

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*

XUEJIAO LIU[†], YU QIAO[†], AND BENZHUO LU[‡]

Abstract. The energy functional, the governing partial differential equation(s) (PDE), and the boundary conditions need to be consistent with each other in a modeling system. In electrolyte solution study, people usually use a free energy form of an infinite domain system (with vanishing potential boundary condition) and the derived PDE(s) for analysis and computing. However, in many real systems and/or numerical computing, the objective domain is bounded, and people still use the similar energy form, PDE(s), but with different boundary conditions, which may cause inconsistency. In this work, (1) we present a mean field free energy functional for the electrolyte solution within a bounded domain with either physical or numerically required artificial boundary. Apart from the conventional energy components (electrostatic potential energy, ideal gas entropy term, and chemical potential term), new boundary interaction terms are added for both Neumann and Dirichlet boundary conditions. These new terms count for physical interactions with the boundary (for a real boundary) or the environment influence on the computational domain system (for a nonphysical but numerically designed boundary). In addition, the boundary energy term also applies to any bounded system described by the Poisson equation. (2) The traditional physical-based Poisson–Boltzmann (PB) equation and Poisson–Nernst–Planck (PNP) equations are proved to be consistent with the complete free energy form, and different boundary conditions can be applied. (3) In particular, for the inhomogeneous electrolyte with ionic concentration-dependent dielectric permittivity, we derive the generalized Boltzmann distribution (thereby the generalized PB equation) for the equilibrium case, and the generalized PNP equations with variable dielectric (VDPNP) for the nonequilibrium case, under different boundary conditions. (4) Furthermore, the energy laws are calculated and compared to study the energy properties of different energy functionals and the resulting PNP systems. Numerical tests are also performed to demonstrate the different consequences resulting from different energy forms and their derived PDE(s).

Key words. free energy functional, electrolyte, boundary conditions, variable dielectric, generalized Poisson–Nernst–Planck/Poisson–Boltzmann equations, energy law

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

DOI. 10.1137/16M1108583

1. Introduction. As a requirement in both physics and mathematics, the system energy functional, the governing partial differential equation(s) (PDE), and the boundary condition(s) (BC) need to be consistent. People usually derive the PDE(s) through minimization of a free energy functional F , in which the information of bound-

*Received by the editors December 19, 2016; accepted for publication (in revised form) January 16, 2018; published electronically April 10, 2018.

<http://www.siam.org/journals/siap/78-2/M110858.html>

Funding: This work was supported by Science Challenge Project (TZ2016003), the National Key Research and Development Program of China (grant 2016YFB0201304), and the China NSF (NSFC 21573274, NSFC 91530102).

[†]State Key Laboratory of Scientific and Engineering Computing, National Center for Mathematics and Interdisciplinary Sciences, 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 (liuxuejiao@lsec.cc.ac.cn, qiaoyu@lsec.cc.ac.cn).

[‡]Corresponding author. State Key Laboratory of Scientific and Engineering Computing, National Center for Mathematics and Interdisciplinary Sciences, 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).

any condition(s) associated with the PDE is, in principle, included. However, a common case is that once a type of PDE is obtained (usually from an energy functional on the whole space), people may study, either theoretically or numerically, the PDE under different boundary conditions. But in this case the changed boundary condition may be inconsistent with the original energy form, and may cause unreasonable results. An example is the electrolyte system, which is the focus of this work.

The electrolyte solution is a charged system mixed with polarizable solvent and mobile ions, which exists in many areas such as chemistry, colloid, fuel cell, material science, and biology systems. An enormous amount of literature can be found in this area. In mean field theory, a Poisson–Boltzmann (PB) equation is a physically reasonable description of the equilibrium state of the electrolyte solution. In a nonequilibrium state (i.e., nonbalanced ionic flow exists), the Poisson–Nernst–Planck (PNP) equations are employed to model the coupling of ionic diffusion processes and the generated electric field. The PB equation and PNP equations are two most commonly used PDE models in the electrolyte solution system. These equations can also be derived from variation of the free energy. As an example in the chemical physics area, Sharp and Honig have used the calculus of variations to provide a unique definition of the total energy and to obtain expressions for the total mean field electrostatic free energy of the electrolyte solution (including fixed macromolecules) for both linear and nonlinear PB equations [30], and later Gilson et al. derived the mean forces based on mean field electrostatic free energies [11]:

$$(1) \quad F = \int \left\{ \rho^f \phi - \frac{1}{2} \epsilon |\nabla \phi|^2 - \beta^{-1} \sum_{i=1}^K c_i^b (e^{-\beta q_i \phi} - 1) \right\} dV.$$

And in turn, the PB equation can also be expected to be derived from these energy functionals. Gilson et al. have shown that if the free energy F is considered as a functional with respect to (w.r.t.) the potential function, the potential which extremizes F is also the potential that satisfies the PB equation [11]. Fogolari and Briggs have pointed out that the potential satisfying the PB equation in fact maximizes the energy functional if it is considered as a functional w.r.t. potential [9]. When the free energy functional is regarded as functional w.r.t. the concentration c rather than the potential ϕ , they proved that the PB distribution is then the only distribution which minimizes the free energy (the Poisson equation is considered as a constraint) [9]. This conclusion was also restated in a more mathematical way later [19]. The energy functional takes the form

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

with a Poisson equation as a constraint. Another advantage of this form is that this form can be applied to study both the equilibrium and nonequilibrium states of the electrolyte solution. It is worth noting that those free energy forms are for the electrolyte solution on the whole space, where the potential (and the derivative) goes to zero at infinity. However, a real physical system and/or a practically computational domain (as appeared in finite element/finite difference methods) are often bounded, and the boundary conditions are usually nontrivial and nonhomogenous. In electrokinetics, most physically interesting properties arise from different nonhomogenous boundary conditions [32, 37, 5, 17, 38]. In these nonhomogenous BC cases for charged system, the system's free energy also needs to include the physical interaction

between the system and the boundary. In other words, the traditional PB equations with general nonhomogenous Dirichlet or/and Neumann BCs cannot be derived from the above free energy form (neither (1) nor (2)) because the boundary term(s) are missed in the energy functional. The issue will be solved in this work. It is worth noting here that even though a real system is infinite, in practical computation as in the finite element approach, only a bounded domain is taken and certain nontrivial BC(s) need to be adopted to simulate the behavior of the whole system. In this case, if we need a, for instance, nonhomogenous Dirichlet BC, an energy term needs to be included in the free energy and represents interaction between the system and the boundary of Dirichlet type (see the detailed physical explanations in section 2). Therefore, in the rest of this paper, we will not distinguish a boundary as a physical (interfacial) boundary or as an artificial boundary, as they will be treated similarly in the energy form.

The free energy functional for an infinite electrolyte solution system can be considered as a special case under the homogenous boundary condition at infinity. If this energy functional is used to derive the PDE with nonhomogenous BC, it may result in “distorted” (nonphysical) equation(s) (see later analysis and discussion). The following nonhomogenous Dirichlet boundary-value problem of Poisson equation (3) is considered, which is a constraint of the potential ϕ in the traditional free energy functional:

$$(3) \quad \begin{aligned} -\nabla \cdot (\epsilon \nabla \phi(c)) &= \rho(c) && \text{in } \Omega, \\ \epsilon \frac{\partial \phi}{\partial n} &= \sigma && \text{on } \Gamma_N, \\ \phi &= \phi_0 && \text{on } \Gamma_D, \end{aligned}$$

where $\frac{\partial \phi}{\partial n}$ denotes the normal derivative at the boundary with n the exterior unit normal. In analysis, we generally need to introduce a corresponding nonhomogeneous boundary-value problem of Poisson equation (4) which has the unique weak solution ϕ_D :

$$(4) \quad \begin{aligned} \nabla \cdot (\epsilon \nabla \phi_D(c)) &= 0 && \text{in } \Omega, \\ \epsilon \frac{\partial \phi_D}{\partial n} &= 0 && \text{on } \Gamma_N, \\ \phi_D &= \phi_0 && \text{on } \Gamma_D. \end{aligned}$$

Using the variational approach to the free energy functional with incomplete boundary terms can lead to a “distorted” Boltzmann distribution and an unusual PB equation as in [19, 20]. Similarly, for the nonequilibrium state and nonhomogeneous boundary-value problem, we will show details in following sections that applying the variational approach to the incomplete free energy functional will lead to a set of PNP equations different from the traditionally established ones as in the following example:

$$(5) \quad -\nabla \cdot (\epsilon \nabla \phi(c)) = \rho^f + \sum_{i=1}^K q_i c_i \quad \text{in } \Omega,$$

$$(6) \quad \frac{\partial c_i}{\partial t} = \nabla \cdot \left(D_i \left[\nabla c_i + \beta c_i \nabla \left(q_i \left[\phi(c) - \frac{1}{2} \phi_D(c) \right] \right) \right] \right) \quad \text{in } \Omega_s, i = 1, 2, \dots, K.$$

In the physics of the electro-diffusion process and in the traditional PNP equations, the drift term $\beta q c \nabla \phi$ is determined by the electric field, i.e., $\nabla \phi$, and should be

irrelevant to ϕ_D . But in (5) and (6), an additional term $-\frac{1}{2}\beta qc\nabla\phi_D$ appears in the drift term and is unavoidable in the variational approach using the incomplete energy functional (see section 2).

To derive the correct PB and PNP equations subject to different BCs (Neumann, Dirichlet or their co-existing case), in this paper we will provide a complete energy functional form by proposing a new energy term, which is consistent with the PDEs and the corresponding BCs. Numerical examples demonstrate significant deviations between the predictions from the inconsistent PB/PNP models (originated from the incomplete energy functional) and those from the PB/PNP models.

Furthermore, to study the system energy property, the energy law is calculated for the complete energy functional and other forms. Analysis and discussion also indicate that the complete energy functional with a new energy term, instead of the usual forms, leads to a physically reasonable energy law.

In addition, a particularly interesting case of this work is to consider the situation when a dielectric coefficient is dependent on ionic concentration. The general free energy functional includes this situation and a variational approach is applied to derive the generalized PB and PNP equations under different boundary conditions. Ionic solutions may be considered to consist of three constituents: the charged anions and cations, “hydration” solvent molecules near the vicinity of the ions, and “free” solvent molecules. The hydration shells will affect the dielectric coefficient in an ionic solution [36, 35]. The effective polarizability is related to the presence of a hydration shell around ions and causes the dielectric decrement characteristic [1, 27]. In the electrolyte, as the solvent dipoles are highly oriented under large electric fields, there are some studies to consider the field-dependent dielectric permittivity [3]. A lot of experiments and theoretical analysis have indicated that the dielectric coefficient decreased with the increase of local ionic concentrations [12, 15, 14, 28, 13, 33, 21], and the phenomenon of depletion of ions near a charged wall can also be captured [20]. In our previous paper [21], we present a variable dielectric PB (VDPB) model for biological study, in which the dielectric coefficient is ionic concentration-dependent. However, the equation is not mathematically consistent with the system’s free energy functional. In this paper, we analyze and discuss a general dependence form of the dielectric coefficient on local concentrations, and the governing equations in both equilibrium and nonequilibrium are consistently given.

2. Theory and method.

2.1. The mean field free energy functional. We consider the general case of an electrolyte solution that contains a solvent, arbitrary number of mobile ion species, and perhaps membrane-molecule(s) or nanopore as well. The macro-object-like biomolecule, if it exists, is treated as a fixed object and usually also carries charges inside or on the surface. Figure 1 represents two typical biophysical models in computational analysis. The domain Ω_s (s for solvent) denotes the solvent region where there is a mixed solution with diffusive ion species, such as mobile ions. The solute region Ω_m (m for molecule) is the domain occupied by (in (a)) the fixed biomolecule, such as protein or DNA, or by (in (b)) the membrane, channel protein/nanopore [25, 31, 32, 34]. In case (b), if necessary, Ω_m can be further divided into different subregions, but this does not affect our following analysis. The whole domain is denoted by $\Omega = \Omega_m \cup \Omega_s$. Figure 1 illustrates a solvated biomolecular system in an open domain $\Omega \in \mathbb{R}^3$. The open subdomain $\Omega_m \subset \Omega$ represents the biomolecule(s), and the remaining space $\Omega_s = \Omega \setminus \Omega_m$ is filled with ionic solution. Domains Ω_m and Ω_s are separated by a molecular surface Γ_m (for simplicity, we call Γ_m the molecular surface

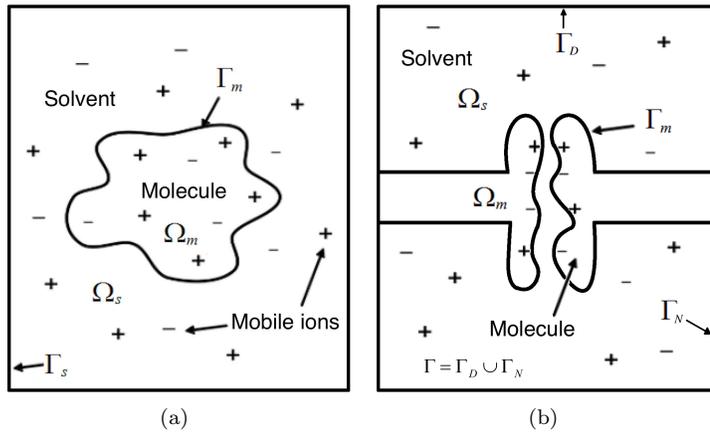


FIG. 1. A two-dimensional (2-D) schematic view of the ionic solution system: (a) with one fixed biomolecule; (b) with an ion channel (or similar a nanopore) embedded in a membrane.

in the rest of the paper, but it also includes the membrane and nanopore surface if they exist). The ionic flow cannot penetrate the nonreactive molecular surface. We use Γ_D and Γ_N to represent boundaries with Dirichlet and Neumann boundary conditions, respectively. According to the property of the physical system and model, both Γ_D and Γ_N can be applied to Γ_s or part of Γ_s . For example, fixed potentials (Dirichlet BC) are usually given on the out boundary Γ_s in PB calculations (Figure 1(a)) and on the upper and lower boundaries of the whole box in PNP simulations (Figure 1(b)). Surface charge density (Neumann BC) is usually applied to the molecular/nanopore surface Γ_m [31, 6, 22], or a simplified molecular surface (do not consider the molecular domain Ω_m) [20] to model the charge amount carried by the molecule. The boundary of the whole region is $\Gamma = \Gamma_D \cup \Gamma_N$.

Free energy discussions in previous works are usually on the whole space with vanishing at infinity and do not consider the nonhomogenous Neumann and Dirichlet boundary effects. If we consider a bounded or a confined region, the variational approach to the derivation of the free energy functional may face problems. For an electrolyte solution system, the Gibbs free energy of the charged system is usually written as [30, 11, 9]

$$\begin{aligned}
 F &= \frac{1}{2} \int_{\Omega} \left(\rho^f + \sum_{i=1}^K q_i c_i \right) \phi dV + k_B T \int_{\Omega} \sum_{i=1}^K c_i [\ln(c_i/c_i^b) - 1] dV \\
 (7) \quad &= \int_{\Omega} \frac{1}{2} \rho \phi dV + \beta^{-1} \sum_{i=1}^K \int_{\Omega} c_i [\ln(\Lambda^3 c_i) - 1] dV - \sum_{i=1}^K \int_{\Omega} \mu_i c_i dV.
 \end{aligned}$$

Here, ρ is the total charge density, defined by

$$(8) \quad \rho = \rho^f + \sum_{i=1}^K q_i c_i,$$

where $q_i = Z_i e$, with Z_i the valence of the i th ionic species and e the elementary charge, K is the number of diffusive ion species in solution that are considered in the

system, and ρ^f is the permanent (fixed) charge distribution

$$\rho^f(x) = \sum_j q_j \delta(x - x_j),$$

which is an ensemble of singular charges q_j located at x_j inside the biomolecule. $\phi = \phi(c)$ is the electrostatic potential with $c = (c_1, \dots, c_K)$, c_i is the concentration for the i th ionic species, and c_i^b is the bulk concentration for the i th ionic species. $\beta^{-1} = k_B T$, 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 for the i th ionic species. The standard PB and PNP equations can be derived by the variational method from this energy form [24, 34].

However, as aforementioned, in many real systems and/or numerical computing, the objective domain is bounded, and people used to adopt the same energy form and study different boundary conditions. This may lead to inconsistency among the energy form, PB/PNP equations, and the boundary conditions, and sometimes even results in a nonphysical PDE model. A satisfactory way is that a PDE model and the BCs can be derived through the energy variational approach (which is necessary for further consistent mathematical analysis), and the energy form is physically reasonable. To obtain the consistent PDE(s), we need include different boundary interactions into the free energy functionals, and these new terms count for physical interactions with the boundary (for real boundary) or the environmental influence on the computational domain system (for an artificially modeled boundary for the numerical goal). Generally, when there exists surface charges (denote the density as σ) on the boundary or part of the boundary (where a Neumann boundary condition can be applied), it is obvious to directly plug a surface energy term ($\frac{1}{2}\phi\sigma$) into the free energy functional. This is physically reasonable because the surface charges cause an additional interaction with the electric field. This “improved” free energy is also often used and studied, as in [20]:

$$(9) \quad F[c] = \int_{\Omega} \frac{1}{2} \rho(c) \phi(c) dV + \int_{\Gamma_N} \frac{1}{2} \sigma \phi(c) dS \\ + \beta^{-1} \sum_{i=1}^K \int_{\Omega} c_i [\ln(\Lambda^3 c_i) - 1] dV - \sum_{i=1}^K \int_{\Omega} \mu_i c_i dV.$$

But this free energy is still not complete, as it lacks the treatment of the Dirichlet boundary condition, which is rarely discussed in previous mathematical and physical work. When a potential is given on a boundary, which means: (1) If the boundary is a physical boundary identified as a certain type of material interface, there must be a mount of “effective” surface charges (denote the density as σ_D^{eff}) to maintain the Dirichlet condition. In physics, the effective surface charge density needs to be equal to $-\epsilon \frac{\partial \phi}{\partial n}$ (induced by exterior region), which thereby causes an additional surface interaction energy $-\frac{1}{2} \epsilon \frac{\partial \phi}{\partial n} \phi$. (2) If the boundary is an artificial boundary (still consider the electrolyte solution system), we are using a boundary condition to model the influence from the “cutoff” outside part which is a polarizable dielectric media (environment). The influence can be approximated by an “effective” surface charge σ_D^{eff} induced by the exterior region as in the physical boundary case. This charge density also should be consistent with the electric potential field and the given surface potential. In other words, the effective charge density σ_D^{eff} is equal to $-\epsilon \frac{\partial \phi}{\partial n}$ and leads to a similar energy term. Therefore, in either of the above two cases, there also needs

to be an energy term in the free energy functional for Dirichlet BC. Here we present a complete free energy functional form:

$$(10) \quad F[c] = \int_{\Omega} \frac{1}{2} \rho(c) \phi(c) dV + \int_{\Gamma_N} \frac{1}{2} \sigma \phi(c) dS - \int_{\Gamma_D} \frac{1}{2} \epsilon(c) \frac{\partial \phi(c)}{\partial n} \phi_0 dS + \beta^{-1} \sum_{i=1}^K \int_{\Omega} c_i [\ln(\Lambda^3 c_i) - 1] dV - \sum_{i=1}^K \int_{\Omega} \mu_i c_i dV,$$

where $\phi = \phi(c)$ is the electrostatic potential determined as the solution to the general boundary-value problem of the Poisson equation

$$(11) \quad \begin{aligned} -\nabla \cdot (\epsilon(c) \nabla \phi(c)) &= \rho(c) && \text{in } \Omega, \\ \epsilon(c) \frac{\partial \phi}{\partial n} &= \sigma && \text{on } \Gamma_N, \\ \phi &= \phi_0 && \text{on } \Gamma_D. \end{aligned}$$

The first three terms in (10) together represent the electrostatic potential energies, and in particular, the second and third terms are the boundary interactions. The fourth term represents the ideal-gas entropy, and the last term in (10) represents the chemical potential of the system that results from the constraint of the total number of ions in each species. It is worth noting that the boundary energy $-\frac{1}{2} \int_{\Gamma_D} \epsilon \frac{\partial \phi}{\partial n} \phi dS \rightarrow 0$ if the domain tends toward infinity. It is also worth mentioning that the ideal-gas entropy will be infinite if the domain tends toward infinity. In fact, the physically meaningful calculation is to calculate the energy difference. The energy difference here is the so-called solvation energy, which is the difference of the energies between the interacting system (the ionic solution and the solvated molecule) and the noninteracting system (separated pure ionic solution and the molecule in a vacuum). In this situation the energy difference can be proved and numerically demonstrated to be always a finite value. As either the original energy form or the energy difference form does not affect the analysis and calculations in this work, we only used the complete energy form as discussed above in the following analysis. In particular, in this work we treat ϵ as a general inhomogeneous dielectric permittivity which can be dependent on ionic concentration. This is another topic of concern in the paper.

Aside from the above physical reasoning for the new boundary energy term, we will try to make an explanation in mathematical point of view. First, considering the Poisson equation as a constraint, using integration by parts and the Gauss theorem in the energy variational derivation will naturally lead to a boundary term with potential for a bounded domain. Second, only considering a Poisson system with Dirichlet BC and electrostatic energy as discussed below, the Euler–Lagrange form for the Poisson equation is shown to lead to exactly the same energy form as proposed in this work, which has a boundary energy term (see 12). Third, analysis on the calculated energy law for different energy forms and corresponding PNP systems indicates again that the additional boundary energy term is necessary to obtain a reasonable energy law (see subsection 2.4.1).

It is also worth noting that there are different energy forms of electrolyte systems appearing in the literature, and in most cases they adopt an underlying assumption of infinite domain but with little discussion and analysis on general cases. We will make some notes on those forms here. Before that, we list two prerequisites: (1) The Poisson equation always holds (from electric field theory). This is why, in most parts of this work, we use the Poisson equation as a constraint instead of a “derived” equation.

(2) Physically, the electrostatic potential energy should naturally take a form like $\int_{\Omega} \frac{1}{2} \rho \phi dV$ (and as demonstrated in this work, we will show that there need to be boundary term(s) in addition to the usual volume integral form). Similarly, we focus our notes only on the Poisson system and electrostatic energy in this paragraph. A familiar energy form is $\int_{\Omega} \frac{\epsilon}{2} |\nabla \phi|^2 dV$, which can be directly interpreted as field energy from electromagnetic field theory (e.g., see [16]). Through integration by parts and supposing the Poisson equation holds, this form can be easily shown to be equivalent to $\int_{\Omega} \frac{1}{2} \rho \phi dV + \frac{1}{2} \int_{\Gamma} \epsilon \frac{\partial \phi}{\partial n} \phi dS$, which is equal to $\int_{\Omega} \frac{1}{2} \rho \phi dV$ only for the infinite domain or vanishing bounded boundary. Similarly, another form is the Euler–Lagrange form that also often appeared in literature such as used in [30, 11],

$$F(\phi, \nabla \phi) = \int_{\Omega} \left(-\frac{\epsilon}{2} |\nabla \phi|^2 + \rho \phi \right) dV.$$

From above note it is easy to see that this form is again equivalent to the form $\int_{\Omega} \frac{1}{2} \rho \phi dV$ when the boundary integral term vanishes. One advantage of this form is that the Euler–Lagrange equation of this energy functional gives exactly the Poisson equation. More specifically, we show in the following that in the case when ϵ is not dependent on ionic concentration c , and under a Dirichlet BC, this form leads to the Poisson equation. Hence the Euler–Lagrange form is a consistent energy form in these situations. The variation is as follows:

$$\begin{aligned} \delta F &= \int_{\Omega} \left(-\epsilon \nabla \phi \cdot \nabla (\delta \phi) - \frac{1}{2} \nabla \phi \cdot \nabla \phi \delta \epsilon + \phi \delta \rho + \rho \delta \phi \right) dV \\ &= \int_{\Omega} (\nabla \cdot (\epsilon \nabla \phi) + \rho) \delta \phi dV - \int_{\Gamma_D} \epsilon \frac{\partial \phi}{\partial n} \delta \phi dS - \frac{1}{2} \int_{\Omega} \nabla \phi \cdot \nabla \phi \delta \epsilon dV + \int_{\Omega} \phi \delta \rho dV. \end{aligned}$$

For a given charge distribution and $\epsilon(r)$, $\delta \rho = \delta \epsilon = 0$, and for a given Dirichlet BC (in which case a unique solution exists), $\delta \phi = 0$ on Γ_D , then the solution function ϕ of the Poisson equation, $-\nabla \cdot (\epsilon \nabla \phi) = \rho$, extremizes the energy F , i.e., $\delta F = 0$. Now, given that the Poisson equation is satisfied in general, this in turn can reach the observation through similar integration by parts that the Euler–Lagrange integral form of the energy differs from the integral of $\frac{1}{2} \rho \phi$ exactly by the boundary integral term $-\int_{\Gamma_D} \frac{1}{2} \epsilon \frac{\partial \phi}{\partial n} \phi_0 dS$ that we are proposing to add in (10):

$$\begin{aligned} &\int_{\Omega} \left(-\frac{1}{2} \epsilon |\nabla \phi|^2 + \rho \phi \right) dV \\ &= \int_{\Omega} \left(\frac{1}{2} \nabla \cdot (\epsilon \nabla \phi) \phi + \rho \phi \right) dV - \frac{1}{2} \int_{\Gamma_D} \epsilon \frac{\partial \phi}{\partial n} \phi_0 dS \\ (12) \quad &= \int_{\Omega} \frac{1}{2} \rho \phi dV - \frac{1}{2} \int_{\Gamma_D} \epsilon \frac{\partial \phi}{\partial n} \phi_0 dS. \end{aligned}$$

However, as shown above, in general cases with nonhomogeneous boundary conditions and with ionic concentration dependent dielectric permittivity, the energy form using $\int_{\Omega} \frac{\epsilon}{2} |\nabla \phi|^2 dV$ could not be obtained physically. One objective of this work is to show that the energy form given by (10) is a physically reasonable and consistent energy form, which will be analyzed and discussed in the following sections.

Consequently, for an electrolyte system *with a given dielectric coefficient* $\epsilon(r)$

under a Dirichlet BC, the following different energy forms are, in fact, equivalent:

$$\begin{aligned}
 F[c] = & \int_{\Omega} \left[-\frac{\epsilon}{2} |\nabla \phi|^2 + \rho(c)\phi(c) \right] dV \\
 & + k_B T \sum_{i=1}^K \int_{\Omega} c_i [\ln(\Lambda^3 c_i) - 1] dV - \sum_{i=1}^K \int_{\Omega} \mu_i c_i dV,
 \end{aligned}
 \tag{13}$$

$$\begin{aligned}
 F[c] = & \int_{\Omega} \frac{\epsilon}{2} |\nabla \phi|^2 dV - \int_{\Gamma_D} \epsilon \frac{\partial \phi(c)}{\partial n} \phi_0 dS \\
 & + k_B T \sum_{i=1}^K \int_{\Omega} c_i [\ln(\Lambda^3 c_i) - 1] dV - \sum_{i=1}^K \int_{\Omega} \mu_i c_i dV,
 \end{aligned}
 \tag{14}$$

and

$$F[c] = \int_{\Omega} \left(\frac{1}{2} \rho(c)\phi(c) + k_B T \sum_{i=1}^K c_i \left[\ln \left(\frac{c_i}{c_i^b} \right) - 1 \right] \right) dV - \frac{1}{2} \int_{\Gamma_D} \epsilon \frac{\partial \phi(c)}{\partial n} \phi_0 dS.
 \tag{15}$$

In the next few subsections, we will use the energetic variational approach to illustrate the appropriateness and consistency of the above-mentioned free energy form, and to derive new equations when dielectric permittivity is dependent on ionic concentration. If the boundary interactions are missed in the free energy functionals, the energetic variational approach will produce some extra terms of boundary integration, and the Boltzmann distribution may or may not be obtained in a distorted form. Of particular interest in the case of ionic concentration-dependent dielectric permittivity, the complete free energy form will consistently lead to two generalized equations under different boundary conditions.

2.2. Energetic variational approach.

2.2.1. First variations. To derive the first variation of F w.r.t. c , we first need the following basic assumptions:

- The dielectric coefficient function $\epsilon(c_1, \dots, c_K) \in C^1([0, \infty))$. Moreover, there are two positive numbers ϵ_{min} and ϵ_{max} such that

$$0 < \epsilon_{min} \leq \epsilon(c_1, \dots, c_K) \leq \epsilon_{max} \quad \forall c_i \geq 0, \quad i = 1, \dots, K.$$

- Ω is bounded and open, $\Gamma = \partial\Omega = \Gamma_N \cup \Gamma_D$.
- We also assume a fixed charged density $\rho^f : \Omega \rightarrow R$, $\rho^f \in L^\infty(\Omega)$, a surface charge density $\sigma : \Gamma_N \rightarrow R$, and a boundary value of the electrostatic potential $\phi_0 : \Gamma_D \rightarrow R$, $\phi_0|_{\Gamma_D} \in W^{2,\infty}(\Omega)$.

We use the standard notion for Sobolev spaces:

$$H_s^1 = \{ \phi \in H^1(\Omega) : \phi = \phi_0 \quad \text{on } \Gamma_D \},$$

$$H_{s,0}^1 = \{ \phi \in H^1(\Omega) : \phi = 0 \quad \text{on } \Gamma_D \}.$$

The weak form of (11) is

$$\int_{\Omega} \nabla \cdot (\epsilon(c)\nabla \phi(c)) v dV = - \int_{\Omega} \rho(c) v dV \quad \forall v \in H_{s,0}^1(\Omega).$$

By the Gauss theorem, we have

$$(16) \quad a(\phi, v) = \int_{\Omega} \epsilon(c) \nabla \phi(c) \cdot \nabla v dV + \int_{\Gamma_N} \sigma v dS \quad \forall v \in H^1_{s,0}(\Omega).$$

Since $L^\infty(\Omega) \cap H^1_{s,0}(\Omega)$ is dense in $H^1_{s,0}(\Omega)$, we can identify u as an element in $H^{-1}_{s,0}(\Omega)$. We denote

$$X = \{c = (c_1, \dots, c_K) \in L^1(\Omega, R^K) : c_i \geq 0 \text{ a.e. } \Omega, i = 1, \dots, K; \sum_{i=1}^K q_i c_i \in H^{-1}_{s,0}(\Omega)\}.$$

Let $c \in X$. It follows from the Lax–Milgram theorem and the Poincaré inequality for functions in $H^1_{s,0}(\Omega)$ that the boundary-value problem of Poisson equation (11) has a unique weak solution $\phi = \phi(c)$.

Let $c = (c_1, \dots, c_K) \in X$ and $d = (d_1, \dots, d_K) \in X$. We define

$$(17) \quad \delta F[c][d] = \lim_{t \rightarrow 0} \frac{F[c + td] - F[c]}{t}.$$

To get the expression of $\delta F[c][d]$, we need the following theorem.

THEOREM 2.1. *Let $c = (c_1, \dots, c_K) \in X$. Assume there exist positive numbers δ_1 and δ_2 such that $\delta_1 \leq c_i(x) \leq \delta_2$ for a.e. $x \in \Omega$ and $i = 1, \dots, K$. Assume also that $d = (d_1, \dots, d_K) \in L^\infty(\Omega, R^K)$. Then*

$$\|\phi(c + td) - \phi(c)\|_{H^1(\Omega)} \rightarrow 0 \text{ as } t \rightarrow 0.$$

A proof of this theorem can be found in [20], and we will not repeat it here.

Now, we decompose the free energy F as

$$F[c] = F_{pot}[c] + F_{entropy}[c],$$

where

$$(18) \quad F_{pot}[c] = \int_{\Omega} \frac{1}{2} \rho(c) \phi(c) dV + \int_{\Gamma_N} \frac{1}{2} \sigma \phi(c) dS - \int_{\Gamma_D} \frac{1}{2} \epsilon(c) \frac{\partial \phi(c)}{\partial n} \phi_0 dS,$$

$$(19) \quad F_{entropy}[c] = \sum_{i=1}^K \int_{\Omega} \{\beta^{-1} c_i [\ln(\Lambda^3 c_i) - 1] - \mu_i c_i\} dV.$$

Based on the definition of (17), we have

$$(20) \quad \delta F_{entropy}[c][d] = \sum_{i=1}^K \int_{\Omega} d_i [\beta^{-1} \ln(\Lambda^3 c_i) - \mu_i] dV.$$

We now deal with another term:

$$(21) \quad \begin{aligned} \delta F_{pot}[c][d] &= \lim_{t \rightarrow 0} \frac{F_{pot}[c + td] - F_{pot}[c]}{t} \\ &= \lim_{t \rightarrow 0} \frac{1}{2} \int_{\Omega} \frac{[\rho(c + td) - \rho(c)] \phi(c + td)}{t} dV + \lim_{t \rightarrow 0} \frac{1}{2} \int_{\Gamma_N} \rho(c) \frac{\phi(c + td) - \phi(c)}{t} dS \\ &+ \lim_{t \rightarrow 0} \left\{ \int_{\Gamma_N} \sigma \frac{\phi(c + td) - \phi(c)}{2t} dS - \frac{1}{2t} \int_{\Gamma_D} \left[\epsilon(c + td) \frac{\partial \phi(c + td)}{\partial n} - \epsilon(c) \frac{\partial \phi(c)}{\partial n} \right] \phi_0 dS \right\}. \end{aligned}$$

By (8) and Theorem 2.1, we have

$$(22) \quad \lim_{t \rightarrow 0} \frac{1}{2} \int_{\Omega} \frac{[\rho(c+td) - \rho(c)]\phi(c+td)}{t} dV = \frac{1}{2} \sum_{i=1}^K \int_{\Omega} d_i q_i \phi(c) dV.$$

Now we deal with the remaining three terms in (21). By the weak formulation (16) for $\phi(c)$ with $v = \frac{\phi(c+td) - \phi(c)}{t} \in H^1_{s,0}$,

$$(23) \quad \begin{aligned} & \lim_{t \rightarrow 0} \frac{1}{2} \int_{\Omega} \rho(c) \frac{\phi(c+td) - \phi(c)}{t} dV + \lim_{t \rightarrow 0} \frac{1}{2} \int_{\Gamma_N} \sigma \frac{\phi(c+td) - \phi(c)}{t} dS \\ & - \lim_{t \rightarrow 0} \frac{1}{2t} \int_{\Gamma_D} \left[\epsilon(c+td) \frac{\partial \phi(c+td)}{\partial n} - \epsilon(c) \frac{\partial \phi(c)}{\partial n} \right] \phi_0 dS \\ & = \lim_{t \rightarrow 0} \frac{1}{2} \int_{\Omega} \epsilon(c) \nabla \phi(c) \cdot \nabla \left[\frac{\phi(c+td) - \phi(c)}{t} \right] dV \\ & - \lim_{t \rightarrow 0} \int_{\Gamma_D} \frac{1}{2t} \left[\epsilon(c+td) \frac{\partial \phi(c+td)}{\partial n} - \epsilon(c) \frac{\partial \phi(c)}{\partial n} \right] \phi_0 dS. \end{aligned}$$

Based on the Poisson equation (11), the following equation holds:

$$\int_{\Omega} -\nabla \cdot (\epsilon(c) \nabla \phi(c)) \phi(c) dV = \int_{\Omega} \rho(c) \phi(c) dV.$$

By integrating the left term by parts and using the divergence theorem

$$(24) \quad \int_{\Omega} \epsilon(c) \nabla \phi(c) \cdot \nabla \phi(c) dV - \int_{\Gamma} \epsilon(c) \frac{\partial \phi(c)}{\partial n} \phi(c) dS = \int_{\Omega} \rho(c) \phi(c) dV.$$

If we consider the Poisson equation (11) at $c+td$, similarly, we have

$$(25) \quad \int_{\Omega} \epsilon(c+td) \nabla \phi(c+td) \cdot \nabla \phi(c) dV - \int_{\Gamma} \epsilon(c+td) \frac{\partial \phi(c+td)}{\partial n} \phi(c) dS = \int_{\Omega} \rho(c+td) \phi(c) dV.$$

If $\epsilon(c)$ is a function of c , we can deduce the equation below from (24) and (25):

$$\begin{aligned} & \sum_{i=1}^K \int_{\Omega} t d_i q_i \phi(c) dV \\ & = \int_{\Omega} [(\epsilon(c+td) - \epsilon(c)) \nabla \phi(c+td) + \epsilon(c) (\nabla \phi(c+td) - \nabla \phi(c))] \cdot \nabla \phi(c) dV \\ & - \int_{\Gamma_N \cup \Gamma_D} \left[\epsilon(c+td) \frac{\partial \phi(c+td)}{\partial n} - \epsilon(c) \frac{\partial \phi(c)}{\partial n} \right] \phi(c) dS \\ & = \int_{\Omega} \left\{ \sum_{i=1}^K [(t d_i \epsilon'_i(c) + o(t)) \nabla \phi(c+td) \cdot \nabla \phi(c)] + [\epsilon(c) (\nabla \phi(c+td) - \nabla \phi(c))] \cdot \nabla \phi(c) \right\} dV \\ & - \int_{\Gamma_D} \left[\epsilon(c+td) \frac{\partial \phi(c+td)}{\partial n} - \epsilon(c) \frac{\partial \phi(c)}{\partial n} \right] \phi_0 dS, \end{aligned}$$

where we denote $\epsilon'_i(c)$ as $\frac{\partial \epsilon(c)}{\partial c_i}$, and take the above equation into (23),

$$\begin{aligned}
 & \lim_{t \rightarrow 0} \frac{1}{2} \int_{\Omega} \rho(c) \frac{\phi(c+td) - \phi(c)}{t} dV + \lim_{t \rightarrow 0} \frac{1}{2} \int_{\Gamma_N} \sigma \frac{\phi(c+td) - \phi(c)}{t} dS \\
 & - \lim_{t \rightarrow 0} \frac{1}{2t} \int_{\Gamma_D} \left[\epsilon(c+td) \frac{\partial \phi(c+td)}{\partial n} - \epsilon(c) \frac{\partial \phi(c)}{\partial n} \right] \phi_0 dS \\
 (26) \quad & = \frac{1}{2} \sum_{i=1}^K \int_{\Omega} d_i q_i \phi(c) dV - \frac{1}{2} \sum_{i=1}^K \int_{\Omega} d_i \epsilon'_i(c) \nabla \phi(c) \cdot \nabla \phi(c) dV.
 \end{aligned}$$

By combining (20), (22), and (26), we finally have

$$\begin{aligned}
 \delta F[c][d] &= \delta F_{entropy}[c][d] + \delta F_{pot}[c][d] \\
 &= \sum_{i=1}^K \int_{\Omega} d_i \{ q_i \phi(c) + \beta^{-1} \ln(\Lambda^3 c_i) - \mu_i - \frac{1}{2} \epsilon'_i(c) \nabla \phi(c) \cdot \nabla \phi(c) \} dV.
 \end{aligned}$$

In the case of the inhomogeneous dielectric coefficient based on these discussions, we can prove the following theorem.

THEOREM 2.2. *Let $c = (c_1, \dots, c_K) \in X$. Assume there exist positive numbers δ_1 and δ_2 such that $\delta_1 \leq c_i(x) \leq \delta_2$ for a.e. $x \in \Omega$ and $i = 1, \dots, K$. Assume also that $d = (d_1, \dots, d_K) \in L^\infty(\Omega, R^K)$. If we consider the complete free energy functional as given in (10), then*

$$(27) \quad \delta F[c][d] = \sum_{i=1}^K \int_{\Omega} d_i \left\{ q_i \phi(c) - \frac{1}{2} \epsilon'_i(c) \nabla \phi(c) \cdot \nabla \phi(c) + \beta^{-1} \ln(\Lambda^3 c_i) - \mu_i \right\} dV.$$

Particularly, if ϵ doesn't depend on c , then

$$(28) \quad \delta F[c][d] = \sum_{i=1}^K \int_{\Omega} d_i \{ q_i \phi(c) + \beta^{-1} \ln(\Lambda^3 c_i) - \mu_i \} dV.$$

2.2.2. Comparison with the result from the incomplete energy form.

To compare with the result from the incomplete energy form, we use the energetic variational approach to the incomplete free energy functional (9) rather than (10) in a bounded domain (or semibounded domain as well), and theoretical analysis will give essentially different results. An extra surface integral occurs in the first variations $\delta F[c][d]$ despite the dependency of the dielectric coefficient on ionic concentrations:

$$\begin{aligned}
 \delta F[c][d] &= \sum_{i=1}^K \int_{\Omega} d_i \left\{ q_i \phi(c) + \beta^{-1} \ln(\Lambda^3 c_i) - \mu_i - \frac{1}{2} \epsilon'_i(c) \nabla \phi(c) \cdot \nabla \phi(c) \right\} dV \\
 (29) \quad & + \lim_{t \rightarrow 0} \frac{1}{2t} \int_{\Gamma_D} \left[\epsilon(c+td) \frac{\partial \phi(c+td)}{\partial n} - \epsilon(c) \frac{\partial \phi(c)}{\partial n} \right] \phi_0 dS.
 \end{aligned}$$

The boundary integration term is introduced by the nonhomogenous Dirichlet boundary condition. A general method to eliminate this effect is to introduce a corresponding boundary-value problem of the Poisson equation as shown in Li, Wen, and Zhou's work [20]:

$$\begin{aligned}
 (30) \quad & \nabla \cdot (\epsilon(c) \nabla \phi_D(c)) = 0 && \text{in } \Omega, \\
 & \epsilon(c) \frac{\partial \phi_D}{\partial n} = 0 && \text{on } \Gamma_N, \\
 & \phi_D = \phi_0 && \text{on } \Gamma_D.
 \end{aligned}$$

Similarly, the weak form of (30) is

$$(31) \quad \int_{\Omega} \epsilon(c) \nabla \phi_D(c) \cdot \nabla v dV = 0 \quad \forall v \in H_{s,0}^1(\Omega).$$

The boundary-value problem of Poisson equation (30) has a unique weak solution $\phi_D = \phi_D(c)$ and only in the special case of homogenous boundary condition $\phi_0 = 0$, the introduced ϕ_D vanishes $\phi_D = 0$.

THEOREM 2.3. (See [19, 18, 20].) *Let $c = (c_1, \dots, c_K) \in X$. Assume there exists positive numbers δ_1 and δ_2 such that $\delta_1 \leq c_i(x) \leq \delta_2$ for a.e. $x \in \Omega$ and $i = 1, \dots, K$. Assume also that $d = (d_1, \dots, d_K) \in L^\infty(\Omega, R^K)$. If we consider the incomplete free energy functional as (9), then*

$$\delta F[c][d] = \sum_{i=1}^K \int_{\Omega} d_i \delta_i F[c] dV,$$

where for each $i(1 \leq i \leq K)$ the function $\delta_i F[c] : \Omega \rightarrow R$ is given by

$$(32) \quad \delta_i F[c] = q_i \left[\phi(c) - \frac{1}{2} \phi_D(c) \right] - \frac{1}{2} \epsilon'_i(c) \nabla \phi(c) \cdot \nabla [\phi(c) - \phi_D(c)] + \beta^{-1} \ln(\Lambda^3 c_i) - \mu_i.$$

Proof. Based on (23) and by the weak formulation in (16) for $\phi(c + td)$ and $\phi(c)$, and by the weak formulation in (31) for ϕ_D with $v = \frac{\phi(c+td) - \phi(c)}{t} \in H_{s,0}^1$ and $v = \phi(c) - \phi_D(c) \in H_{s,0}^1$, we have the following:

$$(33) \quad \begin{aligned} & \lim_{t \rightarrow 0} \frac{1}{2} \int_{\Omega} \epsilon(c) \nabla \phi(c) \cdot \nabla \left[\frac{\phi(c + td) - \phi(c)}{t} \right] dV \\ &= \lim_{t \rightarrow 0} \frac{1}{2} \int_{\Omega} \epsilon(c) \nabla [\phi(c) - \phi_D(c)] \cdot \nabla \left[\frac{\phi(c + td) - \phi(c)}{t} \right] dV \\ &= \lim_{t \rightarrow 0} \left[\frac{1}{2t} \int_{\Omega} (\epsilon(c) - \epsilon(c + td)) \nabla [\phi(c) - \phi_D(c)] \cdot \nabla \phi(c + td) dV \right] \\ &+ \lim_{t \rightarrow 0} \left[\frac{1}{2t} \left\{ \rho(c + td) [\phi(c) - \phi_D(c)] dV + \int_{\Gamma_D} \epsilon(c + td) \frac{\partial \phi(c + td)}{\partial n} [\phi(c) - \phi_D(c)] dS \right\} \right] \\ &- \lim_{t \rightarrow 0} \left[\frac{1}{2t} \left\{ \rho(c) [\phi(c) - \phi_D(c)] dV + \int_{\Gamma_D} \epsilon(c) \frac{\partial \phi}{\partial n} [\phi(c) - \phi_D(c)] dS \right\} \right] \\ &= -\frac{1}{2} \sum_{i=1}^K \int_{\Omega} d_i \epsilon'_i(c) \nabla [\phi(c) - \phi_D(c)] \cdot \nabla \phi(c) dV + \frac{1}{2} \sum_{i=1}^K \int_{\Omega} d_i q_i [\phi(c) - \phi_D(c)] dV. \end{aligned}$$

Combining (20), (22), and (33), we have

$$\begin{aligned} \delta F[c][d] &= \delta F_{entropy}[c][d] + \delta F_{pot}[c][d] \\ &= \sum_{i=1}^K \int_{\Omega} d_i \left\{ q_i \left[\phi(c) - \frac{1}{2} \phi_D(c) \right] + \beta^{-1} \ln(\Lambda^3 c_i) - \mu_i \right\} dV \\ &- \sum_{i=1}^K \int_{\Omega} d_i \frac{1}{2} \epsilon'_i(c) \nabla \phi(c) \cdot \nabla [\phi(c) - \phi_D(c)] dV. \quad \square \end{aligned}$$

This will lead to “distorted” PB and PNP models and obtain incorrect results in physics (see the following subsection). In the next two subsections, we will derive the generalized PB/PNP equations and give detailed discussion.

2.3. Generalized Boltzmann distributions with different boundary conditions. Based on the complete free energy functional (10) and Theorem 2.2, the electrostatic free energy $F = F(c)$ is minimized when $c = (c_1, \dots, c_K) \in X$ satisfies $\delta F[c][d] = 0 \forall d = (d_1, \dots, d_K) \in X$, which means

$$q_i \phi(c) - \frac{1}{2} \epsilon'_i(c) \nabla \phi(c) \cdot \nabla \phi(c) + \beta^{-1} \ln(\Lambda^3 c_i) - \mu_i = 0,$$

and we have

$$(34) \quad \begin{aligned} c_i &= \Lambda^{-3} e^{\beta \mu_i} \exp \left\{ -\beta q_i \phi(c) + \frac{\beta}{2} \epsilon'_i(c) \nabla \phi(c) \cdot \nabla \phi(c) \right\} \\ &= c_i^b \exp \left\{ -\beta q_i \phi(c) + \frac{\beta}{2} \epsilon'_i(c) \nabla \phi(c) \cdot \nabla \phi(c) \right\}, \end{aligned}$$

where $c_i \rightarrow c_i^b$ as $r \rightarrow \infty$ and $\phi \rightarrow 0$. We call these the generalized Boltzmann distributions, as they generalize the classical Boltzmann distributions $c_i = c_i^b e^{-\beta q_i \phi}$ ($i = 1, \dots, K$) of the situation ϵ does not depend on c (no matter what the boundary conditions are). Plugging the generalized Boltzmann distributions (34) into the Poisson equation, we then obtain a generalized PB model under arbitrary Neumann/Dirichlet BCs (this is the self-consistent VDPB model in contrast to our previous one [21]):

$$(35) \quad -\nabla \cdot (\epsilon(c) \nabla \phi(c)) = \rho^f + \sum_{i=1}^K q_i c_i^b \exp \left\{ -\beta q_i \phi(c) + \frac{\beta}{2} \epsilon'_i(c) \nabla \phi(c) \cdot \nabla \phi(c) \right\} \quad \text{on } \Omega.$$

However, if we start from the incomplete free energy functional (7) in a bounded domain (or similarly for semibounded domain) with nonhomogenous Neumann/Dirichlet boundary conditions, $\delta F[c][d]$ takes the form

$$\begin{aligned} \delta F[c][d] &= \sum_{i=1}^K \int_{\Omega} d_i \{ q_i \phi(c) + \beta^{-1} \ln(\Lambda^3 c_i) - \mu_i \} dV \\ &\quad - \lim_{t \rightarrow 0} \left[\int_{\Gamma_N} \frac{1}{2} \sigma \frac{\phi(c+td) - \phi(c)}{t} dS \right] \\ &\quad + \lim_{t \rightarrow 0} \left[\int_{\Gamma_D} \frac{1}{2t} \left[\epsilon \frac{\partial \phi(c+td)}{\partial n} - \epsilon \frac{\partial \phi(c)}{\partial n} \right] \phi_0 dS \right]. \end{aligned}$$

Then we cannot obtain a generalized Boltzmann distribution. Based on Theorem 2.3 and the minimized incomplete energy functional (9), a distorted Boltzmann distribution can be derived (an example can be seen in (37)).

Here we give an example to quantify the difference of these two distributions. If ϵ does not depend on c , the generalized Boltzmann distributions (34) are exactly the same as the classical Boltzmann distributions

$$(36) \quad c_i = c_i^b e^{-\beta q_i \phi},$$

and the “distorted” (nonphysical) Boltzmann distributions take the form [19, 20]

$$(37) \quad c_i = c_i^b \exp \left\{ -\beta q_i \left(\phi(c) - \frac{1}{2} \phi_D(c) \right) \right\}.$$

In this example, we design a virtual (ideal) numerical experiment. Considering a charged sphere in an infinite ionic solution, the bulk concentration ($r \rightarrow \infty$) is

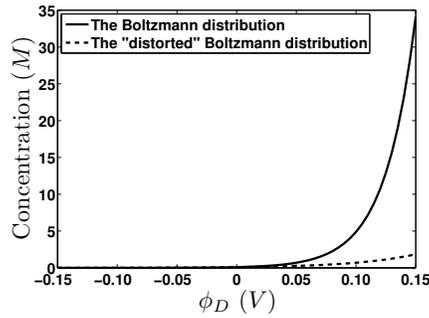


FIG. 2. The traditional (solid line) and “distorted” (dashed line) Boltzmann distributions (supposing $q_i = -1e$) at the Dirichlet boundary as a function of the boundary value ϕ_D . The bulk concentration is set to $0.1M$.

$c_i^b = 0.1M$, and when $r \rightarrow \infty$, $\phi \rightarrow 0$. In numerical calculation, the computational domain is bounded, and we set $\phi = \phi_D$ as the Dirichlet boundary condition on an imaginary spherical boundary at distance $r = R$. Supposing ϕ_D is the real value (depending on the charged sphere and ionic strength) of the real system, the numerical solution should match the realistic potential and concentration distributions. But apparently at $r = R$ (at the boundary) the above two Boltzmann distributions lead to a discrepancy in concentration predictions; one is $c_i^b e^{-\beta q_i \phi_D}$, one is $c_i^b e^{-\frac{1}{2}\beta q_i \phi_D}$. Figure 2 draws the difference as a function of ϕ_D (supposing $q_i = -1e$). It is notable that the gap between the two concentration predictions at the boundary becomes larger with the increase of applied potentials. When the fixed potential is positive, the “distorted” Boltzmann distributions lead to lower concentrations for anions, and higher concentration for cations. For negative boundary potential ϕ_D , the opposite phenomenon occurs. When the fixed potential is zero, the distributions reduce to the same Boltzmann distribution. An alternative example can also be designed as a “semiopen” electrolyte solution system which has a Dirichlet BC ($\phi = \phi_D$) at a “bounded” part of the boundary, and has a homogenous boundary condition at infinity ($\phi \rightarrow 0$, $c_i \rightarrow c_i^b$ as $r \rightarrow \infty$). Similarly as the above example, on the bounded boundary ($\phi = \phi_D$), the generalized Boltzmann distribution is exactly the classical Boltzmann distributions $c_i = c_i^b e^{-\beta q_i \phi_D}$, while the distorted Boltzmann distributions $c_i = c_i^b e^{-\frac{1}{2}\beta q_i \phi_D}$ lead to wrong results.

2.4. Generalized PNP equations with concentration-dependent $\epsilon(c)$ and different boundary conditions. Ionic diffusion in electrolyte solution is an electro-diffusion process that is influenced by the electric field generated by the ion distribution itself, biomolecule(s) (if existing), and the environment. The PNP equations coupling the electric potential and ion concentration distributions provide an ideal model for describing this process [8, 22]. The PNP equations have been widely used to study the ion channels, nanopores, fuel cells, and other research areas [8, 7, 4, 2, 23, 6, 34]. The continuum PNP equations can be derived via different routes. They can be obtained from the microscopic model of Langevin trajectories in the limit of large damping and the absence of correlations of different ionic trajectories [29, 26], or from the variations of the free energy functional that includes the electrostatic free energy and the ideal component of the chemical potential [10]. As aforementioned, the previous variational method can only ensure consistency between the energy form and the PNP equations for vanishing boundary conditions for electric potential ϕ such

as on the whole space because they did not include the boundary interaction terms. In addition, an inhomogeneously concentration-dependent dielectric property has recently caused wide research interest [12, 14, 28, 13, 21, 20]. But little previous study is found to give a consistent dynamic model (such as PNP) for electrolyte solution when the dielectric coefficient is ionic concentration-dependent. This is also to be studied in the current subsection.

We start from the free energy functional given by (10) with generic Dirichlet and Neumann BCs. According to the constitutive relations, the flux J_i and the electrochemical potential μ_i of the i th species satisfy

$$J_i = -m_i c_i \nabla \mu_i.$$

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

$$(38) \quad \mu_i = \frac{\delta F}{\delta c_i} = q_i \phi(c) - \frac{1}{2} \epsilon'_i(c) \nabla \phi(c) \cdot \nabla \phi(c) + \beta^{-1} \ln(c_i/c_i^b).$$

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

$$\begin{aligned} \frac{\partial c_i}{\partial t} &= -\nabla \cdot J_i \\ &= \nabla \cdot \left(\beta D_i c_i \nabla \left\{ q_i \phi(c) - \frac{1}{2} \epsilon'_i(c) \nabla \phi(c) \cdot \nabla \phi(c) + \beta^{-1} \ln(c_i/c_i^b) \right\} \right) \\ &= \nabla \cdot \left(\beta D_i c_i \left(\frac{\nabla c_i}{\beta c_i} + \nabla \left(q_i \phi(c) - \frac{1}{2} \epsilon'_i(c) \nabla \phi(c) \cdot \nabla \phi(c) \right) \right) \right) \\ &= \nabla \cdot \left(D_i \left[\nabla c_i + \beta c_i \nabla \left(q_i \phi(c) - \frac{1}{2} \epsilon'_i(c) \nabla \phi(c) \cdot \nabla \phi(c) \right) \right] \right). \end{aligned}$$

Now we get a set of generalized self-consistent PNP equations with concentration-dependent variable dielectric (VDPNP):

$$(39) \quad -\nabla \cdot (\epsilon(c) \nabla \phi(c)) = \rho^f + \sum_{i=1}^K q_i c_i \quad \text{in } \Omega,$$

$$(40) \quad \frac{\partial c_i}{\partial t} = \nabla \cdot \left(D_i \left[\nabla c_i + \beta c_i \nabla \left(q_i \phi(c) - \frac{1}{2} \epsilon'_i(c) \nabla \phi(c) \cdot \nabla \phi(c) \right) \right] \right) \quad \text{in } \Omega_s, i = 1, 2, \dots, K.$$

$$\begin{aligned} \epsilon(c) \frac{\partial \phi}{\partial n} &= \sigma && \text{on } \Gamma_N, \\ \phi &= \phi_0 && \text{on } \Gamma_D, \\ c_i &= c_i^b && \text{on } \Gamma_D, \\ J_i \cdot n &= 0 && \text{on } \Gamma_m. \end{aligned}$$

If the dielectric coefficient does not depend on local ionic concentrations, (39) and (40) will reduce to the traditional PNP equations with the same boundary conditions:

$$(41) \quad -\nabla \cdot (\epsilon \nabla \phi(c)) = \rho^f + \sum_{i=1}^K q_i c_i \quad \text{in } \Omega,$$

$$(42) \quad \frac{\partial c_i}{\partial t} = \nabla \cdot (D_i[\nabla c_i + \beta c_i \nabla(q_i \phi(c))]) \quad \text{in } \Omega_s, i = 1, 2, \dots, K.$$

However, for simplicity, if ϵ does not depend on c , and based on the same boundary conditions but $\phi_0 \neq 0$, according to Theorem 2.3, the PNP equations from the incomplete energy form (9) take the form of

$$(43) \quad -\nabla \cdot (\epsilon \nabla \phi(c)) = \rho^f + \sum_{i=1}^K q_i c_i \quad \text{in } \Omega,$$

$$(44) \quad \frac{\partial c_i}{\partial t} = \nabla \cdot \left(D_i \left[\nabla c_i + \beta c_i \nabla \left(q_i \left[\phi(c) - \frac{1}{2} \phi_D(c) \right] \right) \right] \right) \quad \text{in } \Omega_s, i = 1, 2, \dots, K.$$

Obviously, this is inconsistent with the established physics in this area. The drift term in the right-hand side of (44) originates from the electric field driving ($\nabla \phi$) and should be irrelevant to ϕ_D , which is introduced only for mathematical analysis of the incomplete free energy form and shouldn't change the physical phenomenon. Therefore, this is actually another main reason to question the previous energy functionals. It also suggests that adding the boundary interactions into the free energy is necessary to make it consistent with PDEs. In subsection 2.4.2, we will give numerical simulations for a cylinder nanopore to further study the different current-voltage predictions from these two derived new PNP models. In the next subsection we will calculate the forms of energy law for different PNP systems and energy forms.

2.4.1. Energy dissipation law. The electro-diffusion process in electrolyte solution is an energy dissipation process (when no external forces or fields are applied). This requires that the evolutionary equation system, such as the PNP equations, need to satisfy the energy dissipation law. This subsection calculates and discusses the forms of energy law for different PNP systems and energy forms. First, consider a constant ϵ , and the total energy of the traditional PNP system (41)–(42) took a form as shown in [37] (please note here a slight difference from the form in [37] is that the entropy term takes $c_i \ln(c_i/c_i^b)$, which is unimportant),

$$(45) \quad F = \int_{\Omega} \left(k_B T \sum_{i=1}^K c_i \left[\ln \left(\frac{c_i}{c_i^b} \right) - 1 \right] + \frac{\epsilon}{2} |\nabla \phi|^2 \right) dV.$$

Consider the change of free energy w.r.t. time t ,

$$\frac{d}{dt} F = \int_{\Omega} \sum_{i=1}^K k_B T \frac{dc_i}{dt} \ln \left(\frac{c_i}{c_i^b} \right) dV + \int_{\Omega} \epsilon \nabla \phi \cdot \nabla \frac{d}{dt} \phi dV.$$

By integrating the second term by parts and using the divergence theorem, we can get

$$\begin{aligned} \frac{d}{dt} F &= \int_{\Omega} \sum_{i=1}^K k_B T \frac{dc_i}{dt} \ln \left(\frac{c_i}{c_i^b} \right) dV - \int_{\Omega} \phi \nabla \cdot \left(\epsilon \nabla \frac{d}{dt} \phi \right) dV + \int_{\Gamma} \phi \epsilon \frac{\partial}{\partial n} \left(\frac{d}{dt} \phi \right) dS \\ &= \int_{\Omega} \sum_{i=1}^K \left[k_B T \ln \left(\frac{c_i}{c_i^b} \right) + q_i \phi \right] \frac{dc_i}{dt} dV + \int_{\Gamma} \phi \frac{d}{dt} \left(\epsilon \frac{\partial \phi}{\partial n} \right) dS. \end{aligned}$$

Then the free energy (45) and the PNP system have been shown to satisfy the following energy law:

$$\begin{aligned}
 (46) \quad \frac{d}{dt}F &= - \int_{\Omega} \sum_{i=1}^K \frac{D_i}{k_B T} c_i |\nabla [k_B T \ln \left(\frac{c_i}{c_i^b} \right) + q_i \phi]|^2 dV + \int_{\Gamma_N} \phi \frac{d}{dt} \sigma dS + \int_{\Gamma_D} \phi_0 \frac{d}{dt} \left(\epsilon \frac{\partial \phi}{\partial n} \right) dS \\
 &+ \int_{\Gamma} \sum_{i=1}^K \frac{D_i}{k_B T} c_i \left(k_B T \ln \left(\frac{c_i}{c_i^b} \right) + q_i \phi \right) \frac{\partial}{\partial n} \left[k_B T \ln \left(\frac{c_i}{c_i^b} \right) + q_i \phi \right] dS \\
 &= - \int_{\Omega} \sum_{i=1}^K \left(\frac{D_i}{k_B T} c_i |\nabla \mu_i|^2 \right) dV + \int_{\Gamma} \sum_{i=1}^K \mu_i \frac{D_i}{k_B T} c_i \frac{\partial \mu_i}{\partial n} dS \\
 &+ \int_{\Gamma_N} \phi \frac{d}{dt} \sigma dS + \int_{\Gamma_D} \phi_0 \frac{d}{dt} \left(\epsilon \frac{\partial \phi}{\partial n} \right) dS,
 \end{aligned}$$

where $\mu_i := \frac{\delta F}{\delta c_i} = k_B T \ln(c_i/c_i^b) + q_i \phi$, which is just the chemical potential. The first two terms have direct physical meanings: energy dissipation and input flux of energy (chemical potential). The third term is a surface energy change due to the surface charge density variation. However, considering $-\epsilon \frac{\partial \phi}{\partial n}$ corresponds to the effective surface charge density σ_D^{eff} induced by the exterior region, the last term (with a minus sign of an energy change rate) has an incorrect sign of energy variation of the system. Whereas in the case when the PNP system has vanishing and nonflux boundary conditions, the system also leads to a correct energy dissipation law:

$$\begin{aligned}
 (47) \quad \frac{d}{dt}F &= \frac{d}{dt} \left[\int_{\Omega} \left(k_B T \sum_{i=1}^K c_i \left[\ln \left(\frac{c_i}{c_i^b} \right) - 1 \right] + \frac{\epsilon}{2} |\nabla \phi|^2 \right) dV \right] \\
 &= - \int_{\Omega} \sum_{i=1}^K \frac{D_i}{k_B T} c_i |\nabla \mu_i|^2 dV \leq 0.
 \end{aligned}$$

Now we consider the complete free energy form (10) with ionic concentration-dependent dielectric coefficient and consider the VDPNP system (39)–(40),

$$(48) \quad F = \int_{\Omega} \left(\frac{1}{2} \rho \phi + k_B T \sum_{i=1}^K c_i \left[\ln \left(\frac{c_i}{c_i^b} \right) - 1 \right] \right) dV + \frac{1}{2} \int_{\Gamma_N} \sigma \phi dS - \frac{1}{2} \int_{\Gamma_D} \epsilon(c) \frac{\partial \phi}{\partial n} \phi_0 dS.$$

We calculate the energy law for the free energy (48) and the VDPNP system (39)–(40),

$$\begin{aligned}
 (49) \quad \frac{d}{dt}F &= \int_{\Omega} \left(\sum_{i=1}^K k_B T \frac{dc_i}{dt} \ln \left(\frac{c_i}{c_i^b} \right) + \frac{1}{2} \frac{d\rho}{dt} \phi + \frac{1}{2} \frac{d\phi}{dt} \rho \right) dV \\
 &+ \frac{1}{2} \int_{\Gamma_N} \frac{d}{dt} (\sigma \phi) dS - \frac{1}{2} \int_{\Gamma_D} \frac{d}{dt} (\epsilon(c) \frac{\partial \phi}{\partial n} \phi_0) dS.
 \end{aligned}$$

By using the Poisson equation and Gauss theorem with nonhomogenous BC,

$$\begin{aligned}
 (50) \quad \int_{\Omega} \frac{1}{2} \frac{d\phi}{dt} \rho dV &= - \int_{\Omega} \frac{1}{2} \nabla \cdot (\epsilon(c) \nabla \phi) \frac{d\phi}{dt} dV \\
 &= \int_{\Omega} \frac{1}{2} \epsilon(c) \nabla \phi \cdot \nabla \frac{d\phi}{dt} dV - \frac{1}{2} \int_{\Gamma} \epsilon(c) \frac{\partial \phi}{\partial n} \frac{d\phi}{dt} dS \\
 &= - \frac{1}{2} \int_{\Omega} \left[\nabla \cdot \left(\epsilon(c) \nabla \frac{d\phi}{dt} \right) \right] \phi dV + \frac{1}{2} \int_{\Gamma} \epsilon(c) \phi \frac{\partial}{\partial n} \frac{d\phi}{dt} dS - \frac{1}{2} \int_{\Gamma} \epsilon(c) \frac{\partial \phi}{\partial n} \frac{d\phi}{dt} dS.
 \end{aligned}$$

As the dielectric coefficient is concentration-dependent, then

$$\begin{aligned}
 \int_{\Omega} \frac{1}{2} \frac{d\phi}{dt} \rho dV &= -\frac{1}{2} \int_{\Omega} \left[\frac{d}{dt} (\nabla \cdot (\epsilon(c) \nabla \phi)) - \nabla \cdot \left(\frac{\partial \epsilon(c)}{\partial c_i} \frac{dc_i}{dt} \nabla \phi \right) \right] \phi dV \\
 &+ \frac{1}{2} \int_{\Gamma} \epsilon(c) \phi \frac{\partial}{\partial n} \frac{d\phi}{dt} dS - \frac{1}{2} \int_{\Gamma} \epsilon(c) \frac{\partial \phi}{\partial n} \frac{d\phi}{dt} dS \\
 &= \frac{1}{2} \int_{\Omega} \frac{d\rho}{dt} \phi dV - \frac{1}{2} \int_{\Omega} \sum_{i=1}^K \frac{\partial \epsilon(c)}{\partial c_i} \frac{dc_i}{dt} |\nabla \phi|^2 dV \\
 (51) \quad &+ \frac{1}{2} \int_{\Gamma} \sum_{i=1}^K \frac{\partial \epsilon(c)}{\partial c_i} \frac{dc_i}{dt} \frac{\partial \phi}{\partial n} \phi dS + \frac{1}{2} \int_{\Gamma} \epsilon(c) \phi \frac{\partial}{\partial n} \frac{d\phi}{dt} dS - \frac{1}{2} \int_{\Gamma} \epsilon(c) \frac{\partial \phi}{\partial n} \frac{d\phi}{dt} dS.
 \end{aligned}$$

Take this equation into (49). Then

$$\begin{aligned}
 \frac{d}{dt} F &= \int_{\Omega} \left(\sum_{i=1}^K k_B T \frac{dc_i}{dt} \ln \left(\frac{c_i}{c_i^b} \right) + \frac{d\rho}{dt} \phi - \frac{1}{2} \sum_{i=1}^K \frac{\partial \epsilon(c)}{\partial c_i} \frac{dc_i}{dt} |\nabla \phi|^2 \right) dV \\
 &+ \frac{1}{2} \int_{\Gamma} \sum_{i=1}^K \frac{\partial \epsilon(c)}{\partial c_i} \frac{dc_i}{dt} \frac{\partial \phi}{\partial n} \phi dS + \frac{1}{2} \int_{\Gamma} \epsilon(c) \phi \frac{d}{dt} \frac{\partial \phi}{\partial n} dS - \frac{1}{2} \int_{\Gamma} \epsilon(c) \frac{\partial \phi}{\partial n} \frac{d\phi}{dt} dS \\
 &+ \frac{1}{2} \int_{\Gamma_N} \frac{d}{dt} (\sigma \phi) dS - \frac{1}{2} \int_{\Gamma_D} \frac{d}{dt} \left(\epsilon(c) \frac{\partial \phi}{\partial n} \phi_0 \right) dS \\
 &= \int_{\Omega} \left(\sum_{i=1}^K \frac{dc_i}{dt} \left[k_B T \ln \left(\frac{c_i}{c_i^b} \right) + q_i \phi - \frac{1}{2} \frac{\partial \epsilon(c)}{\partial c_i} |\nabla \phi|^2 \right] \right) dV \\
 &+ \int_{\Gamma_N} \phi \frac{d}{dt} \sigma dS - \int_{\Gamma_D} \epsilon(c) \frac{\partial \phi}{\partial n} \frac{d}{dt} \phi_0 dS.
 \end{aligned}$$

By using the transport equations,

$$\frac{dc_i}{dt} = \nabla \cdot \left(\frac{D_i}{k_B T} c_i \nabla \left[k_B T \ln \left(\frac{c_i}{c_i^b} \right) + q_i \phi - \frac{1}{2} \frac{\partial \epsilon(c)}{\partial c_i} |\nabla \phi|^2 \right] \right).$$

We then obtain the energy law of form (48) for the generalized PNP system

$$\begin{aligned}
 \frac{d}{dt} F &= - \int_{\Omega} \sum_{i=1}^K \left(\frac{D_i}{k_B T} c_i |\nabla \mu_i^{new}|^2 \right) dV + \int_{\Gamma} \sum_{i=1}^K \mu_i^{new} \frac{D_i}{k_B T} c_i \frac{\partial \mu_i^{new}}{\partial n} dS \\
 (52) \quad &+ \int_{\Gamma_N} \phi \frac{d}{dt} \sigma dS - \int_{\Gamma_D} \epsilon(c) \frac{\partial \phi}{\partial n} \frac{d}{dt} \phi_0 dS,
 \end{aligned}$$

where $\mu_i^{new} = k_B T \ln(c_i/c_i^b) + q_i \phi - \frac{1}{2} \frac{\partial \epsilon(c)}{\partial c_i} |\nabla \phi|^2$, which is just the chemical potential of the generalized system with $\epsilon(c)$ (see (38)). Now, we can see that the chemical potential in the first two terms is replaced by the corresponding modified form μ^{new} in the case of ionic concentration-dependent dielectric permittivity, which is consistent with the generalized PNP equations. At the same time, the four terms also have obvious physical meanings, respectively: energy dissipation, input flux of energy, a surface energy change term due to the surface charge density variation, and a surface energy change term due to the boundary potential variation (with a correct sign here).

If the PNP system has vanishing and nonflux boundary conditions, (52) also leads to an energy dissipation law similar to (47).

As a comparison, we also similarly calculate the energy law for the PNP free energy form without boundary terms as in (7):

$$\begin{aligned}
 \frac{d}{dt} F &= \frac{d}{dt} \left[\int_{\Omega} \left(\frac{1}{2} \rho \phi + k_B T \sum_{i=1}^K c_i \left[\ln \left(\frac{c_i}{c_i^b} \right) - 1 \right] \right) dV \right] \\
 &= - \int_{\Omega} \sum_{i=1}^K \left(\frac{D_i}{k_B T} c_i |\nabla \mu_i|^2 \right) dV + \int_{\Gamma} \sum_{i=1}^K \mu_i \frac{D_i}{k_B T} c_i \frac{\partial \mu_i}{\partial n} dS \\
 (53) \quad &+ \frac{1}{2} \int_{\Gamma_N} \left[\phi \frac{d}{dt} \sigma - \sigma \frac{d}{dt} \phi \right] dS + \frac{1}{2} \int_{\Gamma_D} \left[\phi_0 \frac{d}{dt} \left(\epsilon \frac{\partial \phi}{\partial n} \right) - \epsilon \frac{\partial \phi}{\partial n} \frac{d}{dt} \phi_0 \right] dS,
 \end{aligned}$$

where $\mu_i = k_B T \ln(c_i/c_i^b) + q_i \phi$. Again, as discussed above, we find that in each of the last two surface energy terms there is an incorrect sign of energy changing rate on the boundary, which is inconsistent with the energy law.

The above analysis of energy law is another indication that the addition of the boundary interaction term to the proposed free energy functional in this work is reasonable and necessary.

2.4.2. Numerical simulation in a cylinder nanopore system. In this subsection, we present an example with a cylinder nanopore to further investigate the difference between the standard traditional PNP and the “distorted” PNP models. A cylinder nanopore with a height of 50\AA and a pore radius of 2\AA is placed in the middle of a cubic box of $100\text{\AA} \times 100\text{\AA} \times 100\text{\AA}$. A charge density of $-0.02C/m^2$ is set on the inner surface of the nanopore and the potential on the lower boundary of the cubic box is fixed to be zero, while the upper boundary values (taken as membrane potentials) change from -200mV to 200mV with a step length of 50mV . In this example, we use a finite element method to solve these three-dimensional (3-D) PNP equations in the solvent region Ω_s and do not consider the molecular domain Ω_m . The geometry and a mesh of the cylinder nanopore is illustrated in Figure 3.

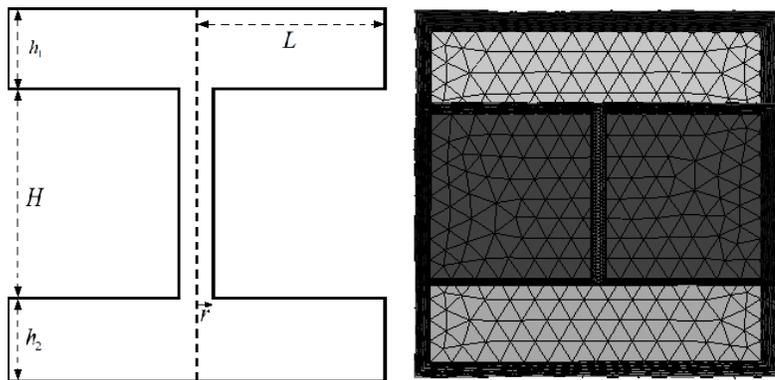


FIG. 3. The geometry and mesh of the cylinder nanopore.

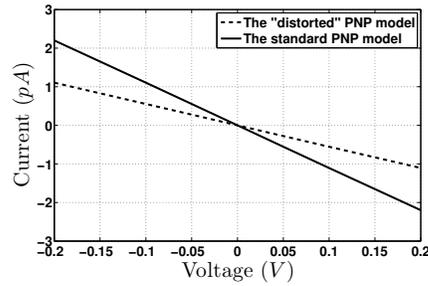


FIG. 4. The current voltage characteristics obtained with the traditional (solid line) and “distorted” (dashed line) PNP models at bulk concentration 0.1M and membrane potential from $-0.2V$ to $0.2V$.

The electrical current of the traditional PNP model across the pore can be calculated as

$$I_z = - \sum_i q_i \int_S D_i \left(\frac{\partial c_i}{\partial z} + \frac{q_i}{k_B T} c_i \frac{\partial \phi}{\partial z} \right) dx dy,$$

where S is a cut plane at any cross section inside the pore. For the distorted PNP model, (43) and (44) from incomplete energy form (9), the electrical current across the pore is calculated as

$$I_z = - \sum_i q_i \int_S D_i \left(\frac{\partial c_i}{\partial z} + \frac{q_i}{k_B T} c_i \frac{\partial (\phi - \frac{1}{2} \phi_D)}{\partial z} \right) dx dy.$$

In the PNP model, the current can be split into two parts: the concentration diffusion part

$$I_{diff} = - \sum_i q_i \int_S D_i \frac{\partial c_i}{\partial z} dx dy$$

and the potential drift part

$$I_{drift} = - \sum_i q_i \int_S D_i \left(\frac{q_i}{k_B T} c_i \frac{\partial \phi}{\partial z} \right) dx dy.$$

The “distorted” PNP from incomplete energy form has a similar concentration diffusion part but a different potential drift part

$$I_{drift} = - \sum_i q_i \int_S D_i \left(\frac{q_i}{k_B T} c_i \frac{\partial (\phi - \frac{1}{2} \phi_D)}{\partial z} \right) dx dy.$$

Through comparison between the currents calculated by the PNP model and the “distorted” PNP model, it is observed that with such a system setup the magnitude of current in the “distorted” PNP model derived from incomplete energy tends to be smaller than that in the traditional PNP model (see Figure 4). The current resulting from the potential drift part is dominant compared to that from the concentration diffusion part (compare the order of magnitude in Figures 5(a) and 5(b)). It is also observed that in the “distorted” PNP model the potential drift part significantly

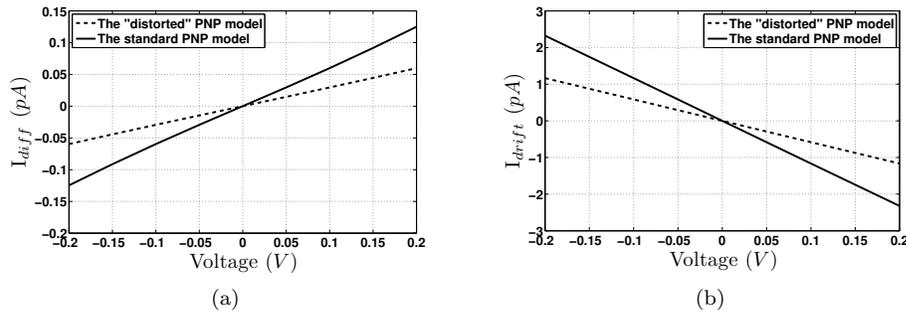


FIG. 5. Contribution of (a) the diffusion and (b) the drift parts of current in the traditional (solid line) and “distorted” (dashed line) PNP models.

underestimates the magnitude of the current, whereas the diffusion part exposes the opposite property.

3. Conclusions. In this paper, we present a mean field free energy functional of a dielectrically inhomogeneous electrolyte solution in a bounded domain with genetic Neumann/Dirichlet boundary conditions for potential. In this complete energy functional with a new boundary energy term, the boundary interaction terms are physically reasonable, and are also crucial in mathematical analysis in order to consistently derive the correct PB, PNP, and other possibly relevant equations. The appropriateness is supported from different aspects: physical interpretation, variational analysis of the functionals and the resulted PDE models, comparison with the Euler–Lagrange form of the Poisson equation, analysis of the energy laws of the corresponding systems, and numerical examples. We also show that in the presence of nonhomogenous Dirichlet boundary conditions for electric potential, the traditional energy form is not consistent with the traditional PB and PNP equations. Using the variational method of the previous energy functional (usually by introducing a corresponding homogeneous problem) may result in “distorted” (nonphysical) Boltzmann distributions and PB/PNP models. Our numerical examples demonstrate the significant deviations of the results originating from the “distorted” models. Furthermore, in a particularly interesting case when the dielectric coefficient of the electrolyte solution depends on the local ionic concentrations, we derive the VDPB and VDPNP equations from our complete free energy functional. In fact, as can be seen in this paper, for any Poisson system (not limited to electrolyte), there should be a similar boundary energy term or other equivalent form in the energy functional when the system is bounded. As for more complicate boundary conditions, it may be still an open question for free energy functional analysis.

Acknowledgments. We gratefully acknowledge the anonymous referees for their helpful comments. The authors thank our group student Hanlin Li for his help.

REFERENCES

- [1] A. ABRASHKIN, D. ANDELMAN, AND H. ORLAND, *Dipolar Poisson-Boltzmann equation: Ions and dipoles close to charge interfaces*, Phys. Rev. Lett., 99 (2007), 077801, <https://doi.org/10.1103/PhysRevLett.99.077801>.

- [2] D. S. BOLINTINEANU, A. SAYYED-AHMAD, H. T. DAVIS, AND Y. N. KAZNESSIS, *Poisson-Nernst-Planck models of nonequilibrium ion electrodiffusion through a protegrin transmembrane Pore*, PLoS Comput. Biol., 5 (2009), e1000277, <https://doi.org/10.1371/journal.pcbi.1000277>.
- [3] F. BOOTH, *Dielectric constant of polar liquids at high field strengths*, J. Chem. Phys., 23 (1955), pp. 453–457, <https://doi.org/10.1063/1.1742009>.
- [4] A. E. CÁRDENAS, R. D. COALSON, AND M. G. KURNIKOVA, *Three-dimensional Poisson-Nernst-Planck theory studies: Influence of membrane electrostatics on gramicidin a channel conductance*, Biophys. J., 79 (2000), pp. 80–93, [https://doi.org/10.1016/S0006-3495\(00\)76275-8](https://doi.org/10.1016/S0006-3495(00)76275-8).
- [5] D. L. CHAPMAN, *A contribution to the theory of electrocapillarity*, Philos. Mag., 25 (1913), pp. 475–481, <https://doi.org/10.1080/14786440408634187>.
- [6] D. CONSTANTIN AND Z. S. SIWY, *Poisson-Nernst-Planck model of ion current rectification through a nanofluidic diode*, Phys. Rev. E, 76 (2007), 041202, <https://doi.org/10.1103/PhysRevE.76.041202>.
- [7] B. EISENBERG, *Ionic channels in biological membranes: Natural nanotubes*, Acc. Chem. Res., 31 (1998), pp. 117–123, <https://doi.org/10.1109/IWCE.1998.742714>.
- [8] R. S. EISENBERG AND D. P. CHEN, *Poisson-Nernst-Planck (PNP) Theory of an open ionic channel*, Biophys. J., 64 (1993), A22.
- [9] F. FOGOLARI AND J. M. BRIGGS, *On the variational approach to Poisson-Boltzmann free energies*, Chem. Phys. Lett., 281 (1997), pp. 135–139, [https://doi.org/10.1016/S0009-2614\(97\)01193-7](https://doi.org/10.1016/S0009-2614(97)01193-7).
- [10] D. GILLESPIE, W. NONNER, AND R. S. EISENBERG, *Coupling Poisson-Nernst-Planck and density functional theory to calculate ion flux*, J. Phys. Condens. Mat., 14 (2002), pp. 12129–12145, <https://doi.org/10.1088/0953-8984/14/46/317>.
- [11] M. K. GILSON, M. E. DAVIS, B. A. LUTY, AND J. A. MCCAMMON, *Computation of electrostatic forces on solvated molecules using the Poisson-Boltzmann equation*, J. Phys. Chem., 97 (1993), pp. 3591–3600, <https://doi.org/10.1021/j100116a025>.
- [12] J. B. HASTED, D. M. RITSON, AND C. H. COLLIE, *Dielectric Properties of Aqueous Ionic Solutions. Parts I and II*, J. Chem. Phys., 16 (1948), pp. 1–21, <https://doi.org/10.1063/1.1746645>.
- [13] B. HESS, C. HOLM, AND N. VAN DER VEGT, *Modeling multibody effects in ionic solutions with a concentration dependent dielectric permittivity*, Phys. Rev. Lett., 96 (2006), 147801, <https://doi.org/10.1103/PhysRevLett.96.147801>.
- [14] J. B. HUBBARD, *Dielectric Dispersion and dielectric friction in electrolyte solutions. II*, J. Chem. Phys., 68 (1978), pp. 1649–1664, <https://doi.org/10.1063/1.435931>.
- [15] J. B. HUBBARD AND L. ONSAGER, *Dielectric Dispersion and Dielectric Friction in Electrolyte Solutions. I*, J. Chem. Phys., 67 (1977), pp. 4850–4857, <https://doi.org/10.1063/1.434664>.
- [16] J. D. JACKSON, *Classical Electrodynamics*, 3rd ed., Wiley, New York, 1999.
- [17] C.-C. LEE, H. LEE, Y. K. HYON, T.-C. LIN, AND C. LIU, *New Poisson-Boltzmann type equations: One-dimensional solutions*, Nonlinearity, 24 (2010), pp. 431–458, <https://doi.org/10.1088/0951-7715/24/2/004>.
- [18] B. LI, *Continuum Electrostatics for ionic solutions with non-uniform ionic sizes*, Nonlinearity, 22 (2009), pp. 811–833, <https://doi.org/10.1088/0951-7715/22/4/007>.
- [19] B. LI, *Minimization of electrostatic free energy and the Poisson-Boltzmann equation for molecular solvation with implicit solvent*, SIAM J. Math. Anal., 40 (2009), pp. 2536–2566, <https://doi.org/10.1137/080712350>.
- [20] B. LI, J. Y. WEN, AND S. G. ZHOU, *Mean-field theory and computation of electrostatics with ionic concentration dependent dielectrics*, Commun. Math. Sci., 14 (2016), pp. 249–271, <https://doi.org/10.4310/CMS.2016.v14.n1.a10>.
- [21] H. L. LI AND B. Z. LU, *An ionic concentration and size dependent dielectric permittivity Poisson-Boltzmann model for biomolecular solvation studies*, J. Chem. Phys., 141 (2014), 024115, <https://doi.org/10.1063/1.4887342>.
- [22] B. Z. LU, M. J. HOLST, J. A. MCCAMMON, AND Y. C. ZHOU, *Poisson-Nernst-Planck equations for simulating biomolecular diffusion-reaction processes I: Finite element solutions*, J. Comput. Phys., 229 (2010), pp. 6979–6994, <https://doi.org/10.1016/j.jcp.2010.05.035>.
- [23] B. Z. 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, <https://doi.org/10.1016/j.bpj.2011.03.059>.
- [24] B. Z. LU, Y. C. ZHOU, M. J. HOLST, AND J. A. MCCAMMON, *Recent progress in numerical methods for the Poisson-Boltzmann equation in biophysical applications*, Commun. Comput. Phys., 3 (2008), pp. 973–1009.

- [25] B. Z. LU, Y. C. ZHOU, G. A. HUBER, S. D. BOND, M. J. HOLST, AND J. A. MCCAMMON, *Electrodifffusion: A continuum modeling framework for biomolecular systems with realistic spatiotemporal resolution*, J. Chem. Phys., 127 (2007), 135102, <https://doi.org/10.1063/1.2775933>.
- [26] B. NADLER, Z. SCHUSS, A. SINGER, AND R. S. EISENBERG, *Ionic diffusion through confined geometries: from Langevin equations to partial differential equations*, J. Phys. Condens. Mat., 16 (2004), pp. S2153–S2165, <https://doi.org/10.1088/0953-8984/16/22/015>.
- [27] 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, <https://doi.org/10.1063/1.4906319>.
- [28] K. NÖRTEMANN, J. HILLAND, AND U. KAATZE, *Dielectric properties of aqueous NaCl solutions at microwave frequencies*, J. Phys. Chem. A, 101 (1997), pp. 6864–6869, <https://doi.org/10.1021/jp971623a>.
- [29] Z. SCHUSS, B. NADLER, AND R. S. EISENBERG, *Derivation of Poisson and Nernst-Planck Equations in a bath and channel from a molecular model*, Phys. Rev. E, 64 (2001), 036116, <https://doi.org/10.1103/PhysRevE.64.036116>.
- [30] K. A. SHARP AND B. HONIG, *Calculating Total electrostatic energies with the nonlinear Poisson-Boltzmann equation*, J. Phys. Chem., 94 (1990), pp. 7684–7692, <https://doi.org/10.1021/j100382a068>.
- [31] Z. S. SIWY, *Ion-current rectification in nanopores and nanotubes with broken symmetry*, Adv. Funct. Mater., 16 (2006), pp. 735–746, <https://doi.org/10.1002/adfm.200500471>.
- [32] B. TU, M. X. CHEN, Y. XIE, L. B. ZHANG, B. EISENBERG, AND B. Z. LU, *A parallel finite element simulator for ion transport through three-dimensional ion channel systems*, J. Comput. Chem., 34 (2013), pp. 2065–2078, <https://doi.org/10.1002/jcc.23329>.
- [33] L. VRBKA, M. LUND, I. KALCHER, J. DZUBIELLA, R. R. NETZ, AND W. KUNZ, *Ion-specific thermodynamics of multicomponent electrolytes: A hybrid HNC/MD approach*, J. Chem. Phys., 131 (2009), 154109, <https://doi.org/10.1063/1.3248218>.
- [34] G. W. WEI, Q. ZHENG, Z. CHEN, AND K. L. XIA, *Variational multiscale models for charge transport*, SIAM Rev., 54 (2012), pp. 699–754, <https://doi.org/10.1137/110845690>.
- [35] Y. Z. WEI, P. CHIANG, AND S. SRIDHAR, *Ion size effects on the dynamic and static dielectric properties of aqueous alkali Solutions*, J. Chem. Phys., 96 (1992), pp. 4569–4573, <https://doi.org/10.1063/1.462792>.
- [36] Y. Z. WEI AND S. SRIDHAR, *Dielectric spectroscopy up to 20 GHz of LiCl/H₂O Solutions*, J. Chem. Phys., 92 (1990), pp. 923–928, <https://doi.org/10.1063/1.458074>.
- [37] S. X. XU, P. SHENG, AND C. LIU, *An energetic variational approach for ion transport*, Commun. Math. Sci., 12 (2013), pp. 779–789, <https://doi.org/10.4310/CMS.2014.v12.n4.a9>.
- [38] Z. L. XU, J. Y. MIAO, N. WANG, W. J. WEN, AND P. SHENG, *Digital flow control of electroosmotic pump: Onsager coefficients and interfacial parameters determination*, Sol. St. Comm., 151 (2011), pp. 440–445, <https://doi.org/10.1016/j.ssc.2010.12.040>.