonic function of the potential ψ . If all ions are cations (i.e., all $z_j > 0$), then this density is always positive, $\rho_i(\infty) = 0$, and $\rho_i(-\infty)$ exists and is finite. If all ions are anions (i.e., all $z_j < 0$), then this density is always negative, $\rho_i(-\infty) = 0$, and $\rho_i(\infty)$ exists and is finite. If both cations and anions exist, then both $\rho_i(-\infty)$ and $\rho_i(\infty)$ exist and are finite, and the density reaches zero at a unique value of the potential ψ . All these are summarized in Figure 2 in Subsection 3.2.
3. A size-modified Debye length, $\hat{\lambda}_D$, is derived with a weak potential limit. A formula of $\hat{\lambda}_D$ is given in (3.23) in Subsection 3.3.

Note that ionizable groups of biomolecules can dissociate in aqueous solution to produce anions or cations. So, studying an ionic system with only cations or only anions is of interest. In general, such a system can serve a model approximation system, as near a charged surface the concentration of coions is usually very low.

We finally consider a charged spherical molecule of radius R_0 in an ionic solution that occupies a region defined by $\{R_0 < |x| < R_\infty\}$ for some $R_\infty > R_0$, and study the PBE, both classical and size-modified. In the case R_∞ is finite, the detailed properties of the equilibrium electrostatic potential are described through two parameters: one is the prescribed surface charge density σ at the boundary $|x| = R_0$ and the other is an effective surface charge density σ_∞ at the boundary $|x| = R_\infty$. This effective density is set by the total charge neutrality. When $\sigma\sigma_\infty < 0$ the potential ψ is monotonic. Otherwise, it decreases then increases, or it increases then decreases. These are summarized in Theorem 4.2 and illustrated in Figure 3 in Section 4. With the same setting of a charged spherical molecule, we numerically minimize the functional (1.2) and confirm our analysis; cf. Figure 4 in

Section 5. If $R_\infty = \infty$, then only in the case that both cations and anions exist and they neutralize in the bulk does the PBE (classical or size-modified) permit a unique solution, the electrostatic potential, that is radially symmetric and monotonic, and vanishes at infinity. We remark that considering a finite R_∞ is of certain interest as it is known that the effect of finite size of charged system can be significant, cf. e.g., [29], and as it is practically useful in numerical computations.

The rest of this paper is organized as follows: In Section 2, we describe the electrostatic free-energy functionals and derive the conditions of equilibrium concentrations. In Section 3, we present an analysis on the equilibrium conditions and on the stratification of counterions of multiple valences and sizes near a charged surface. In Section 4, we study a charged spherical molecule immersed in an ionic solution. In Section 5, we report numerical calculations to confirm our analysis. Finally, in Section 6, we draw conclusions.

2 The Free-Energy Functional and Equilibrium Conditions

We consider an ionic solution with M ($M \geq 1$) ionic species, occupying a region Ω that is a bounded, open, and connected subset of \mathbb{R}^3 with a smooth boundary $\Gamma \neq \emptyset$. The boundary Γ is divided into two disjoint and smooth parts Γ_D and Γ_N (with D for Dirichlet and N for Neumann). We assume that a surface charge density is given on Γ_N and the electrostatic potential is specified on Γ_D . Our set up covers the case that $\Gamma_N = \emptyset$ and $\Gamma_D = \Gamma$ and that $\Gamma_D = \emptyset$ and $\Gamma_N = \Gamma$. It also covers the important case of biomolecular solvation with an implicit solvent: The region Ω is the solvent region and the part of the boundary Γ_N is the solute-solvent interface; cf. Figure 1. The surface charge density on Γ_N effectively replaces the density of partial charges carried by solute atoms.

For each i ($1 \leq i \leq M$), we denote by $c_i = c_i(x)$ the local ionic concentration of the i th ionic species at position $x \in \Omega$. As before, $\rho = \sum_{i=1}^M q_i c_i$ is the ionic charge density. We also denote by v_i ($1 \leq i \leq M$) the volume of an ion of the i th species and by v_0 the volume of a solvent molecule. The local concentration of the solvent, $c_0 = c_0(x)$, is then defined by (1.1). For convenience we denote $c = (c_1, \dots, c_M)$. We consider minimizing the mean-field electrostatic free-energy functional

$$F[c] = \int_{\Omega} \frac{1}{2} \rho \psi \, dV + \int_{\Gamma_N} \frac{1}{2} \sigma \psi \, dS + \beta^{-1} \sum_{i=1}^M \int_{\Omega} c_i [\ln(v_i c_i) - 1] \, dV - \sum_{i=1}^M \int_{\Omega} \mu_i c_i \, dV, \quad (2.1)$$

$$\text{with} \quad \begin{cases} \nabla \cdot \varepsilon \nabla \psi = -\rho & \text{in } \Omega, \\ \psi = \psi_\infty & \text{on } \Gamma_D, \\ \varepsilon \frac{\partial \psi}{\partial n} = \sigma & \text{on } \Gamma_N. \end{cases} \quad (2.2)$$

Here, the first two terms in (2.1) describe the electrostatic potential energy. The electrostatic potential ψ is the unique solution of the boundary-value problem of Poisson's equation (2.2), where $\varepsilon = \varepsilon(x)$ ($x \in \Omega$) is the dielectric coefficient assumed to be Lebesgue measurable and bounded above and below by positive constants, and n denotes the unit exterior normal at the boundary Γ . Both $\psi_\infty : \Gamma_D \rightarrow \mathbb{R}$ and $\sigma : \Gamma_N \rightarrow \mathbb{R}$ are given bounded and smooth functions, representing the electrostatic potential at Γ_D and the surface charge density at Γ_N , respectively. The third term in (2.1) has the form $-TS$ with S being the entropy. The given parameters μ_i ($i = 1, \dots, M$) in the last term in (2.1) are the chemical potentials of the ions.

We define $\psi_D : \Omega \rightarrow \mathbb{R}$ and $\psi_N : \Omega \rightarrow \mathbb{R}$ by

$$\begin{cases} \nabla \cdot \varepsilon \nabla \psi_D = 0 & \text{in } \Omega, \\ \psi_D = \psi_\infty & \text{on } \Gamma_D, \\ \varepsilon \frac{\partial \psi_D}{\partial n} = 0 & \text{on } \Gamma_N, \end{cases} \quad \text{and} \quad \begin{cases} \nabla \cdot \varepsilon \nabla \psi_N = 0 & \text{in } \Omega, \\ \psi_N = 0 & \text{on } \Gamma_D, \\ \varepsilon \frac{\partial \psi_N}{\partial n} = \sigma & \text{on } \Gamma_N, \end{cases}$$

respectively. For a given function $f: \Omega \rightarrow \mathbb{R}$ that is in the Sobolev space $H^{-1}(\Omega)$ [1,13], let us denote by $Lf: \Omega \rightarrow \mathbb{R}$ the unique weak solution to the following boundary-value problem of Poisson's equation

$$\begin{cases} \nabla \cdot \varepsilon \nabla (Lf) = -f & \text{in } \Omega, \\ Lf = 0 & \text{on } \Gamma_D, \\ \varepsilon \frac{\partial (Lf)}{\partial n} = 0 & \text{on } \Gamma_N. \end{cases}$$

(The uniqueness is guaranteed if Γ_D has a nonzero surface measure.) Notice that L is a linear and self-adjoint operator from the space $H^{-1}(\Omega)$ to that consisting of $H^1(\Omega)$ -functions vanishing on Γ_D . With these the solution ψ to the boundary-value problem (2.2) can be decomposed as

$$\psi = \hat{\psi} + \psi_D + \psi_N, \quad (2.3)$$

where $\hat{\psi} = L \left(\sum_{i=1}^M q_i c_i \right)$. By integration by parts, we have

$$\begin{aligned} \int_{\Gamma_N} \sigma \hat{\psi} \, dS &= \int_{\Gamma_N} \varepsilon \frac{\partial \psi_N}{\partial n} \hat{\psi} \, dS = \int_{\Gamma} \varepsilon \frac{\partial \psi_N}{\partial n} \hat{\psi} \, dS \\ &= \int_{\Omega} \hat{\psi} \nabla \cdot \varepsilon \nabla \psi_N \, dV + \int_{\Omega} \varepsilon \nabla \hat{\psi} \cdot \nabla \psi_N \, dV = \int_{\Omega} \varepsilon \nabla \hat{\psi} \cdot \nabla \psi_N \, dV \\ &= \int_{\Omega} \left(-\nabla \cdot \varepsilon \nabla \hat{\psi} \right) \psi_N \, dV = \int_{\Omega} \left(\sum_{i=1}^M q_i c_i \right) \psi_N \, dV. \end{aligned}$$

Therefore the free-energy functional $F[c]$ can now be rewritten as

$$\begin{aligned} F[c] &= \int_{\Omega} \frac{1}{2} \left(\sum_{i=1}^M q_i c_i \right) L \left(\sum_{j=1}^M q_j c_j \right) \, dV \\ &\quad + \sum_{i=1}^M \int_{\Omega} \left[q_i \left(\frac{1}{2} \psi_D + \psi_N \right) - \mu_i \right] c_i \, dV \\ &\quad + \beta^{-1} \sum_{i=0}^M \int_{\Omega} c_i [\ln(v_i c_i) - 1] \, dV \\ &\quad + \int_{\Gamma_N} \frac{1}{2} \sigma (\psi_N + \psi_D) \, dS. \end{aligned}$$

By formal and routine calculations using the decomposition (2.3) and the fact that L is self-adjoint, we obtain the first variations [8,22,23,and 26]

$$\delta_{c_i} F[c] = q_i \left(\psi - \frac{1}{2} \psi_D \right) - \mu_i + \beta^{-1} \left[\ln(v_i c_i) - \frac{v_i}{v_0} \ln(v_0 c_0) \right], \quad i=1, \dots, M, \quad (2.4)$$

where ψ is determined by (2.2) with $\rho = \sum_{i=1}^M q_i c_i$. The equilibrium conditions $\delta_{c_i} F[c] = 0$ ($i=1, \dots, M$) are then given by

$$\frac{v_i}{v_0} \ln(v_0 c_0) - \ln(v_i c_i) = \beta \left[q_i \left(\psi - \frac{1}{2} \psi_D \right) - \mu_i \right], \quad i=1, \dots, M. \quad (2.5)$$

The following result can be proved by the argument used in [22]:

Theorem 2.1

1. *The functional $F[c]$ is convex. Moreover, it has a unique minimizer in the set of all concentrations c_1, \dots, c_M such that $c_i > 0$ ($i = 1, \dots, M$) and $\sum_{i=1}^M v_i c_i \leq 1$ in Ω .*
2. *There exist $\theta_1, \theta_2 \in \mathbb{R}$ with $0 < \theta_1 < \theta_2 < 1$ that bound uniformly from below and above, respectively, the free-energy minimizing ionic concentrations and the corresponding concentration of solvent molecules.*
3. *The minimizer is characterized by the equilibrium conditions (2.5).*

We now consider a different formulation: minimize the electrostatic free-energy functional

$$\hat{F}[c] = \int_{\Omega} \frac{1}{2} \rho \psi \, dV + \int_{\Gamma_N} \frac{1}{2} \sigma \psi \, dS + \beta^{-1} \sum_{i=0}^M \int_{\Omega} c_i [\ln(v_i c_i) - 1] \, dV, \quad (2.6)$$

$$\text{with } \begin{cases} \nabla \cdot \varepsilon \nabla \psi = -\rho & \text{in } \Omega, \\ \psi = \psi_{\infty} & \text{on } \Gamma_D, \\ \varepsilon \frac{\partial \psi}{\partial n} = \sigma & \text{on } \Gamma_N, \end{cases} \quad (2.7)$$

$$\text{subject to } \int_{\Omega} c_i \, dV = N_i, \quad i=1, \dots, M, \quad (2.8)$$

where again $\rho = \sum_{i=1}^M q_i c_i$. Note that the functional $F[c]$ defined in (2.1) has the term of the chemical potentials μ_i . Here the functional $\hat{F}[c]$ does not have that term. On the other hand, the minimization of $\hat{F}[c]$ is subject to the conservation of total number of ions in each of the M ionic species, defined in (2.8) in which N_i ($i = 1, \dots, M$) are given positive numbers. The system (2.7) is the same as (2.2).

It again follows from standard arguments that the functional $\hat{F}[c]$ with (2.7) has a unique minimizer $\hat{c} = (\hat{c}_1, \dots, \hat{c}_M)$ among all $c = (c_1, \dots, c_M)$ subject to (2.8). By a similar argument used in deriving (2.4), we have for any $c = (c_1, \dots, c_M)$ that

$$\delta_{c_i} \hat{F}[c] = q_i \left(\psi - \frac{1}{2} \psi_D \right) + \beta^{-1} \left[\ln(v_i c_i) - \frac{v_i}{v_0} \ln(v_0 c_0) \right], \quad i=1, \dots, M. \quad (2.9)$$

For the minimizer \hat{c} , we have

$$\int_{\Omega} \left(\delta_{c_i} \hat{F}[\hat{c}] \right) d_i dV = 0 \quad \forall d_i: \int_{\Omega} d_i dV = 0, \quad i=1, \dots, M.$$

By Lemma 2.1 below, these lead to the existence of constants, still denoted by μ_i ($i = 1, \dots, M$), such that $\delta_{c_i} F[\hat{c}] = \mu_i$ ($i = 1, \dots, M$). By (2.9), this is exactly (2.5).

We have in fact proved the following:

Theorem 2.2

The variational problem of minimizing the functional (2.1) with (2.2) is equivalent to that of minimizing the functional $F[c]$ with (2.7) and (2.8).

We remark that, if one knows the chemical potentials μ_i ($i = 1, \dots, M$), then the first formulation, i.e., minimizing $F[c]$, can be mathematically and computationally simpler than the second one that has the constraint of total numbers of ions. The question is how the chemical potentials can be estimated by experiment or other models. A similar practical issue for the second formulation with the constraint (2.8) is that one needs to have a good estimate of each N_i , the total number of ions of the i th species in the system.

Lemma 2.1

Let $u \in L^2(\Omega)$ be such that

$$\int_{\Omega} u v dV = 0 \quad \forall v \in L^2(\Omega): \int_{\Omega} v dV = 0.$$

Then there exists a constant $\mu \in \mathbb{R}$ such that $u = \mu$ almost everywhere in Ω .

Proof—Denote for any $w \in L^2(\Omega)$

$$\bar{w} = \int_{\Omega} w dV = \frac{1}{|\Omega|} \int_{\Omega} w dV,$$

where $|\Omega|$ is the volume (i.e., the Lebesgue measure) of Ω . Note that the integral of $w - \bar{w}$ over Ω vanishes. For any $v \in L^2(\Omega)$, we have by the assumption of the lemma that

$$\int_{\Omega} (u - \bar{u}) v dV = \int_{\Omega} (u - \bar{u}) (v - \bar{v}) dV = \int_{\Omega} u (v - \bar{v}) dV = 0.$$

Therefore $u = \bar{u}$ almost everywhere in Ω . Set $\mu = \bar{u}$. The Lemma is proved. **Q.E.D.**

3 Equilibrium Ionic Concentrations and Modified Debye Length

We consider the equilibrium conditions (2.5) that determine the equilibrium ionic concentrations. Introducing a shifted potential $\phi = \psi - \psi_D/2$, we can rewrite (2.5) as

$$\frac{v_i}{v_0} \ln(v_0 c_0) - \ln(v_i c_i) = \beta (q_i \phi - \mu_i), \quad i=1, \dots, M. \quad (3.1)$$

As c_0 is given in (1.1), this is a system of nonlinear algebraic equations for the unknowns c_1, \dots, c_M . In [22], Li proved the following:

Theorem 3.1

1. For each $\phi \in \mathbb{R}$ the system (3.1) has a unique solution $c_i = B_i(\phi) \in (0, v_i^{-1})$ ($i = 1, \dots, M$). Moreover each $B_i: \mathbb{R} \rightarrow (0, v_i^{-1})$ is a smooth function.
2. Define $V: \mathbb{R} \rightarrow \mathbb{R}$ by

$$V(\phi) = - \sum_{i=1}^M \int_0^\phi q_i B_i(\xi) d\xi + V_0, \quad (3.2)$$

where V_0 is a constant. Then the function $V: \mathbb{R} \rightarrow \mathbb{R}$ satisfies $V'' > 0$ on \mathbb{R} and is thus strictly convex.

The relations $c_i = B_i(\phi)$ ($i = 1, \dots, M$) define the generalized Boltzmann distributions for the equilibrium concentrations c_1, \dots, c_M . In general, explicit formulas of such distributions

seem to be unavailable. Notice that $-V'(\phi) = \sum_{i=1}^M q_i B_i(\phi)$ with $\phi = \psi - \psi_D/2$ is the ionic charge density. The proof of $V'' > 0$ in \mathbb{R} given in [22] (cf. the proof of Lemma 5.2 in [22]) applies to our present case; cf. the remark in Subsection 3.1. The electrostatic potential ψ is now the unique solution to the boundary-value problem of the generalized and implicit PBE

$$\nabla \cdot \varepsilon \nabla \psi - V' \left(\psi - \frac{\psi_D}{2} \right) = 0. \quad (3.3)$$

The boundary conditions are the same as in (2.2). The existence and uniqueness of the equilibrium concentrations c_i ($i = 1, \dots, M$) lead to that of the solution to this boundary-value problem.

3.1 Equilibrium ionic concentrations

For convenience, we denote $z_0 = 0$, $q_0 = 0$, and $\mu_0 = 0$. We assume that all the M ionic species have different ionic valence-to-volume ratios. We assume there are $l > 0$ species of anions and $m > 0$ species of cations. So $M = l + m$. If $l = 0$ then all ions are cations. If $m = 0$ then all ions are anions. We label all the M ionic species and the solvent concentration by $-l, \dots, -1, 0, 1, \dots, m$, and assume that

$$\frac{z_{-l}}{v_{-l}} < \dots < \frac{z_{-1}}{v_{-1}} < \frac{z_0}{v_0} = 0 < \frac{z_1}{v_1} < \dots < \frac{z_m}{v_m}. \quad (3.4)$$

For convenience, we denote $J = \{-l, \dots, -1, 0, 1, \dots, m\}$. With our notation, the equilibrium conditions (2.5) then become

$$\frac{v_i}{v_0} \ln(v_0 c_0) - \ln(v_i c_i) = \beta (q_i \phi - \mu_i) \quad \forall i \in J. \quad (3.5)$$

Note that by Theorem 3.1 $c_i = B_i(\phi)$ for any $i \in J$ with $i \neq 0$. We thus have by (1.1) that

$$c_0 = B_0(\phi) = v_0^{-1} \left[1 - \sum_{i \in J, i \neq 0} v_i B_i(\phi) \right]. \quad (3.6)$$

Theorem 3.2—Let $c_i = B_i(\phi)$ ($i \in J$) be the equilibrium concentrations defined by (3.5) and (3.6). Assume (3.4) holds true.

1. Monotonicity of concentrations with the largest and smallest valence-to-volume ratios. We have $c'_{-l}(\phi) > 0$ and $c'_m(\phi) < 0$ for all $\phi \in \mathbb{R}$.
2. Stratification of concentration profiles. If $i \in \{-l, \dots, m-1\}$ then

$$(v_i c_i)^{1/v_i} < (v_{i+1} c_{i+1})^{1/v_{i+1}} \text{ if and only if } \phi < \frac{\mu_{i+1}/v_{i+1} - \mu_i/v_i}{q_{i+1}/v_{i+1} - q_i/v_i}.$$

If $i \in \{-l+1, \dots, m\}$ then

$$(v_i c_i)^{1/v_i} > (v_{i-1} c_{i-1})^{1/v_{i-1}} \text{ if and only if } \phi > \frac{\mu_{i-1}/v_{i-1} - \mu_i/v_i}{q_{i-1}/v_{i-1} - q_i/v_i}.$$

3. Asymptotic behavior of concentrations. We have

$$v_{-l} c_{-l} \rightarrow 1 \text{ and } c_i \rightarrow 0 \text{ (} i = -l+1, \dots, m \text{) as } \phi \rightarrow \infty, \quad (3.7)$$

$$v_m c_m \rightarrow 1 \text{ and } c_i \rightarrow 0 \text{ (} i = -l, \dots, m-1 \text{) as } \phi \rightarrow -\infty. \quad (3.8)$$

Proof: We first prove that

$$(v_i c_i)^{1/v_i} = e^{-\beta(\mu_j/v_j - \mu_i/v_i)} e^{\beta(q_j/v_j - q_i/v_i)\phi} (v_j c_j)^{1/v_j} \quad \forall i, j \in J. \quad (3.9)$$

In fact, it follows immediately from (3.5) that

$$(v_0 c_0)^{1/v_0} = e^{-\beta\mu_i/v_i} e^{\beta(q_i/v_i)\phi} (v_i c_i)^{1/v_i} \quad \forall i \in J. \quad (3.10)$$

This also implies

$$(v_i c_i)^{1/v_i} = e^{\beta\mu_i/v_i} e^{-\beta(q_i/v_i)\phi} (v_0 c_0)^{1/v_0} \quad \forall i \in J. \quad (3.11)$$

It follows from (3.10) and (3.11) that (3.9) holds true if one of i and j is 0. Now let $i, j \in J$ with $i \neq j, i \neq 0$, and $j \neq 0$. We have by (3.5) that

$$\frac{1}{v_i} \ln(v_i c_i) + \frac{\beta q_i}{v_i} \phi - \frac{\beta \mu_i}{v_i} = \frac{1}{v_j} \ln(v_j c_j) + \frac{\beta q_j}{v_j} \phi - \frac{\beta \mu_j}{v_j}.$$

Consequently,

$$(v_i c_i)^{1/v_i} = e^{-\beta(\mu_j/v_j - \mu_i/v_i)} e^{\beta(q_j/v_j - q_i/v_i)\phi} (v_j c_j)^{1/v_j}.$$

This, together with (3.10) and (3.11), implies (3.9).

We now prove parts (1)–(3).

1. Denote $\gamma = v_0 c_0$ and $\eta_i = e^{\beta \mu_i}$ for each $i \in J$. It follows from the equilibrium conditions (3.5) that

$$c_i = \frac{\eta_i}{v_i} \gamma^{v_i/v_0} e^{-\beta q_i \phi} \quad \forall i \in J. \quad (3.12)$$

This and the definition of c_0 (cf. (1.1)) imply

$$\sum_{i \in J} \eta_i \gamma^{v_i/v_0} e^{-\beta q_i \phi} = 1. \quad (3.13)$$

Taking the derivative of both sides of (3.13) with respect to ϕ , and using our notation $z_0 = 0$ and $\mu_0 = 0$, we obtain

$$\gamma'(\phi) = \frac{\beta v_0 \gamma \sum_{i \in J} \eta_i q_i \gamma^{v_i/v_0} e^{-\beta q_i \phi}}{\sum_{i \in J} \eta_i v_i \gamma^{v_i/v_0} e^{-\beta q_i \phi}}.$$

Fix $k \in J$. Taking the derivative of both sides of (3.12) with $i = k$ with respect to ϕ and using the above expression of $\gamma'(\phi)$, we get

$$c'_k(\phi) = \beta \eta_k \gamma^{v_k/v_0} e^{-\beta q_k \phi} \frac{\sum_{i \in J} \eta_i v_i (q_i/v_i - q_k/v_k) \gamma^{v_i/v_0} e^{-\beta q_i \phi}}{\sum_{i \in J} \eta_i v_i \gamma^{v_i/v_0} e^{-\beta q_i \phi}}. \quad (3.14)$$

This, the assumption (3.4), and the definition $q_i = z_i e$ ($i \in J$) imply that $c'_m(\phi) < 0$ and $c'_{-l}(\phi) > 0$.

2. This follows directly from (3.9).
3. Since $0 < v_{-l} c_{-l} < 1$, we have again by (3.9) with $j = -l$ and (3.4) that for any $i \in J$ with $i > -l$

$$(v_i c_i)^{1/v_i} \leq e^{-\beta(\mu_{-l}/v_{-l} - \mu_i/v_i)} e^{\beta(q_{-l}/v_{-l} - q_i/v_i)\phi} \rightarrow 0 \quad \text{as } \phi \rightarrow \infty.$$

Since $\sum_{i \in J} v_i c_i = 1$, we thus also have $v_{-l} c_{-l} \rightarrow 1$ as $\varphi \rightarrow \infty$. This proves (3.7). The proof of (3.8) is similar. **Q.E.D.**

Remark: By (3.14) and the Cauchy–Schwarz inequality, we obtain through a series of calculations that

$$\sum_{k \in J} q_k c'_k(\varphi) = \frac{\beta \left[\left(\sum_{i \in J} q_i v_i c_i \right)^2 - \left(\sum_{i \in J} q_i^2 c_i \right) \left(\sum_{i \in J} v_i^2 c_i \right) \right]}{\sum_{i \in J} v_i^2 c_i} \leq 0.$$

Since $q_i/v_i (i \in J)$ are not all the same, this is a strict inequality. Thus the function $V : \mathbb{R} \rightarrow \mathbb{R}$, defined in (3.2) with $-V'(\varphi)$ being the total ionic charge density, is a strictly convex function of φ ; cf. Theorem 3.1.

3.2 Equilibrium charge density

We now study the properties of the ionic charge density $V'(\varphi) = -\sum_{i \in J} q_i B_i(\varphi)$. By (3.2), the function V is given now by

$$V(\varphi) = -\sum_{i \in J} \int_0^\varphi q_i B_i(\xi) d\xi + V_0. \quad (3.15)$$

We distinguish three cases:

1. $l = 0, m = M$, and $J = \{0, 1, \dots, M\}$;
2. $l = M, m = 0$, and $J = \{-M, \dots, -1, 0\}$;
3. $l = 1, m = 1, l + m = M$, and $J = \{-l, \dots, -1, 0, 1, \dots, m\}$.

We denote $f(-\infty) = \lim_{s \rightarrow -\infty} f(s)$ and $f(\infty) = \lim_{s \rightarrow \infty} f(s)$ if the limits exist.

Theorem 3.3—Assume (3.4) holds true.

1. If $l = 0$ and $m = M$, and $J = \{0, 1, \dots, M\}$, then $V(-\infty) = -q_M/v_M < 0$, $V'(\infty) = 0$, and $V'(\varphi) < 0$ for all $\varphi \in \mathbb{R}$. Moreover, $V(-\infty) = \infty$, and $V(\infty) = 0$ with a suitably chosen constant V_0 in (3.2).
2. If $l = M, m = 0$, and $J = \{-M, \dots, -1, 0\}$, then $V(-\infty) = 0$, $V'(\infty) = -q_{-M}/v_{-M} > 0$, and $V'(\varphi) > 0$ for all $\varphi \in \mathbb{R}$. Moreover, $V(-\infty) = 0$ with a suitably chosen constant V_0 in (3.2), and $V(\infty) = \infty$.
3. If $l = 1, m = 1, l + m = M$, and $J = \{-l, \dots, -1, 0, 1, \dots, m\}$, then $V(-\infty) = -q_m/v_m < 0$, $V'(\infty) = -q_{-l}/v_{-l} > 0$, and $-q_m/v_m < V'(\varphi) < -q_{-l}/v_{-l}$ for all $\varphi \in \mathbb{R}$. Moreover, $\min_{\varphi \in \mathbb{R}} V(\varphi) = 0$ with a suitably chosen constant V_0 in (3.2), $V(-\infty) = \infty$, and $V(\infty) = \infty$.

In Figure 2, we show the schematic behavior of the convex function V for the three different cases.

Proof of Theorem 3.3

1. In this case, we have $V(-\infty) = -q_M/v_M < 0$ by (3.8) and $V'(\infty) = 0$ by (3.7). Since $V'' > 0$ in \mathbb{R} by Theorem 3.1, V' is a strictly increasing function. Therefore, $V'(-\infty)$

< 0 and $V(\infty) = 0$ imply that $V(\varphi) < 0$ for all $\varphi \in \mathbb{R}$. Fix $\varphi_0 \in \mathbb{R}$ so that $V(\varphi_0) < 0$. Then for any $\varphi < \varphi_0$ we have $V(\varphi) = V(\varphi_0) + V'(\xi)(\varphi - \varphi_0)$, where $\xi \in (\varphi, \varphi_0)$. Notice that $V'(\xi) < V'(\varphi_0) < 0$. So, $V(\varphi) \rightarrow \infty$ as $\varphi \rightarrow -\infty$, i.e., $V(-\infty) = \infty$. Finally, setting $j = 0$ in (3.9), we obtain that

$$(v_i B_i(\phi))^{1/v_i} = (v_i c_i)^{1/v_i} \leq \left(\max_{1 \leq i \leq M} e^{\beta \mu_i / v_i} \right) e^{-\beta (q_i / v_i) \phi}.$$

Therefore, the integral of $\sum_{i=1}^M q_i B_i(\phi)$ from 0 to $\varphi > 0$ is a bounded function of φ . Thus, by the definition of V (cf. (3.2)), $V(\varphi)$ is bounded below. Since $V' < 0$ on \mathbb{R} , V decreases. Therefore, $V(\infty)$ exists. Choosing the constant

$$V_0 = \sum_{i \in J} \int_0^\infty q_i B_i(\phi) d\phi$$

in (3.15), we then have $V(\infty) = 0$.

2. This part can be proved similarly.
3. The fact that $V'(-\infty) = -q_m/v_m < 0$ and $V'(\infty) = -q_l/v_l > 0$ can be proved by the same argument used for proving part (1). Since $V'' > 0$ in \mathbb{R} , $V'(\varphi)$ is a strictly increasing function. Therefore, $-q_m/v_m < V'(\varphi) < -q_l/v_l$ for all $\varphi \in \mathbb{R}$. Again by the same argument used in part (1), we have $V(-\infty) = \infty$ and $V(\infty) = \infty$. It is clear now that there exists a unique $\varphi_0 \in \mathbb{R}$ such that $V'(\varphi_0) = 0$ and $V(\varphi_0) = \min_{\varphi \in \mathbb{R}} V(\varphi)$. Setting in (3.15),

$$V_0 = \sum_{i \in J} \int_0^{\phi_0} q_i B_i(\phi) d\phi,$$

we have $\min_{\varphi \in \mathbb{R}} V(\varphi) = 0$. **Q.E.D.**

3.3 Modified Debye length

We now linearize $V'(\varphi)$ at $\varphi = 0$ to obtain a modified Debye length. We first define $c_i^\infty = B_i(0)$ for any $i \in J$. Note that

$$v_0 c_0^\infty = 1 - \sum_{i \in J, i \neq 0} v_i c_i^\infty. \quad (3.16)$$

By (3.10) with $\varphi = 0$ and $\eta_i = e^{\beta \mu_i}$, we also have that

$$(v_0 c_0^\infty)^{v_i/v_0} = \eta_i^{-1} v_i c_i^\infty, \quad i \in J. \quad (3.17)$$

We denote again $\gamma = v_0 c_0$ which depends on φ . We have for $|\varphi| \ll 1$ that

$$\gamma = \tau_0 + \tau_1 \phi + O(\phi^2), \quad (3.18)$$

where τ_0 and τ_1 are two constants to be determined. Using our notation, (1.1) becomes

$$v_0 c_0 = 1 - \sum_{i \in J, i \neq 0} v_i c_i. \quad (3.19)$$

This and (3.16) imply that

$$\tau_0 = v_0 c_0(0) = 1 - \sum_{i \in J, i \neq 0} v_i c_i^\infty = v_0 c_0^\infty. \quad (3.20)$$

Substituting (3.18) into (3.12) for a fixed $i \in J$ with $i \neq 0$, we obtain by (3.20) and (3.17) that

$$\begin{aligned} c_i &= \frac{\eta_i}{v_i} (\tau_0 + \tau_1 \phi + O(\phi^2))^{v_i/v_0} (1 - \beta q_i \phi + O(\phi^2)) \\ &= \frac{\eta_i}{v_i} \tau_0^{v_i/v_0} \left(1 + \frac{\tau_1}{\tau_0} \phi + O(\phi^2)\right)^{v_i/v_0} (1 - \beta q_i \phi + O(\phi^2)) \\ &= c_i^\infty \left(1 + \frac{v_i \tau_1}{v_0 \tau_0} \phi + O(\phi^2)\right) (1 - \beta q_i \phi + O(\phi^2)) \\ &= c_i^\infty + c_i^\infty \left(\frac{v_i \tau_1}{v_0 \tau_0} - \beta q_i\right) \phi + O(\phi^2). \end{aligned} \quad (3.21)$$

It now follows from (3.18), (3.19), (3.21), and (3.20) that

$$\tau_0 + \tau_1 \phi + O(\phi^2) = 1 - \sum_{i \in J, i \neq 0} v_i c_i^\infty - \sum_{i \in J, i \neq 0} v_i c_i^\infty \left(\frac{v_i \tau_1}{v_0 \tau_0} - \beta q_i\right) \phi + O(\phi^2).$$

Comparing the leading-order terms, we obtain exactly (3.20). Comparing the $O(\phi)$ -terms and noting that $z_0 = 0$, we obtain

$$\tau_1 = \frac{\beta v_0^2 c_0^\infty \sum_{i \in J} q_i v_i c_i^\infty}{\sum_{i \in J} v_i^2 c_i^\infty}.$$

This and (3.21) then lead to

$$c_i = c_i^\infty + \beta c_i^\infty \left(\frac{v_i \sum_{j \in J} q_j v_j c_j^\infty}{\sum_{j \in J} v_j^2 c_j^\infty} - q_i\right) \phi + O(\phi^2) \quad \forall i \in J \text{ with } i \neq 0.$$

Consequently,

$$V'(\phi) = - \sum_{i \in J} q_i c_i = - \sum_{i \in J} q_i c_i^\infty - \beta \left[\frac{\left(\sum_{i \in J} q_i v_i c_i^\infty\right)^2}{\sum_{i \in J} v_i^2 c_i^\infty} - \sum_{i \in J} q_i^2 c_i^\infty \right] \phi + O(\phi^2).$$

In the small $|\phi|$ approximation, we then obtain by (3.3) and the shift $\phi = \psi - \psi_D/2$ the linearized PBE with ionic size effects

$$\nabla \cdot \varepsilon \nabla \psi - \varepsilon \hat{\lambda}_D^{-2} \psi = - \sum_{i \in J} q_i c_i^\infty - \frac{1}{2} \varepsilon \hat{\lambda}_D^{-2} \psi_D, \quad (3.22)$$

where $\hat{\lambda}_D > 0$ is defined by

$$\hat{\lambda}_D^{-2} = \frac{\beta}{\varepsilon} \left[\sum_{i \in J} q_i^2 c_i^\infty - \frac{\left(\sum_{i \in J} q_i v_i c_i^\infty \right)^2}{\sum_{i \in J} v_i^2 c_i^\infty} \right]. \quad (3.23)$$

The fact that the right-hand side of the above equation is nonnegative follows from the Cauchy-Schwarz inequality

$$\left(\sum_{i \in J} q_i v_i c_i^\infty \right)^2 \leq \left(\sum_{i \in J} q_i^2 c_i^\infty \right) \left(\sum_{i \in J} v_i^2 c_i^\infty \right).$$

In the case that ε is a constant, $\psi_D = 0$ on Γ_D , and $\sum_{i \in J} q_i c_i^\infty = 0$ which is the charge neutrality, the linearized equation (3.22) simplifies to the familiar equation

$$\Delta \psi - \hat{\lambda}_D^{-2} \psi = 0.$$

We call $\hat{\lambda}_D$ the size-modified Debye length. Recall that the Debye length $\lambda_D > 0$ in the classical Debye-Hückel theory is defined by

$$\lambda_D^{-2} = \frac{\beta}{\varepsilon} \sum_{i \in J} q_i^2 c_i^\infty. \quad (3.24)$$

It is clear that $\hat{\lambda}_D > \lambda_D$. This indicates that finite ionic sizes lead to a longer Debye screening length.

4 A Charged Spherical Molecule: Basic Properties

In this section, we consider a charged spherical molecule, centered at the origin and with radius $R_0 > 0$, immersed in a solvent that occupies the region defined by $R_0 < r < R_\infty$ in the spherical coordinates for some $R_\infty > R_0$, where R_∞ can be finite or infinite. Corresponding to the general setting described in the previous section, we have in this case that

$$\begin{aligned} \Omega &= \{x \in \mathbb{R}^3 : R_0 < |x| < R_\infty\}, \\ \Gamma_N &= \{x \in \mathbb{R}^3 : |x| = R_0\}, \\ \Gamma_D &= \begin{cases} \{x \in \mathbb{R}^3 : |x| = R_\infty\} & \text{if } R_\infty < \infty, \\ \{\infty\} & \text{if } R_\infty = \infty. \end{cases} \end{aligned}$$

We consider the boundary-value problem of the PBE, classical and size-modified, for the electrostatic potential ψ (cf. (2.2) and (3.3)):

$$\begin{cases} \varepsilon \Delta \psi = V'(\psi) & \text{in } \Omega, \\ \varepsilon \frac{\partial \psi}{\partial n} = \sigma & \text{on } \Gamma_N, \\ \psi = 0 & \text{on } \Gamma_D. \end{cases} \quad (4.1)$$

If $\psi = \psi(r) (r = |x|)$ is radially symmetric, then this system is the same as

$$\begin{cases} \varepsilon \left(\psi'' + \frac{2}{r} \psi' \right) = V'(\psi) & \text{if } R_0 < r < R_\infty, \\ \psi'(R_0) = -\frac{\sigma}{\varepsilon}, \\ \psi(R_\infty) = 0. \end{cases} \quad (4.2)$$

Here, we assume both the dielectric coefficient $\varepsilon > 0$ and surface charge density σ are constants. We can consider the inhomogeneous Dirichlet boundary condition $\psi = \psi_\infty$ on Γ_D for a constant ψ_∞ by replacing ψ by $\psi - \psi_\infty$. We assume that $V : \mathbb{R} \rightarrow \mathbb{R}$ is smooth, $V'' > 0$ in \mathbb{R} , and $\inf_{s \in \mathbb{R}} V(s) = 0$. We then have one and only one of the three cases covered in Theorem 3.3: $V' > 0$ in \mathbb{R} , $V' < 0$ in \mathbb{R} , or there exists a unique φ_0 such that $V(s) > V(\varphi_0) = 0$ for any $s \neq \varphi_0$. In the last case, $V' < 0$ in $(-\infty, \varphi_0)$, $V'(\varphi_0) = 0$, and $V' > 0$ in (φ_0, ∞) . The term $-V'(\psi)$ is the ionic charge density that is related to M ionic species with valences and volumes satisfying (3.4).

For the classical PBE, we have $V(\phi) = \sum_{i \in J} c_i^\infty (e^{-\beta q_i \phi} - 1)$, where $c_i^\infty (i \in J, i \neq 0)$ are bulk ionic concentrations. Under the assumption on the charge neutrality $\sum_{i \in J} q_i c_i^\infty = 0$, this V satisfies the properties in the third case in Theorem 3.3 with $\varphi_0 = 0$. So our analysis covers this case.

We first consider the case that $R_\infty < \infty$.

Theorem 4.1

Let $\varepsilon > 0$, $\sigma \in \mathbb{R}$, and $0 < R_0 < R_\infty < \infty$. Assume that $V : \mathbb{R} \rightarrow \mathbb{R}$ is smooth, $V'' > 0$ in \mathbb{R} , and $\inf_{s \in \mathbb{R}} V(s) = 0$. Then the boundary-value problem (4.1) has a unique weak solution. Moreover it is radially symmetric and smooth on Ω .

Proof—We assume that $\sigma > 0$. The case that $\sigma = 0$ can be proved similarly. We denote $H = \{\varphi \in H^1(R_0, R_\infty) : \varphi(R_\infty) = 0\}$ and define $I : H \rightarrow (-\infty, \infty]$ by

$$I[\varphi] = 4\pi \int_{R_0}^{R_\infty} \left[\frac{\varepsilon}{2} \varphi'(r)^2 + V(\varphi) \right] r^2 dr - 4\pi R_0^2 \sigma \varphi(R_0) \quad \forall \varphi \in H. \quad (4.3)$$

If $\varphi \in H$, then we have with $\delta = \varepsilon/(4\sigma) > 0$ that

$$|\varphi(R_0)| = \left| \int_{R_0}^{R_\infty} \varphi'(r) dr \right| \leq \sqrt{R_\infty - R_0} \left(\int_{R_0}^{R_\infty} |\varphi'(r)|^2 dr \right)^{1/2} \leq \frac{R_\infty - R_0}{4\delta} + \delta \int_{R_0}^{R_\infty} |\varphi'(r)|^2 dr,$$

leading to

$$I[\phi] \geq \pi \varepsilon R_0^2 \int_{R_0}^{R_\infty} |\phi'(r)|^2 dr - \frac{4\pi \sigma^2 R_0^2 (R_\infty - R_0)}{\varepsilon} \quad \forall \phi \in H.$$

Notice that by Poincare's inequality, $I[\phi]$ controls $\|\phi\|_{H^1(R_0, R_\infty)}^2$, up to an additive constant. By standard arguments of direct methods in the calculus of variations and by the fact that $H^1(R_0, R_\infty)$ can be compactly embedded into $C([R_0, R_\infty])$, we obtain the existence of a minimizer $\psi \in H$ of the functional $I : H \rightarrow [0, \infty]$. Moreover, the minimum value of I over H is finite. The uniqueness of this minimizer follows from the strict convexity of I . Clearly, the minimizer $\psi = \psi(r)$ is a smooth solution to the corresponding Euler–Lagrange equation, the first equation in (4.2). Moreover, it satisfies the natural boundary condition $\psi'(R_0) = -\sigma/\varepsilon$. Since $\psi \in H$, $\psi(R_\infty) = 0$. If we also denote $\psi(x) = \psi(|x|)$, then it is clear that this function is a radially symmetric solution to (4.1), and is smooth on Ω .

To prove the uniqueness of solution to (4.1), we first note that the solution ψ minimizes the functional

$$Q[\phi] = \int_\Omega \left[\frac{\varepsilon}{2} |\nabla \phi|^2 + V(\phi) \right] dV - \int_{\Gamma_N} \sigma \phi dS$$

over all $\phi \in H^1(\Omega)$ such that $\phi = 0$ on Γ_D . Indeed, for any $\eta \in H^1(\Omega)$ with $\eta = 0$ on Γ_D , we have by integration by parts, the convexity of V , and (4.1) that

$$\begin{aligned} Q[\psi + \eta] - Q[\psi] &= \int_\Omega \left[\frac{\varepsilon}{2} |\nabla \eta|^2 + \varepsilon \nabla \psi \cdot \nabla \eta + V(\psi + \eta) - V(\psi) \right] dV - \int_{\Gamma_N} \sigma \eta dS \\ &\geq \int_\Omega [\varepsilon \nabla \psi \cdot \nabla \eta + V'(\psi) \eta] dV - \int_{\Gamma_N} \sigma \eta dS \\ &\geq \int_\Omega [-\varepsilon \Delta \psi + V'(\psi)] \eta dV + \int_{\Gamma_N} \varepsilon \frac{\partial \psi}{\partial n} \eta dS - \int_{\Gamma_N} \sigma \eta dS \\ &= 0. \end{aligned} \tag{4.4}$$

Now if $\hat{\psi}$ is another solution to (4.1), which is not assumed to be radially symmetric, then both ψ and $\hat{\psi}$ are minimizers of the functional Q . Since Q is strictly convex, it has at most one minimizer. Therefore, $\hat{\psi} = \psi$. **Q.E.D.**

We now study the behavior of the equilibrium potential $\psi = \psi(|x|)$ that is the solution to the boundary-value problem (4.1). We denote by $T(r)$ the total amount of ionic charges in the region $\{x \in \Omega : R_0 < |x| < r\}$:

$$T(r) = -4\pi \int_{R_0}^r V'(\psi(s)) s^2 ds \quad \forall r \in [R_0, R_\infty]. \tag{4.5}$$

Then $T_\infty := T(R_\infty)$ represents the total amount of ionic charges in Ω . If we integrate both sides of Poisson's equation in (4.1), apply integration by parts, and use the boundary condition at $r = R_0$, then we have

$$T_\infty + 4\pi R_0^2 \sigma + 4\pi R_\infty^2 \varepsilon \psi'(R_\infty) = 0. \tag{4.6}$$

This is the charge neutrality of the system, as $\sigma_\infty := \varepsilon \psi'(R_\infty)$ can be viewed as the effective surface charge density on the part of the boundary $\Gamma_D = \{x \in \mathbb{R}^3 : |x| = R_\infty\}$ which is set due to the finiteness of the underlying domain. The surface charge density σ in the boundary

condition and the effective surface charge density $\sigma_\infty = \varepsilon\psi'(R_\infty)$ are the key parameters that determine the monotonicity of the electrostatic potential ψ .

Theorem 4.2

Let $\varepsilon > 0$, $\sigma \in \mathbb{R}$, and $0 < R_0 < R_\infty < \infty$. Assume that $V : \mathbb{R} \rightarrow \mathbb{R}$ is smooth, $V'' > 0$ in \mathbb{R} , and $\inf_{s \in \mathbb{R}} V(s) = 0$. Consider $V' > 0$ in \mathbb{R} , or $V' < 0$ in \mathbb{R} , or $V'(\varphi_0) = 0$ for a unique $\varphi_0 \in \mathbb{R}$. Let $\psi = \psi(|x|)$ be the solution to the boundary-value problem (4.1).

1. If $\sigma > 0$ and $\sigma_\infty > 0$, then there exists a unique $R_c^+ \in (R_0, R_\infty)$ such that $\psi' < 0$ in (R_0, R_c^+) and $\psi' > 0$ in (R_c^+, R_∞) . If $\sigma < 0$ and $\sigma_\infty < 0$, then there exists a unique $R_c^- \in (R_0, R_\infty)$ such that $\psi' > 0$ in (R_0, R_c^-) and $\psi' < 0$ in (R_c^-, R_∞) .
2. If $\sigma\sigma_\infty < 0$ and at least one of σ and σ_∞ is nonzero, then $\psi' > 0$ in (R_0, R_∞) if $\sigma < 0$ or $\sigma_\infty > 0$, and $\psi' < 0$ in (R_0, R_∞) if $\sigma > 0$ or $\sigma_\infty < 0$.
3. The case that $\sigma = \sigma_\infty = 0$ can only occur when $V'(0) = 0$. In this case $\psi = 0$ identically in (R_0, R_∞) .

The main results of Theorem 4.2 are illustrated in Figure 3. To prove the theorem, we first prove a lemma.

Lemma 4.1

Given the assumption as in Theorem 4.2 and $A := \{r \in (R_0, R_\infty) : \psi'(r) = 0\}$.

1. If $V' > 0$ in \mathbb{R} or $V' < 0$ in \mathbb{R} , then either $A = \emptyset$ or A contains exactly one point.
2. If $V'(\varphi_0) = 0$ at some unique $\varphi_0 \in \mathbb{R}$, then either $A = \emptyset$, or A contains exactly one point, or $A = (R_0, R_\infty)$ in which case we have additionally that $\varphi_0 = 0$ and $\psi = 0$ identically in (R_0, R_∞) .

Proof—Suppose there exist $r_1, r_2 \in \mathbb{R}$ such that $R_0 < r_1 < r_2 < R_\infty$ and $\psi'(r_1) = \psi'(r_2) = 0$. Denote $\omega = \{x \in \mathbb{R}^3 : r_1 < |x| < r_2\}$. Then, by the same argument used in proving Theorem 4.1 (cf. (4.4)) and the strict convexity of V , the restriction of ψ onto ω is the unique minimizer among all $\phi \in H^1(\omega)$ of the functional

$$G[\phi] = \int_\omega \left[\frac{\varepsilon}{2} |\nabla \phi|^2 + V(\phi) \right] dV. \quad (4.7)$$

1. Suppose $V' > 0$. Since $\inf_{s \in \mathbb{R}} V(s) = 0$, we have $V(-\infty) = 0$. Thus, with $\varphi_k = -k$ ($k = 1, 2, \dots$), we have $0 = G[\psi] = G[\varphi_k] \rightarrow 0$ as $k \rightarrow \infty$. Thus $G[\psi] = 0$. But this is impossible: If the integral of $|\nabla \psi|^2$ vanishes, then ψ is a constant. But $V(s) > 0$ for any $s \in \mathbb{R}$. Thus the integral of $V(\psi)$ over ω is positive, a contradiction to $G[\psi] = 0$. For this case and similarly the case that $V' < 0$, the set A can then contain at most one point.
2. In this case, $V(\varphi_0) = \min_{s \in \mathbb{R}} V(s) = 0$. Thus, the constant function $\varphi = \varphi_0$ also minimizes G over $H^1(\omega)$. By the uniqueness of minimizer which follows from the strict convexity of G , $\psi = \varphi_0$ in $[r_1, r_2]$ and $[r_1, r_2] \subseteq A$. Let $s = \inf A > R_0$ and $t = \sup A < R_\infty$. At any point in (s, t) , $\psi = \varphi_0$ and ψ' vanishes. Moreover, $\psi' = 0$ in (R_0, s) if $s > R_0$ and in (t, R_∞) if $t < R_\infty$. We prove now $s = R_0$ and $t = R_\infty$. Assume $s > R_0$ and $\psi' > 0$ in (R_0, s) . Differentiating both sides of $\delta\psi = V'(\psi)/\varepsilon$ in $R_0 < r < t$, we obtain

$$\psi'''(r) + \frac{2}{r}\psi''(r) = \left[\frac{1}{\varepsilon}V''(\psi(r)) + \frac{2}{r^2} \right] \psi'(r) \quad \forall r \in (R_0, t). \quad (4.8)$$

Hence, setting $u = \psi'$, we have $Lu := \Delta u + c(r)u = 0$ for $R_0 < r < t$, where $c(r) := -[(1/\varepsilon)V''(\psi(r)) + 2/r^2] < 0$ and $c(r)$ is bounded in (R_0, s) . Clearly $u(s) = 0 = u(r)$ for all $r \in (R_0, t)$. Hence u attains its minimum with the minimum value 0 at any interior point x with $|x| = s$ in $\{x \in \mathbb{R}^3 : R_0 < |x| < t\}$. By the Strong Maximum Principle (cf. Theorem 3.5 of [13]), u must be a constant in $R_0 < r < t$. This contradicts the fact that $u > 0$ in $R_0 < r < s$ and $u = 0$ in $s < r < t$. Hence $\psi' > 0$ in (R_0, s) is impossible. Similarly, $\psi' < 0$ in (R_0, s) is impossible. Therefore $s = R_0$. Similarly, we have $t = R_\infty$. Finally $A = (s, t) = (R_0, R_\infty)$, and since $\psi(R_\infty) = 0$, $\psi = \varphi_0 = 0$ in (R_0, R_∞) . **Q.E.D.**

Proof of Theorem 4.2

1. Assume $\sigma > 0$ and $\sigma_\infty > 0$. Then $\psi'(R_0) < 0$ and $\psi'(R_\infty) > 0$. Hence by Lemma 4.1 there exists a unique $R_c^+ \in (R_0, R_\infty)$ such that $\psi'(R_c^+) = 0$. Clearly, $\psi' < 0$ in (R_0, R_c^+) and $\psi' > 0$ in (R_c^+, R_∞) . The case that $\sigma < 0$ and $\sigma_\infty < 0$ can be proved similarly.
2. Assume $\sigma > 0$ and $\sigma_\infty = 0$, i.e., $\psi'(R_0) < 0$ and $\psi'(R_\infty) = 0$. The other cases can be treated similarly. It suffices to show that ψ' does not vanish in (R_0, R_∞) . Assume there existed $r_0 \in (R_0, R_\infty)$ such that $\psi'(r_0) = 0$. By Lemma 4.1, ψ' does not vanish at other points. Thus there are two cases. Case 1: $\psi' < 0$ in (R_0, r_0) and $\psi' < 0$ in (r_0, R_∞) . Case 2: $\psi' < 0$ in (R_0, r_0) and $\psi' > 0$ in (r_0, R_∞) . We show that each case is impossible.

Consider Case 1. If $V' > 0$ in \mathbb{R} , then $\Delta\psi > 0$ on $\{x \in \mathbb{R}^3 : r_0 < |x| < R_\infty\}$. Let $x_0 \in \mathbb{R}^3$ be such that $|x_0| = r_0$. Since $\psi(|x_0|) > \psi(|x|)$ for any x with $|x| \in (r_0, R_\infty)$. Lemma 3.4 in [13] then implies that $\psi'(r_0) = 0$, a contradiction. If $V' < 0$, we obtain the same contradiction $\psi'(r_0) = 0$ by considering (R_0, r_0) . Finally, assume $V'(\varphi_0) = 0$. If $\psi(r_0) < \varphi_0$, then since $\psi'(r_0) = 0$, $\psi''(r_0) = V'(\varphi(r_0))/\varepsilon < 0$. These imply that ψ' changes its sign at r_0 which is a contradiction in Case 1. Thus Case 1 is impossible.

Consider Case 2. In this case, we must have $\psi'(R_\infty) = 0$, since $\psi'(R_\infty) > 0$ would lead to $\psi'(r_1) = 0$ for some $r_1 \in (r_0, R_\infty)$ which is impossible. Moreover, ψ reaches its minimum at r_0 and in particular $\psi''(r_0) > 0$. If $V' < 0$ then $\Delta\psi < 0$ in Ω . The Strong Maximum Principle then implies that ψ must be a constant for $r \in (R_0, R_\infty)$. This is impossible as $\psi'(R_0) < 0$. If $V' > 0$, then $\Delta\psi > 0$ and $\psi(R_\infty) = 0 > \psi(r)$ for $r \in (r_0, R_\infty)$. By Lemma 3.4 in [13], we must have $\psi'(R_\infty) > 0$, leading to a contradiction. Assume $V'(\varphi_0) = 0$ at some unique φ_0 . We cannot have $\varphi_0 > \psi(r_0)$ as this would imply that $V'(\psi(r_0)) < 0$ and hence $\psi''(r_0) < 0$ which contradicts $\psi''(r_0) > 0$. We cannot have $\varphi_0 < \psi(r_0)$ neither, since otherwise we would have that $V'(\psi) < 0$ and hence $\Delta\psi < 0$ on the region $r_0 < r < R_\infty$. But $\psi(R_\infty) = 0 > \psi(r)$ for any $r \in (r_0, R_\infty)$. Lemma 3.4 in [13] then implies $\psi'(R_\infty) > 0$, a contradiction. Thus Case 2 is also impossible.

3. We have now $\psi'(R_0) = 0$ and $\psi'(R_\infty) = 0$. As in the proof of Lemma 4.1 with $r_1 = R_0$ and $r_2 = R_\infty$, ψ is a constant in $[R_0, R_\infty]$. Since $\psi(R_\infty) = 0$, $\psi = 0$ identically in $[R_0, R_\infty]$. Thus $V'(0) = V'(\psi) = \varepsilon\Delta\psi = 0$. Hence $\varphi_0 = 0$. **Q.E.D.**

We recall that for any $r \in (R_0, R_\infty)$, $T(r)$ is the total amount of ionic charges in the region $\{x \in \Omega : R_0 < |x| < r\}$; cf. (4.5). In the following corollary, we consider a special and useful case but deliver more results:

Corollary 4.1

Let $\varepsilon > 0$, $\sigma \in \mathbb{R}$, and $0 < R_0 < R_\infty < \infty$. Assume that $V: \mathbb{R} \rightarrow \mathbb{R}$ is smooth, $V'' > 0$ in \mathbb{R} , and $V(s) > V(0) = 0$ for any $s \in \mathbb{R}$ with $s \neq 0$. Let $\psi = \psi(|x|)$ be the solution to the boundary-value problem (4.1).

1. If $\sigma = 0$, then $\psi = 0$ and $T = 0$ identically.
2. If $\sigma > 0$, then $\psi' < 0$, $\psi'' > 0$, and $T' < 0$ in (R_0, R_∞) .
3. If $\sigma < 0$, then $\psi' > 0$, $\psi'' < 0$, and $T' > 0$ in (R_0, R_∞) .

Proof

1. It is easy to verify that in this case $\psi = 0$ is the unique solution to (4.1). Moreover, $T'(r) = -V'(\psi(r)) = -V'(0) = 0$ and $T(R_0) = 0$. Hence $T = 0$ in (R_0, R_∞) .
2. Assume $\sigma > 0$. We then have $\sigma_\infty = \varepsilon\psi'(R_\infty) < 0$. Otherwise, $\sigma_\infty > 0$. Then by Theorem 4.2 there exists $R_c \in (R_0, R_\infty)$ such that $\psi' < 0$ in (R_0, R_c) and $\psi' > 0$ in (R_c, R_∞) . We have $\psi(R_c) < \min(\psi(R_0), \psi(R_\infty)) < 0$. Choose $\tau \in \mathbb{R}$ such that $\psi(R_c) < \tau < \min(\psi(R_0), \psi(R_\infty))$. Define $\hat{\psi}$ by $\hat{\psi} = \psi$ if $\psi \geq \tau$ and $\hat{\psi} = \tau$ if $\psi < \tau$. Then $I[\hat{\psi}] < I[\psi]$, where $I[\cdot]$ is defined in (4.3). This is impossible as ψ minimizes $I[\cdot]$ over $H = \{\varphi \in H^1(R_0, R_\infty) : \varphi(R_\infty) = 0\}$ that includes ψ . Now, since $\sigma > 0$ and $\sigma_\infty < 0$, we have $\psi' < 0$ by Theorem 4.2. Since $\psi(R_\infty) = 0$, $\psi > 0$ in (R_0, R_∞) . Hence $V'(\psi) > 0$ in (R_0, R_∞) . Consequently,

$$\psi''(r) = -\frac{2}{r}\psi'(r) + \frac{1}{\varepsilon}V'(\psi(r)) > 0 \quad \text{in } (R_0, R_\infty).$$

Since $V'(\psi) > 0$ in (R_0, R_∞) , we also have $T'(r) < 0$ for all $r \in (R_0, R_\infty)$.

3. This can be proved similarly. **Q.E.D.**

We now consider the case $R_\infty = \infty$.

Theorem 4.3

Let $\varepsilon > 0$, $\sigma \in \mathbb{R}$, and $R_\infty = \infty$.

1. Suppose $V: \mathbb{R} \rightarrow \mathbb{R}$ is smooth and $V(0) < 0$. Then there is no solution to the boundary-value problem (4.1).
2. Suppose $V: \mathbb{R} \rightarrow \mathbb{R}$ is smooth, $V'' > 0$ on \mathbb{R} , $V(-\infty) = \infty$ and $V(\infty) = \infty$, and $V(0) = \inf_{s \in \mathbb{R}} V(s) = 0$. Then there exists a unique solution to the boundary-value problem (4.1). Moreover, this solution $\psi = \psi(|x|)$ is radially symmetric and smooth on Ω , $\psi' < 0$ and $\psi'' > 0$ in $r = |x|$ if $\sigma > 0$, $\psi' > 0$ and $\psi'' < 0$ in $r = |x|$ if $\sigma < 0$, and $\psi = 0$ for all r if $\sigma = 0$.

We remark that in general all charges in an ionic system are in a finite region. Therefore it is natural to impose the far-field condition $\psi(R_\infty) = 0$. The properties on V assumed in part (2) of the theorem are exactly those covered in the third case in Theorem 3.3 but with the minimum of V attained exactly at 0. The theorem states that the solution to (4.1) exists only when $V(0) = 0$. This is precisely the condition of charge neutrality in the bulk. Therefore, for the three cases of V stated in Theorem 3.3, only the third case with $V(0) = 0$ permits a solution to (4.1).

Proof of Theorem 4.3

- (1) Assume $V(0) > 0$. (The case that $V(0) < 0$ is similar.) Assume ψ is a solution to (4.1), which is not assumed to be radially symmetric. Clearly, ψ is smooth on Ω . Since $\psi(\infty) = 0$ and $V(0) > 0$, there exist $A > R_0$ and $\alpha > 0$ such that $\varepsilon \Delta \psi = V'(\psi) - \alpha$ for all $x \in \Omega$ with $|x| \geq A$. In the spherical coordinates (r, θ, φ) ($r > 0, 0 \leq \theta < \pi, 0 \leq \varphi < 2\pi$), $\psi = \psi(r, \theta, \varphi)$, and

$$\Delta \psi = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \varphi^2} \geq \alpha \quad \forall r \geq A. \quad (4.9)$$

Define

$$u(r) = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi \sin \theta \psi(r, \theta, \varphi) \, d\theta d\varphi \quad \forall r > R_0.$$

Clearly, $u(\infty) = 0$, since $\psi \rightarrow 0$ as $r \rightarrow \infty$. Multiplying both sides of the inequality in (4.9) by $\sin \theta / (4\pi)$, and then integrating the resulting sides over $\theta \in [0, \pi]$ and $\varphi \in [0, 2\pi]$, we obtain $(1/r^2) (r^2 u'(r))' \geq \alpha$ for all $r \geq A$. This leads to

$$u'(r) \geq \frac{1}{3} \alpha r + \left[A^2 u'(A) - \frac{1}{3} \alpha A^3 \right] \frac{1}{r^2} \quad \forall r \geq A.$$

With one more time of integration, we get

$$u(r) \geq u(A) + \frac{1}{6} \alpha (r^2 - A^2) - \left[A^2 u'(A) - \frac{1}{3} \alpha A^3 \right] \left(\frac{1}{r} - \frac{1}{A} \right) \quad \forall r \geq A.$$

This contradicts $u(\infty) = 0$. Part (1) is proved.

- (2) We first show the uniqueness. Suppose ψ_1 and ψ_2 are both solutions to (4.1). Clearly they are smooth on $\bar{\Omega} = \{x \in \mathbb{R}^3 : |x| \leq R_0\}$. Let $\eta = \psi_1 - \psi_2$. This function attains its maximum on $\bar{\Omega}$. Suppose $P := \max_{x \in \bar{\Omega}} \eta > 0$. If there exists $x_0 \in \Omega = \{x \in \mathbb{R}^3 : |x| > R_0\}$ such that $\eta(x_0) = P > 0$, then there exists an open ball $B(x_0) \subset \Omega$ centered at x_0 such that $\eta > 0$ on $\bar{B}(x_0)$. Since ψ_1 and ψ_2 are bounded on Ω , $\psi_1(x), \psi_2(x) \in K$ for some compact subset of \mathbb{R} for all $x \in \bar{\Omega}$. Setting $\gamma_0 = \min_{s \in K} V''(s) > 0$, we obtain

$$\varepsilon \Delta \eta = V'(\psi_1) - V'(\psi_2) \geq \gamma_0 \eta > 0 \quad \text{in } B(x_0). \quad (4.10)$$

Since $\eta(x_0) = \max_{x \in B(x_0)} \eta > 0$, the Strong Maximum Principle (cf. Theorem 3.5 of [13]) then implies that η is a constant in $B(x_0)$. Consequently $\Delta \eta = 0$ in $B(x_0)$, and (4.10) implies $\eta = 0$ in $B(x_0)$, contradicting to $\eta(x_0) > 0$. Thus there exists $y_0 \in \bar{\Omega}$ with $|y_0| = R_0$ such that $\eta(y_0) = P > \eta(x)$ for all $x \in \Omega$. But this and (4.10) imply $\eta(y_0) = 0$ by Lemma 3.4 in [13], contradicting $\eta(y_0) = P > 0$ on $\Gamma_D = \{x \in \mathbb{R}^3 : |x| = R_0\}$. Hence $\eta = 0$ and $\psi_1 = \psi_2$ in Ω . Similarly $\psi_2 = \psi_1$ in Ω . Thus $\psi_1 = \psi_2$ in Ω .

We now prove the existence of solution to (4.1) that satisfies all the properties. If $\sigma = 0$ then $\psi = 0$ in Ω is the desired solution. Assume $\sigma > 0$. (The case $\sigma < 0$ is similar.) Choose a sequence $R_k \in \mathbb{R}$ ($k = 1, 2, \dots$) such that $R_0 < R_1 < R_2 < \dots < R_k < \dots$

... and $R_k \rightarrow \infty$ as $k \rightarrow \infty$. For each integer $k \geq 1$, let $\psi_k = \psi_k(|x|)$ be the unique solution to the boundary-value problem

$$\begin{cases} \varepsilon \Delta \psi_k = V'(\psi_k) & \text{in } \Omega^k = \{x \in \mathbb{R}^3 : R_0 < |x| < R_k\}, \\ \varepsilon \frac{\partial \psi_k}{\partial n} = \sigma & \text{on } \Gamma_N^k = \{x \in \mathbb{R}^3 : |x| = R_0\}, \\ \psi_k = 0 & \text{on } \Gamma_D^k = \{x \in \mathbb{R}^3 : |x| = R_k\}. \end{cases} \quad (4.11)$$

By Corollary 4.1, $\psi_k > 0$, $\psi'_k < 0$, and $\psi''_k > 0$ in (R_0, R_k) .

Using the spherical coordinates, we have by the first equation in (4.11) that

$$\psi''_k(r) + \frac{2}{r} \psi'_k(r) = V'(\psi_k(r)) \quad \text{in } (R_0, R_k). \quad (4.12)$$

Multiply both sides of this equation by $\psi'_k(r)$ and integrate the resulting sides over $[R_0, R_k]$. Noting that $\psi'_k \psi''_k = (1/2)(\psi'^2_k)'$ and $\psi'_k V'(\psi_k) = (d/dr) V(\psi_k)$, we then obtain by $\psi'_k(R_0) = -\sigma/\varepsilon$, $\psi_k(R_k) = 0$ and $V(0) = 0$ that

$$\frac{1}{2} \left[(\psi'_k(R_k))^2 - \left(\frac{\sigma}{\varepsilon}\right)^2 \right] + \int_{R_0}^{R_k} \frac{2}{r} (\psi'_k(r))^2 dr = -V(\psi_k(R_0)).$$

Thus, since $V(s) > 0$ for any $s > 0$, we have $0 < V(\psi_k(r)) < \sigma^2/(2\varepsilon^2)$ for all $r \in [R_0, R_k]$ and $k \geq 1$. Since V is positive and strictly increasing in $(0, \infty)$ and $V(\infty) = \infty$, and since $\psi_k(R_0) < \psi_k(r) < \psi_k(R_k)$ for all $r \in [R_0, R_k]$, we have by setting $\varphi_c > 0$ with $V(\varphi_c) = \sigma^2/(2\varepsilon^2)$ that $0 < \psi_k(r) < \varphi_c$ for all $r \in [R_0, R_k]$ and all $k \geq 1$. Moreover, since $\psi''_k > 0$ in (R_0, R_k) , $-\sigma/\varepsilon = \psi'_k(R_0) \leq \psi'_k(r) \leq \psi'_k(R_k) \leq 0$ for all $r \in [R_0, R_k]$ and all $k \geq 1$. Define $\psi_k = 0$ in (R_k, ∞) ($k = 1, 2, \dots$). Then the sequence $\{\psi_k\}_{k=1}^\infty$ is bounded in $W^{1,\infty}(R_0, \infty)$.

There now exists a subsequence $\{\psi_{k,1}\}_{k=1}^\infty$ of $\{\psi_k\}_{k=1}^\infty$ such that $\psi_{k,1} \rightarrow \psi$ in $H^1(R_0, R_1)$ as $k \rightarrow \infty$ for some $\psi \in H^1(R_0, R_1)$. There exists a subsequence $\{\psi_{k,2}\}_{k=1}^\infty$ of $\{\psi_{k,1}\}_{k=1}^\infty$ such that $\psi_{k,2} \rightarrow \varphi$ in $H^1(R_0, R_2)$ as $k \rightarrow \infty$ for some $\varphi \in H^1(R_0, R_2)$ with $\varphi = \psi$ on (R_0, R_1) . We define $\psi = \varphi$ in (R_1, R_2) so that $\psi \in H^1(R_0, R_2)$. Repeating, we obtain $\psi \in C([R_0, \infty))$ with $\psi \in H^1(R_0, R)$ for any $R > R_0$ and subsequences $\{\psi_{k,j}\}_{k=1}^\infty$ of $\{\psi_k\}_{k=1}^\infty$ ($j = 1, 2, \dots$), where for each $j \geq 1$, the sequence $\{\psi_{k,j+1}\}_{k=1}^\infty$ is a subsequence of $\{\psi_{k,j}\}_{k=1}^\infty$. Moreover, $\psi_{k,j} \rightarrow \psi$ in $H^1(R_0, R_j)$ as $k \rightarrow \infty$. Now $\{\psi_{k,k}\}_{k=1}^\infty$ is a subsequence of $\{\psi_k\}_{k=1}^\infty$, and $\{\psi_{k,k}\}_{k=1}^\infty$ converges to ψ in $H^1(R_0, R)$, and hence also in $C([R_0, R])$, for any $R > R_0$.

The limit $\psi = \psi(|x|)$ is clearly radially symmetric. It is a (weak and hence strong) solution to the first two equations in (4.1). We show now that $\lim_{r \rightarrow \infty} \psi(r) = 0$. For each $k \geq 1$, define

$$\eta_k(r) = \begin{cases} \psi_k(R_0) \left(\frac{1}{R_0} - \frac{1}{R_k}\right)^{-1} \left(\frac{1}{r} - \frac{1}{R_k}\right) & \text{if } R_0 \leq r \leq R_k, \\ 0 & \text{if } r > R_k. \end{cases}$$

One easily verifies that $\eta_k(|x|)$ satisfies $\varepsilon\Delta\eta_k=0$ in Ω^k (cf. (4.11) for the definition of Ω^k) and $\eta_k = \psi_k$ on the boundary of Ω^k . Since $\varepsilon\Delta(\psi_k - \eta_k) = 0$ in Ω^k , we thus have by the Maximum Principle that $\psi_k = \eta_k$ in Ω^k and hence in $\Omega = \{x \in \mathbb{R}^3 : |x| > R_0\}$. Denote $\{\eta_{k,k}\}_{k=1}^\infty$ the subsequence of $\{\eta_k\}_{k=1}^\infty$ that corresponds to $\{\psi_{k,k}\}_{k=1}^\infty$. Then we have

$$0 \leq \limsup_{r \rightarrow \infty} \psi(r) = \limsup_{r \rightarrow \infty} \lim_{k \rightarrow \infty} \psi_{k,k}(r) \leq \limsup_{r \rightarrow \infty} \lim_{k \rightarrow \infty} \eta_{k,k}(r) = \limsup_{r \rightarrow \infty} \frac{R_0 \psi(R_0)}{r} = 0,$$

implying $\lim_{r \rightarrow \infty} \psi(r) = 0$.

Since $\psi'_k = 0$ on (R_0, R_k) for all $k \geq 1$, $\psi' = 0$ on (R_0, ∞) . Let $u(r) = \psi'(r)$. Then $u(|x|)$ satisfies $\Delta u - c(r)u = 0$ on $\{x \in \mathbb{R}^3 : |x| > R_0\}$, where $c(r) = -[(1/\varepsilon)V''(\psi(r)) + 2/r^2] < 0$, cf. (4.8). Since $u = 0$ in (R_0, ∞) , the Strong Maximum Principle implies that $u = 0$ in (R_0, ∞) . Hence $u = \psi' < 0$ in (R_0, ∞) . Since $\psi = 0$ and $V(\psi) = 0$, we also have $\psi''(r) = -(2/r)\psi' + V'(\psi) > 0$ for all $r > R_0$. **Q.E.D.**

5 Numerical Results

We now present numerical results to illustrate our analysis. We consider minimizing numerically the free-energy functional (2.6) with (2.7) and (2.8). We choose $\Omega = \{x \in \mathbb{R}^3 : R_0 < |x| < R_\infty\}$, $\Gamma_N = \{x \in \mathbb{R}^3 : |x| = R_0\}$, $\Gamma_D = \{x \in \mathbb{R}^3 : |x| = R_\infty\}$, with $R_0, R_\infty \in \mathbb{R}$ such that $R_0 < R_\infty$. We assume the dielectric coefficient ε and surface charge density σ are both constants. We also set $\psi_D = 0$ on Γ_D . Note that our system is radially symmetric. We use the constrained optimization method developed in our previous work [38] to solve numerically our optimization problem.

We set $R_0 = 10 \text{ \AA}$ and $R_\infty = 80 \text{ \AA}$. We distribute uniformly some negative charges on the sphere $r = R_0$ with the surface charge density $\sigma = -150/(4\pi^2 R_0^2) e/\text{\AA}^2$. We consider three species of counterions K^+ , Ca^{2+} , Al^{3+} , and one species of coions Cl^- in the solution that occupies Ω . So $M = 4$. We label these ionic species by 1, 2, 3, and 4, respectively. We label the solvent (water) by 0. The corresponding valences and ionic volumes are $(z_1, z_2, z_3, z_4) = (+1, +2, +3, -1)$ and $(v_1, v_2, v_3, v_4) = (5.51^3, 4.75^3, 4.1^3, 6.37^3) \text{ \AA}^3$, respectively. The volume of a solvent (water) molecule is $v_0 = 2.75^3 \text{ \AA}^3$. For these real ionic systems, it happens that $a_4 < a_0 = 0 < a_1 < a_2 < a_3$, where $a_k = z_k/v_k$ ($0 \leq k \leq 4$) with $z_0 = 0$. We use a^3 to approximate the volume of an ion of diameter a . The temperature is $T = 300K$. The dielectric coefficient is absorbed into the Bjerrum length $l_B = e^2/(4\pi\varepsilon k_B T)$. We set the Bjerrum length to be $l_B = 7 \text{ \AA}$. We consider two cases of the numbers of ions in different species. Case I: $(N_1, N_2, N_3, N_4) = (60, 30, 20, 50)$. By simple calculations, we have that in this case the effective surface charge density $\sigma_\infty > 0$. Case II: $(N_1, N_2, N_3, N_4) = (50, 50, 50, 50)$. In this case $\sigma_\infty < 0$.

In Figure 4, we plot our computational results of the electrostatic potential ψ and the equilibrium ionic concentrations. For Case I, the potential ψ is monotonically increasing. This is exactly predicted by Theorem 4.2, since in this case, $\sigma < 0$ and $\sigma_\infty > 0$. Notice that the concentration of +3, which has the largest ratio of valence-to-volume among all the species, monotonically decreases, while that of -1 monotonically increases. These are predicted by Theorem 3.2. For Case II, $\sigma < 0$ and $\sigma_\infty > 0$, and the behavior of the potential ψ is again as predicted by Theorem 4.2. We observe the stratification of the counterion concentrations in both cases.

6 Conclusions

We have analyzed a PB-like mean-field model for electrostatic interactions of multivalent ions with finite ionic sizes in an ionic solution near a charged surface. Our work continues that presented in [22] but gives more details on how equilibrium ionic concentrations depend on the electrostatic potential and how the important parameters, the valence-to-volume ratios of ions, determine the properties of ionic concentrations near the charged surface.

Here we discuss some of our main results. First, our analysis shows that for a strong potential, the layering structure of counterion concentrations does depend on the valence-to-volume ratios. In general, the comparison of concentrations for different ionic species can be subtle. Instead of comparing c_i and c_j , one may need to compare $(v_i c_i)^{1/v_i}$ and $(v_j c_j)^{1/v_j}$. The difference of these quantities may only be observed for certain range of the potential. See part (2) of Theorem 3.2.

Second, we characterize the ionic charge density through the function V defined in (3.2); cf. also (3.15). We recall for the classical PB theory that the corresponding function V is defined by

$$V'(\phi) = - \sum_{i \in J, i \neq 0} q_i c_i^\infty e^{-\beta q_i \phi},$$

where c_i^∞ ($i \in J, i \neq 0$) are positive constants. An important difference here is that, when the ionic size effects are included, the function V grows linearly at the $-\infty$ and ∞ , rather than exponentially as in the classical PB theory.

Third, when the ionic size effects are included, the Debye length is then modified. In Table 1 and Table 2, we compare the size-modified Debye length $\hat{\lambda}_D$ defined in (3.23) with the classical Debye length λ_D defined in (3.24) for a few ionic systems. The difference between these two tables is that the diameters of ions listed in Table 1 do not, while those in Table 2, include the size of a hydration shell. It is clear that the modification of the Debye length due to the inclusion of the ionic size effect is not significant. This may suggest that a linearized system may not describe well the size effect. Clearly, further tests are needed on real ionic solutions and biomolecular systems.

Finally, for a spherical charged molecule immersed in an ionic solution occupying a finite region, the qualitative behavior of the electrostatic potential—either it is monotonic or it changes the monotonicity only once in the entire range of the radial variable—is completely determined by the sign of two surface charge densities. One is the prescribed surface charge density and the other is the effective surface charge density. If the region of ionic solution is the entire complement of the sphere in \mathbb{R}^3 , then the ionic charge neutrality is necessary for the existence and uniqueness of the electrostatic potential that vanishes at infinity, governed by the PBE (classical or size-modified). Such a potential is always monotonic.

We conclude with two remarks on the mathematical model we have studied here. First, for the case of a uniform size for all ions and solvent molecules, the free-energy functional (2.1) can be derived from a lattice-gas model; cf. [20]. For a general and more interesting case where the sizes are different, such a derivation seems not available. It is therefore interesting to give a rigorous derivation of such a free-energy functional using the notion of equilibrium statistical mechanics. Second, we have assumed mainly that the region Ω of ionic solution is bounded. The case that Ω has an infinite volume is a tricky situation to define the functional $F[c]$; cf. (2.1) and (2.6). Usually, the concentration c_i is taken to be the bulk value $c_i^\infty (>0)$ at

infinity (or far away from the charged surface). Such a value can be experimentally determined. If Ω is unbounded with an infinite volume, then the integral of c_i over Ω will be just infinite if $c_i=c_i^\infty$ at infinity. The PBE, however, can be defined on an unbounded domain as the electrostatic potential ψ can exist in the entire space.

Acknowledgments

This work was supported by the National Science Foundation (NSF) through grant DMS-0811259 (B.L.), the NSF Center for Theoretical Biological Physics (CTBP) through grant PHY-0822283 (B.L.), the National Institutes of Health through the grant R01GM096188 (B.L.), the Natural Science Foundation of China through grant NSFC-11101276 and NSFC-91130012 (P.L. and Z.X.), and the Alexander von Humboldt Foundation (Z.X.). The authors thank the referee for helpful comments.

References

1. Adams, R. Sobolev Spaces. Academic Press: New York; 1975.
2. Andelman, D. Electrostatic properties of membranes: The Poisson–Boltzmann theory. In: Lipowsky, R.; Sackmann, E., editors. Handbook of Biological Physics. Vol. 1. Elsevier; 1995. p. 603–642.
3. Bai Y, Travers K, Chu VB, Lipfert J, Doniach S, Herschlag D. Quantitative and comprehensive decomposition of the ion atmosphere around nucleic acids. *J Amer Chem Soc.* 2007; 129:14981–14988. [PubMed: 17990882]
4. Bleam ML, Anderson CF, Record MTJ. Relative binding affinities of monovalent cations for double-stranded DNA. *Proc Natl Acad Sci USA.* 1980; 77:3085–3089. [PubMed: 16592827]
5. Borukhov I, Andelman D, Orland H. Steric effects in electrolytes: A modified Poisson–Boltzmann equation. *Phys Rev Lett.* 1997; 79:435–438.
6. Borukhov I, Andelman D, Orland H. Adsorption of large ions from an electrolyte solution: A modified Poisson–Boltzmann equation. *Electrochimica Acta.* 2000; 46:221–229.
7. Boschitsch AH, Danilov PV. Formulation of a new and simple nonuniform size-modified Poisson–Boltzmann description. *J Comput Chem.* 2012; 33:1152–1164. [PubMed: 22370918]
8. Che J, Dzubiella J, Li B, McCammon JA. Electrostatic free energy and its variations in implicit solvent models. *J Phys Chem B.* 2008; 112:3058–3069. [PubMed: 18275182]
9. Chu VB, Bai Y, Lipfert J, Herschlag D, Doniach S. Evaluation of ion binding to DNA duplexes using a size-modified Poisson–Boltzmann theory. *Biophys J.* 2007; 93:3202–3209. [PubMed: 17604318]
10. Davis ME, McCammon JA. Electrostatics in biomolecular structure and dynamics. *Chem Rev.* 1990; 90:509–521.
11. Eisenberg B, Hyon YK, Liu C. Energy variational analysis of ions in water and channels: Field theory for primitive models of complex ionic fluids. *J Chem Phys.* 2011; 133:104104. [PubMed: 20849161]
12. Fogolari F, Brigo A, Molinari H. The Poisson–Boltzmann equation for biomolecular electrostatics: a tool for structural biology. *J Mol Recognit.* 2002; 15:377–392. [PubMed: 12501158]
13. Gilbarg, D.; Trudinger, NS. Elliptic Partial Differential Equations of Second Order. 2nd. Springer-Verlag; 1998.
14. Grochowski P, Trylska J. Continuum molecular electrostatics, salt effects and counterion binding —A review of the Poisson–Boltzmann model and its modifications. *Biopolymers.* 2008; 89:93–113. [PubMed: 17969016]
15. Grosberg AY, Nguyen TT, Shklovskii BI. Colloquium: The physics of charge inversion in chemical and biological systems. *Rev Mod Phys.* 2002; 74:329–345.
16. Hille, B. Ion Channels of Excitable Membranes. 3rd. Sinauer Associates; 2001.
17. Howard JJ, Perkyns JS, Pettitt BM. The behavior of ions near a charged wall—dependence on ion size, concentration, and surface charge. *J Phys Chem B.* 2010; 114:6074–6083. [PubMed: 20405885]
18. Kilic MS, Bazant MZ, Ajdari A. Steric effects in the dynamics of electrolytes at large applied voltages. I. Double-layer charging. *Phys Rev E.* 2007; 75:021502.

19. Kilic MS, Bazant MZ, Ajdari A. Steric effects in the dynamics of electrolytes at large applied voltages. II. Modified Poisson–Nernst–Planck equations. *Phys Rev E*. 2007; 75:021503.
20. Kralj-Igli V, Igli A. A simple statistical mechanical approach to the free energy of the electric double layer including the excluded volume effect. *J Phys II (France)*. 1996; 6:477–491.
21. Lambert D, Leipply D, Shiman R, Draper DE. The influence of monovalent cation size on the stability of RNA tertiary structures. *J Mol Biol*. 2009; 390:791–804. [PubMed: 19427322]
22. Li B. Continuum electrostatics for ionic solutions with nonuniform ionic sizes. Non-linearity. 2009; 22:811–833.
23. Li B. Minimization of electrostatic free energy and the Poisson–Boltzmann equation for molecular solvation with implicit solvent. *SIAM J Math Anal*. 2009; 40:2536–2566.
24. Lockless SW, Zhou M, MacKinnon R. Structural and thermodynamic properties of selective ion binding in a K^+ channel. *PLoS Biology*. 2007; 5:1079–1088.
25. López-García JJ, Horno José. Poisson–Boltzmann description of the electrical double layer including ion size effects. *Langmuir*. 2011; 27:13970–13980. [PubMed: 22035520]
26. Lu BZ, Zhou YC. Poisson–Nernst–Planck equations for simulating biomolecular diffusion-reaction processes II: Size effects on ionic distributions and diffusion-reaction rates. *Biophys J*. 2011; 100:2475–2485. [PubMed: 21575582]
27. Maggs AC. A minimizing principle for the Poisson–Boltzmann equation. *EPL*. 2012; 98:16012.
28. Quesada-Pérez M, Martín-Molina A, Hidalgo-Álvarez R. Simulation of electric double layers with multivalent counterions: Ion size effect. *J Chem Phys*. 2004; 121:8618–8626. [PubMed: 15511188]
29. Schoch RB, Han J, Renaud P. Transport phenomena in nanofluidics. *Rev Mod Phys*. 2008; 80:839–883.
30. Sharp KA, Honig B. Electrostatic interactions in macromolecules: Theory and applications. *Annu Rev Biophys Chem*. 1990; 19:301–332. [PubMed: 2194479]
31. Silalahi ARJ, Boschitsch AH, Harris RC, Fenley MO. Comparing the predictions of the nonlinear Poisson–Boltzmann equation and the ion size-modified Poisson–Boltzmann equation for a low-dielectric charged spherical cavity in an aqueous salt solution. *J Chem Theory Comput*. 2010; 6:3631–3639. [PubMed: 22723750]
32. Strauss UP, Leung YP. Volume changes as a criterion for site binding of counterions by polyelectrolytes. *J Amer Chem Soc*. 1965; 87:1476–1480.
33. Tresset G. Generalized Poisson–Fermi formalism for investigating size correlation effects with multiple ions. *Phys Rev E*. 2008; 78:061506.
34. Valiskó M, Boda D, Gillespie D. Selective adsorption of ions with different diameter and valence and highly charged interfaces. *J Phys Chem C*. 2007; 111:15575–15585.
35. Vlachy V. Ionic effects beyond Poisson–Boltzmann theory. *Annu Rev Phys Chem*. 1999; 50:145–165. [PubMed: 15012409]
36. Vörtler HL, Schäfer K, Smith WR. Simulation of chemical potentials and phase equilibria in two- and three-dimensional square-well fluids: finite size effects. *J Phys Chem B*. 2008; 112:4656–4661. [PubMed: 18358019]
37. Wen J, Zhou S, Xu Z, Li B. Competitive adsorption and ordered packing of counterions near highly charged surfaces: From mean-field theory to Monte Carlo simulations. *Phys Rev E*. 2012; 85:041406.
38. Zhou S, Wang Z, Li B. Mean-field description of ionic size effects with non-uniform ionic sizes: A numerical approach. *Phys Rev E*. 2011; 84:021901.

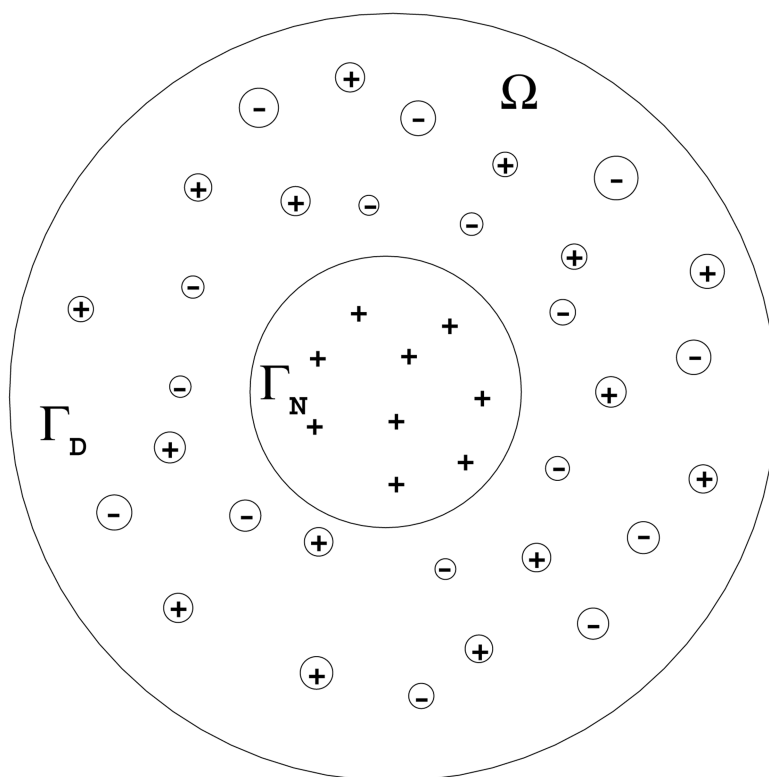


Figure 1. A schematic view of a charged molecule immersed in an ionic solution. The molecule is represented by the inner sphere filled with symbols +.

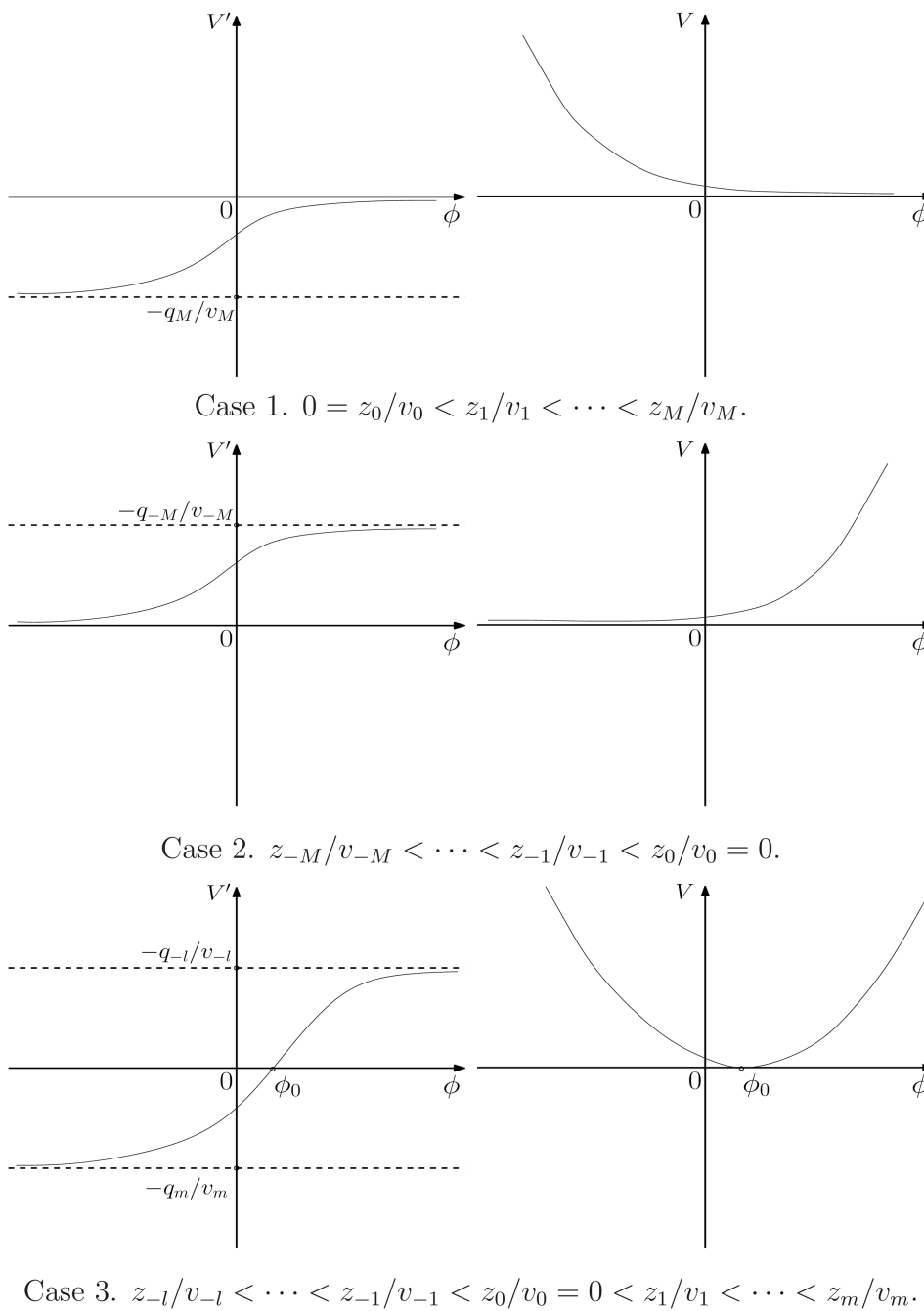


Figure 2. Graphs of $V' = V'(\phi)$ (left) and $V = V(\phi)$ (right) for the three different cases. The value $-V'(\phi)$ is the ionic charge density at a (shifted) electrostatic potential ϕ .

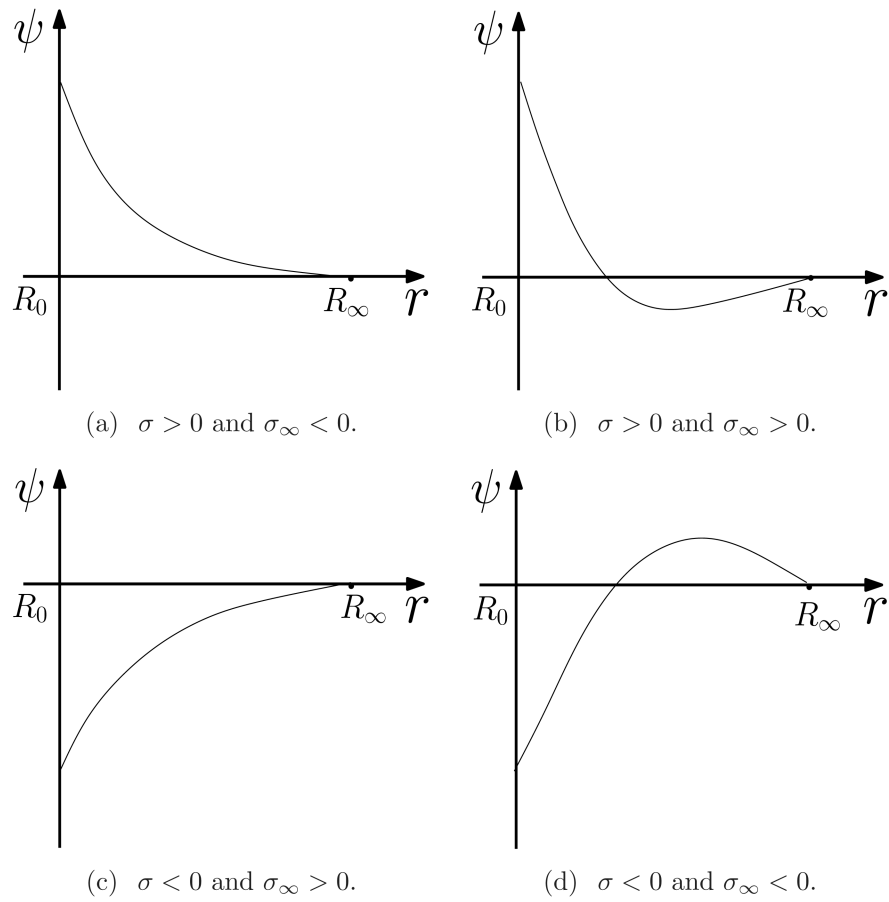


Figure 3.
The graph of electrostatic potential ψ .

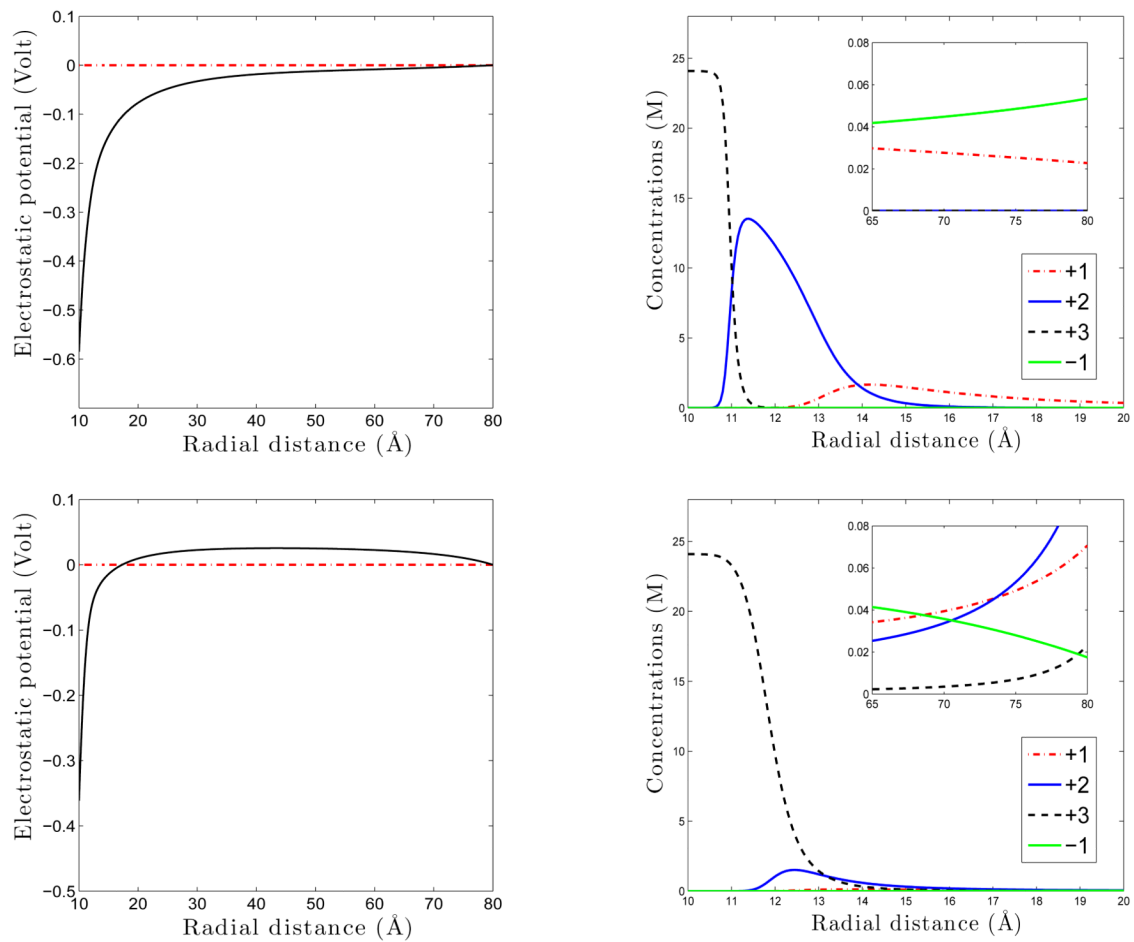


Figure 4.

The electrostatic potential ψ (left) and the equilibrium ionic concentrations (right). Top.

Case I: $(N_1, N_2, N_3, N_4) = (60, 30, 20, 50)$, $\sigma < 0$, and $\sigma_\infty > 0$. Bottom. Case II: $(N_1, N_2, N_3, N_4) = (50, 50, 50, 50)$, $\sigma < 0$, and $\sigma_\infty < 0$. The concentrations profiles are marked by the corresponding ionic valences.

Table 1

A comparison of the Debye length λ_D and the ionic size-modified Debye length $\hat{\lambda}_D$ for a few systems of ionic solutions. The diameter of an ion does not include that of a water molecule (hydration shell). Concentrations mean bulk concentrations.

Ionic systems	Diameters of ions (Å)	Concentrations (M)	λ_D (Å)	$\hat{\lambda}_D$ (Å)
Cl ⁻ , Na ⁺	3.62, 2.04	0.1, 0.1	9.715	9.726
Cl ⁻ , K ⁺	3.62, 2.76	0.1, 0.1	9.715	9.720
Cl ⁻ , Ca ²⁺	3.62, 2.00	0.2, 0.1	5.609	5.618
Cl ⁻ , Na ⁺ , K ⁺	3.62, 2.04, 2.76	0.2, 0.1, 0.1	6.870	6.880
Cl ⁻ , Na ⁺ , Ca ²⁺	3.62, 2.04, 2.00	0.3, 0.1, 0.1	4.858	4.870
Cl ⁻ , Na ⁺ , K ⁺ , Ca ²⁺	3.62, 2.04, 2.76, 2.00	0.4, 0.1, 0.1, 0.1	4.345	4.358
Cl ⁻ , K ⁺ , Ca ²⁺ , Al ³⁺	3.62, 2.76, 2.00, 1.35	0.6, 0.1, 0.1, 0.1	3.072	3.085

Table 2

A comparison of the Debye length λ_D and the ionic size-modified Debye length $\hat{\lambda}_D$ for a few systems of ionic solutions. The diameter of an ion includes that of a water molecule (hydration shell). Concentrations mean bulk concentrations.

Ionic systems	Diameters of ions (Å)	Concentrations (M)	λ_D (Å)	$\hat{\lambda}_D$ (Å)
Cl ⁻ , Na ⁺	6.37, 4.79	0.1, 0.1	9.715	9.847
Cl ⁻ , K ⁺	6.37, 5.51	0.1, 0.1	9.715	9.763
Cl ⁻ , Ca ²⁺	6.37, 4.75	0.2, 0.1	5.609	5.701
Cl ⁻ , Na ⁺ , K ⁺	6.37, 4.79, 5.51	0.2, 0.1, 0.1	6.870	6.970
Cl ⁻ , Na ⁺ , Ca ²⁺	6.37, 4.79, 4.75	0.3, 0.1, 0.1	4.858	4.974
Cl ⁻ , Na ⁺ , K ⁺ , Ca ²⁺	6.37, 4.79, 5.51, 4.75	0.4, 0.1, 0.1, 0.1	4.345	4.449
Cl ⁻ , K ⁺ , Ca ²⁺ , Al ³⁺	6.37, 5.51, 4.75, 4.10	0.6, 0.1, 0.1, 0.1	3.072	3.172