Singular perturbation solutions of steady-state Poisson-Nernst-Planck systems

Xiang-Sheng Wang
Department of Mathematics, Southeast Missouri State University, Cape Girardeau, Missouri 63701, USA

Dongdong He
School of Aerospace Engineering and Applied Mechanics, Tongji University, Shanghai 200092, China

Jonathan J. Wylie
Department of Mathematics, City University of Hong Kong, Tat Chee Avenue, Hong Kong

Huaxiong Huang*
Department of Mathematics and Statistics, York University, Toronto, Ontario, Canada M3J 1P3
(Received 6 April 2013; published 26 February 2014)

We study the Poisson-Nernst-Planck (PNP) system with an arbitrary number of ion species with arbitrary valences in the absence of fixed charges. Assuming point charges and that the Debye length is small relative to the domain size, we derive an asymptotic formula for the steady-state solution by matching outer and boundary layer solutions. The case of two ionic species has been extensively studied, the uniqueness of the solution has been proved, and an explicit expression for the solution has been obtained. However, the case of three or more ions has received significantly less attention. Previous work has indicated that the solution may be nonunique and that even obtaining numerical solutions is a difficult task since one must solve complicated systems of nonlinear equations. By adopting a methodology that preserves the symmetries of the PNP system, we show that determining the outer solution effectively reduces to solving a single scalar transcendental equation. Due to the simple form of the transcendental equation, it can be solved numerically in a straightforward manner. Our methodology thus provides a standard procedure for solving the PNP system and we illustrate this by solving some practical examples. Despite the fact that for three ions, previous studies have indicated that multiple solutions may exist, we show that all except for one of these solutions are unphysical and thereby prove the existence and uniqueness for the three-ion case.

DOI: 10.1103/PhysRevE.89.022722 PACS number(s): 87.16.Vy, 41.20.Cv

I. INTRODUCTION

In biological cells, ionic species flow through cell membranes that are extremely thin (of the order of a few nanometers) and the flux of ions is affected by both ionic concentration gradients and the electric field. Although there are a number of models that have been used to describe such systems (e.g., Maxwell-Boltzmann equations and Langevin systems), the Poisson-Nernst-Planck (PNP) system has the advantage that it can capture many of the important features of cross-membrane flow while being simple enough to be amenable to analysis. Therefore, PNP-type systems are widely used in the modeling of the flow of ions across biological cells [1–9]. Such systems have also proved to be highly adept in modeling electrokinetic problems in industrial electrochemistry [10]. We also note that much of the early work on PNP systems was motivated by the fluxes of electrons and holes in semiconductor physics (see, for example, [11–14]). In fact, the PNP model can be derived from a Langevin model in the limit of large damping and neglecting the finite size of ions and correlations between ionic trajectories [15]. There has been extensive work on incorporating the effects of the finite size of ions [16–38]. However, in general, these models tend to be significantly more complicated than systems composed of point charges and therefore considerably more difficult to analyze. There have also been numerous extensions to the PNP system including [19,20,22–25,31,32] adding fluid flow [14,39] and incorporating the effects of induced charge [15,40]. Transient effects have also been considered by a number of authors [41–43]. In particular, Ghosal and Chen studied a model for capillary electrophoresis and showed that propagating nonlinear waves can result [44,45]. Many studies have focused on the one-dimensional problem, but Bazant [46] showed that the electroneutral Nernst-Planck equations are conformally invariant and that for particular boundary conditions, the solution of a two-dimensional problem in a general geometrical setting can be mapped onto an equivalent one-dimensional problem. In contrast, for boundary conditions that are not conformally invariant, the problem is more complicated and surface conduction of ions can occur [42,47,48].

In the case of two ionic species, there has been extensive analysis of the PNP system to understand its dynamics. The relation between the current and voltage has been studied using asymptotic analysis [49,50]. The qualitative properties of the steady states have been examined using a variety of techniques [51,52]. For the special case (referred to as the 1:−1 case) when there are only two species of ions with unit positive and unit negative charges, Barcilon *et al.* [51] obtained an explicit asymptotic formula using matched asymptotic expansions. Uniqueness of solutions for the special 1:−1 case was obtained in [52]. Asymptotic methods have been used to study the 1:−1 case in a three-dimensional funnel [53]. The system has also been studied using innovative geometric techniques by

*hhuang@yorku.ca

Liu [54], who proved the existence and (local) uniqueness of solutions for the case when the two types of ions have arbitrary valences, referred to as the α:β case hereafter.

Multiple-valued phenomena in biological channels clearly have important consequences for cell dynamics and understanding the mechanisms that underlie these phenomena is crucial if one wishes to manipulate the behavior of cells [55,56]. Therefore, one of the most fundamental scientific questions in the flow of ions through cell membranes is under what circumstances multiple-valued phenomena (nonuniqueness) can occur. Uniqueness has been proven for two ions, but for the case of an additional fixed charge, a number of authors have shown that nonunique behavior can occur [50,57–60]. This raises the interesting question of whether nonunique behavior can occur in systems without fixed charge, but with more than two ions.

Most of the early work focused on the case of only two ions due to the fact that much of the initial interest in PNP systems was motivated by semiconductor devices that only contain electrons and holes. In contrast, in biological channels, multiple ion species are involved in a number of situations. For example, voltage activated sodium channels that are responsible for generating action potentials are known to involve three ions (sodium, chloride, and calcium). Another example involves the loss of hemostasis during a dialysis procedure. In fact, calcium ions are responsible for a number of fundamental mechanisms that are ubiquitous in biological cells. These include acting as a messenger ion and performing signaling operations. In modeling such processes, it is hence imperative to include calcium ions along with the univalent ions (sodium, potassium, and chloride). Therefore, in practice we often need to find solutions of a more general PNP system with more than two species of ions of arbitrary valences. In particular, it is desirable to have a relatively simple expression or solution methodology for computing ion fluxes given by the generic steady-state PNP system for three (or more) ions.

The problem for three or more ions was first considered by Leuchtag [61], who showed that the electric field satisfies a nonlinear high-order ordinary differential equation. However, the nonlinearity and complexity of the ordinary differential equation and the fact that the boundary conditions involve high-order derivatives make obtaining the solution and considering nonuniqueness a formidable task. An important breakthrough was made by Liu [62], who considered the problem for three or more ions using a geometrical framework. He used this framework to address questions of existence and uniqueness and also showed that the problem could be reduced to a complicated system of nonlinear equations. He noted that the multiple-ion case is significantly more challenging than the two-ion case from the viewpoint of rigorous analysis and that even solving such a system numerically represents a challenging task. He was also able to consider a special case in which he was able to find multiple solutions of the nonlinear algebraic equations indicating that multiple solutions may exist for the case of three ions. Liu also noted that his approach allows for the consideration of piecewise constant fixed charge. An analytical solution for the special case of valences 1:−1:2 (representing sodium, chloride, and calcium) has also been obtained by direct integration [63].

In this paper, we assume point charges and derive an asymptotic solution of the general problem in the absence of fixed charges using matched asymptotic expansions. By carefully maintaining the symmetries of the PNP system, we show that the outer solution can be determined by solving a single scalar transcendental equation rather than the systems of equations found by previous authors. The scalar transcendental equation we find is similar to those obtained in the study of delay-differential equations and it can be easily dealt with using standard numerical techniques. The boundary layer solutions are given in terms of a generalization of elliptic integrals that can also be evaluated in a straightforward way. Therefore, in contrast to previous methods, our formulation allows us to determine solutions in a simple and direct way. We demonstrate the effectiveness of our method by solving several practically relevant special cases. If we restrict our attention to physically relevant solutions with non-negative ionic concentrations, we use our framework for three ions to prove the existence and uniqueness of solutions. We note that, in the case $n = 3$, Liu [62] found an example of nonunique solutions to his system of nonlinear equations. However, this example contained a solution of the nonlinear equations that corresponds to a solution of the PNP system that has negative ionic concentrations and is thus unphysical.

The rest of this paper is organized as follows. In Sec. II, we formulate the problem. In Sec. III, we derive the outer solution and boundary layer solutions. As our main result, we present a uniformly valid asymptotic expression for the solution. Two special cases are considered in Sec. IV, namely, the α:β and 2:1:−1 cases, and we validate our results by comparing our asymptotic solution with numerical solutions and those obtained in the literature. The existence and uniqueness of solutions for two and three ions is given in Sec. V. A summary and discussion are given in Sec. VI.

II. FORMULATION

In this paper, we consider a generic PNP problem for point charges that consists of n ion species with valences z_i and concentrations c_i. The electric potential ϕ is governed by the Poisson equation

$$-\nabla \cdot (\epsilon_* \nabla \phi) = \sum_{i=1}^{n} e z_i c_i, \tag{1}$$

where ϵ_* is the permittivity and e is the elementary charge. The concentration of ions is determined by the Nernst-Planck equations

$$\frac{\partial c_i}{\partial t} + \nabla \cdot f_i = 0, \tag{2}$$

where f_i is the concentration flux of the ith ion given by

$$f_i = -D_i \left(\nabla c_i + \frac{e z_i}{k_B T} c_i \nabla \phi \right) \tag{3}$$

$$\equiv -D_i J_i. \tag{4}$$

Here D_i is the diffusion coefficient of the ith ion, k_B is the Boltzmann constant, and T is the absolute temperature. We have also introduced the quantity J_i, which represents the concentration flux divided by the diffusion coefficient for each ion.

We will consider the steady states for the one-dimensional problem of flow of ions across a membrane of width L and constant permittivity with the potential and concentrations of each species prescribed on either side of the membrane. We nondimensionalize lengths by L, the potential ϕ by $k_B T/e$, and the concentrations c_i by the characteristic ionic concentration, which we denote $\mathcal{C}$ to obtain the dimensionless equations

$$-\varepsilon^2 \frac{d^2\phi}{dx^2} = \sum_{i=1}^{n} z_i c_i \tag{5}$$

and

$$\frac{dJ_i}{dx} = 0, \quad -J_i = \frac{dc_i}{dx} + z_i c_i \frac{d\phi}{dx}. \tag{6}$$

Here the normalized fluxes J_i are unknown constants and the dimensionless parameter ε is given by

$$\varepsilon = \sqrt{\frac{\epsilon_* k_B T}{e^2 L^2 \mathcal{C}}}. \tag{7}$$

Physically, ε represents the ratio of the Debye length (which is the length scale over which ions screen electric fields) to the membrane width L [52]. In what follows, we shall assume that this ratio is small, namely,

$$\varepsilon \ll 1. \tag{8}$$

We are interested in obtaining an asymptotic solution to the PNP system with boundary conditions

$$c_i = c_{iL}, \quad \phi = \phi_L \quad \text{for} \quad x = 0; \tag{9}$$

$$c_i = c_{iR}, \quad \phi = \phi_R \quad \text{for} \quad x = 1. \tag{10}$$

We note that for physically meaningful solutions, we will require that the concentrations of all ions are non-negative, namely, $c_i \geqslant 0$. The assumption of constant concentrations at the boundaries is common in biology, but is also used in membrane science [39]. In the latter case, the assumption may break down due to a current-induced membrane discharge effect [64]. Furthermore, in the case of electrodes at which Faradaic reactions occur, the boundary conditions must relate ion fluxes to the rates of reaction [65–68].

III. MAIN RESULT: A UNIFORM ASYMPTOTIC SOLUTION

We can divide the interval $[0,1]$ into two boundary layers ($x \sim 0$ and $x \sim 1$, respectively) and a single outer region away from the boundaries.[1] Posing an asymptotic expansion for small ε and retaining only the leading-order terms, the outer solution satisfies the limited PNP equations

$$0 = \sum_{i=1}^{n} z_i c_i^o, \tag{11}$$

$$-J_i = \frac{dc_i^o}{dx} + z_i c_i^o \frac{d\phi^o}{dx}, \tag{12}$$

where the superscript o represents the leading-order outer solution. By introducing the scale $X = x/\varepsilon$, we obtain the leading-order equations near the left boundary layer $x \sim 0$:

$$-\frac{d^2\phi^l}{dX^2} = \sum_{i=1}^{n} z_i c_i^l, \tag{13}$$

$$0 = \frac{dc_i^l}{dX} + z_i c_i^l \frac{d\phi^l}{dX}, \tag{14}$$

where the superscript l represents the leading-order left boundary solution. Similarly, using the scale $Y = (1-x)/\varepsilon$, the leading-order system near the right boundary layer $x \sim 1$ is given by

$$-\frac{d^2\phi^r}{dY^2} = \sum_{i=1}^{n} z_i c_i^r, \tag{15}$$

$$0 = \frac{dc_i^r}{dY} + z_i c_i^r \frac{d\phi^r}{dY}, \tag{16}$$

where the superscript r represents the leading-order right boundary solution. The boundary conditions (9) and (10) are written as

$$\phi^l(0) = \phi_L, \quad c_i^l(0) = c_{iL}; \tag{17}$$

$$\phi^r(0) = \phi_R, \quad c_i^r(0) = c_{iR}. \tag{18}$$

In the following two subsections, we will obtain explicit solutions to the PNP systems in the outer region and boundary layers, respectively. The unknown fluxes, the values of outer solution and boundary layer solutions in the overlapped region, and the constants of integration are determined by matching the outer and boundary layer solutions. Finally, we present a uniformly valid asymptotic formula as our main result in the last subsection.

A. Outer solution

From (11) and (12) we have

$$\frac{d\phi^o}{dx} = -\frac{\sum_{i=1}^n z_i J_i}{\sum_{i=1}^n z_i^2 c_i^o}.$$

For physical solutions, we require the concentrations $c_i^o \geqslant 0$, which implies that ϕ^o is a monotonic function of x if $\sum_{i=1}^n z_i J_i \neq 0$. The degenerate case $\sum_{i=1}^n z_i J_i = 0$ is significantly simpler than the generic case and will be considered in Sec. III D. For the generic case, the physical outer solution ϕ^o is monotonic and thus invertible. Equation (12) becomes linear if we regard ϕ^o as a variable

$$-J_i \dot{x} = \dot{c}_i^o + z_i c_i^o, \tag{19}$$

where the dot denotes differentiation with respect to ϕ^o. Equation (19) can be written as

$$-J_i e^{z_i \phi^o} \dot{x} = \frac{d}{d\phi^o}\left(e^{z_i \phi^o} c_i^o\right)$$

and since x is monotonic we observe that $e^{z_i \phi^o} c_i^o$ is monotonic. Thus, the concentrations c_i^o are always non-negative since $c_i^o(0)$ and $c_i^o(1)$ are non-negative. Therefore, we have shown that $c_i^o > 0$ for $i = 1, \ldots, n$ if and only if x is a monotonic

[1]This is due to the fact that internal layers cannot exist, as discussed in Sec. VI B.

function of ϕ^o or, alternatively, ϕ^o is a monotonic function of x. That is, only solutions with monotonic $x(\phi^o)$ are physically relevant. We note that the oscillatory outer solutions obtained in Example 5.1 in [62] are not physical because the concentrations are negative in the outer region (even though they have been verified to be positive at the boundaries).

We now proceed to obtain the solution. Following [61], we apply the Vandermonde matrix method and multiply (19) by $(-z_i)^k$ and take the sum over all i to obtain

$$-\sum_{i=1}^{n}(-z_i)^k J_i\dot{x} = \sum_{i=1}^{n}(-z_i)^k \dot{c}_i^o - \sum_{i=1}^{n}(-z_i)^{k+1}c_i^o. \tag{20}$$

For the sake of convenience, we define

$$F_k := \sum_{i=1}^{n}(-z_i)^k c_i^o, \tag{21}$$

$$I_k := \sum_{i=1}^{n}(-z_i)^k J_i. \tag{22}$$

Therefore, (20) can be written as

$$F_{k+1} = I_k\dot{x} + \dot{F}_k. \tag{23}$$

Note that (11) and (21) lead to $F_1 = 0$. By induction, we thus obtain

$$F_{k+1} = I_k\dot{x} + I_{k-1}\ddot{x} + \cdots + I_1 x^{(k)}, \tag{24}$$

where $x^{(k)}$ denotes the kth derivative of x with respect to ϕ^o. Writing (24) in matrix form, we obtain, for any $k \geqslant 1$,

$$\begin{pmatrix} F_2 \\ \vdots \\ F_{k+1} \end{pmatrix} = \begin{pmatrix} I_1 & & \\ \vdots & \ddots & \\ I_k & \cdots & I_1 \end{pmatrix} \begin{pmatrix} \dot{x} \\ \vdots \\ x^{(k)} \end{pmatrix}. \tag{25}$$

From the definition (21) we also have

$$\begin{pmatrix} F_2 \\ \vdots \\ F_{k+1} \end{pmatrix} = \begin{pmatrix} (-z_1)^2 & \cdots & (-z_n)^2 \\ \vdots & & \vdots \\ (-z_1)^{k+1} & \cdots & (-z_n)^{k+1} \end{pmatrix} \begin{pmatrix} c_1^o \\ \vdots \\ c_n^o \end{pmatrix}. \tag{26}$$

From expressions (25) and (26) we obtain (by setting $k = n$)

$$\begin{pmatrix} c_1^o \\ \vdots \\ c_n^o \end{pmatrix} = \begin{pmatrix} (-z_1)^2 & \cdots & (-z_n)^2 \\ \vdots & & \vdots \\ (-z_1)^{n+1} & \cdots & (-z_n)^{n+1} \end{pmatrix}^{-1} \times \begin{pmatrix} I_1 & & \\ \vdots & \ddots & \\ I_n & \cdots & I_1 \end{pmatrix} \begin{pmatrix} \dot{x} \\ \vdots \\ x^{(n)} \end{pmatrix}. \tag{27}$$

This together with (11) yields

$$(z_1 \cdots z_n) \begin{pmatrix} (-z_1)^2 & \cdots & (-z_n)^2 \\ \vdots & & \vdots \\ (-z_1)^{n+1} & \cdots & (-z_n)^{n+1} \end{pmatrix}^{-1} \times \begin{pmatrix} I_1 & & \\ \vdots & \ddots & \\ I_n & \cdots & I_1 \end{pmatrix} \begin{pmatrix} \dot{x} \\ \vdots \\ x^{(n)} \end{pmatrix} = 0.$$

This equation can be rewritten in the form

$$(J_1, \ldots, J_n)A \begin{pmatrix} \dot{x} \\ \vdots \\ x^{(n)} \end{pmatrix} = 0, \tag{28}$$

where

$$A = \begin{pmatrix} 1 & \sum_{i\neq 1} z_i^{-1} & \sum_{i,j\neq 1} z_i^{-1}z_j^{-1} & \cdots & \prod_{i\neq 1} z_i^{-1} \\ \vdots & \vdots & \vdots & & \vdots \\ 1 & \sum_{i\neq n} z_i^{-1} & \sum_{i,j\neq n} z_i^{-1}z_j^{-1} & \cdots & \prod_{i\neq n} z_i^{-1} \end{pmatrix}. \tag{29}$$

Note that the kth row of the matrix A corresponds to the coefficients of the variable z in the polynomial $\Pi_{i\neq k}(z + z_i^{-1})$. It is readily seen that (28) is a linear ordinary differential equation for $\dot{x}$. We note that Liu [62] used different techniques to obtain an equivalent linear system. Generically, we may assume the corresponding equation has $n-1$ distinct roots, which we denote by $\lambda_1, \ldots, \lambda_{n-1}$. We then have an explicit formula for $\dot{x}$:

$$\dot{x} = \sum_{i=1}^{n-1} d_i e^{\lambda_i \phi^o}, \tag{30}$$

where the coefficients d_i, as well as the roots λ_i, will be determined by asymptotic matching.

In the remainder of this subsection, we will derive the explicit relation between the roots of the characteristic polynomial λ_i and the unknown fluxes J_i. Note that the coefficients of the characteristic polynomial of (28) are given by the vector $(J_1 \cdots J_n)A$. In contrast, since the roots of the polynomial are $\lambda_1, \ldots, \lambda_{n-1}$, the coefficients of the characteristic polynomial must be proportional to the vector

$$\left((-1)^{n-1}\prod_{i=1}^{n-1}\lambda_i, \ldots, -\sum_{i=1}^{n}\lambda_i, 1\right).$$

It thus follows that

$$(J_1, \ldots, J_n) = \kappa_0 \left((-1)^{n-1}\prod_{i=1}^{n-1}\lambda_i, \ldots, -\sum_{i=1}^{n}\lambda_i, 1\right) A^{-1} \tag{31}$$

for some nonzero constant κ_0. From (29) we obtain the inverse of A:

$$A^{-1} = \begin{pmatrix} \frac{(-z_1)^{-(n-1)}}{(z_2^{-1}-z_1^{-1})\cdots(z_n^{-1}-z_1^{-1})} & \cdots & \frac{(-z_n)^{-(n-1)}}{(z_1^{-1}-z_n^{-1})\cdots(z_{n-1}^{-1}-z_n^{-1})} \\ \vdots & & \vdots \\ \frac{1}{(z_2^{-1}-z_1^{-1})\cdots(z_n^{-1}-z_1^{-1})} & \cdots & \frac{1}{(z_1^{-1}-z_n^{-1})\cdots(z_{n-1}^{-1}-z_n^{-1})} \end{pmatrix}.$$

It is readily seen from (31) that

$$J_i = \kappa_0(-1)^{n-1}\prod_{j=1}^{n-1}(z_i + \lambda_j)\prod_{j\neq i}(1 - z_i/z_j)^{-1}. \tag{32}$$

The rest of this subsection is dedicated to determining the nonzero constant κ_0 in terms of the characteristic roots $\lambda_1,\ldots,\lambda_{n-1}$. First, from (22) and (32) we obtain

$$I_0 = \kappa_0(-1)^{n-1}\prod_{i=1}^{n-1}\lambda_i. \tag{33}$$

In contrast, from (11), (21), and (23) we obtain

$$I_0\dot{x} + \dot{F}_0 = F_1 = 0.$$

Integrating this equation from $\phi^o(0)$ to $\phi^o(1)$ gives an alternative expression for I_0:

$$I_0 = F_0(0) - F_0(1). \tag{34}$$

Hence, it follows from (33) and (34) that

$$\kappa_0 = (-1)^{n-1}[F_0(0) - F_0(1)]\prod_{i=1}^{n-1}\lambda_i^{-1}. \tag{35}$$

Using (32), we hence obtain

$$J_i = [F_0(0) - F_0(1)]\prod_{j=1}^{n-1}(1 + z_i/\lambda_j)\prod_{j\neq i}(1 - z_i/z_j)^{-1}, \tag{36}$$

which represents an explicit expression for the fluxes J_i in terms of the roots of the characteristic polynomial λ_i. In Sec. III C, we will determine the roots λ_i using asymptotic matching.

B. Boundary layer solutions

It is easily seen from (14) and (17) that

$$c_i^l(X) = c_{iL}e^{-z_i[\phi^l(X)-\phi_L]}. \tag{37}$$

Substituting formula (37) into (13) yields

$$-\frac{d^2\phi^l}{dX^2} = \sum_{i=1}^{n} z_i c_{iL} e^{-z_i[\phi^l(X)-\phi_L]}. \tag{38}$$

Integrating Eq. (38) from X to ∞ gives

$$\left(\frac{d\phi^l}{dX}(X)\right)^2 - \left(\frac{d\phi^l}{dX}(\infty)\right)^2 = \sum_{i=1}^{n} 2c_{iL}[e^{-z_i[\phi^l(X)-\phi_L]} - e^{-z_i[\phi^l(\infty)-\phi_L]}]. \tag{39}$$

Similarly, from (15), (16), and (18) we have

$$c_i^r(Y) = c_{iR}e^{-z_i[\phi^r(Y)-\phi_R]} \tag{40}$$

and

$$\left(\frac{d\phi^r}{dY}(Y)\right)^2 - \left(\frac{d\phi^r}{dY}(\infty)\right)^2 = \sum_{i=1}^{n} 2c_{iR}[e^{-z_i[\phi^r(Y)-\phi_R]} - e^{-z_i[\phi^r(\infty)-\phi_R]}]. \tag{41}$$

As we shall see in the next subsection, the boundary values $\frac{d\phi^l}{dX}(\infty)$, $\phi^l(\infty)$, $\frac{d\phi^r}{dY}(\infty)$, and $\phi^r(\infty)$ can be determined by asymptotic matching.

C. Asymptotic matching

In this subsection, we will first determine the matching values of the outer and boundary layer solutions in the overlapped regions. Then we will find a simple scalar transcendental equation for the characteristic roots $\lambda_1,\ldots,\lambda_{n-1}$. Finally, we will determine the integration constants d_i in (30) in terms of the roots λ_i.

Straightforward matching between the outer and boundary layer solutions yields

$$\phi^o(0) = \phi^l(\infty), \quad c_i^o(0) = c_i^l(\infty); \tag{42}$$

$$\phi^o(1) = \phi^r(\infty), \quad c_i^o(1) = c_i^r(\infty). \tag{43}$$

Note that from (11), (37), and (42) we have

$$c_i^o(0) = c_i^l(\infty) = c_{iL}w_L^{-z_i}, \tag{44}$$

where

$$w_L := e^{\phi^l(\infty)-\phi_L} = e^{\phi^o(0)-\phi_L} > 0. \tag{45}$$

In order to determine w_L, we must solve the algebraic equation

$$\sum_{i=1}^{n} z_i c_{iL} w_L^{-z_i} = 0 \tag{46}$$

that comes from substituting (44) into (11). We note that the left-hand side of this equation is a continuous decreasing function on the positive real line since the concentrations $c_{iL} \geqslant 0$. Moreover, this function has different signs as w_L tends to 0 and ∞. Thus, Eq. (46) possesses a unique positive root. If the difference between the largest and smallest valences is less than or equal to 4, then a closed-form expression for the root can be obtained. Otherwise, the root can easily be obtained numerically using the Jenkins-Traub algorithm [69]. Having obtained the solution, one can use (44) and (45) to determine $c_i^o(0)$ and $\phi^o(0)$. Similarly, from (11), (40), and (43) we have

$$c_i^o(1) = c_i^r(\infty) = c_{iR}w_R^{-z_i}, \tag{47}$$

where

$$w_R := e^{\phi^r(\infty)-\phi_R} = e^{\phi^o(1)-\phi_R} \tag{48}$$

is the unique positive root of the algebraic equation

$$\sum_{i=1}^{n} z_i c_{iR} w_R^{-z_i} = 0. \tag{49}$$

Similarly to the above case, (49) has a unique positive root that one can use to determine $c_i^o(1)$ and $\phi^o(1)$. We note that $c_i^l(\infty) = c_i^o(0)$ and $c_i^r(\infty) = c_i^o(1)$ are independent of ϕ_L and ϕ_R. Recall that $X = x/\varepsilon$ and $Y = (1-x)/\varepsilon$, so we have

$$\frac{d\phi^l}{dX}(\infty) = \varepsilon\frac{d\phi^o}{dx}(0) = O(\varepsilon)$$

and

$$\frac{d\phi^r}{dY}(\infty) = -\varepsilon\frac{d\phi^o}{dx}(1) = O(\varepsilon)$$

as $\varepsilon \to 0$. Thus, by matching at leading order, we have

$$\frac{d\phi^l}{dX}(\infty) = \frac{d\phi^r}{dY}(\infty) = 0. \tag{50}$$

So far, we have determined the matching values of the outer and boundary layer solutions in the overlapped regions, namely, $\phi^o(0) = \phi^l(\infty)$, $c_i^o(0) = c_i^l(\infty)$, $\phi^o(1) = \phi^r(\infty)$, and $c_i^o(1) = c_i^r(\infty)$. We have also shown in (36) that J_i can be expressed in terms of λ_i. It remains to determine the integration constants d_i and the characteristic roots λ_i in the expression for the outer solution (30). As we shall see, the coefficients d_i can be obtained in terms of J_i and λ_i. Thus, the crucial part of this subsection is to find a system of algebraic equations for λ_i. First, substituting (30) into (25) with $k = n-1$ yields

$$\begin{pmatrix} F_2 \\ \vdots \\ F_n \end{pmatrix} = \begin{pmatrix} I_1 & & \\ \vdots & \ddots & \\ I_{n-1} & \cdots & I_1 \end{pmatrix} \begin{pmatrix} \sum_{i=1}^{n-1} d_i e^{\lambda_i \phi^o} \\ \vdots \\ \sum_{i=1}^{n-1} d_i \lambda_i^{n-2} e^{\lambda_i \phi^o} \end{pmatrix}. \quad (51)$$

This equation can be written as

$$\mathcal{F}(x) = \mathcal{I} \mathcal{V} \Lambda(x) D, \quad (52)$$

where

$$\mathcal{F}(x) := [F_2(x), \ldots, F_n(x)]^T, \quad (53)$$

$$\Lambda(x) := \mathrm{diag}\{e^{\lambda_1 \phi^o(x)}, \ldots, e^{\lambda_{n-1}\phi^o(x)}\}, \quad (54)$$

$$D := (d_1, \ldots, d_{n-1})^T, \quad (55)$$

and

$$\mathcal{I} := \begin{pmatrix} I_1 & & \\ \vdots & \ddots & \\ I_{n-1} & \cdots & I_1 \end{pmatrix}, \qquad \mathcal{V} := \begin{pmatrix} 1 & \cdots & 1 \\ \vdots & & \vdots \\ \lambda_1^{n-2} & \cdots & \lambda_{n-1}^{n-2} \end{pmatrix}. \quad (56)$$

Applying (52) at $x = 0$, namely, $\phi^o(x) = \phi^o(0)$, and at $x = 1$, namely, $\phi^o(x) = \phi^o(1)$, we obtain

$$\mathcal{F}(0) = \mathcal{I}\mathcal{V}\Lambda(0)D, \quad \mathcal{F}(1) = \mathcal{I}\mathcal{V}\Lambda(1)D. \quad (57)$$

Eliminating the vector D in Eqs. (57) yields

$$\Lambda(1)^{-1}(\mathcal{I}\mathcal{V})^{-1}\mathcal{F}(1) = \Lambda(0)^{-1}(\mathcal{I}\mathcal{V})^{-1}\mathcal{F}(0), \quad (58)$$

which represents a set of $n-1$ equations. Note from (26) that $\mathcal{F}(0)$ and $\mathcal{F}(1)$ can be determined from the boundary values of c_i^o. Moreover, the components of $\Lambda(0)$ and $\Lambda(1)$ are also explicit functions of λ_i and the boundary values of ϕ^o. It remains to determine the inverse $(\mathcal{I}\mathcal{V})^{-1}$. From (22) and (32) we obtain

$$\begin{aligned} I_1 &= -\kappa_0 \prod_{i=1}^{n} z_i, \\ I_2 &= I_1 \left[\sum_{i=1}^{n}(-z_i) - \sum_{i=1}^{n-1}\lambda_i\right], \\ I_3 &= I_1 \left[\sum_{1\leqslant i\leqslant j\leqslant n}(-z_i)(-z_j) - \left(\sum_{i=1}^{n-1}\lambda_i\right)\left(\sum_{i=1}^{n}(-z_i)\right) \right. \\ &\quad \left. + \sum_{1\leqslant i<j\leqslant n-1}\lambda_i\lambda_j\right], \\ &\vdots . \end{aligned} \quad (59)$$

Using (56) and (59), it is tedious but straightforward to verify that

$$\begin{aligned} (\mathcal{I}\mathcal{V})^{-1} &= I_1^{-1}\begin{pmatrix} \frac{P_{n-2}(\lambda_1)}{(\lambda_1-\lambda_2)\cdots(\lambda_1-\lambda_{n-1})} & \cdots & \frac{P_0(\lambda_1)}{(\lambda_1-\lambda_2)\cdots(\lambda_1-\lambda_{n-1})} \\ \vdots & & \vdots \\ \frac{P_{n-2}(\lambda_{n-1})}{(\lambda_{n-1}-\lambda_1)\cdots(\lambda_{n-1}-\lambda_{n-2})} & \cdots & \frac{P_0(\lambda_{n-1})}{(\lambda_{n-1}-\lambda_1)\cdots(\lambda_{n-1}-\lambda_{n-2})} \end{pmatrix} \\ &= I_1^{-1}\left(P_{n-1-j}(\lambda_i)\prod_{k\neq i}(\lambda_i-\lambda_k)^{-1}\right)_{(n-1)\times(n-1)}, \end{aligned} \quad (60)$$

where $P_k(\lambda)$ is a polynomial of λ given by

$$P_k(\lambda) = \lambda^k + \sum_{i=1}^{n} z_i \lambda^{k-1} + \cdots + \sum_{1\leqslant i_1<i_2<\cdots<i_k\leqslant n} z_{i_1}\cdots z_{i_k}. \quad (61)$$

Substituting into (58), we see that all $n-1$ equations in (58) reduce to the same transcendental equation

$$\sum_{k=2}^{n} P_{n-k}(\lambda)F_k(1) = e^{\lambda V^o}\sum_{k=2}^{n} P_{n-k}(\lambda)F_k(0), \quad (62)$$

where for convenience we define $V^o := \phi^o(1) - \phi^o(0)$. In fact, finding the roots of this single nonlinear equation is equivalent to finding the solution to the system of nonlinear equations obtained by Liu [62]. However, by maintaining the relabeling symmetries of the the system, our approach reduces Liu's system of equations to a single equation. It should be noted that this transcendental equation has infinitely many roots. For instance, there exists a pair of conjugate roots near $[\ln F_2(1) - \ln F_2(0) \pm 2\pi i N]/V^o$ for all sufficiently large integers N. The roots can be obtained numerically using techniques based on Cauchy integrals in the complex plane [70]. In deriving (30) we assumed that the λ_i for $i = 1, \ldots, n-1$ are distinct. Therefore, we must choose $n-1$ of the infinite set of the roots of (62). In practice, we have to choose a set of $n-1$ roots such that the outer solution is real and the concentrations are positive everywhere. The solution must be real, so if we choose a complex root, we must also choose its complex conjugate. For $n \geqslant 3$, it therefore appears that there are an infinite number of solutions. However, in Sec. III A we showed that solutions are physically relevant if and only if $\dot{x} \neq 0$. We note that values of λ with large imaginary component will correspond to functions $\dot{x}$ that are highly oscillatory. Such solutions will have values of ϕ^o for which $\dot{x} = 0$ and are hence unphysical. We will discuss the choice of roots for $n = 2$ and 3 in Sec. V. We also note that oscillatory functions $x(\phi^o)$ correspond to functions $\phi^o(x)$ that are multivalued. In many physical problems, multivaluedness can be resolved by the introduction of internal layers. However, in Sec. VI B we will show that internal layers cannot exist for this problem.

Before ending this subsection, we derive a closed form for $\dot{x}$ that can be used to check if $\dot{x} = 0$ and hence the solution if unphysical. We will use this result in Sec. V to prove existence and uniqueness for $n = 2$ and 3. Setting $k = n-1$ in (26) and using (11) to eliminate c_n^o, we obtain

$$\mathcal{F} = \begin{pmatrix} (-z_1)^2 & \cdots & (-z_n)^2 \\ \vdots & & \vdots \\ (-z_1)^n & \cdots & (-z_n)^n \end{pmatrix} \begin{pmatrix} c_1^o \\ \vdots \\ c_n^o \end{pmatrix}$$
$$= \begin{pmatrix} (-z_1)^2 & \cdots & (-z_n)^2 \\ \vdots & & \vdots \\ (-z_1)^n & \cdots & (-z_n)^n \end{pmatrix}$$
$$\times \begin{pmatrix} 1 & & \\ & \ddots & \\ & & 1 \\ -z_1/z_n & \cdots & -z_{n-1}/z_n \end{pmatrix} \begin{pmatrix} c_1^o \\ \vdots \\ c_{n-1}^o \end{pmatrix}.$$

Premultiplying by $(\mathcal{I}V)^{-1}$ and using (60), we obtain

$$(\mathcal{I}V)^{-1}\mathcal{F}$$
$$= I_1^{-1} \begin{pmatrix} \frac{(\lambda_1+z_2)\cdots(\lambda_1+z_{n-1})}{(\lambda_1-\lambda_2)\cdots(\lambda_1-\lambda_{n-1})} & \cdots & \frac{(\lambda_1+z_1)\cdots(\lambda_1+z_{n-2})}{(\lambda_1-\lambda_2)\cdots(\lambda_1-\lambda_{n-1})} \\ \vdots & & \\ \frac{(\lambda_{n-1}+z_2)\cdots(\lambda_{n-1}+z_{n-1})}{(\lambda_{n-1}-\lambda_1)\cdots(\lambda_{n-1}-\lambda_{n-2})} & \cdots & \frac{(\lambda_{n-1}+z_1)\cdots(\lambda_{n-1}+z_{n-2})}{(\lambda_{n-1}-\lambda_1)\cdots(\lambda_{n-1}-\lambda_{n-2})} \end{pmatrix}$$
$$\times \begin{pmatrix} z_1(z_1-z_n)c_1^o \\ \vdots \\ z_{n-1}(z_{n-1}-z_n)c_{n-1}^o \end{pmatrix}. \quad (63)$$

It then follows from (30), (52), and (63) that

$$\dot{x} = I_1^{-1}\sum_{i=1}^{n-1} e^{\lambda_i[\phi^o-\phi^o(0)]}Q_0(\lambda_i)\prod_{k\neq i,k=1}^{n-1}(\lambda_i-\lambda_k)^{-1}, \quad (64)$$

where

$$Q_0(\lambda) := \left[z_1(z_1-z_n)c_1^o(0)\right]\prod_{k\neq 1,n}(\lambda+z_k)+\cdots$$
$$+\left[z_{n-1}(z_{n-1}-z_n)c_{n-1}^o(0)\right]\prod_{k\neq n-1,n}(\lambda+z_k). \quad (65)$$

We also remark that using (58) and (63), Eq. (62) can be rewritten as

$$Q_1(\lambda) = e^{\lambda V^o}Q_0(\lambda), \quad (66)$$

where $V^o = \phi^o(1) - \phi^o(0)$ and

$$Q_1(\lambda) := \left[z_1(z_1-z_n)c_1^o(1)\right]\prod_{k\neq 1,n}(\lambda+z_k)+\cdots$$
$$+\left[z_{n-1}(z_{n-1}-z_n)c_{n-1}^o(1)\right]\prod_{k\neq n-1,n}(\lambda+z_k). \quad (67)$$

D. Uniformly valid asymptotic solution

In this subsection, we state our main result, which gives a uniformly valid asymptotic solution of the general PNP system. First, we define generalized elliptic integrals by

$$E(\alpha_0,\ldots,\alpha_n;a_0,\ldots,a_n;u) := \int_1^u\left(\sum_{i=0}^n a_i t^{\alpha_i}\right)^{-1/2}dt. \quad (68)$$

Theorem. The PNP system (5) and (6) with boundary conditions (9) and (10) has a uniformly valid asymptotic solution as follows:

$$\phi(x) = \phi^o(x) + \phi^l\left(\frac{x}{\varepsilon}\right) + \phi^r\left(\frac{1-x}{\varepsilon}\right)$$
$$-\phi^o(0) - \phi^o(1) + O(\varepsilon), \quad (69)$$

$$c_i(x) = c_i^o(x) + c_i^l\left(\frac{x}{\varepsilon}\right) + c_i^r\left(\frac{1-x}{\varepsilon}\right)$$
$$-c_i^o(0) - c_i^o(1) + O(\varepsilon), \quad (70)$$

where $\phi^o(x)$ is the inverse function of

$$x = \sum_{i=1}^{n-1}\frac{d_i}{\lambda_i}(e^{\lambda_i\phi^o} - e^{\lambda_i\phi^o(0)}); \quad (71)$$

$\phi^l(X)$ is the inverse function of

$$E(\alpha_0,\ldots,\alpha_n;a_0,\ldots,a_n;e^{\phi^l-\phi_L}) = X\,\mathrm{sgn}\{\phi^l(\infty)-\phi^l(0)\}, \quad (72)$$

with $\alpha_0 = 2$, $\alpha_i = 2 - z_i$, $a_0 = -2F_0(0) = -2\sum_{i=1}^n c_{iL}e^{-z_i[\phi^l(\infty)-\phi_L]}$, and $a_i = 2c_{iL}$; $\phi^r(Y)$ is the inverse function of

$$E(\alpha_0,\ldots,\alpha_n;b_0,\ldots,b_n;e^{\phi^r-\phi_R}) = Y\,\mathrm{sgn}\{\phi^r(\infty)-\phi^r(0)\}, \quad (73)$$

with $\alpha_0 = 2$, $\alpha_i = 2 - z_i$, $b_0 = -2F_0(1) = -2\sum_{i=1}^n c_{iR}e^{-z_i[\phi^r(\infty)-\phi_R]}$, and $b_i = 2c_{iR}$; and $c_i^l(X)$ and $c_i^r(Y)$ are given in (37) and (40), respectively, and $c_i^o(x)$ are determined from (27) and (30).

Proof. The asymptotic formulas (69) and (70) are obtained by asymptotic matching. Equation (71) follows from an integration of (30). Substituting (50) into (39) and (41) gives

$$\frac{d\phi^l}{dX}(X) = \left\{\sum_{i=1}^n 2c_{iL}[e^{-z_i(\phi^l(X)-\phi_L)} - e^{-z_i(\phi^l(\infty)-\phi_L)}]\right\}^{1/2}$$
$$\times\,\mathrm{sgn}\{\phi^l(\infty)-\phi^l(0)\}$$

and

$$\frac{d\phi^r}{dY}(Y) = \left\{\sum_{i=1}^n 2c_{iR}[e^{-z_i[\phi^r(Y)-\phi_R]} - e^{-z_i[\phi^r(\infty)-\phi_R]}]\right\}^{1/2}$$
$$\times\,\mathrm{sgn}\{\phi^r(\infty)-\phi^r(0)\},$$

respectively. Hence, (72) and (73) follow from our definition of the generalized elliptic integrals in (68). ■

IV. EXAMPLES

In this section, we show how straightforward our method is to use by applying it to two examples, the first with two ions that reproduces the results of Barcilon *et al.* [51] and Liu [54] and the second with three ions. Subsequently, these solutions are compared with those obtained by a direct numerical approach and those in the literature. The corresponding current-voltage (I-V) relations are also provided.

A. Example I: Two ions with arbitrary valences α:β

Let $z_1 = \alpha$ and $z_2 = \beta$. First, we solve Eqs. (46) and (49):

$$\alpha c_{1L} w_L^{-\alpha} + \beta c_{2L} w_L^{-\beta} = \alpha c_{1R} w_R^{-\alpha} + \beta c_{2R} w_R^{-\beta} = 0, \tag{74}$$

where $w_L := e^{\phi^l(\infty)-\phi_L} = e^{\phi^o(0)-\phi_L}$ and $w_R := e^{\phi^r(\infty)-\phi_R} = e^{\phi^o(1)-\phi_R}$. The roots are given by

$$w_L = \left(\frac{\alpha c_{1L}}{-\beta c_{2L}}\right)^{1/(\alpha-\beta)}, \quad w_R = \left(\frac{\alpha c_{1R}}{-\beta c_{2R}}\right)^{1/(\alpha-\beta)}. \tag{75}$$

The boundary values (in the matching region) of the concentrations are then obtained from (44) and (47):

$$c_i^o(0) = c_i^l(\infty) = c_{iL} w_L^{-z_i} = c_{iL} e^{-z_i[\phi^l(\infty)-\phi_L]} = c_{iL} e^{-z_i[\phi^o(0)-\phi_L]}$$

and

$$c_i^o(1) = c_i^r(\infty) = c_{iR} w_R^{-z_i} = c_{iR} e^{-z_i[\phi^r(\infty)-\phi_R]} = c_{iR} e^{-z_i[\phi^o(1)-\phi_R]}.$$

Next, we must solve λ_1 from Eq. (62):

$$F_2(1) = e^{\lambda_1 V^o} F_2(0), \tag{76}$$

where $V^o = \phi^o(1) - \phi^o(0)$. Although the equation has infinite number of complex roots for λ_1, we are seeking a real outer solution $\phi^o(x)$ and so we must choose the only real root

$$\lambda_1 = \frac{1}{V^o} \ln \frac{F_2(1)}{F_2(0)}. \tag{77}$$

Consequently, the fluxes can be obtained from (36):

$$J_1 = \frac{[F_0(0) - F_0(1)](1 + \alpha/\lambda_1)}{1 - \alpha/\beta},$$
$$J_2 = \frac{[F_0(0) - F_0(1)](1 + \beta/\lambda_1)}{1 - \beta/\alpha}. \tag{78}$$

Next, we determine the coefficient d_1 from (57):

$$d_1 = e^{-\lambda_1 \phi^o(0)} I_1^{-1} F_2(0) = \frac{\lambda_1 e^{-\lambda_1 \phi^o(0)} F_2(0)}{\alpha\beta[F_0(0) - F_0(1)]}. \tag{79}$$

Consequently, the outer solution is given by (71):

$$x = \frac{d_1}{\lambda_1}[e^{\lambda_1 \phi^o} - e^{\lambda_1 \phi^o(0)}] \tag{80}$$

or, equivalently,

$$\phi^o = \phi^o(0) + \frac{1}{\lambda_1} \ln \left(1 + x \frac{\alpha\beta[F_0(0) - F_0(1)]}{F_2(0)}\right). \tag{81}$$

If $\alpha = 1$ and $\beta = -1$, we have

$$\phi^o(x) = \phi^o(0) + \frac{\phi^o(1) - \phi^o(0)}{\ln\sqrt{c_{1R}c_{2R}} - \ln\sqrt{c_{1L}c_{2L}}} \times \ln\left(1 - x + x\frac{\sqrt{c_{1R}c_{2R}}}{\sqrt{c_{1L}c_{2L}}}\right), \tag{82}$$

which agrees with Eq. (46) in [51]. We now determine the boundary layer solutions. Clearly, $\alpha_0 = 2$, $\alpha_1 = 2 - \alpha$, $\alpha_2 = 2 - \beta$, and

$$a_0 = -2F_0(0), \quad a_1 = 2c_{1L}, \quad a_2 = 2c_{2L},$$
$$b_0 = -2F_0(1), \quad b_1 = 2c_{1R}, \quad b_2 = 2c_{2R},$$

where $F_0(0) = c_{1L} w_L^{-\alpha} + c_{2L} w_L^{-\beta}$ and $F_0(1) = c_{1R} w_R^{-\alpha} + c_{2R} w_R^{-\beta}$. The boundary layer solutions (72) and (73) have explicit formulas for some special values of α and β. For example, when $\alpha = 1$ and $\beta = -1$, we obtain

$$\phi^l(X) = \phi_L + \ln\left(\frac{a^2\left(1 + \frac{1-a}{1+a}e^{-a\sqrt{2c_{2L}}X}\right)^2}{\left(1 - \frac{1-a}{1+a}e^{-a\sqrt{2c_{2L}}X}\right)^2}\right), \tag{83}$$

where $a := (c_{1L}/c_{2L})^{1/4}$, which agrees with Eq. (54) in [51], and

$$\phi^r(Y) = \phi_R + 2\ln\left(\frac{b^2\left(1 + \frac{1-b}{1+b}e^{-b\sqrt{2c_{2R}}Y}\right)^2}{\left(1 - \frac{1-b}{1+b}e^{-b\sqrt{2c_{2R}}Y}\right)^2}\right), \tag{84}$$

where $b := (c_{1R}/c_{2R})^{1/4}$, which agrees with Eq. (57) in [51]. In Fig. 1, we compare our asymptotic solution with a finite-difference solution of the original PNP system [Eq. (87) in [51]]. It can be seen that the two solutions compare reasonably well for $\varepsilon = 0.1$.

B. Example II: Three ions with valences 2:1:−1

Let $z_1 = 2$, $z_2 = 1$, and $z_3 = -1$. First, we obtain two algebraic equations (46) and (49):

$$2c_{1L} w_L^{-2} + c_{2L} w_L^{-1} - c_{3L} w_L = 2c_{1R} w_R^{-2} + c_{2R} w_R^{-1} - c_{3R} w_R = 0, \tag{85}$$

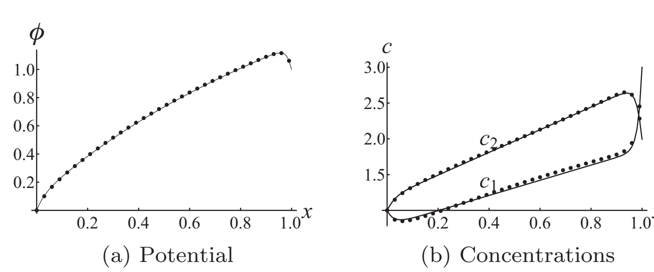


FIG. 1. Comparison of asymptotic solutions (solid lines) with numerical solutions (dotted lines) of the 3:−2 case with the boundary conditions $\phi_L = 0$, $c_{1L} = 1$, $c_{2L} = 1$, $\phi_R = 1$, $c_{1R} = 3$, and $c_{2R} = 2$. Here we choose $\varepsilon = 0.1$.

where $w_L := e^{\phi^l(\infty)-\phi_L} = e^{\phi^o(0)-\phi_L}$ and $w_R := e^{\phi^r(\infty)-\phi_R} = e^{\phi^o(1)-\phi_R}$. These two equations are cubic and hence one can obtain a closed-form expression for the unique positive solutions. The boundary values (in the matching region) of the concentrations are then obtained from (44) and (47):

$$\begin{aligned} c_i^o(0) = c_i^l(\infty) &= c_{iL} w_L^{-z_i} = c_{iL} e^{-z_i[\phi^l(\infty)-\phi_L]} \\ &= c_{iL} e^{-z_i[\phi^o(0)-\phi_L]} \end{aligned}$$

and

$$\begin{aligned} c_i^o(1) = c_i^r(\infty) &= c_{iR} w_R^{-z_i} = c_{iR} e^{-z_i[\phi^r(\infty)-\phi_R]} \\ &= c_{iR} e^{-z_i[\phi^o(1)-\phi_R]}. \end{aligned}$$

Since the two positive roots w_L and w_R are independent of ϕ_L and ϕ_R, we notice that $c_i^o(0) = c_i^l(\infty)$ and $c_i^o(1) = c_i^r(\infty)$ are also independent of ϕ_L and ϕ_R. Next, from (36), we express the fluxes J_1, J_2, and J_3 in terms of characteristic roots λ_1 and λ_2:

$$\begin{aligned} J_1 &= -[F_0(0) - F_0(1)](1 + 2/\lambda_1)(1 + 2/\lambda_2)/3, \\ J_2 &= [F_0(0) - F_0(1)](1 + 1/\lambda_1)(1 + 1/\lambda_2), \\ J_3 &= [F_0(0) - F_0(1)](1 - 1/\lambda_1)(1 - 1/\lambda_2)/3. \end{aligned} \tag{86}$$

The roots λ_1 and λ_2 are solutions to Eq. (62):

$$(\lambda + 2)F_2(1) + F_3(1) = e^{\lambda V^o}[(\lambda + 2)F_2(0) + F_3(0)]. \tag{87}$$

Even though Eq. (87) has infinite many complex roots, we will show in Sec. V that one must choose the roots located in the strip $|V^o \mathrm{Im}\lambda| < \pi$ such that the outer solution in (30) remains real and monotonic. As we shall see later, there exist exactly two characteristic roots in this strip. Next, we determine the coefficients d_1 and d_2 from (57):

$$\begin{aligned} \begin{pmatrix} d_1 \\ d_2 \end{pmatrix} &= \begin{pmatrix} e^{-\lambda_1 \phi^o(0)} & 0 \\ 0 & e^{-\lambda_2 \phi^o(0)} \end{pmatrix} \\ &\quad \times \begin{pmatrix} I_1 & I_1 \\ I_2 + \lambda_1 I_1 & I_2 + \lambda_2 I_1 \end{pmatrix}^{-1} \begin{pmatrix} F_2(0) \\ F_3(0) \end{pmatrix}. \end{aligned} \tag{88}$$

Consequently, the outer solution is given by (71):

$$x = \frac{d_1}{\lambda_1}[e^{\lambda_1 \phi^o} - e^{\lambda_1 \phi^o(0)}] + \frac{d_2}{\lambda_2}[e^{\lambda_2 \phi^o} - e^{\lambda_2 \phi^o(0)}]. \tag{89}$$

We now determine the boundary layer solutions. Clearly,

$$\alpha_0 = 0, \quad \alpha_1 = 0, \quad \alpha_2 = 1, \quad \alpha_3 = 3,$$

$$a_0 = -2F_0(0), \quad a_1 = 2c_{1L}, \quad a_2 = 2c_{2L}, \quad a_3 = 2c_{3L},$$

where $F_0(0) = c_{1L} w_L^{-2} + c_{2L} w_L^{-1} + c_{3L} w_L$ with $w_L := e^{\phi^l(\infty)-\phi_L}$. The generalized elliptic integrals in (68) can be written as

$$\begin{aligned} \int_1^u \big[&-2(c_{1L} w_L^{-2} + c_{2L} w_L^{-1} + c_{3L} w_L)t^2 \\ &+ 2c_{1L} + 2c_{2L} t + 2c_{3L} t^3\big]^{-1/2} dt. \end{aligned}$$

In view of the polynomial equation for w_L in (85), we can factorize the integrand and obtain

$$\int_1^u (2c_{3L})^{-1/2}(t - w_L)\left(t + \frac{c_{1L}}{c_{3L} w_L^2}\right)^{-1/2} dt.$$

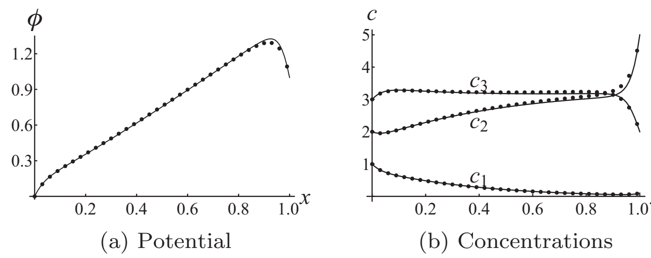


FIG. 2. Comparison of asymptotic solutions (solid lines) with numerical solutions (dotted lines) of the 2:1:−1 case with the boundary conditions $\phi_L = 0$, $c_{1L} = 1$, $c_{2L} = 2$, $c_{3L} = 3$, $\phi_R = 1$, $c_{1R} = 0.1$, $c_{2R} = 5$, and $c_{3R} = 2$. Here we choose $\varepsilon = 0.1$.

For convenience, we define $c := w_L^{-2} c_{1L}/c_{3L}$ and $a := (c + w_L)^{1/2}$. The above integral can be expressed as

$$\frac{1}{a\sqrt{2c_{3L}}} \ln\left(\frac{\sqrt{u+c} - a}{\sqrt{u+c} + a}\frac{\sqrt{1+c} - a}{\sqrt{1+c} + a}\right).$$

Thus, it follows from (68) and (72) that

$$\phi^l(X) = \phi_L + \ln\left(\frac{a^2\big(1 + \frac{\sqrt{1+c}+a}{\sqrt{1+c}-a} e^{a\sqrt{2c_{3L}}X}\big)^2}{\big(1 - \frac{\sqrt{1+c}+a}{\sqrt{1+c}-a} e^{a\sqrt{2c_{3L}}X}\big)^2} - c\right). \tag{90}$$

Similarly, the boundary layer solution near $x \sim 1$ is obtained from (68) and (49):

$$\phi^r(Y) = \phi_R + \ln\left(\frac{b^2\big(1 + \frac{\sqrt{1+d}+b}{\sqrt{1+d}-b} e^{b\sqrt{2c_{3R}}Y}\big)^2}{\big(1 - \frac{\sqrt{1+d}+b}{\sqrt{1+d}-b} e^{b\sqrt{2c_{3R}}Y}\big)^2} - d\right), \tag{91}$$

where $w_R := e^{\phi^r(\infty)-\phi_R}$, $d := w_R^{-2} c_{1R}/c_{3R}$, and $b := (d + w_R)^{1/2}$. In Fig. 2, we plot the numerical solution via a direct iterative method for the PNP system [Eq. (87) in [51]] along with our uniformly valid asymptotic solution. It should be noted that for the special case $F_1 = 0$ (electroneutral), there are no boundary layers (see Fig. 3). Finally, we have presented a comparison between the asymptotic and numerical solutions for a more complicated case 3:2:1:−1:−2 in Fig. 4. The derivation of the asymptotic solution is omitted.

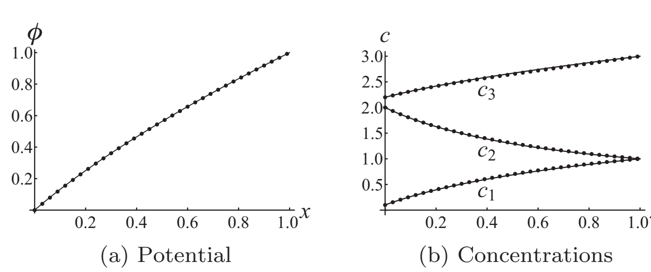
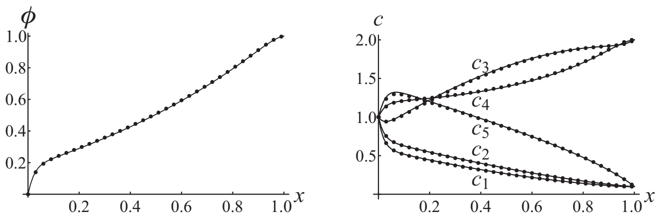


FIG. 3. Comparison of asymptotic solutions (solid lines) with numerical solutions (dotted lines) of the 2:1:−1 case with the (electroneutral) boundary conditions $\phi_L = 0$, $c_{1L} = 0.1$, $c_{2L} = 2$, $c_{3L} = 2.2$, $\phi_R = 1$, $c_{1R} = 1$, $c_{2R} = 1$, and $c_{3R} = 3$. Here we choose $\varepsilon = 0.1$.



(a) Potential (b) Concentrations

FIG. 4. Comparison of asymptotic solutions (solid lines) with numerical solutions (dotted lines) of the 3:2:1:−1:−2 case with the boundary conditions $\phi_L = 0$, $c_{1L} = c_{2L} = c_{3L} = c_{4L} = c_{5L} = 1$, $\phi_R = 1$, $c_{1R} = 0.1$, $c_{2R} = 0.1$, $c_{3R} = 2$, $c_{4R} = 2$, and $c_{5R} = 0.1$. Here we choose $\varepsilon = 0.1$.

C. The *I*-*V* relation

In this subsection, we derive the I-V relation between current $I = -I_1 = \sum_{i=1}^n z_i J_i$ and potential $V = \phi_R - \phi_L = V^o - \ln(w_R/w_L)$. First, we consider the $\alpha{:}\beta$ case ($n = 2$ with $z_1 = \alpha$ and $z_2 = \beta$). It is readily seen from (22), (75), (77), and (78) that

$$I = \frac{-\alpha\beta[F_0(0) - F_0(1)]}{\ln F_2(1) - \ln F_2(0)}\left[V + \frac{1}{\alpha - \beta}\ln\frac{c_{1R}c_{2L}}{c_{1L}c_{2R}}\right]. \tag{92}$$

When $\alpha = 1$ and $\beta = -1$, the relation (92) is

$$I = \frac{2(\sqrt{c_{1L}c_{2L}} - \sqrt{c_{1R}c_{2R}})}{\ln\sqrt{c_{1R}c_{2R}/c_{1L}c_{2L}}}\left[V + \ln\frac{\sqrt{c_{1R}/c_{2R}}}{\sqrt{c_{1L}/c_{2L}}}\right] \tag{93}$$

and so I is a linear function of V, which agrees with Eq. (44) in [51].

Now, we investigate the $\alpha{:}\beta{:}\gamma$ case ($n = 3$ with $z_1 = \alpha$, $z_2 = \beta$, and $z_3 = \gamma$). Making use of (11) and (21), it is easily seen that $(\alpha + \beta + \gamma)F_2 + F_3 = -\alpha\beta\gamma F_0$. Hence, Eq. (62) can be written as

$$\lambda F_2(1) - \alpha\beta\gamma F_0(1) = e^{\lambda V^o}[\lambda F_2(0) - \alpha\beta\gamma F_0(0)].$$

Since $c_i^o > 0$ for any $i = 1,2,3$, we obtain from (21) that $F_0 > 0$ and $F_2 > 0$. For large $V^o > 0$, this equation always has a zero

$$\lambda_1 \sim \frac{1}{V^o}\ln\frac{F_0(1)}{F_0(0)}.$$

The second zero depends on the sign of $\alpha\beta\gamma$:

$$\lambda_2 \sim \begin{cases} \alpha\beta\gamma F_0(1)/F_2(1), & \alpha\beta\gamma < 0 \\ \alpha\beta\gamma F_0(0)/F_2(0), & \alpha\beta\gamma > 0. \end{cases}$$

Note from (22) and (32) that

$$-I_1 \sim [F_0(0) - F_0(1)]\sum_{i=1}^{3}\frac{z_i(1 + z_i/\lambda_2)(1 + z_i/\lambda_1)}{\prod_{j\neq i}(1 - z_i/z_j)}.$$

Since $1/\lambda_1 = O(V^o)$ and $\lambda_2 = O(1)$ for large V^o, we obtain from the above formula and the identities $\sum_{i=1}^3 z_i^2\prod_{j\neq i}(1 - z_i/z_j)^{-1} = 0$ and $\sum_{i=1}^3 z_i^3\prod_{j\neq i}(1 - z_i/z_j)^{-1} = z_1z_2z_3$ that

$$-I_1 \sim \begin{cases} V^o\frac{[F_0(0)-F_0(1)]F_2(1)/F_0(1)}{\ln[F_0(1)/F_0(0)]}, & \alpha\beta\gamma < 0 \\ V^o\frac{[F_0(0)-F_0(1)]F_2(0)/F_0(0)}{\ln[F_0(1)/F_0(0)]}, & \alpha\beta\gamma > 0. \end{cases} \tag{94}$$

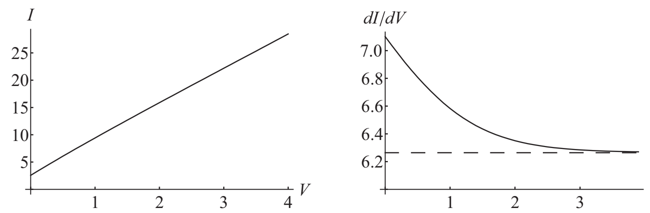


FIG. 5. The I-V relation of the 2:1:−1 case with the boundary conditions $\phi_L = 0$, $c_{1L} = 1$, $c_{2L} = 2$, $c_{3L} = 3$, $\phi_R = V$, $c_{1R} = 0.1$, $c_{2R} = 5$, and $c_{3R} = 2$. The dashed line is calculated via (94).

Note that $I_1 = -I$ and $V^o = V + \ln(w_R/w_L)$. Equation (94) gives an asymptotically linear relation between the current I and the potential V (see Fig. 5). We remark that if the concentrations c_{3L} and c_{3R} are zero, then $F_2/F_0 = -\alpha\beta$ and the relation (94) reduces to the I-V relation (92) for the $\alpha{:}\beta$ case.

V. EXISTENCE AND UNIQUENESS OF SOLUTIONS

In this section, we consider the existence and uniqueness of solutions. Liu proved the existence and (local) uniqueness for $n = 2$ [54], but for $n = 3$ found nonunique solutions [62]. We prove that, for $n = 3$, if we restrict our attention to physically relevant solutions with $c_i > 0$ for $i = 1,\ldots,n$, then the solution must be unique. We observe that Eq. (62) has infinitely many complex roots. However, we have to choose a set of $n - 1$ roots such that $c_i > 0$ for $i = 1,\ldots,n$, which is equivalent to finding a solution of (30) with $\dot{x} \neq 0$.

For the $n = 2$ case, we have seen in the previous section that (76) has exactly one real root that corresponds to the unique physical solution. Moreover, (80) implies that $\dot{x} \neq 0$ and thus $c_i > 0$ for $i = 1,\ldots,n$. This implies the existence of the solution.

In order to prove the existence and uniqueness for the $n = 3$ case, we will show that we must choose the two roots in the strip $|V^o\mathrm{Im}\lambda| < \pi$. The proof of existence and uniqueness of such roots is separated into three steps.

First, it is readily seen from (30) that if the two complex conjugate roots $\lambda^\pm$ are chosen outside the strip $|V^o\mathrm{Im}\lambda| < \pi$, then $\dot{x}$ is a trigonometric function with frequency $2\pi/\mathrm{Im}\lambda^+$:

$$\dot{x} = B\cos(\phi^o\mathrm{Im}\lambda^+ + \theta)e^{\phi^o\mathrm{Re}\lambda^+}$$

for some $B > 0$ and $\theta \in [0,2\pi)$. As ϕ^o varies from $\phi^o(0)$ to $\phi^o(1)$, $\dot{x}$ must change sign at some point because $|V^o\mathrm{Im}\lambda^+| > \pi$ and $V^o = \phi^o(1) - \phi^o(0)$.

Second, we use the fact that the non-negativeness of concentrations implies that $F_2(0) > 0$ and $F_2(1) > 0$ and show that Eq. (62) with $n = 3$ has exactly two roots in the strip $|V^o\mathrm{Im}\lambda| < \pi$ provided $V^o \neq 0$. Upon a linear scaling of λ, it suffices to prove that the transcendental function

$$f(z) := ze^z - a(z-2d) \tag{95}$$

with positive a and real d has exactly two roots (counting multiplicity) in the strip $|\mathrm{Im}z| < \pi$. Note that the derivative $f'(z) = (z+1)e^z - a$ has exactly one real root $z = y_0$ and $f(z) > 0$ as z approaches $\pm\infty$. We conclude that f has two real roots (counting multiplicity) if and only if $f(y_0) = y_0 e^{y_0} - a(y_0 - 2d) \leqslant 0$, where $(y_0+1)e^{y_0} = a$. The condition can be written as $2d \leqslant y_0^2/(y_0+1)$. Since $y_0 > -1$ from its definition, we see that f has exactly two real roots if $d \leqslant 0$. We now turn our attention to the complex roots $z = z_r + iz_i$ of $f(z)$ with $0 < z_i < \pi$. From $f(z) = 0$ we have $1 - 2d/z = e^z/a$. Comparing the imaginary parts of both sides of the equation gives $2dz_i/(z_r^2 + z_i^2) = e^{z_r}\sin z_i/a > 0$, which requires that $d > 0$. Evaluating the real and imaginary parts of $f(z) = ze^z - a(z-2d)$ yields

$$e^{z_r}(z_r \sin z_i + z_i \cos z_i) = az_i, \tag{96}$$

$$e^{z_r}(z_r \cos z_i - z_i \sin z_i) = a(z_r - 2d). \tag{97}$$

We eliminate a from Eqs. (96) and (97) and obtain

$$z_r^2 + z_i^2 = 2d(z_r + z_i \cot z_i). \tag{98}$$

Solving this equation gives

$$z_r = d \pm \sqrt{d^2 - z_i^2 + 2dz_i \cot z_i}. \tag{99}$$

Substituting it into (96) yields $g_\pm(d,z_i) = 0$, where

$$\begin{aligned} g_\pm(d,z_i) &\\ := \exp&\left(d \pm \sqrt{d^2 - z_i^2 + 2dz_i \cot z_i}\right) \\ &\times \left[\left(d \pm \sqrt{d^2 - z_i^2 + 2dz_i\cot z_i}\right)\frac{\sin z_i}{z_i} + \cos z_i\right] - a. \end{aligned}$$

Let $z_i^* \in (0,\pi)$ be the unique solution of the equation $d^2 - z_i^2 + 2dz_i \cot z_i = 0$. It is readily seen that $g_+(d,z_i)$ is a real decreasing function and $g_-(d,z_i)$ is a real increasing function for $z_i \in [0,z_i^*]$. [We remark that if $z_i \in (z_i^*,\pi)$, then $g_\pm(d,z_i)$ is not real and cannot be zero.] Moreover, $g_\pm(d,z_i^*) = e^d - a$ and $g_\pm(0) = (1 + d \pm \sqrt{d^2+2d})\exp(d \pm \sqrt{d^2+2d}) - a$. Therefore, (95) has exactly one complex root $z = z_r + iz_i$ with $z_i \in (0,\pi)$ if and only if

$$\begin{aligned} &(1 + d - \sqrt{d^2+2d})\exp(d - \sqrt{d^2+2d}) \\ &\quad < a < (1 + d + \sqrt{d^2+2d})\exp(d + \sqrt{d^2+2d}). \end{aligned}$$

Recalling that $a = (y_0+1)e^{y_0}$, the above inequality is the same as $d - \sqrt{d^2+2d} < y_0 < d + \sqrt{d^2+2d}$ or, equivalently, $2d > y_0^2/(y_0+1)$. Therefore, we conclude that the transcendental function $f(z) = ze^z - a(z-2d)$ with $a = (y_0 + 1)e^{y_0}$ has exactly two real zeros if and only if $2d \leqslant y_0^2/(y_0+1)$ and exactly two zeros that form a complex conjugate pair $z_r \pm iz_i$ with $0 < z_i < \pi$ if and only if $2d > y_0^2/(y_0+1)$.

Third, for existence, if λ_1 and λ_2 are located in the strip $|V^o \mathrm{Im}\lambda| < \pi$, we have to show that the outer solution in (30) is indeed monotonic. Since Eq. (62) is equivalent to (66) and since $\dot{x}$ in (30) has the explicit formula (64), we need to show that if λ_1 and λ_2 in the strip $|V^o \mathrm{Im}\lambda| < \pi$ satisfies Eq. (66), then the derivative of the outer solution $\dot{x}$ as given in (64) is nowhere near zero as ϕ^o varies from $\phi^o(0)$ to $\phi^o(1)$. Observe from (65) and (67) that the polynomials $Q_0(\lambda)$ and $Q_1(\lambda)$ are linear and with a positive leading coefficient. Without loss of generality, we may assume $\phi^o(0) = 0$, $\phi^o(1) = 1$, $Q_0(\lambda) = \lambda$, and $Q_1(\lambda) = a(\lambda - 2d)$ with $a > 0$. Since λ_1 and λ_2 are two roots of $\lambda e^\lambda = a(\lambda - 2d)$, we have $a = (\lambda_2 e^{\lambda_2} - \lambda_1 e^{\lambda_1})/(\lambda_2 - \lambda_1)$. We will prove by contradiction that if

$$\lambda_1 e^{\lambda_1 \varphi} = \lambda_2 e^{\lambda_2 \varphi} \tag{100}$$

for some $\varphi \in (0,1)$, then a cannot be positive. There are two cases to be considered separately.

Case I: $\lambda_1 < \lambda_2$ are real. It follows from (100) that $\lambda_1\varphi < -1 < \lambda_2\varphi < 0$. If $\lambda_2 \leqslant -1$, then $\lambda_2 e^{\lambda_2} < \lambda_1 e^{\lambda_1}$, which contradicts $a > 0$. If $\lambda_2 > -1$, then $\lambda_2 < \lambda_2\varphi < 0$ and

$$\lambda_2 e^{\lambda_2} < \lambda_2\varphi e^{\lambda_2\varphi} = \lambda_1\varphi e^{\lambda_1\varphi} < \lambda_1 e^{\lambda_1},$$

which again contradicts $a > 0$.

Case II: $\lambda_1 = x - iy$ and $\lambda_2 = x + iy$ with real x and $y \in (0,\pi)$. It follows from (100) that $x = -y\cot(y\varphi) < -y\cot y$. This contradicts the fact that $a = e^x(x \sin y/y + \cos y) > 0$.

A combination of the above three steps yields the existence and uniqueness of a physical solution for $n = 3$. For $n > 3$, we leave it as an open problem.[2]

VI. DISCUSSION AND CONCLUSION

In this paper, we have provided a systematic framework for deriving a uniform asymptotic solution to the steady-state PNP system for point charges with boundary conditions in the absence of fixed charges. On the one hand, the leading-order system of equations in the outer region becomes linear if we view the electric potential as a variable. Consequently, the outer solution can be expressed explicitly as an inverse function of a combination of exponential functions. On the other hand, the leading-order systems of equations near the two boundary layers can be solved in terms of generalized elliptic integrals. In contrast to previous work, which requires the solution of a system of nonlinear equations, our methodology provides a simple numerical procedure to compute membrane fluxes. We note that in biological ion channels, fixed charges are almost always present and it is therefore of significant interest to extend our analysis to include these effects.

We used the framework to prove the uniqueness of the solution for the three-ion case. The physical implication of this result is that hysteresis cannot occur in the PNP framework in the absence of fixed charges. Therefore, additional physical mechanisms are needed to model biological systems that exhibit bistability. As mentioned above, fixed charges are ubiquitous in biological ion channels and the role that these charges play in giving rise to multivalued solutions remains an important open question.

In the absence of fixed charges, if the cross-membrane potential is large, we have derived explicit expressions for the membrane current and all of the ionic fluxes. In the electroneutral case, the boundary layers are absent and our

[2]We will discuss open problems further in Sec. VI.

results show that the potential ϕ and ionic concentrations c_i are all monotonic functions of position. This implies that ϕ and c_i are bounded by their boundary values. We note that in a previous study it was suggested that nonmonotonic behavior can occur. However, we have shown that this is not the case for physically relevant solutions in which all ion concentrations are non-negative.

In the following, we conclude this paper with discussions on the problem of degeneracy and singularity, the nonexistence of internal layer solution, and some open problems.

A. Degeneracy and singularity

The matrix $\mathcal{I}$ in (56) becomes singular when $I_1 = -\sum_{i=1}^n z_i J_i$ defined in (22) vanishes. From (11) and (12) we have

$$0 = \frac{d\phi^o}{dx} \sum_{i=1}^n z_i^2 c_i.$$

Hence $I_1 = 0$ implies that ϕ^o is a constant in the outer region. Consequently, we have $\phi^o(0) = \phi^o(1)$ or, equivalently, the positive solutions of the two algebraic equations (46) and (49) are the same. In contrast, for physically relevant solutions with $c_i^o \geqslant 0$, if $\phi^o(0) = \phi^o(1)$, we conclude from (11) and (12) that $I_1 = 0$. This demonstrates that $I_1 = 0$ is equivalent to $\phi^o(0) = \phi^o(1)$. In this degenerate case, the outer solution is a constant, (12) becomes $dc_i^o/dx = -J_i$ which can be readily solved, and we are only left to find two boundary layer solutions as in (72) and (73).

It should be noted that if some of the fluxes are zero (but the weighted flux $I_1 \neq 0$), then degeneracy does not occur and we can proceed as in the general case. Although it seems possible to reduce the dimension of the PNP system by removing the corresponding ions with zero flux, this reduction will actually lead to full nonlinearity and loss of symmetry so that the reduced system becomes much more complicated to handle than the original one.

If, in particular, all of the fluxes are zero, then we have n algebraic constraints on the boundary conditions by integrating Eq. (6):

$$c_{iR} = c_{iL} e^{-z_i(\phi_R - \phi_L)}.$$

The PNP system can be reduced to a scalar equation

$$-\varepsilon^2 \phi'' = \sum_{i=1}^n z_i c_{iL} e^{-z_i(\phi - \phi_L)} \tag{101}$$

augmented with the boundary conditions $\phi(0) = \phi_L$ and $\phi(1) = \phi_R$. This problem is a special case of our degenerate case ($I_1 = 0$) when the outer solution is a constant and two boundary layer solutions can be expressed in terms of generalized elliptic integrals.

B. Nonexistence of internal layers

One interesting question related to the uniqueness of solutions is whether there exists internal layers for PNP system as those in other systems. Internal layers often occur to resolve multivaluedness in such problems as in the case of the classical shock layer in gas dynamics or as spikes (see [71] for example). Here we provide a simple proof for the nonexistence of internal layers.

Suppose that an internal layer exists at some point x_0. Then it satisfies the following equations:

$$-\frac{d^2\phi^I}{dZ^2} = \sum_{i=1}^n z_i c_i^I, \tag{102}$$

$$0 = \frac{dc_i^I}{dZ} + z_i c_i^I \frac{d\phi^I}{dZ}, \tag{103}$$

where $Z := (x - x_0)/\varepsilon$. By matching, we have electroneutrality as we tend to the edges of the internal layer:

$$\sum_{i=1}^n z_i c_i^I(\pm\infty) = 0.$$

Integrating Eq. (103) from $-\infty$ to ∞ gives

$$c_i^I(\infty) = c_i^I(-\infty) e^{-z_i[\phi^I(\infty) - \phi^I(-\infty)]}.$$

It can shown from these two equations that

$$\sum_{i=1}^n z_i \left(1 - e^{-z_i[\phi^I(\infty) - \phi^I(-\infty)]}\right) c_i^I(-\infty) = 0.$$

This contradicts the non-negativeness of the concentrations c_i^I because all of the coefficients $z_i(1 - e^{-z_i[\phi^I(\infty) - \phi^I(-\infty)]})$ have the same sign. Therefore, physically relevant steady-state internal layer solutions do not exist. In similar systems, previous authors have shown that internal layers can propagate in transient situations giving rise to traveling waves [44,45], but our result shows that stationary waves cannot occur.

C. Open problems

For the special case $n = 2$ (α:β), Liu [54] proved the (local) uniqueness of the solution. For the $n = 3$ case, we are able to show that Eq. (87) has exactly two roots in the strip $|V^o \mathrm{Im}\lambda| < \pi$, which implies the existence and uniqueness of the physical solution. We have performed extensive numerical tests for four or more ions ($n > 3$) and have always found unique solutions. Thus, we conjecture that the general PNP system still has a unique physical solution whose characteristic roots to Eq. (62) are appropriately chosen. We leave the rigorous proof of this statement as an open problem.

In the expression of boundary layer solutions we have made use of the inverse function of generalized elliptic integrals introduced in (68). This definition generalizes the classical elliptic integrals [72] and further investigation is required to understand the generalized elliptic integrals. Again, we leave the more detailed analysis of (68) as an open problem.

ACKNOWLEDGMENTS

This work was done with support as a postdoctoral fellow while X.-S.W. was visiting at York University. X.-S.W. would like to express his gratitude to Professor Jianhong Wu for his generous support. The work of H.H. was supported in part by NSERC. The work of J.J.W. was supported by the Research Grants Council of Hong Kong (Grant No. CityU 104211).

[1] M. Burger, R. S. Eisenberg, and H. W. Engl, SIAM J. Appl. Math. **67**, 960 (2007).
[2] D. P. Chen and R. S. Eisenberg, Biophys. J. **64**, 1405 (1993).
[3] R. D. Coalson, J. Phys. A **41**, 115001 (2009).
[4] R. S. Eisenberg, J. Membr. Biol. **150**, 1 (1996).
[5] R. S. Eisenberg, Adv. Chem. Phys. **148**, 77 (2010).
[6] D. Gillespie and R. S. Eisenberg, Phys. Rev. E **63**, 061902 (2001).
[7] D. Gillespie and R. S. Eisenberg, Eur. Biophys. J. **31**, 454 (2002).
[8] V. Barcilon, SIAM J. Appl. Math. **52**, 1391 (1992).
[9] V. Barcilon, D.-P. Chen, and R. S. Eisenberg, SIAM J. Appl. Math. **52**, 1405 (1992).
[10] M. Z. Bazant, M. S. Kilic, B. D. Storey, and A. Ajdari, Adv. Colloid Interface Sci. **152**, 48 (2009).
[11] J. W. Jerome, *Analysis of Charge Transport: A Mathematical Study of Semiconductor Devices* (Springer, Berlin, 1996).
[12] P. A. Markowich, *The Stationary Semiconductor Device Equations, Computational Microelectronics* (Springer, Vienna, 1986).
[13] P. A. Markowich, C. A. Ringhofer, and C. Schmeiser, *Semiconductor Equations* (Springer, Wien, 1990).
[14] I. Rubinstein, *Electro-diffusion of ions, SIAM Studies in Applied Mathematics*, 11 (Society for Industrial and Applied Mathematics (SIAM), Philadelphia, PA, 1990).
[15] Z. Schuss, B. Nadler, and R. S. Eisenberg, Phys. Rev. E **64**, 036116 (2001).
[16] C. Berti, D. Gillespie, J. P. Bardhan, R. S. Eisenberg, and C. Fiegna, Phys. Rev. E **86**, 011912 (2012).
[17] D. Boda and D. Gillespie, J. Chem. Theor. Comput. **8**, 824 (2012).
[18] E. Csanyi, D. Boda, D. Gillespie, and T. Kristof, Biochim. Biophys. Acta **1818**, 592 (2012).
[19] D. Gillespie, Biophys. J. **94**, 1169 (2008).
[20] D. Gillespie, Biophys. J. **95**, 3706 (2008).
[21] D. Gillespie and D. Boda, Biophys. J. **95**, 2658 (2008).
[22] D. Gillespie, J. Giri, and M. Fill, Biophys. J. **97**, 2212 (2009).
[23] D. Gillespie, W. Nonner, and R. S. Eisenberg, J. Phys.: Condens. Matter **14**, 12129 (2002).
[24] D. Gillespie, W. Nonner, and R. S. Eisenberg, Phys. Rev. E **68**, 031503 (2003).
[25] D. Gillespie, L. Xu, Y. Wang, and G. Meissner, J. Phys. Chem. B **109**, 15598 (2005).
[26] T.-L. Horng, T.-C. Lin, C. Liu, and B. Eisenberg, J. Phys. Chem. B **116**, 11422 (2012).
[27] Y. Hosokawa, K. Yamada, B. Johannesson, and L.-O. Nilsson, Mater. Struct. **44**, 1577 (2011).
[28] Y. Hyon, D. Y. Kwak, and C. Liu, Discrete Cont. Dyn. Syst. Ser. A **26**, 1291 (2010).
[29] Y. Hyon, J. E. Fonseca, B. Eisenberg, and C. Liu, Discrete Cont. Dyn. Syst. Ser. B **17**, 2725 (2102).
[30] B. Johannesson, Transp. Porous Media **85**, 565 (2010).
[31] M. S. Kilic, M. Z. Bazant, and A. Ajdari, Phys. Rev. E **75**, 021503 (2007).
[32] M. Knepley, D. Karpeev, S. Davidovits, R. Eisenberg, and D. Gillespie, J. Chem. Phys. **132**, 124101 (2010).
[33] D. Krauss, B. Eisenberg, and D. Gillespie, Eur. Biophys. J. **40**, 775 (2011).
[34] D. Krauss and D. Gillespie, Eur. Biophys. J. **39**, 1513 (2010).
[35] J.-L. Liu, J. Comput. Phys. **247**, 88 (2013).
[36] Y. Mori, C. Liu, and R. S. Eisenberg, Physica D **240**, 1835 (2011).
[37] G. Wei, Q. Zheng, Z. Chen, and K. Xia, SIAM Rev. **54**, 699 (2012).
[38] Q. Zheng and G.-W. Wei, J. Chem. Phys. **134**, 194101 (2011).
[39] B. Zaltzman and I. Rubinstein, J. Fluid Mech. **579**, 173 (2007).
[40] D. Boda, D. Gillespie, W. Nonner, D. Henderson, and B. Eisenberg, Phys. Rev. E **69**, 046702 (2004).
[41] M. Z. Bazant, K. Thornton, and A. Ajdari, Phys. Rev. E **70**, 021506 (2004).
[42] K. T. Chu and M. Z. Bazant, Phys. Rev. E **74**, 011501 (2006).
[43] L. H. Olesen, M. Z. Bazant, and H. Bruus, Phys. Rev. E **82**, 011501 (2010).
[44] S. Ghosal and Z. Chen, Bull. Math. Biol. **72**, 2047 (2010).
[45] S. Ghosal and Z. Chen, J. Fluid Mech. **697**, 436 (2012).
[46] M. Z. Bazant, Proc. R. Soc. London Ser. A **460**, 1433 (2004).
[47] K. T. Chu and M. Z. Bazant, J. Colloid Interface Sci. **315**, 319 (2007).
[48] K. S. Khair and T. M. Squires, J. Fluid Mech. **640**, 343 (2009).
[49] N. Abaid, R. S. Eisenberg, and W. Liu, SIAM J. Appl. Dyn. Syst. **7**, 1507 (2008).
[50] H. Steinruck, SIAM J. Appl. Math. **49**, 1102 (1989).
[51] V. Barcilon, D.-P. Chen, R. S. Eisenberg, and J. W. Jerome, SIAM J. Appl. Math. **57**, 631 (1997).
[52] J.-H. Park and J. W. Jerome, SIAM J. Appl. Math. **57**, 609 (1997).
[53] A. Singer and J. Norbury, SIAM J. Appl. Math. **70**, 949 (2009).
[54] W. Liu, SIAM J. Appl. Math. **65**, 754 (2005).
[55] J. D. Murray, *Mathematical Biology I: An Introduction* (Springer, New York, 2002).
[56] H. Kitano, *Foundations of Systems Biology* (MIT Press, Cambridge, 2001).
[57] B. Eisenberg and W. Liu, SIAM J. Math. Anal. **38**, 1932 (2007).
[58] M. S. Mock, COMPEL **1**, 165 (1982).
[59] I. Rubinstein, SIAM J. Appl. Math. **47**, 1076 (1987).
[60] A. Singer, D. Gillespie, J. Norbury, and R. S. Eisenberg, Eur. J. Appl. Math. **19**, 541 (2008).
[61] H. R. Leuchtag, J. Math. Phys. **22**, 1317 (1981).
[62] W. Liu, J. Differ. Equ. **246**, 428 (2009).
[63] R. Zhao, M. van Soestbergen, H. H. M. Rijnaarts, A. van der Wal, M. Z. Bazant, and P. M. Biesheuvel, J. Colloid Interface Sci. **384**, 38 (2012).
[64] M. B. Andersen, M. van Soestbergen, A. Mani, H. Bruus, P. M. Biesheuvel, and M. Z. Bazant, Phys. Rev. Lett. **109**, 108301 (2012).
[65] M. Z. Bazant, K. T. Chu, and B. J. Bayly, SIAM J. Appl. Math. **65**, 1463 (2005).
[66] K. T. Chu and M. Z. Bazant, SIAM J. Appl. Math. **65**, 1485 (2005).
[67] P. M. Biesheuvel, M. van Soestbergen, and M. Z. Bazant, Electrochim. Acta **54**, 4857 (2009).
[68] M. van Soestbergen, P. M. Biesheuvel, and M. Z. Bazant, Phys. Rev. E **81**, 021503 (2010).

[69] R. Ralston and P. Rabinowitz, *A First Course in Numerical Analysis* (McGraw-Hill, New York, 1978).
[70] P. Kravanja and M. Van Barel, *Computing the Zeros of Analytic Functions*, Lecture Notes in Mathematics Vol. 1727 (Springer, Berlin, 2000).
[71] C. H. Ou and R. Wong, Stud. Appl. Math. **111**, 377 (2003).
[72] F. W. J. Olver, D. W. Lozier, R. F. Boisvert, and C. W. Clark, eds., *NIST Handbook of Mathematical Functions* (Cambridge University Press, New York, NY, 2010) Print companion to NIST Digital Library of Mathematical Functions, http://dlmf.nist.gov/