Continuum Electrostatics for Ionic Solutions with Nonuniform Ionic Sizes

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Abstract

This work concerns electrostatic properties of an ionic solution with multiple ionic species of possibly different ionic sizes. Such properties are described by the minimization of an electrostatic free-energy functional of ionic concentrations. Bounds are obtained for ionic concentrations with low electrostatic free energies. Such bounds are used to show that there exists a unique set of equilibrium ionic concentrations that minimizes the free-energy functional. The equilibrium ionic concentrations are found to depend sorely on the equilibrium electrostatic potential, resembling the classical Boltzmann distributions that relate the equilibrium ionic concentrations to the equilibrium electrostatic potential. Unless all the ionic and and solvent molecular sizes are assumed to be the same, explicit formulas of such dependence are, however, not available in general. It is nevertheless proved that in equilibrium the ionic charge density is a decreasing function of the electrostatic potential. This determines a variational principle with a convex functional for the electrostatic potential.

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1 Introduction

The Poisson-Boltzmann theory of continuum electrostatics for an ionic solution with M ionic species occupying a region Ω in $\mathbb{R}^3$ is based on the combination of the Poisson equation

$$\nabla \cdot \varepsilon \nabla \psi = -\rho \qquad \text{in } \Omega \tag{1.1}$$

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and the Boltzmann distribution

$$c_i = c_i^\infty e^{-\beta q_i \psi} \qquad \text{in } \Omega, \qquad i = 1, \dots, M, \tag{1.2}$$

cf. [2, 9, 14, 15, 18]. Here, ψ is the electrostatic potential field of the ionic solution, ε the dielectric coefficient that can be position-dependent, ρ the charge density defined by

$$\rho = \rho_f + \sum_{i=1}^{M} q_i c_i \tag{1.3}$$

with ρ_f a fixed charge density and $\sum_{i=1}^{M} q_i c_i$ the induced or ionic charge density, c_i the local concentration of the ith ionic species with c_i^∞ its bulk value, $q_i = z_i e$ with z_i the valence of ith ionic species and e the elementary charge, and β the inverse thermal energy. Inserting (1.2) and (1.3) into (1.1), we obtain the Poisson-Boltzmann equation for the electrostatic potential ψ

$$\nabla \cdot \varepsilon \nabla \psi + \sum_{i=1}^{M} q_i c_i^\infty e^{-\beta q_i \psi} = -\rho_f \qquad \text{in } \Omega.$$

The Boltzmann distributions (1.2) are conditions of equilibrium ionic concentrations of the mean-field electrostatic free-energy functional [3, 6, 15, 18]

$$\int_\Omega \left\{ \frac{1}{2}\rho\psi + \beta^{-1} \sum_{i=1}^{M} c_i \left[\log(\Lambda^3 c_i) - 1 \right] - \sum_{i=1}^{M} \mu_i c_i \right\} dx,$$

where Λ is the thermal de Broglie wavelength and μ_i the chemical potential of the ith ionic species. Here, for a given set of ionic concentrations c_i, the charge density ρ is defined in (1.3) and the potential ψ is determined by the Poisson equation (1.1) together with some boundary conditions. Throughout, we denote by $\log x$ the natural logarithm of $x > 0$.

Despite of its success in many applications, particularly in biomolecular modeling [5, 7, 10, 19], the classical Poisson-Boltzmann theory is known to have some limitations. For instance, it does not in general explain the phenomenon of attraction between like-charged particles in confined geometries [13, 16, 17]. One of the known drawbacks of this classical theory is that it does not describe the ionic finite-size or excluded-volume effect. Presumably, such size effect, particularly when ionic linear sizes are different, is profound in small systems such as ion channels. As pointed out in [1], equilibrium ionic concentrations predicted by the classical Poisson-Boltzmann theory without ionic size effect can be much higher than those predicted by a size-modified Poisson-Boltzmann theory.

In this work, we generalize the classical Poisson-Boltzmann theory for an ionic solution to include the ionic size effect with possibly different ionic sizes. Specifically, we study the mean-field electrostatic free-energy functional

$$F[c] = \int_\Omega \left\{ \frac{1}{2}\rho\psi + \beta^{-1} \sum_{i=0}^{M} c_i \left[\log\left(a_i^3 c_i\right) - 1\right] - \sum_{i=1}^{M} \mu_i c_i \right\} dx, \tag{1.4}$$

where the summation in the β^{-1} term starts from $i = 0$ and

$$c_0(x) = a_0^{-3}\left[1 - \sum_{i=1}^{M} a_i^3 c_i(x)\right] \qquad \forall x \in \Omega \tag{1.5}$$

defines the local concentration of solvent molecules. In (1.4) and (1.5) , the parameter $a_i > 0$ for each $i \in \{1, \ldots, M\}$ represents the linear size of an ion of the ith ionic species and $a_0 > 0$ represents the linear size of a solvent molecule. The charge density $\rho : \Omega \to \mathbb{R}$ is given by (1.3). The electrostatic potential $\psi : \Omega \to \mathbb{R}$ is determined by the Poisson equation (1.1), together with a boundary condition which we take to be

$$\psi = \psi_0 \qquad \text{on } \partial\Omega \tag{1.6}$$

for some given function $\psi_0 : \partial\Omega \to \mathbb{R}$. The first term in (1.4) represents the internal or potential electrostatic energy. The β^{-1} term represents the ideal gas entropy. The last term in (1.4) accounts for a constant chemical potential in the system. The osmotic pressure from the mobile ions is omitted, since it is only an additive constant in the free-energy functional in the present setting.

The special case that all the linear sizes a_i ($i = 0, \ldots, M$) are the same is treated in [11] for a spatially one-dimensional system and in [1] for a two-species system. Rigorous mathematical analysis is also given in [12]. In [4], a two-species system with two different ionic sizes is considered. The form (1.4) of the size-modified electrostatic free-energy functional is known to experts. But it does not seem to be previously available in literature.

It should be pointed out that with a uniform ionic and solvent molecular size a, i.e., $a = a_0 = a_1 = \cdots = a_M$, the equilibrium ionic concentrations and electrostatic potential of the free-energy functionals (1.4) are related by the generalized Boltzmann distributions (cf. [12] and (4.4))

$$c_j(x) = \frac{c_j^\infty e^{-\beta q_j \psi(x)}}{1 + a^3 \sum_{i=1}^{M} c_i^\infty e^{-\beta q_i \psi(x)}} \qquad \forall x \in \Omega, \quad j = 1, \ldots, M,$$

where $c_j^\infty = a^{-3} e^{\beta\mu_j}$ is the bulk concentration of the jth ionic species. This is true for the case $\psi_0 = 0$ in the boundary condition (1.6). For a general case, see (4.4). Such explicit dependence of each equilibrium concentration on the equilibrium electrostatic potential is in general not available, if the sizes of different ions and solvent molecules are not all the same.

Our main results of this work are as follows:

(1) For any concentrations $c = (c_1, \dots, c_M)$, there exist concentrations $\hat{c} = (\hat{c}_1, \dots, \hat{c}_M)$ and constants $\theta_1, \theta_2 \in (0, 1)$ such that $F[\hat{c}] \le F[c]$ and $\theta_1 \le a_i^3 \hat{c}_i(x) \le \theta_2$ for a.e. $x \in \Omega$ and all $i = 0, 1, \dots, M$, cf. Theorem 2.1. This result is proved by constructing concentrations with desired properties, and the construction is based on the perturbation method that is first used in [12];

(2) The free-energy functional (1.4) has a unique minimizer which is also the unique equilibrium, cf. Theorem 3.1. This is essentially a consequence of the fact that the free-energy functional defined in (1.4) is convex;

(3) Each equilibrium concentration depends sorely on the equilibrium electrostatic potential. This can be viewed as generalized, implicit Boltzmann distributions. If all the ionic and solvent molecular sizes are assumed to be the same, then an explicit formula can be found for such distributions, cf. (4.4). Otherwise, the dependence of the equilibrium charge density on the equilibrium electrostatic potential is shown to be a decreasing function. This in turn establishes a variational principle with a convex functional for electrostatic potentials. See Theorem 5.1.

The rest of the paper is organized as follows: In Section 2, we introduce some notation and make some assumptions. We also prove the theorem on the point-wise bounds for ionic concentrations that have low free energies; In Section 3, we prove the existence and uniqueness of the minimizer of the free-energy functional (1.4). We also prove that the free-energy minimizing concentrations are the unique equilibrium concentrations; In Section 4, we derive the generalized Boltzmann distributions for the case of a uniform ionic and solvent molecular size; In Section 5, we prove that, in general for a nonuniform ionic and molecular size, each of the equilibrium ionic concentrations depends sorely on the equilibrium electrostatic potential. We also obtain the monotonicity of the ionic charge density as a function of the potential; Finally, in Section 6, we discuss our main results and draw some conclusions.

2 Bounds on concentrations with low free energies

We make the following assumptions:

(A1) The set $\Omega \subseteq \mathbb{R}^3$ is a bounded domain with a C^1 boundary $\partial\Omega$;

(A2) Both $\rho_f \in L^\infty(\Omega)$ and $\varepsilon \in L^\infty(\Omega)$ are given with $\varepsilon(x) \ge \varepsilon_{min}$ for all $x \in \Omega$ for some constant $\varepsilon_{min} > 0$;

(A3) The integer $M \ge 2$, the positive numbers $a_0, \dots, a_M$ and β, and the real numbers $q_1, \dots, q_M$ and $\mu_1, \dots, \mu_M$ are all given. The numbers $q_1, \dots, q_M$ are non-zero, and do not have the same sign (due to the charge neutrality); (Further assumption on the charge neutrality will be made later, cf. (5.5).)

(A4) The boundary data ψ_0 in (1.6) is the trace of a given function, also denoted by ψ_0, in $W^{1,\infty}(\Omega)$.

We use standard notation for function spaces $L^p(\Omega)$ and $W^{k,p}(\Omega)$, cf. [8].

Let $u \in L^1(\Omega)$. Suppose

$$\sup_{0 \neq \xi \in L^\infty(\Omega) \cap H_0^1(\Omega)} \frac{\int_\Omega u\xi \, dx}{\|\xi\|_{H^1(\Omega)}} < \infty. \tag{2.1}$$

Since $L^\infty(\Omega) \cap H_0^1(\Omega)$ is dense in $H_0^1(\Omega)$, we can identify u as an element in $H^{-1}(\Omega)$, the dual of $H_0^1(\Omega)$, with

$$\langle u, \xi \rangle = \int_\Omega u\xi dx \qquad \forall \xi \in L^\infty(\Omega) \cap H_0^1(\Omega),$$

and we write $u \in L^1(\Omega) \cap H^{-1}(\Omega)$. The $H^{-1}(\Omega)$-norm of u is given by (2.1). We define

$$X = \left\{ (c_1, \dots, c_M) \in L^1(\Omega, \mathbb{R}^M) : \sum_{i=1}^M q_i c_i \in H^{-1}(\Omega) \right\},$$

$$\|c\|_X = \sum_{i=1}^M \|c_i\|_{L^1(\Omega)} + \left\| \sum_{i=1}^M q_i c_i \right\|_{H^{-1}(\Omega)} \qquad \forall c = (c_1, \dots, c_M) \in X.$$

Clearly, $(X, \|\cdot\|_X)$ is a Banach space. We also define

$$K = \left\{ (c_1, \dots, c_M) \in X : \ c_i \geq 0 \ \text{ a.e. } \Omega, \ i = 0, 1, \dots, M \right\}. \tag{2.2}$$

Clearly, K is a nonempty, convex subset of $L^\infty(\Omega, \mathbb{R}^M) \subset X$.

Let $\hat{\psi}_0 \in H^1(\Omega)$ be the weak solution of the boundary-value problem

$$\begin{cases} \nabla \cdot \varepsilon \nabla \hat{\psi}_0 = -\rho_f & \text{in } \Omega, \\ \hat{\psi}_0 = \psi_0 & \text{on } \partial\Omega. \end{cases} \tag{2.3}$$

This means that $\hat{\psi}_0 \in H^1_{\psi_0}(\Omega)$ and

$$\int_\Omega \varepsilon \nabla \hat{\psi}_0 \cdot \nabla v \, dx = \int_\Omega \rho_f v \, dx \qquad \forall v \in H_0^1(\Omega). \tag{2.4}$$

It is clear that $\hat{\psi}_0 \in L^\infty(\Omega)$.

Let $L : H^{-1}(\Omega) \to H_0^1(\Omega)$ be the linear, self-adjoint, elliptic operator defined as follows: for any $f \in H^{-1}(\Omega)$, the function $Lf \in H_0^1(\Omega)$ and

$$\int_\Omega \varepsilon \nabla Lf \cdot \nabla v \, dx = \langle f, v \rangle \qquad \forall v \in H_0^1(\Omega). \tag{2.5}$$

It is easy to verify that $f \mapsto \sqrt{\langle f, Lf\rangle}$ defines a norm on $H^{-1}(\Omega)$ which is equivalent to the $H^{-1}(\Omega)$-norm, cf. [12].

Let $\lambda \in \mathbb{R}$ and define $S_\lambda : [0,\infty) \to \mathbb{R}$ by

$$\begin{cases} S_\lambda(0) = 0 \\ S_\lambda(u) = u(\lambda + \log u) \qquad \text{if } u > 0. \end{cases} \tag{2.6}$$

It is easy to see that S_λ is continuous and bounded below on $[0,\infty)$, and is also strictly convex on $(0,\infty)$. Moreover, if $(c_1,\ldots,c_M) \in K$ then $\int_\Omega S_\lambda(c_i)\,dx < \infty$ for any $\lambda \in \mathbb{R}$ and all $i = 0,1,\ldots,M$.

For a given $c = (c_1,\ldots,c_M) \in K$, the potential ψ defined by (1.1) and (1.6) can be written as

$$\psi = \hat{\psi}_0 + L\left(\sum_{i=1}^M q_i c_i\right). \tag{2.7}$$

Consequently, one verifies that the free-energy functional $F : K \to \mathbb{R}$ defined by (1.4) can be rewritten as

$$F[c] = \int_\Omega \left\{ \frac{1}{2}\left(\sum_{i=1}^M q_i c_i\right) L\left(\sum_{i=1}^M q_i c_i\right) + \beta^{-1}\sum_{i=0}^M S_{-1}(c_i) + \sum_{i=1}^M g_i c_i + f_0 \right] dx, \tag{2.8}$$

where c_0 is defined by (1.5) and

$$\begin{aligned} g_i &= \frac{1}{2} q_i \left(L\rho_f + \hat{\psi}_0\right) + \beta^{-1}\log a_i^3 - \beta^{-1} a_i^3 a_0^{-3}\log a_0^3 - \mu_i, \qquad i = 1,\ldots,M, \\ f_0 &= \frac{1}{2}\rho_f \hat{\psi}_0 + \beta^{-1} a_0^{-3}\log a_0^3. \end{aligned} \tag{2.9}$$

Note that all $g_1,\ldots,g_M$, and f_0 are $L^\infty(\Omega)$-functions.

We denote by $|E|$ the Lebesgue measure of a Lebesgue measurable set $E \subseteq \mathbb{R}^3$.

Theorem 2.1. *Let $c = (c_1,\ldots,c_M) \in K$ and $\delta > 0$. Assume there exists $i_0 \in \{0,1,\ldots,M\}$ such that $\left|\left\{x \in \Omega : a_{i_0}^3 c_{i_0}(x) < \alpha\right\}\right| > 0$ for all $\alpha > 0$. Then there exists $\hat{c} = (\hat{c}_1,\ldots,\hat{c}_M) \in K$ and $\theta_1,\theta_2 \in (0,1)$ with $\theta_1 < \theta_2$ such that $\|\hat{c} - c\|_X < \delta$, $\theta_1 \le a_i^3 \hat{c}_i(x) \le \theta_2$ for a.e. $x \in \Omega$ and all $i = 0,1,\ldots,M$, and $F[\hat{c}] < F[c]$.*

The bounds established in this theorem allow us to derive rigorously the Euler-Lagrange equation and hence define equilibrium concentrations for the functional (1.4), cf. Theorem 3.1.

Our strategy for proving Theorem 2.1 is as follows: given a set of ionic concentrations $c = (c_1,\ldots,c_M) \in K$, we construct the set of ionic concentrations $\hat{c} = (\hat{c}_1,\ldots,\hat{c}_M) \in K$ that satisfies all the desired properties. The construction is done by perturbing the given set of concentrations $c_1, \ldots, c_M$ in two steps. First, if $c_0(x)$ is close to 0 at some point $x \in \Omega$, then we define $\bar{c}_i(x) = c_i(x) - \bar{\alpha}_i(x)$, with $\bar{\alpha}(x) > 0$ small, for those $i \in \{1, \ldots, M\}$ such that $c_i(x)$ is away from 0. Second, if $\bar{c}_j(x)$ is close to 0 for some $j \in \{1, \ldots, M\}$, then we define $\hat{c}_j(x) = \bar{c}_j(x) + \hat{\alpha}_j(x)$ with $\hat{\alpha}_j(x) > 0$ small. The concentrations $(\bar{c}_1, \ldots, \bar{c}_M)$ and $(\hat{c}_1, \ldots, \hat{c}_M)$ remain in the set K. Moreover, they are close to the original set of concentrations $(c_1, \ldots, c_M)$. The change of the potential energy is linear, in leading order, in $\bar{\alpha}_i(x)$ or $\hat{\alpha}_j(x)$. But the entropic change is very negative. For instance, the entropy change due to the change from $\bar{c}_j(x)$ to $\hat{c}_j(x)$ is proportional to $S'_{-1}(\hat{\alpha}_j(x)) = 1/\hat{\alpha}_j(x)$ (cf. (2.6) and (2.8)). Thus the total free-energy change is very negative.

We shall accordingly divide our proof into two major steps. First, we construct $\bar{c} = (\bar{c}_1, \ldots, \bar{c}_M) \in K$ so that the corresponding solvent concentration $\bar{c}_0$ has a lower bound away from 0. Second, we use $\bar{c}$ to construct the desired $\hat{c}$.

Proof of Theorem 2.1. We first construct $\bar{c} = (\bar{c}_1, \ldots, \bar{c}_M) \in K$ such that

$$a_0^3 \bar{c}_0(x) := 1 - \sum_{i=1}^{M} a_i^3 \bar{c}_i(x) \geq \tau_1 \qquad \text{a.e. } x \in \Omega \tag{2.10}$$

for some constant $\tau_1 \in (0, 1)$, $\|\bar{c} - c\|_X < \delta/2$, and $F[\bar{c}] \leq F[c]$ with a strict inequality if $|\{x \in \Omega : a_0^3 c_0(x) < \alpha\}| > 0$ for all $\alpha > 0$. For convenience, we denote for any $\alpha > 0$

$$\omega_0(\alpha) = \{x \in \Omega : a_0^3 c_0(x) < \alpha\}.$$

If there exists a constant $\alpha_1 > 0$ such that $|\omega_0(\alpha_1)| = 0$, i.e., $a_0^3 c_0(x) \geq \alpha_1$ a.e. Ω, then $(\bar{c}_1, \ldots, \bar{c}_M) = (c_1, \ldots, c_M) \in K$ satisfies all the desired properties with $\tau_1 = \alpha_1/(1+\alpha_1) \in (0, 1)$. Suppose $|\omega_0(\alpha)| > 0$ for any $\alpha > 0$. Let $0 < \alpha < 1/(4M)$. Let

$$H_i(\alpha) = \left\{ x \in \omega_0(\alpha) : a_i^3 c_i(x) \geq \frac{1}{2M} \right\}, \qquad i = 1, \ldots, M.$$

Let $x \in \omega_0(\alpha)$. Then there exists some $j = j(x) \in \{1, \ldots, M\}$ such that $a_j^3 c_j(x) \geq 1/(2M)$. In fact, if this were not true, then $a_i^3 c_i(x) < 1/(2M)$ for all $i = 1, \ldots, M$. Hence, $a_0^3 c_0(x) = 1 - \sum_{i=1}^M a_i^3 c_i(x) > 1/2 > \alpha$. This would mean that $x \notin \omega_0(\alpha)$, a contradiction. Therefore, we have $\omega_0(\alpha) = \cup_{i=1}^M H_i(\alpha)$.

Since $|\omega_0(\alpha)| > 0$, we have $|H_{j_1}(\alpha)| > 0$ for some j_1 $(1 \leq j_1 \leq M)$. If $|H_j(\alpha) \setminus H_{j_1}(\alpha)| = 0$ for all $j \neq j_1$, then we have $\omega_0(\alpha) = \tilde{K}_1(\alpha) \cup H_{j_1}(\alpha)$ for some $\tilde{K}_1(\alpha) \subset \omega_0(\alpha)$ with $|\tilde{K}_1(\alpha)| = 0$. Otherwise, $|H_{j_2}(\alpha) \setminus H_{j_1}(\alpha)| > 0$ for some $j_2 \neq j_1$. In case $|\omega_0(\alpha) \setminus [H_{j_1}(\alpha) \cup H_{j_2}(\alpha)]| = 0$, we have $\omega_0(\alpha) = \tilde{K}_2(\alpha) \cup H_{j_1}(\alpha) \cup [H_{j_2}(\alpha) \setminus H_{j_1}(\alpha)]$ for some $\tilde{K}_2(\alpha) \subset \omega_0(\alpha)$ with $|\tilde{K}_2(\alpha)| = 0$. By induction, we see that there exist $m \in \{1, \ldots, M\}$, $\tilde{K}_m(\alpha) \subset \omega_0(\alpha)$ with $|\tilde{K}_m(\alpha)| = 0$, and mutually disjoint sets $K_{j_1}(\alpha), \ldots, K_{j_m}(\alpha) \subseteq \omega_0(\alpha)$ such that $K_{j_i}(\alpha) \subseteq H_{j_i}(\alpha)$ and $|K_{j_i}(\alpha)| > 0$ for $i = 1, \ldots, m$, and $\omega_0(\alpha) = \tilde{K}_m(\alpha) \cup [\cup_{i=1}^m K_{j_i}(\alpha)]$. By relabeling, we may assume that $j_i = i$ for $i = 1, \ldots, m$.

Define now

$$
\bar{c}_j(x) = \begin{cases} c_i(x) - \alpha a_i^{-3} \chi_{K_i(\alpha)}(x) & \forall x \in \Omega, \ i = 1, \ldots, m, \\ c_i(x) & \forall x \in \Omega, \ i = m+1, \ldots, M, \end{cases} \tag{2.11}
$$

$$
\bar{c}_0(x) = a_0^{-3} \left[1 - \sum_{i=1}^{M} a_i^3 \bar{c}_i(x) \right] \qquad \forall x \in \Omega,
$$

where χ_E denotes the characteristic function of the set E. It is easy to see that $\bar{c} = (\bar{c}_1, \ldots, \bar{c}_M) \in K$. Moreover,

$$
a_0^3 \bar{c}_0(x) = a_0^3 c_0(x) + \alpha \chi_{\omega_0(\alpha)}(x) \geq \alpha \qquad \forall x \in \Omega. \tag{2.12}
$$

This implies (2.10) with $\tau_1 = \alpha \in (0,1)$. Clearly,

$$
\sum_{i=1}^{M} \|\bar{c}_i - c_i\|_{L^1(\Omega)} \leq \alpha \sum_{i=1}^{m} a_i^{-3} |K_i(\alpha)|.
$$

Moreover,

$$
\left\| \sum_{i=1}^{M} q_i \bar{c}_i - \sum_{i=1}^{M} q_i c_i \right\|_{H^{-1}(\Omega)} \leq \alpha \left\| \sum_{i=1}^{m} q_i a_i^{-3} \chi_{K_i(\alpha)} \right\|_{L^2(\Omega)} \leq \alpha \sqrt{\sum_{i=1}^{m} q_i^2 a_i^{-6} |K_j(\alpha)|}.
$$

Therefore, $\|\bar{c} - c\|_X < \delta/2$, provided that $\alpha > 0$ is small enough.

If $x \in K_j(\alpha) \subseteq H_j(\alpha)$ for some j with $1 \leq j \leq m$, then $c_j(x) \geq 1/(2Ma_j^3)$, and $\bar{c}_j(x) \geq 1/(4Ma_j^3)$ since $0 < \alpha < 1/(4M)$. By the Mean-Value Theorem and the fact that $S_{-1}'(u) = \log u$ for any $u > 0$, there exists $\eta_j(x)$ with $\bar{c}_j(x) \leq \eta_j(x) \leq c_j(x)$ such that

$$
S_{-1}(\bar{c}_j(x)) - S_{-1}(c_j(x)) = [\bar{c}_j(x) - c_j(x)] \log \eta_j(x) \leq -\alpha a_j^{-3} \log \bar{c}_j(x) \leq \alpha a_j^{-3} \log \left(4Ma_j^3 \right).
$$

By the same argument, using (2.12) and the definition of $\omega_0(\alpha)$ which together imply that $a_0^3 \bar{c}_0(x) \leq 2\alpha$ for any $x \in \omega_0(\alpha)$, we obtain

$$
S_{-1}(\bar{c}_0(x)) - S_{-1}(c_0(x)) \leq \alpha a_0^{-3} \log(2a_0^{-3}\alpha) \qquad \forall x \in \omega_0(\alpha).
$$

Consequently, we have by (2.8), the embedding $L^2(\Omega) \hookrightarrow H^{-1}(\Omega)$, and the Hölder inequality that

$$
\begin{aligned}
F[\bar{c}] - F[c] = \frac{1}{2} \int_\Omega \left(\sum_{i=1}^{M} q_i c_i - \alpha \sum_{i=1}^{m} q_i a_i^{-3} \chi_{K_i(\alpha)} \right) L \left(\sum_{i=1}^{M} q_i c_i - \alpha \sum_{i=1}^{m} q_i a_i^{-3} \chi_{K_j(\alpha)} \right) dx \\
- \frac{1}{2} \int_\Omega \left(\sum_{i=1}^{M} q_i c_i \right) L \left(\sum_{i=1}^{M} q_i c_i \right) dx - \alpha \sum_{i=1}^{m} \int_{K_i(\alpha)} a_i^{-3} g_i dx
\end{aligned}
$$

$$
\begin{aligned}
&\quad + \beta^{-1} \sum_{i=0}^{m} \int_{\omega_0(\alpha)} [S_{-1}(\bar{c}_i) - S_{-1}(c_i)]\, dx \\
&\le \frac{1}{2}\alpha^2 \int_\Omega \left(\sum_{i=1}^{m} q_i a_i^{-3} \chi_{K_i(\alpha)} \right) L \left(\sum_{i=1}^{m} q_i a_i^{-3} \chi_{K_i(\alpha)} \right) dx \\
&\quad - \alpha \int_\Omega \left(\sum_{i=1}^{m} q_i a_i^{-3} \chi_{K_i(\alpha)} \right) L \left(\sum_{i=1}^{M} q_i c_i \right) dx + \alpha \sum_{i=1}^{m} \| a_i^{-3} g_i \|_{L^\infty(\Omega)} |K_i(\alpha)| \\
&\quad + \beta^{-1} \alpha \log \left(2 a_0^{-3} \alpha \right) |\omega_0(\alpha)| + \beta^{-1}\alpha \left[\sum_{i=1}^{m} a_i^{-3} \log \left(4 M a_i^3 \right) \right] |\omega_0(\alpha)| \\
&\le C\alpha^2 \left\| \sum_{i=1}^{m} q_i a_i^{-3} \chi_{K_i(\alpha)} \right\|^2_{L^2(\Omega)} + \alpha \left\| L \left(\sum_{i=1}^{M} q_i c_i \right) \right\|_{L^\infty(\Omega)} \sum_{i=1}^{m} |q_i| a_i^{-3} |K_i(\alpha)| \\
&\quad + \left(\beta^{-1} \alpha \log \alpha + C\alpha \right) |\omega_0(\alpha)| \\
&\le C\alpha (1 + \log \alpha) \sum_{i=1}^{m} |K_i(\alpha)|,
\end{aligned}
$$

where $C > 0$ is a generic constant independent of α. Thus, $F[\bar{c}] \le F[c]$ for $\alpha > 0$ sufficiently small, and $F[\bar{c}] < F[c]$ if $|\omega_0(\alpha)| = \sum_{j=1}^{m} |K_j(\alpha)| > 0$ for all $\alpha > 0$.

We now construct $\hat{c} = (\hat{c}_1, \dots, \hat{c}_M) \in K$ that satisfies

$$
a_i^3 \hat{c}_i(x) \ge \theta_0 \qquad \text{a.e. } x \in \Omega, \quad i = 0, 1, \dots, M, \tag{2.13}
$$

for some constant $\theta_0 \in (0,1)$, $\|\hat{c} - \bar{c}\|_X < \delta/2$, and $F[\hat{c}] \le F[\bar{c}]$ with a strict inequality if there exists $j \in \{1, \dots, M\}$ such that $|\{x \in \Omega : a_j^3 c_j(x) < \gamma\}| > 0$ for all $\gamma > 0$. All these imply that $\hat{c} \in K$ satisfies all the desired properties with $\theta_1 = \theta_0 \in (0,1)$ and $\theta_2 = 1 - \theta_0 \in (0,1)$.

If there exists $\tau_2 \in (0,1)$ such that $a_i^3 c_i(x) \ge \tau_2$ for a.e. $x \in \Omega$ and all $i = 1, \dots, M$, then $\hat{c} = \bar{c}$, with $0 < \alpha < \tau_2/2$ additionally, satisfies all the desired properties with $\theta_0 = \alpha$ (cf. (2.11) and (2.12)). Assume otherwise there exists $j_0 \in \{1, \dots, M\}$ such that $|\{x \in \Omega : a_{j_0}^3 c_{j_0}(x) < \gamma\}| > 0$ for all $\gamma > 0$. This means by (2.11) that $|\{x \in \Omega : a_{j_0}^3 \bar{c}_{j_0}(x) < \gamma\}| > 0$ for all $\gamma > 0$.

Define

$$
\begin{aligned}
&\sigma_j(\gamma) = \{x \in \Omega : a_j^3 \bar{c}_j(x) < \gamma\} \qquad \forall \gamma > 0, \quad j = 1, \dots, M, \\
&J_0 = \{j \in \{1, \dots, M\} : |\sigma_j(\gamma)| > 0 \ \forall \gamma > 0\}, \\
&J_1 = \{1, \dots, M\} \setminus J_0.
\end{aligned}
$$

We have $J_0 \ne \emptyset$ since $j_0 \in J_0$. If $J_1 \ne \emptyset$, then there exists $\gamma_1 > 0$ such that

$$
a_j^3 \bar{c}_j(x) \ge \gamma_1 \qquad \text{a.e. } x \in \Omega, \quad \forall j \in J_1. \tag{2.14}
$$

Define for $0 < \gamma < \min(\gamma_1, \tau_1/M)$ (cf. (2.10) for the definition of τ_1) and $1 \le i \le M$

$$\hat{c}_i(x) = \begin{cases} \bar{c}_i(x) + \gamma a_i^{-3} \chi_{\sigma_i(\gamma)}(x) & \text{if } i \in J_0 \\ \bar{c}_i(x) & \text{if } i \in J_1 \end{cases} \qquad \forall x \in \Omega. \tag{2.15}$$

$$\hat{c}_0(x) = a_0^{-3} \left[1 - \sum_{i=1}^{M} a_i^3 \hat{c}_i(x) \right] \qquad \forall x \in \Omega.$$

Notice by (2.10) that

$$a_0^3 \hat{c}_0(x) = a_0^3 \bar{c}_0(x) - \gamma \sum_{i \in J_0} \chi_{\sigma_i(\gamma)}(x) \ge \tau_1 - \gamma M > 0 \qquad \text{a.e. } x \in \Omega. \tag{2.16}$$

Thus, $\hat{c} = (\hat{c}_1, \dots, \hat{c}_M) \in K$. Moreover, (2.14)–(2.16) imply (2.13) with $\theta_0 = \min(\gamma_1, \gamma, \tau_1 - \gamma M)$. Applying the same argument used above, we obtain that $\|\hat{c} - \bar{c}\|_X < \delta/2$ for $\gamma > 0$ small enough.

We have now by the Mean-Value Theorem and the definition of $\sigma_j(\gamma)$ for $j \in J_0$ that

$$\begin{aligned} \sum_{i=1}^{M} \int_\Omega [S_{-1}(\hat{c}_i) - S_{-1}(\bar{c}_i)] \, dx &= \sum_{i \in J_0} \int_{\sigma_i(\gamma)} [S_{-1}(\hat{c}_i) - S_{-1}(\bar{c}_i)] \, dx \\ &\le \sum_{i \in J_0} \gamma a_i^{-3} \log \left(2\gamma a_i^{-3} \right) |\sigma_j(\gamma)|. \end{aligned}$$

Similarly, we obtain by (2.10) and (2.16) that

$$\int_\Omega [S_{-1}(\hat{c}_0) - S_{-1}(\bar{c}_0)] \, dx \le -a_0^{-3} \gamma \log \left(a_0^{-3} (\tau_1 - \gamma M) \right) \sum_{i \in J_0} |\sigma_i(\gamma)|.$$

Consequently, we have for $\gamma > 0$ small enough that

$$\begin{aligned} F[\hat{c}] - F[\bar{c}] = &\frac{1}{2} \int_\Omega \left(\sum_{i=1}^{M} q_i \bar{c}_i + \gamma \sum_{i \in J_0} a_i^{-3} q_i \chi_{\sigma_i(\gamma)} \right) L \left(\sum_{i=1}^{M} q_i \bar{c}_i + \gamma \sum_{i \in J_0} a_i^{-3} q_i \chi_{\sigma_i(\gamma)} \right) dx \\ &- \frac{1}{2} \int_\Omega \left(\sum_{i=1}^{M} q_i \bar{c}_i \right) L \left(\sum_{i=1}^{M} q_i \bar{c}_i \right) dx + \gamma \sum_{i \in J_0} a_i^{-3} \int_{\sigma_i(\gamma)} g_i dx \\ &+ \beta^{-1} \sum_{i \in J_0} \int_{\sigma_i(\gamma)} [S_{-1}(\hat{c}_i) - S_{-1}(\bar{c}_i)] \, dx + \beta^{-1} \int_\Omega [S_{-1}(\hat{c}_0) - S_{-1}(\bar{c}_0)] \, dx \\ \le C\gamma^2 &\left\| \sum_{i \in J_0} q_i a_i^{-3} \chi_{\sigma_i(\gamma)} \right\|_{L^2(\Omega)}^2 + \gamma \left\| L \left(\sum_{i=1}^{M} q_i \bar{c}_i \right) \right\|_{L^\infty(\Omega)} \sum_{i \in J_0} |q_i| a_i^{-3} |\sigma_j(\gamma)| \\ &+ \gamma \sum_{i \in J_0} a_i^{-3} \|g_i\|_{L^\infty(\Omega)} + \gamma \beta^{-1} \sum_{i \in J_0} a_i^{-3} \log \left(2\gamma a_i^{-3} \right) |\sigma_i(\gamma)| \end{aligned}$$

$$
\begin{aligned}
&\quad - \gamma\beta^{-1} a_0^{-3} \log\left(a_0^{-3}(\tau_1 - \gamma M)\right) \sum_{i\in J_0} |\sigma_i(\gamma)| \\
&\le C\gamma(1+\log\gamma) \sum_{i\in J_0} |\sigma_i(\gamma)|,
\end{aligned}
$$

where $C > 0$ is a generic constant independent of γ. Since $J_0 \neq \emptyset$, this is strictly negative if $\gamma > 0$ is sufficiently small. The case that $J_1 = \emptyset$ can be treated similarly. **Q.E.D.**

3 Free-energy minimization

We recall for a given $c = (c_1, \dots, c_M) \in K$ with K defined in (2.2) the functions c_0, $\hat{\psi}_0$, and g_i ($i = 1, \dots, M$) are defined by (1.5), (2.3), and (2.9), respectively, and that the functional $F : K \to \mathbb{R}$ is given in (2.8).

Theorem 3.1. *There exists a unique $c = (c_1, \dots, c_M) \in K$ such that*

$$F[c] = \min_{d\in K} F[d]. \tag{3.1}$$

This minimizer is also the unique local minimizer of $F : K \to \mathbb{R}$, defined by $c \in K$ and

$$F[c] = \min_{d\in K, \|d-c\|_X < \delta} F[d] \tag{3.2}$$

for some $\delta > 0$. Moreover, it is characterized by the following two conditions:

(1) *Bounds. There exist constants $\theta_1, \theta_2 \in (0,1)$ such that*

$$\theta_1 \le a_i^3 c_i(x) \le \theta_2 \qquad a.e.\ x \in \Omega, \quad i = 0, 1, \dots, M; \tag{3.3}$$

(2) *Equilibrium conditions.*

$$\left(\frac{a_i}{a_0}\right)^3 \log\left(a_0^3 c_0\right) - \log\left(a_i^3 c_i\right) = \beta\left[q_i\left(\psi - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2}\right) - \mu_i\right] \qquad a.e.\ \Omega,\ i = 1, \dots, M, \tag{3.4}$$

where ψ is the corresponding equilibrium electrostatic potential given by (2.7).

The existence and uniqueness of a global minimizer, which is also the unique equilibrium defined by conditions (1) and (2) in the theorem, can be proved by the direct method in the calculus of variations, using the fact that the functional $F : K \to \mathbb{R}$ is a convex functional defined on the convex set K. This proof is similar to that in [12]. For completeness we shall give a brief proof. But, first, to see the convexity of $F : K \to \mathbb{R}$, we notice that $S_{-1}(c_i)$ is a strict convex function of c_i for each $i \in \{1, \dots, M\}$. Therefore, we need only to check the convexity of $S_{-1}(c_0)$ as a function of $c_1, \ldots, c_M$. By the definition of c_0 (cf. (1.5)), it suffices to show the convexity of the function

$$h(u_1, \ldots, u_M) := \left(1 - \sum_{k=1}^{M} a_k^3 u_k\right) \left[\log\left(1 - \sum_{k=1}^{M} a_k^3 u_k\right) - 1\right] \tag{3.5}$$

in the domain of $(u_1, \ldots, u_M)$ defined by $u_1 > 0, \ldots, u_M > 0$, and $\sum_{k=1}^{M} a_k^3 u_k < 1$. (Here and below, $A := B$ means that A is defined by B.) In fact, simple calculations lead to

$$\partial_{u_i}\partial_{u_j} h(u) = \frac{a_i^3 a_j^3}{1 - \sum_{k=1}^{M} a_k^3 u_k}, \qquad i, j = 1, \ldots, M.$$

Therefore, for any $v_1, \ldots, v_M \in \mathbb{R}$,

$$\sum_{i,j=1}^{M} \partial_{u_i}\partial_{u_j} h(u) v_i v_j = \frac{\left(\sum_{i=1}^{M} a_i^3 v_i\right)^2}{1 - \sum_{k=1}^{M} a_k^3 u_k} \geq 0. \tag{3.6}$$

Hence the function $h = h(u_1, \ldots, u_M)$ is convex.

Proof of Theorem 3.1. It follows from the definition (2.8) that there exist positive numbers C_1 and t as well as a real number C_2 such that

$$F[c] \geq C_1 \left\| \sum_{i=1}^{M} q_i c_i \right\|_{H^{-1}(\Omega)}^2 + \beta^{-1} \sum_{i=1}^{M} \int_\Omega S_{-t}(c_i) dx + C_2 \qquad \forall c = (c_1, \ldots, c_M) \in K. \tag{3.7}$$

Let $z = \inf_{c \in K} F[c]$. Since $S_{-t} : [0, \infty) \to \mathbb{R}$ is bounded below, z is finite.

Let $c^{(k)} = \left(c_1^{(k)}, \ldots, c_M^{(k)}\right) \in K$ $(k = 1, 2, \ldots)$ be such that $\lim_{k\to\infty} F\left[c^{(k)}\right] = z$. It follows from (3.7) that $\left\{\int_\Omega S_{-t}\left(c_i^{(k)}\right) dx\right\}$ is bounded for each $i \in \{1, \ldots, M\}$. Since S_{-t} is convex, and super-linear, i.e., $S_{-t}(u)/u \to \infty$ as $u \to \infty$, there is a subsequence of $\left\{c_i^{(k)}\right\}$, not relabeled, that converges weakly in $L^1(\Omega)$ to some $c_i \in L^1(\Omega)$ for $i = 1, \ldots, M$ (cf. e.g., Lemma 3.3 in [12]). It is clear that all $c_i \geq 0$ a.e. in Ω for $i = 0, 1, \ldots, M$ with c_0 defined by (1.5). Moreover, the convexity of $S_{-t}(c_i)$ $(i = 1, \ldots, M)$ and that of $S_{-t}(c_0)$ with respect to $(c_1, \ldots, c_M)$ lead to

$$\int_\Omega S_{-t}(c_i)\, dx \leq \liminf_{k\to\infty} \int_\Omega S_{-t}\left(c_i^{(k)}\right) dx < \infty, \qquad i = 0, 1, \ldots, M. \tag{3.8}$$

By (3.7), $\left\{\sum_{i=1}^{M} q_i c_i^{(k)}\right\}$ is bounded in the Hilbert space $H^{-1}(\Omega)$. It thus has a subsequence, again not relabeled, converging weakly to some $G \in H^{-1}(\Omega)$. One easily verifies that $G = \sum_{i=1}^{M} q_i c_i \in H^{-1}(\Omega)$. Hence $c = (c_1, \dots, c_M) \in K$. By (3.8) and the fact that the norm of a Banach space is sequentially weakly lower semi-continuous, we have $z = \liminf_{k\to\infty} F\left[c^{(k)}\right] \ge F[c] \ge z$, leading to (3.1).

The uniqueness of a minimizer follows from the strict convexity of $F : K \to \mathbb{R}$.

Let $\hat{c} = (\hat{c}_1, \dots, \hat{c}_M) \in K$ be a local minimizer of $F : K \to \mathbb{R}$. Then $d_\lambda := \lambda c + (1 - \lambda)\hat{c} \in K$ for any $\lambda \in (0, 1)$ and $\|d_\lambda - \hat{c}\|_X \to 0$ as $\lambda \to 0$, where $c \in K$ is the (global) minimizer of $F : K \to \mathbb{R}$. Since $\hat{c}$ is a local minimizer and $F : K \to \mathbb{R}$ is convex, we have

$$F[\hat{c}] \le F[d_\lambda] = F[\lambda c + (1-\lambda)\hat{c}] \le \lambda F[c] + (1-\lambda)F[\hat{c}],$$

leading to $F[\hat{c}] \le F_0[c]$. Thus $\hat{c} \in K$ is also a global minimizer of $F : K \to \mathbb{R}$. The uniqueness now implies that $\hat{c} = c$.

By Theorem 2.1, the minimizer $c \in K$ satisfies (3.3). Fix i with $1 \le i \le M$. Let $d_i \in L^\infty(\Omega)$. Then it follows from (3.3) that $(c_1, \dots, c_{i-1}, c_i + td_i, c_{i+1}, \dots, c_M) \in K$ for $t \in \mathbb{R}$ with $|t|$ sufficiently small. Hence

$$F[c_1, \dots, c_{i-1}, c_i + td_i, c_{i+1}, \dots, c_M] \le F[c],$$

if $|t|$ is small enough. Consequently,

$$\left.\frac{d}{dt}\right|_{t=0} F[c_1, \dots, c_{i-1}, c_i + td_i, c_{i+1}, \dots, c_M] = 0 \qquad \forall d_i \in L^\infty(\Omega).$$

This, together with a series of calculations, leads to (3.4).

Assume now $c = (c_1, \dots, c_M) \in K$ satisfies both (3.3) and (3.4). We show that c is a minimizer of $F : K \to \mathbb{R}$. By Theorem 2.1, we need only to show that $F[c] \le F[d]$ for any $d = (d_1, \dots, d_M) \in K$ such that $\gamma_1 \le a_i^3 d_i(x) \le \gamma_2$ for a.e. $x \in \Omega$, $i = 0, 1, \dots, M$, and some constants $\gamma_1, \gamma_2 \in (0, 1)$. In fact, setting $e = (e_1, \dots, e_M) = d - c \in X \cap L^\infty(\Omega, \mathbb{R}^M)$, we have by the convexity of $S_{-1} : [0, \infty) \to \mathbb{R}$ that

$$S_{-1}(d_i) - S_{-1}(c_i) \ge (d_i - c_i) S'_{-1}(c_i) = e_i \log c_i \qquad \text{a.e. } \Omega,\ i = 1, \dots, M.$$

Notice that $S_{-1}(c_0) = S_{-1}\left(a_0^{-3}\left(1 - \sum_{k=1}^{M} a_k^3 c_k\right)\right)$ is a convex function of $(c_1, \dots, c_M)$, cf. (3.5) and (3.6). Hence, with $d_0 = a_0^{-3}(1 - \sum_{k=1}^{M} a_k^3 d_k)$, we have

$$S_{-1}(d_0) - S_{-1}(c_0) \ge \sum_{i=1}^{M} (d_i - c_i) \frac{\partial S_{-1}(c_0)}{\partial c_i} = -\sum_{i=1}^{M} \left(\frac{a_i}{a_0}\right)^3 e_i \log c_0.$$

Consequently, it follows from (2.8), (2.7), (2.9), and (3.4) that

$$F[d] - F[c] = \int_\Omega \left\{ \frac{1}{2} \left(\sum_{i=1}^{M} q_i e_i\right) L \left(\sum_{i=1}^{M} q_i e_i\right) + \left(\sum_{i=1}^{M} q_i e_i\right) L \left(\sum_{i=1}^{M} q_i c_i\right)\right.$$

$$
\begin{aligned}
&+\beta^{-1}\sum_{i=0}^{M}\left[S_{-1}(d_i)-S_{-1}(c_i)\right]+\sum_{i=1}^{M}g_ie_i\Bigg\}\,dx\\
\geq{}&\sum_{i=1}^{M}\int_\Omega\left[q_iL\left(\sum_{j=1}^{M}q_jc_j\right)+\beta^{-1}\log c_i-\beta^{-1}\left(\frac{a_i}{a_0}\right)^3\log c_0+g_i\right]e_i dx\\
={}&\sum_{i=1}^{M}\int_\Omega\Bigg[q_i\left(\psi-\frac{\hat{\psi}_0}{2}+\frac{L\rho_f}{2}\right)\\
&+\beta^{-1}\log\left(a_i^3c_i\right)-\beta^{-1}\left(\frac{a_i}{a_0}\right)^3\log\left(a_0^3c_0\right)-\mu_i\Bigg]e_i dx\\
={}&0.
\end{aligned}
$$

Hence $F[c]\leq F[d]$. **Q.E.D.**

4 Generalized Boltzmann distributions for the case of a uniform ionic size

Let $c=(c_1,\ldots,c_M)\in K$ be the unique minimizer of the free-energy functional $F:K\to\mathbb{R}$, cf. (2.2) for the definition of K and (1.4) and (2.8) for that of F. Let ψ be the corresponding, equilibrium electrostatic potential, which is the weak solution to the Poisson equation (1.1) and the boundary condition (1.6). By Theorem 3.1, $c_1,\ldots,c_M$ satisfy the Euler-Lagrange equations (3.4). We seek the dependence of each of the concentration components c_i on the potential ψ, i.e., the possible generalized Boltzmann distribution $c_i=c_i(\psi)$.

Consider first the case that all the linear sizes of the ions and solvent molecules are the same, say, they are equal to $a>0$: $a_0=a_1=\cdots=a_M=a$. In this case, we have from (2.9) that

$$g_i=\frac{1}{2}q_i\left(L\rho_f+\hat{\psi}_0\right)-\mu_i,\qquad i=1,\ldots,M.$$

The Euler-Lagrange equation (3.4) then leads to

$$c_i=c_0a^3c_i^\infty e^{-\beta q_i\left(\psi-\hat{\psi}_0/2+L\rho_f/2\right)}\qquad\text{a.e. }\Omega,\ i=1,\ldots,M,\tag{4.1}$$

where

$$c_i^\infty=a^{-3}e^{\beta\mu_i}\tag{4.2}$$

is the chemical potential of the ith ionic species ($i=1,\ldots,M$). Multiplying both sides of the equation in (4.1) by a^3 and then summing the resulting equation over all $i=1,\ldots,M$, we obtain

$$1 - a^3 c_0 = a^3 c_0 \sum_{i=1}^{M} a^3 c_i^\infty e^{-\beta q_i \left(\psi - \hat{\psi}_0/2 + L\rho_f/2\right)} \qquad \text{a.e. } \Omega,$$

where we used the definition of c_0 (cf. (1.5)). Hence,

$$c_0 = \frac{a^{-3}}{1 + \sum_{i=1}^{M} a^3 c_i^\infty e^{-\beta q_i \left(\psi - \hat{\psi}_0/2 + L\rho_f/2\right)}} \qquad \text{a.e. } \Omega. \tag{4.3}$$

This and (4.1) imply the following generalized Boltzmann distributions:

$$c_i(x) = \frac{c_i^\infty e^{-\beta q_i \left[\psi(x) - \hat{\psi}_0(x)/2 + L\rho_f(x)/2\right]}}{1 + \sum_{j=1}^{M} a^3 c_j^\infty e^{-\beta q_j \left[\psi(x) - \hat{\psi}_0(x)/2 + L\rho_f(x)/2\right]}} \qquad \text{a.e. } x \in \Omega, \ i = 1, \dots, M. \tag{4.4}$$

Notice that the electrostatic potential in the generalized Boltzmann distributions is modified via the "potentials" $\hat{\psi}_0$ (cf. (2.3)) and $L\rho_f$ (cf. (2.5)) through the boundary condition (1.6) and the fixed charge density ρ_f, respectively. This modification is essentially due to the inhomogeneous Dirichlet boundary data ψ_0 (cf. (1.6)): if $\psi_0 = 0$ on $\partial\Omega$, then $\hat{\psi}_0 = L\rho_f$.

By the generalized Boltzmann distributions (4.4), we can derive an expression of the minimum electrostatic free energy using only the equilibrium electrostatic potential ψ. By (4.3), (4.2), and the fact that $a^3 \sum_{i=0}^{M} c_i = 1$ (cf. (1.5)), we have for a.e. $x \in \Omega$ that

$$\begin{aligned}
&\beta^{-1} \sum_{i=0}^{M} c_i \left[\log\left(a^3 c_i\right) - 1\right] - \sum_{i=1}^{M} \mu_i c_i \\
&\quad = \beta^{-1} \left(\sum_{i=0}^{M} c_i \right) \left(\log a^3 - 1\right) + \beta^{-1} c_0 \log c_0 + \beta^{-1} \sum_{i=1}^{M} c_i \log c_i - \sum_{i=1}^{M} \mu_i c_i \\
&\quad = \beta^{-1} a^{-3} \left(\log a^3 - 1\right) + \beta^{-1} c_0 \left[\log a^{-3} - \log \left(1 + \sum_{i=1}^{M} a^3 c_i^\infty e^{-\beta q_i (\psi - \hat{\psi}_0/2 + L\rho_f/2)} \right) \right] \\
&\qquad + \beta^{-1} \sum_{i=1}^{M} c_i \left[\log c_i^\infty - \beta q_i \left(\psi - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2} \right) \right. \\
&\qquad \left. - \log \left(1 + \sum_{j=1}^{M} a^3 c_j^\infty e^{-\beta q_j (\psi - \hat{\psi}_0/2 + L\rho_f/2)} \right) \right] - \sum_{i=1}^{M} \mu_i c_i \\
&\quad = \beta^{-1} a^{-3} \left(\log a^3 - 1\right) + \beta^{-1} c_0 \log a^{-3} \\
&\qquad - \beta^{-1} c_0 \log \left(1 + \sum_{i=1}^{M} a^3 c_i^\infty e^{-\beta q_i (\psi - \hat{\psi}_0/2 + L\rho_f/2)} \right)
\end{aligned}$$

$$
\begin{aligned}
&+ \beta^{-1} \sum_{i=1}^{M} c_i \left[\log a^{-3} + \beta \mu_i - \beta q_i \left(\psi - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2} \right) \right] \\
&- \beta^{-1} \left(\sum_{i=1}^{M} c_i \right) \log \left(1 + \sum_{j=1}^{M} a^3 c_j^\infty e^{-\beta q_j (\psi - \hat{\psi}_0/2 + L\rho_f/2)} \right) - \sum_{i=1}^{M} \mu_i c_i \\
= &-\beta^{-1} a^{-3} - \beta^{-1} a^{-3} \log \left(1 + \sum_{i=1}^{M} a^3 c_i^\infty e^{-\beta q_i (\psi - \hat{\psi}_0/2 + L\rho_f/2)} \right) \\
&- \left(\sum_{i=1}^{M} q_i c_i \right) \left(\psi - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2} \right).
\end{aligned}
$$

The minimum free energy is therefore

$$
\begin{aligned}
F[c] = \int_\Omega \Bigg[&\frac{1}{2} \rho \psi - \left(\sum_{i=1}^{M} q_i c_i \right) \left(\psi - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2} \right) \\
&-\beta^{-1} a^{-3} - \beta^{-1} a^{-3} \log \left(1 + \sum_{i=1}^{M} a^3 c_i^\infty e^{-\beta q_i (\psi - \hat{\psi}_0/2 + L\rho_f/2)} \right) \Bigg] dx.
\end{aligned}
$$

By (1.3), (2.3), (2.4), (2.5), and the fact that both $\psi - \hat{\psi}_0$ and $L\rho_f$ vanish on the boundary $\partial\Omega$, we have

$$
\begin{aligned}
&\int_\Omega \left[\frac{1}{2} \rho \psi - \left(\sum_{i=1}^{M} q_i c_i \right) \left(\psi - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2} \right) \right] dx \\
&= \int_\Omega \left[\frac{1}{2} \rho \psi - (\rho - \rho_f) \left(\psi - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2} \right) \right] dx \\
&= \frac{1}{2} \int_\Omega \rho \left(\hat{\psi}_0 - \psi \right) dx - \frac{1}{2} \int_\Omega \rho L\rho_f \, dx + \int_\Omega \rho_f \left(\psi - \hat{\psi}_0 \right) dx \\
&\quad + \frac{1}{2} \int_\Omega \rho_f L\rho_f \, dx + \frac{1}{2} \int_\Omega \rho_f \hat{\psi}_0 \, dx \\
&= \frac{1}{2} \int_\Omega \varepsilon \nabla \psi \cdot \nabla \left(\hat{\psi}_0 - \psi \right) dx - \frac{1}{2} \int_\Omega \varepsilon \nabla \psi \cdot \nabla L\rho_f \, dx + \int_\Omega \varepsilon \nabla L\rho_f \cdot \nabla \left(\psi - \hat{\psi}_0 \right) dx \\
&\quad + \frac{1}{2} \int_\Omega \varepsilon \nabla \hat{\psi}_0 \cdot \nabla L\rho_f \, dx + \frac{1}{2} \int_\Omega \rho_f \hat{\psi}_0 \, dx \\
&= \frac{1}{2} \int_\Omega \varepsilon \nabla \psi \cdot \nabla \left(\hat{\psi}_0 - \psi \right) dx + \frac{1}{2} \int_\Omega \varepsilon \nabla L\rho_f \cdot \nabla \left(\psi - \hat{\psi}_0 \right) dx + \frac{1}{2} \int_\Omega \rho_f \hat{\psi}_0 \, dx \\
&= \frac{1}{2} \int_\Omega \varepsilon \nabla \psi \cdot \nabla \left(\hat{\psi}_0 - \psi \right) dx + \frac{1}{2} \int_\Omega L\rho_f \left(\psi - \hat{\psi}_0 \right) dx + \frac{1}{2} \int_\Omega \rho_f \hat{\psi}_0 \, dx \\
&= \frac{1}{2} \int_\Omega \varepsilon \nabla \psi \cdot \nabla \left(\hat{\psi}_0 - \psi \right) dx + \frac{1}{2} \int_\Omega \varepsilon \nabla \hat{\psi}_0 \cdot \nabla \left(\psi - \hat{\psi}_0 \right) dx + \frac{1}{2} \int_\Omega \rho_f \hat{\psi}_0 \, dx
\end{aligned}
$$

$$= \frac{1}{2}\int_\Omega \rho_f \hat{\psi}_0 \, dx - \frac{1}{2}\int_\Omega \left|\nabla\left(\psi - \hat{\psi}_0\right)\right|^2 dx. \tag{4.5}$$

Inserting this into the previous expression of $F[c]$, we obtain the minimum free energy

$$\min_{d\in K} F[d] = F[c] = \int_\Omega \left\{ \frac{1}{2}\rho_f \hat{\psi}_0 - \frac{\varepsilon}{2}\left|\nabla\left(\psi - \hat{\psi}_0\right)\right|^2 \right.$$
$$\left. -\beta^{-1}a^{-3}\left[1 + \log\left(1 + \sum_{i=1}^{M} a^3 c_i^\infty e^{-\beta q_i(\psi - \hat{\psi}_0/2 + L\rho_f/2)}\right)\right]\right\} dx. \tag{4.6}$$

The generalized Boltzmann distributions (4.4) and the Poisson equation (1.1) yield the generalized Poisson-Boltzmann equation

$$\nabla\cdot\varepsilon\nabla\psi + \frac{\sum_{i=1}^M q_i c_i^\infty e^{-\beta q_i\left(\psi - \hat{\psi}_0/2 + L\rho_f/2\right)}}{1 + \sum_{i=1}^M a^3 e^{-\beta q_i\left(\psi - \hat{\psi}_0/2 + L\rho_f/2\right)}} = -\rho_f \qquad \text{in } \Omega. \tag{4.7}$$

This equation can be viewed as the Euler-Lagrange equation of the functional $I : H^1_{\psi_0}(\Omega) \to \mathbb{R}\cup\{+\infty\}$ defined by

$$I[\phi] = \int_\Omega \left[\frac{1}{2}\varepsilon|\nabla\phi|^2 - \rho_f\phi + \beta^{-1}a^{-3}\log\left(1 + \sum_{i=1}^M a^3 c_i^\infty e^{-\beta q_i\left(\phi - \hat{\psi}_0/2 + L\rho_f/2\right)}\right)\right] dx, \tag{4.8}$$

where

$$H^1_{\psi_0}(\Omega) = \left\{\phi \in H^1(\Omega : \phi = \psi_0 \text{ on } \partial\Omega\right\}.$$

Setting $q_0 = 0$ and $c_0^\infty = a^{-3}$, we obtain by direct calculations and the Cauchy-Schwarz inequality that

$$\frac{d^2}{d\phi^2}\log\left(1 + \sum_{i=1}^M a^3 c_i^\infty e^{-\beta q_i\phi}\right)$$
$$= \frac{\left(\sum_{i=1}^M a^3\beta^2 q_i^2 c_i^\infty e^{-\beta q_i\phi}\right)\left(1 + \sum_{i=1}^M a^3 c_i^\infty e^{-\beta q_i\phi}\right) - \left(\sum_{i=1}^M a^3\beta q_i c_i^\infty e^{-\beta q_i\phi}\right)^2}{\left(1 + \sum_{i=1}^M a^3 c_i^\infty e^{-\beta q_i\phi}\right)^2}$$
$$= \frac{a^6\beta^2\left[\left(\sum_{i=0}^M q_i^2 c_i^\infty e^{-\beta q_i\phi}\right)\left(\sum_{i=0}^M c_i^\infty e^{-\beta q_i\phi}\right) - \left(\sum_{i=0}^M q_i\sqrt{c_i^\infty e^{-\beta q_i\phi}}\sqrt{c_i^\infty e^{-\beta q_i\phi}}\right)^2\right]}{\left(1 + \sum_{i=1}^M a^3 c_i^\infty e^{-\beta q_i\phi}\right)^2}$$
$$\geq 0 \qquad \forall\phi\in\mathbb{R}.$$

The inequality is in fact strict, since $q_1, \ldots, q_M$ do not have the same sign. Therefore, the log term in (4.8) is strictly convex. Hence, the functional $I : H^1_{\psi_0}(\Omega) \to \mathbb{R}\cup\{+\infty\}$ is strictly convex.

We summarize our discussions in the following theorem which can be proved by the same argument used in [12]. (Notice that it is unnecessary to assume that $\chi_{\Omega_s} B(u) \in L^2(\Omega)$ in the definition of the set $\mathcal{K}$ in the proof of Theorem 2.1 and Theorem 2.2 in [12].) See also the proof of Theorem 5.1 which treats the general case:

Theorem 4.1. *Assume $a_0 = a_1 = \cdots = a_M = a > 0$. Then the following hold true:*

(1) *The functional $I : H^1_{\psi_0}(\Omega) \to \mathbb{R} \cup \{+\infty\}$ is convex and admits a unique minimizer $\psi \in H^1_{\psi_0}(\Omega)$ which is also the unique weak solution of* (4.7)*;*

(2) *If we define $c_i(x)$ by* (4.4) *for all $i = 1, \ldots, M$, then $(c_1, \ldots, c_M) \in K$ is the unique set of equilibrium ionic concentrations and ψ is the unique equilibrium electrostatic potential, as described in Theorem 3.1;*

(3) *The minimum electrostatic free energy is given by* (4.6).

5 Implicit Boltzmann distributions for the case of a nonuniform ionic size

We now consider a general ionic system with possibly nonuniform sizes of ions and solvent molecules. We shall show that the Euler-Lagrange equations (3.4) determine the relations $c_i = c_i(\psi)$ $(i = 1, \ldots, M)$ for the equilibrium ionic concentrations $c_1, \ldots, c_M$ as functions of the equilibrium electrostatic potential ψ. These relations can be viewed as implicit Boltzmann distributions.

Let

$$D_M = \left\{ (u_1, \ldots, u_M) \in \mathbb{R}^M : u_1 > 0, \ldots, u_M > 0, \text{ and } \sum_{i=1}^M a_i^3 u_i < 1 \right\}.$$

Clearly, $D_M \subset \prod_{i=1}^M (0, a_i^{-3})$. Denote for any $u = (u_1, \ldots, u_M) \in D_M$

$$u_0 = a_0^{-3} \left(1 - \sum_{j=1}^M a_j^3 u_j \right). \tag{5.1}$$

Define $\hat{f} = (\hat{f}_1, \ldots, \hat{f}_M) : D_M \to \mathbb{R}^M$ by

$$\hat{f}_i(u) = \left(\frac{a_i}{a_0} \right)^3 \log \left(a_0^3 u_0 \right) - \log \left(a_i^3 u_i \right) \qquad \forall u = (u_1, \ldots, u_M) \in D_M, \ i = 1, \ldots, M. \tag{5.2}$$

Lemma 5.1. *The mapping $\hat{f} : D_M \to \mathbb{R}^M$ is a C^∞, bijective mapping.*

Proof. Clearly, $\hat{f} : D_M \to \mathbb{R}^M$ is a C^∞ mapping. By simple calculations, we have

$$\frac{\partial \hat{f}_i}{\partial u_j} = -\frac{a_i^3 a_j^3}{a_0^3 u_0} - \frac{\delta_{ij}}{u_i}, \qquad i, j = 1, \ldots, M,$$

where $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ if $i \neq j$. Denote $p = (a_1^3, \ldots, a_M^3)^T \in \mathbb{R}^M$. Denote also by W the diagonal $M \times M$ matrix with the diagonal entries $1/u_1, \ldots, 1/u_M$. The inverse W^{-1} of W is the diagonal matrix with the diagonal entries $u_1, \ldots, u_M$. The gradient matrix $\nabla \hat{f}(u)$ for any $u = (u_1, \ldots, u_M) \in D_M$ is then the $M \times M$ matrix

$$\nabla \hat{f}(u) = \left[\frac{\partial \hat{f}_i}{\partial u_j} \right]_{i,j=1}^{M} = -W - \frac{1}{a_0^3 u_0} p \otimes p = -W \left(I_M + \frac{1}{a_0^3 u_0} W^{-1} p \otimes p \right),$$

where I_M denotes the $M \times M$ identity matrix. Consequently, the Jacobian of the mapping $\hat{f}$ at u is

$$\det \nabla \hat{f}(u) = (-1)^M \det W \left(1 + \frac{1}{a_0^3 u_0} W^{-1} p \cdot p \right) = \frac{(-1)^M}{u_1 \cdots u_M} \left(1 + \frac{1}{a_0^3 u_0} \sum_{i=1}^{M} a_i^6 u_i \right) \neq 0.$$

Here we have used the fact that for any $v, w \in \mathbb{R}^M$,

$$\det(I_M + v \otimes w) = 1 + v \cdot w.$$

This can be directly verified. Since the Jacobian of $\hat{f}$ at any $u \in D_M$ is non-zero, the mapping $\hat{f} : D_M \to \mathbb{R}^M$ is injective.

Let $r_i \in \mathbb{R}$ $(i = 1, \ldots, M)$. We show that there exists $u = (u_1, \ldots, u_M) \in D_M$ such that $\hat{f}_i(u) = r_i$ $(i = 1, \ldots, M)$. To do so, let us denote $t_i = -1 + \log a_i^3$ for $i = 0, 1, \ldots, M$ and define $z : \overline{D_M} \to \mathbb{R}$ by

$$z(u) = \sum_{i=0}^{M} S_{t_i}(u_i) + \sum_{i=1}^{M} r_i u_i \qquad \forall u = (u_1, \ldots, u_M) \in \overline{D_M},$$

where $\overline{D_M}$ is the closure of D_M in $\mathbb{R}^M$ and u_0 is defined by (5.1). Notice for $u_i > 0$ $(0 \leq i \leq M)$ that $S_{t_i}(u_i) = u_i[\log(a_i^3 u_i) - 1]$, cf. (2.6). It is easy to see that z is continuous on the compact set $\overline{D_M}$, and hence it attains its minimum in $\overline{D_M}$. Moreover, z is clearly smooth on D_M, and by simple calculations

$$\frac{\partial z}{\partial u_i} = r_i - \hat{f}_i(u) \qquad \forall u = (u_1, \ldots, u_M) \in D_M, \ i = 1, \ldots, M.$$

Therefore, it suffices to show that the minimum of $z : \overline{D_M} \to \mathbb{R}$ is in fact attained at some $u \in D_M$ at which we have $\partial z / \partial u_i = 0$ for $i = 1, \ldots, M$.

In the rest of the proof, we use the idea similar to that used in the proof of Theorem 2.1. Fix $u = (u_1, \ldots, u_M) \in \overline{D_M}$. Assume that $u_0 = 0$, i.e., $\sum_{i=1}^{M} a_i^3 u_i = 1$. Let σ be the set of indices i with $1 \leq i \leq M$ such that $u_i > 0$. Clearly, σ is non-empty. Let $\alpha_0 = \min_{i \in \sigma} u_i$. Let $0 < \alpha < \alpha_0/2$ and define $\bar{u}_i = u_i - \alpha$ for each $i \in \sigma$ and $\bar{u}_i = u_i$

for each $i \notin \sigma$. Clearly, $\bar{u} = (\bar{u}_1, \ldots, \bar{u}_M) \in \overline{D_M}$ but $\sum_{i=1}^M a_i^3 \bar{u}_i < 1$. By the Mean-Value Theorem, there exists $\xi \in [u_i - \alpha, u_i]$ for each $i \in \sigma$ such that

$$\begin{aligned}
z(\bar{u}) - z(u) = &\sum_{i\in\sigma} \left\{(u_i - \alpha)\left[\log\left(a_i^3(u_i-\alpha)\right) - 1\right] - u_i\left[\log\left(a_i^3 u_i\right) - 1\right]\right\} \\
&\quad + \bar{u}_0\left[\log\left(a_0^3\bar{u}_0\right) - 1\right] \\
&= \sum_{i\in\sigma}(-\alpha)\log\left(a_i^3\xi_i\right) + \alpha a_0^{-3}\left(\sum_{i\in\sigma} a_i^3\right)\left[\log\left(\alpha\sum_{j\in\sigma} a_j^3\right) - 1\right] \\
&\le -\alpha\sum_{i\in\sigma}\log\left(\frac{a_i^3\alpha_0}{2}\right) + \alpha a_0^{-3}\left(\sum_{i\in\sigma} a_i^3\right)\left[\log\alpha + \log\left(\sum_{j\in\sigma} a_j^3\right) - 1\right] \\
&= \alpha\sum_{i\in\sigma}\left\{a_0^{-3}a_i^3\log\alpha + a_0^{-3}a_i^3\left[\log\left(\sum_{j\in\sigma} a_j^3\right) - 1\right] - \log\left(\frac{a_i^3\alpha_0}{2}\right)\right\} \\
&< 0,
\end{aligned}$$

if $\alpha \in (0, \alpha_0/2)$ is small enough. This means that the minimum of z is not attained at any point $u \in \overline{D_M}$ with $u_0 = 0$.

Now let us consider $u \in \overline{D_M}$ with $u_0 > 0$ but $u_i = 0$ for some i ($1 \le i \le M$). Denote by τ the non-empty set of indices i such that $1 \le i \le M$ and $u_i = 0$. Let $\gamma_0 = a_0^3\left(\sum_{i=1}^M a_i^3\right)^{-1} u_0$ and $0 < \gamma < \gamma_0/2$. Define $\hat{u}_i = \gamma$ for $i \in \tau$ and $\hat{u}_i = u_i$ for $i \notin \tau$. Clearly $\hat{u} = (\hat{u}_1, \ldots, \hat{u}_M) \in D_M$. Moreover, by the Mean-Value Theorem, there exists $\eta_0 \in [\hat{u}_0, u_0] = \left[u_0 - a_0^{-3}\left(\sum_{i\in\tau} a_i^3\right)\gamma, u_0\right] \subseteq [u_0/2, u_0]$, where $\hat{u}_0 = a_0^{-3}\left(1 - \sum_{i=1}^M a_i^3\hat{u}_i\right)$, such that

$$\begin{aligned}
\hat{u}_0\left[\log\left(a_0^3\hat{u}_0\right) - 1\right] - u_0\left[\log\left(a_0^3 u_0\right) - 1\right] &= \left(\hat{u}_0 - u_0\right)\log\left(a_0^3\eta_0\right) \\
&\le \gamma a_0^{-3}\left(\sum_{i\in\tau} a_i^3\right)\log\left(a_0^3 u_0\right).
\end{aligned}$$

Consequently,

$$\begin{aligned}
z(\hat{u}) - z(u) &= \sum_{i\in\tau}\gamma\left[\log\left(a_i^3\gamma\right) - 1\right] + \hat{u}_0\left[\log\left(a_0^3\hat{u}_0\right) - 1\right] - u_0\left[\log\left(a_0^3 u_0\right) - 1\right] \\
&\le \gamma\sum_{i\in\tau}\left(\log\gamma + \log a_i^3 - 1\right) + \gamma a_0^{-3}\left(\sum_{i\in\tau} a_i^3\right)\log\left(a_0^3 u_0\right) \\
&= \gamma\sum_{i\in\tau}\left[\log\gamma + \log a_i^3 - 1 + a_0^{-3}a_i^3\log\left(a_0^3 u_0\right)\right] \\
&< 0,
\end{aligned}$$

if $\gamma \in (0, \gamma_0/2)$ is small enough. This means that the minimum of z is not attained at any point $u \in \overline{D_M}$ with $u_i = 0$ for some i $(1 \le i \le M)$. Therefore, the minimum of z is attained at some $u = (u_1, \dots, u_M) \in D_M$. Consequently, $\partial z/\partial u_i = r_i - \hat{f}_i(u) = 0$ for all $i = 1, \dots, M$. This implies that $\hat{f} : D_M \to \mathbb{R}^M$ is surjective. Therefore, it is bijective. **Q.E.D.**

Let $\hat{g} = (\hat{g}_1, \dots, \hat{g}_M) : \mathbb{R}^M \to D_M$ be the inverse mapping of $\hat{f} : D_M \to \mathbb{R}^M$. This means that $\hat{f}_i(u_1, \dots, u_M) = r_i$ $(i = 1, \dots, M)$ if and only if $\hat{g}_i(r_1, \dots, r_M) = u_i$ $(i = 1, \dots, M)$. Define for each $i \in \{1, \dots, M\}$

$$B_i(\phi) = \hat{g}_i \left(\beta(q_1\phi - \mu_1), \dots, \beta(q_M\phi - \mu_M)\right) \qquad \forall \phi \in \mathbb{R}. \tag{5.3}$$

This means that

$$\left(\frac{a_i}{a_0}\right)^3 \log\left(a_0^3 B_0(\phi)\right) - \log\left(a_i^3 B_i(\phi)\right) = \beta\left(q_i\phi - \mu_i\right), \qquad i = 1, \dots, M, \tag{5.4}$$

where

$$B_0(\phi) := a_0^{-3}\left[1 - \sum_{j=1}^M a_j^3 B_j(\phi)\right] > 0 \qquad \forall \phi \in \mathbb{R}.$$

Clearly, each $B_i : \mathbb{R} \to (0, a_i^{-3})$ is a C^∞ function. It follows from (3.4) and Lemma 5.1 that, if ϕ is the "modified" equilibrium potential, i.e., $\phi = \psi - \hat{\psi}_0/2 + L\rho_f/2$ at some point $x \in \Omega$, then $B_i(\phi)$ is the corresponding equilibrium concentration of the ith ionic species. If the potential ϕ vanishes at some spatial point, then the corresponding induced charge density should also vanish at such a point. Therefore, we shall assume that the following neutrality condition holds true:

$$\text{The neutrality condition:} \qquad \sum_{i=1}^M q_i B_i(0) = 0. \tag{5.5}$$

Define

$$V(\phi) = -\sum_{i=1}^M q_i \int_0^\phi B_i(\xi)\, d\xi \qquad \forall \phi \in \mathbb{R}. \tag{5.6}$$

Clearly, $V : \mathbb{R} \to \mathbb{R}$ is a C^∞ function. Moreover, $V' : \mathbb{R} \to \mathbb{R}$, given by $V'(\phi) = -\sum_{i=1}^M q_i B_i(\phi)$ $(\phi \in \mathbb{R})$ is a bounded function, since each $B_i : \mathbb{R} \to (0, a_i^{-3})$ is bounded $(1 \le i \le M)$.

Lemma 5.2. *The function $V : \mathbb{R} \to \mathbb{R}$ is strictly convex. Moreover,*

$$V'(\phi) \begin{cases} > 0 & \text{if } \phi > 0, \\ = 0 & \text{if } \phi = 0, \\ < 0 & \text{if } \phi < 0, \end{cases}$$

$V(\phi) > V(0) = 0$ for all $\phi \in \mathbb{R}$ with $\phi \ne 0$, and $V(\pm\infty) = \infty$.

Proof. We show that $V''(\phi) > 0$ for all $\phi \in \mathbb{R}$. Taking the derivative with respect to ϕ on both sides of the equation (5.4), we get

$$-\left(\frac{a_i}{a_0}\right)^3 \sum_{j=1}^{M} \left(\frac{a_j}{a_0}\right)^3 \frac{B_j'(\phi)}{B_0(\phi)} - \frac{B_i'(\phi)}{B_i(\phi)} = \beta q_i,$$

leading to

$$B_i'(\phi) = -\beta q_i B_i(\phi) - \left(\frac{a_i}{a_0}\right)^3 \frac{B_i(\phi)}{B_0(\phi)} \left[\sum_{j=1}^{M} \left(\frac{a_j}{a_0}\right)^3 B_j'(\phi)\right]. \tag{5.7}$$

Multiplying both sides of this equation by $(a_i/a_0)^3$ and summing the result over all $i = 1, \ldots, M$, we get

$$\sum_{i=1}^{M} \left(\frac{a_i}{a_0}\right)^3 B_i'(\phi) = -\sum_{i=1}^{M} \left(\frac{a_i}{a_0}\right)^3 \beta q_i B_i(\phi) - \left[\sum_{i=1}^{M} \left(\frac{a_i}{a_0}\right)^6 \frac{B_i(\phi)}{B_0(\phi)}\right] \left[\sum_{j=1}^{M} \left(\frac{a_j}{a_0}\right)^3 B_j'(\phi)\right].$$

Consequently,

$$\sum_{j=1}^{M} \left(\frac{a_j}{a_0}\right)^3 B_j'(\phi) = \frac{-\beta B_0(\phi) \sum_{i=1}^{M} \left(\frac{a_i}{a_0}\right)^3 q_i B_i(\phi)}{B_0(\phi) + \sum_{i=1}^{M} \left(\frac{a_i}{a_0}\right)^6 B_i(\phi)}.$$

This and (5.7) lead to

$$\begin{aligned} V''(\phi) &= -\sum_{i=1}^{M} q_i B_i'(\phi) \\ &= \beta \sum_{i=1}^{M} q_i^2 B_i(\phi) + \left[\sum_{i=1}^{M} \left(\frac{a_i}{a_0}\right)^3 q_i \frac{B_i(\phi)}{B_0(\phi)}\right] \left[\sum_{j=1}^{M} \left(\frac{a_j}{a_0}\right)^3 B_j'(\phi)\right] \\ &= \frac{\beta \left[\sum_{i=1}^{M} q_i^2 B_i(\phi)\right] \left[B_0(\phi) + \sum_{i=1}^{M} \left(\frac{a_i}{a_0}\right)^6 B_i(\phi)\right] - \beta \left[\sum_{i=1}^{M} \left(\frac{a_i}{a_0}\right)^3 q_i B_i(\phi)\right]^2}{B_0(\phi) + \sum_{i=1}^{M} \left(\frac{a_i}{a_0}\right)^6 B_i(\phi)}. \end{aligned} \tag{5.8}$$

Setting $q_0 = 0$ and applying the Cauchy-Schwarz inequality, we get

$$\begin{aligned} \left[\sum_{i=1}^{M} \left(\frac{a_i}{a_0}\right)^3 q_i B_i(\phi)\right]^2 &= \left[\sum_{i=0}^{M} q_i \sqrt{B_i(\phi)} \cdot \left(\frac{a_i}{a_0}\right)^3 \sqrt{B_i(\phi)}\right]^2 \\ &\leq \left[\sum_{i=1}^{M} q_i^2 B_i(\phi)\right] \left[B_0(\phi) + \sum_{i=1}^{M} \left(\frac{a_i}{a_0}\right)^6 B_i(\phi)\right]. \end{aligned}$$

This is in fact a strict inequality, since $q_1, \dots, q_M$ do not have the same sign, which implies that $(a_i/a_0)^3/q_i$ is not a constant for all $i = 1, \dots, M$. Therefore, $V''(\phi) > 0$ for all $\phi \in \mathbb{R}$. Hence $V : \mathbb{R} \to \mathbb{R}$ is strictly convex.

Notice from (5.6) that $V'(\phi) = -\sum_{i=1}^{M} q_i B_i(\phi)$ for all $\phi \in \mathbb{R}$. The fact that $V'(0) = 0$ follows then from the neutrality condition (5.5). Since $V''(\phi) > 0$ for all $\phi \in \mathbb{R}$, V' is an increasing function. Therefore, $V'(\phi) < V'(0) = 0$ for $\phi < 0$ and $V'(\phi) > V'(0) = 0$ for $\phi > 0$. Since $V' < 0$ on $(-\infty, 0)$, we have $V(\phi) > V(0) = 0$ for all $\phi < 0$. Similarly, since $V' > 0$ on $(0, \infty)$, we have $V(\phi) > V(0) = 0$ for all $\phi > 0$. Therefore, $V(\phi) > 0$ for all $\phi \neq 0$. Finally, for any $\phi > 1$, there exists $\xi = \xi(\phi) \in [1, \phi]$ such that

$$V(\phi) - V(1) = V'(\xi)(\phi - 1) \geq V'(1)(\phi - 1) \to \infty \qquad \text{as } \phi \to \infty.$$

Hence $V(\infty) = \infty$. Similarly, $V(-\infty) = \infty$. **Q.E.D.**

The following is our main result for an ionic solution with nonuniform ionic and solvent molecular sizes:

Theorem 5.1. (1) *The unique minimizer $c = (c_1, \dots, c_M) \in K$ of the free-energy functional $F : K \to \mathbb{R}$ and the corresponding equilibrium potential ψ are related by*

$$c_i = B_i\left(\psi - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2}\right) \qquad \text{a.e. } \Omega,\ i = 1, \dots, M. \tag{5.9}$$

The minimum electrostatic free energy is given by

$$\begin{aligned}\min_{d \in K} F[d] = F[c] = \int_\Omega \left[\frac{1}{2}\rho_f \hat{\psi}_0 - \frac{\varepsilon}{2}\left|\nabla\left(\psi - \hat{\psi}_0\right)\right|^2\right] dx \\ + \beta^{-1} a_0^{-3} \int_\Omega \left[\log\left(1 - \sum_{i=1}^{M} a_i^3 B_i\left(\psi - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2}\right)\right) - 1\right. \\ \left. + \sum_{i=1}^{M}\left(a_i^3 - a_0^3\right) B_i\left(\psi - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2}\right)\right] dx.\end{aligned} \tag{5.10}$$

(2) *The functional $J : H^1_{\psi_0}(\Omega) \to \mathbb{R} \cup \{+\infty\}$, defined by*

$$J[\phi] = \int_\Omega \left[\frac{1}{2}|\nabla\phi|^2 - \rho_f \phi + V\left(\phi - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2}\right)\right] dx \qquad \forall \phi \in H^1_{\psi_0}(\Omega),$$

admits a unique minimizer $\tilde{\psi} \in H^1_{\psi_0}(\Omega)$. This function $\tilde{\psi}$ is also the unique weak solution to the boundary-value problem of the implicit Poisson-Boltzmann equation

$$\nabla \cdot \varepsilon \nabla \phi - V'\left(\phi - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2}\right) = -\rho_f \qquad \text{in } \Omega. \tag{5.11}$$

and the boundary condition $\phi = \psi_0$ on $\partial\Omega$.

(3) *Let* $\tilde{\psi} \in H^1_{\psi_0}(\Omega)$ *be the same as in Part* (2). *Define* $\tilde{c}_i : \Omega \to \mathbb{R}$ $(i = 1, \dots, M)$ *by* (5.9) *with* c_i $(i = 1, \dots, M)$ *and* ψ *replaced by* $\tilde{c}_i$ $(i = 1, \dots, M)$ *and* $\tilde{\psi}$, *respectively. Then* $\tilde{c}_i = c_i$ $(i = 1, \dots, M)$ *and* $\tilde{\psi} = \psi$ *a.e. on* Ω, *i.e.,* $\tilde{c}_1, \dots, \tilde{c}_M$ *are the equilibrium concentrations and* $\tilde{\psi}$ *is the equilibrium electrostatic potential.*

The relations (5.9) are the implicit Boltzmann distributions of the equilibrium ionic concentrations $c_1, \dots, c_M$ expressed in terms of functions of the equilibrium electrostatic potential ψ. In the case that all the ionic and solvent molecular sizes are the same, say, $a_1 = \cdots = a_M = a$, then $\hat{f}_i(u_1, \dots, u_M) = \log(u_0/u_i)$ $(i = 1, \dots, M)$, cf. (5.2). One easily finds that the inverse mapping $\hat{g} = (\hat{g}_1, \dots, \hat{g}_M)$ is given by

$$\hat{g}_i(r_1, \dots, r_M) = \frac{a^{-3} e^{-r_i}}{1 + \sum_{j=1}^M e^{-r_j}}, \qquad i = 1, \dots, M.$$

This, together with (5.3) and (5.9), yield the generalized Boltzmann distributions (4.4) for the case of a uniform ionic and solvent molecular size.

Part (2) of Theorem 5.1 is a variational principle for the equilibrium electrostatic potential.

Proof of Theorem 5.1. (1) The implicit Boltzmann distributions (5.9) follow from Theorem 3.1 (cf. (3.4)) and the definition of $\hat{g}_i$ and $B_i(\phi)$ with $\phi = \psi - \hat{\psi}_0/2 + L\rho_f/2$ a.e. Ω $(i = 1, \dots, M)$, cf. (5.3) and (5.4).

To prove (5.10), we use the equilibrium conditions (3.4) and the fact that $\sum_{i=0}^M a_i^3 c_i = 1$ to get

$$\begin{aligned}
&\beta^{-1} \sum_{i=0}^M c_i \left[\log\left(a_i^3 c_i\right) - 1\right] - \sum_{i=1}^M \mu_i c_i \\
&\quad = \beta^{-1} c_0 \left[\log\left(a_0^3 c_0\right) - 1\right] + \beta^{-1} \sum_{i=1}^M c_i \left[\left(\frac{a_i}{a_0}\right)^3 \log\left(a_0^3 c_0\right) - 1\right] \\
&\qquad - \left(\sum_{i=1}^M q_i c_i\right)\left(\psi - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2}\right) \\
&\quad = -\beta^{-1} \sum_{i=0}^M c_i + \beta^{-1} a_0^{-3} \log\left(a_0^3 c_0\right) - \left(\sum_{i=1}^M q_i c_i\right)\left(\psi - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2}\right) \\
&\quad = \beta^{-1} a_0^{-3} \log\left(1 - \sum_{i=1}^M a_i^3 c_i\right) - \beta^{-1} a_0^{-3} \left[1 - \sum_{i=1}^M \left(a_i^3 - a_0^3\right) c_i\right] \\
&\qquad - \left(\sum_{i=1}^M q_i c_i\right)\left(\psi - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2}\right).
\end{aligned}$$

By the same argument as in obtaining (4.5), we have

$$\int_\Omega \left[\frac{1}{2}\rho\psi - \left(\sum_{i=1}^M q_i c_i\right)\left(\psi - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2}\right)\right] dx = \int_\Omega \left[\frac{1}{2}\rho_f \hat{\psi}_0 - \frac{\varepsilon}{2}\left|\nabla\left(\psi - \hat{\psi}_0\right)\right|^2\right] dx.$$

Combining the above two equations, together with (5.9), we obtain (5.10).

(2) Since $V \geq 0$ by Lemma 5.2, we have by applying Poincaré's inequality that

$$J[\phi] \geq C_3\|\phi\|^2_{H^1(\Omega)} + C_4 \qquad \forall \phi \in H^1_{\psi_0}(\Omega),$$

where $C_3 > 0$ and $C_4 \in \mathbb{R}$ are two constants. This and the fact that $\psi_0 \in H^1_{\psi_0}(\Omega)$ imply that the infimum of J over $H^1_{\psi_0}(\Omega)$ is finite. Moreover, it allows us to extract from an infimizing sequence $\{\psi_k\}$ of $J : H^1_{\psi_0}(\Omega) \to \mathbb{R} \cup \{+\infty\}$ a subsequence, not relabeled, that converges weakly in $H^1(\Omega)$ to some $\tilde{\psi} \in H^1_{\psi_0}(\Omega)$ and almost everywhere to $\tilde{\psi}$ on Ω. These and Fatou's lemma imply that $\liminf_{k\to\infty} J[\psi_k] \geq J[\tilde{\psi}]$. Hence the functional $J : H^1_{\psi_0}(\Omega) \to \mathbb{R}\cup\{+\infty\}$ has a minimizer. The uniqueness of this minimizer follows from the strict convexity of the functional $J : H^1_{\psi_0}(\Omega) \to \mathbb{R} \cup \{+\infty\}$.

Notice that $V' = -\sum_{i=1}^M q_i B_i$ is a bounded function, since $B_i(s) \in (0, a_i^{-3})$ for any $s \in \mathbb{R}$ and all $i = 1, \ldots, M$. The Mean-Value Theorem then implies that, for any $\phi \in C_c^\infty(\Omega)$ and $t \in \mathbb{R}$ with $t \neq 0$,

$$\left|\frac{V(\tilde{\psi} + t\phi - \hat{\psi}_0/2 + L\rho_f/2) - V(\tilde{\psi} - \hat{\psi}_0/2 + L\rho_f/2)}{t}\right| \leq \|\phi\|_{L^\infty(\Omega)} \max_{s\in\mathbb{R}} |V'(s)| \qquad \text{in } \Omega.$$

Therefore, by the Lebesgue Dominated Convergence Theorem,

$$\begin{aligned}\lim_{t\to 0} \int_\Omega &\frac{V(\tilde{\psi} + t\phi - \hat{\psi}_0/2 + L\rho_f/2) - V(\tilde{\psi} - \hat{\psi}_0/2 + L\rho_f/2)}{t} dx \\ &= \int_\Omega V'\left(\tilde{\psi} - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2}\right)\phi\, dx.\end{aligned}$$

Consequently, we have by a usual argument that $\tilde{\psi} \in H^1_{\psi_0}(\Omega)$ satisfies

$$\int_\Omega \left[\varepsilon\nabla\tilde{\psi}\cdot\nabla\phi - \rho_f\phi + V'\left(\tilde{\psi} - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2}\right)\phi\right] dx = 0 \tag{5.12}$$

for all $\phi \in C_c^\infty(\Omega)$. Since V' is bounded, (5.12) holds true for all $\phi \in H^1_0(\Omega)$. This means exactly that $\tilde{\psi}$ is the claimed weak solution.

Conversely, let us assume that $\tilde{\phi} \in H^1_{\psi_0}(\Omega)$ is a weak solution of (5.11), i.e., (5.12) holds true with $\tilde{\psi}$ replaced by $\tilde{\phi}$ for all $\phi \in H^1_0(\Omega)$. This and the convexity of V imply that for any $\phi \in H^1_0(\Omega)$ there exists $\xi \in H^1(\Omega)$ such that

$$J[\tilde{\phi} + \phi] - J[\tilde{\phi}] = \int_\Omega \left[\frac{\varepsilon}{2}|\nabla\phi|^2 + \frac{1}{2}V''(\xi)\phi^2\right] dx \geq 0.$$

Therefore, $\tilde{\phi}$ is a minimizer of $J : H^1_{\psi_0}(\Omega) \to \mathbb{R} \cup \{+\infty\}$. The uniqueness of weak solution follows from that of the minimizer.

(3) By the standard regularity theory [8], we have that the weak solution $\tilde{\psi} \in C(\overline{\Omega})$. Thus, there exists a compact set $Y \subset \mathbb{R}^M$ such that

$$(\beta(q_1(\tilde{\psi} - \hat{\psi}_0/2 + L\rho_f/2) - \mu_1), \ldots, \beta(q_1(\tilde{\psi} - \hat{\psi}_0/2 + L\rho_f/2) - \mu_1)) \in Y \qquad \text{a.e. } \Omega.$$

Now the image of Y under the mapping $\hat{g} : \mathbb{R}^M \to D_M$ is also compact. Therefore, by (5.3) and (5.9), $(\tilde{c}_1, \ldots, \tilde{c}_M)$ lies in a compact subset of D_M a.e. Ω. Hence (3.3) holds true with $\tilde{c}_i$ replacing c_i (with $\tilde{c}_0$ defined in a similar way) for some constants $\theta_1, \theta_2 \in (0, 1)$.

By (5.6) and (5.9) (with c_i and ψ replaced by $\tilde{c}_i$ and $\tilde{\psi}$, respectively), we have

$$V'\left(\tilde{\psi} - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2}\right) = -\sum_{i=1}^M q_i B_i\left(\tilde{\psi} - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2}\right) = -\sum_{i=1}^M q_i \tilde{c}_i \qquad \text{in } \Omega.$$

Therefore, $\tilde{\psi} \in H^1_{\psi_0}(\Omega)$ is the weak solution of

$$-\nabla \cdot \varepsilon \nabla \tilde{\psi} = \rho_f + \sum_{i=1}^M q_i \tilde{c}_i \qquad \text{in } \Omega.$$

Moreover, the definition $\tilde{c}_i = B_i(\tilde{\psi} - \hat{\psi}_0/2 + L\rho_f/2)$ $(i = 1, \ldots, M)$, (5.3), and (5.4) imply that

$$\left(\frac{a_i}{a_0}\right)^3 \log\left(a_0^3 \tilde{c}_0\right) - \log\left(a_i^3 \tilde{c}_i\right) = \beta\left[q_i\left(\tilde{\psi} - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2}\right) - \mu_i\right] \quad \text{a.e. } \Omega,\ i = 1, \ldots, M.$$

Therefore, the two conditions in Theorem 3.1 ((1) bounds and (2) equilibrium conditions) are satisfied for $(\tilde{c}_1, \ldots, \tilde{c}_M)$ and $\tilde{\psi}$. Hence $\tilde{c}_1, \ldots, \tilde{c}_M$ are the unique equilibrium ionic concentrations and $\tilde{\psi}$ is the unique equilibrium electrostatic potential. **Q.E.D.**

6 Conclusions

We have studied a continuum free-energy functional of the electrostatics for an ionic solution. We include the ionic finite-size effect in the functional by simply adding the excluded volumes of the ions and solvent molecules in the entropy term. Our detailed mathematical analysis shows that the resulting theory is qualitatively similar to the classical Poisson-Boltzmann theory of the electrostatics for ionic solutions without including the finite-size effect.

The upper bound for equilibrium ionic concentrations with the finite-size effect included can be much smaller than that without the finite-size effect included. Lower bounds for equilibrium ionic concentrations, however, always exist, with or without the finite-size effect included in an underlying free-energy functional. (For the case without finite-size effect, see [12].) This implies that, in any small region of the ionic solution, there is always certain amount of concentrations of each of the ionic species, in contrast to the reality where positives ions accumulate near a fixed, negatively charged object in an ionic solution. Although one can argue that the precise value of any of these bounds is still unknown, the simply size-modified Poisson-Boltzmann theory of continuum electrostatics, as developed in this work, does not seem to qualitatively capture molecular details.

Of much interest is the result that even no explicit, generalized Boltzmann distributions are available in general, there exist always implicit Boltzmann distributions that relate equilibrium ionic concentrations with the equilibrium electrostatic potential. Moreover, the induced charge density is an increasing function of the potential. This property resembles that for the classical Poisson-Boltzmann theory. It provides a variational principle for the electrostatic potential: the potential minimizes a convex functional. The convexity is an important property.

In the case that explicit, generalized Boltzmann distributions are available, one needs only to solve the generalized Poisson-Boltzmann equation to get the potential, and then to get the equilibrium concentrations using the explicit, generalized Boltzmann distributions. Otherwise, to get the potential, one needs to solve a constrained optimization problem: minimizing a convex functional constrained by a linear, inhomogeneous, partial differential equation, together with some boundary conditions. How to accurately and very efficiently solve such a minimization problem is of much practical interest. A possible alternative strategy can be to first obtain the numerical values of the functions $B_i : \mathbb{R} \to (0, a_i^{-3})$ $(i = 1, \ldots, M)$, defined by (5.4), and then use them to solve numerically the implicit Poisson-Boltzmann equation (5.11) to get the equilibrium potential ψ, and to get the equilibrium concentrations $c_1, \ldots, c_M$ by (5.9). This needs more studies.

By Lemma 5.2 and the Taylor expansion, we have the small potential expansion

$$V'(\phi) \approx V'(0) + V''(0)\phi \qquad \text{if } |\phi| \ll 1.$$

This and (5.11) lead to a generalized Debye-Hückel approximation

$$\nabla \cdot \varepsilon \nabla \phi - V''(0) \left(\phi - \frac{\hat{\psi}_0}{2} + \frac{L\rho_f}{2} \right) = -\rho_f \qquad \text{in } \Omega. \tag{6.1}$$

Notice that by (5.8)

$$V''(0) = \beta \sum_{i=1}^{M} q_i^2 B_i(0) - \frac{\beta \left[\sum_{i=1}^{M} a_i{}^3 q_i B_i(0) \right]^2}{\sum_{i=0}^{M} a_i^6 B_i(0)}.$$

Solving once the system (5.4) for $\phi = 0$, we can get the value of $V''(0)$. Therefore, (6.1) can be practically useful.

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