SIAM J. APPL. MATH.
Vol. 78, No. 6, pp. 2973–2995

LEGENDRE TRANSFORMS OF ELECTROSTATIC FREE-ENERGY FUNCTIONALS*

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Abstract. In the Poisson–Boltzmann (PB) theory, the electrostatic free-energy functional of all possible electrostatic potentials for an ionic solution is often formulated in such a way that the Euler–Lagrange equation of such a functional is exactly the PB equation. However, such a PB functional is concave downward and maximized at its critical point, making it inconsistent in many applications where a macroscopic free-energy functional is minimized. Maggs [*Europhys. Lett.*, 98 (2012), 16012] proposed a Legendre transformed form of the electrostatic free-energy functional of all possible dielectric displacements. This new functional is convex and minimized at the displacement corresponding to the critical point of the PB functional, and the minimum value is exactly the equilibrium electrostatic free energy. In this work, we study mathematically the Legendre transformed electrostatic free-energy functionals and the related variational principles. We first prove that the PB functional and its Legendre transformed functional are equivalent. We then consider a phenomenological electrostatic free-energy functional that includes a higher-order gradient term, proposed by Bazant, Storey, and Kornyshev [*Phys. Rev. Lett.*, 106 (2011), 046102] to describe charge-charge correlations. For such a functional, we introduce the corresponding Legendre transformed functional and obtain the related equivalence. We further consider the case without ions. We show that the electrostatic energy functional is equivalent to a Legendre transformed energy functional with constraint, and we prove the convergence of the Legendre transform of a perturbed electrostatic energy functional. Finally, we apply the Legendre transform to the dielectric boundary electrostatic free energy in molecular solvation.

Key words. electrostatic free-energy functionals, Legendre transforms, variational principles

AMS subject classification. 49S05

DOI. 10.1137/18M1167644

1. Introduction.

We consider an ionic solution that consists of M ionic species together with solvent and that occupies a bounded region $\Omega \subseteq \mathbb{R}^3$. A commonly used electrostatic free-energy functional, often termed the Poisson–Boltzmann (PB) electrostatic free-energy functional, takes the form [2, 8, 11, 17, 19, 25, 34, 36]

$$I[\phi] = \int_\Omega \left[-\frac{\varepsilon}{2}|\nabla\phi|^2 + f\phi - B(\phi) \right] dx. \tag{1.1}$$

Here, $\phi : \Omega \to \mathbb{R}$ is any possible electrostatic potential, $\varepsilon : \Omega \to \mathbb{R}$ is the dielectric coefficient that can vary spatially in the region Ω, and $f : \Omega \to \mathbb{R}$ is the density of fixed charges. In the classical PB theory, the function $B : \mathbb{R} \to \mathbb{R}$ is given by

$$B(\phi) = \beta^{-1} \sum_{i=1}^{M} c_i^\infty \left(e^{-\beta q_i \phi} - 1 \right), \tag{1.2}$$

*Received by the editors January 29, 2018; accepted for publication (in revised form) September 19, 2018; published electronically November 1, 2018.
http://www.siam.org/journals/siap/78-6/M116764.html

Funding: The first author's work was supported in part by a Frieda Daum Urey Academic and Oceanids Memorial Fellowship, University of California, San Diego, 2016–2017. The second author's work was supported by the National Science Foundation through grant DMS-1620487.

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where $\beta = (k_\mathrm{B}T)^{-1}$ with k_B the Boltzmann constant and T the absolute temperature, c_i^∞ is the bulk concentration of the ith ionic species, and $q_i = Z_i e$ is the charge of an ion in the ith ionic species with Z_i the valence of such an ion and e the elementary charge. Note that the function $B = B(s)$ is smooth and strictly convex and is minimized at $s = 0$ under the usual assumption of charge neutrality: $B'(0) = \sum_{i=1}^M c_i^\infty q_i = 0$. The Euler–Lagrange equation of the functional $I = I[\phi]$ is

$$\nabla \cdot \varepsilon \nabla \phi - B'(\phi) = -f. \tag{1.3}$$

This is exactly the PB equation for the equilibrium electrostatic potential ϕ. Moreover, the functional value $I[\phi]$ at this critical point ϕ, which is the same as the maximum value of the functional I, is exactly the (macroscopic) electrostatic free energy.

The functional I defined in (1.1) is an expression of the electrostatic free energy through the equilibrium electrostatic potential of an underlying ionic system. It can be derived from minimizing the following effective electrostatic free-energy functional of all the ionic concentrations $c_i : \Omega \to [0, \infty)$ $(1 \le i \le M)$ [8, 17, 25, 34]:

$$F[c] = \int_\Omega \left\{ \frac{1}{2}\left(f + \sum_{i=1}^M q_i c_i \right)\phi + \beta^{-1} \sum_{i=1}^M c_i \left[\ln\left(\Lambda^3 c_i\right) - 1 \right] - \sum_{i=1}^M \mu_i c_i - \beta^{-1} \sum_{i=1}^M c_i^\infty \right\} dx, \tag{1.4}$$

where $c = (c_1, \dots, c_M)$. (We define $s \ln s = 0$ for $s = 0$.) The first part of the free energy $F[c]$ is the electrostatic potential energy, where $f + \sum_{i=1}^M q_i c_i$ is the total charge density and $\phi : \Omega \to \mathbb{R}$ is the corresponding electrostatic potential defined as the solution to Poisson's equation

$$\nabla \cdot \varepsilon \nabla \phi = -\left(f + \sum_{i=1}^M q_i c_i \right), \tag{1.5}$$

together with some boundary conditions. The second part, where Λ is the thermal de Broglie wavelength, is the entropy of the ions. The third part of the free energy $F[c]$ arises from the constraint of a fixed total number of ions in each ionic species. Here μ_i is the chemical potential for an ion of the ith species and is related to other parameters by $\mu_i = \beta^{-1} \ln(\Lambda^3 c_i^\infty)$ [8]. The last part of the free energy $F[c]$ is the ionic pressure. Note that the functional F is strictly convex. The equilibrium ionic concentrations $c_i = c_i(x)$ $(1 \le i \le M)$, defined by the vanishing of the first variations $\delta_{c_i} F[c] = 0$ $(1 \le i \le M)$, and the corresponding equilibrium electrostatic potential ϕ, satisfy the Boltzmann distributions $c_i(x) = c_i^\infty e^{-\beta q_i \phi(x)}$ for $x \in \Omega$ and $i = 1, \dots, M$. These and Poisson's equation (1.5) lead to the PB equation (1.3), where

$$-B'(\phi) = \sum_{i=1}^M c_i^\infty q_i e^{-\beta q_i \phi} = \sum_{i=1}^M q_i c_i$$

is exactly the local density of the ionic charges. Moreover, the free energy F is minimized at the equilibrium concentrations, and this minimum value is exactly $I[\phi]$, the (macroscopic) electrostatic free energy; see, e.g., [8, 25, 34] for more details.

We remark that the variational approach in the PB theory has been generalized to include the ionic size effect (or excluded volume effect); cf. [6, 23, 24, 25] and also [4, 7, 9, 14, 15, 20, 21, 22, 27, 29, 30, 38, 40]. Let us denote by v_i the volume of an ion in the ith ionic species $(1 \le i \le M)$. Let us also denote by $c_0 = c_0(x)$ $(x \in \Omega)$

the local concentration of solvent molecules and by v_0 the volume of a solvent molecule. Then $\sum_{i=0}^{M} v_i c_i(x) = 1$ for all $x \in \Omega$. This means that the solvent concentration is determined by all the ionic concentrations. The generalized, size-modified electrostatic free-energy functional of all the ionic concentrations is the same as the functional $F[c]$ defined in (1.4), except that the entropy integrand term (i.e., the logarithmic term in the integrand) is replaced by $\beta^{-1} \sum_{i=0}^{M} [c_i \ln(v_i c_i) - 1]$, where the sum starts from $i = 0$ [6, 23, 24]. The new functional is strictly convex and admits a unique set of free-energy minimizing concentrations that are determined by the equilibrium conditions (i.e., the vanishing of first variations) [24, 25, 27]:

$$\frac{v_i}{v_0} \ln(v_0 c_0) - \ln(v_i c_i) = \beta (q_i \phi - \mu_i) \qquad \text{in } \Omega, \quad i = 1, \ldots, M, \tag{1.6}$$

where ϕ is the corresponding electrostatic potential. This set of nonlinear algebraic equations determine uniquely the generalized Boltzmann distributions $c_i = c_i(\phi)$ $(i = 1, \ldots, M)$. If all v_i $(i = 0, 1, \ldots, M)$ are the same, say, $v_i = v$, then such distributions are given by

$$c_i = \frac{c_i^\infty e^{-\beta q_i \phi}}{1 + \sum_{j=1}^{M} v c_j^\infty \left(e^{-\beta q_j \phi} - 1\right)} \qquad \text{in } \Omega, \quad i = 1, \ldots, M, \tag{1.7}$$

where $c_i^\infty = v^{-1} e^{\beta \mu_i} / (1 + \sum_{j=1}^{M} e^{\beta \mu_j})$ $(i = 1, \ldots, M)$. If the sizes are nonuniform, then explicit formulas of Boltzmann distributions $c_i = c_i(\phi)$ $(i = 1, \ldots, M)$ seem unavailable. (Numerically, one can minimize the free-energy functional of concentrations using Poisson's equation (1.5) as a constraint; cf. [40]. Alternatively, one can obtain such distributions by solving numerically the system of equations (1.6) for a set of values of ϕ.) In any case (with or without the size effect included, and uniform or nonuniform size when the size effect is included), the minimum electrostatic free energy can be written in terms of the electrostatic potential ϕ as in (1.1), where the function $B : \mathbb{R} \to \mathbb{R}$ is defined by

$$-B'(\phi) = \sum_{i=1}^{M} q_i c_i(\phi) \qquad \text{and} \qquad B(0) = 0, \tag{1.8}$$

The condition of the charge neutrality is now $B'(0) = 0$. It is shown in [24] that B is smooth, strictly convex, and minimized uniquely at 0. The generalized PB equation has exactly the same form as in (1.3).

An advantage of the PB theory (classical or size-modified) is that once the equilibrium potential ϕ is determined by solving the PB equation, all the ionic concentrations are also known. However, the fact that the critical point ϕ *maximizes* the functional I defined in (1.1), due to the negative quadratic term in the functional, makes it inconsistent to couple the PB electrostatic free energy with other macroscopic energies, such as the surface energy of a dielectric boundary, that are often minimized to yield a stable equilibrium state. Naturally, one tries to construct a free-energy functional that is satisfactory in several ways. First, such a functional should have a unique minimizer and the corresponding minimum value should be the exact (macroscopic) electrostatic free energy. Second, the minimizer should satisfy the PB equation. It turns out that this is impossible as shown in [8].

To see the idea, let us only consider the case in which there are no mobile ionic charges; and hence set the B-term to be 0. The electrostatic energy is given by

$$E = \int_\Omega \frac{1}{2} f \phi \, dx, \tag{1.9}$$

where ϕ is the solution to Poisson's equation

$$\nabla \cdot \varepsilon \nabla \phi = -f, \tag{1.10}$$

together with some boundary conditions. Using this equation, we have by integration by parts that

$$\begin{aligned} E &= \int_\Omega \left(f\phi - \frac{1}{2} f\phi \right) dx \\ &= \int_\Omega \left[f\phi + \frac{1}{2}(\nabla \cdot \varepsilon \nabla \phi)\phi \right] dx \\ &= \int_\Omega \left(f\phi - \frac{\varepsilon}{2}|\nabla \phi|^2 \right) dx + \text{ some boundary terms.} \end{aligned}$$

If the region Ω is large enough, with its boundary far away from the support of f (the closure of the set of points where f is not zero), then the boundary terms are small and can be neglected. This derivation shows how the negative quadratic term appears. Now the electrostatic potential ϕ, the solution to Poisson's equation (1.10), maximizes this functional (without the boundary terms). One may try the following functional:

$$\int_\Omega \left(a|\nabla \phi|^2 + b\phi \right) \, dx$$

for some a and b that can depend on f and ε but not on ϕ. If the functional is minimized at some ϕ that solves Poisson's equation and the minimum value is the same as (1.9), then the only choice of a and b is that $a = -\varepsilon/2$ and $b = f$; cf. [8].

To resolve the issue of concavity of the PB free-energy functional, Maggs [31] constructed a Legendre transformed electrostatic free-energy functional of all possible electrostatic displacements $D : \Omega \to \mathbb{R}^3$:

$$D \mapsto \int_\Omega \left[\frac{1}{2\varepsilon}|D|^2 + B^*(f - \nabla \cdot D) \right] dx. \tag{1.11}$$

Here B^* is the Legendre transform of the function B. Indeed, the dielectric displacement is related to the electrostatic potential ϕ by $D = -\varepsilon \nabla \phi$. This allows us to rewrite

$$-\frac{\varepsilon}{2}|\nabla \phi|^2 = \frac{1}{2\varepsilon}|D|^2 + D \cdot \nabla \phi.$$

With this and an integration by parts, we can then rewrite the original PB functional (1.1) into

$$\begin{aligned} &\int_\Omega \left[-\frac{\varepsilon}{2}|\nabla \phi|^2 + f\phi - B(\phi) \right] dx \\ &\quad = \int_\Omega \left[\frac{1}{2\varepsilon}|D|^2 + (f - \nabla \cdot D)\phi - B(\phi) \right] dx + \text{boundary term.} \end{aligned}$$

Now, the terms $(f - \nabla \cdot D)\phi - B(\phi)$ are related to the Legendre transform of the convex function B evaluated at $f - \nabla \cdot D$. Therefore, it is natural to construct the functional (1.11) [31]. Pujos and Maggs [33] applied this approach to develop models for computer simulations of fluctuations in ionic solution. Maggs and Podgornik [32] and Blossey, Maggs, and Podgornik [5] have also used the Legendre transformed functional to study the asymmetric steric effect and correlations in electrostatic interactions.

We recall that the Legendre transform $h^* : \mathbb{R} \to \mathbb{R} \cup \{+\infty\}$ for a given function $h : \mathbb{R} \to \mathbb{R}$ is defined by [35, 41]

$$h^*(\xi) = \sup_{s\in\mathbb{R}} [s\xi - h(s)] \qquad \forall \xi \in \mathbb{R}.$$

If h is smooth, strictly convex, and minimized at some critical point, then $h^* : \mathbb{R} \to \mathbb{R}$ is also smooth and strictly convex, and

$$h^*(\xi) = s^*\xi - h(s^*), \qquad h'(s^*) = \xi, \qquad \text{and} \qquad {h^*}'(\xi) = s^*. \tag{1.12}$$

In this work, we study mathematically Maggs' Legendre transformed functional with extension to several cases and with application to dielectric boundary implicit-solvent models for the solvation of charged molecules.

(1) We give a rigorous proof of the equivalence of the Legendre transformed functional (cf. (1.11)) and the original PB functional (cf. (1.1)). This means in particular that the minimizing displacement field D of the Legendre transformed functional is exactly the one that corresponds to the maximizing potential ϕ of the PB functional: $D = -\varepsilon\nabla\phi$. We also derive the interface conditions for the equilibrium displacement for the case with a dielectric boundary.

(2) We study a phenomenological free-energy functional that includes higher-order gradients of the electrostatic potential, proposed by Bazant, Storey, and Kornyshev [3] for describing charge-charge correlations. In a simple setting (e.g., without the surface charges), this functional can be written as

$$\phi \mapsto \int_\Omega \left[-\frac{\varepsilon}{2} \left(|\nabla\phi|^2 + l_c^2 |\Delta\phi|^2 \right) + f\phi - B(\phi) \right] dx,$$

where $l_c > 0$ is the (constant) correlation length. We shall introduce a corresponding Legendre transformed functional and prove that these functionals are equivalent.

(3) We consider the case where there are no mobile ions in an underlying electrostatic system. The electrostatic energy of such a system is the same as (1.1) except the B-term is not included. This setting is simpler but is in fact more subtle to understand, as the Legendre transform of the zero function is $+\infty$ everywhere except at 0. We shall first show that the electrostatic energy functional is equivalent to the Legendre transformed functional

$$D \mapsto \int_\Omega \frac{1}{2\varepsilon} |D|^2 dx \tag{1.13}$$

that is to be minimized over the class of displacements D such that $\nabla \cdot D = f$ in Ω. Following the suggestion in [31], we also consider a perturbed electrostatic energy functional

$$I_\mu[\phi] = \int_\Omega \left[-\frac{\varepsilon}{2} |\nabla\phi|^2 + f\phi - \frac{\mu}{2} |\phi|^2 \right] dx,$$

where $\mu > 0$ is a small parameter. We apply the Legendre transform to this functional and prove that the minimizing displacement and minimum value of the transformed energy converge as $\mu \to 0$ to the displacement of the maximizing electrostatic potential and maximum value of the original, unperturbed functional.

(4) We consider the dielectric boundary electrostatic free-energy functional in the implicit-solvent model for the solvation of charged molecules [12, 13, 26, 39]

$$I_\Gamma[\phi] = \int_\Omega \left[-\frac{\varepsilon_\Gamma}{2} |\nabla \phi|^2 + f\phi - \chi_+ B(\phi) \right] dx.$$

Here, Γ is the dielectric boundary—an interface that separates a solute region (i.e., the region of charged molecules) Ω_- from the solvent (e.g., salted water) region Ω_+ in which there are mobile ions, f represents the fixed charges of solute atoms, and $\chi_+ = \chi_{\Omega_+}$ is the characteristic function of the solvent region. The dielectric coefficient ε_Γ is a constant in Ω_- and another constant in Ω_+. The term $\chi_+ B(\phi)$ results from a usual assumption in the implicit-solvent modeling that the mobile ions do not penetrate into the solute region. Based on our analysis of the corresponding Legendre transform of the integrand of $I_\Gamma[\phi]$, we propose to use the same Legendre transformed electrostatic free-energy functional (1.11) but identify the admissible electrostatic displacements to be those vector fields $D : \Omega \to \mathbb{R}^3$ such that $\nabla \cdot D = f$ in Ω_-. With such a setting, we again prove the equivalence of the two free-energy functionals.

The rest of this paper is organized as follows. In section 2, we prove the equivalence of the PB (classic or size-modified) free-energy functional and its Legendre transformed functional. In section 3, we consider a phenomenological electrostatic free-energy functional that involves a higher-order gradient term. We introduce its Legendre transformed functional and prove the equivalence of these two formulations. In section 4, we consider the case without ions. We show that the electrostatic energy functional is equivalent to a Legendre transformed energy functional with constraint. We also show the convergence of the Legendre transform of the perturbed electrostatic energy functional. In section 5, we study the Legendre transformed electrostatic free-energy functional for the dielectric boundary implicit-solvent model for the solvation of charged molecules. Finally, in section 6, we draw conclusions and present a brief discussion of our results.

2. Equivalence of two free-energy functionals.

Let Ω be a bounded domain in $\mathbb{R}^3$ with a C^2 boundary $\partial\Omega$, $f \in L^2(\Omega)$, and $g \in W^{1,\infty}(\Omega)$. (We use standard notation of Lebesgue and Sobolev spaces as in [1, 18].) Denote

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

Here and below, the boundary values are understood in the sense of trace [1, 18]. Let $\varepsilon \in L^\infty(\Omega)$ be such that $\varepsilon_{\min} \le \varepsilon(x) \le \varepsilon_{\max}$ for all $x \in \Omega$, where $\varepsilon_{\min}$ and $\varepsilon_{\max}$ are two positive constants. Let $B \in C^3(\mathbb{R})$ be such that

(1) B is strictly convex in $\mathbb{R}$;
(2) B is minimized at 0 with minimum value $B(0) = 0$; and
(3) $B(\pm\infty) = \infty$, and either $B'(\pm\infty) = \pm\infty$ or B' is bounded.

In the classical PB theory, the function B is given in (1.2), and hence $B'(\pm\infty) = \pm\infty$. In the size-modified PB theory, it is shown in [24] that B' is bounded. Note that the Legendre transform $B^* : \mathbb{R} \to \mathbb{R}$ is a strictly convex and C^2 function. In particular, $B^*(0) = 0$, since $B'(0) = 0$. We define $I : H^1_g(\Omega) \to \mathbb{R} \cup \{-\infty\}$ by (1.1). Note that $I[\phi] < \infty$ for any $\phi \in H^1_g(\Omega)$.

THEOREM 2.1. *The functional $I : H^1_g \to \mathbb{R} \cup \{-\infty\}$ has a unique maximizer $\phi_B \in H^1_g(\Omega)$ and the maximum value is finite. Moreover, ϕ_B is the unique weak solution to the boundary-value problem of PB equation*

$$\int_\Omega [\varepsilon \nabla \phi_B \cdot \nabla \eta + B'(\phi_B)\eta]\, dx = \int_\Omega f\eta\, dx \qquad \forall \eta \in H_0^1(\Omega), \tag{2.1}$$

and $\phi_B \in L^\infty(\Omega)$.

Proof. For the classical PB functional where the function B is given in (1.2), this is similar to the proof of Theorem 2.1 in [26]. For the size-modified PB functional, where B is given by (1.7) or implicitly by (1.8), this is similar to the proof of Theorem 5.1 in [24], where the fact that $\phi_B \in L^\infty(\Omega)$ is a direct consequence of the PB equation and regularity theory [18, Chapter 8]. ∎

We denote

$$H(\text{div}, \Omega) = \left\{ D \in \left[L^2(\Omega)\right]^3 : \nabla \cdot D \in L^2(\Omega) \right\},$$

where the divergence $\nabla \cdot D$ is defined in the weak sense:

$$\int_\Omega \nabla \cdot D\, \eta\, dx = -\int_\Omega D \cdot \nabla \eta\, dx \qquad \forall \eta \in H_0^1(\Omega). \tag{2.2}$$

We recall that $H(\text{div}, \Omega)$ is a Hilbert space with the inner product [37]

$$\langle D, G \rangle = \int_\Omega \left[D \cdot G + (\nabla \cdot D)(\nabla \cdot G) \right] \, dx \qquad \forall D, G \in H(\text{div}, \Omega).$$

If $D \in H(\text{div}, \Omega)$, then the trace $D \cdot n : \partial\Omega \to \mathbb{R}$ is in $L^2(\partial\Omega)$, where n is the unit exterior normal at the boundary $\partial\Omega$, and

$$\int_\Omega (\nabla \cdot D)\, \eta\, dx = -\int_\Omega D \cdot \nabla \eta\, dx + \int_{\partial\Omega} (D \cdot n)\, \eta\, dS \qquad \forall \eta \in H^1(\Omega); \tag{2.3}$$

see [37]. We define $J : H(\text{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ by

$$J[D] = \int_\Omega \left[\frac{1}{2\varepsilon}|D|^2 + B^*(f - \nabla \cdot D) \right] dx + \int_{\partial\Omega} g D \cdot n\, dS. \tag{2.4}$$

Note that we have an additional boundary integral term in this functional, compared with the functional defined in (1.11). Formal calculations show that the Euler–Lagrange equation for the functional $J : H(\text{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ is

$$\frac{D}{\varepsilon} + \nabla(B^{*\prime}(f - \nabla \cdot D)) = 0 \qquad \text{in } \Omega. \tag{2.5}$$

Let us denote

$$H_0(\text{div}, \Omega) = \{ D \in H(\text{div}, \Omega) : D \cdot n = 0 \text{ on } \partial\Omega \}.$$

(Note that this is not the subspace of $H(\text{div}, \Omega)$ that consists of divergence-free vector fields. The subscript 0 here indicates a vanishing normal component of the vector field on the boundary.) We call $D \in H(\text{div}, \Omega)$ a weak solution to the Euler–Lagrange equation (2.5) if

$$\int_\Omega \left[\frac{D \cdot G}{\varepsilon} - B^{*\prime}(f - \nabla \cdot D)(\nabla \cdot G) \right] dx = 0 \qquad \forall G \in H_0(\text{div}, \Omega). \tag{2.6}$$

The following theorem indicates that the PB electrostatic free-energy functional I defined in (1.1) and its Legendre transformed free-energy functional J defined in (2.4) are equivalent.

THEOREM 2.2. *We have*

$$I[\phi] \le J[D] \qquad \forall \phi \in H_g^1(\Omega) \quad \forall D \in H(\mathrm{div}, \Omega). \tag{2.7}$$

Moreover, if $\phi_B \in H_g^1(\Omega)$ *is the unique maximizer of* $I : H_g^1(\Omega) \to \mathbb{R} \cup \{-\infty\}$ *and* $D_B = -\varepsilon \nabla \phi_B$, *then* $D_B \in H(\mathrm{div}, \Omega)$ *and*

$$I[\phi_B] = \max_{\phi \in H_g^1(\Omega)} I[\phi] = \min_{D \in H(\mathrm{div}, \Omega)} J[D] = J[D_B]. \tag{2.8}$$

In particular, D_B *is the unique minimizer of* $J : H(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ *with a finite minimum value, and* D_B *is also the unique weak solution to the boundary-value problem of the Euler–Lagrange equation for the functional* $J : H(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$

$$\frac{D}{\varepsilon} + \nabla({B^*}'(f - \nabla \cdot D)) = 0 \qquad \text{in } \Omega, \tag{2.9}$$

$${B^*}'(f - \nabla \cdot D) = g \qquad \text{on } \partial\Omega. \tag{2.10}$$

We note that the inequality (2.7) shows that the functional of two-variable (ϕ, D) derived in [31] (cf. equation (17) there) is convex in D and concave in ϕ. We also note that if $D = D_B$, then the Euler–Lagrange equation (2.9) is just the constitutive relation $D_B = -\varepsilon \nabla \phi_B$, and the boundary condition (2.10) is just the boundary condition for ϕ_B: $\phi_B = g$ on $\partial\Omega$.

Proof of Theorem 2.2. Let $\phi \in H_g^1(\Omega)$ and $D \in H(\mathrm{div}, \Omega)$. By the definition of the Legendre transform and integration by parts, we obtain

$$\begin{aligned} I[\phi] &= \int_\Omega \left[-\frac{\varepsilon}{2} |\nabla \phi|^2 + f\phi - B(\phi) \right] dx \\ &\le \int_\Omega \left[-\frac{\varepsilon}{2} |\nabla \phi|^2 + f\phi - B(\phi) + \frac{1}{2\varepsilon} |D + \varepsilon \nabla \phi|^2 \right] dx \\ &= \int_\Omega \left[\frac{1}{2\varepsilon} |D|^2 + f\phi - B(\phi) + D \cdot \nabla \phi \right] dx \\ &= \int_\Omega \left[\frac{1}{2\varepsilon} |D|^2 + (f - \nabla \cdot D)\phi - B(\phi) \right] dx + \int_{\partial\Omega} g D \cdot n \, dS \\ &\le \int_\Omega \left[\frac{1}{2\varepsilon} |D|^2 + B^*(f - \nabla \cdot D) \right] dx + \int_{\partial\Omega} g D \cdot n \, dS \\ &= J[D]. \end{aligned} \tag{2.11}$$

This proves (2.7).

Now let $\phi_B \in H_g^1(\Omega)$ be the unique maximizer of I over $H_g^1(\Omega)$ and let $D_B = -\varepsilon \nabla \phi_B$. Clearly, $D_B \in [L^2(\Omega)]^3$. By (2.1) and (2.2), $\nabla \cdot D_B = f - B'(\phi_B) \in L^2(\Omega)$. Hence $D_B \in H(\mathrm{div}, \Omega)$. Moreover,

$$f - \nabla \cdot D_B = B'(\phi_B) \in H^1(\Omega). \tag{2.12}$$

This and (1.12) imply that

$$B^*(f - \nabla \cdot D_B) = (f - \nabla \cdot D_B)\phi_B - B(\phi_B) \qquad \text{a.e. } \Omega, \tag{2.13}$$

$${B^*}'(f - \nabla \cdot D_B) = \phi_B \qquad \text{a.e. } \Omega. \tag{2.14}$$

Repeating similar steps in (2.11) above, we have then by (2.13) that

$$
\begin{aligned}
I[\phi_B] &= \int_\Omega \left[-\frac{\varepsilon}{2}|\nabla\phi_B|^2 + f\phi_B - B(\phi_B)\right] dx \\
&= \int_\Omega \left[-\frac{\varepsilon}{2}|\nabla\phi_B|^2 + f\phi_B - B(\phi_B) + \frac{1}{2\varepsilon}|D_B + \varepsilon\nabla\phi_B|^2\right] dx \\
&= \int_\Omega \left[\frac{1}{2\varepsilon}|D_B|^2 + f\phi_B - B(\phi_B) + D\cdot\nabla\phi_B\right] dx \\
&= \int_\Omega \left[\frac{1}{2\varepsilon}|D_B|^2 + (f - \nabla\cdot D_B)\phi_B - B(\phi_B)\right] dx + \int_{\partial\Omega} gD_B\cdot n\, dS \\
&= \int_\Omega \left[\frac{1}{2\varepsilon}|D_B|^2 + B^*(f - \nabla\cdot D_B)\right] dx + \int_{\partial\Omega} gD_B\cdot n\, dS \\
&= J[D_B]. \qquad (2.15)
\end{aligned}
$$

By (2.11) and (2.15), we have for any $D \in H(\mathrm{div}, \Omega)$ that $J[D_B] = I[\phi_B] \le J[D]$. This implies (2.8), and D_B minimizes J over $H(\mathrm{div}, \Omega)$. Since the Legendre transform takes convex functions to convex functions, the uniqueness of minimizer of $J : H(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ follows from the strict convexity of J. Clearly, the minimum value $J[D_B]$ is finite.

By Theorem 2.1, $\phi_B \in H^1(\Omega) \cap L^\infty(\Omega)$, and hence, by (2.12), $f - \nabla\cdot D_B \in H^1(\Omega) \cap L^\infty(\Omega)$. Consequently, for any $G \in [C^1(\overline{\Omega})]^3 \subset H(\mathrm{div}, \Omega)$, we conclude from that fact that $\delta J[D_B][G] := (d/dt)|_{t=0} J[D_B + tG] = 0$, and from Lebesgue's dominated convergence theorem allowing the exchange of the limit and integration that

$$
\delta J[D_B][G] = \int_\Omega \left[\frac{D_B\cdot G}{\varepsilon} + B^{*\prime}(f - \nabla\cdot D_B)(-\nabla\cdot G)\right] dx + \int_{\partial\Omega} gG\cdot n\, dS = 0. \qquad (2.16)
$$

By (2.14), $B^{*\prime}(f - \nabla\cdot D_B) = \phi_B \in H^1(\Omega) \cap L^\infty(\Omega)$. Note that $[C^1(\overline{\Omega})]^3$ is dense in $H(\mathrm{div}, \Omega)$. It then follows that (2.16) holds true for any $G \in H(\mathrm{div}, \Omega)$. In particular, (2.6) is true for any $G \in H_0(\mathrm{div}, \Omega)$, implying that D_B is a weak solution to (2.9). It follows from (2.3) and (2.16) with $G \in H(\mathrm{div}, \Omega)$ that

$$
\int_\Omega \left[\frac{D_B}{\varepsilon} + \nabla\left(B^{*\prime}(f - \nabla\cdot D_B)\right)\right]\cdot G\, dx + \int_{\partial\Omega} \left[g - B^{*\prime}(f - \nabla\cdot D_B)\right] G\cdot n\, dS = 0. \qquad (2.17)
$$

By choosing $G \in H_0(\mathrm{div}, \Omega)$, we obtain (2.9) with $D = D_B$. The two equations (2.9) and (2.17) then imply that the second integral in (2.17) vanishes for any $G \in H(\mathrm{div}, \Omega)$. This leads to (2.10) with $D = D_B$. The uniqueness of the weak solution follows from the strict convexity of B^* and a usual argument; cf., e.g., the proof of Theorem 2.1 in [26]. ∎

Let us denote

$$
W = \{D \in H(\mathrm{div}, \Omega) :\ \text{there exists } \phi \in H^1(\Omega) \text{ such that } D = -\varepsilon\nabla\phi\}.
$$

Clearly, this is a linear subspace of $H(\mathrm{div}, \Omega)$. The following is a direct consequence of Theorem 2.2:

COROLLARY 2.3. *Let D_B be the minimizer of the functional $J : H(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ as stated in Theorem* 2.2. *Then, $D_B \in W$ and*

$$
J[D_B] = \min_{D\in H(\mathrm{div},\Omega)} J[D] = \min_{D\in W} J[D].
$$

We now consider the dielectric boundary problem and the interface conditions for the minimizer of the Legendre transformed functional. Let Γ be a C^2, closed surface such that $\Gamma \subset \Omega$. Denote Ω_- the interior of Γ and $\Omega_+ = \Omega \setminus \overline{\Omega_-}$. So, both Ω_- and Ω_+ are bounded open sets in $\mathbb{R}^3$, and $\Omega = \Omega_- \cup \Omega_+ \cup \Gamma$. We assume now that the dielectric coefficient is given by

$$\varepsilon(x) = \varepsilon_\Gamma(x) = \begin{cases} \varepsilon_- & \text{if } x \in \Omega_-, \\ \varepsilon_+ & \text{if } x \in \Omega_+, \end{cases} \tag{2.18}$$

where ε_- and ε_+ are two distinct positive numbers. We denote by $[\![u]\!] = u|_{\Omega_+} - u|_{\Omega_-}$ the jump across Γ of a function $u : \Omega \to \mathbb{R}$ from Ω_+ to Ω_-. We also denote by n the unit normal at Γ pointing from Ω_- to Ω_+. Since the piecewise constant function $\varepsilon \in L^\infty(\Omega)$, Theorem 2.2 still holds true. It follows from routine calculations [25, 26] that the maximizer $\phi_B \in H^1_g(\Omega)$ of $I : H^1_g(\Omega) \to \mathbb{R} \cup \{-\infty\}$ is characterized by the following set of equations:

$$\begin{cases} \varepsilon_- \Delta\phi_B - B'(\phi_B) = -f & \text{in } \Omega_-, \\ \varepsilon_+ \Delta\phi_B - B'(\phi_B) = -f & \text{in } \Omega_+, \\ [\![\phi_B]\!] = 0 \quad \text{and} \quad [\![\varepsilon_\Gamma \nabla\phi_B \cdot n]\!] = 0 & \text{on } \Gamma, \\ \phi_B = g & \text{on } \partial\Omega. \end{cases} \tag{2.19}$$

In particular, $\phi_B|_{\Omega_\pm} \in H^2(\Omega_\pm)$. The spaces $H^2(\Omega_\pm)$ can be replaced by $H^3(\Omega_\pm)$ if $f \in H^1(\Omega)$.

The following theorem provides a similar set of conditions that characterize the minimizer D_B of the Legendre transformed functional $J : H(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$.

THEOREM 2.4. *Assume $f \in H^1(\Omega)$. Let $D \in [L^2(\Omega)]^3$ be such that $D|_{\Omega_-} \in [H^2(\Omega_-)]^3$ and $D|_{\Omega_+} \in [H^2(\Omega_+)]^3$. Then $D = D_B \in H(\mathrm{div}, \Omega)$ (the unique minimizer of $J : H(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ as in Theorem 2.2) if and only if D satisfies the following set of equations:*

$$\begin{cases} \dfrac{D}{\varepsilon_-} + \nabla\left(B^{*\prime}(f - \nabla \cdot D)\right) = 0 & \text{in } \Omega_-, \\ \dfrac{D}{\varepsilon_+} + \nabla\left(B^{*\prime}(f - \nabla \cdot D)\right) = 0 & \text{in } \Omega_+, \\ [\![D \cdot n]\!] = 0 \quad \text{and} \quad [\![\nabla \cdot D]\!] = 0 & \text{on } \Gamma, \\ B^{*\prime}(f - \nabla \cdot D) = g & \text{on } \partial\Omega. \end{cases} \tag{2.20}$$

We note that if $D = D_B$, the unique minimizer of $J : H(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$, then $D = -\varepsilon_\Gamma \nabla\phi_B$ with ϕ_B the unique maximizer of $I : H^1_g(\Omega) \to \mathbb{R} \cup \{-\infty\}$. Consequently, the first interface condition $[\![D \cdot n]\!] = 0$ on Γ in (2.20) is exactly the second interface condition $[\![\varepsilon_\Gamma \nabla\phi_B \cdot n]\!] = 0$ on Γ in (2.19), and, as shown below in the proof of Theorem 2.4, the second interface condition $[\![\nabla \cdot D]\!] = 0$ on Γ in (2.20) is exactly the first interface condition $[\![\phi_B]\!] = 0$ on Γ in (2.19). Moreover, the last equations in (2.20) and (2.19) are exactly the same.

Proof of Theorem 2.4. Clearly, the minimizer $D_B = -\varepsilon_\Gamma \nabla\phi_B \in [L^2(\Omega)]^3$, where $\phi_B \in H^1_g(\Omega)$ is the maximizer of $I : H^1_g(\Omega) \to \mathbb{R} \cup \{-\infty\}$. Moreover, by the regularity of ϕ_B, we have $D_B|_{\Omega_\pm} \in [H^2(\Omega_\pm)]^3$. It follows from (2.16), the divergence theorem, and the fact that the unit normal n points from Ω_- to Ω_+ that

$$
\begin{aligned}
0 &= \delta J[D_B][G] \\
&= \int_{\Omega_-} \left[\frac{D_B \cdot G}{\varepsilon} + B^{*\prime}(f - \nabla \cdot D_B)(-\nabla \cdot G) \right] dx \\
&\quad + \int_{\Omega_+} \left[\frac{D_B \cdot G}{\varepsilon} + B^{*\prime}(f - \nabla \cdot D_B)(-\nabla \cdot G) \right] dx + \int_{\partial\Omega} gG \cdot n \, dS \\
&= \int_{\Omega_-} \left[\frac{D_B}{\varepsilon} + \nabla \left(B^{*\prime}(f - \nabla \cdot D_B) \right) \right] \cdot G \, dx \\
&\quad + \int_{\Omega_+} \left[\frac{D_B}{\varepsilon} + \nabla \left(B^{*\prime}(f - \nabla \cdot D_B) \right) \right] \cdot G \, dx + \int_{\Gamma} [\![B^{*\prime}(f - \nabla \cdot D_B)]\!] G \cdot n \, dS \\
&\quad + \int_{\partial\Omega} \left[g - B^{*\prime}(f - \nabla \cdot D_B) \right] G \cdot n \, dS \qquad \forall G \in H(\mathrm{div}, \Omega).
\end{aligned} \tag{2.21}
$$

Choosing G with its support inside Ω_+ and Ω_- implies the first two equations in (2.20), respectively. As a result, the above equation is reduced to the one without any volume integrals. Choosing G supported inside Ω implies that $[\![B^{*\prime}(f - \nabla \cdot D_B)]\!] = 0$, which further implies that $[\![\nabla \cdot D_B]\!] = 0$ on Γ, since $B^{*\prime}$ is a strictly monotonic function and the trace of $f \in H^1(\Omega)$ on Γ is well defined. The above equation is then further reduced to the one with the right-hand side being only the integral over $\partial\Omega$. This then finally leads to the boundary condition in the last equation of (2.20). The first interface condition $[\![D_B \cdot n]\!] = 0$ follows from the relation $D_B = -\varepsilon_\Gamma \nabla \phi_B$ and the continuity $[\![\varepsilon_\Gamma \nabla \phi_B \cdot n]\!] = 0$ on Γ in (2.19).

Assume now $D \in [L^2(\Omega)]^3$ with $D|_{\Omega_\pm} \in [H^2(\Omega_\pm)]^3$. Define $q \in L^2(\Omega)$ by $q = \nabla \cdot D$ in $\Omega_- \cup \Omega_+$. Since $[\![D \cdot n]\!] = 0$ on Γ and n points from Ω_- to Ω_+,

$$
\begin{aligned}
\int_\Omega qu \, dx &= \int_{\Omega_-} (\nabla \cdot D) u \, dx + \int_{\Omega_+} (\nabla \cdot D) u \, dx \\
&= -\int_{\Omega_-} D \cdot \nabla u \, dx - \int_{\Omega_+} D \cdot \nabla u \, dx - \int_\Gamma [\![D \cdot n]\!] u \, dS \\
&= -\int_\Omega D \cdot \nabla u \, dx \qquad \forall u \in H_0^1(\Omega).
\end{aligned}
$$

Hence, $q = \nabla \cdot D$ and $D \in H(\mathrm{div}, \Omega)$. If D also satisfies (2.20), then we have by similar calculations as before (cf. (2.16) and (2.21)) that $\delta J[D][G] = 0$ for all $G \in H(\mathrm{div}, \Omega)$. Since J is strictly convex, D is the unique minimizer of J, and hence $D = D_B$. ◻

3. The case with a higher-order gradient term. In this (and only in this) section, we shall assume that ε is a constant for simplicity. We also assume that the boundary of Ω and the function f and g on Ω are all sufficiently smooth so that the solution to an underlying boundary-value problem of partial differential equation is regular enough. Let $\sigma > 0$ be a constant. We define

$$
H_g^2(\Omega) = \{ \phi \in H^2(\Omega) : \phi = g \text{ and } \partial_n \phi = \partial_n g \text{ on } \partial\Omega \},
$$

and $\hat{I} : H_g^2(\Omega) \to \mathbb{R} \cup \{-\infty\}$ by [3]

$$
\hat{I}[\phi] = \int_\Omega \left[-\frac{\sigma}{2} (\Delta \phi)^2 - \frac{\varepsilon}{2} |\nabla \phi|^2 + f\phi - B(\phi) \right] dx.
$$

Here the higher-order gradient term $-(\sigma/2)|\Delta\phi|^2$ describes the ion-ion correlation with $\sqrt{\sigma/\varepsilon}$ the correlation length [3]. This functional is the same as the phenomenological electrostatic free-energy functional proposed in [3] except we drop the surface charge term for simplicity. By formal calculations, the Euler–Lagrange equation of the functional $\hat{I}$ is

$$\sigma\Delta^2\phi - \varepsilon\Delta\phi + B'(\phi) = f \qquad \text{in } \Omega.$$

A function $\phi \in H_g^2(\Omega)$ is a weak solution to this equation if

$$\int_\Omega [\sigma\Delta\phi\Delta\eta + \varepsilon\nabla\phi\cdot\nabla\eta + B'(\phi)\eta]\, dx = \int_\Omega f\eta\, dx \qquad \forall\eta \in H_0^2(\Omega). \tag{3.1}$$

THEOREM 3.1. *There exists a unique* $\hat{\phi} \in H_g^2(\Omega)$ *such that* $\hat{I}[\hat{\phi}] = \max_{\phi\in H_g^2(\Omega)} \hat{I}[\phi]$ *with a finite maximum value. Moreover,* $\hat{\phi}$ *is the unique weak solution to the boundary-value problem*

$$\sigma\Delta^2\phi - \varepsilon\Delta\phi + B'(\phi) = f \qquad \textit{in } \Omega, \tag{3.2}$$

$$\phi = g \quad \textit{and} \quad \partial_n\phi = \partial_n g \qquad \textit{on } \partial\Omega. \tag{3.3}$$

Proof. We consider equivalently the minimization of the functional $-\hat{I}$. Note that $u \mapsto \|\Delta u\|_{L^2(\Omega)}$ is a norm of $H_0^2(\Omega)$ that is equivalent to the $H^2(\Omega)$-norm. Therefore, since $B \geq 0$, there exist constants $C_1 > 0$ and $C_2 \geq 0$ such that

$$-\hat{I}[u] \geq C_1\|u\|^2_{H^2(\Omega)} - C_2 \qquad \forall u \in H_g^2(\Omega). \tag{3.4}$$

Now, let $\alpha = \inf_{\phi\in H_g^2(\Omega)}(-\hat{I})[\phi] > -\infty$. Clearly, $\alpha \leq (-\hat{I})[g] < \infty$ and hence α is finite. Let $\phi_j \in H_g^2(\Omega)$ $(j = 1, 2, \ldots)$ be such that $(-\hat{I})[\phi_j] \to \alpha$. Then, it follows from (3.4) that $\{\phi_j\}$ is bounded in $H^2(\Omega)$. Since $H^2(\Omega)$ is a Hilbert space and can be compactly embedded into $H^1(\Omega)$ and $C(\overline{\Omega})$, there exists a subsequence, not relabeled, of $\{\phi_j\}$ that converges weakly in $H^2(\Omega)$, strongly in $H^1(\Omega)$, and uniformly on $\overline{\Omega}$ to some $\hat{\phi} \in H^2(\Omega)$. Since $H_g^2(\Omega)$ is convex and closed in $H^2(\Omega)$ by the trace theorem [16, 18], it is weakly closed in $H_g^2(\Omega)$. Hence $\hat{\phi} \in H_g^2(\Omega)$. Clearly, $-\hat{I}$ is strictly convex. Moreover, it is continuous with respect to the strong convergence of $H^2(\Omega)$. Therefore, $-\hat{I}$ is weakly lower-semicontinuous, and hence $\liminf_{j\to\infty}(-\hat{I})[\phi_j] \geq (-\hat{I})[\hat{\phi}]$. This implies that $(-\hat{I})[\hat{\phi}] = \alpha$ and that $\hat{\phi}$ is a minimizer of $-\hat{I}$ over $H_g^2(\Omega)$. The uniqueness of such a minimizer is a consequence of the strict convexity of the functional $-\hat{I}$. Finally, noting that $\hat{\phi} \in C(\overline{\Omega})$, we obtain (3.1), with $\hat{\phi}$ replacing ϕ, by routine calculations; hence $\hat{\phi} \in H_g^2(\Omega)$ is a weak solution to the boundary-value problem (3.2) and (3.3). The uniqueness of such a weak solution again follows from the strict convexity of the functional $-\hat{I}$. ∎

We define

$$H^2(\text{div}, \Omega) = \{D \in [H^2(\Omega)]^3 : \nabla\cdot D \in H^2(\Omega)\}.$$

Note that if $D \in H^2(\text{div}, \Omega)$, then

$$\int_\Omega \Delta(\nabla\cdot D)\,\eta\, dx = -\int_\Omega \nabla(\nabla\cdot D)\cdot\nabla\eta\, dx + \int_{\partial\Omega} \partial_n(\nabla\cdot D)\,\eta\, dS \qquad \forall\eta \in H^1(\Omega).$$

We define the Legendre transformed functional $\hat{J} : H^2(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ of the functional $\hat{I} : H_g^2(\Omega) \to \mathbb{R} \cup \{-\infty\}$ by

$$\hat{J}[D] = \int_\Omega \left[\frac{1}{2\varepsilon}|D|^2 + \frac{\sigma}{2\varepsilon}|\nabla \cdot D|^2 + B^* \left(f - \nabla \cdot D + \frac{\sigma}{\varepsilon}\Delta(\nabla \cdot D) \right) \right] dx + \int_{\partial\Omega} \left\{ \left[D \cdot n - \frac{\sigma}{\varepsilon}\partial_n(\nabla \cdot D) \right] g + \frac{\sigma}{\varepsilon}(\nabla \cdot D)\partial_n g \right\} dS.$$

The following theorem is parallel to Theorem 2.2.

THEOREM 3.2. *We have*

$$\hat{I}[\phi] \le \hat{J}[D] \qquad \forall \phi \in H_g^2(\Omega) \quad \forall D \in H^2(\mathrm{div}, \Omega). \tag{3.5}$$

Moreover, if $\hat{\phi} \in H_g^2(\Omega)$ is the unique maximizer of $\hat{I} : H_g^2(\Omega) \to \mathbb{R} \cup \{-\infty\}$ and $\hat{D} = -\varepsilon\nabla\hat{\phi}$, then $\hat{D} \in H^2(\mathrm{div}, \Omega)$ and

$$\hat{I}[\hat{\phi}] = \max_{\phi \in H_g^2(\Omega)} \hat{I}[\phi] = \min_{D \in H^2(\mathrm{div},\Omega)} \hat{J}[D] = \hat{J}[\hat{D}]. \tag{3.6}$$

In particular, $\hat{D}$ is the unique minimizer of $\hat{J} : H^2(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ with a finite minimum value.

Proof. Fix $\phi \in H_g^2(\Omega)$ and $D \in H^2(\mathrm{div}, \Omega)$. We have by the definition of $\hat{I}[\phi]$ and $\hat{J}[D]$, integration by parts, and the fact that $\phi = g$ and $\partial_n \phi = \partial_n g$ on $\partial\Omega$ that

(3.7)

$$\begin{aligned}
\hat{I}[\phi] &= \int_\Omega \left[-\frac{\sigma}{2}(\Delta\phi)^2 - \frac{\varepsilon}{2}|\nabla\phi|^2 + f\phi - B(\phi) \right] dx \\
&\le \int_\Omega \left[-\frac{\sigma}{2}(\Delta\phi)^2 - \frac{\varepsilon}{2}|\nabla\phi|^2 + f\phi - B(\phi) + \frac{\sigma}{2\varepsilon^2}|\nabla \cdot D + \varepsilon\Delta\phi|^2 + \frac{1}{2\varepsilon}|D + \varepsilon\nabla\phi|^2 \right] dx \\
&= \int_\Omega \left[\frac{\sigma}{2\varepsilon^2}|\nabla \cdot D|^2 + \frac{1}{2\varepsilon}|D|^2 + f\phi - B(\phi) + \frac{\sigma}{\varepsilon}(\nabla \cdot D)\Delta\phi + D \cdot \nabla\phi \right] dx \\
&= \int_\Omega \left[\frac{\sigma}{2\varepsilon^2}|\nabla \cdot D|^2 + \frac{1}{2\varepsilon}|D|^2 + f\phi - B(\phi) - \frac{\sigma}{\varepsilon}\nabla(\nabla \cdot D) \cdot \nabla\phi - (\nabla \cdot D)\phi \right] dx \\
&\quad + \int_{\partial\Omega} \left[\frac{\sigma}{\varepsilon}(\nabla \cdot D)\partial_n g + (D \cdot n)g \right] dS \\
&= \int_\Omega \left[\frac{\sigma}{2\varepsilon^2}|\nabla \cdot D|^2 + \frac{1}{2\varepsilon}|D|^2 + \phi \left(f - \nabla \cdot D + \frac{\sigma}{\varepsilon}\Delta(\nabla \cdot D) \right) - B(\phi) \right] dx \\
&\quad + \int_{\partial\Omega} \left[\frac{\sigma}{\varepsilon}(\nabla \cdot D)\partial_n g + (D \cdot n)g - \frac{\sigma}{\varepsilon}\partial_n(\nabla \cdot D)g \right] dS \\
&\le \int_\Omega \left[\frac{1}{2\varepsilon}|D|^2 + \frac{\sigma}{2\varepsilon^2}|\nabla \cdot D|^2 + B^* \left(f - \nabla \cdot D + \frac{\sigma}{\varepsilon}\Delta(\nabla \cdot D) \right) \right] dx \\
&\quad + \int_{\partial\Omega} \left\{ \left[D \cdot n - \frac{\sigma}{\varepsilon}\partial_n(\nabla \cdot D) \right] g + \frac{\sigma}{\varepsilon}(\nabla \cdot D)\partial_n g \right\} dS. \\
&= \hat{J}[D].
\end{aligned}$$

This proves (3.5).

Now let $\hat{\phi} \in H_g^2(\Omega)$ be the unique maximizer of $\hat{I}$ over $H_g^2(\Omega)$ and let $\hat{D} = -\varepsilon\nabla\hat{\phi}$. Since $\hat{\phi}$ satisfies (3.2) and all Ω, f, and g are sufficiently smooth, we have $\hat{\phi} \in H^3(\Omega)$

and $\Delta\hat{\phi} \in H^2(\Omega)$. These imply that $\hat{D} \in H^2(\mathrm{div}, \Omega)$. Moreover, by (3.2) again, we have

$$f - \nabla \cdot \hat{D} + \frac{\sigma}{\varepsilon}\Delta(\nabla \cdot \hat{D}) = B'(\hat{\phi}) \qquad \text{a.e. } \Omega. \tag{3.8}$$

This and (1.12) imply that

$$B^*\left(f - \nabla \cdot \hat{D} + \frac{\sigma}{\varepsilon}\Delta(\nabla \cdot \hat{D})\right) = \hat{\phi}\left(f - \nabla \cdot \hat{D} + \frac{\sigma}{\varepsilon}\Delta(\nabla \cdot \hat{D}\right) - B(\hat{\phi}) \qquad \text{a.e. } \Omega. \tag{3.9}$$

Repeating (3.7) above with $\hat{\phi}$ and $\hat{D}$ replacing ϕ and D, respectively, noting that the two inequalities are in fact equalities in this case, we then obtain $\hat{I}[\hat{\phi}] = \hat{J}[\hat{D}]$. This implies (3.6). Hence $\hat{D}$ minimizes $\hat{J}$ over $H^2(\mathrm{div}, \Omega)$. Since the Legendre transform takes convex functions to convex functions, the uniqueness of the minimizer of $\hat{J} : H^2(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ follows from the strict convexity of $\hat{J}$. Clearly, the minimum value $\hat{J}[\hat{D}]$ is finite. ∎

4. The case without ions. We define $I_0 : H^1_g(\Omega) \to \mathbb{R}$ by

$$I_0[\phi] = \int_\Omega \left(-\frac{\varepsilon}{2}|\nabla\phi|^2 + f\phi\right) dx \qquad \forall \phi \in H^1_g(\Omega). \tag{4.1}$$

This functional is the same as $I[\phi]$ with $B(\phi)$ replaced by the 0 function. Let us denote by B_0 the 0 function, i.e., $B_0(s) = 0$ for all $s \in \mathbb{R}$. As in the previous case, we define $\tilde{J}_0 : H(\mathrm{div}, \Omega) \to \mathbb{R} \cup \{+\infty\}$ by

$$\tilde{J}_0[D] = \int_\Omega \left[\frac{1}{2\varepsilon}|D|^2 + B_0^*(f - \nabla \cdot D)\right] dx + \int_{\partial\Omega} gD \cdot n\, dS \qquad \forall D \in H(\mathrm{div}, \Omega).$$

However, by the definition of Legendre transform, $B_0^*(\xi) = \infty$ if $\xi \neq 0$ and $B_0^*(0) = 0$. Hence, $\tilde{J}_0[D] = +\infty$ for all $D \in H(\mathrm{div}, \Omega)$ except those that satisfy $\nabla \cdot D = f$ a.e. in Ω. We therefore consider the following constrained variational problem: Minimize the functional $J_0 : H(\mathrm{div}_f, \Omega) \to \mathbb{R}$, defined by

$$J_0[D] = \int_\Omega \frac{1}{2\varepsilon}|D|^2 dx + \int_{\partial\Omega} gD \cdot n\, dS \qquad \forall D \in H(\mathrm{div_f}, \Omega),$$

where

$$H(\mathrm{div_f}, \Omega) = \{\mathrm{D} \in \mathrm{H}(\mathrm{div}, \Omega) : \nabla \cdot \mathrm{D} = \mathrm{f \ a.e.\ } \Omega\}.$$

Note that J_0 differs from the functional defined in (1.13) by the boundary integral term.

We recall that there exists a unique $\phi_0 \in H^1_g(\Omega)$ that maximizes I_0 over $H^1_g(\Omega)$, and the maximizer ϕ_0 is the unique weak solution to $\nabla \cdot \varepsilon\nabla\phi_0 = -f$ in Ω and $\phi_0 = g$ on $\partial\Omega$; cf. [16, 18, 25].

THEOREM 4.1. *We have*

$$I_0[\phi] \leq J_0[D] \qquad \forall \phi \in H^1_g(\Omega) \quad \forall D \in H(\mathrm{div_f}, \Omega). \tag{4.2}$$

Moreover, if $\phi_0 \in H^1_g(\Omega)$ is the unique maximizer of $I_0 : H^1_g(\Omega) \to \mathbb{R}$ and $D_0 = -\varepsilon\nabla\phi_0$, then $D_0 \in H(\mathrm{div_f}, \Omega)$ and

$$J_0[D_0] = \min_{D \in H(\mathrm{div_f}, \Omega)} J[D] = \max_{\phi \in H^1_g(\Omega)} I_0[\phi] = I_0[\phi_0]. \tag{4.3}$$

In particular, D_0 is the unique minimizer of $J_0 : H(\mathrm{div_f}, \Omega) \to \mathbb{R}$ and the minimum value is finite.

Proof. Let $\phi \in H_g^1(\Omega)$ and $D \in H(\mathrm{div_f}, \Omega)$. Similar to the proof of (2.11) but with the fact that $\nabla \cdot D = f$ a.e. in Ω, we have

$$\begin{aligned} I_0[\phi] &= \int_\Omega \left(-\frac{\varepsilon}{2}|\nabla\phi|^2 + f\phi\right) dx \\ &\le \int_\Omega \left(-\frac{\varepsilon}{2}|\nabla\phi|^2 + f\phi + \frac{1}{2\varepsilon}|D + \varepsilon\nabla\phi|^2\right) dx \\ &= \int_\Omega \left(\frac{1}{2\varepsilon}|D|^2 + f\phi + D\cdot\nabla\phi\right) dx \\ &= \int_\Omega \frac{1}{2\varepsilon}|D|^2 dx + \int_{\partial\Omega} gD\cdot n\, dS \\ &= J_0[D]. \end{aligned}$$

This proves (4.2). Clearly, $D_0 \in H(\mathrm{div_f}, \Omega)$, since ϕ_0 is the weak solution to $\nabla\cdot\varepsilon\nabla\phi_0 = -f$. To prove (4.3), we notice that the above inequality is in fact an equality if we replace ϕ by ϕ_0 and D by D_0, respectively. This equality and (4.2) then lead to (4.3). Now (4.3) implies that D_0 is a minimizer of J_0 over $H(\mathrm{div_f}, \Omega)$. It is the unique minimizer, since J_0 is convex. ∎

We now consider a different approach as suggested in [31]. We approximate the functional I_0 by $I_\mu : H_g^1(\Omega) \to \mathbb{R}$ with $\mu > 0$, defined by

$$I_\mu[\phi] = \int_\Omega \left(-\frac{\varepsilon}{2}|\nabla\phi|^2 + f\phi - \frac{\mu}{2}\phi^2\right) dx \qquad \forall\phi \in H_g^1(\Omega). \tag{4.4}$$

For any $\mu > 0$, let us define $B_\mu : \mathbb{R} \to \mathbb{R}$ by $B_\mu(s) = \mu s^2/2$. It is easy to verify that the Legendre transform of B_μ is given by $B_\mu^*(\xi) = \xi^2/2\mu$ for any $\xi \in \mathbb{R}$. Correspondingly, for each $\mu > 0$, we define the Legendre transformed functional $J_\mu : H(\mathrm{div}, \Omega) \to \mathbb{R}$ by

$$J_\mu[D] = \int_\Omega \left(\frac{1}{2\varepsilon}|D|^2 + \frac{1}{2\mu}|f - \nabla\cdot D|^2\right) dx + \int_{\partial\Omega} gD\cdot n\, dS \qquad \forall D \in H(\mathrm{div}, \Omega).$$

THEOREM 4.2.

(1) *For each $\mu \ge 0$, there exists a unique $\phi_\mu \in H_g^1(\Omega)$ that maximizes $I_\mu : H_g^1(\Omega) \to \mathbb{R}$ and that is also the unique weak solution to the boundary-value problem*

$$\begin{cases} \nabla\cdot\varepsilon\nabla\phi_\mu - \mu\phi_\mu = -f & \text{in } \Omega, \\ \phi_\mu = g & \text{on } \partial\Omega. \end{cases} \tag{4.5}$$

(2) *We have for any $\mu > 0$ that*

$$I_\mu[\phi] \le J_\mu[D] \qquad \forall\phi \in H_g^1(\Omega) \quad \forall D \in H(\mathrm{div}, \Omega). \tag{4.6}$$

Let ϕ_μ be the maximizer of $I_\mu : H_g^1(\Omega) \to \mathbb{R}$ and $D_\mu = -\varepsilon\nabla\phi_\mu$ $(\mu \ge 0)$. Then we have for any $\mu > 0$ that

$$I_\mu[\phi_\mu] = \max_{\phi\in H_g^1(\Omega)} I_\mu[\phi] = \min_{D\in H(\mathrm{div},\Omega)} J_\mu[D] = J_\mu[D_\mu]. \tag{4.7}$$

In particular, D_μ is the unique minimizer of $J_\mu : H(\mathrm{div}, \Omega) \to \mathbb{R}$.

(3) *There exist constants $C > 0$ and $\mu_0 > 0$, depending only on Ω, f, g, and $\varepsilon_{\min}$ and $\varepsilon_{\max}$, such that for all $\mu \in (0, \mu_0]$*

$$\|D_\mu - D_0\|_{L^2(\Omega)} \le \varepsilon_{\max}\|\phi_\mu - \phi_0\|_{H^1(\Omega)} \le C\mu, \tag{4.8}$$

$$|J_\mu[D_\mu] - I_0[\phi_0]| = |I_\mu[\phi_\mu] - I_0[\phi_0]| \le C\mu. \tag{4.9}$$

Proof. (1) This part is standard; cf. [16, 18].

(2) The proof of this part is the same as that of Theorem 2.2 with B_μ, ϕ_μ, and D_μ replacing B, ϕ_B, and D_B, respectively.

(3) By (1), ϕ_μ ($\mu > 0$) and ϕ_0 satisfy

$$\int_\Omega (\varepsilon \nabla \phi_\mu \cdot \nabla \eta + \mu \phi_\mu \eta)\, dx = \int_\Omega f \eta \, dx \qquad \forall \eta \in H_0^1(\Omega), \tag{4.10}$$

$$\int_\Omega \varepsilon \nabla \phi_0 \cdot \nabla \eta \, dx = \int_\Omega f \eta \, dx \qquad \forall \eta \in H_0^1(\Omega), \tag{4.11}$$

respectively. Letting $\eta = \phi_\mu - \phi_0 \in H_0^1(\Omega)$ and subtracting (4.11) from (4.10), we get

$$\int_\Omega \varepsilon |\nabla \phi_\mu - \nabla \phi_0|^2 dx = -\mu \int_\Omega \phi_\mu (\phi_\mu - \phi_0)\, dx.$$

It then follows from Poincaré's inequality and the Cauchy–Schwarz inequality that

$$\|\phi_\mu - \phi_0\|_{H^1(\Omega)}^2 \le C\mu \|\phi_\mu\|_{L^2(\Omega)} \|\phi_\mu - \phi_0\|_{L^2(\Omega)}.$$

Here C denotes a generic constant that only depends on Ω, f, g, ε_-, and ε_+. Consequently,

$$\|\phi_\mu - \phi_0\|_{H^1(\Omega)} \le C\mu \|\phi_\mu\|_{L^2(\Omega)} \le C\mu \|\phi_\mu - \phi_0\|_{L^2(\Omega)} + C\mu \|\phi_0\|_{L^2(\Omega)}.$$

Note ϕ_0 only depends on Ω, f, g, ε_-, and ε_+. Hence, we obtain the second inequality in (4.8) for all $\mu \in (0, \mu_0]$ for some $\mu_0 > 0$ sufficiently small and depending only on Ω, f, g, ε_-, and ε_+. The first inequality in (4.8) follows from $D_\mu = -\varepsilon \nabla \phi_\mu (\mu \ge 0)$ and $0 < \varepsilon_{\min} \le \varepsilon \le \varepsilon_{\max}$ in Ω.

It now follows from the definition of I_μ (cf. (4.4)) and I_0 (cf. (4.1)), and (4.8), that for all $\mu \in (0, \mu_0]$

$$\begin{aligned} |I_\mu[\phi_\mu] - I_0[\phi_0]| &= \left| \int_\Omega \left[-\frac{\varepsilon}{2} \left(|\nabla \phi_\mu|^2 - |\nabla \phi_0|^2 \right) + f(\phi_\mu - \phi_0) - \frac{\mu}{2} \phi_\mu^2 \right] dx \right| \\ &\le \frac{\varepsilon_{\max}}{2} \|\nabla \phi_\mu - \nabla \phi_0\|_{L^2(\Omega)} \|\nabla \phi_\mu + \nabla \phi_0\|_{L^2(\Omega)} \\ &\qquad + \|f\|_{L^2(\Omega)} \|\phi_\mu - \phi_0\|_{L^2(\Omega)} + \frac{\mu}{2} \|\phi_\mu\|_{L^2(\Omega)}^2 \\ &\le C\mu \left(\|\nabla \phi_\mu + \nabla \phi_0\|_{L^2(\Omega)} + 1 + \|\phi_\mu\|_{L^2(\Omega)}^2 \right) \\ &\le C\mu \Big(\|\nabla \phi_\mu - \nabla \phi_0\|_{L^2(\Omega)} + 2\|\nabla \phi_0\|_{L^2(\Omega)} + 1 \\ &\qquad + 2\|\phi_\mu - \phi_0\|_{L^2(\Omega)}^2 + 2\|\phi_0\|_{L^2(\Omega)}^2 \Big) \\ &\le C\mu \left(\mu + 2\mu^2 + 1 \right). \end{aligned}$$

This proves (4.9). ∎

5. Application to dielectric boundary implicit solvation. We now consider the dielectric boundary problem in molecular solvation. Let again Γ be a C^2, closed surface such that $\Gamma \subset \Omega$. Denote Ω_- the interior of Γ and $\Omega_+ = \Omega \setminus \overline{\Omega_-}$. So, $\Omega = \Omega_- \cup \Omega_+ \cup \Gamma$. Here, Ω_- and Ω_+ are the solute and solvent regions, respectively, and Γ is the dielectric boundary. As before, we denote by n the unit normal at Γ pointing from Ω_- to Ω_+. The piecewise constant, dielectric coefficient $\varepsilon_\Gamma : \Omega \to \mathbb{R}$ is defined again in (2.18) with ε_- and ε_+ two distinct positive constants. Denote again by χ_+ the characteristic function of Ω_+. We define $I_\Gamma : H_g^1(\Omega) \cup \{-\infty\}$ by

$$I_\Gamma[\phi] = \int_\Omega \left[-\frac{\varepsilon_\Gamma}{2} |\nabla \phi|^2 + f\phi - \chi_+ B(\phi) \right] dx \qquad \forall \phi \in H_g^1(\Omega). \tag{5.1}$$

Clearly, $I[\phi] < \infty$ for any $\phi \in H_g^1(\Omega)$. We consider the maximization of the functional $I_\Gamma : H_g^1(\Omega) \cup \{-\infty\}$ and the boundary-value problem of the PB equation

$$\nabla \cdot \varepsilon_\Gamma \nabla \phi - \chi_+ B'(\phi) = -f \qquad \text{in } \Omega, \tag{5.2}$$
$$\phi = g \qquad \text{on } \partial\Omega. \tag{5.3}$$

The following theorem collects some useful results proved in [10, 25, 26, 28].

Theorem 5.1.
(1) *The functional* $I_\Gamma : H_g^1(\Omega) \to \mathbb{R} \cup \{-\infty\}$ *has a unique* maximizer $\phi_\Gamma \in H_g^1(\Omega)$. *Moreover, the maximum value is finite, and*

$$\|\phi_\Gamma\|_{H^1(\Omega)} + \|\phi_\Gamma\|_{L^\infty(\Omega)} \le C$$

for some constant $C > 0$ *depending on* ε_-, ε_+, f, g, B, *and* Ω *but not on* Γ.
(2) *The maximizer* ϕ_Γ *is the unique solution to the boundary-value problem of the PB equation* (5.2) *and* (5.3).
(3) *The boundary-value problem of the PB equation* (5.2) *and* (5.3) *is equivalent to the elliptic interface problem*

$$\begin{cases} \varepsilon_- \Delta \phi = -f & \text{in } \Omega_-, \\ \varepsilon_+ \Delta \phi - B'(\phi) = -f & \text{in } \Omega_+, \\ [\![\phi]\!] = [\![\varepsilon_\Gamma \nabla \phi \cdot n]\!] = 0 & \text{on } \Gamma, \\ \phi = g & \text{on } \partial\Omega. \end{cases} \tag{5.4}$$

In particular, $\phi|_{\Omega_-} \in H^2(\Omega_-)$ *and* $\phi|_{\Omega_+} \in H^2(\Omega_+)$. *The spaces* $H^2(\Omega_-)$ *and* $H^2(\Omega_+)$ *can be replaced by* $H^3(\Omega_-)$ *and* $H^3(\Omega_+)$, *respectively, if* $f \in H^1(\Omega)$.

We now denote

$$V_\Gamma = \{D \in H(\mathrm{div}, \Omega) : \nabla \cdot D = f \text{ a.e. } \Omega_-\}$$

and define $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{+\infty\}$ by

$$J_\Gamma[D] = \int_\Omega \left[\frac{1}{2\varepsilon_\Gamma} |D|^2 + B^*(f - \nabla \cdot D) \right] dx + \int_{\partial\Omega} gD \cdot n \, dS.$$

Note that V_Γ is a convex subset of $H(\mathrm{div}, \Omega)$. Note also that $J_\Gamma[D]$ is the same as $J[D]$ defined in (2.4) (with ε_Γ replacing ε). Here we use the subscript Γ to indicate that J_Γ is defined on V_Γ. It is clear that $J_\Gamma[D] > -\infty$ for any $D \in V_\Gamma$.

Theorem 5.2. *We have for any* $\phi \in H_g^1(\Omega)$ *and any* $D \in V_\Gamma$ *that* $I_\Gamma[\phi] \le J_\Gamma[D]$. *If we denote* $\phi_\Gamma \in H_g^1(\Omega)$ *the unique maximizer of* $I_\Gamma : H_g^1(\Omega) \to \mathbb{R}$ *and* $D_\Gamma = -\varepsilon_\Gamma \nabla \phi_\Gamma$, *then* $D_\Gamma \in V_\Gamma$, *and* D_Γ *is the unique minimizer of* $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{+\infty\}$. *Moreover,*

$$J_\Gamma[D_\Gamma] = \min_{D \in V_\Gamma} J_\Gamma[D] = \max_{\phi \in H_g^1(\Omega)} I_\Gamma[\phi] = I_\Gamma[\phi_\Gamma]. \tag{5.5}$$

Proof. Let $\phi \in H_g^1(\Omega)$ and $D \in V_\Gamma$. Since $\nabla \cdot D = f$ in Ω_- and $B^*(0) = 0$, we have $B^*(f - \nabla \cdot D) = 0$ a.e. Ω_-. Therefore, by integration by parts, we obtain that

$$\begin{aligned}
I_\Gamma[\phi] &= \int_\Omega \left[-\frac{\varepsilon_\Gamma}{2} |\nabla \phi|^2 + f\phi - \chi_+ B(\phi) \right] dx \\
&\le \int_\Omega \left[-\frac{\varepsilon_\Gamma}{2} |\nabla \phi|^2 + f\phi - \chi_+ B(\phi) + \frac{1}{2\varepsilon_\Gamma} |D + \varepsilon_\Gamma \nabla \phi|^2 \right] dx \\
&= \int_\Omega \left[\frac{1}{2\varepsilon_\Gamma} |D|^2 + f\phi - \chi_+ B(\phi) + D \cdot \nabla \phi \right] dx \\
&= \int_\Omega \left[\frac{1}{2\varepsilon_\Gamma} |D|^2 + f\phi - \chi_+ B(\phi) - \phi \nabla \cdot D \right] dx + \int_{\partial\Omega} g D \cdot n \, dS \\
&= \int_\Omega \left[\frac{1}{2\varepsilon_\Gamma} |D|^2 + \chi_+ \left(\phi(f - \nabla \cdot D) - B(\phi) \right) \right] dx + \int_{\partial\Omega} g D \cdot n \, dS \\
&\le \int_\Omega \left[\frac{1}{2\varepsilon_\Gamma} |D|^2 + \chi_+ B^*(f - \nabla \cdot D) \right] dx + \int_{\partial\Omega} g D \cdot n \, dS \\
&= \int_\Omega \left[\frac{1}{2\varepsilon_\Gamma} |D|^2 + B^*(f - \nabla \cdot D) \right] dx + \int_{\partial\Omega} g D \cdot n \, dS \\
&= J_\Gamma[D]. \qquad (5.6)
\end{aligned}$$

Let $\phi_\Gamma \in H_g^1(\Omega)$ be the unique maximizer of $I_\Gamma : H_g^1(\Omega) \to \mathbb{R} \cup \{-\infty\}$ and $D_\Gamma = -\varepsilon_\Gamma \nabla \phi_\Gamma \in [L^2(\Omega)]^3$. Since ϕ_Γ is the unique weak solution to the boundary-value problem of PB equation (5.2) and (5.3), we have by (5.2) that $\nabla \cdot D_\Gamma = f - \chi_+ B'(\phi_\Gamma) \in L^2(\Omega)$. Hence $D_\Gamma \in H(\mathrm{div}, \Omega)$. By the first equation in (5.4), $\nabla \cdot D_\Gamma = f$ a.e. Ω_-. Hence, $D_\Gamma \in V_\Gamma$. By the second equation in (5.4), we have

$$B'(\phi_\Gamma) = f - \nabla \cdot D_\Gamma \qquad \text{in } \Omega_+. \tag{5.7}$$

Consequently,

$$B^*(f - \nabla \cdot D_\Gamma) = \phi_\Gamma(f - \nabla \cdot D_\Gamma) - B(\phi_\Gamma) \qquad \text{in } \Omega_+.$$

Therefore, we can repeat those steps in (5.6) with ϕ_Γ and D_Γ replacing ϕ and D, respectively, to get

$$\begin{aligned}
I_\Gamma[\phi_\Gamma] &= \int_\Omega \left[-\frac{\varepsilon_\Gamma}{2} |\nabla \phi_\Gamma|^2 + f\phi_\Gamma - \chi_+ B(\phi_\Gamma) \right] dx \\
&= \int_\Omega \left[-\frac{\varepsilon_\Gamma}{2} |\nabla \phi_\Gamma|^2 + f\phi_\Gamma - \chi_+ B(\phi_\Gamma) + \frac{1}{2\varepsilon_\Gamma} |D_\Gamma + \varepsilon_\Gamma \nabla \phi_\Gamma|^2 \right] dx \\
&= \int_\Omega \left[\frac{1}{2\varepsilon_\Gamma} |D_\Gamma|^2 + f\phi_\Gamma - \chi_+ B(\phi_\Gamma) + D_\Gamma \cdot \nabla \phi_\Gamma \right] dx \\
&= \int_\Omega \left[\frac{1}{2\varepsilon_\Gamma} |D_\Gamma|^2 + f\phi_\Gamma - \chi_+ B(\phi_\Gamma) - \phi_\Gamma \nabla \cdot D_\Gamma \right] dx + \int_{\partial\Omega} g D_\Gamma \cdot n \, dS \\
&= \int_\Omega \left[\frac{1}{2\varepsilon_\Gamma} |D_\Gamma|^2 + \chi_+ \left(\phi_\Gamma(f - \nabla \cdot D_\Gamma) - B(\phi_\Gamma) \right) \right] dx + \int_{\partial\Omega} g D_\Gamma \cdot n \, dS \\
&= \int_\Omega \left[\frac{1}{2\varepsilon_\Gamma} |D_\Gamma|^2 + \chi_+ B^*(f - \nabla \cdot D_\Gamma) \right] dx + \int_{\partial\Omega} g D_\Gamma \cdot n \, dS \\
&= \int_\Omega \left[\frac{1}{2\varepsilon_\Gamma} |D_\Gamma|^2 + B^*(f - \nabla \cdot D_\Gamma) \right] dx + \int_{\partial\Omega} g D_\Gamma \cdot n \, dS \\
&= J_\Gamma[D_\Gamma].
\end{aligned}$$

This and (5.6), together with the fact that ϕ_Γ maximizes $I_\Gamma : H^1_g(\Omega) \to \mathbb{R} \cup \{-\infty\}$, imply (5.5). The inequality (5.6) and (5.5) imply that D_Γ minimizes $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{\infty\}$. This minimizer is unique since the functional $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{\infty\}$ is convex. ∎

Denote

$$W_\Gamma = \{D \in V_\Gamma : \text{ there exists } \phi \in H^1(\Omega) \text{ such that } D = -\varepsilon_\Gamma \nabla\phi \text{ in } \Omega\}.$$

Clearly, W_Γ is a convex subset of V_Γ. The following is a direct consequence of Theorem 5.2.

COROLLARY 5.3. *Let D_Γ be the minimizer of the functional $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{+\infty\}$ as stated in Theorem* 5.2. *Then, $D_\Gamma \in W_\Gamma$ and*

$$J_\Gamma[D_\Gamma] = \min_{D\in V_\Gamma} J[D] = \min_{D\in W_\Gamma} J[D].$$

The following theorem provides a set of conditions, similar to those in (5.4), that characterize the minimizer D_Γ of the Legendre transformed functional $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{+\infty\}$.

THEOREM 5.4. *Assume $f \in H^1(\Omega)$. Let $D \in [L^2(\Omega)]^3$ be such that $D|_{\Omega_-} \in [H^2(\Omega_-)]^3$ and $D|_{\Omega_+} \in [H^2(\Omega_+)]^3$, and $D = -\varepsilon_- \nabla\phi_-$ in Ω_- for some $\phi_- \in H^1(\Omega_-)$. Then $D = D_\Gamma \in V_\Gamma$ (the unique minimizer of $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{+\infty\}$ as in Theorem* 5.2*) if and only if D satisfies the following set of equations:*

$$(5.8)\quad \begin{cases} \nabla \cdot D = f & \text{in } \Omega_-, \\ \dfrac{D}{\varepsilon_+} + \nabla\left(B^{*\prime}(f - \nabla\cdot D)\right) = 0 & \text{in } \Omega_+, \\ [\![D\cdot n]\!] = 0 & \text{on } \Gamma, \\ \dfrac{1}{\varepsilon_-} D|_{\Omega_-}\cdot\tau = -\partial_\tau\left(B^{*\prime}(f-\nabla\cdot D)|_{\Omega_+}\right) & \forall \text{ unit vector } \tau \text{ tangential to } \Gamma, \\ B^{*\prime}(f - \nabla\cdot D) = g & \text{on } \partial\Omega. \end{cases}$$

Several remarks are in order. First, if $D = D_\Gamma$, the unique minimizer of $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{+\infty\}$, then $D_\Gamma = -\varepsilon_\Gamma \nabla\phi_\Gamma$ with ϕ_Γ the unique maximizer of $I_\Gamma : H^1_g(\Omega) \to \mathbb{R} \cup \{-\infty\}$. Consequently, as shown in the proof of the theorem, the equations in (5.8) are equivalent to those in (5.4). Second, the second interface condition (i.e., the fourth equation in (5.8)) is not the jump across Γ of a very same quantity. This is because the B part is only for the solvent region Ω_+ as it models the ionic contribution. Therefore, the Legendre transform is only applied to part of the entire region Ω. Finally, we require D to be the gradient of a function in Ω_-. Otherwise, the divergence-free vector field $D + \varepsilon_- \nabla\phi_\Gamma$ in Ω_- may be nonzero in Ω_-. (It will be a curl of a vector field if Ω_- is simply connected.) Note the minimizer D_Γ fulfills this requirement. Moreover, in terms of numerical implementation, solving the equation $\nabla \cdot D = f$ in Ω_- can be converted to solving a more well-defined equation $-\varepsilon_- \Delta\phi_- = f$ in Ω_-.

Proof of Theorem 5.4. Clearly, the minimizer $D_\Gamma \in V_\Gamma$ of the functional $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{+\infty\}$ satisfies $D_\Gamma \in [L^2(\Omega)]^3$. Since $D_\Gamma = -\varepsilon_\Gamma \nabla\phi_\Gamma$ with ϕ_Γ the maximizer of $I_\Gamma : H^1_g(\Omega) \to \mathbb{R} \cup \{-\infty\}$, we have by Theorem 5.1 that $D_\Gamma|_{\Omega_\pm} \in [H^2(\Omega_\pm)]^3$ and that clearly $D_\Gamma = -\varepsilon_- \nabla\phi_\Gamma$ in Ω_- with $\phi_\Gamma \in H^1(\Omega)$. We show that D_Γ satisfies (5.8). The first equation in (5.8) with D_Γ replacing D follows from the definition of V_Γ and the fact that $D_\Gamma \in V_\Gamma$. Note from (5.7) and (1.12) that

$$(5.9)\qquad B^{*\prime}(f - \nabla\cdot D_\Gamma) = \phi_\Gamma \qquad \text{in } \Omega_+.$$

This and the relation $D_\Gamma = -\varepsilon_\Gamma \nabla \phi_\Gamma$ imply the second equation in (5.8) with D_Γ replacing D. The third equation in (5.8) follows from the second interface condition in the third equation of (5.4) with D_Γ and ϕ_Γ replacing D and ϕ, respectively. With $D = D_\Gamma = -\varepsilon_\Gamma \nabla \phi_\Gamma$ and (5.9), the fourth equation in (5.8) becomes $\partial_\tau \phi_\Gamma|_{\Omega_-} = \partial_\tau \phi_\Gamma|_{\Omega_+}$ on Γ for any unit vector tangential to Γ. This is true, since $\phi_\Gamma|_{\Omega_-} = \phi_\Gamma|_{\Omega_+}$ on Γ by the continuity of ϕ_Γ; cf. the first interface condition in (5.4). Finally, by (5.9) and the fact that $\partial\Omega$ is a subset of $\partial\Omega_+$, the last equation of (5.8) with $D = D_\Gamma$ is the same as the last equation in (5.4).

Assume now $D \in [L^2(\Omega)]^3$ satisfies $D|_{\Omega_-} \in [H^2(\Omega_-)]^3$ and $D|_{\Omega_+} \in [H^2(\Omega_+)]^3$, and $D = -\varepsilon_- \nabla \phi_-$ in Ω_- for some $\phi_- \in H^1(\Omega_-)$. Assume also that D satisfies (5.8). Then by the third equation in (5.8), we have $D \in H(\mathrm{div}, \Omega)$; cf. the last part of the proof of Theorem 2.4. Moreover, $D \in V_\Gamma$ by the first equation in (5.8). It now suffices to show that D is a critical point of the strictly convex functional $J_\Gamma : V_\Gamma \to \mathbb{R} \cup \{+\infty\}$, i.e.,

$$\delta J_\Gamma[D][G] = \left.\frac{d}{dt}\right|_{t=0} J_\Gamma[D + tG] = 0 \qquad \forall G \in H(\mathrm{div}, \Omega) \text{ such that } \nabla \cdot G = 0 \text{ in } \Omega_-.$$

Fix $G \in H(\mathrm{div}, \Omega)$ with $\nabla \cdot G = 0$ in Ω_-. Suppose $\Omega_- = \cup_i \Omega_-^{(i)}$, where $\Omega_-^{(i)}$ are countably many, disjoint, connected components of Ω_-. Denote $\Gamma^{(i)} = \partial \Omega_-^{(i)}$. Hence, we have the disjoint union $\Gamma = \cup_i \Gamma^{(i)}$. For each i, $\Gamma^{(i)}$ is a connected smooth surface. Therefore, by the fourth equation in (5.8) and the relation $D \cdot \tau = -\varepsilon_- \partial_\tau \phi_-$, we have $B^{*\prime}(f - \nabla \cdot D|_{\Omega_+}) - \phi_-|_{\Omega_-} = c_i$ on $\Gamma^{(i)}$ for some constant $c_i \in \mathbb{R}$. It now follows from the second and fifth equations in (5.8), the divergence theorem, and the fact that the unit normal n points from Ω_- to Ω_+ that

$$\begin{aligned}
\delta J_\Gamma[D][G] &= \int_{\Omega_-} \frac{D \cdot G}{\varepsilon_-}\, dx + \int_{\Omega_+} \left[\frac{D \cdot G}{\varepsilon_+} + B^{*\prime}(f - \nabla \cdot D)(-\nabla \cdot G) \right] dx + \int_{\partial\Omega} g G \cdot n \, dS \\
&= -\int_{\Omega_-} \nabla \phi_- \cdot G \, dx + \int_{\Omega_+} \left[\frac{D}{\varepsilon_+} + \nabla \left(B^{*\prime}(f - \nabla \cdot D) \right) \right] \cdot G \, dx \\
&\quad + \int_\Gamma B^{*\prime}(f - \nabla \cdot D|_{\Omega_+})(G \cdot n)\, dS + \int_{\partial\Omega} \left[g - B^{*\prime}(f - \nabla \cdot D) \right] G \cdot n \, dS \\
&= -\sum_i \int_{\Omega_-^{(i)}} \nabla(\phi_- + c_i) \cdot G \, dx + \int_\Gamma B^{*\prime}(f - \nabla \cdot D|_{\Omega_+})(G \cdot n)\, dS \\
&= \sum_i \int_{\Gamma^{(i)}} \left[B^{*\prime}(f - \nabla \cdot D|_{\Omega_+}) - (\phi_-|_{\Omega_-} + c_i) \right] (G \cdot n)\, dS \\
&= 0.
\end{aligned}$$

This completes the proof. ∎

6. Conclusions. A commonly used electrostatic free-energy functional of electrostatic potential is concave downward and its critical point is the maximizer of such a functional. Maggs [31] proposed a Legendre transformed functional of electrostatic displacements. This new functional is convex and is therefore minimized at the critical point. Here, we first present a rigorous proof of the equivalence of these two functionals. We then generalize this approach to several cases, including the case with a higher-order gradient term and that without ions, to establish the related variational principles. We finally apply this approach to the dielectric boundary model of molecular solvation.

Potentially, a Legendre transformed functional can be coupled with other energy functionals to minimize consistently the total energy. For example, in a continuum model of molecular solvation, the electrostatic free energy with a dielectric boundary is often coupled with the surface energy of such a boundary. In such a situation, using the Legendre transformed electrostatic free-energy functional of dielectric displacements can be advantageous, as each part of the total energy is to be minimized. A practical issue in using a Legendre transformed electrostatic free-energy functional is to find the Legendre transform B^* of B. Only for a special case (1:1 salt), the explicit form of B^* seems to be available [31]. In general, the function B^* can be numerically determined and tabulated. A disadvantage of using a Legendre transformed functional is that the corresponding Euler–Lagrange equation is more complicated, particularly for the case of the functional with a higher-order gradient term. Further work is therefore needed to demonstrate how the new forms of electrostatic free-energy functionals are both theoretically and practically useful.

Our main contributions here are twofold. One is to provide some mathematical insight into the Legendre transformed electrostatic free-energy functional in various situations. The other is to apply this framework to the solvation of charged molecules. This includes the construction of a new Legendre transformed electrostatic free-energy functional for the molecular electrostatics with a dielectric boundary and the derivation of a set of interface conditions for the equilibrium electrostatic displacement. Our follow-up work will be to develop numerical methods for molecular solvation with our newly constructed Legendre transformed electrostatic free-energy functional.

Acknowledgment. The second author thanks Dr. Anthony Maggs for helpful discussions on the Legendre transformed electrostatic free-energy functional, Dr. Martin Bazant for bringing to his attention the papers [3, 4], and Dr. Yongcheng Zhou for a brief discussion on the form of electrostatic energy functionals in the case without ions. The authors also thank the anonymous referees for their critical reviews and helpful suggestions.

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