

ION TRANSPORT IN DIPOLAR MEDIUM I: A LOCAL DIELECTRIC POISSON–NERNST–PLANCK/POISSON–BOLTZMANN MODEL*

SHENG GUI[†], BENZHUO LU[‡], AND WEILIN YU[§]

Abstract. In this paper, an energetic variational method is employed to derive a set of ion transportation and electrostatic models of general electrolyte solution with a locally and mathematically rigorously determined dielectric permittivity of the dipolar solvent under certain assumptions. The model could be called the local dielectric Poisson–Nernst–Planck (LDPNP)/Poisson–Boltzmann (LDPB) model, which couples the Poisson–Nernst–Planck and Poisson–Boltzmann equations with a novel moment equation of dipolar molecules. A feature of this new model is that the system consistently determines the dipole moment distribution, thereby the local dielectric permittivity of the ionic aqueous solution, whereas this information is lacking and a constant assumption is usually adopted for the dielectric permittivity in traditional PNP simulations. We investigate the energy dissipation law of the derived LDPNP equations. For a planar bounded radially symmetric domain, we prove the existence and uniqueness of the equilibrium solution of LDPNP equations.

Key words. dipolar media, local dielectric Poisson–Nernst–Planck (LDPNP) model, local dielectric Poisson–Boltzmann (LDPB) model

MSC codes. 35J, 35Q, 49S, 82D, 92C

DOI. 10.1137/24M1633959

1. Introduction. The Poisson–Boltzmann (PB) equation and Poisson–Nernst–Planck (PNP) equations are two commonly used PDE models in the electrolyte solution system. The PB equation serves as a physically reasonable and efficient mathematical description of the equilibrium state of the electrolyte solution [2, 13, 14, 15, 19]. It models the electrostatic interactions involving charged solutes, mobile ions, and a polarized solvent which influences the stability and dynamics of biological molecules in aqueous solutions [13, 26, 30, 35, 36]. In a nonequilibrium state (i.e., unbalanced ionic flow exists), the PNP model, which couples the electrostatic potential equation with convection–diffusion equations, describes the electrodiffusion process of ions in an electrolyte solution. It has been widely used in the biological ion channel [25, 28, 31] and nanopore systems [10, 12, 52]. In both models, a basic hypothesis is that the background solute and solvent molecules can be treated as dielectric media characterized by their dielectric permittivity. Though the dielectric permittivity in electrolytes was often assumed as constant or piecewise constant in many electrostatic modelings,

*Received by the editors January 24, 2024; accepted for publication (in revised form) July 9, 2024; published electronically October 9, 2024.

<https://doi.org/10.1137/24M1633959>

Funding: The work of the first and second authors was supported by the Strategic Priority Research Program of Chinese Academy of Sciences through grant XDB0500000 and by the National Natural Science Foundation of China through grants 12371413 and 22073110. The work of the third author was supported by the China Postdoctoral Science Foundation through grant 2023M730333.

[†]LSEC, NCMIS, Academy of Mathematics and Systems Science, Chinese Academy of Sciences, Beijing 100190, China, and School of Mathematical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China (shenggui@lsec.cc.ac.cn).

[‡]Corresponding author. LSEC, NCMIS, Academy of Mathematics and Systems Science, Chinese Academy of Sciences, Beijing 100190, China, and School of Mathematical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China (bzlu@lsec.cc.ac.cn).

[§]Corresponding author. School of Mathematics and Statistics, and Jiangxi Provincial Center for Applied Mathematics, Jiangxi Normal University, Nanchang, Jiangxi 330022, China (weilinyu@amss.ac.cn).

such as in PB/PNP calculations, it is usually not a constant and has a complicated dependence on the density of surface/interface charge, domain geometry, and the ionic strength of the solution [22, 24, 29, 30, 38].

Dielectric decrement, referring to the reduction in the dielectric constant (or permittivity) of a solution, is a general phenomenon observed in electrolytes which results from the ordering of the polarized water due to the presence of ions or polar molecules in a solution (see Figure 1). A number of experimental and numerical measurements have confirmed that the dielectric properties of the fluid close to interfaces drastically differ from the bulk properties [6, 16, 46]. The low dielectric region can reach distances of a few nanometers from the interface (such as water-membrane, water-protein interfaces and others), which is independent of the sign of the surface charges [11]. This phenomenon is significant in various contexts, including electrochemical processes, biological systems, and transport phenomena. For instance, the low dielectric permittivity of water at the membrane interface affects the protonmotive force (the transmembrane difference in electrochemical potential of protons), and thereby the proton motion which drives adenosine triphosphate (ATP) synthesis in bacteria, mitochondria, and chloroplasts. Nevertheless, when simulating interfacial phenomena, using a homogeneous dielectric constant of water in calculations leads to an underestimation of the occurrence of electrostatic forces [11]. Investigations were conducted for dielectric modulation of ion transport near interfaces [3], as well as the effects on electrokinetic phenomena, including electroosmosis and electrophoresis [53]. The heterogeneity of the dielectric constant also has a significant influence on the structure of the electric double-layer region [5, 18, 23, 29, 37, 44] and charge transfer [27]. Additionally, a good understanding of the dielectric properties of a solvent is crucial for an accurate description of molecular-level studies of macromolecules [17].

As for ion channel studies, besides many factors like quantum effects [9, 45, 50], protein conformation dynamics [7, 4, 21], ion size effects [8, 33, 43], and correlation effects [34, 42, 41] to be considered, the dielectric permittivity is also an influential parameter in continuum modeling. It is not entirely clear what dielectric value should be used in continuum studies of biological ion channels. The quantity is hard to measure experimentally, with very few studies known to date [20, 40], and the complicated geometries and composition of the proteins makes this value difficult to compute analytically. A number of attempts have been made to determine the dielectric constant of liquid water [1, 39, 47], water inside an artificial narrow pore [48, 49], and water within the channel protein/pore [40].

In this paper, we consider diffusion and migration of positively and negatively charged particles in a general electrolyte solution (not limited to ion channel) with a dipolar medium. This work aims to present a general model to calculate the heterogeneous dielectric coefficient in electrolytes (not limited to ion channel systems) that is locally determined by an interplay of dipole distribution, surrounding charges, electric fields, and domain geometry. A particularly interesting case of this work is to consider the situation that the dielectric coefficient is dependent on ionic concentration and polarization of water molecules. The general free energy functional includes additional energy terms of the interaction between dipole and electric field. The variational approach is employed to derive the local dielectric PNP (LDPNP)/PB (LDPB) equations in dipolar medium under boundary conditions.

The dielectric permittivity ϵ has complicated local dependence on the ionic densities and polarization of the media, and these quantities and relations are usually difficult to determine and experimentally measure in inhomogeneous material. The main point of this work is to treat the dielectric permittivity as a generic function

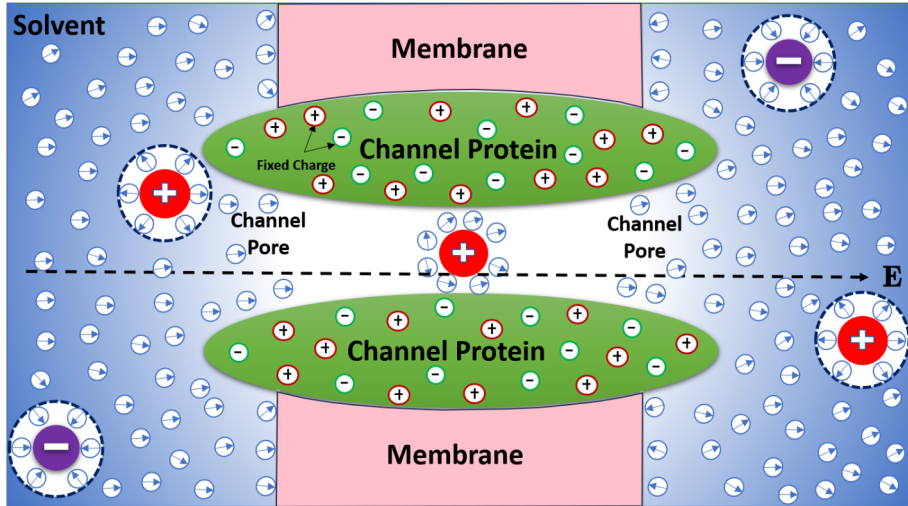


FIG. 1. A diagram of the heterogeneous dielectric implicit solvent model in an ionic solvent.

of polarization and ionic densities. The function forms were widely studied and can be seen elsewhere; for instance, the dependence of ϵ on polarization \mathbf{P} has a common physical relation, $\epsilon = (1 + \chi_e)/\epsilon_0$, where the electric susceptibility χ_e describes a proportional relation between the polarization and the strength of the electric field as $\mathbf{P} = \epsilon_0 \chi_e \mathbf{E}$, and ϵ_0 is the vacuum permittivity.

It is worth noting here that if ϵ assumes an explicitly given function of position x , $\epsilon(x)$, this is the usual treatment as in commonly used PNP/PB modeling, and is not the focus of the current work. If ϵ depends only on the ionic densities and the general free energy does not depend on the dipole effect, $\epsilon(c_i)$, this resumes our previously studied ionic density-dependent dielectric model [31]. Our LDPNP model couples the PNP equations with a dipole moment equation describing the interactions and dynamics among electrostatic potential $\phi = \phi(x, t)$, the density of the i th ion species $c_i = c_i(x, t)$, and the dipole polarization field $\mathbf{p} = \mathbf{p}(x, t)$. In the microscopic scale, there are polarized charges due to dipole polarization, $\nabla \cdot \mathbf{p}$. But in the macroscopic scale we still regard a water molecule as an electrically neutral particle, and hence in Gauss's law the field sources are all the ions, which implies that the electrostatic potential ϕ is formed only by all ions and the boundary layers.

We organize the rest of the paper as follows: In section 2, we give a complete free energy functional with dipole moment. In section 3, we derive the first variations of the free energy functional, the generalized Boltzmann distributions, the LDPB model, and the LDPNP model. Furthermore, we prove the energy dissipation law of the LDPNP model, and the existence and uniqueness of the solution for the stationary LDPNP model. Finally, in section 4, we draw our conclusions.

2. The mean field free energy functional. In this section, we will derive the free energy functional with dipole moment. When considering charged ions in a water medium in a domain $\Omega \subset \mathbb{R}^N$, $N = 2, 3$, and the dielectric permittivity ϵ local dependence on the ionic densities, the Gibbs free energy of the charged system is usually written as

$$(2.1) \quad F[c] = \int_{\Omega} \frac{1}{2} \rho(c) \phi(c) dV + \beta^{-1} \sum_{i=1}^K \int_{\Omega} c_i [\log(\Lambda^3 c_i) - 1] dV - \sum_{i=1}^K \int_{\Omega} \mu_i c_i dV.$$

Here, ρ is the total charge density, K is the number of diffusive ion species in the solution that are considered in the system, $\phi = \phi(c)$ is the electrostatic potential with $c = (c_1, \dots, c_K)$, c_i is the concentration for the i th ionic species, $\beta = 1/k_B T$ is inverse Boltzmann energy, where k_B is the Boltzmann constant and T the temperature, Λ is the thermal de Broglie wavelength, and μ_i is the chemical potential of the i th ion species. The classical PB equation and PNP equations can be derived by the variational method from this energy form [32, 51].

However, this free energy is not complete. When a potential is given on a boundary, this means (1) if the boundary is a physical boundary identified as a certain type of material interfaces, there must be a mount of “effective” surface charges $\sigma_D^{\text{eff}} = -\epsilon \frac{\partial \phi}{\partial n}$, which then causes an additional surface interaction energy $-\frac{1}{2} \epsilon \frac{\partial \phi}{\partial n} \phi$; (2) the boundary is artificial, and the influence can be approximated by “effective” surface charges $\sigma_D^{\text{eff}} = -\epsilon \frac{\partial \phi}{\partial n}$, which leads to a similar energy term. Based on these two observations, Liu, Qiao, and Lu [31] put forward a complete free energy functional form for the Dirichlet boundary condition:

$$(2.2) \quad F[c] = \int_{\Omega} \frac{1}{2} \rho(c) \phi(c) dV - \int_{\partial\Omega} \frac{1}{2} \epsilon(c) \frac{\partial \phi(c)}{\partial n} \phi_0 dS + \beta^{-1} \sum_{i=1}^K \int_{\Omega} c_i [\log(\Lambda^3 c_i) - 1] dV - \sum_{i=1}^K \int_{\Omega} \mu_i c_i dV.$$

Using this energy form, they derive a generalized self-consistent PB equation/PNP equations.

In the present paper, we further add the polarization effect to this system, in which the dielectric permittivity ϵ has local dependence not only on the ionic densities, but also on the polarization of the media.

For a dipole moment $\mathbf{p} = (p_1, \dots, p_N)$ in a electric field $E = -\nabla \phi$, the total energy includes two parts: one is the electric potential energy of the outside electric field E given by $U_1 = -\mathbf{p} \cdot E = \mathbf{p} \cdot \nabla \phi$, and the other is the electric potential energy given by $U_2 = -\frac{k^* q_1 q_2}{l} = \frac{k^* |\mathbf{p}|^2}{l^3}$ where k^* is Coulomb’s constant, $l = |\mathbf{d}|$ is the length of a dipole, and \mathbf{d} is the vector that represents a dipole (see Figure 2). Therefore, we present the free energy functional as follows:

$$(2.3) \quad F[a] = \int_{\Omega} \frac{1}{2} \rho(c) \phi(a) dV - \int_{\partial\Omega} \frac{1}{2} \epsilon(a) \frac{\partial \phi(a)}{\partial n} \phi_0 dS + \beta^{-1} \sum_{i=1}^K \int_{\Omega} c_i [\log(\Lambda^3 c_i) - 1] dV - \sum_{i=1}^K \int_{\Omega} \mu_i c_i dV + \int_{\Omega} \rho_{\omega} \mathbf{p} \cdot \nabla \phi(a) dV + \int_{\Omega} \frac{k^*}{l^3} \rho_{\omega} |\mathbf{p}|^2 dV,$$

where the electrostatic potential $\phi(a)$ satisfies the Poisson equation:

$$(2.4) \quad \begin{cases} -\nabla \cdot (\epsilon(a) \nabla \phi(a)) = \rho(c) & \text{in } \Omega, \\ \phi(a) = \phi_0 & \text{on } \partial\Omega. \end{cases}$$

Here, $a = (c_1, \dots, c_K; p_1, \dots, p_N)$, $c = (c_1, \dots, c_K)$, c_i is the density of i th ion species, $\beta = 1/K_B T$ is inverse Boltzmann energy, Λ is thermal de Broglie wavelength, μ_i is

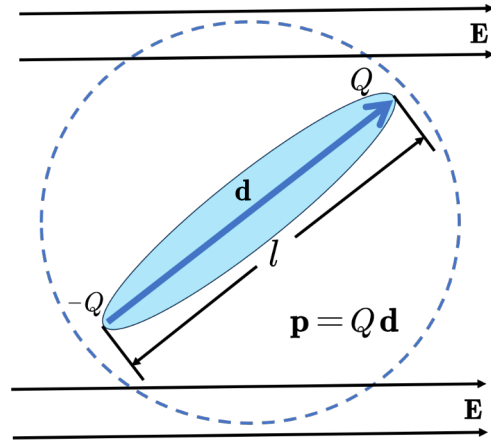


FIG. 2. A diagram of the dipole in the external electric field.

the chemical potential of the i th ion species, ρ_w is the number density of water, and $\rho = \rho(c)$ is the total charge density, defined by

$$\rho(c) = \sum_{i=1}^K q_i c_i, \quad q_i = z_i e, \quad i = 1, \dots, K,$$

where z_i is the valence of the i th species and e is the charge of one electron. In (2.3), The first two terms together represent the electrostatic potential energies, and the second term is the boundary interaction. The third term represents the ideal-gas entropy, and the fourth term represents the chemical potential of the system that results from the constraint of the total number of ions in each species. The last two terms represent the total energy of dipoles.

3. Energetic variational approach. In this section, we will use the energetic variational approach from the energy functional form (2.3) to derive LDPNP/LDPB models. For this purpose, we need the following basic assumptions:

(i) $a \in \mathbb{X}$, where

$$\mathbb{X} = \{a = (c_1, \dots, c_K, p_1, \dots, p_N) : c_i > 0, c_i \in W^{1,\infty}(\Omega), p_i \in L^2(\Omega) \cap W^{1,\infty}(\Omega)\}.$$

(ii) The dielectric coefficient function $\epsilon(a) \in C^1(\overline{\mathbb{R}}_+^{K+N}, \mathbb{R})$. Moreover, there are two positive numbers ϵ_{\min} and ϵ_{\max} such that

$$0 < \epsilon_{\min} \leq \epsilon(a) \leq \epsilon_{\max} \quad \forall a \in \mathbb{X},$$

where $\overline{\mathbb{R}}_+ = [0, \infty)$.

(iii) The boundary electrostatic potential ϕ_0 belongs to $H^{\frac{3}{2}}(\partial\Omega)$.

Before deriving the first variation of F with respect to a , we state the following results for Poisson equation (2.4).

THEOREM 3.1. *Poisson equation (2.4) has a unique solution $\phi = \phi(a) \in H^2(\Omega)$. Moreover, by the trace theorem, $\phi(a) \in H^{\frac{3}{2}}(\partial\Omega)$.*

Proof. Let us decompose $\phi(a)$ as follows:

$$\phi(a) = \phi_1(a) + \phi_2(a),$$

where $\phi_1(a)$ satisfies

$$(3.1) \quad \begin{cases} -\nabla \cdot (\epsilon(a)\nabla\phi_1(a)) = 0 & \text{in } \Omega, \\ \phi_1(a) = \phi_0 & \text{on } \partial\Omega, \end{cases}$$

and $\phi_2(a)$ satisfies

$$(3.2) \quad \begin{cases} -\nabla \cdot (\epsilon(a)\nabla\phi_2(a)) = \rho(c) & \text{in } \Omega, \\ \phi_2(a) = 0 & \text{on } \partial\Omega. \end{cases}$$

It is well known that for $\phi_0 \in H^{\frac{3}{2}}(\partial\Omega)$, there exists a unique harmonic function $\phi_{1,1} \in H^2(\Omega)$, such that $\phi_{1,1} = \phi_0$ on $\partial\Omega$. If we take $\phi_1(a) = \phi_{1,1} + \phi_{1,2}(a)$, then $\phi_{1,2}(a)$ satisfies

$$(3.3) \quad \begin{cases} -\nabla \cdot (\epsilon(a)\nabla\phi_{1,2}(a)) = \sum_{i=1}^K \frac{\partial\epsilon(a)}{\partial c_i} (\nabla c_i \cdot \nabla\phi_{1,1}) + \sum_{i=1}^N \frac{\partial\epsilon(a)}{\partial p_i} (\nabla p_i \cdot \nabla\phi_{1,1}) & \text{in } \Omega, \\ \phi_{1,2}(a) = 0 & \text{on } \partial\Omega. \end{cases}$$

Define the bilinear form

$$B(u, v) = \int_{\Omega} \epsilon(a)\nabla u \cdot \nabla v \, dV \quad \forall u, v \in H_0^1(\Omega).$$

It follows from assumption (ii) that B is a bounded, coercive bilinear form. Since $a \in \mathbb{X}$ and $\phi_{1,1} \in H^2(\Omega)$, by our assumption (ii) again, the right-hand side of (3.3) belongs to $L^2(\Omega)$ and hence $H^{-1}(\Omega)$. Using the Lax–Milgram theorem, (3.3) has a unique solution $\phi_{1,2}(a)$ in $H_0^1(\Omega)$. Using the elliptic regularity theorem, $\phi_{1,2}(a) \in H^2(\Omega)$. As a result, (3.1) has a unique solution $\phi_1(a) \in H^2(\Omega)$.

Since $a \in \mathbb{X}$, we have $\rho(c) \in H^{-1}(\Omega)$. Using the Lax–Milgram theorem again, (3.2) also has a unique solution $\phi_2(a)$ in $H_0^1(\Omega)$. The elliptic regularity theorem implies that $\phi_2(a) \in H^2(\Omega)$.

Hence, we have proved that the boundary-value problem of Poisson equation (2.4) has a unique solution $\phi = \phi(a) \in H^2(\Omega)$. \square

Based on Theorem 3.1, the complete free energy (2.3) is well-defined. We now begin to calculate the first variation of F with respect to a .

3.1. First variations. Let $a = (c_1, \dots, c_K, p_1, \dots, p_N) \in \mathbb{X}$ and $\bar{a} = (\bar{c}_1, \dots, \bar{c}_K, \bar{p}_1, \dots, \bar{p}_N) \in X$. We define the Gateaux derivative by

$$(3.4) \quad \delta F[a][\bar{a}] = \lim_{t \rightarrow 0} \frac{F[a + t\bar{a}] - F[a]}{t}.$$

To get the expression of $\delta F[a][\bar{a}]$, some lemmas are needed.

For $t \in \mathbb{R}$ and $t \neq 0$, we define

$$(3.5) \quad \Phi_t[a][\bar{a}] = \frac{\phi(a + t\bar{a}) - \phi(a)}{t}.$$

Then we can state the first lemma.

LEMMA 3.2. *We have $\Phi_t[a][\bar{a}] \in H_0^1(\Omega)$. As $t \rightarrow 0$,*

$$(3.6) \quad \|\Phi_t[a][\bar{a}]\|_{H^1(\Omega)} \leq C.$$

As a consequence,

$$(3.7) \quad \phi(a + t\bar{a}) \rightarrow \phi(a) \quad \text{strongly in } H^1(\Omega) \text{ as } t \rightarrow 0.$$

Proof. Since $\phi(a)$ solves (2.4) and $\phi(a + t\bar{a})$ is a solution of

$$(3.8) \quad \begin{cases} -\nabla \cdot (\epsilon(a + t\bar{a}) \nabla \phi(a + t\bar{a})) = \rho(c + t\bar{c}) & \text{in } \Omega, \\ \phi(a + t\bar{a}) = \phi_0 & \text{on } \partial\Omega, \end{cases}$$

we have $\phi(a + t\bar{a}) - \phi(a) \in H_0^1(\Omega)$ (hence $\Phi_t[a][\bar{a}] \in H_0^1(\Omega)$) and

$$(3.9) \quad \begin{aligned} & -\nabla \cdot (\epsilon(a) \nabla (\phi(a + t\bar{a}) - \phi(a))) \\ & = \rho(c + t\bar{c}) - \rho(c) + \nabla \cdot ((\epsilon(a + t\bar{a}) - \epsilon(a)) \nabla \phi(a + t\bar{a})) \quad \text{in } \Omega. \end{aligned}$$

Testing $\phi(a + t\bar{a}) - \phi(a)$ to (3.9) and the integral in Ω , we get

$$(3.10) \quad \begin{aligned} & \int_{\Omega} \epsilon(a) |\nabla (\phi(a + t\bar{a}) - \phi(a))|^2 dV \\ & = \int_{\Omega} (\rho(c + t\bar{c}) - \rho(c)) (\phi(a + t\bar{a}) - \phi(a)) dV \\ & \quad + \int_{\Omega} (\epsilon(a + t\bar{a}) - \epsilon(a)) \nabla \phi(a + t\bar{a}) \cdot \nabla (\phi(a + t\bar{a}) - \phi(a)) dV. \end{aligned}$$

Since $\phi(a + t\bar{a}) - \phi(a) \in H_0^1(\Omega)$, by the Poincaré inequality we have

$$(3.11) \quad \|\phi(a + t\bar{a}) - \phi(a)\|_{L^2(\Omega)} \leq C \|\nabla (\phi(a + t\bar{a}) - \phi(a))\|_{L^2(\Omega)}.$$

Then the first term on the right-hand side of (3.10) has the following estimate:

$$\begin{aligned} \int_{\Omega} (\rho(c + t\bar{c}) - \rho(c)) (\phi(a + t\bar{a}) - \phi(a)) dV &= \sum_{i=1}^K q_i t \int_{\Omega} \bar{c}_i (\phi(a + t\bar{a}) - \phi(a)) dV \\ &\leq C |t| \|\phi(a + t\bar{a}) - \phi(a)\|_{L^2(\Omega)} \\ &\leq C |t| \|\nabla (\phi(a + t\bar{a}) - \phi(a))\|_{L^2(\Omega)}. \end{aligned}$$

On the other hand, fixing $\delta > 0$, for any $|t| < \delta$, $\|\nabla \phi(a + t\bar{a})\|_{L^2(\Omega)} \leq C$ via the elliptic regularity theory. Thus, the second term on the right-hand side of (3.10) has the estimate

$$\begin{aligned} & \int_{\Omega} (\epsilon(a + t\bar{a}) - \epsilon(a)) \nabla \phi(a + t\bar{a}) \cdot \nabla (\phi(a + t\bar{a}) - \phi(a)) dV \\ &= \int_{\Omega} \left(\sum_{i=1}^K \frac{\partial \epsilon(a + st\bar{a})}{\partial c_i} t \bar{c}_i + \sum_{i=1}^N \frac{\partial \epsilon(a + st\bar{a})}{\partial p_i} t \bar{p}_i \right) \nabla \phi(a + t\bar{a}) \cdot \nabla (\phi(a + t\bar{a}) - \phi(a)) dV \\ &\leq C |t| \|\nabla (\phi(a + t\bar{a}) - \phi(a))\|_{L^2(\Omega)}, \end{aligned}$$

where $0 \leq s \leq 1$.

Hence, we obtain that

$$\begin{aligned} \epsilon_{\min} \int_{\Omega} |\nabla (\phi(a + t\bar{a}) - \phi(a))|^2 dV &\leq \int_{\Omega} \epsilon(a) |\nabla (\phi(a + t\bar{a}) - \phi(a))|^2 dV \\ &\leq C |t| \|\nabla (\phi(a + t\bar{a}) - \phi(a))\|_{L^2(\Omega)}, \end{aligned}$$

which gives

$$(3.12) \quad \|\nabla (\phi(a + t\bar{a}) - \phi(a))\|_{L^2(\Omega)} \leq C |t|.$$

The conclusion (3.6) follows from (3.11) and (3.12). \square

Furthermore, we have the following.

LEMMA 3.3. As $t \rightarrow 0$,

$$(3.13) \quad \Phi_t[a][\bar{a}] \rightarrow v_0 \quad \text{strongly in } H_0^1(\Omega),$$

where v_0 is a solution of

$$(3.14) \quad \begin{cases} -\nabla \cdot (\epsilon(a)\nabla v_0) = \sum_{i=1}^K q_i \bar{c}_i + \nabla \cdot \left(\left(\sum_{i=1}^K \frac{\partial \epsilon(a)}{\partial c_i} \bar{c}_i + \sum_{i=1}^N \frac{\partial \epsilon(a)}{\partial p_i} \bar{p}_i \right) \nabla \phi(a) \right) & \text{in } \Omega, \\ v_0 = 0 & \text{on } \partial\Omega. \end{cases}$$

Proof. Note that $\Phi_t[a][\bar{a}] \in H_0^1(\Omega)$ satisfies

$$(3.15) \quad -\nabla \cdot (\epsilon(a)\nabla \Phi_t[a][\bar{a}]) = \sum_{i=1}^K q_i \bar{c}_i + \nabla \cdot \left(\frac{\epsilon(a + t\bar{a}) - \epsilon(a)}{t} \nabla \phi(a + t\bar{a}) \right) \quad \text{in } \Omega.$$

By Lemma 3.2, $\Phi_t[a][\bar{a}]$ is bounded in $H_0^1(\Omega)$. So there exists $v_0 \in H_0^1(\Omega)$ such that

$$\Phi_t[a][\bar{a}] \rightarrow v_0 \quad \text{weakly in } H_0^1(\Omega) \text{ as } t \rightarrow 0.$$

By letting $t \rightarrow 0$ in (3.15), we have

$$-\nabla \cdot (\epsilon(a)\nabla v_0) = \sum_{i=1}^K q_i \bar{c}_i + \nabla \cdot \left(\left(\sum_{i=1}^K \frac{\partial \epsilon(a)}{\partial c_i} \bar{c}_i + \sum_{i=1}^N \frac{\partial \epsilon(a)}{\partial p_i} \bar{p}_i \right) \nabla \phi(a) \right) \text{ in } \Omega,$$

which, together with (3.15), gives

$$(3.16) \quad \begin{aligned} & -\nabla \cdot (\epsilon(a)\nabla(\Phi_t[a][\bar{a}] - v_0)) \\ &= \nabla \cdot \left(\frac{\epsilon(a + t\bar{a}) - \epsilon(a)}{t} \nabla \phi(a + t\bar{a}) - \left(\sum_{i=1}^K \frac{\partial \epsilon(a)}{\partial c_i} \bar{c}_i + \sum_{i=1}^N \frac{\partial \epsilon(a)}{\partial p_i} \bar{p}_i \right) \nabla \phi(a) \right) \quad \text{in } \Omega. \end{aligned}$$

Testing $\Phi_t[a][\bar{a}] - v_0$ to (3.16) and the integral in Ω , we get from assumption (ii) and Lemma 3.2 that

$$\begin{aligned} & \int_{\Omega} \epsilon(a) |\nabla(\Phi_t[a][\bar{a}] - v_0)|^2 dV \\ &= - \int_{\Omega} \frac{\epsilon(a + t\bar{a}) - \epsilon(a)}{t} \nabla \phi(a + t\bar{a}) \cdot \nabla(\Phi_t[a][\bar{a}] - v_0) dV \\ & \quad + \int_{\Omega} \left(\sum_{i=1}^K \frac{\partial \epsilon(a)}{\partial c_i} \bar{c}_i + \sum_{i=1}^N \frac{\partial \epsilon(a)}{\partial p_i} \bar{p}_i \right) \nabla \phi(a) \cdot \nabla(\Phi_t[a][\bar{a}] - v_0) dV \\ &= - \int_{\Omega} \left(\sum_{i=1}^K \frac{\partial \epsilon(a + st\bar{a})}{\partial c_i} \bar{c}_i + \sum_{i=1}^N \frac{\partial \epsilon(a + st\bar{a})}{\partial p_i} \bar{p}_i \right) \nabla \phi(a + t\bar{a}) \cdot \nabla(\Phi_t[a][\bar{a}] - v_0) dV \end{aligned}$$

$$\begin{aligned}
& + \int_{\Omega} \left(\sum_{i=1}^K \frac{\partial \epsilon(a)}{\partial c_i} \bar{c}_i + \sum_{i=1}^N \frac{\partial \epsilon(a)}{\partial p_i} \bar{p}_i \right) \nabla \phi(a) \cdot \nabla (\Phi_t[a][\bar{a}] - v_0) dV \\
= & - \int_{\Omega} \sum_{i=1}^K \left(\frac{\partial \epsilon(a + st\bar{a})}{\partial c_i} - \frac{\partial \epsilon(a)}{\partial c_i} \right) \bar{c}_i \nabla \phi(a + t\bar{a}) \cdot \nabla (\Phi_t[a][\bar{a}] - v_0) dV \\
& - \int_{\Omega} \sum_{i=1}^K \frac{\partial \epsilon(a)}{\partial c_i} \bar{c}_i \nabla (\phi(a + t\bar{a}) - \phi(a)) \cdot \nabla (\Phi_t[a][\bar{a}] - v_0) dV \\
& - \int_{\Omega} \sum_{i=1}^N \left(\frac{\partial \epsilon(a + st\bar{a})}{\partial p_i} - \frac{\partial \epsilon(a)}{\partial p_i} \right) \bar{p}_i \nabla \phi(a + t\bar{a}) \cdot \nabla (\Phi_t[a][\bar{a}] - v_0) dV \\
& - \int_{\Omega} \sum_{i=1}^N \frac{\partial \epsilon(a)}{\partial p_i} \bar{p}_i \nabla (\phi(a + t\bar{a}) - \phi(a)) \cdot \nabla (\Phi_t[a][\bar{a}] - v_0) dV \\
(3.17) \quad & \leq o_t(1) \|\nabla(\Phi_t[a][\bar{a}] - v_0)\|_{L^2(\Omega)},
\end{aligned}$$

where $o_t(1)$ denotes that $o_t(1) \rightarrow 0$ as $t \rightarrow 0$. Since $\epsilon(a) \geq \epsilon_{\min} > 0$, we finally obtain that

$$(3.18) \quad \|\nabla(\Phi_t[a][\bar{a}] - v_0)\|_{L^2(\Omega)} \leq o_t(1).$$

It follows from the Poincaré inequality that

$$(3.19) \quad \|\Phi_t[a][\bar{a}] - v_0\|_{L^2(\Omega)} \leq o_t(1).$$

We complete the proof. \square

Let $G_{\epsilon(a)}(y, x)$ be the Green's function for $-\nabla(\epsilon(a)\nabla)$ in Ω , such that

$$\begin{cases} -\nabla_y \cdot (\epsilon(a)\nabla_y G_{\epsilon(a)}(y, x)) = \delta(y - x) & \text{in } \Omega, \\ G_{\epsilon(a)}(y, x) = 0 & \text{on } \partial\Omega, \end{cases}$$

where δ is the Dirac function. Then $G_{\epsilon(a)}(y, x)$ has the form

$$G_{\epsilon(a)}(y, x) = G(y, x) + R_{\epsilon(a)}(y, x),$$

where $G(y, x)$ is the Green's function for $-\Delta$ in Ω with zero boundary condition and $R_{\epsilon(a)}(y, x)$ is a correction term. Using the Green's function $G_{\epsilon(a)}(y, x)$, we can represent v_0 as follows:

$$(3.20) \quad v_0(x) = \int_{\Omega} G_{\epsilon(a)}(y, x) \left[\sum_{i=1}^K q_i \bar{c}_i + \nabla \cdot \left(\left(\sum_{i=1}^K \frac{\partial \epsilon(a)}{\partial c_i} \bar{c}_i + \sum_{i=1}^N \frac{\partial \epsilon(a)}{\partial p_i} \bar{p}_i \right) \nabla \phi(a) \right) \right] (y) dy.$$

Based on the above discussions, we are ready to calculate $\delta F[a][\bar{a}]$. Let us decompose the free energy F as

$$F[a] = F_{\text{pot}}[a] + F_{\text{entropy}}[c] + F_{\text{dipole}}[a],$$

where

$$(3.21) \quad F_{\text{pot}}[a] = \int_{\Omega} \frac{1}{2} \rho(c) \phi(a) dV - \int_{\partial\Omega} \frac{1}{2} \epsilon(a) \frac{\partial\phi(a)}{\partial n} \phi_0 dS,$$

$$(3.22) \quad F_{\text{entropy}}[c] = \sum_{i=1}^K \int_{\Omega} \{ \beta^{-1} c_i [\log(\Lambda^3 c_i) - 1] - \mu_i c_i \} dV,$$

$$(3.23) \quad F_{\text{dipole}}[a] = \int_{\Omega} \rho_{\omega} \mathbf{p} \cdot \nabla \phi(a) dV + \int_{\Omega} \frac{k^*}{l^3} \rho_{\omega} |\mathbf{p}|^2 dV.$$

By the definition of (3.4), we have

$$(3.24) \quad \delta F_{\text{entropy}}[c][\bar{c}] = \lim_{t \rightarrow 0} \frac{F_{\text{entropy}}[c + t\bar{c}] - F_{\text{entropy}}[c]}{t} = \sum_{i=1}^K \int_{\Omega} \bar{c}_i [\beta^{-1} \log(\Lambda^3 c_i) - \mu_i] dV.$$

We now deal with the derivative of electrostatic potential energy. Clearly,

$$(3.25) \quad \begin{aligned} \delta F_{\text{pot}}[a][\bar{a}] &= \lim_{t \rightarrow 0} \frac{F_{\text{pot}}[a + t\bar{a}] - F_{\text{pot}}[a]}{t} \\ &= \lim_{t \rightarrow 0} \frac{1}{2t} \left(\int_{\Omega} (\rho(c + t\bar{c}) - \rho(c)) \phi(a + t\bar{a}) dV + \int_{\Omega} \rho(c) (\phi(a + t\bar{a}) - \phi(a)) dV \right) \\ &\quad - \lim_{t \rightarrow 0} \frac{1}{2t} \int_{\partial\Omega} \left(\epsilon(a + t\bar{a}) \frac{\partial\phi(a + t\bar{a})}{\partial n} - \epsilon(a) \frac{\partial\phi(a)}{\partial n} \right) \phi_0 dS \\ &= \lim_{t \rightarrow 0} \frac{1}{2} \sum_{i=1}^K \int_{\Omega} q_i \bar{c}_i \phi(a + t\bar{a}) dV + \lim_{t \rightarrow 0} \frac{1}{2t} \int_{\Omega} \rho(c) (\phi(a + t\bar{a}) - \phi(a)) dV \\ &\quad - \lim_{t \rightarrow 0} \frac{1}{2t} \int_{\partial\Omega} \left(\epsilon(a + t\bar{a}) \frac{\partial\phi(a + t\bar{a})}{\partial n} - \epsilon(a) \frac{\partial\phi(a)}{\partial n} \right) \phi_0 dS. \end{aligned}$$

By (3.7),

$$(3.26) \quad \lim_{t \rightarrow 0} \frac{1}{2} \sum_{i=1}^K \int_{\Omega} q_i \bar{c}_i \phi(a + t\bar{a}) dV = \frac{1}{2} \sum_{i=1}^K \int_{\Omega} q_i \bar{c}_i \phi(a) dV.$$

Since $\phi(a)$ is a solution of (2.4), we can test (2.4) by $\phi(a)$ to get that

$$(3.27) \quad \int_{\Omega} \epsilon(a) \nabla \phi(a) \cdot \nabla \phi(a) dV - \int_{\partial\Omega} \epsilon(a) \frac{\partial\phi(a)}{\partial n} \phi_0 dS = \int_{\Omega} \rho(c) \phi(a) dV.$$

Similarly, testing (3.8) by $\phi(a)$ we have

$$(3.28) \quad \int_{\Omega} \epsilon(a + t\bar{a}) \nabla \phi(a + t\bar{a}) \cdot \nabla \phi(a) dV - \int_{\partial\Omega} \epsilon(a + t\bar{a}) \frac{\partial\phi(a + t\bar{a})}{\partial n} \phi_0 dS = \int_{\Omega} \rho(c + t\bar{c}) \phi(a) dV.$$

Combining this with (3.27) and (3.28), one sees

$$\begin{aligned}
 & - \lim_{t \rightarrow 0} \frac{1}{2t} \int_{\partial\Omega} \left(\epsilon(a + t\bar{a}) \frac{\partial\phi(a + t\bar{a})}{\partial n} - \epsilon(a) \frac{\partial\phi(a)}{\partial n} \right) \phi_0 dS \\
 & = \lim_{t \rightarrow 0} \frac{1}{2t} \int_{\Omega} (\rho(c + t\bar{c}) - \rho(c)) \phi(a) dV \\
 (3.29) \quad & - \lim_{t \rightarrow 0} \frac{1}{2t} \int_{\Omega} (\epsilon(a + t\bar{a}) \nabla\phi(a + t\bar{a}) - \epsilon(a) \nabla\phi(a)) \cdot \nabla\phi(a) dV \\
 & = \frac{1}{2} \sum_{i=1}^K \int_{\Omega} q_i \bar{c}_i \phi(a) dV - \lim_{t \rightarrow 0} \frac{1}{2t} \int_{\Omega} (\epsilon(a + t\bar{a}) - \epsilon(a)) \nabla\phi(a + t\bar{a}) \cdot \nabla\phi(a) dV \\
 & - \lim_{t \rightarrow 0} \frac{1}{2t} \int_{\Omega} \epsilon(a) \nabla(\phi(a + t\bar{a}) - \phi(a)) \cdot \nabla\phi(a) dV.
 \end{aligned}$$

It follows from Lemma 3.2 that

$$\begin{aligned}
 (3.30) \quad & \lim_{t \rightarrow 0} \frac{1}{2t} \int_{\Omega} (\epsilon(a + t\bar{a}) - \epsilon(a)) \nabla\phi(a + t\bar{a}) \cdot \nabla\phi(a) dV \\
 & = \frac{1}{2} \int_{\Omega} \left(\sum_{i=1}^K \frac{\partial\epsilon(a)}{\partial c_i} \bar{c}_i + \sum_{i=1}^N \frac{\partial\epsilon(a)}{\partial p_i} \bar{p}_i \right) |\nabla\phi(a)|^2 dV.
 \end{aligned}$$

Since $\phi(a + t\bar{a}) - \phi(a) = 0$ on $\partial\Omega$, we have

$$\begin{aligned}
 (3.31) \quad & \lim_{t \rightarrow 0} \frac{1}{2t} \int_{\Omega} \epsilon(a) \nabla(\phi(a + t\bar{a}) - \phi(a)) \cdot \nabla\phi(a) dV \\
 & = \lim_{t \rightarrow 0} \frac{1}{2t} \int_{\Omega} -\nabla \cdot (\epsilon(a) \nabla\phi(a)) (\phi(a + t\bar{a}) - \phi(a)) dV \\
 & = \lim_{t \rightarrow 0} \frac{1}{2t} \int_{\Omega} \rho(c) (\phi(a + t\bar{a}) - \phi(a)) dV.
 \end{aligned}$$

Then by (3.25), (3.26), (3.29), (3.30), and (3.31), we obtain

$$\begin{aligned}
 (3.32) \quad \delta F_{\text{pot}}[a][\bar{a}] & = \sum_{i=1}^K \int_{\Omega} q_i \bar{c}_i \phi(a) dV \\
 & - \frac{1}{2} \int_{\Omega} \left(\sum_{i=1}^K \frac{\partial\epsilon(a)}{\partial c_i} \bar{c}_i + \sum_{i=1}^N \frac{\partial\epsilon(a)}{\partial p_i} \bar{p}_i \right) |\nabla\phi(a)|^2 dV.
 \end{aligned}$$

Finally, we deal with the derivative of the dipole's energy. We have

$$\begin{aligned}
 (3.33) \quad \delta F_{\text{dipole}}[a][\bar{a}] & = \lim_{t \rightarrow 0} \frac{F_{\text{dipole}}[a + t\bar{a}] - F_{\text{dipole}}[a]}{t} \\
 & = \lim_{t \rightarrow 0} \frac{1}{t} \int_{\Omega} \rho_{\omega} \mathbf{P} \cdot \nabla(\phi(a + t\bar{a}) - \phi(a)) dV \\
 & + \lim_{t \rightarrow 0} \int_{\Omega} \rho_{\omega} \bar{\mathbf{P}} \cdot \nabla\phi(a + t\bar{a}) dV \\
 & + \int_{\Omega} \frac{2k^*}{l^3} \rho_{\omega} \mathbf{P} \cdot \bar{\mathbf{P}} dV.
 \end{aligned}$$

By (3.7), we have

$$(3.34) \quad \lim_{t \rightarrow 0} \int_{\Omega} \rho_{\omega} \bar{\mathbf{P}} \cdot \nabla\phi(a + t\bar{a}) dV = \int_{\Omega} \rho_{\omega} \bar{\mathbf{P}} \cdot \nabla\phi(a) dV.$$

On the other hand, by Lemma 3.3 we have

$$\begin{aligned}
 \lim_{t \rightarrow 0} \frac{1}{t} \int_{\Omega} \rho_{\omega} \mathbf{p} \cdot \nabla (\phi(a + t\bar{a}) - \phi(a)) dV &= \lim_{t \rightarrow 0} \int_{\Omega} \rho_{\omega} \mathbf{p} \cdot \nabla \Phi_t[a][\bar{a}] \\
 (3.35) \qquad \qquad \qquad &= \int_{\Omega} \rho_{\omega} \mathbf{p} \cdot \nabla v_0 dV \\
 &= - \int_{\Omega} \rho_{\omega} (\nabla \cdot \mathbf{p}) v_0 dV.
 \end{aligned}$$

From the expansion (3.20), we obtain that

$$\begin{aligned}
 \int_{\Omega} \rho_{\omega} (\nabla \cdot \mathbf{p}) v_0 dV &= \int_{\Omega} \int_{\Omega} G_{\epsilon(a)}(y, x) [\rho_{\omega} (\nabla \cdot \mathbf{p})](x) \\
 &\quad \cdot \left[\sum_{i=1}^K q_i \bar{c}_i + \nabla \cdot \left(\left(\sum_{i=1}^K \frac{\partial \epsilon(a)}{\partial c_i} \bar{c}_i + \sum_{i=1}^N \frac{\partial \epsilon(a)}{\partial p_i} \bar{p}_i \right) \nabla \phi(a) \right) \right] (y) dx dy \\
 (3.36) \qquad \qquad \qquad &= \int_{\Omega} H_{\epsilon(a)} \left[\sum_{i=1}^K q_i \bar{c}_i + \nabla \cdot \left(\left(\sum_{i=1}^K \frac{\partial \epsilon(a)}{\partial c_i} \bar{c}_i + \sum_{i=1}^N \frac{\partial \epsilon(a)}{\partial p_i} \bar{p}_i \right) \nabla \phi(a) \right) \right] dV \\
 &= \sum_{i=1}^K \int_{\Omega} \left(q_i H_{\epsilon(a)} - \frac{\partial \epsilon(a)}{\partial c_i} \nabla \phi(a) \cdot \nabla H_{\epsilon(a)} \right) \bar{c}_i dV \\
 &\quad - \sum_{i=1}^N \int_{\Omega} \frac{\partial \epsilon(a)}{\partial p_i} (\nabla \phi(a) \cdot \nabla H_{\epsilon(a)}) \bar{p}_i dV,
 \end{aligned}$$

where

$$(3.37) \qquad \qquad \qquad H_{\epsilon(a)}(x) = \int_{\Omega} G_{\epsilon(a)}(y, x) [\rho_{\omega} (\nabla \cdot \mathbf{p})](y) dy.$$

Hence we obtain that

$$\begin{aligned}
 (3.38) \qquad \delta F_{\text{dipole}}[a][\bar{a}] &= - \sum_{i=1}^K \int_{\Omega} \left(q_i H_{\epsilon(a)} - \frac{\partial \epsilon(a)}{\partial c_i} \nabla \phi(a) \cdot \nabla H_{\epsilon(a)} \right) \bar{c}_i dV \\
 &\quad + \sum_{i=1}^N \int_{\Omega} \left(\frac{2k^*}{l^3} \rho_{\omega} p_i + \rho_{\omega} \frac{\partial \phi(a)}{\partial x_i} + \frac{\partial \epsilon(a)}{\partial p_i} (\nabla \phi(a) \cdot \nabla H_{\epsilon(a)}) \right) \bar{p}_i dV.
 \end{aligned}$$

Combining (3.24), (3.32), and (3.38), the derivative $\delta F[a][\bar{a}]$ can be stated as follows.

THEOREM 3.4. *Suppose (i)–(iii) hold and $\bar{a} \in \mathbb{X}$. Then*

$$\begin{aligned}
 (3.39) \qquad \delta F[a][\bar{a}] &= \sum_{i=1}^K \int_{\Omega} \left(q_i (\phi(a) - H_{\epsilon(a)}) - \left(\frac{1}{2} |\nabla \phi(a)|^2 - \nabla H_{\epsilon(a)} \cdot \nabla \phi(a) \right) \frac{\partial \epsilon(a)}{\partial c_i} \right. \\
 &\quad \left. + \beta^{-1} \log(\Lambda^3 c_i) - \mu_i \right) \bar{c}_i dV \\
 &\quad + \sum_{i=1}^N \int_{\Omega} \left(\frac{2k^*}{l^3} \rho_{\omega} p_i + \rho_{\omega} \frac{\partial \phi(a)}{\partial x_i} \right. \\
 &\quad \left. + \left(-\frac{1}{2} |\nabla \phi(a)|^2 + \nabla H_{\epsilon(a)} \cdot \nabla \phi(a) \right) \frac{\partial \epsilon(a)}{\partial p_i} \right) \bar{p}_i dV.
 \end{aligned}$$

That is,

$$(3.40) \quad \frac{\delta F[a]}{\delta c_i} = q_i(\phi(a) - H_{\epsilon(a)}) - \left(\frac{1}{2} |\nabla \phi(a)|^2 - \nabla H_{\epsilon(a)} \cdot \nabla \phi(a) \right) \frac{\partial \epsilon(a)}{\partial c_i} + \beta^{-1} \log(\Lambda^3 c_i) - \mu_i$$

and

$$(3.41) \quad \frac{\delta F[a]}{\delta p_i} = \frac{2k^*}{l^3} \rho_\omega p_i + \rho_\omega \frac{\partial \phi(a)}{\partial x_i} + \left(-\frac{1}{2} |\nabla \phi(a)|^2 + \nabla H_{\epsilon(a)} \cdot \nabla \phi(a) \right) \frac{\partial \epsilon(a)}{\partial p_i}.$$

From the definition of $H_{\epsilon(a)}$, we have the following remark.

Remark 3.5. The function $H_{\epsilon(a)}$ introduced in (3.37) satisfies

$$\begin{cases} -\nabla \cdot (\epsilon(a) \nabla H_{\epsilon(a)}) = \rho_\omega (\nabla \cdot \mathbf{p}) & \text{in } \Omega, \\ H_{\epsilon(a)} = 0 & \text{on } \partial\Omega. \end{cases}$$

Thus, $H_{\epsilon(a)}$ is the electrostatic potential of the dipole and its equivalent charge distribution is $\rho_\omega (\nabla \cdot \mathbf{p})$.

3.2. Generalized Boltzmann distributions with dipole moment and local dielectric Poisson–Boltzmann Model. For $a \in \mathbb{X}$, we call it an equilibrium if the first variation $\delta F[a][\bar{a}]$ exists and equals zero for any $\bar{a} \in \mathbb{X}$. If $a \in \mathbb{X}$ is an equilibrium, then $\delta F[a][\bar{a}] = 0$ for all $\bar{a} \in \mathbb{X}$, which means

$$(3.42) \quad \mu_i = q_i(\phi(a) - H_{\epsilon(a)}) - \left(\frac{1}{2} |\nabla \phi(a)|^2 - \nabla H_{\epsilon(a)} \cdot \nabla \phi(a) \right) \frac{\partial \epsilon(a)}{\partial c_i} + \beta^{-1} \log(\Lambda^3 c_i),$$

$$(3.43) \quad \frac{2k^*}{l^3} \rho_\omega p_i + \rho_\omega \frac{\partial \phi(a)}{\partial x_i} + \left(-\frac{1}{2} |\nabla \phi(a)|^2 + \nabla H_{\epsilon(a)} \cdot \nabla \phi(a) \right) \frac{\partial \epsilon(a)}{\partial p_i} = 0.$$

A straightforward calculation implies that

$$(3.44) \quad \begin{aligned} c_i &= \Lambda^{-3} e^{\beta \mu_i} \exp \left\{ \beta \left(-q_i(\phi(a) - H_{\epsilon(a)}) + \left(\frac{1}{2} |\nabla \phi(a)|^2 - \nabla H_{\epsilon(a)} \cdot \nabla \phi(a) \right) \frac{\partial \epsilon(a)}{\partial c_i} \right) \right\} \\ &= c_i^\infty \exp \left\{ \beta \left(-q_i(\phi(a) - H_{\epsilon(a)}) + \left(\frac{1}{2} |\nabla \phi(a)|^2 - \nabla H_{\epsilon(a)} \cdot \nabla \phi(a) \right) \frac{\partial \epsilon(a)}{\partial c_i} \right) \right\}, \end{aligned}$$

where as $r \rightarrow \infty$, $c_i \rightarrow c_i^\infty$ and $\phi(a) \rightarrow 0$. Compared with the classical Boltzmann distributions $c_i = c_i^\infty e^{-\beta q_i \phi}$, this is the generalized Boltzmann distributions. Plugging the generalized Boltzmann distributions (3.44) into the Poisson equation, and combining with (3.43), we then obtain an LDPB model under an arbitrary Dirichlet boundary condition:

$$(3.45) \quad \begin{aligned} -\nabla \cdot (\epsilon(a) \nabla \phi(a)) &= \sum_{i=1}^K q_i c_i^\infty e^{\beta \left(-q_i(\phi(a) - H_{\epsilon(a)}) + \left(\frac{1}{2} |\nabla \phi(a)|^2 - \nabla H_{\epsilon(a)} \cdot \nabla \phi(a) \right) \frac{\partial \epsilon(a)}{\partial c_i} \right)} & \text{in } \Omega, \\ \frac{2k^*}{l^3} \rho_\omega p_i + \rho_\omega \frac{\partial \phi(a)}{\partial x_i} + \left(-\frac{1}{2} |\nabla \phi(a)|^2 + \nabla H_{\epsilon(a)} \cdot \nabla \phi(a) \right) \frac{\partial \epsilon(a)}{\partial p_i} &= 0 & \text{in } \Omega, \\ \phi(a) &= \phi_0 & \text{on } \partial\Omega. \end{aligned}$$

3.3. Local dielectric Poisson–Nernst–Planck model. According to the constitutive relations, the flux J_i and the electrochemical potential $\tilde{\mu}_i$ of the i th species satisfy

$$J_i = -m_i c_i \nabla \tilde{\mu}_i,$$

where m_i is the ion mobility that relates to its diffusivity D_i through Einstein’s relation $D_i = \beta^{-1} m_i$, and $\tilde{\mu}_i$ is the variation of F with respect to c_i :

$$\tilde{\mu}_i = \frac{\delta F}{\delta c_i}.$$

Then the following transport equations are obtained from the mass and current conservation law:

$$\begin{aligned} \frac{\partial c_i}{\partial t} &= -\nabla \cdot J_i = \nabla \cdot (\beta D_i c_i \nabla \tilde{\mu}_i) \\ &= \nabla \cdot \left(\beta D_i c_i \nabla \left(q_i (\phi(a) - H_{\epsilon(a)}) - \left(\frac{1}{2} |\nabla \phi(a)|^2 - \nabla H_{\epsilon(a)} \cdot \nabla \phi(a) \right) \frac{\partial \epsilon(a)}{\partial c_i} \right) \right) \\ &\quad + \nabla \cdot (\beta D_i c_i \nabla (\beta^{-1} \log(\Lambda^3 c_i))) \\ &= \nabla \cdot \left(\beta D_i c_i \nabla \left(q_i (\phi(a) - H_{\epsilon(a)}) - \left(\frac{1}{2} |\nabla \phi(a)|^2 - \nabla H_{\epsilon(a)} \cdot \nabla \phi(a) \right) \frac{\partial \epsilon(a)}{\partial c_i} \right) \right) \\ &\quad + \nabla \cdot (D_i \nabla c_i). \end{aligned}$$

Next, we want to derive the equations corresponding to the dipole moment field \mathbf{p} via the conservation law of spin angular momentum. As an approximation model, we assume that the masses of positive charge q_2 and negative charge q_1 in the dipole \mathbf{p} are equal to each other, that is, $\frac{1}{2} m_w$, where m_w is the mass of a molecule of water, and they rotate around the center O of the line between the positive charge and the negative charge. Thus the spin angular momentum L of dipole \mathbf{p} is given by

$$\begin{aligned} L &= \mathbf{r}_1 \times m_1 \mathbf{v}_1 + \mathbf{r}_2 \times m_2 \mathbf{v}_2 \\ &= -\frac{1}{2} \mathbf{d} \times \frac{1}{2} m_w \frac{d}{dt} \left(-\frac{1}{2} \mathbf{d} \right) + \frac{1}{2} \mathbf{d} \times \frac{1}{2} m_w \frac{d}{dt} \left(\frac{1}{2} \mathbf{d} \right) \\ &= \frac{m_w}{4} \mathbf{d} \times \frac{d\mathbf{d}}{dt} = \frac{m_w}{16e^2} \mathbf{p} \times \frac{d\mathbf{p}}{dt}, \end{aligned}$$

where for $i = 1, 2$, \mathbf{r}_i is the vector from O to q_i , m_i is the mass of q_i , and \mathbf{v}_i is the rotation velocity of q_i .

On the other hand, for a dipole moment \mathbf{p} in an electric field E , the moment of force is given by

$$M = \mathbf{p} \times E.$$

When we consider the permittivity coefficient ϵ not depending on \mathbf{p} , the electric field $E = -\nabla \phi - \frac{2k^*}{l^3} \mathbf{p}$ and it equals $-\frac{1}{\rho_w} \nabla_{\mathbf{p}} F_{\text{dipole}}$, where $\nabla_{\mathbf{p}} = (\frac{\delta}{\delta p_1}, \dots, \frac{\delta}{\delta p_N})$. But for ϵ depending on \mathbf{p} , we amend the electric field to $-\frac{1}{\rho_w} \nabla_{\mathbf{p}} F$. So we have

$$M = -\mathbf{p} \times \frac{1}{\rho_w} \nabla_{\mathbf{p}} F[a].$$

By the conservation law of spin angular momentum, we have

$$M = \frac{dL}{dt},$$

namely,

$$\frac{m_\omega}{16e^2} \mathbf{p} \times \frac{d^2 \mathbf{p}}{dt^2} = -\frac{1}{\rho_\omega} \mathbf{p} \times \nabla_{\mathbf{p}} F[a],$$

since

$$\frac{d}{dt} \left(\mathbf{p} \times \frac{d\mathbf{p}}{dt} \right) = \frac{d\mathbf{p}}{dt} \times \frac{d\mathbf{p}}{dt} + \mathbf{p} \times \frac{d^2 \mathbf{p}}{dt^2} = \mathbf{p} \times \frac{d^2 \mathbf{p}}{dt^2}.$$

Collecting all those above equations, we get a set of generalized self-consistent LDPNP equations:

$$(3.46) \quad -\nabla \cdot (\epsilon(a) \nabla \phi(a)) = \sum_{i=1}^K q_i c_i \quad \text{in } \Omega,$$

$$(3.47) \quad \frac{\partial c_i}{\partial t} = \nabla \cdot \left(\beta D_i c_i \nabla \left(q_i (\phi(a) - H_{\epsilon(a)}) - \left(\frac{1}{2} |\nabla \phi(a)|^2 - \nabla H_{\epsilon(a)} \cdot \nabla \phi(a) \right) \frac{\partial \epsilon(a)}{\partial c_i} \right) \right) \\ + \nabla \cdot (D_i \nabla c_i) \quad \text{in } \Omega,$$

$$(3.48) \quad \mathbf{p} \times \frac{d^2 \mathbf{p}}{dt^2} = -\frac{16e^2}{m_\omega \rho_\omega} \mathbf{p} \times \left(\frac{2k^*}{l^3} \rho_\omega \mathbf{p} + \rho_\omega \nabla \phi(a) \right. \\ \left. + \left(-\frac{1}{2} |\nabla \phi(a)|^2 + \nabla H_{\epsilon(a)} \cdot \nabla \phi(a) \right) \nabla_{\mathbf{p}} \epsilon(a) \right) \quad \text{in } \Omega,$$

with the boundary conditions

$$\begin{aligned} \phi &= \phi_0 && \text{on } \partial\Omega, \\ c_i &= c_i^b && \text{on } \partial\Omega, \\ p_i &= p_i^b && \text{on } \partial\Omega, \\ J_i \cdot n &= 0 && \text{on } \partial\Omega. \end{aligned}$$

It is easy to see that (3.48) is equivalent to

$$(3.49) \quad \frac{d^2 \mathbf{p}}{dt^2} = -\gamma \mathbf{p} - \frac{16e^2}{m_\omega} \nabla \phi(a) - \frac{16e^2}{m_\omega \rho_\omega} \left(-\frac{1}{2} |\nabla \phi(a)|^2 + \nabla H_{\epsilon(a)} \cdot \nabla \phi(a) \right) \nabla_{\mathbf{p}} \epsilon(a)$$

for some function γ .

3.3.1. Energy dissipation law. In this section, we show the energy dissipation law as follows.

THEOREM 3.6 (energy dissipation law). *If (c, \mathbf{p}, ϕ) is a solution of the LDPNP equations (3.46)–(3.48) so that $|\mathbf{p}| = 2le$, then we have*

$$\frac{d}{dt} E^{\text{total}}[a] = -\sum_{i=1}^K \int_{\Omega} m_i c_i |\nabla \tilde{\mu}_i|^2 dV \leq 0,$$

where $E^{\text{total}}[a]$ is given by $E^{\text{total}}[a] := F[a] + \frac{\rho_\omega m_\omega}{32e^2} \int_{\Omega} \left| \frac{d\mathbf{p}}{dt} \right|^2 dV$.

Proof. It is clear that

$$\frac{d}{dt} F[a] = \delta F[a] \left[\frac{da}{dt} \right] = \sum_{i=1}^K \int_{\Omega} \frac{\delta F}{\delta c_i} \frac{dc_i}{dt} dV + \sum_{i=1}^N \int_{\Omega} \frac{\delta F}{\delta p_i} \frac{dp_i}{dt} dV$$

$$\begin{aligned}
 &= - \sum_{i=1}^K \int_{\Omega} \frac{\delta F}{\delta c_i} \nabla \cdot J_i dV + \sum_{i=1}^N \int_{\Omega} \frac{\delta F}{\delta p_i} \frac{dp_i}{dt} dV \\
 &= - \sum_{i=1}^K \int_{\partial\Omega} \frac{\delta F}{\delta c_i} n \cdot J_i dS + \sum_{i=1}^K \int_{\Omega} \nabla \frac{\delta F}{\delta c_i} \cdot J_i dV + \sum_{i=1}^N \int_{\Omega} \frac{\delta F}{\delta p_i} \frac{dp_i}{dt} dV \\
 &= - \sum_{i=1}^K \int_{\Omega} m_i c_i \left| \nabla \frac{\delta F}{\delta c_i} \right|^2 dV + \sum_{i=1}^N \int_{\Omega} \frac{\delta F}{\delta p_i} \frac{dp_i}{dt} dV \\
 &= - \sum_{i=1}^K \int_{\Omega} m_i c_i |\nabla \tilde{\mu}_i|^2 dV + \sum_{i=1}^N \int_{\Omega} \frac{\delta F}{\delta p_i} \frac{dp_i}{dt} dV.
 \end{aligned}$$

By (3.49), for $\gamma_1 = \gamma - \frac{32k^*e^2}{m_\omega l^3}$ we get

$$\sum_{i=1}^N \int_{\Omega} \frac{\delta F}{\delta p_i} \frac{dp_i}{dt} dV = - \frac{\rho_\omega m_\omega}{16e^2} \int_{\Omega} \left(\frac{d^2 \mathbf{p}}{dt^2} - \gamma_1 \mathbf{p} \right) \cdot \frac{d\mathbf{p}}{dt} dV = - \frac{\rho_\omega m_\omega}{32e^2} \frac{d}{dt} \int_{\Omega} \left| \frac{d\mathbf{p}}{dt} \right|^2 dV,$$

since from $|\mathbf{p}|^2 = 4l^2 e^2$ we have $\mathbf{p} \cdot \frac{d}{dt} \mathbf{p} = 0$. □

3.3.2. Analysis of stationary models. In order to demonstrate the new model of mathematical posedness, we will investigate the analysis of the stationary LDPNP model. In this section, we mainly focus on the existence of stationary LDPNP equations in a bounded domain Ω . For simplicity, we assume that $K = 2$, $q_1 = 1$, $q_2 = -1$, $\beta = 1$, $D_i = 1$, $e = 1$, $\rho_\omega = 1$, $m_\omega = 16$, and $\epsilon = \epsilon^2$, where $\epsilon > 0$ is a small constant. We also denote $\phi = \phi(a)$, $H = H_{\epsilon(a)}$. Then the stationary LDPNP system can be stated as follows:

$$(3.50) \quad -\epsilon^2 \Delta \phi = c_1 - c_2 \quad \text{in } \Omega,$$

$$(3.51) \quad \nabla \cdot (\nabla c_1 + c_1 \nabla(\phi - H)) = 0 \quad \text{in } \Omega,$$

$$(3.52) \quad \nabla \cdot (\nabla c_2 - c_2 \nabla(\phi - H)) = 0 \quad \text{in } \Omega,$$

$$(3.53) \quad \gamma \mathbf{p} + \nabla \phi = \mathbf{0} \quad \text{in } \Omega,$$

$$(3.54) \quad -\epsilon^2 \Delta H = \nabla \cdot \mathbf{p} \quad \text{in } \Omega,$$

with the boundary conditions

$$(3.55) \quad \phi = \phi_0 \quad \text{on } \partial\Omega,$$

$$(3.56) \quad H = 0 \quad \text{on } \partial\Omega,$$

$$(3.57) \quad c_i = c_i^b \quad \text{on } \partial\Omega,$$

$$(3.58) \quad p_i = p_i^b \quad \text{on } \partial\Omega,$$

$$(3.59) \quad (\nabla c_1 + c_1 \nabla(\phi - H)) \cdot n = 0 \quad \text{on } \partial\Omega,$$

$$(3.60) \quad (\nabla c_2 - c_2 \nabla(\phi - H)) \cdot n = 0 \quad \text{on } \partial\Omega.$$

Based on the mass conservation law, we may assume that

$$(3.61) \quad \int_{\Omega} c_1 dx = \alpha > 0, \quad \int_{\Omega} c_2 dx = \beta > 0.$$

THEOREM 3.7 (existence). *Let Ω be a planar bounded, radially symmetric domain. We assume that $\phi_0 = \text{constant}$ on each connected component of $\partial\Omega$. We further assume that γ is a radially symmetric function, $\gamma \in C^1(\bar{\Omega})$, and $M_1 < \gamma < +\infty$ with*

$M_1\varepsilon^2 > 1$. Then there exist boundary data c_i^b, p_i^b such that the system (3.50)–(3.54) with boundary conditions (3.55)–(3.60) and constraint (3.61) has a classical solution $(\phi, H, c_1, c_2, p_1, p_2)$, namely, $\phi, H, c_1, c_2 \in C^2(\bar{\Omega})$ and $p_1, p_2 \in C^1(\bar{\Omega})$.

We will prove Theorem 3.7 by reducing the stationary LDPNP system to an elliptic equation with Dirichlet boundary condition. Let us outline its proof.

We note that the equilibrium solution of LDPNP is

$$(3.62) \quad c_1 = \alpha \frac{e^{-(\phi-H)}}{\int_{\Omega} e^{-(\phi-H)} dx}, \quad c_2 = \beta \frac{e^{\phi-H}}{\int_{\Omega} e^{\phi-H} dx},$$

which satisfies (3.51)–(3.52), the boundary conditions (3.59)–(3.60), and the constraint (3.61). Thus, the system (3.50)–(3.54) with boundary conditions (3.55)–(3.60) and the constraint (3.61) can be reduced to the following system:

$$(3.63) \quad \begin{cases} -\varepsilon^2 \Delta \phi = \alpha \frac{e^{-(\phi-H)}}{\int_{\Omega} e^{-(\phi-H)} dx} - \beta \frac{e^{\phi-H}}{\int_{\Omega} e^{\phi-H} dx} & \text{in } \Omega, \\ \gamma \mathbf{p} + \nabla \phi = \mathbf{0} & \text{in } \Omega, \\ -\varepsilon^2 \Delta H = \nabla \cdot \mathbf{p} & \text{in } \Omega, \\ \phi = \phi_0, \quad H = 0 & \text{on } \partial\Omega. \end{cases}$$

Since $\gamma > M_1 > 0$, from the second equation of (3.63) we have

$$(3.64) \quad \mathbf{p} = -\frac{1}{\gamma} \nabla \phi.$$

Inserting it into the third equation of (3.63), one sees

$$(3.65) \quad \varepsilon^2 \Delta H = \nabla \cdot \left(\frac{1}{\gamma} \nabla \phi \right).$$

Let $u = \phi - H$. Then by (3.65) we have

$$(3.66) \quad \nabla \cdot \left(\left(\varepsilon^2 - \frac{1}{\gamma} \right) \nabla H - \frac{1}{\gamma} \nabla u \right) = 0.$$

If we want to find radial solutions ϕ, H , then there exists a radially symmetric function $f = f(r)$ with $r = |x|$ so that

$$\left(\varepsilon^2 - \frac{1}{\gamma} \right) \nabla H = \frac{1}{\gamma} \nabla u + \nabla^\perp f,$$

where $\nabla^\perp = (\partial_2, -\partial_1)$. Since $\gamma\varepsilon^2 > M_1\varepsilon^2 > 1$, we obtain that

$$(3.67) \quad \nabla H = \frac{1}{\gamma\varepsilon^2 - 1} \nabla u + \frac{\gamma}{\gamma\varepsilon^2 - 1} \nabla^\perp f.$$

As a result,

$$(3.68) \quad \Delta H = \nabla \cdot \left(\frac{1}{\gamma\varepsilon^2 - 1} \nabla u \right) + \nabla \cdot \left(\frac{\gamma}{\gamma\varepsilon^2 - 1} \nabla^\perp f \right) = \nabla \cdot \left(\frac{1}{\gamma\varepsilon^2 - 1} \nabla u \right),$$

since

$$\begin{aligned} \nabla \cdot \left(\frac{\gamma}{\gamma\varepsilon^2 - 1} \nabla^\perp f \right) &= \nabla \cdot \left(\frac{\gamma}{\gamma\varepsilon^2 - 1} \right) \cdot \nabla^\perp f + \frac{\gamma}{\gamma\varepsilon^2 - 1} \nabla \cdot \nabla^\perp f \\ &= \left(\frac{\gamma}{\gamma\varepsilon^2 - 1} \right)' (r) f'(r) \left(\frac{x_1}{r}, \frac{x_2}{r} \right) \cdot \left(\frac{x_2}{r}, -\frac{x_1}{r} \right) + \frac{\gamma}{\gamma\varepsilon^2 - 1} \nabla \cdot \nabla^\perp f \\ &= 0. \end{aligned}$$

Hence, the system (3.63) becomes

$$(3.69) \quad \begin{cases} -\varepsilon^2 \nabla \cdot \left(\frac{\gamma \varepsilon^2}{\gamma \varepsilon^2 - 1} \nabla u \right) = \alpha \frac{e^{-u}}{\int_{\Omega} e^{-u} dx} - \beta \frac{e^u}{\int_{\Omega} e^u dx} & \text{in } \Omega, \\ u = \phi_0 & \text{on } \partial\Omega. \end{cases}$$

Note that if we find a radial solution u of (3.69), then H can be recovered by

$$H(x) = \int_{\Omega} G(y, x) \left[\nabla \cdot \left(\frac{1}{\gamma \varepsilon^2 - 1} \nabla u \right) \right] (y) dy,$$

$\phi = u + H$, and \mathbf{p} is given by (3.64), where G is the Green’s function of $-\Delta$ with zero Dirichlet boundary condition.

The proof of Theorem 3.7 can be derived directly from the following result.

THEOREM 3.8. *Under the assumptions of Theorem 3.7, problem (3.69) has a unique solution $u \in C^2(\bar{\Omega})$, which is radially symmetric.*

Proof. Let η be the unique solution of the following equation:

$$(3.70) \quad \nabla \cdot \left(\frac{\gamma \varepsilon^2}{\gamma \varepsilon^2 - 1} \nabla \eta \right) = 0 \quad \text{in } \Omega, \quad \eta = \phi_0 \quad \text{on } \partial\Omega.$$

We replace u by $u + \eta$. Then (3.69) becomes

$$(3.71) \quad \begin{cases} -\varepsilon^2 \nabla \cdot \left(\frac{\gamma \varepsilon^2}{\gamma \varepsilon^2 - 1} \nabla u \right) = \alpha \frac{e^{-(u+\eta)}}{\int_{\Omega} e^{-(u+\eta)} dx} - \beta \frac{e^{u+\eta}}{\int_{\Omega} e^{u+\eta} dx} & \text{in } \Omega, \\ u = 0 & \text{on } \partial\Omega. \end{cases}$$

Let us point out that (3.71) is the Euler–Lagrange equation of the energy

$$E(u) = \frac{\varepsilon^2}{2} \int_{\Omega} \frac{\gamma \varepsilon^2}{\gamma \varepsilon^2 - 1} |\nabla u|^2 dx + \alpha \log \left(\int_{\Omega} e^{-(u+\eta)} dx \right) + \beta \log \left(\int_{\Omega} e^{u+\eta} dx \right).$$

We first show that E is a coercive functional bounded from below. By the convexity of the exponential and by the Poincaré inequality,

$$\begin{aligned} E(u) &= \frac{\varepsilon^2}{2} \int_{\Omega} \frac{\gamma \varepsilon^2}{\gamma \varepsilon^2 - 1} |\nabla u|^2 dx + \alpha \log \left(\int_{\Omega} e^{-(u+\eta)} dx \right) + \beta \log \left(\int_{\Omega} e^{u+\eta} dx \right) \\ &\geq \frac{\varepsilon^2}{2} \int_{\Omega} \frac{\gamma \varepsilon^2}{\gamma \varepsilon^2 - 1} |\nabla u|^2 dx - \alpha \int_{\Omega} (u + \eta) dx + \beta \int_{\Omega} (u + \eta) dx \\ &\geq \frac{\varepsilon^2}{2} \int_{\Omega} |\nabla u|^2 dx - C \|u\|_{L^2(\Omega)} - C \geq \frac{\varepsilon^2}{2} \|\nabla u\|_{L^2(\Omega)}^2 - C \|\nabla u\|_{L^2(\Omega)} - C, \end{aligned}$$

where $C > 0$ is a constant. Thus, $E(u) \geq -\frac{1}{2\varepsilon^2} C^2 - C$, and $E(u) \rightarrow +\infty$ as $\|u\|_{H^1} \rightarrow +\infty$. We now define

$$(3.72) \quad c_{\varepsilon} = \inf_{u \in H_0^1(\Omega)} E(u).$$

Let $\{u_n\} \subset H_0^1(\Omega)$ be a sequence so that $E(u_n) \rightarrow c_{\varepsilon}$ as $n \rightarrow +\infty$. It is clear that u_n is bounded in $H_0^1(\Omega)$. Up to a subsequence, we may assume that as $n \rightarrow +\infty$,

$$\begin{aligned} u_n &\rightharpoonup u \quad \text{weakly in } H_0^1(\Omega), \\ u_n &\rightarrow u \quad \text{strongly in } L^2(\Omega), \\ u_n &\rightarrow u \quad \text{a.e. } \Omega. \end{aligned}$$

By Fatou's lemma,

$$c_\varepsilon \leq E(u) \leq \lim_{n \rightarrow +\infty} E(u_n) = c_\varepsilon.$$

Thus, $E(u) = c_\varepsilon$ and u is a minimizer. By the Ekeland variational principle, $E'(u) = 0$, namely, u is a solution of (3.71).

Next we show that the solution of (3.71) is unique. To do this, we only need to show that E is a strictly convex functional on $H_0^1(\Omega)$.

Let $u_1, u_2 \in H_0^1(\Omega)$ so that $u_1 \neq u_2$. Then $\nabla u_1 \neq \nabla u_2$. As a result, for each $\lambda \in (0, 1)$ we have

$$\begin{aligned} & \frac{\varepsilon^2}{2} \int_{\Omega} \frac{\gamma \varepsilon^2}{\gamma \varepsilon^2 - 1} |\nabla(\lambda u_1 + (1 - \lambda)u_2)|^2 dx \\ & < \lambda \frac{\varepsilon^2}{2} \int_{\Omega} \frac{\gamma \varepsilon^2}{\gamma \varepsilon^2 - 1} |\nabla u_1|^2 dx + (1 - \lambda) \frac{\varepsilon^2}{2} \int_{\Omega} \frac{\gamma \varepsilon^2}{\gamma \varepsilon^2 - 1} |\nabla u_2|^2 dx. \end{aligned}$$

Otherwise, by the Hölder inequality we have

$$\begin{aligned} \log \left(\int_{\Omega} e^{-(\lambda u_1 + (1 - \lambda)u_2 + \eta)} dx \right) &= \log \left(\int_{\Omega} e^{-(\lambda(u_1 + \eta) + (1 - \lambda)(u_2 + \eta))} dx \right) \\ &\leq \log \left(\left(\int_{\Omega} e^{-(u_1 + \eta)} dx \right)^\lambda \left(\int_{\Omega} e^{-(u_2 + \eta)} dx \right)^{1 - \lambda} \right) \\ &= \lambda \log \left(\int_{\Omega} e^{-(u_1 + \eta)} dx \right) + (1 - \lambda) \log \left(\int_{\Omega} e^{-(u_2 + \eta)} dx \right), \end{aligned}$$

and similarly,

$$\log \left(\int_{\Omega} e^{\lambda u_1 + (1 - \lambda)u_2 + \eta} dx \right) \leq \lambda \log \left(\int_{\Omega} e^{u_1 + \eta} dx \right) + (1 - \lambda) \log \left(\int_{\Omega} e^{u_2 + \eta} dx \right).$$

Thus, we get that

$$E(\lambda u_1 + (1 - \lambda)u_2) < \lambda E(u_1) + (1 - \lambda)E(u_2).$$

So, E is a strictly convex functional on $H_0^1(\Omega)$.

Hence, $u + \eta$ is a unique solution of (3.69). \square

4. Conclusion. In this paper, an energetic variational method is applied to derive a set of ion transport and electrostatic models of the general electrolyte solution (not limited to ion channel) with a locally and mathematically strictly determined dielectric permittivity of the dipolar solvent under certain assumptions. The main feature of the LDPNP model is that the system consistently determines the dipole moment distribution and hence the local permittivity of the ionic aqueous solution, whereas in traditional PNP simulations this information is lacking and a constant assumption is usually made for the permittivity. Furthermore, in order to demonstrate the reasonableness of our model, we investigate the energy dissipation law of the derived LDPNP model, and the existence and uniqueness of the solution for the stationary LDPNP model. A quantitative comparison between the dipole effects and other effects has not been conducted in the current work due to the lack of model simulations; this, as well as tackling the numerical challenges in solving the complicated model equations, is our next goal.

Acknowledgment. We gratefully acknowledge the anonymous referees for their helpful comments.

REFERENCES

- [1] H. E. ALPER AND R. M. LEVY, *Computer simulations of the dielectric properties of water: Studies of the simple point charge and transferrable intermolecular potential model*, J. Chem. Phys., 91 (1989), pp. 1242–1251.
- [2] D. ANDELMAN, *Electrostatic properties of membranes: The Poisson-Boltzmann theory*, in Handbook of Biological Physics, Vol. 1, Elsevier, 1995, pp. 603–642.
- [3] H. S. ANTILA AND E. LUIJTEN, *Dielectric modulation of ion transport near interfaces*, Phys. Rev. Lett., 120 (2018).
- [4] K. A. BAKER, C. TZITZILONIS, W. KWIATKOWSKI, S. CHOE, AND R. RIEK, *Conformational dynamics of the KcsA potassium channel governs gating properties*, Nat. Struct. Mol. Biol., 14 (2007), pp. 1089–1095.
- [5] D. BEN-YAAKOV, D. ANDELMAN, AND R. PODGORNİK, *Dielectric decrement as a source of ion-specific effects*, J. Chem. Phys., 134 (2011), 074705.
- [6] H. BERTHOUMIEUX AND F. PAILLUSSON, *Dielectric response in the vicinity of an ion: A nonlocal and nonlinear model of the dielectric properties of water*, J. Chem. Phys., 150 (2019), 094507.
- [7] P. BJELKMAR, P. S. NIEMELA, I. VATTULAINEN, AND E. LINDAHL, *Conformational changes and slow dynamics through microsecond polarized atomistic molecular simulation of an integral Kv1.2 ion channel*, PLoS Comput. Biol., 5 (2009), e1000289.
- [8] I. BORUKHOV, D. ANDELMAN, AND H. ORLAND, *Steric effects in electrolytes: A modified Poisson-Boltzmann equation*, Phys. Rev. Lett., 79 (1997), pp. 435–438.
- [9] D. BUCHER AND U. ROTHLSBERGER, *Molecular simulations of ion channels: A quantum chemist's perspective*, J. Gen. Physiol., 135 (2010), pp. 549–554.
- [10] J. H. CHAUDHRY, J. COMER, A. AKSIMENTIEV, AND L. N. OLSON, *A stabilized finite element method for modified Poisson–Nernst–Planck equations to determine ion flow through a nanopore*, Commun. Comput. Phys., 15 (2014), pp. 93–125.
- [11] D. CHEREPANOV, B. FENIOUK, W. JUNGE, AND A. MULKIDJANIAN, *Low dielectric permittivity of water at the membrane interface: Effect on the energy coupling mechanism in biological membranes*, Biophys. J., 85 (2003), pp. 1307–1316.
- [12] H. DAIGUJI, P. YANG, AND A. MAJUMDAR, *Ion transport in nanoftuidic channels*, Nano Lett., 4 (2004), pp. 137–142.
- [13] M. E. DAVIS AND J. A. MCCAMMON, *Electrostatics in biomolecular structure and dynamics*, Chem. Rev., 90 (1990), pp. 509–521.
- [14] M. FIXMAN, *The Poisson–Boltzmann equation and its application to polyelectrolytes*, J. Chem. Phys., 70 (1979), pp. 4995–5005.
- [15] F. FOGOLARI, A. BRIGO, AND H. MOLINARI, *The Poisson–Boltzmann equation for biomolecular electrostatics: A tool for structural biology*, J. Mol. Recognit., 15 (2002), pp. 377–392.
- [16] L. FUMAGALLI, A. ESFANDIAR, R. FABREGAS, S. HU, P. ARES, A. JANARDANAN, Q. YANG, B. RADHA, T. TANIGUCHI, K. WATANABE, ET AL., *Anomalously low dielectric constant of confined water*, Science, 360 (2018), pp. 1339–1342.
- [17] N. GAVISH AND K. PROMISLOW, *Dependence of the dielectric constant of electrolyte solutions on ionic concentration: A microfield approach*, Phys. Rev. E, 94 (2016), 012611.
- [18] N. GAVISH AND K. PROMISLOW, *On the structure of generalized Poisson-Boltzmann equations*, Eur. J. Appl. Math., 27 (2016), pp. 667–685.
- [19] P. GROCHOWSKI AND J. TRYLSKA, *Continuum molecular electrostatics, salt effects, and counterion binding—a review of the Poisson–Boltzmann theory and its modifications*, Biopolymers Original Research on Biomolecules, 89 (2008), pp. 93–113.
- [20] M. GUTMAN, Y. TSFADIA, A. MASAD, AND E. NACHLIEL, *Quantitation of physical-chemical properties of the aqueous phase inside the phoE ionic channel*, Biochim. Biophys. Acta, 1109 (1992), pp. 141–148.
- [21] M. HAN AND J. Z. H. ZHANG, *Molecular dynamic simulation of the Kv1.2 voltage-gated potassium channel in open and closed state conformations*, J. Phys. Chem. B, 112 (2008), pp. 16966–16974.
- [22] J. HASTED, D. RITSON, AND C. COLLIE, *Dielectric properties of aqueous ionic solutions. Parts I and II*, J. Chem. Phys., 16 (1948), pp. 1–21.
- [23] M. M. HATLO, R. VAN ROIJ, AND L. LUE, *The electric double layer at high surface potentials: The influence of excess ion polarizability*, Europhys. Lett., 97 (2012), 28010.

- [24] R. HILFER, *Geometric and dielectric characterization of porous media*, Phys. Rev. B, 44 (1991), pp. 60–75.
- [25] U. HOLLERBACH, D.-P. CHEN, AND R. S. EISENBERG, *Two- and three-dimensional Poisson–Nernst–Planck simulations of current flow through gramicidin A*, J. Sci. Comput., 16 (2001), pp. 373–409.
- [26] B. HONIG AND A. NICHOLLS, *Classical electrostatics in biology and chemistry*, Science, 268 (1995), pp. 1144–1149.
- [27] J. F. JOUNG, S. KIM, AND S. PARK, *Effect of NaCl salts on the activation energy of excited-state proton transfer reaction of coumarin 183*, J. Phys. Chem. B, 119 (2015), pp. 15509–15515.
- [28] M. G. KURNIKOVA, R. D. COALSON, P. GRAF, AND A. NITZAN, *A lattice relaxation algorithm for three-dimensional Poisson–Nernst–Planck theory with application to ion transport through the gramicidin A channel*, Biophys. J., 76 (1999), pp. 642–656.
- [29] B. LI, J. WEN, AND S. ZHOU, *Mean-field theory and computation of electrostatics with ionic concentration dependent dielectrics*, Commun. Math. Sci., 14 (2016), pp. 249–271.
- [30] H. LI AND B. LU, *An ionic concentration and size dependent dielectric permittivity Poisson–Boltzmann model for biomolecular solvation studies*, J. Chem. Phys., 141 (2014), 024115.
- [31] X. LIU, Y. QIAO, AND B. LU, *Analysis of the mean field free energy functional of electrolyte solution with nonhomogenous boundary conditions and the generalized PB/PNP equations with inhomogeneous dielectric permittivity*, SIAM J. Appl. Math., 78 (2018), pp. 1131–1154, <https://doi.org/10.1137/16M1108583>.
- [32] B. LU, Y. ZHOU, M. HOLST, AND J. MCCAMMON, *Recent progress in numerical methods for the Poisson–Boltzmann equation in biophysical applications*, Commun. Comput. Phys., 3 (2008), pp. 973–1009.
- [33] B. LU AND Y. C. ZHOU, *Poisson–Nernst–Planck equations for simulating biomolecular diffusion–reaction processes II: Size effects on ionic distributions and diffusion–reaction rates*, Biophys. J., 100 (2011), pp. 2475–2485.
- [34] M. MA, Z. XU, AND L. ZHANG, *Modified Poisson–Nernst–Planck model with Coulomb and hard-sphere correlations*, SIAM J. Appl. Math., 81 (2021), pp. 1645–1667, <https://doi.org/10.1137/19M1310098>.
- [35] J. A. MCCAMMON, *Darwinian biophysics: Electrostatics and evolution in the kinetics of molecular binding*, Proc. Natl. Acad. Sci. USA, 106 (2009), pp. 7683–7684.
- [36] S. McLAUGHLIN, *The electrostatic properties of membranes*, Annu. Rev. Biophys. Biophys. Chem., 18 (1989), pp. 113–136.
- [37] Y. NAKAYAMA AND D. ANDELMAN, *Differential capacitance of the electric double layer: The interplay between ion finite size and dielectric decrement*, J. Chem. Phys., 142 (2015), 044706.
- [38] M. NAVARRO-RODRIGUEZ, E. PALACIOS-LIDON, AND A. M. SOMOZA, *The surface charge decay: A theoretical and experimental analysis*, Appl. Surf. Sci., 610 (2023), 155437.
- [39] M. NEUMANN, *Dielectric-relaxation in water. Computer simulations with the TIP4P potential*, J. Chem. Phys., 85 (1986), pp. 1567–1580.
- [40] J. A. NG, T. VORA, V. KRISHNAMURTHY, AND S.-H. CHUNG, *Estimating the dielectric constant of the channel protein and pore*, Eur. Biophys. J. Biophys. Lett., 37 (2008), pp. 213–222.
- [41] Y. QIAO, C. LIAN, B. LU, AND J. WU, *Modeling selective ion adsorption into cylindrical nanopores*, Chem. Phys. Lett., 709 (2018), pp. 116–124.
- [42] Y. QIAO, X. LIU, M. CHEN, AND B. LU, *A local approximation of fundamental measure theory incorporated into three dimensional Poisson–Nernst–Planck equations to account for hard sphere repulsion among ions*, J. Stat. Phys., 163 (2016), pp. 156–174.
- [43] Y. QIAO, B. TU, AND B. LU, *Ionic size effects to molecular solvation energy and to ion current across a channel resulted from the nonuniform size-modified PNP equations*, J. Chem. Phys., 140 (2014), 174102.
- [44] E. RUCKENSTEIN AND M. MANCIU, *Specific ion effects via ion hydration: II. Double layer interaction*, Adv. Colloid Interfac., 105 (2003), pp. 177–200.
- [45] V. SALARI, N. MORADI, M. SAJADI, F. FAZILEH, AND F. SHAHBAZI, *Quantum decoherence time scales for ionic superposition states in ion channels*, Phys. Rev. E, 91 (2015), 032704.
- [46] C. SCHAAF AND S. GEKLE, *Dielectric response of the water hydration layer around spherical solutes*, Phys. Rev. E, 92 (2015), 032718.
- [47] T. SIMONSON, *Accurate calculation of the dielectric constant of water from simulations of a microscopic droplet in vacuum*, Chem. Phys. Lett., 250 (1996), pp. 450–454.
- [48] T. SIMONSON AND D. PERAHIA, *Internal and interfacial dielectric properties of cytochrome c from molecular dynamics in aqueous solution*, Proc. Natl. Acad. Sci. USA, 92 (1995), pp. 1082–1086.

- [49] T. SIMONSON AND D. PERAHIA, *Microscopic dielectric properties of cytochrome c from molecular dynamics simulations in aqueous solution*, J. Amer. Chem. Soc., 117 (1995), pp. 7987–8000.
- [50] J. SUMMHAMMER, G. SULYOK, AND G. BERNROIDER, *Quantum dynamics and non-local effects behind ion transition states during permeation in membrane channel proteins*, Entropy, 20 (2018), 558.
- [51] G.-W. WEI, Q. ZHENG, Z. CHEN, AND K. XIA, *Variational multiscale models for charge transport*, SIAM Rev., 54 (2012), pp. 699–754, <https://doi.org/10.1137/110845690>.
- [52] J. XU, B. LU, AND L. ZHANG, *A time-dependent finite element algorithm for simulations of ion current rectification and hysteresis properties of 3D nanopore system*, IEEE Trans. Nanotechnol., 17 (2018), pp. 513–519.
- [53] H. ZHAO AND S. ZHAI, *The influence of dielectric decrement on electrokinetics*, J. Fluid Mech., 724 (2013), pp. 69–94.