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MINIMIZATION OF ELECTROSTATIC FREE ENERGY AND THE POISSON–BOLTZMANN EQUATION FOR MOLECULAR SOLVATION WITH IMPLICIT SOLVENT*

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Abstract. In an implicit-solvent description of the solvation of charged molecules (solutes), the electrostatic free energy is a functional of concentrations of ions in the solvent. The charge density is determined by such concentrations together with the point charges of the solute atoms, and the electrostatic potential is determined by the Poisson equation with a variable dielectric coefficient. Such a free-energy functional is considered in this work for both the case of point ions and that of ions with a uniform finite size. It is proved for each case that there exists a unique set of equilibrium concentrations that minimize the free energy and that are given by the corresponding Boltzmann distributions through the equilibrium electrostatic potential. Such distributions are found to depend on the boundary data for the Poisson equation. Pointwise upper and lower bounds are obtained for the free-energy minimizing concentrations. Proofs are also given for the existence and uniqueness of the boundary-value problem of the resulting Poisson–Boltzmann equation that determines the equilibrium electrostatic potential. Finally, the equivalence of two different forms of such a boundary-value problem is proved.

Key words. implicit solvent, electrostatic free energy, ionic concentrations, electrostatic potentials, the Poisson–Boltzmann equation, variational methods, nonlinear elliptic interface problems

AMS subject classifications. 35J, 35Q, 49S, 82D, 92C

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1. Introduction.

It has long been realized that the electrostatic potential of a charged molecular system extremizes an electrostatic free-energy functional [3, 6, 12, 13, 15, 18, 20, 26, 28, 29]. In a simple setting, this functional is given by

$$F[c_1,\ldots,c_M;\psi] = \int \left\{ -\frac{\varepsilon}{8\pi}|\nabla\psi|^2 + \rho\psi + \beta^{-1}\sum_{j=1}^{M} c_j\left[\ln\left(\Lambda^3 c_j\right) - 1\right] - \sum_{j=1}^{M}\mu_j c_j \right\} dx,$$

where $c_1,\ldots,c_M$ are ionic concentrations, ψ is an electrostatic potential, ε is the dielectric constant, ρ is the charge density defined to be a linear combination of the ionic concentrations, β is the inverse thermal energy, Λ is the thermal de Broglie wavelength, and μ_j is the chemical potential of the jth ionic species. Throughout, we use the electrostatics CGS units. We also use $\log x$ to denote the natural logarithm of $x > 0$. Extremizing this functional with respect to the concentrations and the potential lead to the Boltzmann distribution of concentrations and the Poisson equation for the equilibrium potential, respectively [3, 6, 12, 13, 15, 26, 28]. Notice, however, that this free-energy functional is concave with respect to the electrostatic potential. Therefore, the extremizing concentrations and potential do not minimize this free-energy functional, rather they form an unstable saddle point of the system [1, 6, 12, 13]. This flaw of theory is removed in the free-energy minimization approach that was proposed

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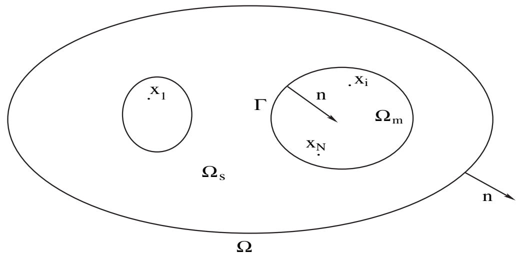

FIG. 1. *The geometry of a solvation system with an implicit solvent.*

in [12, 20]. The key point in this new approach is that the electrostatic free-energy functional depends solely on the ionic concentrations and the electrostatic potential is determined by such concentrations through the Poisson equation. In the recent article [5], this free-energy minimization approach was revisited and applied to the implicit-solvent (or continuum-solvent) description of solvation.

The present work is a mathematical study of the free-energy minimization approach to the electrostatics applied to the solvation of molecules with an implicit-solvent. Such application introduces additional mathematical complications due to the presence of point charges in solutes and the dielectric boundaries. We consider both the case of point ions—ions modeled as points without volumes—and that of ions with a uniform finite size. The finite-size effect of ions is known to be important in continuum modeling of electrostatics in molecular systems. Our analysis shows particularly that the free-energy minimizing ionic concentrations are uniformly bounded from above and away from zero at each spatial point. This uniform boundedness, which is proved by somewhat tedious constructions, is a consequence of the property that the free-energy minimizing concentrations have a large entropy. We do not consider the more general case of ions with different sizes for which there seems no explicit Boltzmann distributions.

Consider now the solvation of charged molecules with an implicit solvent [27]. We divide the entire region Ω of the solvation system into the region of solute molecules $\Omega_m \subset \mathbb{R}^3$ that is possibly multiply connected, the region of solvent (such as salted water) $\Omega_s \subset \mathbb{R}^3$, and the solute-solvent interface $\Gamma = \partial\Omega_m \cap \partial\Omega_s$; cf. Figure 1. This interface Γ serves as the dielectric boundary. Assume the solutes consist of N atoms with the ith one located at x_i and carrying a charge Q_i. Assume also there are M ionic species in the solvent with $q_j = ez_j$ the buck charge of the jth ionic species, where e is the elementary charge and z_j the valence of jth ionic species. Denote by $c_j = c_j(x)$ the local concentration at $x \in \Omega_s$ of the jth ionic species. Following the common assumption that the mobile ions in the solvent cannot penetrate the dielectric boundary Γ, we define $c_j(x) = 0$ for all $x \in \Omega_m$ and $1 \le j \le M$.

We consider two mean-field approximations of the electrostatic free energy of the solvation system as functionals of the local ionic concentrations $c = (c_1, \dots, c_M)$ in the solvent region. In the first one, point ions are assumed, and the related electrostatic free-energy functional is given by [5, 12, 19, 20, 26]

$$\begin{aligned} F_0[c] = {} & \frac{1}{2}\sum_{i=1}^{N} Q_i(\psi - \psi_{vac})(x_i) + \frac{1}{2}\int_{\Omega_s}\left(\sum_{j=1}^{M} q_j c_j\right)\psi dx \\ & + \beta^{-1}\sum_{j=1}^{M}\int_{\Omega_s} c_j\left[\log\left(a^3 c_j\right) - 1\right]dx - \sum_{j=1}^{M}\int_{\Omega_s}\mu_j c_j dx. \end{aligned} \tag{1.1}$$

In the second approximation, all ions are assumed to have a uniform linear size, and the related free-energy functional is given by [3, 20]

$$
\begin{aligned}
F_a[c] = {} & \frac{1}{2}\sum_{i=1}^{N} Q_i(\psi - \psi_{vac})(x_i) + \frac{1}{2}\int_{\Omega_s}\left(\sum_{j=1}^{M} q_j c_j\right)\psi dx \\
& + \beta^{-1}\sum_{j=0}^{M}\int_{\Omega_s} c_j\left[\log\left(a^3 c_j\right) - 1\right] dx - \sum_{j=1}^{M}\int_{\Omega_s}\mu_j c_j\, dx,
\end{aligned} \tag{1.2}
$$

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

$$
c_0(x) = a^{-3}\left[1 - \sum_{j=1}^{M} a^3 c_j(x)\right] \qquad \forall x \in \Omega_s. \tag{1.3}
$$

In (1.1) and (1.2), ψ is the electrostatic potential of the solvation system,

$$
\psi_{vac}(x) = \sum_{i=1}^{N} \frac{Q_i}{\varepsilon_m |x - x_i|} \tag{1.4}
$$

defines the electrostatic potential generated by all the point charges Q_i at x_i in a medium with the dielectric constant ε_m (usually taken as that in the vacuum), $a > 0$ is a constant, and μ_j is the constant chemical potential of the jth ionic species. The constant $a > 0$ represents in (1.1) a nonphysical cut-off which is often chosen to be the thermal de Broglie wavelength and in (1.2) the uniform linear size of ions.

The electrostatic potential ψ is determined by the Poisson equation

$$
\nabla \cdot \varepsilon_\Gamma \nabla \psi = -4\pi\rho \qquad \text{in } \Omega, \tag{1.5}
$$

where ε_Γ is the dielectric coefficient and ρ is the charge density, together with a boundary condition which is usually taken to be

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

where ψ_0 is a given function. The dielectric coefficient is defined to be

$$
\varepsilon_\Gamma(x) = \begin{cases} \varepsilon_m & \text{if } x \in \Omega_m, \\ \varepsilon_s & \text{if } x \in \Omega_s, \end{cases} \tag{1.7}
$$

where ε_m and ε_s are the dielectric constants of the solutes and the solvent, respectively. The charge density is given by

$$
\rho = \sum_{i=1}^{N} Q_i \delta_{x_i} + \sum_{j=1}^{M} q_j c_j \qquad \text{in } \Omega, \tag{1.8}
$$

where δ_{x_i} denotes the Dirac delta function centered at x_i.

The first two terms in (1.1) or (1.2) represent the internal electrostatic energy, which are often written formally as the integral of $\rho\psi/2$ over the entire region Ω. Based on Born's definition [2], the contribution to the electrostatic free energy due to the solute point charges is given as the first term in (1.1) or (1.2) though the reaction field $\psi - \psi_{vac}$. The β^{-1} term represents the ideal gas entropy. The term $1-\sum_{j=1}^{M} a^3 c_j$ in (1.2) is the concentration of solvent molecules. It describes the effect of finite size of ions. The last term in (1.1) or (1.2) accounts for a constant chemical potential in the system. The osmotic pressure from the mobile ions is dropped, since it is only an additive constant to the free-energy functional in the present setting. We remark that the use of notations F_0 and F_a does not indicate that we can obtain the functional F_0 by simply setting $a = 0$ in F_a.

In this work, we prove the following results:

(1) For each of the free-energy functionals (1.1) and (1.2), there admits a unique minimizer $c_1, \ldots, c_M$, which is also the unique equilibrium, in an admissible set of concentrations. Moreover, such concentrations and the corresponding equilibrium electrostatic potential ψ are related by the boundary-data dependent Boltzmann distributions

$$
(1.9)\quad c_j(x) = \begin{cases} c_j^\infty e^{-\beta q_j\left[\psi(x) - \hat{\psi}_0(x)/2\right]} & \text{for point ions,} \\ \dfrac{c_j^\infty e^{-\beta q_j[\psi(x)-\hat{\psi}_0(x)/2]}}{1 + a^3 \sum_{i=1}^{M} c_i^\infty e^{-\beta q_i[\psi(x)-\hat{\psi}_0(x)/2]}} & \text{for finite-size ions,} \end{cases}
$$

for a.e. $x \in \Omega_s$ and $1 \le j \le M$, where $c_j^\infty = a^{-3} e^{\beta \mu_j}$ and $\hat{\psi}_0 \in H^1(\Omega)$ is determined by

$$
(1.10)\qquad \begin{cases} \displaystyle\int_\Omega \varepsilon_\Gamma \nabla \hat{\psi}_0 \cdot \nabla \eta dx = 0 & \forall \eta \in H_0^1(\Omega), \\ \hat{\psi}_0 = \psi_0 & \text{on } \partial\Omega. \end{cases}
$$

The free-energy minimizing concentrations are shown to be uniformly bounded above and below away from zero. These results are summarized in Theorems 2.3–2.5 and Lemmas 3.4 and 3.5.

(2) The equilibrium electrostatic potential ψ is the unique solution to the boundary-data dependent Poisson–Boltzmann equation (PBE) [3, 4, 10, 11, 16, 17, 20, 31], together with the boundary condition (1.6),

$$
(1.11)\quad \nabla \cdot \varepsilon_\Gamma \nabla \psi + 4\pi \chi_{\Omega_s} \sum_{j=1}^{M} q_j c_j^\infty e^{-\beta q_j\left(\psi - \hat{\psi}_0/2\right)} = -4\pi \sum_{i=1}^{N} Q_i \delta_{x_i} \qquad \text{in } \Omega
$$

for the case of point ions, and

$$
(1.12)\quad \nabla \cdot \varepsilon_\Gamma \nabla \psi + 4\pi \chi_{\Omega_s} \sum_{j=1}^{M} \frac{q_j c_j^\infty e^{-\beta q_j\left(\psi - \hat{\psi}_0/2\right)}}{1 + a^3 \sum_{i=1}^{M} c_i^\infty e^{-\beta q_i\left(\psi - \hat{\psi}_0/2\right)}} = -4\pi \sum_{i=1}^{N} Q_i \delta_{x_i} \qquad \text{in } \Omega
$$

for the case of finite-size ions, where χ_{Ω_s} is the characteristic function of Ω_s. These equations can be written together as

$$
(1.13)\qquad \nabla \cdot \varepsilon_\Gamma \nabla \psi - 4\pi \chi_{\Omega_s} B'\left(\psi - \frac{\hat{\psi}_0}{2}\right) = -4\pi \sum_{i=1}^{N} Q_i \delta_{x_i} \qquad \text{in } \Omega,
$$

where B' is the derivative of the function $B : \mathbb{R} \to \mathbb{R}$ defined by
(1.14)

$$B(\psi) = \begin{cases} \displaystyle\sum_{j=1}^{M} \beta^{-1} c_j^\infty e^{-\beta q_j \psi} & \text{for point ions,} \\ \displaystyle\beta^{-1} a^{-3} \log\left(1 + a^3 \sum_{j=1}^{M} c_j^\infty e^{-\beta q_j \psi}\right) & \text{for finite-size ions.} \end{cases}$$

See Theorem 2.1.

(3) The boundary-value problem of the PBE (1.13) and (1.6) is equivalent to the elliptic interface problem

$$\begin{cases} \nabla \cdot \varepsilon_m \nabla \psi = -4\pi \displaystyle\sum_{i=1}^{N} Q_i \delta_{x_i} & \text{in } \Omega_m, \\ \nabla \cdot \varepsilon_s \nabla \psi - 4\pi B'\left(\psi - \dfrac{\hat{\psi}_0}{2}\right) = 0 & \text{in } \Omega_s, \\ [\![\psi]\!] = [\![\varepsilon_\Gamma \nabla \psi \cdot n]\!] = 0 & \text{on } \Gamma, \\ \psi = \psi_0 & \text{on } \Omega. \end{cases} \tag{1.15}$$

Here and below, we denote for any function u on Ω, $u_m = u|_{\Omega_m}$, $u_s = u|_{\Omega_s}$,, and $[\![u]\!] = u_s - u_m$ on Γ. See Theorem 2.2.

Two variations of the PBE (1.11) with $\psi_0 = 0$ are commonly used [8, 15, 29]. First, we have by the Taylor expansion and the electrostatic neutrality $\sum_{j=1}^{M} c_j^\infty = 0$ that

$$\sum_{j=1}^{M} q_j c_j^\infty e^{-\beta q_j \psi} \approx -\left(\sum_{j=1}^{M} \beta q_j^2 c_j^\infty\right) \psi,$$

if $|\psi|$ is small, leading to the linearized PBE [9]

$$\nabla \cdot \varepsilon_\Gamma \nabla \psi - \varepsilon_s \kappa^2 \chi_{\Omega_s} \psi = -4\pi \sum_{i=1}^{N} Q_i \delta_{x_i} \qquad \text{in } \Omega,$$

where $\kappa = \sqrt{4\pi\beta \sum_{i=1}^{M} q_j^2 c_j^\infty / \varepsilon_s^2}$ is the ionic strength or the inverse Debye–Hückel screening length. Clearly, all of our results for the nonlinear PBE (1.11) hold true for the linearized PBE. Second, for the common $z : -z$ type of salt such as NaCl in the solution, we have $M = 2$, $c_1^\infty = c_2^\infty$, and $q_1 = -q_2 = ze$. The PBE (1.11) reduces to the following sinh PBE:

$$\nabla \cdot \varepsilon_\Gamma \nabla \psi - 8\pi z e c_1^\infty \chi_{\Omega_s} \sinh(\beta z e \psi) = -4\pi \sum_{i=1}^{N} Q_i \delta_{x_i} \qquad \text{in } \Omega.$$

In proving the existence of minimizers of the functionals F_0 and F_a, we use de la Vallée Poussin's criterion [25] of the sequential compactness in $L^1(\Omega)$. The uniqueness of such minimizers follows basically from the convexity of these functionals. A crucial step in defining and deriving equilibriums of F_0 and F_a is the construction of

L^∞-concentrations that are bounded below in Ω_s by a positive constant and that have low free energies. Such constructions are made by increasing the entropy of ionic concentrations through their small perturbations. The effect of inhomogeneous Dirichlet boundary data to the Boltzmann distributions and, hence, to the PBE can be useful to guide practical numerical computations. The equivalence of the two formulations is a common property for many physical problems. The interface formulation of the boundary-value problem of the PBE has been used for numerical computations using boundary integral method [22–24]. The finite-size effect is important in modeling electrostatics [3, 20].

The rest of the paper is organized as follows: In section 2, we state our main results; in section 3, we provide some lemmas; in section 4, we prove our theorems on the boundary-value problem of PBE; in section 5, we prove our theorems on the free-energy minimization. Finally, in Appendix, we give the proof of two lemmas.

2. Main results. Throughout the rest of the paper, we make the following assumptions:

A1. The set $\Omega \subset \mathbb{R}^3$ is nonempty, bounded, open, and connected. The sets $\Omega_m \subset \mathbb{R}^3$ and $\Omega_s \subset \mathbb{R}^3$ are nonempty, bounded, and open, and satisfy that $\overline{\Omega_m} \subset \Omega$ and $\Omega_s = \Omega \setminus \overline{\Omega_m}$. The N points $x_1, \dots, x_N$ for some integer $N \geq 1$ belong to Ω_m. Both $\partial\Omega$ and Γ are of C^2. The unit exterior normal at the boundary of Ω_s is denoted by n; cf. Figure 1.

A2. $M \geq 2$ is an integer. All $a > 0$, $\beta > 0$, $Q_i \in \mathbb{R}$ $(1 \leq i \leq N)$, $q_j \in \mathbb{R}$ and $\mu_j \in \mathbb{R}$ $(1 \leq j \leq M)$, $\varepsilon_m > 0$, and $\varepsilon_s > 0$ are constants;

A3. The functions ψ_{vac} and ε_Γ are defined in (1.4) and (1.7), respectively. The boundary data ψ_0 is the trace of a given function, also denoted by ψ_0, in $W^{2,\infty}(\Omega)$.

Boundary values are understood as traces. When no confusion arises, the capital letter C, with or without a subscript, denotes a positive constant that can depend on all Ω_m, Ω_s, Ω, Γ, ε_m, ε_s, a, β, N, M, x_i, and Q_i $(1 \leq i \leq N)$, q_j and μ_j $(1 \leq j \leq M)$, and ψ_0.

For any open set $U \subseteq \mathbb{R}^3$ that contains all $x_1, \dots, x_N$, we denote

$$H^1_*(U) = \left\{ u \in W^{1,1}(U) : u|_{U_\alpha} \in H^1(U_\alpha)\, \forall \alpha > 0 \right\},$$

where $U_\alpha = U \setminus (\cup_{i=1}^N \overline{B(x_i, \alpha)})$ and $B(x_i, \alpha)$ denotes the ball centered at x_i with radius α.

Definition 2.1. *A function $\psi \in H^1_*(\Omega)$ is a weak solution to the boundary-value problem of the PBE* (1.13) *and* (1.6)*, if $\psi = \psi_0$ on $\partial\Omega$, $\chi_{\Omega_s} B(\psi) \in L^2(\Omega_s)$, and*

(2.1)
$$\int_\Omega \left[\varepsilon_\Gamma \nabla\psi \cdot \nabla\eta + 4\pi \chi_{\Omega_s} B'\left(\psi - \frac{\hat{\psi}_0}{2}\right)\eta \right] dx = 4\pi \sum_{i=1}^N Q_i \eta(x_i) \qquad \forall \eta \in C_c^\infty(\Omega).$$

We remark that if $\phi \in H^1(U)$ for some bounded and smooth domain $U \subset \mathbb{R}^3$, then e^ϕ and, hence, $B(\phi)$ may not be in $L^1(U)$. For example, let $U = B(0,1)$ be the unit ball of $\mathbb{R}^3$ and $\alpha \in (0, 1/2)$. Define $\phi(x) = |x|^{-\alpha}$ for any $x \in U$. Then $\phi \in H^1(U)$ and that $e^\phi \notin L^1(U)$. Notice by (1.14) that $\chi_{\Omega_s} B(\psi) \in L^2(\Omega_s)$ is equivalent to $\chi_{\Omega_s} e^{-\beta q_j \psi} \in L^2(\Omega_s)$ or $\chi_{\Omega_s} e^{-\beta q_j (\psi - \hat{\psi}_0/2)} \in L^2(\Omega_s)$ $(j = 1, \dots, M)$, which in turn are equivalent to $\chi_{\Omega_s} B(\psi - \hat{\psi}_0/2) \in L^2(\Omega_s)$.

Theorem 2.1. *There exists a unique weak solution $\psi \in H^1_*(\Omega)$ to the boundary-value problem of the PBE* (1.13) *and* (1.6)*. Moreover, $\psi \in C(\overline{\Omega} \setminus (\cup_{i=1}^N \overline{B(x_i, \alpha)})$*

for any $\alpha > 0$ such that the closure of $\cup_{i=1}^N B(x_i, \alpha)$ is contained in Ω_m, and $\psi \in C^\infty((\Omega_m \setminus \{x_1, \dots, x_N\}) \cup \Omega_s)$.

Definition 2.2. *A function $\psi : \Omega \to \mathbb{R}$ is a weak solution of the interface problem* (1.15), *if the following are satisfied: $\psi_m \in H^1_*(\Omega_m)$ and*

$$\int_{\Omega_m} \varepsilon_m \nabla \psi \cdot \nabla \eta dx = 4\pi \sum_{i=1}^N Q_i \eta(x_i) \qquad \forall \eta \in C_c^\infty(\Omega_m); \tag{2.2}$$

$\psi_s \in H^1(\Omega_s)$, $\chi_{\Omega_s} B(\psi) \in L^2(\Omega_s)$, and

$$\int_{\Omega_s} \left[\varepsilon_s \nabla \psi \cdot \nabla \eta + 4\pi \chi_{\Omega_s} B' \left(\psi - \frac{\hat{\psi}_0}{2} \right) \eta \right] dx = 0 \qquad \forall \eta \in C_c^\infty(\Omega_s); \tag{2.3}$$

and the third and fourth equations in (1.15) *hold true.*

Theorem 2.2. *A function $\psi : \Omega \to \mathbb{R}$ is a weak solution to the boundary-value problems* (1.13) *and* (1.6), *if and only if it is a weak solution to the boundary-value problem* (1.15).

Let $U \subset \mathbb{R}^3$ be a nonempty, bounded, and open set. Let $f \in L^1(U)$. Assume

$$\sup_{0 \neq \xi \in L^\infty(U) \cap H^1_0(U)} \frac{\int_U f \xi \, dx}{\|\xi\|_{H^1(U)}} < \infty. \tag{2.4}$$

Since $L^\infty(U) \cap H^1_0(U)$ is dense in $H^1_0(U)$, we can identify f as an element in $H^{-1}(U)$, the dual of $H^1_0(U)$, with

$$\langle f, \xi \rangle = \int_U f \xi dx \qquad \forall \xi \in L^\infty(U) \cap H^1_0(U),$$

and we write $f \in L^1(U) \cap H^{-1}(U)$. The $H^{-1}(U)$ norm of f is given by (2.4). We define

$$X = \left\{ c = (c_1, \dots, c_M) \in L^1\left(\Omega, \mathbb{R}^M\right) : c = 0 \text{ a.e. } \Omega_m \text{ and } \sum_{j=1}^M q_j c_j \in H^{-1}(\Omega) \right\},$$

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

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

Let $\alpha \in \mathbb{R}$ and define $S_\alpha : [0, \infty) \to \mathbb{R}$ by $S_\alpha(0) = 0$ and $S_\alpha(u) = u(\alpha + \log u)$ if $u > 0$. It is easy to see that S_α is bounded below on $[0, \infty)$ and strictly convex on $(0, \infty)$. Define

$$V_0 = \left\{ (c_1, \dots, c_M) \in X : \ c_j \geq 0 \text{ a.e. } \Omega_s \text{ and } \int_\Omega S_0(c_j) \, dx < \infty, \ j = 1, \dots, M \right\},$$

$$W_0 = \left\{ (c_1, \dots, c_M) \in V_0 : \text{ there exists } p > \frac{3}{2} \text{ such that } c_j \in L^p(\Omega), j = 1, \dots, M \right\},$$

$$V_a = \left\{ (c_1, \dots, c_M) \in V_0 : \ c_0 = a^{-3} \left(1 - \sum_{j=1}^M a^3 c_j \right) \geq 0 \text{ a.e. } \Omega_s \right\}.$$

Clearly, all V_0, W_0, and V_a are nonempty and convex. For any $c = (c_1, \ldots, c_M) \in V_0$, there exists a unique weak solution $\psi = \psi(c)$ of the boundary-value problem (1.5) and (1.6) with the charge density ρ given by (1.8); in particular, $\psi - \psi_{vac}$ is harmonic in Ω_m, cf. Lemma 3.2. We shall call $\psi = \psi(c)$ the electrostatic potential corresponding to c. Therefore, $F_0 : V_0 \to \mathbb{R}$ and $F_a : V_a \to \mathbb{R}$ are well defined. We use V, F to denote V_0, F_0 or W_0, F_0 or V_a, F_a.

DEFINITION 2.3. *An element $c = (c_1, \ldots, c_M) \in V$ is an equilibrium of $F : V \to \mathbb{R}$, if*

$$\text{there exist } \gamma_1 > 0 \text{ and } \gamma_2 > 0 \text{ such that } \gamma_1 \le c_j(x) \le \gamma_2 \text{ a.e. } x \in \Omega_s,\ j = 1, \ldots, M, \tag{2.5}$$

for the case of point ions, or

$$\text{there exists } \theta_0 \in (0,1) \text{ such that } a^3 c_j(x) \ge \theta_0 \text{ a.e. } x \in \Omega_s,\ j = 0, 1, \ldots, M, \tag{2.6}$$

for the case of finite-size ions; and

$$\delta F[c]e := \lim_{t \to 0} \frac{F[c + te] - F[c]}{t} = 0 \qquad \forall e \in X \cap L^\infty\left(\Omega, \mathbb{R}^M\right).$$

DEFINITION 2.4. *An element $c \in V$ is a local minimizer of $F : V \to \mathbb{R}$, if there exists $\varepsilon > 0$ such that $F[d] \ge F[c]$ for any $d \in V$ with $\|d - c\|_X < \varepsilon$.*

THEOREM 2.3. *There exists a unique minimizer of $F_0 : V_0 \to \mathbb{R}$. It is also the unique local minimizer of $F_0 : V_0 \to \mathbb{R}$.*

It is an open question if the unique minimizer of $F_0 : V_0 \to \mathbb{R}$ is an equilibrium of $F_0 : V_0 \to \mathbb{R}$ as defined in Definition 2.3. The answer to this question would be yes if this minimizer were in W_0 or if $\min_{d \in V_0} F_0[d] = \min_{d \in W_0} F_0[d]$, neither of which is clearly true. This is the reason we introduce the class of concentrations W_0. See the proof of Lemma 3.4 in Appendix.

THEOREM 2.4.

(1) *There exists a unique equilibrium $c = (c_1, \ldots, c_M)$ of $F_0 : W_0 \to \mathbb{R}$. It is also the unique global minimizer and the unique local minimizer of $F_0 : W_0 \to \mathbb{R}$.*
(2) *If $\psi = \psi(c)$ is the corresponding electrostatic potential, then the Boltzmann distributions* (1.9) *for point ions holds true and ψ is the unique weak solution to the corresponding boundary-value problem of PBE* (1.11) *and* (1.6). *Moreover,*

$$\begin{aligned}\min_{d \in W_0} F_0[d] = {} & \frac{1}{2} \sum_{i=1}^N Q_i (\psi - \psi_{vac})(x_i) + \int_\Gamma \frac{1}{8\pi} \left(\psi - \hat{\phi}_0\right) \varepsilon_\Gamma \partial_n \left(\psi - \hat{\psi}_0\right) dS \\ & - \int_{\Omega_s} \frac{\varepsilon_s}{8\pi} \left|\nabla \left(\psi - \hat{\psi}_0\right)\right|^2 dx - \beta^{-1} \sum_{j=1}^M \int_{\Omega_s} c_j^\infty e^{-\beta q_j \left(\psi - \hat{\psi}_0/2\right)} dx.\end{aligned} \tag{2.7}$$

THEOREM 2.5.

(1) *There exists a unique equilibrium $c = (c_1, \ldots, c_M)$ of $F_a : V_a \to \mathbb{R}$. It is also the unique global minimizer and the unique local minimizer of $F_a : V_a \to \mathbb{R}$.*
(2) *If $\psi = \psi(c)$ is the corresponding electrostatic potential, then the Boltzmann distributions* (1.9) *for finite-size ions holds true and ψ is the unique weak solution to the corresponding boundary-value problem of PBE* (1.12) *and* (1.6).

Moreover,

$$\begin{aligned}\min_{d\in V_a} F_a[d] = {} & \frac{1}{2}\sum_{i=1}^N Q_i(\psi-\psi_{vac})(x_i) + \int_\Gamma \frac{1}{8\pi}\left(\psi-\hat{\phi}_0\right)\varepsilon_\Gamma \partial_n\left(\psi-\hat{\psi}_0\right) dS \\ & - \int_{\Omega_s} \frac{\varepsilon_\Gamma}{8\pi}\left|\nabla\left(\psi-\hat{\psi}_0\right)\right|^2 dx - \beta^{-1}a^{-3}\int_{\Omega_s} \\ & \left[1+\log\left(1+a^3\sum_{j=1}^M c_j^\infty e^{-\beta q_j\left(\psi-\hat{\psi}_0/2\right)}\right)\right] dx.\end{aligned} \tag{2.8}$$

3. Some lemmas. The key point of our first lemma below is the existence and continuity across the interface Γ of the normal flux for a solution of an elliptic interface problem. In terms of electrostatics, this means that the electrostatic potential and the normal component of electrostatic displacement are continuous across dielectric boundaries. These seem to be known results. For completeness, we give a proof here.

LEMMA 3.1. *Let $U \subset \mathbb{R}^3$ be an open set such that $\Gamma \subset U \subseteq \Omega$. Let $g \in L^1(U) \cap H^{-1}(U)$. Suppose $u \in H^1(U)$ satisfies*

$$\int_U \varepsilon_\Gamma \nabla u \cdot \nabla \eta dx = \int_U g\eta dx \qquad \forall \eta \in C_c^\infty(U). \tag{3.1}$$

Then $[\![u]\!] = 0$ on Γ. If in addition $g \in L^2(U)$, then $[\![\varepsilon_\Gamma \partial_n u]\!] = 0$ on Γ.

Proof. Fix an open ball $B \subset U$ such that $\Gamma \cap B \neq \emptyset$. Let $\eta \in C_c^\infty(U)$ with $\operatorname{supp}\eta \subset B$. Let n_j with $1 \le j \le 3$ be the jth component of n, the unit normal at the Γ, pointing from Ω_s to Ω_m. It follows from the fact that $u \in H^1(\Omega)$ and integration by parts that

$$\begin{aligned}-\int_B u\partial_j\eta\, dx &= \int_B (\partial_j u)\eta\, dx \\ &= \int_{B\cap\Omega_m} (\partial_j u)\eta\, dx + \int_{B\cap\Omega_s} (\partial_j u)\eta\, dx \\ &= -\int_{B\cap\Omega_m} u\partial_j\eta\, dx - \int_{\Gamma\cap B} u_m\eta n_j\, dS - \int_{B\cap\Omega_s} u\partial_j\eta\, dx + \int_{\Gamma\cap B} u_s\eta n_j\, dS \\ &= -\int_B u\partial_j\eta\, dx + \int_{\Gamma\cap B}(u_s-u_m)\eta n_j\, dS, \qquad j=1,2,3.\end{aligned}$$

This and the arbitrariness of η imply $[\![u]\!] = 0$ on Γ.

To show the continuity of $\varepsilon_\Gamma \nabla u \cdot n$ across Γ, we fix an open set $U_0 \subset \mathbb{R}^3$ such that $\Gamma \subset U_0 \subset \overline{U_0} \subset U$ and that the boundary ∂U_0 is C^2. By the fact that $u \in H^1(U)$ and $g \in L^2(U)$, and by (3.1), we have

$$(\varepsilon_t \nabla u_t)|_{U_0\cap\Omega_t} \in L^2\left(U_0\cap\Omega_t, \mathbb{R}^3\right) \quad \text{and} \quad (\nabla\cdot\varepsilon_t\nabla u_t)|_{U_0\cap\Omega_t} = -g \in L^2(U_0\cap\Omega_t), \quad t=m,s.$$

Therefore, by Theorem 1.2 in [30], the trace of $(\varepsilon_t\nabla u_t)|_{U_0\cap\Omega_t}\cdot\nu \in H^{-1/2}(\partial(U_0\cap\Omega_t))$ exists, and also by (3.1),

$$\int_{U_0\cap\Omega_t} \varepsilon_t\nabla u_t\cdot\nabla\eta dx = \int_{U_0\cap\Omega_t} g\eta dx + \int_{\partial(U_0\cap\Omega_t)} (\varepsilon_t\nabla u_t\cdot\nu)\eta dS \quad \forall\eta\in C_c^\infty(U_0\cap\Omega_t), \tag{3.2}$$

where ν denotes the unit exterior normal of the boundary $\partial(U_0 \cap \Omega_t)$ which contains Γ and $t = m, s$. Notice that the normals ν at Γ from both sides $U_0 \cap \Omega_m$ and $U_0 \cap \Omega_s$ are in opposite directions.

These traces are determined independent of the choice of U_0. In fact, if $Q_0 \subset \mathbb{R}^3$ is another open set such that $\Gamma \subset Q_0 \subset \overline{Q_0} \subset U$ and the boundary ∂Q_0 is C^2, then the traces $(\varepsilon_m \nabla u_m)|_{Q_0\cap\Omega_m} \cdot \nu \in H^{-1/2}(\partial(Q_0 \cap \Omega_m))$ and $(\varepsilon_s \nabla u_s)|_{Q_0\cap\Omega_s} \cdot \nu \in H^{-1/2}(\partial(Q_0 \cap \Omega_m))$ exist, and (3.2) holds true for $t = m, s$ when U_0 is replaced by Q_0. Consider now (3.2) with $t = m$. Choose any $\eta \in C^1_c(U_0 \cap Q_0)$ such that $\eta = 0$ on $\partial(U_0 \cap \Omega_m) \setminus \Gamma$ and on $\partial(Q_0 \cap \Omega_m) \setminus \Gamma$. Extend η by $\eta = 0$ to outside $U_0 \cap Q_0$. By (3.2) with $t = m$ and the corresponding equation with U_0 replaced by Q_0, we obtain that

$$\int_{\partial(U_0\cap\Omega_m)} (\varepsilon_m \nabla u_m \cdot \nu)\eta dS = \int_{\partial(Q_0\cap\Omega_m)} (\varepsilon_m \nabla u_m \cdot \nu)\eta dS.$$

The arbitrariness of η then implies that the trace of $(\varepsilon_m \nabla u_m \cdot \nu)|_{U_0\cap\Omega_m}$ on Γ determined by U_0 is the same as that determined by Q_0. By the same argument, we see that the trace of $(\varepsilon_s \nabla u_s \cdot n)|_{U_0\cap\Omega_s}$ on Γ determined by U_0 is the same as that determined by Q_0.

Now, by the fact that $U_0 = (U_0 \cap \Omega_m) \cup (U_0 \cap \Omega_s)$ and $(U_0 \cap \Omega_m) \cap (U_0 \cap \Omega_s) = \emptyset$, and by our convention for the direction of the unit normal n along Γ, we obtain from (3.1) and (3.2) that for any $\eta \in C^\infty_c(U)$ with $\operatorname{supp} \eta \subset U_0$

$$\int_\Gamma \left(\varepsilon_m \frac{\partial u_m}{\partial n} - \varepsilon_s \frac{\partial u_s}{\partial n} \right) \eta dS = 0.$$

The arbitrariness of η implies $[\![\varepsilon_\Gamma \partial_n u]\!] = 0$ on Γ. $\square$

Let $L : H^{-1}(\Omega) \to H^1(\Omega)$ be the linear operator defined as follows: for any $\xi \in H^{-1}(\Omega)$, $L\xi \in H^1_0(\Omega)$ is the unique function in $H^1_0(\Omega)$ that satisfies

$$\frac{1}{4\pi} \int_\Omega \varepsilon_\Gamma \nabla (L\xi) \cdot \nabla v \, dx = \xi(v) \qquad \forall v \in H^1_0(\Omega). \tag{3.3}$$

It is easy to see that $\langle \xi, \eta \rangle = \xi(L\eta)$ defines an inner product of $H^{-1}(\Omega)$. Denote by $|\!|\!| \cdot |\!|\!|$ the corresponding norm of $H^{-1}(\Omega)$, i.e., $|\!|\!|\xi|\!|\!| = \sqrt{\langle \xi, \xi \rangle} = \sqrt{\xi(L\xi)}$ for any $\xi \in H^{-1}(\Omega)$. One can verify that there exist $C_1 = C_1(\Omega, \varepsilon_m, \varepsilon_s) > 0$ and $C_2 = C_2(\varepsilon_m, \varepsilon_s) > 0$ such that

$$C_1 |\!|\!|\xi|\!|\!| \le \|\xi\|_{H^{-1}(\Omega)} \le C_2 |\!|\!|\xi|\!|\!| \qquad \forall \xi \in H^{-1}(\Omega). \tag{3.4}$$

It follows from [21] (with minor modifications) that there exists a unique $G \in H^1_*(\Omega)$ such that $G = 0$ on $\partial\Omega$ and

$$\int_\Omega \varepsilon_\Gamma \nabla G \cdot \nabla \eta dx = 4\pi \sum_{i=1}^N Q_i \eta(x_i) \qquad \forall \eta \in C^\infty_c(\Omega). \tag{3.5}$$

Clearly, $G - \psi_{vac}$ is harmonic in Ω_m and $G \in W^{1,p}(\Omega)$ for any $p \in [1, 3/2)$. Notice that the function $\hat{\psi}_0 \in H^1(\Omega)$ defined in (1.10) is harmonic in $\Omega_m \cup \Omega_s$.

The next lemma gives a solution decomposition of the Poisson equation (1.5) with its right-hand side consisting of Dirac masses and a function in $H^{-1}(\Omega)$ that represents the density of ionic charges. This decomposition is a mathematical formulation of the Born cycle [2].

LEMMA 3.2. *Let $f \in L^1(\Omega) \cap H^{-1}(\Omega)$ be such that $f = 0$ in Ω_m. Then $\psi := G + \hat{\psi}_0 + Lf$ is the unique function in $H^1_*(\Omega)$ that satisfies $\psi = \psi_0$ on $\partial\Omega$ and*

$$\int_\Omega \varepsilon_\Gamma \nabla\psi \cdot \nabla\eta dx = 4\pi \sum_{i=1}^N Q_i \eta(x_i) + 4\pi \int_{\Omega_s} f\eta dx \qquad \forall \eta \in C_c^\infty(\Omega). \tag{3.6}$$

Moreover, Lf and $\psi - \psi_{vac}$ are harmonic in Ω_m, and

$$\sum_{i=1}^N Q_i \left(Lf\right)(x_i) = \int_{\Omega_s} Gf dx. \tag{3.7}$$

Proof. From the definition of G, $\hat{\psi}_0$, and L (cf. (3.5), (1.10), and (3.3)), we easily verify that the function ψ is in $H^1_*(\Omega)$, $\psi = \psi_0$ on $\partial\Omega$, and (3.6) holds true. If $\bar{\psi} \in H^1_*(\Omega)$ satisfies $\bar{\psi} = 0$ on $\partial\Omega$ and $\int_\Omega \varepsilon_\Gamma \nabla\bar{\psi} \cdot \nabla\eta \, dx = 0$ for all $\eta \in C_c^\infty(\Omega)$, then clearly $\bar{\psi} \in H^1_0(\Omega)$ and in fact $\bar{\psi} = 0$ a.e. Ω. This proves the needed uniqueness.

By the fact that $f = 0$ in Ω_m and the definition of L (cf. (3.3)), Lf is harmonic in Ω_m. The fact that $\psi - \psi_{vac}$ is harmonic in Ω_m follows from (3.6) with $\eta \in C_c^\infty(\Omega)$ so chosen that $\operatorname{supp}\eta \subset \Omega_m$ and

$$\int_{\Omega_m} \varepsilon_m \nabla\psi_{vac} \cdot \nabla\eta dx = 4\pi \sum_{i=1}^N Q_i \eta(x_i) \qquad \forall \eta \in C_c^\infty(\Omega_m).$$

It remains to prove (3.7). Denote $\psi_c = Lf \in H^1_0(\Omega)$. Let $\alpha > 0$ be sufficiently small and let $B_\alpha = \cup_{i=1}^N B(x_i, \alpha)$. By the fact that G is harmonic in $\Omega_m \setminus B_\alpha$ and $G - \psi_{vac}$ is harmonic in Ω_m, we obtain by a series of routine calculations that

$$\begin{aligned}
\int_{\Omega_m} \varepsilon_m \nabla G \cdot \nabla\psi_c dx &= \int_{\Omega_m \setminus B_\alpha} \varepsilon_m \nabla G \cdot \nabla\psi_c dx + \int_{B_\alpha} \varepsilon_m \nabla G \cdot \nabla\psi_c dx \\
&= -\int_{\Omega_m \setminus B_\alpha} \varepsilon_m (\Delta G)\psi_c dx + \int_{\partial(\Omega_m \setminus B_\alpha)} \varepsilon_m \psi_c \frac{\partial G}{\partial\nu} dS + O(\alpha) \\
&= -\int_\Gamma \varepsilon_m \psi_c|_m \frac{\partial G|_m}{\partial n} dS + \int_{\partial B_\alpha} \varepsilon_m \psi_c \frac{\partial G}{\partial\nu} dS + O(\alpha) \\
&= -\int_\Gamma \varepsilon_m \psi_c|_m \frac{\partial G|_m}{\partial n} dS + \int_{\partial B_\alpha} \varepsilon_m \psi_c \frac{\partial\left(G - \psi_{vac}\right)}{\partial\nu} dS \\
&\quad + \sum_{i=1}^N \int_{\partial B(x_i,\alpha)} \varepsilon_m \psi_c \frac{\partial\psi_{vac}}{\partial\nu} dS + O(\alpha) \\
&\to -\int_\Gamma \varepsilon_m \psi_c|_m \frac{\partial G|_m}{\partial n} dS + 4\pi \sum_{i=1}^N Q_i \psi_c(x_i) \qquad \text{as } \alpha \to 0,
\end{aligned}$$

where ν is the exterior unit normal of $\partial(\Omega_m \setminus B_\alpha)$ and $\nu = -n$ on Γ by our convention for the direction of n. Consequently, by the continuity of $\varepsilon_\Gamma \nabla G \cdot n$ across Γ (cf.

Lemma 3.1), the fact that G is harmonic in Ω_s, and $G = \psi_c = 0$ on $\partial\Omega$, we obtain

$$
\begin{aligned}
4\pi \sum_{i=1}^{N} Q_i \psi_c(x_i) &= \int_\Gamma \varepsilon_s \psi_c|_s \frac{\partial G|_s}{\partial n} dS + \int_{\Omega_m} \varepsilon_m \nabla G \cdot \nabla \psi_c dx \\
&= \int_{\Omega_s} \varepsilon_s (\Delta G) \psi_c dx + \int_{\Omega_s} \varepsilon_s \nabla G \cdot \nabla \psi_c dx + \int_{\Omega_m} \varepsilon_m \nabla G \cdot \nabla \psi_c dx \\
&= \int_\Omega \varepsilon_\Gamma \nabla G \cdot \nabla \psi_c dx. \qquad (3.8)
\end{aligned}
$$

Since $\psi_c = Lf \in H_0^1(\Omega)$ is harmonic in Ω_m, we also have by the properties of G (cf. [21]) and integration by parts that

$$
\begin{aligned}
\int_{\Omega_m} \varepsilon_m \nabla G \cdot \nabla \psi_c dx &= \int_{\Omega_m \setminus B_\alpha} \varepsilon_m \nabla G \cdot \nabla \psi_c dx + \int_{B_\alpha} \varepsilon_m \nabla G \cdot \nabla \psi_c dx \\
&= -\int_{\Omega_m \setminus B_\alpha} \varepsilon_m G \Delta \psi_c dx + \int_{\partial(\Omega_m \setminus B_\alpha)} \varepsilon_m G \frac{\partial \psi_c}{\partial \nu} dS + O(\alpha) \\
&= -\int_\Gamma \varepsilon_m G|_m \frac{\partial \psi_c|_m}{\partial n} dS + \int_{\partial B_\alpha} \varepsilon_m G \frac{\partial \psi_c}{\partial \nu} dS + O(\alpha) \\
&\to -\int_\Gamma \varepsilon_m G|_m \frac{\partial \psi_c|_m}{\partial n} dS \qquad \text{as } \alpha \to 0. \qquad (3.9)
\end{aligned}
$$

Let $\hat{G} \in H^1(\Omega_m)$ be such that $\hat{G} = G$ on $\Gamma = \partial\Omega_m$. Replacing G in (3.9) by $\hat{G}$ and repeating the same calculations, we obtain

$$
\int_{\Omega_m} \varepsilon_m \nabla G \cdot \nabla \psi_c dx = \int_{\Omega_m} \varepsilon_m \nabla \hat{G} \cdot \nabla \psi_c dx. \qquad (3.10)
$$

Define $\overline{G} : \Omega \to \mathbb{R}$ by $\overline{G}(x) = \hat{G}(x)$ if $x \in \overline{\Omega_m}$ and by $\overline{G}(x) = G(x)$ if $x \in \Omega_s$. Clearly, $\overline{G} \in H_0^1(\Omega)$. Since $\psi_c = Lf$ and $f = 0$ in Ω_m, we, thus, have by (3.8) and (3.10) that

$$
\begin{aligned}
4\pi \sum_{i=1}^{N} Q_i \psi_c(x_i) &= \int_{\Omega_m} \varepsilon_m \nabla \hat{G} \cdot \nabla \psi_c dx + \int_{\Omega_s} \varepsilon_s \nabla G \cdot \nabla \psi_c dx \\
&= \int_\Omega \varepsilon_\Gamma \nabla \overline{G} \cdot \nabla \psi_c dx = 4\pi \int_\Omega \overline{G} f dx = 4\pi \int_{\Omega_s} G f dx.
\end{aligned}
$$

This implies (3.7). $\square$

By Lemma 3.2, the potential $\psi = \psi(c_1, \dots, c_M)$ corresponding to a set of concentrations $(c_1, \dots, c_M)$ is well defined with $f = \sum_{j=1}^{M} q_j c_j$ and is given by

$$
\psi(c_1, \dots, c_M) = G + \hat{\psi}_0 + L\left(\sum_{j=1}^{M} q_j c_j\right). \qquad (3.11)
$$

Moreover, the functional $F_0 : V_0 \to \mathbb{R}$ and $F_a : V_a \to \mathbb{R}$ can be rewritten as

$$F_0[c] = \frac{1}{2}\int_{\Omega_s}\left(\sum_{j=1}^M q_j c_j\right) L \left(\sum_{j=1}^M q_j c_j\right) dx + \sum_{j=1}^M \int_{\Omega_s} \mu_{0j} c_j dx \\ + \beta^{-1}\sum_{j=1}^M \int_{\Omega_s} S_{-1}(c_j)dx + E_0, \qquad \forall c = (c_1, \ldots, c_M) \in V_0, \tag{3.12}$$

$$F_a[c] = \frac{1}{2}\int_{\Omega_s}\left(\sum_{j=1}^M q_j c_j\right) L \left(\sum_{j=1}^M q_j c_j\right) dx + \sum_{j=1}^M \int_{\Omega_s} \mu_{aj} c_j dx \\ + \beta^{-1}\sum_{j=0}^M \int_{\Omega_s} S_{-1}(c_j)dx + E_a \qquad \forall c = (c_1, \ldots, c_M) \in V_a, \tag{3.13}$$

respectively, where

$$\mu_{0j}(x) = q_j G(x) + \frac{1}{2} q_j \hat{\psi}_0(x) + 3\beta^{-1}\log a - \mu_j \qquad \forall x \in \Omega_s,\ j = 1, \ldots, M, \tag{3.14}$$

$$E_0 = \frac{1}{2}\sum_{i=1}^N Q_i \left(G + \hat{\psi}_0 - \psi_{vac}\right)(x_i), \tag{3.15}$$

$$\mu_{aj}(x) = q_j G(x) + \frac{1}{2} q_j \hat{\psi}_0(x) - \mu_j \qquad \forall x \in \Omega_s,\ j = 1, \ldots, M, \tag{3.16}$$

$$E_a = \frac{1}{2}\sum_{i=1}^N Q_i \left(G + \hat{\psi}_0 - \psi_{vac}\right)(x_i) + 3\beta^{-1} a^{-3}(\log a)|\Omega_s|, \tag{3.17}$$

where $|E|$ denotes the Lebesgue measure of a Lebesgue measurable set $E \subset \mathbb{R}^3$.

LEMMA 3.3. *Let $D \subset \mathbb{R}^3$ be a bounded and open set. Let $\alpha \in \mathbb{R}$. Let $\{u^{(k)}\}$ be a sequence of functions in $L^1(D)$ such that $u^{(k)} \geq 0$ a.e. D for each $k \geq 1$ and that*

$$\sup_{k\geq 1} \int_D S_\alpha\left(u^{(k)}\right) dx < \infty.$$

Then there exists a subsequence $\{u^{(k_j)}\}$ of $\{u^{(k)}\}$ such that $\{u^{(k_j)}\}$ converges weakly in $L^1(D)$ to some $u \in L^1(D)$ with $u \geq 0$ a.e. D and

$$\int_D S_\alpha(u)\, dx \leq \liminf_{k\to\infty} \int_D S_\alpha\left(u^{(k)}\right) dx.$$

Proof. Since $S_\alpha : [0, \infty) \to \mathbb{R}$ is bounded below, by passing to a subsequence if necessary, we may assume that the limit

$$A := \lim_{k\to\infty} \int_D S_\alpha\left(u^{(k)}\right) dx = \liminf_{k\to\infty} \int_D S_\alpha\left(u^{(k)}\right) dx \tag{3.18}$$

exists and is finite. Since $S_\alpha(\lambda)/\lambda \to +\infty$ as $\lambda \to +\infty$, $\{u^{(k)}\}$ is weakly sequentially compact in $L^1(D)$ by de la Vallée Poussin's criterion [25]. Therefore, this sequence has a subsequence, not relabeled, that converges weakly in $L^1(D)$ to some $u \in L^1(D)$. Clearly, $u \geq 0$ a.e. D.

Let $\varepsilon > 0$. By (3.18), there exists an integer $K > 0$ such that

$$\int_D S_\alpha\left(u^{(k)}\right) dx \leq A + \varepsilon \qquad \forall k > K. \tag{3.19}$$

By Mazur's theorem [7, 32], there exist convex combinations $v^{(k)}$ of $u^{(K+1)}, \dots, u^{(K+k)}$ for all $k \geq 1$ such that $v^{(k)} \to u$ in $L^1(D)$. Let $v^{(k)} = \sum_{j=1}^k \lambda_{k,j} u^{(K+j)}$ with $\lambda_{k,j} \geq 0$ for all j and k, and $\sum_{j=1}^k \lambda_{k,j} = 1$ for all k. Since $S_\alpha : [0,\infty) \to \mathbb{R}$ is convex, we have by Jensen's inequality and (3.19) that

$$S_\alpha\left(v^{(k)}\right) \leq \sum_{j=1}^k \lambda_{k,j} S_\alpha\left(u^{(K+j)}\right) \leq \sum_{j=1}^k \lambda_{k,j}(A+\varepsilon) = A + \varepsilon \qquad \forall k \geq 1. \tag{3.20}$$

Since $v^{(k)} \to u$ in $L^1(D)$, there exists a subsequence $\{v^{(k_j)}\}$ of $\{v^{(k)}\}$ such that $v^{k_j}(x) \to u(x)$ a.e. $x \in D$. Consequently, since $S_\alpha : [0,\infty) \to \mathbb{R}$ is continuous and bounded below, we have by Fatou's lemma and (3.20) that

$$\int_D S_\alpha(u(x))\, dx = \int_D \lim_{j\to\infty} S_\alpha\left(v^{k_j}(x)\right) dx \leq \liminf_{j\to\infty} \int_D S_\alpha\left(v^{k_j}(x)\right) dx \leq A + \varepsilon,$$

concluding the proof by the arbitrariness of $\varepsilon > 0$. ∎

The next two lemmas state some boundedness of concentrations that have low free energies. Their proofs are somewhat tedious, and are given in Appendix A.

LEMMA 3.4. *Let $c = (c_1, \dots, c_M) \in W_0$ satisfy that $c \notin L^\infty(\Omega, \mathbb{R}^M)$ or there exists $j \in \{1, \dots, M\}$ with $|\{x \in \Omega_s : c_j(x) < \alpha\}| > 0$ for all $\alpha > 0$. Then for any $\varepsilon > 0$ there exist $\hat{c} = (\hat{c}_1, \dots, \hat{c}_M) \in W_0$ that satisfies* (2.5) *with c replaced by $\hat{c}$, $\|\hat{c} - c\|_X < \varepsilon$, and $F_0[\hat{c}] < F_0[c]$.*

LEMMA 3.5. *Let $c = (c_1, \dots, c_M) \in V_a$ and c_0 be defined by* (1.3). *Assume there exists $j \in \{0, 1, \dots, M\}$ such that $|\{x \in \Omega_s : a^3 c_j(x) < \alpha\}| > 0$ for all $\alpha > 0$. Let $\varepsilon > 0$. Then there exists $\hat{c} = (\hat{c}_1, \dots, \hat{c}_M) \in V_a$ that satisfies* (2.6) *with c replaced by $\hat{c}$, $\|\hat{c} - c\|_X < \varepsilon$, and $F_a[\hat{c}] < F_a[c]$.*

4. The Poisson–Boltzmann equation: Proof of Theorems 2.1 and 2.2.

Proof of Theorem 2.1. It is easy to verify that the function $B : \mathbb{R} \to \mathbb{R}$ defined in (1.14) is convex for both the case of point ions and that of finite-size ions. Let

$$\mathcal{K} := \left\{u \in H^1(\Omega) : u = \psi_0 \text{ on } \partial\Omega \text{ and } \chi_{\Omega_s} B(u) \in L^2(\Omega)\right\}.$$

Clearly, $\mathcal{K} \neq \emptyset$ since $\psi_0 \in \mathcal{K}$ and $\mathcal{K}$ is convex since $B : \mathbb{R} \to \mathbb{R}$ is convex. We show now that $\mathcal{K}$ is closed in $H^1(\Omega)$. Let $u_k \in \mathcal{K}$ $(k = 1, 2, \dots)$ and $u_k \to u$ in $H^1(\Omega)$

for some $u \in H^1(\Omega)$. Clearly, $u = \psi_0$ on $\partial\Omega$. Up to a subsequence, not relabeled, $u_k(x) \to u(x)$ a.e. $x \in \Omega$. Since $B : \mathbb{R} \to \mathbb{R}$ is convex and positive, we have

$$\frac{d^2}{dv^2}\left([B(v)]^2\right) = 2[B'(v)]^2 + 2B(v)B''(v) > 0 \qquad \forall v \in \mathbb{R}.$$

Thus, $v \mapsto [B(v)]^2$ is convex. It then follows from Fatou's lemma, Jensen's inequality, and the $H^1(\Omega)$-boundedness of $\{u_k\}$ that

$$\begin{aligned}\frac{1}{|\Omega_s|}\int_{\Omega_s}[B(u)]^2\,dx &\le \liminf_{k\to\infty}\frac{1}{|\Omega_s|}\int_{\Omega_s}[B(u_k)]^2\,dx \\ &\le \liminf_{k\to\infty}\left[B\left(\frac{1}{|\Omega_s|}\int_{\Omega_s}u_k dx\right)\right]^2 < \infty.\end{aligned}$$

This implies that $u \in \mathcal{K}$. Therefore, $\mathcal{K}$ is closed in $H^1(\Omega)$. Since $\mathcal{K}$ is convex, it is also weakly closed in $H^1(\Omega)$.

Define now $J : \mathcal{K} \to \mathbb{R}$ by

$$J[u] = \int_\Omega \left[\frac{\varepsilon_\Gamma}{2}|\nabla u|^2 + 4\pi\chi_{\Omega_s}B\left(u + G - \frac{\hat{\psi}_0}{2}\right)\right]dx \qquad \forall u \in \mathcal{K},$$

where G and $\hat{\psi}_0$ are defined in (3.5) and (1.10), respectively. Note that $\psi_0 \in \mathcal{K}$ and that $J[\psi_0] < \infty$. By the Poincaré inequality, there exist constants $C_3 > 0$ and $C_4 \ge 0$ such that $J[u] \ge C_3\|u\|^2_{H^1(\Omega)} - C_4$ for all $u \in \mathcal{K}$. Thus, $\alpha := \inf_{u\in\mathcal{K}} J[u]$ is finite. Let $v_k \in \mathcal{K}$ $(k = 1, 2 \dots)$ be such that $\lim_{k\to\infty} J[v_k] = \alpha$. Then, $\{v_k\}$ is bounded in $H^1(\Omega)$ and, hence, it has a subsequence, not relabeled, that weakly converges to some $v \in H^1(\Omega)$. Since $\mathcal{K}$ is weakly closed, $v \in \mathcal{K}$. Since the embedding $H^1(\Omega) \hookrightarrow L^2(\Omega)$ is compact, up to a further subsequence, again not relabeled, $v_k \to v$ a.e. in Ω. Therefore, since $B : \mathbb{R} \to \mathbb{R}$ is continuous and nonnegative, Fatou's lemma implies

$$\liminf_{k\to\infty}\int_\Omega \chi_{\Omega_s}B\left(v_k + G - \frac{\hat{\psi}_0}{2}\right)dx \ge \int_\Omega \chi_{\Omega_s}B\left(v + G - \frac{\hat{\psi}_0}{2}\right)dx.$$

Since $u \mapsto \int_\Omega \varepsilon_\Gamma|\nabla u|^2 dx$ is convex and $H^1(\Omega)$ continuous, it is sequentially weakly lower semicontinuous. Consequently, $\liminf_{k\to\infty} J[v_k] \ge J[v]$. Thus, v is a minimizer of $J : \mathcal{K} \to \mathbb{R}$.

Notice that $\chi_{\Omega_s}B'(v + G - \hat{\psi}_0/2) \in L^2(\Omega_s)$. Simple calculations of the first variation of $J : \mathcal{K} \to \mathbb{R}$ at any $\eta \in C_c^\infty(\Omega)$ leads to

$$\int_\Omega \left[\varepsilon_\Gamma \nabla v \cdot \nabla\eta + 4\pi\chi_{\Omega_s}B'\left(v + G - \frac{\hat{\psi}_0}{2}\right)\eta\right]dx = 0 \qquad \forall \eta \in C_c^\infty(\Omega).$$

The function $\psi = v + G$ is, thus, a needed solution.

We now prove the uniqueness. Let ϕ be another weak solution. Let $\xi = \psi - \phi$. Then, $\xi \in H^1_*(\Omega)$, $\xi = 0$ on $\partial\Omega$, and

$$\int_\Omega \left\{\varepsilon_\Gamma \nabla\xi \cdot \nabla\eta + 4\pi\chi_{\Omega_s}\left[B'\left(\psi - \frac{\hat{\psi}_0}{2}\right) - B'\left(\phi - \frac{\hat{\psi}_0}{2}\right)\right]\eta\right\}dx = 0 \qquad \forall \eta \in C_c^\infty(\Omega).$$

Choosing the test functions $\eta \in C_c^\infty(\Omega)$ so that $\operatorname{supp}\eta \subset \Omega_m$, we find that ξ is harmonic in Ω_m. This and the fact that $\xi \in H_*^1(\Omega)$ imply that $\xi \in H_0^1(\Omega)$. Thus, the above test functions η can be chosen from $H_0^1(\Omega)$. In particular, setting $\eta = \xi$ and using the convexity of $B : \mathbb{R} \to \mathbb{R}$, we obtain that $\xi = 0$ and, hence, $\psi = \phi$ in $H^1(\Omega)$.

Let $\sigma > 0$ be such that the closure of $B_\sigma := \cup_{i=1}^N B(x_i, \sigma)$ is contained in Ω_m. Clearly, the unique weak solution $\psi \in H_*^1(\Omega)$ satisfies

$$\int_{\Omega\setminus\overline{B_\sigma}} \varepsilon_\Gamma \nabla\psi \cdot \nabla\eta dx = \int_{\Omega\setminus\overline{B_\sigma}} g\eta dx \qquad \forall \eta \in C_c^\infty\left(\Omega \setminus \overline{B_\sigma}\right), \tag{4.1}$$

where $g = -4\pi\chi_{\Omega_s} B'(\psi - \hat{\psi}_0/2) \in L^2(\Omega \setminus \overline{B_\sigma})$. Therefore, $\psi \in C(\overline{\Omega} \setminus B_\sigma)$ by the standard regularity theory [14]. Since $\varepsilon_\Gamma = \varepsilon_m$ in Ω_m and $\varepsilon_\Gamma = \varepsilon_s$ in Ω_s, ψ is harmonic in $\Omega_m \setminus \overline{B_\sigma}$. Hence, $\psi \in C^\infty(\Omega_m \setminus \overline{B_\sigma})$. Notice that $B \in C^\infty(\mathbb{R})$; thus, we have $\psi \in C^\infty(\Omega_s)$ by a standard bootstrapping argument. ∎

Proof of Theorem 2.2. Let $\psi \in H_*^1(\Omega)$ be a weak solution to the boundary-value problem (1.13) and (1.6). Clearly, $\psi_m \in H_*^1(\Omega_m)$. For any $\eta \in C_c^\infty(\Omega_m)$, we extend η to the entire Ω by defining $\eta = 0$ outside Ω_m. Then, we obtain (2.2) from (2.1). Since all $x_i \in \Omega_m$ $(i = 1, \ldots, N)$, we have $\psi_s \in H^1(\Omega_s)$. Since $\chi_{\Omega_s} B(\psi) \in L^2(\Omega_s)$, it follows from (1.14) that $\chi_{\Omega_s} B'(\psi) \in L^2(\Omega_s)$. For any $\eta \in C_c^\infty(\Omega_s)$, we, again, extend η to Ω by defining $\eta = 0$ outside Ω_s. Then, we obtain (2.3) from (2.1). Finally, by Lemma 3.1, (4.1), and (1.6), the last two equations in (1.15) hold true. Hence, ψ is a weak solution to (1.15).

Now let $\psi : \Omega \to \mathbb{R}$ be a solution to the boundary-value problem (1.15). We first show that $\psi \in H_*^1(\Omega)$. Let $\sigma > 0$ be small enough so that the closure of $B_\sigma := \cup_{i=1}^N B(x_i, \sigma)$ is contained in Ω_m. Since $\psi_m \in H_*^1(\Omega_m)$, $\psi_m \in H^1(\Omega_m \setminus \overline{B_\sigma})$. Thus, the trace $\psi_m|_\Gamma \in L^2(\Gamma)$, and is independent on the choice of σ. Similarly, $\psi_s \in H^1(\Omega_s)$, and, hence, $\psi_s|_\Gamma \in L^2(\Gamma)$. Fix $j \in \{1, 2, 3\}$. Define $\xi_j : \Omega \setminus \overline{B_\sigma} \to \mathbb{R}$ by $\xi_j = \partial_j \psi_m$ in $\Omega_m \setminus \overline{B_\sigma}$ and $\xi_j = \partial_j \psi_s$ in Ω_s. Clearly, $\xi_j \in L^2(\Omega \setminus \overline{B_\sigma})$. Let n_j be the jth component of the unit exterior normal n at Γ, pointing from Ω_s to Ω_m. Then, for any $\eta \in C_c^\infty(\Omega \setminus \overline{B_\sigma})$, we have

$$\begin{aligned}
\int_{\Omega\setminus\overline{B_\sigma}} \xi_j \eta \, dx &= \int_{\Omega_m\setminus\overline{B_\sigma}} (\partial_j \psi_m)\eta \, dx + \int_{\Omega_s} (\partial_j \psi_s)\eta \, dx \\
&= -\int_{\Omega_m\setminus\overline{B_\sigma}} \psi \partial_j \eta \, dx - \int_\Gamma \psi_m \eta n_j \, dS - \int_{\Omega_s} \psi \partial_j \eta \, dx + \int_\Gamma \psi_s \eta n_j \, dS \\
&= -\int_{\Omega\setminus\overline{B_\sigma}} \psi \partial_j \eta \, dx + \int_\Gamma [\![\psi]\!] n_j \eta \, dS \\
&= -\int_{\Omega\setminus\overline{B_\sigma}} \psi \partial_j \eta \, dx,
\end{aligned}$$

where in the last step we used the fact that $[\![\psi]\!] = 0$ on Γ. Thus, $\xi_j = \partial_j \psi \in L^2(\Omega \setminus \overline{B_\sigma})$, and, hence, $\psi \in H_*^1(\Omega)$ by the arbitrariness of $\sigma > 0$.

Clearly, $\chi_{\Omega_s} B'(\psi) \in L^2(\Omega_s)$ and $\psi = \psi_0$ on $\partial\Omega$. It remains to show that (2.1) holds true. Let $\eta \in C_c^\infty(\Omega)$. Let V_1 and V_2 be two open sets in $\mathbb{R}^3$ such that ∂V_1 and ∂V_2 are of C^2, $x_i \notin V_2$ for $i = 1, \ldots, N$, and $\Gamma \subset V_1 \subset \overline{V}_1 \subset V_2 \subset \overline{V}_2 \subset \Omega$. Let

$\zeta \in C_c^\infty(\Omega)$ be such that $\operatorname{supp} \zeta \subset V_2$ and $\zeta = 1$ on V_1. Then, $(1-\zeta)\eta|_{\Omega_m} \in C_c^\infty(\Omega_m)$, $(1-\zeta)\eta|_{\Omega_s} \in C_c^\infty(\Omega_s)$, and $(1-\zeta(x_i))\eta(x_i) = \eta(x_i)$, $i = 1, \dots, N$. We, thus, have by (2.2) and (2.3) that

$$
\begin{aligned}
&\int_\Omega \left[\varepsilon_\Gamma \nabla\psi \cdot \nabla\eta + 4\pi\chi_{\Omega_s} B'\left(\psi - \frac{\hat{\psi}_0}{2}\right)\eta \right] dx \\
&\quad = \int_\Omega \left[\varepsilon_\Gamma \nabla\psi \cdot \nabla((1-\zeta)\eta) + 4\pi\chi_{\Omega_s} B'\left(\psi - \frac{\hat{\psi}_0}{2}\right)(1-\zeta)\eta \right] dx \\
&\qquad + \int_\Omega \left[\varepsilon_\Gamma \nabla\psi \cdot \nabla(\zeta\eta) + 4\pi\chi_{\Omega_s} B'\left(\psi - \frac{\hat{\psi}_0}{2}\right)\zeta\eta \right] dx \\
&\quad = \int_{\Omega_m} \varepsilon_\Gamma \nabla\psi \cdot \nabla((1-\zeta)\eta) dx \\
&\qquad + \int_{\Omega_s} \left[\varepsilon_\Gamma \nabla\psi \cdot \nabla((1-\zeta)\eta) + 4\pi\chi_{\Omega_s} B'\left(\psi - \frac{\hat{\psi}_0}{2}\right)(1-\zeta)\eta \right] dx \\
&\qquad + \int_{V_2} \left[\varepsilon_\Gamma \nabla\psi \cdot \nabla(\zeta\eta) + 4\pi\chi_{\Omega_s} B'\left(\psi - \frac{\hat{\psi}_0}{2}\right)\zeta\eta \right] dx \\
&\quad = 4\pi \sum_{i=1}^N Q_i \eta(x_i) + \int_{V_2} \left[\varepsilon_\Gamma \nabla\psi \cdot \nabla(\zeta\eta) + 4\pi\chi_{\Omega_s} B'\left(\psi - \frac{\hat{\psi}_0}{2}\right)\zeta\eta \right] dx. \qquad (4.2)
\end{aligned}
$$

We now show that the second term in (4.2) is zero. Notice that $\psi|_{V_2} \in H^1(V_2)$ and $x_i \notin V_2$ $(1 \le i \le N)$. Denoting $V_m = V_2 \cap \Omega_m$ and $V_s = V_2 \cap \Omega_s$, we have by (2.2) and (2.3) that

$$
\begin{aligned}
&\int_{V_m} \varepsilon_m \nabla\psi \cdot \nabla\xi \, dx = 0 \qquad \forall \xi \in C_c^\infty(V_m), \\
&\int_{V_s} \varepsilon_s \nabla\phi \cdot \nabla\xi \, dx = -4\pi \int_{V_s} B'\left(\psi - \frac{\hat{\psi}_0}{2}\right)\xi \, dx \qquad \forall \xi \in C_c^\infty(V_s).
\end{aligned}
$$

Consequently, since $\chi_{\Omega_s} B'(\psi - \hat{\psi}_0/2) \in L^2(\Omega_s)$, we infer from the regularity theory of elliptic boundary-value problems [14] that $\psi|_{V_m} \in H^2(V_m)$ and $\psi|_{V_s} \in H^2(V_s)$, and that

$$
\begin{aligned}
\nabla \cdot \varepsilon_m \nabla\psi &= 0 \qquad \text{a.e. } V_m, \\
\nabla \cdot \varepsilon_s \nabla\psi - 4\pi B'\left(\psi - \frac{\hat{\psi}_0}{2}\right) &= 0 \qquad \text{a.e. } V_s.
\end{aligned}
$$

Therefore, the trace of $\varepsilon_m \nabla\psi \cdot n$ and that of $\varepsilon_s \nabla\psi \cdot n$ on Γ both exist. Moreover,

$$
\begin{aligned}
&\int_{V_2} \left[\varepsilon_\Gamma \nabla\psi \cdot \nabla(\zeta\eta) + 4\pi\chi_{\Omega_s} B' \left(\psi - \frac{\hat{\psi}_0}{2} \right) \zeta\eta \right] dx \\
&= \int_{V_m} \varepsilon_m \nabla\psi \cdot \nabla(\zeta\eta) dx + \int_{V_s} \left[\varepsilon_s \nabla\psi \cdot \nabla(\zeta\eta) + 4\pi\chi_{\Omega_s} B' \left(\psi - \frac{\hat{\psi}_0}{2} \right) \zeta\eta \right] dx \\
&= -\int_{V_m} (\nabla \cdot \varepsilon_m \nabla\psi)\zeta\eta \, dx - \int_\Gamma (\varepsilon_m \nabla\psi \cdot n)\zeta\eta \, dS \\
&\quad + \int_{V_s} \left[-(\nabla \cdot \varepsilon_s \nabla\psi)(\zeta\eta) + 4\pi\chi_{\Omega_s} B' \left(\psi - \frac{\hat{\psi}_0}{2} \right) \zeta\eta \right] dx + \int_\Gamma (\varepsilon_s \nabla\psi \cdot n)\zeta\eta \, dS \\
&= \int_\Gamma [\![\varepsilon \nabla\psi \cdot n]\!] \zeta\eta \, dS \\
&= 0,
\end{aligned}
\tag{4.3}
$$

where in the last step, we used the third equation of (1.15). Now, since $\eta \in C_c^\infty(\Omega)$ is arbitrary, we obtain (2.1) from (4.2) and (4.3). ∎

5. Minimization of the electrostatic free energy: Proof of Theorems 2.3, 2.4, and 2.5.

Proof of Theorem 2.3. Let $t = 1 + \beta \max_{1\le j\le M} \|\mu_{0j}\|_{L^\infty(\Omega_s)}$, where μ_{0j} ($j = 1, \dots, M$) are defined in (3.14). It follows from (3.12) and (3.4) that there exists $C_5 > 0$ such that

$$
F_0[c] \ge C_5 \left\| \sum_{j=1}^M q_j c_j \right\|_{H^{-1}(\Omega)}^2 + \beta^{-1} \sum_{j=1}^M \int_{\Omega_s} S_{-t}(c_j) dx + E_0 \qquad \forall c = (c_1, \dots, c_M) \in V_0,
\tag{5.1}
$$

where E_0 is defined in (3.15). Let $z = \inf_{c\in V_0} F_0[c]$. Since $S_{-t} : [0, \infty) \to \mathbb{R}$ is bounded below, z is finite.

Let $c^{(k)} = (c_1^{(k)}, \dots, c_M^{(k)}) \in V_0$ ($k = 1, 2, \dots$) be such that $\lim_{k\to\infty} F_0[c^{(k)}] = z$. It follows from (5.1) that $\{\int_{\Omega_s} S_{-t}(c_j^{(k)})dx\}$ is bounded for each $j = 1, \dots, M$. Therefore, by Lemma 3.3, up to a subsequence that is not relabeled, $\{c_j^{(k)}\}$ converges weakly in $L^1(\Omega_s)$ to some $c_j \in L^1(\Omega_s)$, and

$$
\int_{\Omega_s} S_{-t}(c_j) \, dx \le \liminf_{k\to\infty} \int_{\Omega_s} S_{-t}\left(c_j^{(k)} \right) dx < \infty \qquad j = 1, \dots, M.
\tag{5.2}
$$

Define $c_j = 0$ on Ω_m for all $j = 1, \dots, M$. By (5.1), $\{\sum_{j=1}^M q_j c_j^{(k)}\}$ is bounded in $H^{-1}(\Omega)$. Since $H^{-1}(\Omega)$ is a Hilbert space, $\{\sum_{j=1}^M q_j c_j^{(k)}\}$ has a subsequence, again not relabeled, that weakly converges to some $F \in H^{-1}(\Omega)$. Let $\xi \in L^\infty(\Omega) \cap H_0^1(\Omega)$. We have

$$
F(\xi) = \lim_{k\to\infty} \int_\Omega \left(\sum_{j=1}^M q_j c_j^{(k)} \right) \xi dx = \int_\Omega \left(\sum_{j=1}^M q_j c_j \right) \xi dx.
$$

Therefore, $\sum_{j=1}^M q_j c_j \in H^{-1}(\Omega)$ and, hence, $c = (c_1, \dots, c_M) \in V_0$.

By (5.2) and the fact that the norm of a Banach space is sequentially weakly lower semicontinuous, we have $z = \liminf_{k\to\infty} F_0[c^{(k)}] \geq F_0[c] \geq z$. This implies that $c \in V_0$ is a global minimizer of $F_0 : V_0 \to \mathbb{R}$.

Let $d = (d_1, \dots, d_M) \in V_0$ be a local minimizer of $F_0 : V_0 \to \mathbb{R}$. Then for $\lambda \in (0,1)$ close to 0, we have by the convexity of $F_0 : V_0 \to \mathbb{R}$ that

$$F_0[d] \leq F_0[\lambda c + (1-\lambda)d] \leq \lambda F_0[c] + (1-\lambda)F_0[d],$$

leading to $F_0[d] \leq F_0[c]$. Thus, d is also a global minimizer of $F_0 : V_0 \to \mathbb{R}$. Clearly, $(c+d)/2 \in V_0$. Consequently, it follows from the definition of the norm $\||\cdot\||$ and the Cauchy–Schwarz inequality with respect to the inner product $\langle \xi, \eta \rangle = \xi(L\eta)$ $(\xi, \eta \in H^{-1}(\Omega))$ that

$$\begin{aligned}
0 &\leq F_0\left[\frac{c+d}{2}\right] - \min_{e\in V_0} F_0[e] \\
&= F_0\left[\frac{c+d}{2}\right] - \frac{1}{2}F_0[c] - \frac{1}{2}F_0[d] \\
&= \frac{1}{8}\left\|\left|\sum_{j=1}^M q_j(c_j+d_j)\right|\right\|^2 - \frac{1}{4}\left\|\left|\sum_{j=1}^M q_j c_j\right|\right\|^2 - \frac{1}{4}\left\|\left|\sum_{j=1}^M q_j d_j\right|\right\|^2 \\
&\quad + \beta^{-1}\sum_{j=1}^M \int_{\Omega_s}\left[S_{-1}\left(\frac{c_j+d_j}{2}\right) - \frac{1}{2}S_{-1}(c_j) - \frac{1}{2}S_{-1}(d_j)\right]dx \\
&\leq \beta^{-1}\sum_{j=1}^M \int_{\Omega_s}\left[S_{-1}\left(\frac{c_j+d_j}{2}\right) - \frac{1}{2}S_{-1}(c_j) - \frac{1}{2}S_{-1}(d_j)\right]dx.
\end{aligned}$$

This, together with the convexity of S_{-1} on $[0,\infty)$, implies that

$$S_{-1}\left(\frac{c_j(x)+d_j(x)}{2}\right) = \frac{1}{2}S_{-1}(c_j(x)) + \frac{1}{2}S_{-1}(d_j(x)) \qquad \forall j = 1,\dots,M,\ \forall x \in \Omega_s \backslash \omega_s,$$

for some $\omega_s \subset \Omega_s$ with $|\omega_s| = 0$. Let $x \in \Omega_s \setminus \omega_s$. Then it follows from the definition of $S_{-1} : [0,\infty) \to \mathbb{R}$ that $c_j(x) = 0$ if and only if $d_j(x) = 0$ for all $j = 1,\dots,M$. The strict convexity of S_0 on $(0,\infty)$ then implies that $c = d$ a.e. Ω_s. Hence, $c = d$ in V_0. ◻

Proof of Theorem 2.4. (1) Let $c = (c_1,\dots,c_M) \in W_0$. We show that the following four statements are equivalent:

(i) c is an equilibrium of $F_0 : W_0 \to \mathbb{R}$;

(ii) The property (2.5) holds true, and

$$q_j L\left(\sum_{j=1}^M q_j c_j\right) + \mu_{0j} + \beta^{-1}\log c_j = 0 \qquad \text{a.e. } \Omega_s, \quad j = 1,\dots,M; \tag{5.3}$$

(iii) c is a global minimizer of $F_0 : W_0 \to \mathbb{R}$;

(iv) c is a local minimizer of $F_0 : W_0 \to \mathbb{R}$.

Assume (i) is true. Then (2.5) holds true by Definition 2.3. Let $e = (e_1,\dots,e_M) \in X \cap L^\infty(\Omega,\mathbb{R}^M)$. Notice that $S_{-1}'(u) = \log u$ for any $u > 0$. Thus, for each $j \in \{1,\dots,M\}$ and each $x \in \Omega_s$, the mean-value theorem implies the existence of $\theta_j(x) \in [0,1]$ such that

$$S_{-1}(c_j(x) + te_j(x)) - S_{-1}(c_j(x)) = te_j(x)\log(c_j(x) + t\theta_j(x)e_j(x)).$$

Hence, by the Lebesgue dominated convergence theorem,

$$\lim_{t\to 0}\int_{\Omega_s}\frac{S_{-1}(c_j+te_j)-S_{-1}(c_j)}{t}dx=\int_{\Omega_s}e_j\log c_j\,dx,\qquad j=1,\dots,M.$$

Therefore, it follows from Definition 2.3, the definition of the norm $\|\!|\cdot|\!\|$, (3.12), and (3.4) that

$$\begin{aligned}
0&=\delta F_0[c]e\\
&=\lim_{t\to 0}\frac{F_0[c+te]-F_0[c]}{t}\\
&=\lim_{t\to 0}\left\{\frac{1}{2}t\left|\!\left|\!\left|\sum_{j=1}^M q_je_j\right|\!\right|\!\right|^2+\int_{\Omega_s}\left(\sum_{j=1}^M q_je_j\right)L\left(\sum_{j=1}^M q_jc_j\right)dx\right.\\
&\qquad\left.+\sum_{j=1}^M\int_{\Omega_s}\mu_{0j}e_jdx+\beta^{-1}\sum_{j=1}^M\int_{\Omega_s}\frac{1}{t}\left[S_{-1}(c_j+te_j)-S_{-1}(c_j)\right]dx\right\}\\
&=\sum_{j=1}^M\int_{\Omega_s}\left[q_jL\left(\sum_{j=1}^M q_jc_j\right)+\mu_{0j}+\beta^{-1}\log c_j\right]e_jdx\qquad\forall e\in X\cap L^\infty\left(\Omega,\mathbb{R}^M\right).
\end{aligned}\tag{5.4}$$

This implies (5.3). Hence, (ii) is true.

Assume (ii) is true. We show that (iii) is true. By Lemma 3.4, we need only to show that $F_0[c]\le F_0[d]$ for any fixed $d=(d_1,\dots,d_M)\in W_0$ that satisfies (2.5) with c replaced by d. 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

$$S_{-1}(d_j)-S_{-1}(c_j)\ge(d_j-c_j)S'_{-1}(c_j)=e_j\log c_j\qquad\text{a.e. }\Omega_s.$$

Therefore, it follows from (3.12) and (5.3) that

$$\begin{aligned}
F_0[d]-F_0[c]&=\frac{1}{2}\int_{\Omega_s}\left(\sum_{j=1}^M q_je_j\right)L\left(\sum_{j=1}^M q_je_j\right)dx+\int_{\Omega_s}\left(\sum_{j=1}^M q_je_j\right)L\left(\sum_{j=1}^M q_jc_j\right)dx\\
&\qquad+\sum_{j=1}^M\int_{\Omega_s}\mu_{0j}e_jdx+\beta^{-1}\sum_{j=1}^M\int_{\Omega_s}\left[S_{-1}(d_j)-S_{-1}(c_j)\right]dx\\
&\ge\sum_{j=1}^M\int_{\Omega_s}\left[q_jL\left(\sum_{i=1}^M q_ic_i\right)+\mu_{0j}+\beta^{-1}\log c_j\right]e_jdx\\
&=0.
\end{aligned}$$

Hence, $F_0[c]\le F_0[d]$, and (iii) is true.

Clearly, (iii) implies (iv).

Finally, assume (iv) is true. By Lemma 3.4, (2.5) holds true. For any $e\in X\cap L^\infty(\Omega,\mathbb{R}^M)$, it is easy to see that $\delta F_0[c]e$ exists, cf. (5.4). Since $F_0[c+te]\ge F_0[c]$ for $|t|$ small enough, we have $\delta F_0[c]e=0$. Therefore, c is an equilibrium of $F_0:W_0\to\mathbb{R}$, and (i) is true.

Let now $\psi \in H^1_*(\Omega)$ be the unique weak solution to the boundary-value problem of the PBE (1.11) and (1.6), cf. Theorem 2.1. Define $c = (c_1, \dots, c_M) : \Omega \to \mathbb{R}$ by (1.9) for point ions and $c_j(x) = 0$ for all $x \in \Omega_m$ and all $j = 1, \dots, M$. Clearly, $c \in W_0$. Moreover, by Theorem 2.1, $\psi|_{\Omega_s} \in C(\overline{\Omega_s})$. This implies (2.5). It follows from (1.11), (1.6), (1.9) for point ions, and Lemma 3.2 with $f = \sum_{j=1}^M q_j c_j$ that ψ is the electrostatic potential corresponding to c; i.e., $\psi = G + \hat{\psi}_0 + L(\sum_{j=1}^M q_j c_j)$. This, together with the Boltzmann relations (1.9) for point ions and (3.14), implies (5.3). Hence, c is an equilibrium, and, thus, a local and global minimizer, of $F_0 : W_0 \to \mathbb{R}$. The uniqueness of equilibria or local minimizers is equivalent to that of global minimizers, and can be proved by the same argument used in the proof of Theorem 2.3.

(2) It is clear that from our definition of c and ψ that we need only to prove (2.7). Since c is the unique minimizer of $F_0 : W_0 \to \mathbb{R}$ and ψ is the corresponding electrostatic potential determined by (3.11), we have by (1.1) and (1.9) for point ions that

$$\begin{aligned}
\min_{d \in W_0} F_0[d] &= F_0[c] \\
&= \frac{1}{2} \sum_{i=1}^N Q_i(\psi - \psi_{vac})(x_i) + \frac{1}{2} \int_{\Omega_s} \left(\sum_{j=1}^M q_j c_j \right) \psi dx \\
&\quad + \beta^{-1} \sum_{j=1}^M \int_{\Omega_s} c_j \left[\log\left(a^3 c_j\right) - 1 \right] dx - \sum_{j=1}^M \int_{\Omega_s} \mu_j c_j dx \\
&= \frac{1}{2} \sum_{i=1}^N Q_i(\psi - \psi_{vac})(x_i) - \frac{1}{2} \sum_{j=1}^M \int_{\Omega_s} q_j c_j^\infty e^{-\beta q_j \left(\psi - \hat{\psi}_0/2\right)} \left(\psi - \hat{\psi}_0\right) dx \\
&\quad - \beta^{-1} \sum_{j=1}^M \int_{\Omega_s} c_j^\infty e^{-\beta q_j \left(\psi - \hat{\psi}_0/2\right)} dx.
\end{aligned} \tag{5.5}$$

Since ψ is the unique solution to the boundary-value problem of PBE (1.11) and (1.6), and since $\hat{\psi}_0$ is harmonic in Ω_s by (1.10), we have

$$\varepsilon_s \Delta \left(\psi - \hat{\psi}_0\right) + 4\pi \sum_{j=1}^M q_j c_j^\infty e^{-\beta q_j \left(\psi - \hat{\psi}_0/2\right)} = 0 \qquad \text{a.e. } \Omega_s.$$

Multiplying both sides of this equation by $\psi - \hat{\psi}_0$ and integrate the resulting terms over Ω_s, we obtain by integration by parts and the fact that by Lemma 3.1 both $\psi - \hat{\psi}_0$ and $\varepsilon_\Gamma \partial_n(\psi - \hat{\psi}_0)$ are continuous across Γ,

$$\begin{aligned}
&- \int_{\Omega_s} \varepsilon_s \left| \nabla \left(\psi - \hat{\psi}_0\right) \right|^2 dx + \int_\Gamma \varepsilon_\Gamma \left(\psi - \hat{\psi}_0\right) \partial_n \left(\psi - \hat{\psi}_0\right) dS \\
&\quad + 4\pi \sum_{j=1}^M \int_{\Omega_s} q_j c_j^\infty e^{-\beta q_j \left(\psi - \hat{\psi}_0/2\right)} \left(\psi - \hat{\psi}_0\right) dx = 0.
\end{aligned}$$

This and (5.5) imply (2.7). $\square$

Proof of Theorem 2.5. (1) We first show that $F_a : V_a \to \mathbb{R}$ is a convex functional. Define $T_M = \{(u_1, \ldots, u_M) \in \mathbb{R}^M : u_j > 0 \text{ for } j = 1, \ldots, M, \text{ and } \sum_{j=1}^M u_j < 1\}$ and

$$h(u) = \left(1 - \sum_{j=1}^M u_j\right) \left[\log\left(1 - \sum_{j=1}^M u_j\right) - 1\right] \qquad \forall u = (u_1, \ldots, u_M) \in T_M.$$

Clearly, T_M is convex. We have $\partial_{u_i u_j} h(u) = (1 - \sum_{k=1}^M u_k)^{-1}$ for all $1 \le i, j \le M$. Let $H(u) = (\partial_{u_i u_j} h)$ be the Hessian of $h : T_M \to \mathbb{R}$. Then, for any $y = (y_1, \ldots, y_M) \in R^M$, we have $y \cdot H(u) y = (\sum_{k=1}^M y_k)^2 / (1 - \sum_{k=1} u_k) \ge 0$. Therefore, $H(u)$ is symmetric, semidefinite for any $u \in T_M$. Hence, $h : T_M \to \mathbb{R}$ is convex. Consequently, since V_a is a convex subset of X and $S_{-1} : [0, \infty) \to \mathbb{R}$ is convex, we conclude by (3.13) that $F_a : V_a \to \mathbb{R}$ is convex.

Let now $c = (c_1, \ldots, c_M) \in V_a$. By the same argument used in the proof of Theorem 2.4, we obtain the equivalence of the following four statements:

(i) c is an equilibrium of $F_a : V_a \to \mathbb{R}$;

(ii) The property (2.6) holds true, and

$$(5.6) \quad q_j L\left(\sum_{i=1}^M q_i c_i\right) + \mu_{aj} + \beta^{-1} \log\left(\frac{a^3 c_j}{1 - a^3 \sum_{i=1}^M c_i}\right) = 0 \qquad \text{a.e. } \Omega_s, \quad j = 1, \ldots, M;$$

(iii) c is a global minimizer of $F_a : V_a \to \mathbb{R}$;

(iv) c is a local minimizer of $F_a : V_a \to \mathbb{R}$.

Let $\psi \in H^1_*(\Omega)$ be the unique weak solution to the boundary-value problem of the PBE (1.12) and (1.6), cf. Theorem 2.1. Define $c = (c_1, \ldots, c_M) : \Omega \to \mathbb{R}$ by (1.9) for finite-size ions and $c_j(x) = 0$ for all $x \in \Omega_m$ and all $j = 1, \ldots, M$. Clearly, $c \in V_a$. Moreover, by Theorem 2.1, $\psi|_{\Omega_s} \in C(\overline{\Omega_s})$. This implies (2.6). By (1.9) for finite-size ions, we have

$$a^3 \sum_{j=1}^M c_j(x) = 1 - \frac{1}{1 + a^3 \sum_{i=1}^M c_i^\infty e^{-\beta q_i \left(\psi - \hat{\psi}_0/2\right)}}.$$

This together with (1.9) for finite-size ions imply that

$$(5.7) \qquad \frac{c_j}{1 - a^3 \sum_{i=1}^M c_i} = c_j^\infty e^{-\beta q_j \left(\psi - \hat{\psi}_0/2\right)}, \qquad j = 1, \ldots, M.$$

It follows from (1.12), (1.6), (1.9) for finite-size ions, and Lemma 3.2 with $f = \sum_{j=1}^M q_j c_j$ that ψ is the electrostatic potential corresponding to c, i.e., $\psi = G + \hat{\psi}_0 + L(\sum_{j=1}^M q_j c_j)$. This, together with (5.7) and (3.16), implies (5.6). Hence, c is an equilibrium, and, thus, a local and global minimizer, of $F_a : V_a \to \mathbb{R}$. The uniqueness of equilibria or local minimizers is equivalent to that of global minimizers, and can be proved by the same argument used in the proof of Theorem 2.3.

(2) We need only to prove (2.8). Since c is the unique minimizer of $F_a : V_a \to \mathbb{R}$ and ψ is the corresponding electrostatic potential determined by (3.11), we have by

(1.2), (1.3), and (1.9) for finite-size ions that

$$
\begin{aligned}
\min_{d\in V_a} F_a[d] = F_a[c]&\\
&= \frac{1}{2}\sum_{i=1}^{N} Q_i(\psi-\psi_{vac})(x_i) + \frac{1}{2}\int_{\Omega_s}\left(\sum_{j=1}^{M} q_j c_j\right)\psi dx\\
&\quad + \beta^{-1}\sum_{j=0}^{M}\int_{\Omega_s} c_j\left[\log\left(a^3 c_j\right)-1\right]dx - \sum_{j=1}^{M}\int_{\Omega_s}\mu_j c_j dx\\
&= \frac{1}{2}\sum_{i=1}^{N} Q_i(\psi-\psi_{vac})(x_i) - \frac{1}{2}\sum_{j=1}^{M}\int_{\Omega_s}\frac{q_j c_j^\infty e^{-\beta q_j\left(\psi-\hat\psi_0/2\right)}\left(\psi-\hat\psi_0\right)}{1+a^3\sum_{i=1}^{M} c_i^\infty e^{-\beta q_i\left(\psi-\hat\psi_0/2\right)}}dx\\
&\quad - \beta^{-1}a^{-3}\int_{\Omega_s}\left[1+\log\left(1+a^3\sum_{i=1}^{M} c_i^\infty e^{-\beta q_i\left(\psi-\hat\psi_0/2\right)}\right)\right]dx.
\end{aligned}
\tag{5.8}
$$

Since ψ is the unique solution to the boundary-value problem of PBE (1.12) and (1.6), and since $\hat\psi_0$ is harmonic in Ω_s by (1.10), we have

$$
\varepsilon_s\Delta\left(\psi-\hat\psi_0\right) + 4\pi\sum_{j=1}^{M}\frac{q_j c_j^\infty e^{-\beta q_j\left(\psi-\hat\psi_0/2\right)}}{1+a^3\sum_{i=1}^{M} c_i^\infty e^{-\beta q_i\left(\psi-\hat\psi_0/2\right)}} = 0 \qquad \text{a.e. } \Omega_s.
$$

Multiplying both sides of this equation by $\psi-\hat\psi_0$ and integrating the resulting terms over Ω_s, we obtain by integration by parts and the fact that by Lemma 3.1 both $\psi-\hat\psi_0$ and $\varepsilon_\Gamma\partial_n(\psi-\hat\psi_0)$ are continuous across Γ,

$$
\begin{aligned}
-\int_{\Omega_s}\varepsilon_s\left|\nabla\left(\psi-\hat\psi_0\right)\right|^2 dx + \int_\Gamma \varepsilon_\Gamma\left(\psi-\hat\psi_0\right)\partial_n\left(\psi-\hat\psi_0\right)dS&\\
+ 4\pi\sum_{j=1}^{M}\int_{\Omega_s}\frac{q_j c_j^\infty e^{-\beta q_j\left(\psi-\hat\psi_0/2\right)}\left(\psi-\hat\psi_0\right)}{1+a^3\sum_{i=1}^{M} c_i^\infty e^{-\beta q_i\left(\psi-\hat\psi_0/2\right)}}dx &= 0.
\end{aligned}
$$

This and (5.8) imply (2.8). ∎

Appendix A.

We now prove Lemma 3.4 and Lemma 3.5 by constructing ionic concentrations that satisfy required conditions and that have lower free energies. The key idea here is based on the following observation: the function $S_\alpha : [0,\infty)\to\mathbb{R}$, defined for any $\alpha\in\mathbb{R}$ by $S_\alpha(0)=0$ and $S_\alpha(u)=u(\alpha+\log u)$ if $u>0$, has a unique minimizer which is a positive number. Moreover, the magnitude $|S'_\alpha(u)|$ is very large if u is close to 0 or ∞. Notice that $-S_\alpha$ represents the entropy of the system. Therefore, small changes of concentrations near zero or infinity can largely increase the corresponding entropy and, hence, decrease the free energy.

Proof of Lemma 3.4. We first construct $\bar c\in W_0$ that satisfies

$$
\bar c_j(x)\le \gamma_2' \qquad \text{a.e. } x\in\Omega_s,\ j=1,\dots,M, \tag{A.1}
$$

for some constant $\gamma_2'>0$, $\|\bar c - c\|_X<\varepsilon/2$, and $F_0[\bar c]\le F_0[c]$ with a strict inequality if $c\notin L^\infty(\Omega,\mathbb{R}^M)$. Let $A>0$. Define $\bar c=(\bar c_1,\dots,\bar c_M):\Omega\to\mathbb{R}$ by

$$
\bar c_j(x) = \begin{cases} c_j(x) & \text{if } c_j(x)\le A\\ 0 & \text{if } c_j(x)>A\end{cases} \qquad \forall x\in\Omega,\ j=1,\dots,M. \tag{A.2}
$$

Clearly, $\bar{c} \in W_0$ and (A.1) holds true with $\gamma_2' = A$. Moreover, $\sum_{j=1}^M \|\bar{c}_j - c_j\|_{L^1(\Omega)} < \varepsilon/4$ for $A > 0$ large enough.

Denote

$$\tau_j(A) = \{x \in \Omega_s : c_j(x) > A\}, \qquad j = 1, \dots, M.$$

Since $c \in W_0$, there exists $p > 3/2$ such that each $c_j \in L^p(\Omega)$ $(1 \le j \le M)$. Thus,

$$\sum_{j=1}^M q_j \bar{c}_j - \sum_{j=1}^M q_j c_j = -\sum_{j=1}^M q_j \chi_{\tau_j(A)} c_j \to 0 \qquad \text{in } L^p(\Omega) \quad \text{as } A \to \infty.$$

By the definition of $L : H^{-1}(\Omega) \to H_0^1(\Omega)$ and the regularity theory for elliptic problems [14], we have $L(\sum_{j=1}^M q_j \chi_{\tau_j(A)} c_j)|_{\Omega_s} \in W^{2,p}(\Omega_s)$ and

$$\left\| L\left(\sum_{j=1}^M q_j \chi_{\tau_j(A)} c_j\right)\right\|_{W^{2,p}(\Omega_s)} \le C \left\|\sum_{j=1}^M q_j \chi_{\tau_j(A)} c_j\right\|_{L^p(\Omega_s)} \to 0 \qquad \text{as } A \to \infty.$$

Hence, by (3.4) and the embedding $W^{2,p}(\Omega_s) \hookrightarrow L^\infty(\Omega_s)$ that

$$\begin{aligned}
\left\|\sum_{j=1}^M q_j \bar{c}_j - \sum_{j=1}^M q_j c_j\right\|^2_{H^{-1}(\Omega)} &\le C \int_{\Omega_s} \left(\sum_{j=1}^M q_j \chi_{\tau_j(A)} c_j\right) L\left(\sum_{j=1}^M q_j \chi_{\tau_j(A)} c_j\right) dx \\
&\le C \left\|\sum_{j=1}^M q_j \chi_{\tau_j(A)} c_j\right\|_{L^1(\Omega_s)} \left\| L\left(\sum_{j=1}^M q_j \chi_{\tau_j(A)} c_j\right)\right\|_{L^\infty(\Omega_s)} \\
&\le C \left\|\sum_{j=1}^M q_j \chi_{\tau_j(A)} c_j\right\|_{L^p(\Omega_s)} \left\| L\left(\sum_{j=1}^M q_j \chi_{\tau_j(A)} c_j\right)\right\|_{W^{2,p}(\Omega_s)} \\
&\le C \left\|\sum_{j=1}^M q_j \chi_{\tau_j(A)} c_j\right\|^2_{L^p(\Omega_s)} \\
&\to 0 \qquad \text{as } A \to \infty.
\end{aligned}$$

Therefore, $\|\bar{c} - c\|_X < \varepsilon$ if $A > 0$ is large enough.

Notice that $\bar{c}_j = c_j - \chi_{\tau_j(A)} c_j$ for all $j = 1, \dots, M$. Thus,

$$\begin{aligned}
&\frac{1}{2}\int_{\Omega_s} \left(\sum_{j=1}^M q_j \bar{c}_j\right) L\left(\sum_{j=1}^M q_j \bar{c}_j\right) dx - \frac{1}{2}\int_{\Omega_s} \left(\sum_{j=1}^M q_j c_j\right) L\left(\sum_{j=1}^M q_j c_j\right) dx \\
&\qquad = -\frac{1}{2}\int_{\Omega_s} \left(\sum_{j=1}^M q_j \chi_{\tau_j(A)} c_j\right) L\left(\sum_{j=1}^M q_j c_j + \sum_{j=1}^M q_j \bar{c}_j\right) dx \\
&\qquad \le \frac{1}{2}\sum_{j=1}^M |q_j| d_j(A) \int_{\tau_j(A)} c_j dx, \qquad \text{(A.3)}
\end{aligned}$$

where

$$d_j(A) = \left\| L\left(\sum_{j=1}^M q_j c_j\right)\right\|_{L^\infty(\Omega_s)} + \left\| L\left(\sum_{j=1}^M q_j \bar{c}_j\right)\right\|_{L^\infty(\Omega_s)}.$$

Since

$$\begin{aligned}\left\| L\left(\sum_{j=1}^M q_j \bar{c}_j\right)\right\|_{L^\infty(\Omega_s)} &\le C\left\| L\left(\sum_{j=1}^M q_j \bar{c}_j\right)\right\|_{W^{2,p}(\Omega_s)} \\ &\le C\left\|\sum_{j=1}^M q_j \bar{c}_j\right\|_{L^p(\Omega_s)} \to \left\|\sum_{j=1}^M q_j c_j\right\|_{L^p(\Omega_s)}\end{aligned}$$

as $A \to \infty$, we have $\max_{1\le j\le M} d_j(A) \le C$ as $A > 0$ large enough. For each fixed $j \in \{1, \dots, M\}$ and $x \in \tau_j(A)$, we also have

(A.4) $\quad S_{-1}(\bar{c}_j(x)) - S_{-1}(c_j(x)) = -S_{-1}(c_j(x)) = -c_j(x)\log c_j(x) \le -c_j(x)\log A.$

Therefore, it follows from (3.12), (A.3), and (A.4) that

$$F_0[\bar{c}] - F_0[c] \le \sum_{j=1}^M \left(\frac{1}{2}|q_j| d_j(A) + \|\mu_{0j}\|_{L^\infty(\Omega_s)} - \beta^{-1}\log A\right)\int_{\tau_j(A)} c_j dx.$$

If $A > 0$ is large enough, this is nonpositive. If $c \notin L^\infty(\Omega, \mathbb{R}^M)$, then there exists $j \in \{1, \dots, M\}$ such that $|\tau_j(A)| > 0$ for all $A > 0$. In this case, we have the strict inequality $F_0[\bar{c}] < F_0[c]$.

We now construct $\hat{c} \in W_0$ that satisfies (2.5) with c replaced by $\hat{c}$, $\|\hat{c} - \bar{c}\|_X < \varepsilon/2$, and $F_0[\hat{c}] \le F_0[\bar{c}]$ with a strict inequality if there exists $j \in \{1, \dots, M\}$ such that $|\{x \in \Omega_s : c_j(x) < \alpha\}| > 0$ for all $\alpha > 0$, all these implying that $\hat{c}$ satisfies all the desired properties. If there exists $\gamma_1' > 0$ such that $c_j(x) \ge \gamma_1'$ for a.e. $x \in \Omega_s$ and $j = 1, \dots, M$, then $\hat{c} = \bar{c}$ with $A \ge \gamma_1'$ (cf. (A.2)) satisfies all the desired properties with $\gamma_1 = \gamma_1'$ and $\gamma_2 = \gamma_2'$. Assume otherwise there exists $j_0 \in \{1, \dots, M\}$ such that $|\{x \in \Omega_s : c_{j_0}(x) < \alpha\}| > 0$ for all $\alpha > 0$. This means that $|\{x \in \Omega_s : \bar{c}_{j_0}(x) < \alpha\}| > 0$ for all $\alpha > 0$.

Define

$$\begin{aligned}&\rho_j(\alpha) = \{x \in \Omega_s : \bar{c}_j(x) < \alpha\} \qquad \forall \alpha > 0, \quad j = 1, \dots, M,\\ &I_0 = \{j \in \{1, \dots, M\} : |\rho_j(\alpha)| > 0 \ \forall \alpha > 0\},\\ &I_1 = \{1, \dots, M\} \setminus I_0.\end{aligned}$$

Clearly, $I_0 \ne \emptyset$. If $I_1 \ne \emptyset$, then there exists $\alpha_1 > 0$ such that

$$\bar{c}_j(x) \ge \alpha_1 \qquad \text{a.e. } x \in \Omega_s, \quad \forall j \in I_1.$$

Define for $0 < \alpha < \alpha_1$ and $1 \le j \le M$

$$\hat{c}_j(x) = \begin{cases} \bar{c}_j(x) + \alpha\chi_{\rho_j(\alpha)}(x) & \text{if } j \in I_0 \\ \bar{c}_j(x) & \text{if } j \in I_1 \end{cases} \qquad \forall x \in \Omega.$$

Clearly, $\hat{c} = (\hat{c}_1, \dots, \hat{c}_M) \in W_0$ and (2.5) holds true with c replaced by $\hat{c}$, $\gamma_1 = \alpha$, and $\gamma_2 = \gamma_2' + \alpha$. Moreover, $\sum_{j=1}^M \|\hat{c}_j - \bar{c}_j\|_{L^1(\Omega)} < \varepsilon/4$ if $\alpha > 0$ is small enough.

Furthermore,

$$
\begin{aligned}
\left\| \sum_{j=1}^{M} q_j \hat{c}_j - \sum_{j=1}^{M} q_j \bar{c}_j \right\|_{H^{-1}(\Omega)} &= \alpha \left\| \sum_{j\in I_0} q_j \chi_{\rho_j(\alpha)} \right\|_{H^{-1}(\Omega)} \le \alpha \left\| \sum_{j\in I_0} q_j \chi_{\rho_j(\alpha)} \right\|_{L^2(\Omega)} \\
&\le \alpha \sum_{j\in I_0} |q_j| \sqrt{|\rho_j(\alpha)|} \to 0 \qquad \text{as } \alpha \to 0.
\end{aligned} \tag{A.5}
$$

Hence, $\|\hat{c} - \bar{c}\|_X < \varepsilon/2$ if $\alpha > 0$ is small enough.

By the mean-value theorem and the fact that $S'_{-1}(u) = \log u$ for any $u > 0$,

$$
\begin{aligned}
\sum_{j=1}^{M} \int_{\Omega_s} [S_{-1}(\hat{c}_j) - S_{-1}(\bar{c}_j)]\, dx &= \sum_{j\in I_0} \int_{\rho_j(\alpha)} [S_{-1}(\hat{c}_j) - S_{-1}(\bar{c}_j)]\, dx \\
&\le \alpha \log(2\alpha) \sum_{j\in I_0} |\rho_j(\alpha)|.
\end{aligned}
$$

Consequently, it follows from (3.13), (3.4), (A.5) that

$$
\begin{aligned}
F_0[\hat{c}] - F_0[\bar{c}] &= \frac{1}{2}\int_{\Omega_s} \left(\sum_{j=1}^{M} q_j \bar{c}_j + \alpha \sum_{j\in I_0} q_j \chi_{\rho_j(\alpha)} \right) L \left(\sum_{j=1}^{M} q_j \bar{c}_j + \alpha \sum_{j\in I_0} q_j \chi_{\rho_j(\alpha)} \right) dx \\
&\quad - \frac{1}{2}\int_{\Omega_s} \left(\sum_{j=1}^{M} q_j \bar{c}_j \right) L \left(\sum_{j=1}^{M} q_j \bar{c}_j \right) dx + \alpha \sum_{j\in I_0} \int_{\rho_j(\alpha)} \mu_{0j}\, dx \\
&\quad + \beta^{-1} \sum_{j\in I_0} \int_{\rho_j(\alpha)} [S_{-1}(\hat{c}_j) - S_{-1}(\bar{c}_j)]\, dx \\
&\le \frac{\alpha^2}{2} \int_{\Omega_s} \left(\sum_{j\in I_0} q_j \chi_{\rho_j(\alpha)} \right) L \left(\sum_{j\in I_0} q_j \chi_{\rho_j(\alpha)} \right) dx \\
&\quad + \alpha \int_{\Omega_s} \left(\sum_{j\in I_0} q_j \chi_{\rho_j(\alpha)} \right) L \left(\sum_{j=1}^{M} q_j \bar{c}_j \right) dx \\
&\quad + \alpha \sum_{j\in I_0} \|\mu_{0j}\|_{L^\infty(\Omega_s)} |\rho_j(\alpha)| + \alpha \sum_{j\in I_0} \beta^{-1} \log(2\alpha) |\rho_j(\alpha)| \\
&\le \frac{\alpha^2}{2} \left(\sum_{i\in I_0} q_i^2 \right) \sum_{j\in I_0} |\rho_j(\alpha)| + \alpha \left\| L \left(\sum_{j=1}^{M} q_j \bar{c}_j \right) \right\|_{L^\infty(\Omega_s)} \sum_{j\in I_0} |q_j| |\rho_j(\alpha)| \\
&\quad + \alpha \sum_{j\in I_0} \|\mu_{0j}\|_{L^\infty(\Omega_s)} |\rho_j(\alpha)| + \alpha \sum_{j\in I_0} \beta^{-1} \log(2\alpha) |\rho_j(\alpha)| \\
&= \alpha \sum_{j\in J_0} \left[\frac{\alpha}{2} \left(\sum_{j\in I_0} q_j^2 \right) + |q_j| \left\| L \left(\sum_{j=1}^{M} q_j \bar{c}_j \right) \right\|_{L^\infty(\Omega_s)} \right. \\
&\qquad \left. + \|\mu_{0j}\|_{L^\infty(\Omega_s)} + \beta^{-1} \log(2\alpha) | \right] \rho_j(\alpha)|.
\end{aligned}
$$

Since $I_0 \neq \emptyset$, this is strictly negative if $\alpha > 0$ is small enough.

Proof of Lemma 3.5. We first construct $\bar{c} = (\bar{c}_1, \ldots, \bar{c}_M) \in V_a$ such that

$$a^3 \bar{c}_0(x) = 1 - a^3 \sum_{j=1}^{M} \bar{c}_j(x) \geq \theta_1 \qquad \text{a.e. } x \in \Omega_s \tag{A.6}$$

for some constant $\theta_1 \in (0,1)$, $\|\bar{c} - c\|_X < \varepsilon/2$, and $F_a[\bar{c}] \leq F_a[c]$ with a strict inequality if $|\{x \in \Omega_s : a^3 c_0(x) < \alpha\}| > 0$ for all $\alpha > 0$.

Denote for any $\alpha > 0$

$$\omega_0(\alpha) = \left\{ x \in \Omega_s : a^3 c_0(x) < \alpha \right\}.$$

If there exists a constant $\alpha_1 > 0$ such that $|\omega_0(\alpha_1)| = 0$, i.e., $a^3 c_0(x) \geq \alpha_1$ a.e. Ω_s, then $(\bar{c}_1, \ldots, \bar{c}_M) = (c_1, \ldots, c_M) \in V_a$ satisfies all the desired properties with $\theta_1 = \alpha_1/(1 + \alpha_1) \in (0,1)$. Suppose $|\omega_0(\alpha)| > 0$ for any $\alpha > 0$. Let $0 < \alpha < 1/(4M)$. Let $x \in \omega_0(\alpha)$. Then there exists some $j = j(x) \in \{1, \ldots, M\}$ such that $a^3 c_j(x) \geq 1/(2M)$. In fact, if this were not true, then $a^3 c_i(x) < 1/(2M)$ for all $i = 1, \ldots, M$. Hence, $a^3 c_0(x) = 1 - a^3 \sum_{i=1}^{M} c_i(x) > 1/2 > \alpha$. This would mean that $x \notin \omega_0(\alpha)$, a contradiction. Denoting

$$H_j(\alpha) = \left\{ x \in \omega_0(\alpha) : a^3 c_j(x) \geq \frac{1}{2M} \right\}, \qquad j = 1, \ldots, M,$$

we, thus, have $\omega_0(\alpha) = \cup_{j=1}^{M} H_j(\alpha)$. 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

$$\bar{c}_j(x) = \begin{cases} c_j(x) - \alpha a^{-3} \chi_{K_j(\alpha)}(x) & \forall x \in \Omega, \ j = 1, \ldots, m, \\ c_j(x) & \forall x \in \Omega, \ j = m+1, \ldots, M, \end{cases} \tag{A.7}$$

$$\bar{c}_0(x) = a^{-3} \left[1 - a^3 \sum_{j=1}^{M} \bar{c}_j(x) \right] \qquad \forall x \in \Omega_s.$$

It is easy to see that $(\bar{c}_1, \ldots, \bar{c}_M) \in V_a$. Moreover,

$$a^3 \bar{c}_0(x) = a^3 c_0(x) + \alpha \chi_{\omega_0(\alpha)}(x) \geq \alpha \qquad \text{a.e. } x \in \Omega_s, \tag{A.8}$$

implying (A.6) with $\theta_1 = \alpha$. Clearly, $\sum_{j=1}^{M} \|\bar{c}_j - c_j\|_{L^1(\Omega)} \leq \alpha a^{-3} \sum_{j=1}^{m} |K_j(\alpha)|$. Moreover,

$$\left\| \sum_{j=1}^{M} q_j \bar{c}_j - \sum_{j=1}^{M} q_j c_j \right\|_{H^{-1}(\Omega)} \leq \alpha a^{-3} \left\| \sum_{j=1}^{m} q_j \chi_{K_j(\alpha)} \right\|_{L^2(\Omega)} \leq \alpha a^{-3} \sqrt{\sum_{j=1}^{m} q_j^2 |K_j(\alpha)|}.$$

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

If $x \in K_j(\alpha)$ for some j with $1 \le j \le m$, then $c_j(x) \ge 1/(2Ma^3)$, and $\bar{c}_j(x) \ge 1/(4Ma^3)$ 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 $\bar{c}_j(x) \le \eta_j(x) \le c_j(x)$ such that

$$\begin{aligned} S_{-1}\left[\bar{c}_j(x)\right] - S_{-1}\left[c_j(x)\right] &= \left[\bar{c}_j(x) - c_j(x)\right]\log \eta_j(x) \\ &\le -\alpha a^{-3} \log \bar{c}_j(x) \le \alpha a^{-3} \log\left(4Ma^3\right). \end{aligned}$$

By the same argument using (A.8) and the definition of $\omega_0(\alpha)$, we obtain

$$S_{-1}\left(\bar{c}_0(x)\right) - S_{-1}\left(c_0(x)\right) \le \alpha a^{-3} \log\left(a^{-3}\alpha\right) \qquad \text{a.e. } x \in \omega_0(\alpha).$$

Consequently, we have by (3.13), (3.4), and the embedding $L^2(\Omega_s) \hookrightarrow H^{-1}(\Omega_s)$ that

$$\begin{aligned} F_a[\bar{c}] - F_a[c] = \frac{1}{2}\int_{\Omega_s} &\left(\sum_{j=1}^M q_j c_j - \alpha a^{-3}\sum_{j=1}^m q_j \chi_{K_j(\alpha)}\right) \\ &L\left(\sum_{j=1}^M q_j c_j - \alpha a^{-3}\sum_{j=1}^m q_j \chi_{K_j(\alpha)}\right) dx \\ &- \frac{1}{2}\int_{\Omega_s}\left(\sum_{j=1}^M q_j c_j\right) L\left(\sum_{j=1}^M q_j c_j\right) dx - \alpha a^{-3}\sum_{j=1}^m \int_{K_j(\alpha)} \mu_{aj}\, dx \\ &+ \beta^{-1}\sum_{j=0}^m \int_{\omega_0(\alpha)} \left[S_{-1}(\bar{c}_j) - S_{-1}(c_j)\right] dx \\ \le{}& \frac{1}{2}\alpha^2 a^{-6}\int_{\Omega_s}\left(\sum_{j=1}^m q_j \chi_{K_j(\alpha)}\right) L\left(\sum_{j=1}^m q_j \chi_{K_j(\alpha)}\right) dx \\ &- \alpha a^{-3}\int_{\Omega_s}\left(\sum_{j=1}^m q_j \chi_{K_j(\alpha)}\right) L\left(\sum_{j=1}^m q_j c_j\right) dx \\ &+ \alpha a^{-3}\sum_{j=1}^m \|\mu_{aj}\|_{L^\infty(\Omega_s)} |K_j(\alpha)| \\ &+ \beta^{-1}\alpha a^{-3}\log\left(a^{-3}\alpha\right)|\omega_0(\alpha)| + \beta^{-1}\alpha a^{-3}\log\left(4Ma^3\right)|\omega_0(\alpha)| \\ \le{}& C\alpha^2 a^{-6}\left\|\sum_{j=1}^m q_j \chi_{K_j(\alpha)}\right\|^2_{L^2(\Omega_s)} \\ &+ \alpha a^{-3}\left\| L\left(\sum_{j=1}^M q_j c_j\right)\right\|_{L^\infty(\Omega)} \sum_{j=1}^m |q_j||K_j(\alpha)| \\ &+ \alpha a^{-3}\sum_{j=1}^m \|\mu_{aj}\|_{L^\infty(\Omega_s)}|K_j(\alpha)| + \beta^{-1}\alpha a^{-3}\log\left(8Ma^3\alpha\right)\sum_{j=1}^m |K_j(\alpha)| \\ ={}& \alpha\sum_{j=1}^M \Bigg[C\alpha a^{-6} q_j^2 + a^{-3}|q_j|\left\| L\left(\sum_{j=1}^M q_j c_j\right)\right\|_{L^\infty(\Omega)} + a^{-3}\|\mu_{aj}\|_{L^\infty(\Omega_s)} \\ &+ \beta^{-1} a^{-3}\log\left(8Ma^3\alpha\right)\Bigg]|K_j(\alpha)|, \end{aligned}$$

where $C > 0$ is a constant independent of α. Thus, $F_a[\bar{c}] - F_a[c]$ is nonpositive for $\alpha > 0$ sufficiently small. It is strictly negative, if $|\omega_0(\alpha)| = \sum_{j=1}^m |K_j(\alpha)| > 0$ for all $\alpha > 0$, i.e., if $|\{x \in \Omega_s : a^3 c_0(x) < \alpha\}| > 0$ for all $\alpha > 0$.

We now construct $\hat{c} \in V_a$ that satisfies (2.6) with c replaced by $\hat{c}$, $\|\hat{c} - \bar{c}\|_X < \varepsilon/2$, and $F_a[\hat{c}] \le F_a[\bar{c}]$ with a strict inequality if there exists $j \in \{1, \ldots, M\}$ such that $|\{x \in \Omega_s : a^3 c_j(x) < \alpha\}| > 0$ for all $\alpha > 0$, all these implying that $\hat{c}$ satisfies all the desired properties. If there exists $\theta_2 \in (0,1)$ such that $c_j(x) \ge \theta_2$ for a.e. $x \in \Omega_s$ and all $j = 1, \ldots, M$, then $\hat{c} = \bar{c}$ with $0 < \alpha < \theta_2/2$ (cf. (A.7)) satisfies all the desired properties with $\theta_0 = \min(\theta_1, \theta_2/2)$. Assume otherwise there exists $j_0 \in \{1, \ldots, M\}$ such that $|\{x \in \Omega_s : c_{j_0}(x) < \alpha\}| > 0$ for all $\alpha > 0$. This means that $|\{x \in \Omega_s : \bar{c}_{j_0}(x) < \alpha\}| > 0$ for all $\alpha > 0$.

Define

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

Clearly, $J_0 \ne \emptyset$. If $J_1 \ne \emptyset$, then there exists $\alpha_2 > 0$ such that

$$
a^3 \bar{c}_j(x) \ge \alpha_2 \qquad \text{a.e. } x \in \Omega_s, \quad \forall j \in J_1.
$$

Define for $0 < \alpha < \min\{\alpha_2, \theta_1/M\}$ and $1 \le j \le M$

$$
\hat{c}_j(x) = \begin{cases} \bar{c}_j(x) + \alpha a^{-3} \chi_{\sigma_j(\alpha)}(x) & \text{if } j \in J_0 \\ \bar{c}_j(x) & \text{if } j \in J_1 \end{cases} \qquad \forall x \in \Omega.
$$

$$
\hat{c}_0(x) = a^{-3} \left[1 - \sum_{j=1}^M a^3 \hat{c}_j(x) \right] \qquad \forall x \in \Omega_s.
$$

Notice by (A.6) that

$$
\begin{aligned}
a^3 \hat{c}_0(x) &= 1 - \sum_{j=1}^M a^3 \hat{c}_j(x) = 1 - \sum_{j=1}^M a^3 \bar{c}_j(x) - \alpha \sum_{j \in J_0} \chi_{\sigma_j(\alpha)} \\
&\ge \theta_1 - \alpha M > 0 \qquad \text{a.e. } x \in \Omega_s.
\end{aligned}
$$

Thus, $\hat{c} = (\hat{c}_1, \ldots, \hat{c}_M) \in V_a$. Clearly, (2.6) holds true for $\theta_0 = \min\{\alpha, \alpha_2, \theta_1 - \alpha M\}$. Applying the same argument used above, we obtain that $\|\hat{c} - \bar{c}\|_X < \varepsilon/2$ for $\alpha > 0$ small enough.

We have now by the mean-value theorem that

$$
\begin{aligned}
\sum_{j=1}^M \int_{\Omega_s} [S_{-1}(\hat{c}_j) - S_{-1}(\bar{c}_j)]\, dx &= \sum_{j \in J_0} \int_{\sigma_j(\alpha)} [S_{-1}(\hat{c}_j) - S_{-1}(\bar{c}_j)]\, dx \\
&\le \alpha a^{-3} \log\left(2\alpha a^{-3}\right) \sum_{j \in J_0} |\sigma_j(\alpha)|.
\end{aligned}
$$

Similarly, we have by (2.6) that

$$
\int_{\Omega_s} [S_{-1}(\hat{c}_0) - S_{-1}(\bar{c}_0)]\, dx \le -\alpha a^{-3} \log\left(a^{-3}\theta_0\right) \sum_{j \in J_0} |\sigma_j(\alpha)|.
$$

Consequently, we have by (3.13) and a similar argument that

$$
\begin{aligned}
F_a[\hat{c}] - F_a[\bar{c}] = \frac{1}{2}\int_{\Omega_s} & \left(\sum_{j=1}^{M} q_j \bar{c}_j + \alpha a^{-3} \sum_{j\in J_0} q_j \chi_{\sigma_j(\alpha)}\right) \\
& L\left(\sum_{j=1}^{M} q_j \bar{c}_j + \alpha a^{-3} \sum_{j\in J_0} q_j \chi_{\sigma_j(\alpha)}\right) dx \\
& - \frac{1}{2}\int_{\Omega_s} \left(\sum_{j=1}^{M} q_j \bar{c}_j\right) L\left(\sum_{j=1}^{M} q_j \bar{c}_j\right) dx + \alpha a^{-3} \sum_{j\in J_0} \int_{\sigma_j(\alpha)} \mu_{aj} dx \\
& + \beta^{-1} \sum_{j\in J_0} \int_{\sigma_j(\alpha)} \left[S_{-1}(\hat{c}_j) - S_{-1}(\bar{c}_j)\right] dx \\
& + \beta^{-1} \int_{\Omega_s} \left[S_{-1}(\hat{c}_0) - S_{-1}(\bar{c}_0)\right] dx \\
\le C\alpha^2 a^{-6} & \left\| \sum_{j\in J_0} q_j \chi_{\sigma_j(\alpha)} \right\|_{L^2(\Omega_s)}^2 + \alpha a^{-3} \left\| \sum_{j=1}^{M} q_j \bar{c}_j \right\|_{L^\infty(\Omega_s)} \sum_{j\in J_0} |q_j||\sigma_j(\alpha)| \\
& + \alpha a^{-3} \sum_{j\in J_0} \|\mu_{aj}\|_{L^\infty(\Omega_s)} |\sigma_j(\alpha)| + \beta^{-1}\alpha a^{-3} \log(2\alpha/\theta_0) \sum_{j\in J_0} |\sigma_j(\alpha)| \\
\le \alpha \sum_{j\in J_0} & \left[C\alpha a^{-6} q_j^2 + a^{-3}|q_j| \left\| \sum_{j=1}^{M} q_j \bar{c}_j \right\|_{L^\infty(\Omega_s)} + a^{-3} \|\mu_{aj}\|_{L^\infty(\Omega_s)} \right. \\
& \left. + \beta^{-1} a^{-3} \log(2\alpha/\theta_0) \right] |\sigma_j(\alpha)|.
\end{aligned}
$$

Since $J_0 \neq \emptyset$, this is strictly negative if $\alpha > 0$ is sufficiently small. The case that $J_1 = \emptyset$ can be treated similarly. ∎

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