Variational Analysis of the Classical and Ionic Size-Modified Poisson–Boltzmann Electrostatics

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Abstract

This work concerns both the classical and the ionic size-modified Poisson–Boltzmann (PB) models of the continuum electrostatics for an ionic solution with different cases of charges involved. A unified approach is developed to analyze the minimizers of the PB electrostatic free-energy functionals of ionic concentrations and the solutions to the corresponding PB and the generalized PB equations. Key results of the analysis are the uniform positive bounds for the equilibrium concentrations and the uniform bounds for the solutions of the PB equations. Penalized and constraint-free PB energy functionals are constructed that can be used for solving the underlying variational problems and partial differential equations by machine learning with application to complex charged molecular systems. In addition to the existence and uniqueness of minimizers of such new functionals, uniform bounds with respect to the penalization parameters are obtained for such minimizers. The convergence of the penalized models is finally established.

Key words. Electrostatic free energy, variational models, Poisson–Boltzmann equation, penalty methods, uniform bounds, convergence.

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1 Introduction

We consider an ionic solution with $M(\geq 1)$ ionic species, occupying a bounded region $\Omega \subset \mathbb{R}^3$ and study two electrostatic free-energy functionals of the ionic concentrations. One is the classical and the other an ionic size-modified Poisson–Boltzmann (PB) functional of the ionic concentrations. They are given by the following unified form [2, 3, 5, 12, 13, 14, 20, 21]:

$$F[c] = \int_\Omega \left[\frac{1}{2}\rho\phi + S(c) - \sum_{i=1}^{M} \mu_i c_i \right] dx, \tag{1.1}$$

where $c = (c_1, \dots, c_M)$ with $c_i : \Omega \to [0, \infty)$ denoting the concentration of ions of the ith species ($i = 1, \dots, M$). The first part of $F[c]$ is the electrostatic potential energy. The function

$\rho : \Omega \to \mathbb{R}$ is the charge density, defined by $\rho = f + \sum_{i=1}^{M} q_i c_i$, where $f : \Omega \to \mathbb{R}$ is a given function representing a fixed charge density and each q_i is the charge of an ion of the ith ionic species ($1 \le i \le M$). The function $\phi : \Omega \to \mathbb{R}$ is the electrostatic potential, uniquely determined as the solution to the boundary-value problem of Poisson's equation

$$\begin{cases} \nabla \cdot \varepsilon \nabla \phi = -\rho & \text{in } \Omega, \\ \phi = g & \text{on } \partial\Omega, \end{cases} \tag{1.2}$$

where $\varepsilon : \Omega \to \mathbb{R}$ is the dielectric coefficient which is a known function assumed to satisfy

$$\varepsilon_{\min} \le \varepsilon(x) \le \varepsilon_{\max} \qquad \forall x \in \Omega, \tag{1.3}$$

with $\varepsilon_{\min}$ and $\varepsilon_{\max}$ two positive constants, and $g : \partial\Omega \to \mathbb{R}$ is a given function. The second part of the free-energy function $F[c]$ in (1.1) is the entropy, defined by

$$S(c) = \begin{cases} \beta^{-1} \sum_{i=1}^{M} c_i \left[\log(\Lambda^3 c_i) - 1\right] & \text{without the size effect,} \\ \beta^{-1} \sum_{i=0}^{M} c_i \left[\log(v_i c_i) - 1\right] & \text{with the size effect,} \end{cases} \tag{1.4}$$

where $\beta = (k_{\rm B} T)^{-1}$ with $k_{\rm B}$ the Boltzmann constant and T the temperature. Here and below, log denotes the natural logarithm. For the case of no ionic size effect included, $\Lambda > 0$ is the de Broglie wavelength, a known cut-off length. For the case of the ionic size effect included, the summation is from $i = 0$ to $i = M$. For each i with $1 \le i \le M$, v_i denotes the effective volume of an ion of the ith species. The term for $i = 0$ is the entropy of the solvent, where $c_0 : \Omega \to [0, v_0^{-1}]$ is the solvent concentration, defined by $\sum_{i=0}^{M} v_i c_i = 1$, i.e.,

$$c_0 = v_0^{-1} \left(1 - \sum_{i=1}^{M} v_i c_i \right) \qquad \text{in } \Omega, \tag{1.5}$$

where v_0 is the effective volume of a solvent molecule. The last part of $F[c]$ in (1.1) is the Lagrange multiplier for the constraint of the conservation of ionic concentrations, where μ_i ($1 \le i \le M$) is the chemical potential for the ith ionic species. In the model, all T, Λ, q_i, μ_i, and v_i for all i are known constants.

Heuristically, the functional F is convex and admits a unique minimizer in a suitable admissible set of concentrations. This unique minimizer is determined by the vanishing of the first variation $\delta F[c] = 0$, which leads to the Boltzmann distributions for the equilibrium ionic concentrations and the corresponding electrostatic potential $c_i = c_i(\phi)$ in Ω for all $i = 1, \ldots, M$. In the case of no ionic size effects, these are the classical Boltzmann distributions, $c_i = c_i^{\infty} e^{-\beta q_i \phi}$ in Ω for $i = 1, \ldots, M$, where c_i^{∞} is the bulk concentration of the ith ionic species in the system. With the ionic size effect included, explicit formulas of such relations seem to be only available for the special case of a uniform size, i.e., all the ionic sizes and the solvent molecular size are the same [10, 11, 14, 16, 17, 23]. With the Boltzmann distributions, the charge density is $\rho = f + \sum_{i=1}^{M} q_i c_i(\phi)$ and the Poisson equation in (1.2) becomes the generalized Poisson–Boltzmann (PB) equation (PBE)

$$\nabla \cdot \varepsilon \nabla \phi - B'(\phi) = -f \qquad \text{in } \Omega, \tag{1.6}$$

where the function $B : \mathbb{R} \to \mathbb{R}$ is defined through the Boltzmann distributions $c_i = c_i(\phi)$ $(i = 1, \dots, M)$ by $B'(\phi) = -\sum_{i=1}^M q_i c_i(\phi)$.

In this work, we first examine the functional $F[c]$ defined in (1.1) and the related PBE (1.6) for the case that the ionic charges are all positive (cations only), or all negative (anions only), or a mixture of both positive and negative charges. We then study the penalized functionals

$$G_\lambda[c, \phi] = \int_\Omega \left[\frac{\varepsilon}{2} |\nabla \phi|^2 + S(c) - \sum_{i=1}^M \mu_i c_i \right] dx + \lambda_1 \int_\Omega \left(\nabla \cdot \varepsilon \nabla \phi + f + \sum_{i=1}^M q_i c_i \right)^2 dx + \lambda_2 \int_{\partial\Omega} (\phi - g)^2 \, dS, \tag{1.7}$$

where $\lambda = (\lambda_1, \lambda_2)$ with $\lambda_1 > 0$ and $\lambda_2 > 0$. Note that the function ϕ in the definition of $F[c]$ is constrained by Poisson's equation in (1.2) while ϕ in $G_\lambda[c, \phi]$ is a free variable. It follows from Poisson's equation in (1.2) and integration by parts that the first term in $F[c]$ is

$$\int_\Omega \frac{1}{2} \rho \phi \, dx = \int_\Omega \frac{\varepsilon}{2} |\nabla \phi|^2 \, dx - \int_{\partial\Omega} \frac{1}{2} \varepsilon \partial_n \phi g \, dS,$$

where n is the unit exterior normal at $\partial\Omega$. If we neglect the boundary integral term by approximation, we obtain the first term in $G_\lambda[c, \phi]$. The penalty terms (i.e., the λ_1 and λ_2 terms) in $G_\lambda[c, \phi]$ force ϕ to satisfy Poisson's equation and the boundary condition (1.2) with the penalty coefficients $\lambda_1, \lambda_2 \to +\infty$. The constraint-free penalized energy functionals G_λ are designed for numerical studies of the PB electrostatics, particularly applied to charged molecules with complex surfaces, using a machine learning approach [6, 9].

Our main results are the following:

(1) We consider a family of the PB equations with fixed charge densities f_k and boundary values g_k $(k = 1, 2, \dots)$ and prove that each of the boundary-value problems of the PBE has a unique weak solution ϕ_k. Moreover, $\sup_{k \geq 1} \|\phi_k\|_{L^\infty(\Omega)} < \infty$. The proof relies on a variational structure of the PB equation and an improved comparison argument [15].

(2) Using the direct method in the calculus of variations, we prove the existence of minimizers of the PB electrostatic free-energy functions on suitably defined spaces of ionic concentrations that have minimum regularity requirement; cf. [13, 14]. Moreover, we use the uniformly bounded electrostatic potentials that are solutions to the PBE and the expected Boltzmann distributions to construct the unique free-energy minimizing ionic concentrations that are bounded below and above by positive constants. This is different from previous work that obtains such bounds by a technical construction of lower energy concentrations [13, 14].

(3) Given any penalty coefficient $\lambda = (\lambda_1, \lambda_2) > 0$, we prove the existence and uniqueness of the minimizer for the penalized functional G_λ defined in (1.7). A key step in the proof is a "change of variable" argument that allows us to disintegrate the penalty terms from other terms in the functionals. We also prove the convergence of the penalized energy functionals to the classical electrostatic energy functionals with respect to the energy minimizers and the minimum energy values.

The rest of the paper is organized as follows. In section 2, we prove the uniform boundedness for solutions of the PBE with a sequence of charge densities and boundary values. In section 3, we prove the existence and uniqueness of the minimizer of the PB energy functionals and also obtain the positive bounds for such minimizers. In section 4, we prove the existence and uniqueness of the minimizers for penalized PB energy functionals and the convergence of such functionals.

2 The PB Equation

In what follows, we assume that $B \in C^{\infty}(\mathbb{R})$ is a strictly convex function and $\inf_{s\in\mathbb{R}} B(s) = 0$. Moreover, it satisfies the following additional properties corresponding to three different cases:

Case 1. There exist $i, j \in \{1, \dots, M\}$ such that $q_i > 0$ and $q_j < 0$. In this case, $B(-\infty) = +\infty$ and $B(+\infty) = +\infty$. Moreover, $B'(-\infty) = -\infty$ or $B'(-\infty)$ exists and is negative, and $B'(+\infty) = +\infty$ or $B'(+\infty)$ exists and is positive.

Case 2. All $q_i > 0$ $(i = 1, \dots, M)$. In this case, B is monotonically decreasing with $B(-\infty) = +\infty$ and $B(+\infty) = 0$. Moreover, $B'(-\infty) = -\infty$ or $B'(-\infty)$ exists and is negative, and $B'(+\infty) = 0$.

Case 3. All $q_i < 0$ $(i = 1, \dots, M)$. In this case, B is monotonically increasing with $B(-\infty) = 0$ and $B(+\infty) = +\infty$. Moreover, $B'(-\infty) = 0$, and $B'(+\infty) = +\infty$ or $B'(+\infty)$ exists and is positive.

Figure 2.1 shows schematic of the graph of the function B for the three cases. We remark that these properties of the function B are satisfied in general [2, 5, 13, 14].

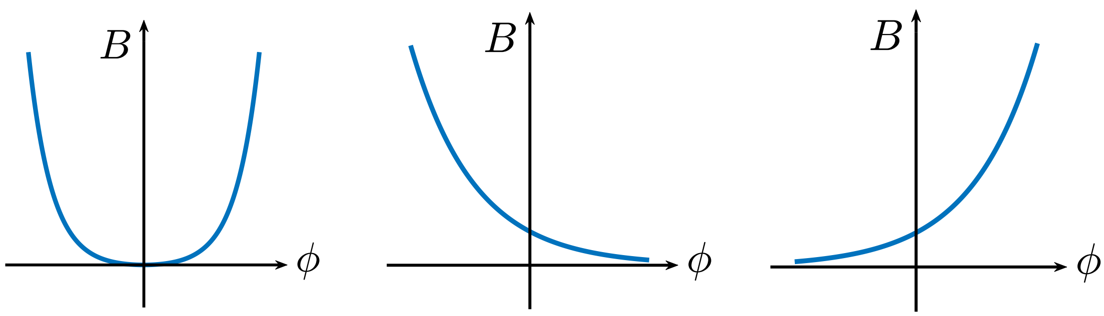

Figure 2.1: Schematic of the three cases of the function B.

We assume $\Omega \subset \mathbb{R}^3$ is a bounded domain with a Lipschitz-continuous boundary $\partial\Omega$. Let $\varepsilon \in L^{\infty}(\Omega)$ satisfy (1.3), $f \in L^2(\Omega)$, and $g \in H^1(\Omega)$. Denote

$$H^1_g(\Omega) = \{\phi \in H^1(\Omega) : \phi = g \text{ on } \partial\Omega\}.$$

Here and below, we use the standard notation of Sobolev spaces; cf. e.g., [1, 7, 8].

Definition 2.1. *A function $\phi \in H^1_g(\Omega)$ is a weak solution to the boundary-value problem of PBE* (1.6) *with the boundary condition $\phi = g$ on $\partial\Omega$ if $B'(\phi) \in L^2(\Omega)$ and*

$$\int_\Omega \left[\varepsilon \nabla\phi \cdot \nabla\xi + B'(\phi)\xi\right] dx = \int_\Omega f\xi \, dx \qquad \forall \xi \in H^1_0(\Omega).$$

Let $f_k \in L^2(\Omega)$ and $g_k \in H^1(\Omega)$ $(k = 1, 2, \dots)$. For each $k \geq 1$, we define the functional $J_k : H^1_{g_k}(\Omega) \to \mathbb{R} \cup \{+\infty\}$ by

$$J_k[\phi] = \int_\Omega \left[\frac{\varepsilon}{2}|\nabla\phi|^2 + B(\phi) - f_k\phi\right] dx \qquad \forall \phi \in H^1_{g_k}(\Omega). \tag{2.1}$$

The boundary-value problem for the corresponding Euler–Lagrange equation, which is the PB equation, is

$$\begin{cases} \nabla \cdot \varepsilon\nabla\phi - B'(\phi) = -f_k & \text{in } \Omega, \\ \phi = g_k & \text{on } \partial\Omega. \end{cases} \tag{2.2}$$

Theorem 2.1. *Assume either*

(1) $\Omega \subset \mathbb{R}^3$ *is a bounded domain with a* C^1 *boundary* $\partial\Omega$, $\varepsilon \in L^\infty(\Omega)$ *satisfy* (1.3), *and* $f_k \in L^2(\Omega)$ *and* $g_k \in W^{1,\infty}(\Omega)$ $(k = 1, 2, \dots)$ *satisfy*

$$\sup_{k\geq 1} \|f_k\|_{L^2(\Omega)} < \infty \qquad \textit{and} \qquad \sup_{k\geq 1} \|g_k\|_{W^{1,\infty}(\Omega)} < \infty, \tag{2.3}$$

respectively; or

(2) $\Omega \subset \mathbb{R}^3$ *is a bounded domain with a* C^2 *boundary* $\partial\Omega$, $\varepsilon \in W^{1,\infty}(\Omega)$ *satisfy* (1.3), *and* $f_k \in L^2(\Omega)$ *and* $g_k \in H^2(\Omega)$ $(k = 1, 2, \dots)$ *satisfy*

$$\sup_{k\geq 1} \|f_k\|_{L^2(\Omega)} < \infty \qquad \textit{and} \qquad \sup_{k\geq 1} \|g_k\|_{H^2(\Omega)} < \infty, \tag{2.4}$$

respectively. Then, for each $k \geq 1$, *the functional* $J_k : H^1_{g_k}(\Omega) \to \mathbb{R} \cup \{+\infty\}$ *admits a unique minimizer* $\phi_k \in H^1_{g_k}(\Omega)$. *Moreover, the following hold true under the assumption* (1) *or* (2), *respectively:*

(1) *For each* $k \geq 1$, $\phi_k \in L^\infty(\Omega)$ *and is the unique weak solution to* (2.2), *and*

$$\sup_{k\geq 1} \|\phi_k\|_{L^\infty(\Omega)} < \infty; \tag{2.5}$$

(2) *For each* $k \geq 1$, $\phi_k \in H^2(\Omega)$ *and is the unique weak solution to* (2.2), *and*

$$\sup_{k\geq 1} \|\phi_k\|_{H^2(\Omega)} < \infty. \tag{2.6}$$

Remark. *The two different assumptions in the theorem will also be used in several lemmas and theorems below. The first assumption is less restrictive and serves as a general result while the second one is made particularly for studying the penalized and constraint-free energy functionals in sections 4.*

Proof of Theorem 2.1. Fix $k \geq 1$. Note that $B \geq 0$ and J_k is strictly convex. The existence and uniqueness of its minimizer ϕ_k over the set $H^1_{g_k}(\Omega)$ follows from a standard argument using the direct method in the calculus of variations; cf. e.g., [7, 13, 14, 15]. Once it is shown that $\phi_k \in L^\infty(\Omega)$ in Case (1) or $\phi_k \in H^2(\Omega) \hookrightarrow L^\infty(\Omega)$ in Case (2), then by direct calculations following the definition of the first variation and the Lebesgue Dominated Convergence theorem, we have

$$\int_\Omega [\varepsilon \nabla\phi_k \cdot \nabla\xi + B'(\phi_k)\xi - f_k\xi] \, dx = 0$$

first for any $\xi \in C^1_c(\Omega)$ and then for any $\xi \in H^1_0(\Omega)$ as $C^1_c(\Omega)$ is dense in $H^1_0(\Omega)$. Therefore, ϕ_k is also a weak solution to the corresponding PBE by Definition 2.1. The uniqueness of such a solution follows from the strict convexity of B. Therefore, we only need to prove (2.5) in Case (1) and (2.6) in Case (2).

To continue, we first "shift" out f_k in J_k and then apply a comparison argument to obtain the uniform bound (2.5) and (2.6). Fix $k \geq 1$. There exists a unique $\eta_k \in H^1_{g_k}(\Omega)$, such that

$$\int_\Omega \varepsilon \nabla\eta_k \cdot \nabla\xi \, dx = \int_\Omega f_k \xi \, dx \qquad \forall \xi \in H^1_0(\Omega). \tag{2.7}$$

In Case (1), $g_k \in W^{1,\infty}(\Omega)$. Thus, it follows from (2.3), the solution boundedness (cf. Theorem 8.16 in [8]) and the embedding $W^{1,\infty}(\Omega) \hookrightarrow L^\infty(\partial\Omega)$ that $\eta_k \in L^\infty(\Omega)$ $(k = 1, 2, \dots)$, and there exists a constant $C = C(\Omega)$ such that

$$\sup_{k\geq 1} \|\eta_k\|_{L^\infty(\Omega)} \leq C \sup_{k\geq 1} \left(\|f_k\|_{L^2(\Omega)} + \|g_k\|_{W^{1,\infty}(\Omega)} \right) < \infty. \tag{2.8}$$

In Case (2), $\varepsilon \in W^{1,\infty}(\Omega)$ and $g_k \in H^2(\Omega)$. By (2.4), the regularity theory (cf. Theorem 8.12 in [8]) and the Sobolev embedding $H^2(\Omega) \hookrightarrow L^\infty(\Omega)$, we have

$$\sup_{k\geq 1} \|\eta_k\|_{H^2(\Omega)} < \infty \qquad \text{and} \qquad \sup_{k\geq 1} \|\eta_k\|_{L^\infty(\Omega)} < \infty. \tag{2.9}$$

For any $\phi \in H^1_{g_k}(\Omega)$, let $w = \phi - \eta_k \in H^1_0(\Omega)$. By (2.7) with ξ replaced by w, we have by direct calculations that

$$J_k[\phi] = J^{(k)}[w] + \int_\Omega \left(\frac{\varepsilon}{2} |\nabla \eta_k|^2 - f_k \eta_k \right) dx,$$

where the integral term is a constant for a fixed k and

$$J^{(k)}[w] = \int_\Omega \left[\frac{\varepsilon}{2} |\nabla w|^2 + B(w + \eta_k) \right] dx \qquad \forall w \in H^1_0(\Omega).$$

Therefore, the minimization of J_k over $\phi \in H^1_{g_k}(\Omega)$ is equivalent to the minimization of $J^{(k)}$ over $w \in H^1_0(\Omega)$. By the direct method in the calculus of variations, there exists a unique $w_k \in H^1_0(\Omega)$ that minimizes $J^{(k)} : H^1_0(\Omega) \to \mathbb{R} \cup \{+\infty\}$. Clearly, $\phi_k = w_k + \eta_k$. By (2.8) and (2.9), it now suffices to prove

$$\text{For Case (1):} \qquad \sup_{k\geq 1} \|w_k\|_{L^\infty(\Omega)} < \infty, \tag{2.10}$$

$$\text{For Case (2):} \qquad \sup_{k\geq 1} \|w_k\|_{H^2(\Omega)} < \infty. \tag{2.11}$$

We consider three cases.

Case (i). There exist i and j such that $q_i > 0$ and $q_j < 0$. In this case, $B'(-\infty) = -\infty$ or it exists and is negative, and $B'(+\infty) = +\infty$ or it exists and is positive. By (2.8) and (2.9), there exist $\lambda > 0$ and $a > 0$ independent of k, such that

$$B'(\lambda + \eta_k) \geq a \qquad \text{and} \qquad B'(-\lambda + \eta_k) \leq -a \quad \text{a.e. } \Omega. \tag{2.12}$$

Now for each k, we define $w_{k,\lambda} : \Omega \to \mathbb{R}$ by

$$w_{k,\lambda}(x) = \begin{cases} -\lambda & \text{if } w_k(x) < -\lambda, \\ w_k(x) & \text{if } -\lambda \leq w_k(x) \leq \lambda, \\ \lambda & \text{if } w_k(x) > \lambda. \end{cases}$$

We verify that $w_{k,\lambda} \in H^1_0(\Omega)$ and $|\nabla w_{k,\lambda}| \leq |\nabla w_k|$ a.e. in Ω. Since $J^{(k)}[w_k] \leq J^{(k)}[w_{k,\lambda}]$, it follows that

$$\int_\Omega B(w_{k,\lambda} + \eta_k)\, dx \geq \int_\Omega B(w_k + \eta_k)\, dx.$$

Consequently, we have by the convexity of B and (2.12) that

$$
\begin{aligned}
0 &\geq \int_\Omega B(w_k + \eta_k)\,dx - \int_\Omega B(w_{k,\lambda} + \eta_k)\,dx \\
&= \int_{\{w_k < -\lambda\}} [B(w_k + \eta_k) - B(-\lambda + \eta_k)]\,dx + \int_{\{w_k > \lambda\}} [B(w_k + \eta_k) - B(\lambda + \eta_k)]\,dx \\
&\geq \int_{\{w_k < -\lambda\}} B'(-\lambda + \eta_k)\,(w_k + \lambda)\,dx + \int_{\{w_k > \lambda\}} B'(\lambda + \eta_k)\,(w_k - \lambda)\,dx \\
&\geq \int_{\{w_k < -\lambda\}} -a(w_k + \lambda)\,dx + \int_{\{w_k > \lambda\}} a(w_k - \lambda)\,dx \\
&= \int_{\{w_k < -\lambda\}} a\,(|w_k| - \lambda)\,dx + \int_{\{w_k > \lambda\}} a\,(|w_k| - \lambda)\,dx \\
&= \int_{\{|w_k| > \lambda\}} a\,(|w_k| - \lambda)\,dx \\
&\geq 0.
\end{aligned}
$$

Thus, $|w_k| \leq \lambda$ a.e. Ω. Hence, (2.10) holds true as λ is independent of k. Moreover, $w_k \in H_0^1(\Omega)$ is a weak solution to $\nabla \cdot \varepsilon \nabla w_k = B'(w_k + \eta_k)$ in Ω. The assumptions on ε and Ω in Case (2), (2.9), and the regularity theory (cf. Theorem 8.12 in [8]) imply that $w_k \in H^2(\Omega)$ and (2.11).

Case (ii). All $q_i > 0$ ($i = 1, \ldots, M$). In this case, $B'(-\infty) = -\infty$ or it exists and is negative. By the same argument, there exists $\lambda > 0$ and $b > 0$, independent of k, such that

$$
B'(-\lambda + \eta_k) \leq -b \qquad \text{a.e. } \Omega. \tag{2.13}
$$

For each k, we define $w_{k,\lambda} : \Omega \to \mathbb{R} \cup \{+\infty\}$ by

$$
w_{k,\lambda}(x) = \begin{cases} -\lambda & \text{if } \ w_k(x) < -\lambda, \\ w_k(x) & \text{if } \ w_k(x) \geq -\lambda. \end{cases}
$$

We have $w_{k,\lambda} \in H_0^1(\Omega)$ and $|\nabla w_{k,\lambda}| \leq |\nabla w_k|$ a.e. in Ω. Since $J^{(k)}[w_k] \leq J^{(k)}[w_{k,\lambda}]$,

$$
\int_\Omega B(w_{k,\lambda} + \eta_k)\,dx \geq \int_\Omega B(w_k + \eta_k)\,dx.
$$

Thus, we have by the convexity of B and (2.13) that

$$
\begin{aligned}
0 &\geq \int_\Omega B(w_k + \eta_k)\,dx - \int_\Omega B(w_{k,\lambda} + \eta_k)\,dx \\
&= \int_{\{w_k < -\lambda\}} [B(w_k + \eta_k) - B(-\lambda + \eta_k)]\,dx \\
&\geq \int_{\{w_k < -\lambda\}} B'(-\lambda + \eta_k)\,(w_k + \lambda)\,dx \\
&\geq \int_{\{w_k < -\lambda\}} -b(w_k + \lambda)\,dx \\
&\geq 0.
\end{aligned}
$$

Consequently, we have

$$w_k \geq -\lambda \quad \text{a.e. } \Omega \quad \forall k \geq 1. \tag{2.14}$$

Since λ is independent of k, this and (2.8) or (2.9), together with the fact that $B'(+\infty) = 0$ in this case, imply that $[B(w_k + \eta_k + t\xi) - B(w_k + \eta_k)]/t$ $(0 < |t| < 1)$ are uniformly essentially bounded in Ω for any $\xi \in C_c^1(\Omega)$. Therefore, since $w_k \in H_0^1(\Omega)$ minimizes $J^{(k)}$ over $H_0^1(\Omega)$, we have by the routine calculations using the Lebesgue Dominated Convergence theorem that

$$\int_\Omega [\varepsilon \nabla w_k \cdot \nabla \xi + B'(w_k + \eta_k)\xi]\, dx = 0 \qquad \forall \xi \in C_c^1(\Omega).$$

This is also true if $\xi \in H_0^1(\Omega)$, since $C_c^1(\Omega)$ is dense in $H_0^1(\Omega)$. Thus, $w_k \in H_0^1(\Omega)$ is a weak solution to $\nabla \cdot \varepsilon \nabla w_k = B'(w_k + \eta_k)$. For Case (1), since $\sup_{k \geq 1} \|B'(w_k + \eta_k)\|_{L^\infty(\Omega)} < \infty$ by (2.8) and (2.14), we obtain (2.10) by the solution boundedness (cf. Theorem 8.16 in [8]). Similarly, with the assumptions on Ω and ε in Case (2), we have by (2.9) and the regularity theory (cf. Theorem 8.12 in [8]) that $w_k \in H^2(\Omega)$ and (2.11) holds true.

Case (iii). All $q_i < 0$ $(i = 1, \ldots, M)$. This is similar to Case (ii). □

3 The PB Free-Energy Functional

In this section, we study the PB functional $F[c]$ defined in (1.1), which is rewritten as

$$F[c] = \int_\Omega \left[\frac{1}{2}\rho\phi + W(c) \right] dx \tag{3.1}$$

and the related PB functional

$$\hat{F}[c] = \int_\Omega \left[\frac{\varepsilon}{2} |\nabla \phi|^2 + W(c) \right] dx. \tag{3.2}$$

Here, $\Omega \subset \mathbb{R}^3$ is a bounded domain, $c = (c_1, \ldots, c_M)$,

$$W(c) = S(c) - \sum_{i=1}^{M} \mu_i c_i, \tag{3.3}$$

and ϕ is the unique weak solution to (1.2) defined by $\phi \in H_g^1(\Omega)$ and

$$\int_\Omega \varepsilon \nabla \phi \cdot \nabla \xi \, dx = \langle \rho, \xi \rangle \qquad \forall \xi \in H_0^1(\Omega), \tag{3.4}$$

where $\rho = f + \sum_{i=1}^M q_i c_i$ and $\langle \rho, \xi \rangle = \rho(\xi)$ if $\rho \in H^{-1}(\Omega)$. If the integral of $\rho\xi$ over Ω exists, then $\langle \rho, \xi \rangle$ is the same as that integral. Note that $\hat{F}[c]$ is the first part of the penalized functional $G_\lambda[c, \phi]$ defined in (1.7).

We first define a suitable set $Y_+ \subset [L^1(\Omega)]^M$ of admissible concentrations and reformulate these functionals into new and equivalent ones for all $c \in Y_+$ which have the minimal regularity. Let $\Omega \subset \mathbb{R}^3$ be a bounded domain with a Lipschitz-continuous boundary $\partial\Omega$. We consider functions $\rho \in L^1(\Omega)$ such that

$$\sup_{0 \neq \xi \in H_0^1(\Omega) \cap L^\infty(\Omega)} \frac{1}{\|\xi\|_{H^1(\Omega)}} \left| \int_\Omega \rho \xi \, dx \right| < \infty. \tag{3.5}$$

We define

$$X = \left\{ \rho \in L^1(\Omega) : \text{condition (3.5) holds true} \right\}. \tag{3.6}$$

Clearly, X is a vector subspace of $L^1(\Omega)$. The following elementary lemma indicates that each $\rho \in X$ can be extended uniquely to an element in $H^{-1}(\Omega)$ and we omit its proof:

Lemma 3.1. *Let $\rho \in X$. There exists a unique $T_\rho \in H^{-1}(\Omega)$ such that*

$$\begin{aligned}
&T_\rho(\xi) = \int_\Omega \rho\xi \, dx \qquad \forall \xi \in H_0^1(\Omega) \cap L^\infty(\Omega), \\
&T_\rho(\xi) = \lim_{k\to\infty} \int_\Omega \rho\xi_k \, dx \qquad \forall \xi \in H_0^1(\Omega), \\
&\qquad \textit{where } \xi_k \in H_0^1(\Omega) \cap L^\infty(\Omega) \ (k \geq 1) \ \ \textit{and } \xi_k \to \xi \quad \textit{in } H^1(\Omega), \\
&\|T_\rho\|_{H^{-1}(\Omega)} = \sup_{0 \neq \xi \in H_0^1(\Omega)\cap L^\infty(\Omega)} \frac{1}{\|\xi\|_{H^1(\Omega)}} \left| \int_\Omega \rho\xi \, dx \right|.
\end{aligned}$$

Moreover, the space X is a Banach space with the norm $\|\rho\|_X = \|\rho\|_{L^1(\Omega)} + \|T_\rho\|_{H^{-1}(\Omega)}$. □

We denote $\langle T, \xi \rangle = T(\xi)$ for any $T \in H^{-1}(\Omega)$ and $\xi \in H_0^1(\Omega)$. If $\rho \in X$, then we shall identify $T_\rho = \rho$. If $\xi \in H_0^1(\Omega)$, then $\langle \rho, \xi \rangle = \langle T_\rho, \xi \rangle$. If $\xi \in H_0^1(\Omega) \cap L^\infty(\Omega)$, then $\langle \rho, \xi \rangle$ is the integral of $\rho\xi$ over Ω. We define

$$Y = \left\{ c = (c_1, \ldots, c_M) \in [L^1(\Omega)]^M : \rho(c) := \sum_{i=1}^M q_i c_i \in X \right\}, \tag{3.7}$$

$$Y_+ = \left\{ c = (c_1, \ldots, c_M) \in Y : c_i \in [L^1_+(\Omega)]^M, i = 1, \ldots, M \right\}, \tag{3.8}$$

where $L^p_+(\Omega) = \{u \in L^p(\Omega) : u \geq 0 \text{ a.e. } \Omega\}$ for any p: $1 \leq p \leq \infty$. For any $c \in Y$, define

$$\|c\|_Y = \sum_{i=1}^M \|c_i\|_{L^1(\Omega)} + \|\rho(c)\|_{H^{-1}(\Omega)}.$$

We can verify that $(Y, \|\cdot\|_Y)$ is a Banach space, Y_+ is a convex and closed subset of Y, and $[L^2_+(\Omega)]^M \subset Y_+ \subset [L^1_+(\Omega)]^M$.

Now let $\varepsilon \in L^\infty(\Omega)$ satisfy (1.3). Note that if $c \in Y_+$ and $\phi \in H_g^1(\Omega)$ is the weak solution to $\nabla \cdot \varepsilon \nabla \phi = -(f + \rho(c))$ with $\rho(c) = \sum_{i=1}^M q_i c_i$, then the integral of $\rho(c)\phi$ is not well defined in general. Therefore, we reformulate the functional $F[c]$. We also reformulate the functional $\hat{F}[c]$ for a unified treatment. To do so, we first define $L_\varepsilon : H^{-1}(\Omega) \to H_0^1(\Omega)$ as follows: for any $h \in H^{-1}(\Omega)$, $L_\varepsilon h \in H_0^1(\Omega)$ is the unique weak solution to $\nabla \cdot \varepsilon \nabla L_\varepsilon h = -h$, defined by

$$\int_\Omega \varepsilon \nabla (L_\varepsilon h) \cdot \nabla \xi \, dx = \langle h, \xi \rangle \qquad \forall \xi \in H_0^1(\Omega). \tag{3.9}$$

It is clear that the operator $L_\varepsilon : H^{-1}(\Omega) \to H_0^1(\Omega)$ is linear, continuous, and self-adjoint,

$$\langle h_1, L_\varepsilon h_2 \rangle = \langle h_2, L_\varepsilon h_1 \rangle = \int_\Omega \varepsilon \nabla L_\varepsilon h_1 \cdot \nabla L_\varepsilon h_2 \, dx \qquad \forall h_1, h_2 \in H^{-1}(\Omega). \tag{3.10}$$

Moreover, $(h_1, h_2) \mapsto \langle h_1, L_\varepsilon h_2\rangle$ defined by (3.10) is an inner product of $H^{-1}(\Omega)$. It induces the norm $\|h\|_\varepsilon := \sqrt{\langle h, L_\varepsilon h\rangle}$ on $H^{-1}(\Omega)$ and the norm is equivalent to the $H^{-1}(\Omega)$-norm.

Let $f \in L^2(\Omega)$ and $g \in H^1(\Omega)$. For any $c \in Y_+$, we have $\rho = f + \rho(c) \in H^{-1}(\Omega) \cap L^1(\Omega)$. Let $\phi_f \in H^1_g(\Omega)$ be the unique weak solution to $\nabla \cdot \varepsilon \nabla \phi_f = -f$ defined by

$$\int_\Omega \varepsilon \nabla \phi_f \cdot \nabla \xi \, dx = \int_\Omega f \xi \, dx \qquad \forall \xi \in H^1_0(\Omega). \tag{3.11}$$

If $\phi_f \in H^1_g(\Omega) \cap L^\infty(\Omega)$, then $\phi_f \rho(c) \in L^1(\Omega)$. In this case we define $E : Y_+ \to \mathbb{R} \cup \{+\infty\}$ by

$$E[c] = \int_\Omega \left[\frac{\varepsilon}{2} |\nabla L_\varepsilon \rho(c)|^2 + \frac{1}{2} f L_\varepsilon \rho(c) + \frac{1}{2} \phi_f \rho(c) + W(c) \right] dx + \int_\Omega \frac{1}{2} f \phi_f \, dx. \tag{3.12}$$

We also define $\hat{E} : Y_+ \to \mathbb{R} \cup \{+\infty\}$ by

$$\hat{E}[c] = \int_\Omega \left[\frac{\varepsilon}{2} |\nabla L_\varepsilon \rho(c)|^2 + f L_\varepsilon \rho(c) + W(c) \right] dx + \int_\Omega \frac{\varepsilon}{2} |\nabla \phi_f|^2 \, dx. \tag{3.13}$$

Lemma 3.2. *Assume either*

(1) *$\Omega \subset \mathbb{R}^3$ is a bounded domain with a C^1 boundary $\partial\Omega$, $\varepsilon \in L^\infty(\Omega)$ satisfy* (1.3)*, $f \in L^2(\Omega)$, and $g \in W^{1,\infty}(\Omega)$; or*

(2) *$\Omega \subset \mathbb{R}^3$ is a bounded domain with a C^2 boundary $\partial\Omega$, $\varepsilon \in W^{1,\infty}(\Omega)$ satisfy* (1.3)*, $f \in L^2(\Omega)$, and $g \in H^2(\Omega)$.*

Then $E[c] = F[c]$ for any $c \in [L^2_+(\Omega)]^M$ and $\hat{E}[c] = \hat{F}[c]$ for any $c \in Y_+$.

Proof. We first note that $\phi_f \in L^\infty(\Omega)$ by the global boundedness of solution (cf. Theorem 8.16 in [8]) with the assumption (1) or by the regularity of solution (cf. Theorem 8.12 in [8]) and the Sobolev embedding $H^2(\Omega) \hookrightarrow L^\infty(\Omega)$ (cf. [1, 8]) with the assumption (2). Thus, $E[c]$ is well defined for any $c \in Y_+$. We also note the following: for any $c \in Y_+$, by setting $h = \rho(c)$ and $\xi = L_\varepsilon \rho(c)$ in (3.9), we obtain

$$\|\rho(c)\|^2_\varepsilon = \langle \rho(c), L_\varepsilon \rho(c)\rangle = \int_\Omega \varepsilon |\nabla L_\varepsilon \rho(c)|^2 \, dx. \tag{3.14}$$

Let $c \in [L^2_+(\Omega)]^M$, then $c \in Y_+$. We show that $E[c] = F[c]$ with the assumption (1) or (2). Note that $\rho = f + \rho(c) \in L^2(\Omega)$. Let $\phi \in H^1_g(\Omega)$ be given by (3.4). With ϕ_f given by (3.11), we have $\phi = \phi_f + L_\varepsilon \rho(c) \in H^1_g(\Omega)$. It thus follows from (3.14) that

$$\begin{aligned}
\int_\Omega \frac{1}{2} \rho \phi \, dx &= \int_\Omega \frac{1}{2} (f + \rho(c))(\phi_f + L_\varepsilon \rho(c)) \, dx \\
&= \int_\Omega \left[\frac{1}{2} \rho(c) L_\varepsilon \rho(c) + \frac{1}{2} f L_\varepsilon \rho(c) + \frac{1}{2} \phi_f \rho(c) + \frac{1}{2} f \phi_f \right] dx \\
&= \int_\Omega \left[\frac{\varepsilon}{2} |\nabla L_\varepsilon \rho(c)|^2 + \frac{1}{2} f L_\varepsilon \rho(c) + \frac{1}{2} \phi_f \rho(c) \right] dx + \int_\Omega \frac{1}{2} f \phi_f \, dx.
\end{aligned}$$

Comparing this with the definition of $F[c]$ (cf. (3.1)) and $E[c]$ (cf. (3.12)), we see that they are the same.

Now, let $c \in Y_+$. We still have $\phi = \phi_f + L_\varepsilon \rho(c)$. Hence, by (3.11) with $\xi = L_\varepsilon \rho(c)$, we obtain

$$\begin{aligned}\int_\Omega \frac{\varepsilon}{2}|\nabla\phi|^2\,dx &= \int_\Omega \left[\frac{\varepsilon}{2}|\nabla(\phi-\phi_f)|^2 + \varepsilon\nabla(\phi-\phi_f)\cdot\nabla\phi_f + \frac{\varepsilon}{2}|\nabla\phi_f|^2\right]dx \\ &= \int_\Omega \left[\frac{\varepsilon}{2}|\nabla L_\varepsilon\rho(c)|^2 + \varepsilon\nabla L_\varepsilon\rho(c)\cdot\nabla\phi_f + \frac{\varepsilon}{2}|\nabla\phi_f|^2\right]dx \\ &= \int_\Omega \left[\frac{\varepsilon}{2}|\nabla L_\varepsilon\rho(c)|^2 + fL_\varepsilon\rho(c) + \frac{\varepsilon}{2}|\nabla\phi_f|^2\right]dx.\end{aligned}$$

Consequently, it follows from the definition of $\hat{F}[c]$ (cf. (3.2)) and $\hat{E}[c]$ (cf. (3.13)) that they are the same. □

We now calculate the first variation of E and $\hat{E}$ at a set of concentrations $c = (c_1, \dots, c_M) \in [L^\infty_+(\Omega)]^M$ such that each component of c is bounded below by a positive constant and derive the corresponding (generalized) Boltzmann distributions and the PB equation [5, 13, 14, 17]. Our approach is then to use the boundedness of solution to the PB equation established in Theorem 2.1 and the derived Boltzmann distributions to construct the ionic concentrations and show that they minimize the free-energy functional.

First, let

$$u_g = \phi_f - L_\varepsilon f \in H^1_g(\Omega). \tag{3.15}$$

Note that $u_g \in H^1_g(\Omega)$ is the unique weak solution to $\nabla\cdot\varepsilon\nabla u_g = 0$ defined by

$$\int_\Omega \varepsilon\nabla u_g\cdot\nabla\xi\,dx = 0 \qquad \forall\xi\in H^1_0(\Omega). \tag{3.16}$$

Now let $c = (c_1, \dots, c_M) \in Y_+$ and $d = (d_1, \dots, d_M) \in [C^1_{\rm c}(\Omega)]^M$. By the definition of L_ε (cf. (3.9)), ϕ (cf. (3.4)), ϕ_f (cf. (3.11)), and u_g (cf. (3.15)), we obtain $L_\varepsilon\rho(c) + L_\varepsilon f = \phi - u_g$ and $\phi_f = u_g + L_\varepsilon f$. Therefore, we have

$$\begin{aligned}\delta E[c][d] &= \left.\frac{d}{dt}\right|_{t=0} E[c+td] \\ &= \int_\Omega\left[\varepsilon\nabla L_\varepsilon\rho(c)\cdot\nabla L_\varepsilon\rho(d) + \frac{1}{2}fL_\varepsilon\rho(d) + \frac{1}{2}\phi_f\rho(d) + \nabla W(c)\cdot d\right]dx \\ &= \int_\Omega\left[(L_\varepsilon\rho(c))\rho(d) + \frac{1}{2}(L_\varepsilon f + \phi_f)\rho(d) + \nabla W(c)\cdot d\right]dx \\ &= \int_\Omega\left[\left(L_\varepsilon\rho(c) + \frac{1}{2}(L_\varepsilon f + \phi_f)\right)\rho(d) + \nabla W(c)\cdot d\right]dx \\ &= \sum_{i=1}^M \int_\Omega\left[\partial_{c_i}W(c) + q_i\left(\phi - \frac{u_g}{2}\right)\right]d_i\,dx.\end{aligned}$$

Since $W(c)$ is given in (3.3), we thus obtain

$$\delta_{c_i}E[c] = \partial_{c_i}S(c) - \mu_i + q_i\left(\phi - \frac{u_g}{2}\right), \quad i = 1,\dots,M. \tag{3.17}$$

Setting $\delta E[c] = 0$, we obtain the equilibrium concentration c. Similarly, we have for $\hat{E}$ that

$$\delta_{c_i}\hat{E}[c] = \partial_{c_i}S(c) - \mu_i + q_i\left(\phi - u_g\right), \quad i = 1,\dots,M. \tag{3.18}$$

In this case, the equilibrium concentration c is determined by $\delta \hat{E}[c] = 0$.

The following proposition indicates that the equilibrium conditions (3.17) or (3.18) determine a one-to-one correspondence between the equilibrium concentrations $c = (c_1, \ldots, c_M)$ and the equilibrium electrostatic potential ϕ:

Proposition 3.1. (1) *The system of equations*

$$\partial_{c_i} S(B_1(\phi), \ldots, B_M(\phi)) - \mu_i + q_i \phi = 0, \qquad i = 1, \ldots, M, \tag{3.19}$$

define the bijection $B_i : \mathbb{R} \to (0, \infty)$ $(i = 1, \ldots, M)$ with each $B_i \in C^\infty(\mathbb{R})$ and $B_i^{-1} \in C^\infty((0, \infty))$. Moreover, $B_i(A) \subset (0, \infty)$ is compact in $(0, \infty)$ if $A \subset \mathbb{R}$ is compact in $\mathbb{R}$.

(2) *The function $B : \mathbb{R} \to \mathbb{R}$ defined by*

$$B(\phi) = -\sum_{i=1}^{M} q_i \int_0^\phi B_i(\xi)\, d\xi + B_0, \tag{3.20}$$

with B_0 a constant such that $\inf_{s \in \mathbb{R}} B(s) = 0$, satisfies all the properties assumed in section 2.

We shall call $c_i = B_i(\phi)$ in Ω $(i = 1, \ldots, M)$ the (generalized) Boltzmann distributions of ionic concentrations $c = (c_1, \ldots, c_M)$ with respect to the electrostatic potential $\phi = \phi(x)$ $(x \in \Omega)$.

Proof of Proposition 3.1. We consider two different cases, without and with size effects, defined in (1.4). For the case of no size effect, we have for each i $(1 \le i \le M)$ that $\partial_{c_i} S(c) = \beta^{-1} \log(\Lambda^3 c_i)$. Hence, Eq. (3.19) defines $B_i(\phi) = c_i^\infty e^{-\beta q_i \phi}$ with $c_i^\infty = \Lambda^{-3} e^{\beta \mu_i}$. Since $q_i \neq 0$, B_i is a bijection from $\mathbb{R}$ to $(0, \infty)$. It is clear that both B_i and B_i^{-1} are C^∞-functions and that B_i maps a compact subset of $\mathbb{R}$ to a compact subset of $(0, \infty)$. In this case, we have by (3.20) that $B(\phi) = \beta^{-1} \sum_{i=1}^{M} c_i^\infty e^{-\beta q_i \phi} + b_0$, where b_0 is a constant so that $\inf_{s \in \mathbb{R}} B(s) = 0$. Direct calculations verify that the function $B \in C^\infty(\mathbb{R})$ satisfies all the properties for B in section 2. For the case of size effect included, these results are proved in [13, 14, 16]. □

We note that, if the size is uniform with the volume being v for an ion of any species and for a solvent molecule, then [3, 13, 14]

$$B_i(\phi) = \frac{c_i^\infty e^{-\beta q_i \phi}}{1 + v \sum_{j=1}^{M} c_j^\infty (e^{-\beta q_j \phi} - 1)} \quad \text{with} \quad c_i^\infty = \frac{v^{-1} e^{\beta \mu_i}}{1 + \sum_{j=1}^{M} e^{\beta \mu_j}}, \quad i = 1, \ldots, M.$$

However, such an analytical formula seems not available for ions with non-uniform sizes.

Note that for each set of concentrations $c = (c_1, \ldots, c_M)$, the corresponding electrostatic potential $\phi \in H_g^1(\Omega)$ is the unique weak solution to the Poisson equation corresponding to the charge density $\rho = f + \rho(c)$; cf. (3.4). If c is an equilibrium, i.e., $\delta E[c] = 0$ or $\delta \hat{E}[c] = 0$, then it follows from (3.17), (3.18), and Proposition 3.1 that

$$\text{For } E[c]: \qquad \rho(c) = \sum_{i=1}^{M} q_i c_i = -B'\left(\phi - \frac{u_g}{2}\right), \tag{3.21}$$

$$\text{For } \hat{E}[c]: \qquad \rho(c) = \sum_{i=1}^{M} q_i c_i = -B'(\phi - u_g). \tag{3.22}$$

The Poisson equation (cf. (3.4)) then becomes the (generalized) PB equation for the equilibrium electrostatic potential ϕ, given by

$$\text{For } E[c]: \qquad \nabla\cdot\varepsilon\nabla\phi - B'\left(\phi - \frac{u_g}{2}\right) = -f \qquad \text{in } \Omega, \tag{3.23}$$

$$\text{For } \hat{E}[c]: \qquad \nabla\cdot\varepsilon\nabla\phi - B'(\phi - u_g) = -f \qquad \text{in } \Omega. \tag{3.24}$$

We conclude from our calculations that if c minimizes E or $\hat{E}$, and if each component of c is bounded below and above by positive constants, then the corresponding $\phi \in H_g^1(\Omega)$ defined by (3.4) solves the PBE (3.23) or (3.24). Conversely, if ϕ solves the PBE (3.23) or (3.24), then we can construct the concentration $c = (c_1, \dots, c_M)$ by $c_i = B_i(\phi - u_g/2)$ or $c_i = B_i(\phi - u_g)$ $(i = 1, \dots, M)$ to minimize E or $\hat{E}$.

The following is our main result in this section:

Theorem 3.1. *Assume either (1) or (2) as in Lemma 3.2. Then there exist a unique minimizer $d = (d_1, \dots, d_M)$ of $E : Y_+ \to \mathbb{R} \cup \{+\infty\}$ and a unique minimizer $\hat{d} = (\hat{d}_1, \dots, \hat{d}_M)$ of $\hat{E} : Y_+ \to \mathbb{R} \cup \{+\infty\}$, given respectively by*

$$d_i = B_i\left(\psi - \frac{u_g}{2}\right) \quad \text{and} \quad \hat{d}_i = B_i\left(\hat{\psi} - u_g\right) \quad \text{in } \Omega,\ i = 1, \dots, M, \tag{3.25}$$

where $\psi, \hat{\psi} \in H_g^1(\Omega) \cap L^\infty(\Omega)$ with the assumption (1) *and $\psi, \hat{\psi} \in H_g^1(\Omega) \cap H^2(\Omega)$ with the assumption* (2) *are the unique weak solution to the PB equation* (3.23) *and* (3.24)*, respectively. In particular, $d, \hat{d} \in [L_+^\infty(\Omega) \cap H^1(\Omega)]^M$ and there exist positive constants θ_i and $\hat{\theta}_i$ $(i = 1, 2)$ such that*

$$\theta_1 \le d_i \le \theta_2 \quad \text{and} \quad \hat{\theta}_1 \le \hat{d}_i \le \hat{\theta}_2 \quad \text{a.e. } \Omega,\ i = 1, \dots, M. \tag{3.26}$$

Proof. We only consider the functional E as the proof for the functional $\hat{E}$ is similar.

Step 1. We first establish the existence and uniqueness of the minimizer of E. Since $L_\varepsilon : H^{-1}(\Omega) \to H_0^1(\Omega)$ is self-adjoint, and $L_\varepsilon f \in L^\infty(\Omega)$ following the assumption (1) or (2), we have

$$\int_\Omega f L_\varepsilon \rho(c)\, dx = \int_\Omega (L_\varepsilon f)\rho(c)\, dx \qquad \forall c \in Y_+.$$

Denoting $\eta = (L_\varepsilon f + \phi_f)/2 \in L^\infty(\Omega)$ and $V(c) = \eta\rho(c) + W(c)$ for any $c \in Y_+$, we can rewrite the energy $E[c]$ (cf. (3.12)) as

$$E[c] = \int_\Omega \left[\frac{\varepsilon}{2}|\nabla L_\varepsilon \rho(c)|^2 + V(c)\right] dx + \int_\Omega \frac{1}{2} f\phi_f\, dx \qquad \forall c \in Y_+.$$

By (1.4) and (3.3), we have

$$V(c) = \begin{cases} \beta^{-1}\displaystyle\sum_{i=1}^M c_i\left[\log c_i + \sigma_i\right] & \text{without size effect,} \\ \beta^{-1}\displaystyle\sum_{i=1}^M c_i\left[\log c_i + \tau_i\right] + \beta^{-1}c_0\left[\log(v_0 c_0) - 1\right] & \text{with size effect,} \end{cases} \tag{3.27}$$

where σ_i and τ_i are some functions in $L^\infty(\Omega)$ that are independent of $c \in Y_+$ and c_0 is a function of $(c_1, \dots, c_M)$ as defined in (1.5). Note that V is bounded below and it is also convex [13, 14]. Therefore, by setting $h_1 = h_2 = \rho(c)$ in (3.10) and by the remark below (3.10), we have

$$E[c] \geq C_1 \|\rho(c)\|^2_{H^{-1}(\Omega)} + \int_\Omega V(c)\, dx + C_2 \qquad \forall c \in Y_+,$$

where $C_1 > 0$ and C_2 are two constants.

Let $\gamma = \inf_{c \in Y_+} E[c]$. Since $V(c)$ is bounded below for any $c \in Y_+$, γ is finite. Let $c^{(k)} = (c_1^{(k)}, \dots, c_M^{(k)}) \in Y_+$ $(k = 1, 2, \dots)$ be such that $E[c^{(k)}] \to \gamma$. We have

$$\sup_{k \geq 1} \|\rho(c^{(k)})\|_{H^{-1}(\Omega)} < \infty \qquad \text{and} \qquad \sup_{k \geq 1} \int_\Omega V(c^{(k)})\, dx < \infty. \tag{3.28}$$

We claim that, up to a subsequence that is not relabeled, $c^{(k)} \rightharpoonup d$ in $[L^1(\Omega)]^M$ for some $d = (d_1, \dots, d_M) \in [L^1_+(\Omega)]^M$. In the case of no size effect included, this follows from that fact that $V(c)$ is superlinear (cf. (3.27)), the second inequality in (3.28), and de la Vallée Poussin's criterion [18] (cf. the proof of Lemma 3.3 in [14]). In the case with the size effect included, this follows from the fact that all the concentrations are bounded (cf. (1.5)) and hence, there exists a subsequence of $\{c^{(k)}\}$ that converges weakly in $[L^2(\Omega)]^M$ and hence weakly in $[L^1(\Omega)]^M$ to some $d = (d_1, \dots, d_M) \in [L^2_+(\Omega)]^M \subset Y_+$. Since $c^{(k)} \rightharpoonup d$ in $[L^1(\Omega)]^M$, we have by the convexity of $V(c)$ for both of the cases that [13, 14]

$$\liminf_{k \to \infty} \int_\Omega V(c^{(k)})\, dx \geq \int_\Omega V(d)\, dx. \tag{3.29}$$

By the first inequality in (3.28), there exists a subsequence of $\{c^{(k)}\}$, not relabeled, such that $\rho(c^{(k)}) \rightharpoonup h$ in $H^{-1}(\Omega)$ for some $h \in H^{-1}(\Omega)$. Since $c^{(k)} \rightharpoonup d$ in $[L^1(\Omega)]^M$, by the definition of $\rho(c)$ for any $c \in Y_+$ (cf. (3.7) and (3.8)), $\rho(c^{(k)}) \rightharpoonup \rho(d)$ in $L^1(\Omega)$. Thus,

$$h(\xi) = \lim_{k \to \infty} \int_\Omega \rho(c^{(k)}) \xi\, dx = \int_\Omega \rho(d) \xi\, dx \qquad \forall \xi \in H^1_0(\Omega) \cap L^\infty(\Omega).$$

Consequently, $\rho(d) = h \in X$ and hence $d \in Y_+$. Since $\rho(c^{(k)}) \rightharpoonup \rho(d)$ in $H^{-1}(\Omega)$, we have $\lim_{k \to \infty} \langle \rho(c^{(k)}) - \rho(d), L_\varepsilon \rho(d) \rangle = 0$. Splitting the terms, we have by (3.10) that

$$\begin{aligned}
&\liminf_{k \to \infty} \int_\Omega \frac{\varepsilon}{2} |\nabla L_\varepsilon \rho(c^{(k)})|^2\, dx \\
&\quad \geq \liminf_{k \to \infty} \int_\Omega \left[\frac{\varepsilon}{2} |\nabla L_\varepsilon \rho(c^{(k)}) - \nabla L_\varepsilon \rho(d)|^2 + \frac{\varepsilon}{2} |\nabla L_\varepsilon \rho(d)|^2 \right] dx \\
&\qquad + \liminf_{k \to \infty} \int_\Omega \varepsilon \left(\nabla L_\varepsilon \rho(c^{(k)}) - \nabla L_\varepsilon \rho(d) \right) \cdot \nabla L_\varepsilon \rho(d)\, dx \\
&\quad \geq \int_\Omega \frac{\varepsilon}{2} |\nabla L_\varepsilon \rho(d)|^2\, dx + \liminf_{k \to \infty} \langle \rho(c^{(k)}) - \rho(d), L_\varepsilon \rho(d) \rangle \\
&\quad = \int_\Omega \frac{\varepsilon}{2} |\nabla L_\varepsilon \rho(d)|^2\, dx.
\end{aligned}$$

This and (3.29) imply $\gamma = \liminf_{k \to \infty} E[c^{(k)}] \geq E[d] \geq \gamma$. Hence $d \in Y_+$ is a minimizer of $E : Y_+ \to \mathbb{R} \cup \{+\infty\}$.

Assume $\tilde{d} \in Y_+$ is also a minimizer of E over Y_+. Clearly, $(\tilde{d}+d)/2 \in Y_+$. Since E is convex, we have $(\tilde{d}+d)/2$ is also a minimizer of E over Y_+. Therefore, by direct calculations, we have

$$
\begin{aligned}
0 &= E\left[\frac{\tilde{d}+d}{2}\right] - \frac{1}{2}E[\tilde{d}] - \frac{1}{2}E[d] \\
&= -\int_\Omega \frac{\varepsilon}{8}|\nabla L_\varepsilon \rho(\tilde{d}) - \nabla L_\varepsilon \rho(d)|^2\,dx + \int_\Omega \left[V\left(\frac{\tilde{d}+d}{2}\right) - \frac{1}{2}V(\tilde{d}) - \frac{1}{2}V(d)\right] dx \\
&\le \int_\Omega \left[V\left(\frac{\tilde{d}+d}{2}\right) - \frac{1}{2}V(\tilde{d}) - \frac{1}{2}V(d)\right] dx.
\end{aligned}
$$

Since V is convex on $[0,\infty)$, the integrand of the last integral is non positive and therefore vanishes a.e. in Ω. Moreover, since $c_0 \log(v_0 c_0)$ is convex in $(c_1,\dots,c_M)$ [13] for the case of size effect included, we have by the definition of V (cf. (3.27)) that

$$
V_i\left(\frac{\tilde{d}+d}{2}\right) = \frac{1}{2}V_i(\tilde{d}) + \frac{1}{2}V_i(d) \qquad \text{in } \Omega_i,\ i=1,\dots,M, \tag{3.30}
$$

where $\Omega_i \subseteq \Omega$ with the measure $|\Omega \setminus \Omega_i| = 0$ and $V_i(c) = \beta^{-1}\sum_{i=1}^M c_i(\log c_i + \gamma_i)$ with $\gamma_i = \sigma_i$ or τ_i $(i=1,\dots,M)$. Note that each V_i is convex at every point in Ω_i. Fix i. We verify from (3.30) that $\tilde{d}_i(x) = 0$ if and only if $d_i(x) = 0$ for any $x \in \Omega_i$. If both $\tilde{d}_i(x)$ and $d_i(x)$ are nonzero for some $x \in \Omega_i$, then by (3.30) and the strict convexity of V_i on $(0,\infty)$, we infer that $\tilde{d}_i(x) = d_i(x)$. Therefore, $\tilde{d} = d$ a.e. Ω and the minimizer is unique.

Step 2. We establish the bounds for d and show that $d \in [H^1(\Omega)]^M$. To do so, we construct the set of concentrations using Boltzmann distributions and verify that it is indeed the minimizer d and it satisfies the desired properties.

By Theorem 2.1 with $f_k = f$ and $g_k = g/2$ for every k, there exists a unique $\psi_f \in H^1_{g/2}(\Omega)$ that minimizes $J : H^1_{g/2}(\Omega) \to \mathbb{R} \cup \{+\infty\}$ defined by

$$
J[\psi] = \int_\Omega \left[\frac{\varepsilon}{2}|\nabla\psi|^2 - f\psi + B(\psi)\right] dx, \qquad \forall \psi \in H^1_{g/2}(\Omega),
$$

where B is defined in (3.20) in Proposition 3.1. Moreover, $\psi_f \in H^1_{g/2}(\Omega) \cap L^\infty(\Omega)$ with the assumption (1) and $\psi_f \in H^1_{g/2}(\Omega) \cap H^2(\Omega) \subset H^1_{g/2}(\Omega) \cap L^\infty(\Omega)$ with the assumption (2) is the unique weak solution to the corresponding PB equation defined by

$$
\int_\Omega [\varepsilon \nabla\psi_f \cdot \nabla\xi + B'(\psi_f)\xi]\,dx = \int_\Omega f\xi\,dx \qquad \forall \xi \in H^1_0(\Omega). \tag{3.31}
$$

Recall that $u_g \in H^1_g(\Omega)$ is defined in (3.16). We have $u_g \in H^1_g(\Omega) \cap L^\infty(\Omega)$ under the assumption (1) and $u_g \in H^1_g(\Omega) \cap H^2(\Omega) \subset H^1_g(\Omega) \cap L^\infty(\Omega)$ under the assumption (2). Define

$$
\psi = \psi_f + \frac{u_g}{2} \in H^1_g(\Omega) \cap L^\infty(\Omega). \tag{3.32}
$$

Note that $\psi \in H^1_g(\Omega) \cap H^2(\Omega)$ with the assumption (2). By (3.15), (3.16), and (3.31), we infer that ψ is the weak solution to the PB equation (3.23), i.e.,

$$
\int_\Omega \left[\varepsilon \nabla\psi \cdot \nabla\xi + B'\left(\psi - \frac{u_g}{2}\right)\xi\right] dx = \int_\Omega f\xi\,dx \qquad \forall \xi \in H^1_0(\Omega). \tag{3.33}
$$

Now, let us define $b = (b_1, \ldots, b_M) : \Omega \to \mathbb{R}^M$ by

$$b_i = B_i\left(\psi - \frac{u_g}{2}\right), \qquad i = 1, \ldots, M, \tag{3.34}$$

where each B_i is defined in Proposition 3.1. By the definition of B (cf. (3.20)),

$$\rho(b) = \sum_{i=1}^{M} q_i b_i = -B'\left(\psi - \frac{u_g}{2}\right).$$

By the definition of $L_\varepsilon : H^{-1}(\Omega) \to H_0^1(\Omega)$ (cf. (3.9)) and the fact that $\psi \in H_g^1(\Omega) \cap L^\infty(\Omega)$ (defined in (3.32)) is the weak solution to the PBE (cf. (3.33)), we have

$$\psi = u_g + L_\varepsilon f + L_\varepsilon \rho(b). \tag{3.35}$$

Clearly, $b \in [H^1(\Omega)]^M$ as $\psi - u_g/2 \in H^1(\Omega) \cap L^\infty(\Omega)$ and $B_i \in C^\infty(\mathbb{R})$ by Proposition 3.1. Moreover, since $\psi - u_g/2 \in L^\infty(\Omega)$, it follows from (3.34) and Proposition 3.1 that there exist positive constants $\theta_1 > 0$ and $\theta_2 > 0$ such that $\theta_1 \le b_i \le \theta_2$ a.e. Ω $(i = 1, \ldots, M)$.

It remains to show that the constructed concentrations $b = (b_1, \ldots, b_M)$ (cf. (3.34)) is in fact a minimizer of $E : Y_+ \to \mathbb{R} \cup \{+\infty\}$. Once this is shown, then by *Step 1* of the proof, $b = d$, which is the unique minimizer of E over Y_+, and by the bounds on b, d satisfies the desired inequality.

For any $c \in Y_+$, we have

$$\begin{aligned} E[c] - E[b] = &\int_\Omega \frac{\varepsilon}{2} \nabla \left(L_\varepsilon \rho(c) - L\rho(b)\right) \cdot \nabla \left(L_\varepsilon \rho(c) + L_\varepsilon \rho(b)\right) dx \\ &+ \int_\Omega \left(\frac{1}{2} f L_\varepsilon \rho(c) - \frac{1}{2} f L_\varepsilon \rho(b)\right) dx + \int_\Omega \left(\frac{1}{2}\rho(c)\phi_f - \frac{1}{2}\rho(b)\phi_f\right) dx \\ &+ \int_\Omega \left(W(c) - W(b)\right) dx \\ := &\ A_1 + A_2 + A_3. \end{aligned}$$

By the definition of the operator L_ε (3.9), we obtain

$$\begin{aligned} &\int_\Omega \varepsilon \nabla L_\varepsilon \rho(c) \cdot \nabla \left(L_\varepsilon \rho(c) + L_\varepsilon \rho(b)\right) dx = \langle \rho(c),\ L_\varepsilon \rho(c) + L_\varepsilon \rho(b) \rangle, \\ &\int_\Omega \varepsilon \nabla L_\varepsilon \rho(b) \cdot \nabla \left(L_\varepsilon \rho(c) + L_\varepsilon \rho(b)\right) dx = \langle \rho(b),\ L_\varepsilon \rho(c) + L_\varepsilon \rho(b) \rangle, \end{aligned}$$

leading to

$$A_1 = \int_\Omega \frac{\varepsilon}{2} \nabla \left(L_\varepsilon \rho(c) - L_\varepsilon \rho(b)\right) \cdot \nabla \left(L_\varepsilon \rho(c) + L_\varepsilon \rho(b)\right) dx = \frac{1}{2} \langle \rho(c) - \rho(b),\ L_\varepsilon \rho(c) + L_\varepsilon \rho(b) \rangle.$$

Since $L_\varepsilon : H^{-1}(\Omega) \to H_0^1(\Omega)$ is self-adjoint, we have

$$A_2 = \int_\Omega \left(\frac{1}{2} f L_\varepsilon \rho(c) - \frac{1}{2} f L_\varepsilon \rho(b)\right) dx + \int_\Omega \left(\frac{1}{2}\rho(c)\phi_f - \frac{1}{2}\rho(b)\phi_f\right) dx$$

$$= \frac{1}{2}\langle \rho(c) - \rho(b), L_\varepsilon f\rangle + \frac{1}{2}\int_\Omega [\rho(c) - \rho(b)]\, \phi_f \, dx.$$

Note that $W(c)$ and $S(c)$ are related by (3.3). By our definition of b_i (cf. (3.34)) and Proposition 3.1, we have $\partial_{c_i} W(b) = \partial_{c_i} S(b) - \mu_i = -q_i\,(\psi - u_g/2)$ $(i = 1, \dots, M)$. Therefore, by the convexity of W, the bounds $\theta_1 \le b_i \le \theta_2$ a.e. Ω $(i = 1, \dots, M)$, and the fact that $u_g \in L^\infty(\Omega)$ (cf. (3.15)) and $\psi \in L^\infty(\Omega)$ (cf. (3.32)), we have

$$A_3 = \int_\Omega [W(c) - W(b)]\, dx \ge \int_\Omega \left[\sum_{i=1}^M \partial_{c_i} W(b)(c_i - b_i)\right] dx = \frac{1}{2}\int_\Omega [\rho(c) - \rho(b)]\,(u_g - 2\psi)\, dx.$$

By (3.15) and (3.35), $\phi_f + u_g - 2\psi = -L_\varepsilon f - 2L_\varepsilon \rho(b) \in H_0^1(\Omega)$. Consequently, it follows the estimates of A_1, A_2, and A_3 and the definition of L_ε (cf. (3.9)) that

$$\begin{aligned} E[c] - E[b] &\ge \frac{1}{2}\langle \rho(c) - \rho(b),\, L_\varepsilon\rho(c) + L_\varepsilon\rho(b)\rangle + \frac{1}{2}\langle \rho(c) - \rho(b),\, L_\varepsilon f\rangle \\ &\quad - \frac{1}{2}\int_\Omega [\rho(c) - \rho(b)]\ [L_\varepsilon f + 2L_\varepsilon \rho(b)]\ dx \\ &= \frac{1}{2}\langle \rho(c) - \rho(b),\, L_\varepsilon\rho(c) - L_\varepsilon\rho(b)\rangle \\ &= \int_\Omega \frac{\varepsilon}{2}|\nabla\,[L_\varepsilon\rho(c) - L_\varepsilon\rho(b)]\,|^2\, dx \\ &\ge 0. \end{aligned}$$

Hence b is a minimizer of E over Y_+. □

Let $f_k \in L^2(\Omega)$ and $g_k \in H^1(\Omega)$ $(k = 1, 2, \dots)$. For each $k \ge 1$, we define $\hat{F}_k : [L^2_+(\Omega)]^M \to \mathbb{R} \cup \{+\infty\}$ by (cf. (3.2))

$$\hat{F}_k[c] = \int_\Omega \left[\frac{\varepsilon}{2}|\nabla\phi_k|^2 + W(c)\right] dx,$$

where $\phi_k = \phi_k(c) \in H^1_{g_k}(\Omega)$ is determined by

$$\int_\Omega \varepsilon\nabla\phi_k \cdot \nabla\xi\, dx = \int_\Omega \left(f_k + \sum_{i=1}^M q_i c_i\right)\xi\, dx \qquad \forall \xi \in H_0^1(\Omega). \tag{3.36}$$

The following corollary generalizes the above theorem and will be used in the next section:

Corollary 3.1. *Let $\Omega \subset \mathbb{R}^3$ be a bounded domain with a C^2 boundary $\partial\Omega$, $\varepsilon \in W^{1,\infty}(\Omega)$ satisfy (1.3), and $f_k \in L^2(\Omega)$ and $g_k \in H^1(\Omega)$ $(k = 1, 2, \dots)$. Assume $\sup_{k\ge 1}\|f_k\|_{L^2(\Omega)} < \infty$. For each $k \ge 1$, let $\hat{\psi}^{(k)} \in H_0^1(\Omega)$ be the unique weak solution to the PB equation*

$$\nabla\cdot\varepsilon\nabla\hat{\psi}^{(k)} - B'(\hat{\psi}^{(k)}) = -f_k \qquad \text{in } \Omega. \tag{3.37}$$

Then, each $\hat{\psi}^{(k)} \in H^2(\Omega)$ and $\sup_{k\ge1}\|\hat{\psi}^{(k)}\|_{H^2(\Omega)} < \infty$. Moreover, if $\hat{d}_k = (\hat{d}_{k,1}, \dots, \hat{d}_{k,M}) : \Omega \to \mathbb{R}^M$ is defined by $\hat{d}_{k,i} = B_i(\hat{\psi}^{(k)})$ $(i = 1, \dots, M)$, then each $\hat{d}_k \in [L^2_+(\Omega)]^M$ is the unique minimizer of $\hat{F}_k : [L^2_+(\Omega)]^M \to \mathbb{R} \cup \{+\infty\}$, $\hat{d}_k \in [L^\infty_+(\Omega) \cap H^1(\Omega)]^M$ $(k = 1, 2, \dots)$, $\sup_{k\ge1}\|\hat{d}_{k,i}\|_{H^1(\Omega)} < \infty$ $(i = 1, \dots, M)$, and there are positive constants $\hat{\theta}_1$ and $\hat{\theta}_2$ such that

$$0 < \hat{\theta}_1 \le \hat{d}_{k,i} \le \hat{\theta}_2 \qquad \text{a.e. } \Omega,\ \forall i = 1, \dots, M,\ \forall k \ge 1. \tag{3.38}$$

Proof. For each $k \geq 1$, let $\eta_k \in H^1_{g_k}(\Omega)$ be defined uniquely by

$$\int_\Omega \varepsilon \nabla \eta_k \cdot \nabla \xi \, dx = 0 \qquad \forall \xi \in H^1_0(\Omega). \tag{3.39}$$

Let $c \in [L^2_+(\Omega)]^M$ and $\phi_k = \phi_k(c) \in H^1_{g_k}(\Omega)$ be given in (3.36). Let $\psi_k(c) = \phi_k(c) - \eta_k \in H^1_0(\Omega)$. Then we have

$$\int_\Omega \varepsilon \nabla \psi_k(c) \cdot \nabla \xi \, dx = \int_\Omega \left(f_k + \sum_{i=1}^M q_i c_i \right) \xi \, dx \qquad \forall \xi \in H^1_0(\Omega).$$

Regularity theory (cf. Theorem 8.12 in [8]) implies that $\psi_k(c) \in H^2(\Omega)$. Direct calculations using (3.39) with $\psi_k(c)$ replacing ξ lead to

$$\hat{F}_k[c] = \hat{F}^{(k)}[c] + \int_\Omega \frac{\varepsilon}{2} |\nabla \eta_k|^2 \, dx,$$

where

$$\hat{F}^{(k)}[c] = \int_\Omega \left[\frac{\varepsilon}{2} |\nabla \psi_k(c)|^2 + W(c) \right] dx \qquad \forall c \in [L^2_+(\Omega)]^M.$$

Thus, for each $k \geq 1$, the minimization of $\hat{F}_k$ over $[L^2_+(\Omega)]^M$ is equivalent to the minimization of $\hat{F}^{(k)}$ over $[L^2_+(\Omega)]^M$.

By Theorem 3.1, with $\hat{F}$, f, and g there replaced by $\hat{F}^{(k)}$, f_k, and 0, respectively, for each $k \geq 1$, there exists a unique minimizer $\hat{d}_k = (\hat{d}_{k,1}, \dots, \hat{d}_{k,M})$ of $\hat{F}^{(k)}$ over $[L^2_+(\Omega)]^M$ and $\hat{d}_k \in [L^\infty_+(\Omega) \cap H^1(\Omega)]^M$. Moreover, by (3.25) and the fact that $u_g = 0$ (cf. (3.16)) since $g = 0$, we have $\hat{d}_{k,i} = B_i(\hat{\psi}^{(k)})$ $(i = 1, \dots, M)$, where $\hat{\psi}^{(k)} \in H^1_0(\Omega)$ is the unique weak solution to the PB equation (3.37). By Case (2) of Theorem 2.1, $\sup_{k \geq 1} \|\hat{\psi}^{(k)}\|_{H^2(\Omega)} < \infty$, and hence by embedding $\sup_{k \geq 1} \|\hat{\psi}^{(k)}\|_{L^\infty(\Omega)} < \infty$. Therefore, since $\hat{d}_{k,i} = B_i(\hat{\psi}^{(k)})$ $(i = 1, \dots, M)$, (3.38) holds true, and further, since each B_i is smooth, $\sup_{k \geq 1} \|\hat{d}_{k,i}\|_{H^1(\Omega)} < \infty$ $(i = 1, \dots, M)$. □

4 Penalized PB Free-Energy Functionals

We now consider the penalized functionals $G_\lambda[c, \phi]$ defined in (1.7). Using the function W defined in (3.3) and the notation $\rho(c) = \sum_{i=1}^M q_i c_i$ for $c = (c_1, \dots, c_M)$, we rewrite the functional G_λ as

$$\begin{aligned} G_\lambda[c, \phi] = & \int_\Omega \left[\frac{\varepsilon}{2} |\nabla \phi|^2 + W(c) \right] dx \\ & + \lambda_1 \int_\Omega (\nabla \cdot \varepsilon \nabla \phi + f + \rho(c))^2 \, dx + \lambda_2 \int_{\partial\Omega} (\phi - g)^2 \, dS. \end{aligned} \tag{4.1}$$

We define $H = H(\Omega)$ by $H = \{ u \in H^1(\Omega) : \Delta u \in L^2(\Omega) \}$, where Δu is defined in the weak sense, i.e., $\Delta u \in L^2(\Omega)$ is determined by

$$\int_\Omega \Delta u \, \xi \, dx = \int_\Omega u \Delta \xi \, dx \qquad \forall \xi \in C^\infty_c(\Omega).$$

If $u \in H^1(\Omega)$ then we have equivalently

$$\int_\Omega \Delta u \, \xi \, dx = -\int_\Omega \nabla u \cdot \nabla \xi \, dx \qquad \forall \xi \in H_0^1(\Omega). \tag{4.2}$$

We define for any $u, v \in H$

$$\langle u, v \rangle_H = \int_\Omega (uv + \nabla u \cdot \nabla v + \Delta u \Delta v) \, dx \qquad \text{and} \qquad \|u\|_H = \sqrt{\langle u, u \rangle}_H. \tag{4.3}$$

We can verify directly that $\langle \cdot, \cdot \rangle_H$ and $\| \cdot \|_H$ are an inner product and the corresponding norm on H, respectively, and H is a Hilbert space.

Let $\varepsilon \in W^{1,\infty}(\Omega)$ satisfy (1.3) and $u \in L^2(\Omega)$. If there exists $w \in L^2(\Omega)$ such that

$$\int_\Omega w \, \xi \, dx = \int_\Omega u(\nabla \cdot \varepsilon \nabla \xi) \, dx \qquad \forall \xi \in C_c^\infty(\Omega),$$

then we say $\nabla \cdot \varepsilon \nabla u$ exists in the weak sense and $\nabla \cdot \varepsilon \nabla u = w$. If $u \in H^1(\Omega)$ then equivalently

$$\int_\Omega (\nabla \cdot \varepsilon \nabla u) \xi \, dx = -\int_\Omega \varepsilon \nabla u \cdot \nabla \xi \, dx \qquad \forall \xi \in H_0^1(\Omega). \tag{4.4}$$

Assume $u \in H^1(\Omega)$ and $\Delta u \in L^2(\Omega)$ exists. Setting $\xi = \varepsilon \eta$ in (4.2) for any $\eta \in H_0^1(\Omega)$, we see from (4.4) that $\nabla \cdot \varepsilon \nabla u = \nabla u \cdot \nabla \varepsilon + \varepsilon \Delta u \in L^2(\Omega)$. Similarly, assume $u \in H^1(\Omega)$ and $\nabla \cdot \varepsilon \nabla u \in L^2(\Omega)$. Setting $\xi = \eta / \varepsilon$ in (4.4) for any $\eta \in H_0^1(\Omega)$, we see from (4.2) that $\Delta u = (\nabla \cdot \varepsilon \nabla u - \nabla u \cdot \nabla \varepsilon)/\varepsilon \in L^2(\Omega)$. Therefore, if $u \in H^1(\Omega)$ then $\Delta u \in L^2(\Omega)$ (which implies that $u \in H$) if and only if $\nabla \cdot \varepsilon \nabla u \in L^2(\Omega)$. In this case, $\nabla \cdot \varepsilon \nabla u = \nabla \varepsilon \cdot \nabla u + \varepsilon \Delta u$ a.e. in Ω.

Theorem 4.1. *Let $\Omega \subset \mathbb{R}^3$ be a bounded domain with a C^2 boundary $\partial\Omega$, $\varepsilon \in W^{1,\infty}(\Omega)$ satisfy (1.3), $f \in L^2(\Omega)$, and $g \in H^2(\Omega)$. Let $\lambda_1^{(0)} > 0$ and $\lambda_2^{(0)} > 0$. For any $\lambda_1 \geq \lambda_1^{(0)}$ and $\lambda_2 \geq \lambda_2^{(0)}$, there exists a unique $(c_\lambda, \phi_\lambda) \in [L_+^2(\Omega)]^M \times H$ such that*

$$G_\lambda[c_\lambda, \phi_\lambda] = \min_{(c,\phi) \in [L_+^2(\Omega)]^M \times H} G_\lambda[c, \phi]. \tag{4.5}$$

Moreover, there exist constants $\theta_1 > 0$ and $\theta_2 > 0$, independent of λ_1 and λ_2, such that

$$0 < \theta_1 \leq c_{\lambda,i} \leq \theta_2 \quad \text{a.e. in } \Omega, \; i = 1, \dots, M.$$

Proof. Fix $\lambda = (\lambda_1, \lambda_2)$ with $\lambda_1 \geq \lambda_1^{(0)}$ and $\lambda_2 \geq \lambda_2^{(0)}$. We divide our proof into five steps.

Step 1. We first reformulate the energy functional using a new pair of variables. For any $c \in [L_+^2(\Omega)]^M$, we define $\psi = \psi(c) \in H_g^1(\Omega)$ by

$$\int_\Omega \varepsilon \nabla \psi(c) \cdot \nabla \xi \, dx = \int_\Omega \left(f + \sum_{i=1}^M q_i c_i \right) \xi \, dx \qquad \forall \xi \in H_0^1(\Omega). \tag{4.6}$$

Regularity theory (cf. Theorem 8.12 in [8]) implies that $\psi(c) \in H^2(\Omega)$. We define $\tilde{G}_\lambda$: $[L_+^2(\Omega)]^M \times H \to \mathbb{R} \cup \{+\infty\}$ by

$$\tilde{G}_\lambda[c, u] = \int_\Omega \left[\frac{\varepsilon}{2} |\nabla \psi(c) - \nabla u|^2 + W(c) \right] dx + \lambda_1 \int_\Omega (\nabla \cdot \varepsilon \nabla u)^2 \, dx + \lambda_2 \int_{\partial\Omega} u^2 \, dS \tag{4.7}$$

and verify that

$$G_\lambda[c,\phi] = \tilde{G}_\lambda[c,u] \quad \text{with } u = \psi(c) - \phi \in H \qquad \forall (c,\phi) \in [L^2_+(\Omega)]^M \times H. \tag{4.8}$$

Note that (c,ϕ) minimizes G_λ over $[L^2_+(\Omega)]^M \times H$ if and only if $(c,u) = (c,\psi(c)-\phi)$ minimizes $\tilde{G}_\lambda$ over $[L^2_+(\Omega)]^M \times H$. Hence, it suffices to show the existence of a unique minimizer of $\tilde{G}_\lambda$ over $[L^2_+(\Omega)]^M \times H$.

Step 2. We employ the direct method in the calculus of variations and specify an energy-minimizing sequence. Denote

$$\alpha_\lambda = \inf_{(c,u)\in[L^2_+(\Omega)]^M\times H} \tilde{G}_\lambda[c,u] = \inf_{(c,\phi)\in[L^2_+(\Omega)]^M\times H} G_\lambda[c,\phi]. \tag{4.9}$$

Choose $c^{(0)} = 0 \in [L^2_+(\Omega)]^M$ and let $\phi^{(0)} \in H^1_g(\Omega) \cap H^2(\Omega)$ be such that $\nabla\cdot\varepsilon\nabla\phi^{(0)} = -f$ in Ω. Then $A := G_\lambda[c^{(0)},\phi^{(0)}]$ is independent of λ. Since Ω is bounded and W is bounded below, we have $-\infty < \alpha_\lambda \le A$. Therefore, there exist $(c^\lambda_k, u^\lambda_k) \in [L^2_+(\Omega)]^M \times H$ $(k = 1,2,\dots)$ such that

$$\alpha_\lambda \le \tilde{G}_\lambda[c^\lambda_k, u^\lambda_k] < \alpha_\lambda + \frac{1}{k} \le A+1 \qquad \forall k \ge 1. \tag{4.10}$$

These inequalities and (4.7) imply that

$$\sup_{k\ge1,\lambda_1\ge\lambda_1^{(0)},\lambda_2\ge\lambda_2^{(0)}} \|\nabla\cdot\varepsilon\nabla u^\lambda_k\|_{L^2(\Omega)} < \infty \quad \text{and} \quad \sup_{k\ge1,\lambda_1\ge\lambda_1^{(0)},\lambda_2\ge\lambda_2^{(0)}} \|u^\lambda_k\|_{L^2(\partial\Omega)} < \infty. \tag{4.11}$$

Step 3. Fix $k \ge 1$ and hence u^λ_k. We minimize $\tilde{G}_\lambda[\cdot, u^\lambda_k]$ over $[L^2_+(\Omega)]^M$. By the definition of $\tilde{G}_\lambda$ (cf. (4.7)) and $\psi(c)$ (cf. (4.6)), this is equivalent to minimizing $\hat{F}^\lambda_k[c]$ over $[L^2_+(\Omega)]^M$, defined by

$$\hat{F}^\lambda_k[c] = \int_\Omega \left[\frac{\varepsilon}{2}|\nabla\phi^\lambda_k(c)|^2 + W(c)\right] dx \qquad \forall c \in [L^2_+(\Omega)]^M, \tag{4.12}$$

where $\phi^\lambda_k(c) = \psi(c) - u^\lambda_k \in H$. The function $\phi^\lambda_k(c)$ is determined by $\phi^\lambda_k(c) \in H^1_{g-u^\lambda_k}(\Omega)$ and

$$\int_\Omega \varepsilon\nabla\phi^\lambda_k(c)\cdot\nabla\xi\,dx = \int_\Omega \left(f + \nabla\cdot\varepsilon\nabla u^\lambda_k + \sum_{i=1}^M q_i c_i\right)\xi\,dx \qquad \forall \xi \in H^1_0(\Omega). \tag{4.13}$$

Note by (4.11) that $\sup_{k\ge1,\lambda_1\ge\lambda_1^{(0)},\lambda_2\ge\lambda_2^{(0)}} \|f + \nabla\cdot\varepsilon\nabla u^\lambda_k\|_{L^2(\Omega)} < \infty$. Thus by Corollary 3.1, for each $k \ge 1$, there exists a unique $d^\lambda_k = (d^\lambda_{k,1},\dots,d^\lambda_{k,M}) \in [L^\infty_+(\Omega)\cap H^1(\Omega)]^M$ such that

$$\hat{F}^\lambda_k[d^\lambda_k] = \min_{c\in[L^2_+(\Omega)]^M} \hat{F}^\lambda_k[c], \tag{4.14}$$

$$\sup_{k\ge1,\lambda_1\ge\lambda_1^{(0)},\lambda_2\ge\lambda_2^{(0)}} \|d^\lambda_{k,i}\|_{H^1(\Omega)} < \infty, \qquad i = 1,\dots,M, \tag{4.15}$$

$$0 < \theta_1 \le d^\lambda_{k,i}(x) \le \theta_2 \quad \text{a.e. in } \Omega,\ i = 1,\dots,M, \quad \forall k \ge 1, \tag{4.16}$$

where $\theta_1 > 0$ and $\theta_2 > 0$ are positive constants independent of k and $\lambda = (\lambda_1,\lambda_2)$ with $\lambda_1 \ge \lambda_1^{(0)}$ and $\lambda_2 \ge \lambda_2^{(0)}$. It follows from the definition of $\hat{F}^\lambda_k$ (cf. (4.12)) and $\tilde{G}_\lambda$ (cf. (4.7)), and (4.10) that

$$\alpha_\lambda \le \tilde{G}_\lambda[d^\lambda_k, u^\lambda_k] = \min_{c\in[L^2_+(\Omega)]^M} \tilde{G}_\lambda[c, u^\lambda_k] \le \tilde{G}_\lambda[c^\lambda_k, u^\lambda_k] < A+1 \qquad \forall k \ge 1. \tag{4.17}$$

Step 4. We show that, up to a subsequence, the new energy-minimizing sequence $\{(d_k^\lambda, u_k^\lambda)\}$ converges weakly to some limit that is in fact a minimizer of $\tilde{G}_\lambda$ over $[L_+^2(\Omega)]^M \times H$.

By the definition of $\psi(d_k^\lambda)$ (cf. (4.6)), the uniform bound (4.15) and (4.11), and the regularity theory (cf. Theorem 8.12 in [8]), we have

$$\sup_{k\geq 1, \lambda_1 \geq \lambda_1^{(0)}, \lambda_2 \geq \lambda_2^{(0)}} \|\psi(d_k^\lambda)\|_{H^2(\Omega)} < \infty. \tag{4.18}$$

By (4.7) and (4.12), $\hat{F}_k^\lambda[d_k^\lambda] \leq \tilde{G}_\lambda[d_k^\lambda, u_k^\lambda]$. This and (4.17), together with the fact that W is bounded below, lead to

$$\sup_{k\geq 1, \lambda_1 \geq \lambda_1^{(0)}, \lambda_2 \geq \lambda_2^{(0)}} \int_\Omega \frac{\varepsilon}{2} |\nabla \psi(d_k^\lambda) - \nabla u_k^\lambda|^2 \, dx < \infty.$$

The above two inequalities imply that $\sup_{k\geq 1, \lambda_1 \geq \lambda_1^{(0)}, \lambda_2 \geq \lambda_2^{(0)}} \|\nabla u_k^\lambda\|_{L^2(\Omega)} < \infty$. This, together with (4.11) and Friedrichs' inequality [22], implies that

$$\sup_{k\geq 1, \lambda_1 \geq \lambda_1^{(0)}, \lambda_2 \geq \lambda_2^{(0)}} \|u_k^\lambda\|_{H^1(\Omega)} < \infty. \tag{4.19}$$

It follows from the bounds (4.11), (4.15), (4.18) and (4.19) that the following hold true:

(1) There exists $d_\lambda = (d_{\lambda,1}, \ldots, d_{\lambda,M}) \in [L_+^\infty(\Omega) \cap H^1(\Omega)]^M$ such that, up to a subsequence, $d_k^\lambda \to d_\lambda$ weakly in $[H^1(\Omega)]^M$, strongly in $[L^2(\Omega)]^M$, and a.e. in Ω as $k \to \infty$.

(2) There exist $u_\lambda \in H^1(\Omega)$ and $h_\lambda \in L^2(\Omega)$ such that, up to a subsequence, $u_k^\lambda \to u_\lambda$ weakly in $H^1(\Omega)$, strongly in $L^2(\Omega)$ and $L^2(\partial\Omega)$, a.e. in Ω as $k \to \infty$, and $\nabla \cdot \varepsilon \nabla u_k^\lambda \to h_\lambda$ weakly in $L^2(\Omega)$. For any $\xi \in C_c^\infty(\Omega)$, we have

$$\int_\Omega h_\lambda \, \xi \, dx = \lim_{k\to\infty} \int_\Omega (\nabla \cdot \varepsilon \nabla u_k^\lambda) \xi \, dx = \lim_{k\to\infty} -\int_\Omega \varepsilon \nabla u_k^\lambda \cdot \nabla \xi \, dx = -\int_\Omega \varepsilon \nabla u_\lambda \cdot \nabla \xi \, dx.$$

Thus, $h_\lambda = \nabla \cdot \varepsilon \nabla u_\lambda$, and further $u_\lambda \in H$.

(3) There exists $\psi_\lambda \in H^2(\Omega)$ such that, up to a subsequence, $\psi(d_k^\lambda) \to \psi_\lambda$ weakly in $H^2(\Omega)$, strongly in $H^1(\Omega)$ and $L^2(\partial\Omega)$, and a.e. in Ω as $k \to \infty$. By the definition of $\psi(c)$ for any $c \in [L_+^2(\Omega)]^M$ (cf. (4.6)) and the regularity theory, we have $\psi_\lambda = \psi(d_\lambda) \in H_g^1(\Omega) \cap H^2(\Omega)$. In particular, $\psi_\lambda \in H$.

Consequently, it follows from the definition of $\tilde{G}_\lambda$ (cf. (4.7)) and Fatou's lemma that

$$\begin{aligned}
\alpha_\lambda &= \lim_{k\to\infty} \tilde{G}_\lambda[d_k^\lambda, u_k^\lambda] \\
&\geq \int_\Omega \left[\frac{\varepsilon}{2} |\nabla \psi_\lambda - \nabla u_\lambda|^2 + W(d_\lambda) \right] dx + \lambda_1 \int_\Omega (\nabla \cdot \varepsilon \nabla u_\lambda)^2 \, dx + \lambda_2 \int_{\partial\Omega} (u_\lambda)^2 \, dS \\
&= \tilde{G}_\lambda[d_\lambda, u_\lambda] \\
&\geq \alpha_\lambda.
\end{aligned}$$

Hence, (d_λ, u_λ) is a minimizer of $\tilde{G}_\lambda$ over $[L_+^2(\Omega)]^M \times H$ and $(c_\lambda, \phi_\lambda) := (d_\lambda, \psi(d_\lambda) - u_\lambda)$ is a minimizer of G_λ over $[L_+^2(\Omega)]^M \times H$. By (4.15) and (4.16), $c_\lambda \in [L_+^\infty(\Omega) \cap H^1(\Omega)]^M$ and it satisfies the desired boundedness.

Step 5. We show the uniqueness of the minimizer. Suppose $(\hat{c}_\lambda, \hat{\phi}_\lambda) \in [L^2_+(\Omega)]^M \times H$ is another minimizer of G_λ. Define $(\tilde{c}_\lambda, \tilde{\phi}_\lambda) = ((\hat{c}_\lambda, \hat{\phi}_\lambda) + (c_\lambda, \phi_\lambda))/2 \in [L^2_+(\Omega)]^M \times H$. Since G_λ is convex, we have $\alpha_\lambda = G_\lambda[\tilde{c}_\lambda, \tilde{\phi}_\lambda] = G_\lambda[c_\lambda, \phi_\lambda] = G_\lambda[\hat{c}_\lambda, \hat{\phi}_\lambda]$. By the convexity of W and direct calculations, we obtain

$$
\begin{aligned}
0 &= G_\lambda[\tilde{c}_\lambda, \tilde{\phi}_\lambda] - \frac{1}{2} G_\lambda[c_\lambda, \phi_\lambda] - \frac{1}{2} G_\lambda[\hat{c}_\lambda, \hat{\phi}_\lambda] \\
&= - \int_\Omega \frac{\varepsilon}{8} |\nabla \hat{\phi}_\lambda - \nabla \phi_\lambda|^2 \, dx + \int_\Omega \left[W\left(\frac{\hat{c}_\lambda + c_\lambda}{2} \right) - \frac{1}{2} W(\hat{c}_\lambda) - \frac{1}{2} W(c_\lambda) \right] dx \\
&\quad - \frac{\lambda_1}{4} \int_\Omega \left[\nabla \cdot \varepsilon \nabla \hat{\phi}_\lambda + \sum_{i=1}^M q_i \hat{c}_{\lambda,i} - \nabla \cdot \varepsilon \nabla \phi_\lambda - \sum_{i=1}^M q_i c_{\lambda,i} \right]^2 dx \\
&\quad - \frac{\lambda_2}{4} \int_{\partial\Omega} |\hat{\phi}_\lambda - \phi_\lambda|^2 \, dS \\
&\le 0.
\end{aligned}
$$

Therefore, we have

$$
\int_\Omega \frac{\varepsilon}{8} |\nabla \hat{\phi}_\lambda - \nabla \phi_\lambda|^2 \, dx = \int_\Omega \left[W\left(\frac{\hat{c}_\lambda + c_\lambda}{2} \right) - \frac{1}{2} W(\hat{c}_\lambda) - \frac{1}{2} W(c_\lambda) \right] dx = \int_{\partial\Omega} |\hat{\phi}_\lambda - \phi_\lambda|^2 \, dS = 0.
$$

The first and third equation lead to $\hat{\phi}_\lambda = \phi_\lambda$ a.e. in Ω. Applying the argument in the proof of Theorem 3.1, we can infer from the second part being zero that $\hat{c}_\lambda = c_\lambda$ a.e. in Ω. Thus the minimizer of G_λ is unique. □

Theorem 4.2. *Let Ω, ε, f, and g be the same as in Theorem 4.1. Let $\lambda_k = (\lambda_{1k}, \lambda_{2k})$ with $\lambda_{1k} > 0$ and $\lambda_{2k} > 0$ $(k = 1, 2, \dots)$ and assume $\lambda_{1k} \nearrow +\infty$ and $\lambda_{2k} \nearrow +\infty$. For each $k \ge 1$, we denote $G_k = G_{\lambda_k}$, the functional defined in (4.1), and $(c_k, \phi_k) = (c_{\lambda_k}, \phi_{\lambda_k})$, the corresponding minimizer of G_k over $[L^2_+(\Omega)]^M \times H$ as given in Theorem 4.1. Let $\hat{c} \in [L^2_+(\Omega)]^M \subset Y_+$ be the unique minimizer of $\hat{E} : Y_+ \to \mathbb{R} \cup \{+\infty\}$ and $\hat{\psi} \in H^1_g(\Omega) \cap H^2(\Omega)$ be the solution to the corresponding PBE (3.24) as given in Theorem 3.1. Then,*

$$
G_k[c_k, \phi_k] = \min_{(c,\phi) \in [L^2_+(\Omega)]^M \times H} G_k[c, \phi] \to \min_{c \in Y_+} \hat{E}[c] = \hat{E}[\hat{c}] \quad \text{as } k \to \infty, \tag{4.20}
$$

$$
c_k \to \hat{c} \quad \text{in } [L^2(\Omega)]^M \quad \text{and} \quad \phi_k \to \hat{\psi} \quad \text{in } H \quad \text{as } k \to \infty. \tag{4.21}
$$

Proof. It suffices to show that any subsequence of $\{\lambda_k\}$, not relabeled, has a further subsequence, again not relabeled, for which the convergence in (4.20) and (4.21) hold true. We divide our proof into three steps. First, we prove the energy convergence (4.20). Then, we prove the convergence $c_k \to \hat{c}$ in $[L^1(\Omega)]^M$ and $\phi_k \to \hat{\psi}$ in $H^1(\Omega)$. Finally, we prove (4.21).

Step 1. We first note that the sequence $\{G_k[c_k, \phi_k]\}_{k=1}^\infty$ is monotonically increasing. We also note that $\hat{\psi}$ and $\hat{c}$ are related by $\nabla \cdot \varepsilon \nabla \hat{\psi} = -(f + \sum_{i=1}^M q_i \hat{c}_i)$ a.e Ω; cf. (3.4), (3.22), and (3.24). Thus, by the definition of G_λ (cf. (4.1)) and $\hat{F}$ (cf. (3.2)), and Lemma 3.2, we have

$$
G_k[c_k, \phi_k] \le G_k[\hat{c}, \hat{\psi}] = \hat{F}[\hat{c}] = \hat{E}[\hat{c}]. \tag{4.22}
$$

Consequently, the sequence $\{G_k[c_k, \phi_k]\}_{k=1}^\infty$ converges. Moreover, writing $c_k = (c_{k,1}, \dots, c_{k,M})$, we have

$$
\sup_{k \ge 1} \|\nabla \phi_k\|_{L^2(\Omega)} < \infty, \tag{4.23}
$$

$$\sup_{k\ge 1}\int_\Omega W(c_k)\,dx < \infty, \tag{4.24}$$

$$\left\| \nabla\cdot\varepsilon\nabla\phi_k + f + \sum_{i=1}^M q_i c_{k,i}\right\|_{L^2(\Omega)} \to 0 \quad \text{as } k\to\infty, \tag{4.25}$$

$$\|\phi_k - g\|_{L^2(\partial\Omega)} \to 0 \quad \text{as } k\to\infty. \tag{4.26}$$

By (4.23), (4.26), and Friedrichs' inequality, we have $\sup_{k\ge1}\|\phi_k\|_{H^1(\Omega)} < \infty$. Thus, by the compact embedding $H^1(\Omega)\hookrightarrow L^2(\Omega)$ and $H^1(\Omega)\hookrightarrow L^2(\partial\Omega)$ [1, 7, 8, 19], there exists $\phi_\infty \in H^1_g(\Omega)$, such that, passing to a further subsequence if necessary, $\phi_k \rightharpoonup \phi_\infty$ in $H^1(\Omega)$, $\phi_k\to\phi_\infty$ in $L^2(\Omega)$, and $\phi_k\to\phi_\infty$ a.e. Ω. It follows from (4.24) that, up to a further subsequence, $c_k \rightharpoonup c_\infty = (c_{\infty,1},\dots,c_{\infty,M})$ in $[L^1(\Omega)]^M$ for some $c_\infty\in[L^1_+(\Omega)]^M$ and

$$\int_\Omega c_{\infty,i}\log c_{\infty,i}\,dx \le \liminf_{k\to\infty}\int_\Omega c_{k,i}\log c_{k,i}\,dx, \qquad i=1,\dots,M; \tag{4.27}$$

cf. Lemma 3.3 in [14]. Consequently,

$$\int_\Omega W(c_\infty)\,dx \le \liminf_{k\to\infty}\int_\Omega W(c_k)\,dx. \tag{4.28}$$

Since for any $k\ge1$ and any $\xi\in H^1_0(\Omega)\cap L^\infty(\Omega)$,

$$\int_\Omega\left(\nabla\cdot\varepsilon\nabla\phi_k + f + \sum_{i=1}^M q_i c_{k,i}\right)\xi\,dx = -\int_\Omega \varepsilon\nabla\phi_k\cdot\nabla\xi\,dx + \int_\Omega\left(f+\sum_{i=1}^M q_i c_{k,i}\right)\xi\,dx,$$

we have by taking $k\to\infty$ and using (4.25) and the weak convergence $\phi_k\rightharpoonup\phi_\infty$ in $H^1(\Omega)$ that

$$\int_\Omega \varepsilon\nabla\phi_\infty\cdot\nabla\xi\,dx = \int_\Omega \rho_\infty\xi\,dx, \qquad \forall\xi\in H^1_0(\Omega)\cap L^\infty(\Omega), \tag{4.29}$$

where $\rho_\infty = f+\rho(c_\infty) = f+\sum_{i=1}^M q_i c_{\infty,i}\in L^1(\Omega)$. Moreover,

$$\sup_{0\ne\xi\in H^1_0(\Omega)\cap L^\infty(\Omega)}\frac{|\int_\Omega\rho_\infty\xi\,dx|}{\|\xi\|_{H^1(\Omega)}} = \sup_{0\ne\xi\in H^1_0(\Omega)\cap L^\infty(\Omega)}\frac{|\int_\Omega\varepsilon\nabla\phi_\infty\cdot\nabla\xi\,dx|}{\|\xi\|_{H^1(\Omega)}} \le \|\varepsilon\nabla\phi_\infty\|_{L^2(\Omega)}<\infty.$$

Therefore, $\rho_\infty\in X$ and thus $c_\infty\in Y_+$.

Recall that $\phi_f\in H^1_g(\Omega)$ is given by (3.11). It then follows from (4.29) that $\phi_\infty = \phi_f + L_\varepsilon\rho(c_\infty)$. Now, define G_0 to be the same as G_λ in (4.1), with the penalty terms excluded by setting $\lambda_1=\lambda_2=0$. By Lemma 3.2, we have $G_0[c_\infty,\phi_\infty] = \hat F[c_\infty] = \hat E[c_\infty]$. Therefore, it follows from various convergence of ϕ_k to ϕ_∞, the weak convergence $c_k\rightharpoonup c_\infty$ in $[L^1_+(\Omega)]^M$, (4.28), and (4.22) that

$$\begin{aligned}\hat E[\hat c] &\le \hat E[c_\infty] = G_0[c_\infty,\phi_\infty] \le \liminf_{k\to\infty} G_0[c_k,\phi_k]\\ &\le \liminf_{k\to\infty} G_k[c_k,\phi_k] \le \limsup_{k\to\infty} G_k[c_k,\phi_k] \le \hat E[\hat c],\end{aligned} \tag{4.30}$$

leading to (4.20).

Step 2. It follows from (4.30) and the uniqueness of a minimizer of $\hat{E}$ over Y_+ that $c_\infty = \hat{c}$. Therefore, $c_k \rightharpoonup \hat{c}$ in $[L^1(\Omega)]^M$ as $k \to \infty$. Additionally, by the assumption on $\hat{\psi}$ and (4.29), both ϕ_∞ and $\hat{\psi}$ are the solutions to (3.4) with (c, ϕ) replaced by (c_∞, ϕ_∞) and $(\hat{c}, \hat{\psi})$, respectively. Since $c_\infty = \hat{c}$, we get that $\phi_\infty = \hat{\psi} \in H^1_g(\Omega) \cap H^2(\Omega)$ and that $\phi_k \to \hat{\psi}$ weakly in $H^1(\Omega)$, strongly in $L^2(\Omega)$, and a.e. in Ω.

Now, since $G_k[c_k, \phi_k] \to \hat{E}[\hat{c}] = \hat{F}[\hat{c}]$ and $\{G_k[c_k, \phi_k]\}_{k=1}^\infty$ is an increasing sequence, we have

$$
\begin{aligned}
0 &\geq G_k[c_k, \phi_k] - \hat{F}[\hat{c}] \\
&= \int_\Omega \frac{\varepsilon}{2} \left(|\nabla \phi_k|^2 - |\nabla \hat{\psi}|^2 \right) dx + \int_\Omega (W(c_k) - W(\hat{c}))\, dx \\
&\quad + \lambda_{1k} \int_\Omega \left(\nabla \cdot \varepsilon \nabla \phi_k + f + \sum_{i=1}^M q_i c_{k,i} \right)^2 dx + \lambda_{2k} \int_{\partial\Omega} (\phi_k - g)^2\, dS \\
&:= A_k + B_k + C_k + D_k \qquad \forall k \geq 1.
\end{aligned}
$$

We have $\liminf_{k\to\infty} C_k \geq 0$ and $\liminf_{k\to\infty} D_k \geq 0$. Since $\phi_k \to \hat{\psi}$ in $H^1(\Omega)$ weakly, we have

$$
\begin{aligned}
\liminf_{k\to\infty} A_k &= \liminf_{k\to\infty} \int_\Omega \frac{\varepsilon}{2} \left(|\nabla \phi_k|^2 - |\nabla \hat{\psi}|^2 \right) dx \\
&= \liminf_{k\to\infty} \left[\int_\Omega \frac{\varepsilon}{2} |\nabla(\phi_k - \hat{\psi})|^2\, dx + \int_\Omega \varepsilon \nabla(\phi_k - \hat{\psi}) \cdot \nabla \hat{\psi}\, dx \right] \\
&= \liminf_{k\to\infty} \int_\Omega \frac{\varepsilon}{2} |\nabla(\phi_k - \hat{\psi})|^2\, dx \geq 0.
\end{aligned}
$$

By (4.28), we obtain $\liminf_{k\to\infty} B_k \geq 0$. Combining these results, we have

$$
0 \geq \liminf_{k\to\infty} (A_k + B_k + C_k + D_k) \geq \liminf_{k\to\infty} A_k + \liminf_{k\to\infty} B_k + \liminf_{k\to\infty} C_k + \liminf_{k\to\infty} D_k \geq 0,
$$

hence we have

$$
\liminf_{k\to\infty} A_k = \liminf_{k\to\infty} B_k = \liminf_{k\to\infty} C_k = \liminf_{k\to\infty} D_k = 0.
$$

Passing to a further subsequence if necessary, we have $\lim_{k\to\infty} A_k = 0$ and $\lim_{k\to\infty} B_k = 0$. This implies that as $k \to \infty$,

$$
\int_\Omega \frac{\varepsilon}{2} |\nabla(\phi_k - \hat{\psi})|^2\, dx \to 0 \quad \text{and} \quad \int_\Omega W(c_k)\, dx \to \int_\Omega W(\hat{c})\, dx.
$$

Thus $\phi_k \to \hat{\psi}$ in $H^1(\Omega)$ strongly. Since $c_k \rightharpoonup \hat{c}$ in $[L^1(\Omega)]^M$, we have by (4.27) and a result in [4] (Lemma 2.5 and the proof of Theorem 2.7) that $c_k \to \hat{c}$ in $[L^1(\Omega)]^M$ strongly.

Step 3. Since $\lambda_{1k} \to +\infty$ and $\lambda_{2k} \to +\infty$ as $k \to \infty$, there exists an integer $K \geq 1$ such that $\lambda_{1k} \geq 1$ and $\lambda_{2k} \geq 1$ for any $k \geq K$. It follows from Theorem 4.1 applied to the sequence (c_k, ϕ_k) $(k = K+1, K+2, \dots)$ that there exist $\hat{\Theta}_1 > 0$ and $\hat{\Theta}_2 > 0$ such that $0 < \hat{\Theta}_1 \leq c_{k,i}(x) \leq \hat{\Theta}_2$ a.e. Ω $(i = 1, \dots, M)$ for all $k \geq K$. Consequently, since $c_k \to \hat{c}$ in $[L^1(\Omega)]^M$ strongly, for $i = 1, \dots, M$, we have

$$
\int_\Omega (c_{k,i} - \hat{c}_i)^2\, dx \leq (\hat{\Theta}_2 + \hat{\theta}_2) \int_\Omega |c_{k,i} - \hat{c}_i|\, dx \to 0 \quad \text{as } k \to \infty,
$$

where $\hat{\theta}_2$ is the upper bound for $\hat{c}$; cf. (3.26). Hence $c_k \to \hat{c}$ in $[L^2(\Omega)]^M$ strongly.

Finally, by (4.25), the strong convergence $c_k \to \hat{c}$ in $[L^2(\Omega)]^M$ as $k \to \infty$, and the fact that (3.4) holds true with (c, ϕ) replaced by $(\hat{c}, \hat{\psi})$, we can infer that $\nabla \cdot \varepsilon \nabla \phi_k \to \nabla \cdot \varepsilon \nabla \hat{\psi}$ in $L^2(\Omega)$ and thus $\Delta \phi_k \to \Delta \hat{\psi}$ in $L^2(\Omega)$ as $k \to \infty$. This leads to $\phi_k \to \hat{\psi}$ in H. $\square$

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