Mathematical analysis of Poisson-Nernst-Planck models with permanent charges and boundary layers: Studies on individual fluxes

Jianing Chen,∗ Yiwei Wang† Lijun Zhang‡ and Mingji Zhang§¶

Abstract

This work focuses on a one-dimensional Poisson-Nernst-Planck system including small permanent charges for ionic flows with one cation and one anion through a membrane channel. Our main interest is to examine the qualitative properties of the individual fluxes with boundary layers that is more realistic for ion channel problem study. Our result shows that the individual fluxes depend sensitively on multiple system parameters such as permanent charges, channel geometry, boundary conditions (concentrations and potentials) and boundary layers. For the relatively simple setting and assumptions of the model in this work, we are able to characterize the different effects of the nonlinear interaction among these system parameters in detail and gain a better understanding of the internal dynamics of ionic flows through membrane channels. Our analysis indicates that the small positive permanent charge cannot strengthen the flux of cation while reduce that of anion. Critical electric potentials which play crucial roles in studying ionic flow properties are identified. Some can be estimated experimentally. Numerical simulations are further performed and numerical results are consistent with our analytical ones.

Key Words. Poisson-Nernst-Planck systems, permanent charges, individual fluxes, boundary layers, critical potentials

AMS subject classification. 34A26, 34B16, 34D15, 37D10, 92C35

Abbreviated title. Boundary layer effects on individual fluxes via PNP system

1 Introduction

The study of electrodiffusion is an extraordinarily plentiful area for multidisciplinary research with various applications in different research fields, such as physics, chemistry and biology. More specifically, semiconductor technology controls the migration and diffusion of quasi-particles of charge in transistors and integrated circuits

∗Department of Mathematics, New Mexico Institute of Mining and Technology, Socorro, NM 87801, USA, E-mail: jianing.chen@student.nmt.edu
†Zhejiang Sci-Tech University, Hangzhou, Zhejiang 310018, China, E-mail: yiwei_1223@163.com
‡College of Mathematics and Systems Science, Shandong University of Science and Technology, Qingdao, Shandong 266510, China, Email: li-jun0608@163.com
§Department of Mathematics, New Mexico Institute of Mining and Technology, Socorro, NM 87801, USA, E-mail: mingji.zhang@nmt.edu.
¶Corresponding author: Mingji Zhang
problems ([45, 49]), chemical science deals with charged molecules in water ([7, 11, 12]), and biology occurs in plasma of ions and charged organic molecules in water ([3, 14, 25, 50]). Not surprisingly, the physics of electrodiffusion is of such universal importance: systems of moving charge have rich behaviors that can be occasionally controlled easily by boundary conditions, and the actual goal of technology is to control systems to allow useful behavior.

Control is important to biological sciences, and almost all biology occurs in plasmas, in which ions move much as they move in gaseous plasmas, or as quasi-particles move in semiconductors ([16, 17, 18]). In semiconductor and biological devices, macroscopic flows of charges are driven through atomic scale channels which link one macroscopic reservoir to another. The reservoirs are macroscopic regions where the concentration of charges and electrical potentials are almost constant. Engineers and biophysicists control flow by setting the electric potential at the boundaries usually called contacts, terminals, or baths. Besides the external driving forces (boundary electric potentials and boundary concentrations), the flow through the atomic scale channel is also affected by other variables, namely, the shape of its pore (channel geometry) and the distribution of permanent charge along its interior wall ([15, 17, 18, 21]).

Mathematical analysis plays essential and unique roles for revealing mechanisms of observed biological phenomena and for discovering new ones, assuming a more or less explicit solution of the associated mathematical model can be achieved. The recent accomplishments ([8, 9, 19, 20, 31, 33, 37, 36, 41, 44, 52]) in analyzing Poisson-Nernst-Planck (PNP) model for ionic flows through membrane channels provides deep insights and better understanding of qualitative properties of ionic flows, especially, the internal dynamics. In this work, we examine boundary layers effects (due to the violation of electroneutrality boundary concentration conditions) on ionic flows via one-dimensional classical PNP models with nonzero but small permanent charges. Of particular interest is to characterize the nonlinear interplays among system parameters, such as channel geometry, small permanent charge, boundary conditions (concentration and potential) and boundary layers, which provides some efficient ways to control the ionic flows through membrane channels by adjusting boundary conditions (mainly boundary electric potentials).

1.1 Ionic flows and the PNP model

Ionic flows are governed by fundamental physical laws of electrodiffusion which relate rates of quantities of interest. Two most relevant biological properties of a channel are permeation and selectivity, both of which are characterized by the current-
voltage relations measured experimentally under different ionic conditions. However, to better understand the ionic flow properties of interest, it is important to examine properties of individual fluxes because most experiments (with some exceptions) can only measure the total flux while individual fluxes contain much more information on channel functions [26, 31].

Considering the structural characteristics, the basic continuum model for ionic flows is the PNP system which can be extracted as a reduced model from molecular dynamics ([46]), Boltzmann equations ([4]), and variational principles ([28, 29, 30]). The simplest PNP system is the classical Poisson-Nernst-Planck (cPNP) system that includes the ideal component \( \mu_{id}^k(X) \) in (7) only. The ideal component \( \mu_{id}^k \) contains contributions by considering ion particles as point charges. For a wide range of purposes, the classical PNP models have been simulated ([14, 23, 27, 43, 53] and the reference therein) and analyzed (see, e.g., [1, 4, 5, 6, 47, 48, 51]) extensively.

For ionic solutions with \( n \) ion species, the PNP system reads

\[
\nabla \cdot \left( \epsilon_r(r) \varepsilon_0 \nabla \Phi \right) = -e \left( \sum_{s=1}^{n} z_s c_s + Q(r) \right),
\]

\[
\nabla \cdot \mathbf{J}_k = 0,
\]

\[
-\mathbf{J}_k = 1 \frac{k_B T}{D_k(r)} c_k \nabla \mu_k, \quad k = 1, 2, \ldots, n,
\]

where \( r \in \Omega \) with \( \Omega \) being a three-dimensional cylindrical-like domain representing the channel, \( Q(r) \) is the permanent charge density, \( \varepsilon(r) \) is the relative dielectric coefficient, \( \varepsilon_0 \) is the vacuum permittivity, \( e \) is the elementary charge, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature; \( \Phi \) is the electric potential. Also, for the \( k \)th ion species, \( c_k \) is the concentration, \( z_k \) is the valence (the number of charges per particle), \( \mu_k \) is the electrochemical potential depending on \( \Phi \) and \( \{c_j\} \), \( \mathbf{J}_k \) is the flux density, and \( D_k(r) \) is the diffusion coefficient.

Based on the fact that ion channels have narrow cross-sections relative to their lengths, reduction of the three-dimensional steady-state PNP systems (1) to a quasi-one-dimensional models was first proposed in [43] and was rigorously justified in [40] for special cases. A quasi-one-dimensional steady-state PNP model takes the form

\[
\frac{1}{h(x)} \frac{d}{dx} \left( \varepsilon_r(x) \varepsilon_0 h(x) \frac{d\Phi}{dx} \right) = -e \left( \sum_{s=1}^{n} z_s c_s + Q(x) \right),
\]

\[
\frac{d\mathbf{J}_k}{dx} = 0, \quad -\mathbf{J}_k = 1 \frac{k_B T}{D_k(x) h(x)} c_k \frac{d\mu_k}{dx}, \quad k = 1, 2, \ldots, n,
\]

where \( x \in [0, 1] \) is the coordinate along the axis of the channel that is normalized to \( [0, 1] \), \( h(x) \) is the area of cross-section of the channel over the location \( x \).

For system (2), we have the following boundary conditions (see [19] for a reasoning), for \( k = 1, 2, \ldots, n \),

\[
\Phi(0) = \mathcal{V}, \quad c_k(0) = L_k > 0; \quad \Phi(1) = 0, \quad c_k(1) = R_k > 0, \quad k = 1, 2, \ldots, n.
\]

1.2 Permanent charges

While some information may be obtained by ignoring the permanent charge and focusing on the effects of boundary conditions, the charges and sizes of ions, etc.,
we believe that different channel types differ mainly in the distribution of permanent charge ([21]). For both ion channels and semiconductors, permanent charges add an additional component—probably the most important one—to their rich behavior, in particular, for ion channels, a permanent charge reflects the structure of the channel protein. Permanent charge density may depend on the location of many atoms, the shape of the protein (channel geometry), and so on ([20]). In general, the permanent charge \( Q(x) \) is modeled by a piecewise constant function, that is, we assume, for a partition \( x_0 = 0 < x_1 < \cdots < x_{m-1} < x_m = l \) of \([0, l] \) into \( m \) subintervals, \( Q(x) = Q_j \) for \( x \in (x_{j-1}, x_j) \) where \( Q_j \)'s are constants with \( Q_1 = Q_m = 0 \) (the intervals \([x_0, x_1] \) and \([x_{m-1}, x_m] \) are viewed as the reservoirs without permanent charges).

In [19], under the framework of geometric singular perturbation theory, the existence and uniqueness (local) was established for the boundary value problem (2)-(3) with one cation and one anion and the permanent charge function modeled by

\[
Q(x) = 0 \text{ if } 0 < x < a; \quad Q(x) = Q_0 \text{ if } a < x < b; \quad Q(x) = 0 \text{ if } b < x < 1, \tag{4}
\]

where \( Q_0 \) is some nonzero constant. Due to the challenge in obtaining explicit expressions of the I-V relation with nonzero permanent charges, in [33], the author studied the case with \( Q_0 \) in (4) being small and employed regular perturbation analysis (viewing \( Q_0 \) as a small perturbation to the solutions of the system (2)-(3)) to further study the effects on ionic flows from the permanent charges. The analysis in [33] (Proposition 4.11 and its following discussion) indicates that to optimize the effect of the permanent charge, a short and narrow neck within which the permanent charge is confined, is expected. This indicates the critical role that the permanent charge plays in the study of ionic flow properties of interest.

1.3 Electroneutrality conditions and boundary layers

To describe the actual behavior of channels or useful transistors, macroscopic reservoirs linked by ion channels must be included ([13, 22, 23, 24]). Macroscopic boundary conditions that describe such reservoirs introduce boundary layers of concentration and charge. If those boundary layers reach into the part of the device that performs atomic control, they prominently influence its behavior. Particularly, boundary layers of charge are probably to produce artifacts over long distances because the electric field spreads a long way.

The boundary layer problem should be considered more carefully in the study of such problems, particularly, for ion channel problems. In [19, 37, 38], under the framework of geometric singular perturbation analysis, the authors studied the classical PNP system and mainly focused on the existence and local uniqueness result. The boundary layer is characterized in the study of the limiting fast system (see Corollary 3.3 in [19] and Proposition 3.3 in [38] for details), from which two landing points (for convenience in our following discussion, we let \( \phi_{[0,r]} \) and \( c_k^{[0,r]} \) be the corresponding components of the landing point at the left boundary \( x = 0 \) and let \( \phi_{[1,l]} \) and \( c_k^{[1,l]} \) be the corresponding components of the landing point at the right boundary \( x = 1 \) ) are obtained, which provide new boundary conditions for the limiting slow system (mainly for the electric potential and concentration, see Section 3.1.2 in [19] and Section 3.1.2 in [38] for detailed discussion). The approximated individual fluxes/I-V relations can then be derived from the solution of the limiting slow system under
those new boundary conditions that include boundary layer effects. However, this is not studied in any of these works.

On the other hand, very often, when examine the qualitative properties of ionic flows in terms of I-V relations and individual fluxes, which characterize the two most relevant properties (permeation and selectivity) of ion channels, electroneutrality boundary conditions are naturally enforced at both ends of the channel (see, e.g., [1, 8, 9, 10, 32, 33, 34, 36, 39, 53]), which are defined as

$$\sum_{s=1}^{n} z_s L_s = \sum_{s=1}^{n} z_s R_s = 0. \tag{5}$$

However, under the condition (5), the two boundary layers disappear, and the \(\phi\)- and \(c_k\)-components of the landing points are nothing but the original boundary conditions, that is, \(\phi^{[0,j]} = \phi(0), \ c_k^{[0,j]} = c_k(0)\) and \(\phi^{[1,j]} = \phi(1), \ c_k^{[1,j]} = c_k(1)\), where \(\phi(0)\) and \(c_k(0)\) are the boundary conditions at \(x = 0\); \(\phi(1)\) and \(c_k(1)\) are the one at \(x = 1\). Although the difficulty in analyzing the dynamics of ionic flows is reduced to a great extent, the effects on ionic flows from boundary layers that carries much more rich information cannot be examined.

To better understand the mechanism of ionic flows through membrane channels, one need to consider the boundary layer effects during the study. Due to the sensitivity of electric potentials on boundary layers, a first but natural step is to study the state that is not neutral but close to. This is more challenging but more realistic to study dynamics of ionic flows. Following this idea, the author in [54] considered the cPNP system for one cation and one anion with zero permanent charges focusing on the qualitative properties of ionic flows. More precisely, the author assumes

$$-z_2 L_2 = \sigma(z_1 L_1) \quad \text{and} \quad -z_2 R_2 = \rho(z_1 R_1), \tag{6}$$

where \(\sigma\) and \(\rho\) are some positive constants close to but not equal to 1 simultaneously (\(\sigma = 1 = \rho\) in (6) implies neutral state). More rich qualitative properties of ionic flows were observed compared to the one with electroneutrality conditions. More recently, the authors in [52] further studied the cPNP system with two cations and one anion focusing on the competitions between cations that further depend on boundary conditions. Some special cases were also studied in [2, 42]. All the works indicate the importance of the role played by the boundary layer in the analysis of ionic flow properties of interest, and encourage us to further study the effects from boundary layer while a nonzero but small permanent charge is included in the PNP model.

1.4 Brief discussion of main results

Our interest in this work is to study the qualitative properties of ionic flows through membrane channels via the cPNP system for two oppositely charged particles with small permanent charges \(Q(x)\) defined by (4) and under the assumption (6) as \((\sigma, \rho) \rightarrow (1, 1)\). This is a more realistic but more challenging approach to study the properties of ionic flows related to ion channel problems. Particularly, we focus on the case with \((\sigma, \rho) \rightarrow (1^+, 1^+)\), while other cases can be analyzed similarly. We take advantage of the work in [33] to provide a detailed explanation of how these physical parameters interact to produce a wide spectrum of behaviors for ionic flows with boundary layers.
For convenience, we now give a brief discussion of our main results. To get started, we write the individual fluxes of the form with \(Q_0 > 0\) (\(Q_0 < 0\) case can be analyzed similarly)

\[J_k(V; Q_0; L_1, R_1; \sigma, \rho) = J_{k0}(V; L_1, R_1; \sigma, \rho) + Q_0 J_{k1}(V; L_1, R_1; \sigma, \rho) + o(Q_0), \quad k = 1, 2,\]

where \(J_{k1}\) is the leading term containing small permanent charges with boundary layers characterized through the parameters \(\sigma\) and \(\rho\). In our following discussion, we use \(J_k^{EN}, J_{k0}^{EN}\) and \(J_{k1}^{EN}\) to denote the case under electroneutrality boundary conditions.

(i) As the leading term containing permanent charge effects, the sign of \(J_{k1}\) is crucial. Our first key result deals with the dependence of signs of \(J_{k1}\) on channel geometry with boundary layers, from which the small permanent charge effects on the magnitude of the individual fluxes \(|J_k(V)|, \ k = 1, 2\) (equivalent to analyzing the sign of \(J_{k0}(V)J_{k1}(V)\)) are studied. Two critical potentials \(V_1^*\) and \(V_2^*\) are identified by \(J_{11}(V_1^*) = 0\) and \(J_{21}(V_2^*) = 0\), which play key role in our analysis; see Theorem 3.5 in Section 3.2.

(ii) Further depending on the nonlinear interplays among channel geometry \((\alpha, \beta)\), boundary conditions \((L_1, R_1)\) and boundary layers \((\sigma, \rho)\), the order of \(V_1^*\) and \(V_2^*\) is provided, which splits the electric potential region into three subregions, over which distinct effects from permanent charge on individual fluxes are able to be characterized. More interestingly, we observed that (small) positive permanent charges

- can reduce the cation flux and enhance the anion flux;
- can enhance both cation and anion fluxes;
- can reduce both cation and anion fluxes;
- but cannot enhance the cation flux while reduce the anion flux;

see Theorem 3.10 in Section 3.2.

(iii) Partial order (see Proposition 3.12) and total order (see Proposition 3.16) of the critical potentials \(V_1^*, V_2^*, V_q^1\) and \(V_q^2\) are provided, from which the effects from boundary layers on individual fluxes are analyzed to a great extent. Here, \(V_q^1\) and \(V_q^2\) are defined by \(J_{11}^{EN}(V_q^1) = 0\) and \(J_{21}^{EN}(V_q^2) = 0\). Taking the partial order of \(V_1^*\) and \(V_q^1\) for example, with \(V_q^1 < V_1^*\), one has \(J_{10}^{EN} J_{11}^{EN} > 0\) while \(J_{10} J_{11} < 0\) for \(V_q^1 < V < V_1^*\), from which one can tell clearly that the qualitative properties of the individual flux \(J_1\) is totally different, and the difference is caused by the boundary layers; see Theorems 3.14 and 3.15, and Table 1 given in Section 3.3.2.

(iv) To further study the boundary layer effects on individual fluxes, we consider the term \(J_{kd}\) defined by

\[J_{kd}(V; \sigma, \rho) = J_k(V; \sigma, \rho) - J_k^{EN}(V; 1, 1) = G_{k0}(V; \sigma, \rho) + Q_0 G_{k1}(V; \sigma, \rho),\]

where \(G_{k0} = J_{k0} - J_{k0}^{EN}\) and \(G_{k1} = J_{k1} - J_{k1}^{EN}\). Two critical potentials \(V_{1N}^*\) and \(V_{2N}^*\) are defined by \(G_{11}(V_{1N}^*) = 0\) and \(G_{21}(V_{2N}^*) = 0\), together with the interaction among other system parameters, particularly the small permanent
charges and channel geometry, different cases for the sign of $G_{k0}(V)G_{k1}(V)$ are observed and characterized that further indicates the important roles played by the boundary layers in the study of ionic flows properties; see Theorem 3.18 in Section 3.4.

We comment that for the relatively simple setting of the PNP model, our analysis almost completely characterizes the nonlinear interplays among different system parameters, such as, channel geometry, small permanent charges, boundary conditions and boundary layers. Most importantly, the sensitive dependence of ionic flows properties on boundary layers is examined in great detail. Most of the results are far away from intuitive, especially the observation discussed in (ii) above. The study in this work provides some deep insights and better understanding of the mechanism of ionic flows through membrane channels, and meanwhile provides efficient ways to observe different qualitative properties of ionic flows by controlling/adjusting boundary conditions, particularly, the boundary electric potential. The identification of the two critical potentials $V_1^*$ and $V_2^*$ that balance the small permanent charge effects is critical in our study, which can be estimated experimentally (see the discussion in Section 4). Compared to the work done in [33], the dynamics of ionic flows are more rich due to the more complicated interaction among the parameters, and more importantly, the existence of boundary layers (for example, one may compare Theorem 3.5 and Proposition 3.8 in current work with Theorem 4.8 in [33]). We believe the analysis in this work will provide useful information for future studies both numerically and analytically, and even experimentally.

We organize the rest of this paper as follows: in Section 2, we set up the problem with some further restrictions consistent with those in [33]. Some results from [33] are recalled, which will be the starting point of our analysis; Section 3 provides boundary layer effects on individual fluxes in great detail under the condition (6) as $(\sigma, \rho) \to (1, 1)$. Several critical potentials are identified, which play critical role in characterizing the small permanent charge effects on individual fluxes with boundary layers. Numerical simulations are further performed to provide a more intuitive understanding of our analytical results, and they are consistent. The conclusion and the summary for this work is included in Section 4.

2 Problem set-up and some previous results

The PNP model is briefly described, and some results from [33], which will be used in our later discussion, are recalled.

2.1 The steady-state boundary value problem and assumptions

Our main interest is to examine the boundary layer effect on ionic flows via the PNP system (2)-(3) with small permanent charges.

To be specific, the same setting as that in [33] but without assuming electroneutrality boundary conditions: $z_1L_1 + z_2L_2 = z_1R_1 + z_2R_2 = 0$, is taken, which includes:

(A1). We consider two charged particles $(n = 2)$ with $z_1 > 0$ and $z_2 < 0$. 

(A2). The PNP model only includes the ideal component \( \mu_{k}^{id}(X) \) of the electrochemical potential defined by

\[
\mu_{k}^{id}(x) = z_{k}e\Phi(x) + k_{B}T\ln\frac{c_{k}(x)}{c_{0}},
\]

where \( c_{0} \) is some characteristic number density.

(A3). \( \varepsilon_{r}(X) = \varepsilon_{r} \) and \( D_{t}(X) = D_{t} \).

We will assume (A1)–(A3) from now on. We first make the following dimensionless rescaling ([33]). Let

\[
J = \frac{e_{0}k_{B}T}{c_{0}}J,
\]

\[
V = \frac{e_{0}k_{B}T}{c_{0}}V,
\]

\[
\varepsilon^{2} = \frac{\varepsilon_{r}e_{0}k_{B}T}{e^{2}},
\]

\[
J_{k} = \frac{J_{k}}{D_{k}},
\]

Correspondingly, the boundary value problem (2)-(3) becomes

\[
\frac{\varepsilon^{2}}{h(x)}\frac{d}{dx}\left(h(x)\frac{d}{dx}\phi\right) = -z_{1}c_{1} - z_{2}c_{2} - Q(x),
\]

\[
h(x)\frac{d\phi}{dx} + z_{k}h(x)c_{k}\frac{d\phi}{dx} = -J_{k},
\]

\[
\frac{dJ_{k}}{dx} = 0, \quad k = 1, 2
\]

with the boundary conditions

\[
\phi(0) = V, \quad c_{k}(0) = L_{k}; \quad \phi(1) = 0, \quad c_{k}(1) = R_{k}, \quad k = 1, 2.
\]

We point out that both the variable \( c \) and the function \( h(x) \) in the equation (8) are dimensionless.

### 2.2 Some previous results

We recall some results from [33] that are fundamental for our analysis. The authors in [33] treat \( |Q_{0}| \) small compared to the boundary concentrations \( L_{k} \)'s and \( R_{k} \)'s, and derive approximations for the individual fluxes expanded in \( Q_{0} \):

\[
J_{k}(V; Q_{0}) = J_{k_{0}}(V) + J_{k_{1}}(V; \lambda)Q_{0} + o(Q_{0}),
\]

where \( J_{k} = D_{k}J_{k} \) (correspondingly, \( J_{k_{0}} = D_{k}J_{k_{0}} \) and \( J_{k_{1}} = D_{k}J_{k_{1}} \)) and

\[
J_{10} = \frac{(c_{1}^{L} - c_{1}^{R})(z_{1}V + \ln L_{1} - \ln R_{1})}{H(1)(\ln c_{1}^{L} - \ln c_{1}^{R})},
\]

\[
J_{20} = \frac{(c_{2}^{L} - c_{2}^{R})(z_{2}V + \ln L_{2} - \ln R_{2})}{H(1)(\ln c_{2}^{L} - \ln c_{2}^{R})},
\]

\[
J_{11} = \frac{A(z_{2}(1 - B)\lambda + 1)}{(z_{1} - z_{2})H(1)}(z_{1}\lambda + 1), \quad J_{21} = \frac{A(z_{1}(1 - B)\lambda + 1)}{(z_{2} - z_{1})H(1)}(z_{2}\lambda + 1),
\]

with

\[
\lambda = \frac{\phi^{L} - \phi^{R}}{\ln c_{1}^{L} - \ln c_{1}^{R}}, \quad A = \frac{(c_{1}^{L} - c_{1}^{R})(c_{10}^{b} - c_{10}^{a})}{c_{10}^{a}c_{10}^{b}(\ln c_{1}^{L} - \ln c_{1}^{R})},
\]

\[
B = \frac{\ln c_{10}^{a} - \ln c_{10}^{b}}{A} = \frac{(\ln c_{1}^{L} - \ln c_{1}^{R})(\ln c_{10}^{b} - \ln c_{10}^{a})}{(c_{1}^{L} - c_{1}^{R})(c_{10}^{b} - c_{10}^{a})}.\]
Here,

\[
\phi^L = V - \frac{1}{z_1 - z_2} \ln \frac{-z_2 L_2}{z_1 L_1}, \quad z_1 c_1^L = -z_2 c_2^L = (z_1 L_1) \frac{-z_2}{z_1 - z_2} (z_2 L_2) \frac{z_1}{z_1 - z_2},
\]

\[
\phi^R = -\frac{1}{z_1 - z_2} \ln \frac{-z_2 R_2}{z_1 L_1}, \quad z_1 c_1^R = -z_2 c_2^R = (z_1 R_1) \frac{-z_2}{z_1 - z_2} (z_2 R_2) \frac{z_1}{z_1 - z_2}, \tag{13}
\]

\[
c_{10}^a = c_1^L + \alpha(c_1^R - c_1^L), \quad c_{10}^b = c_1^L + \beta(c_1^R - c_1^L),
\]

where, with \( H(x) = \int_0^x \frac{1}{h(s)} \, ds, \)

\[
\alpha = \frac{H(a)}{H(1)} \quad \text{and} \quad \beta = \frac{H(b)}{H(1)}. \tag{14}
\]

The quantities \( J_{11} \) and \( J_{21} \) are the leading terms containing permanent charges and channel geometry effects on individual fluxes and will be studied in detail.

We define the following function, which will be used often in our analysis. For \( t > 0 \), set

\[
\gamma(t) = \frac{t \ln t - t + 1}{(t - 1) \ln t} \quad \text{for} \quad t \neq 1 \quad \text{and} \quad \gamma(1) = \frac{1}{2}. \tag{15}
\]

One establishes easily that

**Lemma 2.1.** For \( t > 0 \), one has \( 0 < \gamma(t) < 1, \gamma'(t) > 0 \), \( \lim_{t \to 0} \gamma(t) = 0 \) and \( \lim_{t \to \infty} \gamma(t) = 1. \)

### 3 Boundary layer effects on individual fluxes

Of particular interest in this section is to examine the effects on individual fluxes from boundary layers, which further depend on other system parameters, particularly, the permanent charge and channel geometry. More precisely, we study the qualitative properties of individual fluxes under the assumption (6).

#### 3.1 Expansions of individual fluxes at \((\sigma^*, \rho^*) = (1, 1)\)

For the \( k \)th ion species, upon introducing \( \mu_k^\delta \) to denote the difference between its electrochemical potentials at the two boundaries, one has

\[
\mu_k^\delta := \mu_k^\delta(V; L_k, R_k) = \mu_k(0) - \mu_k(1) = k_B T(z_k V + \ln L_k - \ln R_k). \tag{16}
\]

Together with the assumption (6), (11) can be rewritten as

\[
\begin{align*}
J_{10} &= \frac{-z_1}{H(1)} \left( \frac{z_1 - z_2}{z_1 - z_2} \ln \frac{\rho}{\sigma} + \ln \frac{L_1}{R_1} \right) k_B T \mu_1^\delta, \\
J_{20} &= -\frac{z_1}{z_2} \left( \frac{z_1 - z_2}{z_1 - z_2} \ln \frac{\rho}{\sigma} + \ln \frac{L_1}{R_1} \right) k_B T \mu_2^\delta, \\
J_{11} &= \frac{-z_2 (f(\sigma, \rho) + g(\sigma, \rho)) V + f_1(\sigma, \rho) + g_1(\sigma, \rho)}{(z_1 - z_2) H(1)} k_B T \mu_1^\delta, \\
J_{21} &= \frac{z_1 (f(\sigma, \rho) + g(\sigma, \rho)) V - f_2(\sigma, \rho) + g_2(\sigma, \rho)}{(z_1 - z_2) H(1)} k_B T \mu_2^\delta,
\end{align*}
\]
where, with

\[
A = - \frac{\beta - \alpha}{(1 - \alpha)\sigma^{\frac{1}{z_1 - z_2}} L_1 - \rho^{\frac{1}{z_1 - z_2}} R_1} \cdot \frac{1}{(1 - \beta)\sigma^{\frac{1}{z_1 - z_2}} L_1 + \beta\rho^{\frac{1}{z_1 - z_2}} R_1},
\]

\[
f(\sigma, \rho) = \ln \frac{(1 - \beta)\sigma^{\frac{1}{z_1 - z_2}} L_1 + \beta\rho^{\frac{1}{z_1 - z_2}} R_1}{(1 - \alpha)\sigma^{\frac{1}{z_1 - z_2}} L_1 + \alpha\rho^{\frac{1}{z_1 - z_2}} R_1}
\]

\[
g(\sigma, \rho) = -\frac{A}{(z_1 - z_2)\ln \frac{\sigma}{\rho} + \ln \frac{L_1}{R_1}}^2,
\]

\[
f_1(\sigma, \rho) = \frac{z_2 \ln \frac{\sigma}{\rho}}{(z_1 - z_2)\ln \frac{\sigma}{\rho} + \ln \frac{L_1}{R_1}^2},
\]

\[
g_1(\sigma, \rho) = \frac{A(z_1 - z_2)\ln \frac{\sigma}{\rho} + \ln \frac{L_1}{R_1}^2}{(z_1 - z_2)\ln \frac{\sigma}{\rho} + \ln \frac{L_1}{R_1}^2},
\]

\[
f_2(\sigma, \rho) = \frac{z_1 \ln \frac{\sigma}{\rho}}{(z_1 - z_2)\ln \frac{\sigma}{\rho} + \ln \frac{L_1}{R_1}^2},
\]

\[
g_2(\sigma, \rho) = \frac{-A(z_1 - z_2)\ln \frac{\sigma}{\rho} + \ln \frac{L_1}{R_1}^2}{(z_1 - z_2)\ln \frac{\sigma}{\rho} + \ln \frac{L_1}{R_1}^2}.
\]

We focus on the dynamics of individual fluxes near the neutral state, which is the case with \((\sigma, \rho) \to (1, 1)\) under our assumption. We first expand \(J_{k0}\) and \(J_{k1}\) at \((\sigma^*, \rho^*) = (1, 1)\) up to the first order (higher order terms are neglected). For simplicity, we let \(t = L_1/R_1\), and always assume \(t > 1\) in our following discussions. Similar argument can be applied for the case with \(t < 1\). Then, one has

\[
J_{10} = \frac{R_1 M}{H(1)\ln^2 t k_B T}, \quad J_{20} = -\frac{z_1}{z_2} \frac{R_1 M}{H(1)\ln^2 t k_B T},
\]

\[
J_{11} = -\frac{z_2 NV + E}{(z_1 - z_2)H(1) k_B T}, \quad J_{21} = \frac{z_1 NV + F}{(z_1 - z_2)H(1) k_B T},
\]

where \(M = M(\sigma, \rho), \ N = N(\sigma, \rho), \ E = E(\sigma, \rho)\) and \(F = F(\sigma, \rho)\) are given by

\[
M = (t - 1) \ln t + \frac{z_1}{z_1 - z_2} \left[ (\sigma - 1) t \ln t + (1 - \rho) t \ln t + (\rho - \sigma)(t - 1) \right],
\]

\[
N = g(1, 1) + f(1, 1) + \left( \frac{\partial g}{\partial \sigma}(1, 1) + \frac{\partial f}{\partial \sigma}(1, 1) \right)(\sigma - \rho),
\]

\[
E = g_1(1, 1) + f_1(1, 1) + \left( \frac{\partial g_1}{\partial \sigma}(1, 1) + \frac{\partial f_1}{\partial \sigma}(1, 1) \right)(\sigma - \rho),
\]

\[
F = g_2(1, 1) - f_2(1, 1) + \left( \frac{\partial g_2}{\partial \sigma}(1, 1) - \frac{\partial f_2}{\partial \sigma}(1, 1) \right)(\sigma - \rho).
\]
Here, with $\omega(x) = (1 - x)t + x$, we have

$$g(1, 1) + f(1, 1) = \frac{\omega(\alpha)\omega(\beta) \ln t \ln \frac{\omega(\beta)}{\omega(\alpha)} + (\beta - \alpha)(t - 1)^2}{\omega(\alpha)\omega(\beta) \ln^3 t},$$

$$\frac{\partial g}{\partial \sigma}(1, 1) + \frac{\partial f}{\partial \sigma}(1, 1) = \frac{1}{2} \frac{2z_1}{z_1 - z_2} \omega^2(\alpha)\omega^2(\beta) \ln^3 t \left[ (\beta - \alpha) \left( \omega(\alpha)\omega(\beta) \left( t^2 - t \right) \ln t - \frac{t}{2} \ln^2 t - \frac{3}{2} (t - 1)^2 \right) - (1 - \alpha)(1 - \beta)t^2 + (\beta + \alpha - 2\alpha\beta) \frac{t}{2} \ln t \right]$$

$$- \omega^2(\alpha)\omega^2(\beta) \ln t \ln \frac{\omega(\beta)}{\omega(\alpha)};$$

$$g_1(1, 1) + f_1(1, 1) = \frac{(\alpha - \beta)(t - 1)^2}{\omega(\alpha)\omega(\beta) \ln^2 t},$$

$$\frac{\partial g_1}{\partial \sigma}(1, 1) + \frac{\partial f_1}{\partial \sigma}(1, 1) = \frac{1}{2} \frac{2z_1}{z_1 - z_2} \omega^2(\alpha)\omega^2(\beta) \ln^3 t \left[ (\alpha - \beta) \left( \omega(\alpha)\omega(\beta) \left( t^2 - t \right) \ln t - \frac{t}{2} \ln^2 t - \frac{3}{2} (t - 1)^2 \right) - (1 - \alpha)(1 - \beta)t^2 + (\beta + \alpha - 2\alpha\beta) \frac{t}{2} \ln t \right]$$

$$- \omega^2(\alpha)\omega^2(\beta) \ln t \ln \frac{\omega(\beta)}{\omega(\alpha)};$$

$$g_2(1, 1) - f_2(1, 1) = \frac{(\beta - \alpha)(t - 1)^2}{\omega(\alpha)\omega(\beta) \ln^2 t},$$

$$\frac{\partial g_2}{\partial \sigma}(1, 1) - \frac{\partial f_2}{\partial \sigma}(1, 1) = \frac{1}{2} \frac{2z_1}{z_1 - z_2} \omega^2(\alpha)\omega^2(\beta) \ln^3 t \left[ \frac{2z_1}{z_1 - z_2} (\beta - \alpha) \left( \omega(\alpha)\omega(\beta) \left( t^2 - t \right) \ln t - \frac{t}{2} \ln^2 t - \frac{3}{2} (t - 1)^2 \right) - (1 - \alpha)(1 - \beta)t^2 + (\beta + \alpha - 2\alpha\beta) \frac{t}{2} \ln t \right]$$

$$- \frac{z_1}{z_1 - z_2} \omega^2(\alpha)\omega^2(\beta) \ln t \ln \frac{\omega(\beta)}{\omega(\alpha)}.\]

**Remark 3.1.** One has

(i) Direct calculations gives

$$\frac{\partial g}{\partial \rho}(1, 1) + \frac{\partial f}{\partial \rho}(1, 1) = - \frac{\partial g}{\partial \rho}(1, 1) - \frac{\partial f}{\partial \rho}(1, 1),$$

$$\frac{\partial g_1}{\partial \rho}(1, 1) + \frac{\partial f_1}{\partial \rho}(1, 1) = - \frac{\partial g_1}{\partial \rho}(1, 1) - \frac{\partial f_1}{\partial \rho}(1, 1),$$

$$\frac{\partial g_2}{\partial \rho}(1, 1) - \frac{\partial f_2}{\partial \rho}(1, 1) = - \frac{\partial g_2}{\partial \rho}(1, 1) + \frac{\partial f_2}{\partial \rho}(1, 1).$$

(ii) Under the assumption (6), for $t > 1$ and $(\sigma, \rho) \to (1^+, 1^+)$, one has $J_{k0}$ is positively proportional to $\mu^k$ from formulas (18).

(iii) For $J_{11}, J_{21}$ in the formulas (18), if $\sigma = \rho = 1$, we will get the same results as those under electroneutrality conditions in [33].
3.2 Dependence of signs of $J_{k1}$ on channel geometry with boundary layers

We now consider the signs of $J_{k1}$’s relative to those of $J_{k0}$’s via boundary condition $(V, L, R)$ and channel geometry $(\alpha, \beta)$.

We first consider the sign of the quantity $f(1,1) + g(1,1)$, which will be used later for our analysis. To get started, we write it as

$$f(1,1) + g(1,1) = \frac{p(\beta)}{\omega(\alpha)\omega(\beta)\ln^3 t},$$

where

$$p(\beta) = \omega(\alpha)\omega(\beta)\ln t\ln \frac{\omega(\beta)}{\omega(\alpha)} + (\beta - \alpha)(t - 1)^2.$$ 

For $p(\beta)$, the following result can be established.

**Lemma 3.2.** Assume $t > 1$. Then,

(i) for $\alpha < \gamma(t)$, there exists a unique $\beta_1 \in (\alpha, 1)$ such that

$$p(\beta) < 0 \text{ if } \beta \in (\alpha, \beta_1) \text{ and } p(\beta) > 0 \text{ if } \beta \in (\beta_1, 1);$$

(ii) for $\alpha \geq \gamma(t)$, $p(\beta) > 0$.

Notice that $\omega(\alpha) > 0$ and $\omega(\beta) > 0$. One has, for $t > 1$, $g(1,1) + f(1,1)$ has the same sign as that of $p(\beta)$.

**Lemma 3.3.** Let $t = L_1/R_1 > 1$ and $\gamma(t)$ be as in (15). Define $s(\beta)$ as

$$s(\beta) = \frac{\partial g}{\partial \sigma}(1,1) + \frac{\partial f}{\partial \sigma}(1,1) = \frac{1}{z_1 - z_2\omega(\alpha)\omega(\beta)\ln^3 t} s_1(\beta),$$

where

$$s_1(\beta) = (\beta - \alpha)\left[\omega(\alpha)\omega(\beta)\left((t^2 - t)\ln t - \frac{t}{2}\ln^2 t - \frac{3}{2}(t - 1)^2\right) - (t - 1)^2\right]$$

$$\times (1 - \alpha)(1 - \beta)t^2 + (\beta + \alpha - 2\alpha\beta)\frac{t}{2}\ln t - \omega(\alpha)\omega(\beta)\ln t\ln \frac{\omega(\beta)}{\omega(\alpha)}.$$

One has

(i) For $0 < \alpha < \gamma(t)$,

(1) if $0 < \alpha \leq \alpha_1$, then, $s(\beta) > 0$;

(2) if $\alpha_1 < \alpha < \gamma(t)$, then, $s(\beta) < 0$.

(ii) For $\gamma(t) \leq \alpha < 1$,

(iii) if $\gamma(t) \leq \alpha < \alpha_2$, then, there exists a unique $\beta_2 \in (\alpha, 1)$ such that

$$s(\beta) < 0 \text{ for } \beta \in (\alpha, \beta_2) \text{ and } s(\beta) > 0 \text{ for } \beta \in (\beta_2, 1);$$
(ii2) if \( \alpha_2 \leq \alpha < 1 \), then, \( s(\beta) > 0 \).

Here \( \alpha_1 \) and \( \alpha_2 \) are two roots of
\[
s_2(\alpha) = (t^2 - t) \ln t - \frac{t}{2} \omega(\alpha) \ln^2 t - \frac{3}{2}(t - 1)^2 \omega(\alpha) + (t - 1) \omega^2(\alpha) \ln t = 0
\]
given by
\[
\begin{align*}
\alpha_1 &= \frac{2t(t - 1) \ln t - \frac{t}{2} \ln^2 t - \frac{3}{2}(t - 1)^2 - \sqrt{\frac{t^2 \ln^4 t}{4} + \frac{9(t - 1)^4}{4} - \frac{5(t - 1)^2 \ln^2 t}{2}}}{2(t - 1)^2 \ln t}, \\
\alpha_2 &= \frac{2t(t - 1) \ln t - \frac{t}{2} \ln^2 t - \frac{3}{2}(t - 1)^2 + \sqrt{\frac{t^2 \ln^4 t}{4} + \frac{9(t - 1)^4}{4} - \frac{5(t - 1)^2 \ln^2 t}{2}}}{2(t - 1)^2 \ln t}.
\end{align*}
\]

**Proof.** The proof is complicated by straightforward. We omit it here. \( \square \)

**Remark 3.4.** It is easy to check numerically, for \( t > 1 \), \( \alpha_1 > 0.29 \) and \( \alpha_2 > 0.7 \).

**Theorem 3.5.** For \( N \neq 0 \), define \( V_1^* \) and \( V_2^* \) by \( J_{11}(V_1^*) = 0 \) and \( J_{21}(V_2^*) = 0 \), respectively, which are given by
\[
V_1^* = \frac{E}{z_2 N} \quad \text{and} \quad V_2^* = -\frac{F}{z_1 N}.
\]
(20)

Then, for \( t = L_1/R_1 > 1 \), \( \sigma, \rho \rightarrow (1^+, 1^+) \) with \( \sigma > \rho \), one has

(i) For \( \gamma(t) \leq \alpha < 1 \),

(i1) if \( \alpha_2 \leq \alpha < 1 \) or \( \gamma(t) \leq \alpha < \alpha_2 \) and \( \beta \in (\beta_2, 1) \) or \( \gamma(t) \leq \alpha < \alpha_2 \) and \( \beta \in (\alpha, \beta_2) \) and \( \sigma - \rho < -\frac{f(1, 1) + g(1, 1)}{s(\beta)} \), then, \( N > 0 \); furthermore,

(i11) \( J_{10}J_{11} < 0 \) (resp. \( J_{10}J_{11} > 0 \)) if \( V < V_1^* \) (resp. \( V > V_1^* \));

(i12) \( J_{20}J_{21} < 0 \) (resp. \( J_{20}J_{21} > 0 \)) if \( V < V_2^* \) (resp. \( V > V_2^* \));

or equivalently, for \( V < V_1^* \), (small) positive \( Q_0 \) reduces \( |J_1| \) and, for \( V > V_1^* \), (small) positive \( Q_0 \) strengthens \( |J_1| \); and for \( V < V_2^* \), (small) positive \( Q_0 \) reduces \( |J_2| \) and, for \( V > V_2^* \), (small) positive \( Q_0 \) strengthens \( |J_2| \);

(ii) if \( \gamma(t) \leq \alpha < \alpha_2 \) and \( \beta \in (\alpha, \beta_2) \) and \( \sigma - \rho < -\frac{f(1, 1) + g(1, 1)}{s(\beta)} \), then, \( N < 0 \); and,

(ii1) \( J_{10}J_{11} > 0 \) (resp. \( J_{10}J_{11} < 0 \)) if \( V < V_1^* \) (resp. \( V > V_1^* \));

(ii2) \( J_{20}J_{21} > 0 \) (resp. \( J_{20}J_{21} < 0 \)) if \( V < V_2^* \) (resp. \( V > V_2^* \));

or equivalently, for \( V < V_1^* \), (small) positive \( Q_0 \) strengthens \( |J_1| \) and, for \( V > V_1^* \), (small) positive \( Q_0 \) reduces \( |J_1| \); and for \( V < V_2^* \), (small) positive \( Q_0 \) strengthens \( |J_2| \) and, for \( V > V_2^* \), (small) positive \( Q_0 \) reduces \( |J_2| \);

(ii) For \( 0 < \alpha < \gamma(t) \),

(iii) if \( \beta \in (\alpha, \beta_1) \) and \( 0 < \alpha < \gamma(t) \), then, \( N < 0 \); and,

(iii1) \( J_{10}J_{11} > 0 \) (resp. \( J_{10}J_{11} < 0 \)) if \( V < V_1^* \) (resp. \( V > V_1^* \));
Remark 3.6. Actually, the term $V_{j1}$, where $J_{j2}$ is the sign of $\mu_{k}$, Lemma 3.7. Let $\alpha_{1} < \alpha < \gamma(t)$ and $\sigma - \rho < -\frac{f(1,1)+g(1,1)}{s(\beta)}$, then, $N > 0$; and,

(iii) if $\beta \in (\beta_{1}, 1)$, $\alpha_{1} < \alpha < \gamma(t)$ and $\sigma - \rho < -\frac{f(1,1)+g(1,1)}{s(\beta)}$, then, $N < 0$; and, (ii11) $J_{0}\mathcal{J}_{11} > 0$ (resp. $J_{0}\mathcal{J}_{11} < 0$) if $V < V_{1}^{*}$ (resp. $V > V_{1}^{*}$); (iii11) $J_{0}\mathcal{J}_{11} > 0$ (resp. $J_{0}\mathcal{J}_{11} < 0$) if $V < V_{1}^{*}$ (resp. $V > V_{1}^{*}$); or equivalently, for $V < V_{1}^{*}$, (small) positive $Q_{0}$ reduces $|J_{1}|$ and, for $V > V_{1}^{*}$, (small) positive $Q_{0}$ strengthens $|J_{2}|$; and, for $V > V_{2}^{*}$, (small) positive $Q_{0}$ reduces $|J_{2}|$.

We now compare the two critical potentials $V_{1}^{*}$ and $V_{2}^{*}$. Direct calculation gives

\[ V_{1}^{*} - V_{2}^{*} = \frac{k_{1} + (\sigma - \rho)k_{2}}{z_{1}z_{2}N}, \]

where

\[
\begin{align*}
k_{1} &= \frac{(z_{1} - z_{2})(\alpha - \beta)(t - 1)^{2}}{(\omega(\alpha)(\omega(\beta)\ln^{2} t)} , \\
k_{2} &= \frac{2z_{1}(\alpha - \beta)}{\omega^{2}(\alpha)(\omega(\beta))\ln^{3} t} \left[ (t - 1)\omega(\alpha)(\omega(\beta)(t \ln t - (t - 1)) \\
&\quad - (t - 1)^{2}((1 - \alpha)(1 - \beta)t^{2} + (\beta + \alpha - 2\alpha\beta_{1}t) \ln t] .
\end{align*}
\]

Remark 3.6. Actually, the term $J_{11}(V)$, as a function of the potential $V$, has two zeros, one is identified in the Theorem 3.5, the other is the value $V_{c}^{k1}$ such that $\mu_{k}^{\delta}(V_{c}^{k1}) = 0$, which is also a zero of $J_{k0}(V)$. Since our main interest in the Theorem 3.5 is the sign of $J_{k0}(V)J_{k1}(V)$, we did not focus on the critical potential $V_{c}^{k1}$.

Lemma 3.7. Let $\alpha_{3} = \frac{t - t - t \ln t}{(t - 1)^{2}}$ with $t = L_{1}/R_{1} > 1$. For $k_{2}$, one has

(i) For $0 < \alpha \leq \alpha_{1}$ or $\beta \in (\beta_{1}, 1)$, there exists a unique $\beta_{3} \in (\alpha, 1)$ such that $k_{2} > 0$ if $\beta \in (\alpha, \beta_{3})$; and $k_{2} < 0$ if $\beta \in (\beta_{3}, 1)$;

(ii) For $\alpha_{3} \leq \alpha < 1$, $k_{2} < 0$.

It follows that
Proposition 3.8. Let \( t = L_1/R_1 > 1 \), \( \sigma > \rho \) and \( (\sigma, \rho) \to (1^+, 1^+) \). Suppose \( \beta_1 < \beta_2 < \beta_3 \). One has

(i) \( V_1^* > V_2^* \) under one of the following conditions

\[
\text{(i1)} \quad \alpha > \alpha_3; \\
\text{(i2)} \quad \gamma(t) < \alpha < \alpha_3 \text{ and } \beta \in (\beta_3, 1); \\
\text{(i3)} \quad 0 < \alpha < \alpha_1 \text{ and } \beta \in (\beta_3, 1); \\
\text{(i4)} \quad \alpha_2 < \alpha < \alpha_3, \beta \in (\alpha, \beta_3) \text{ and } 0 < \sigma - \rho < -\frac{k_1}{k_2}; \\
\text{(i5)} \quad \gamma(t) < \alpha < \alpha_2, \beta \in (\beta_2, \beta_3) \text{ and } 0 < \sigma - \rho < -\frac{k_1}{k_2}; \\
\text{(i6)} \quad 0 < \alpha < \alpha_1, \beta \in (\beta_1, \beta_3) \text{ and } 0 < \sigma - \rho < -\frac{k_1}{k_2}; \\
\text{(i7)} \quad \gamma(t) < \alpha < \alpha_2, \beta \in (\alpha, \beta_2) \text{ and } 0 < \sigma - \rho < -\frac{f(1.1) + g(1.1)}{s(\beta)}; \\
\text{(i8)} \quad \gamma(t) < \alpha < \alpha_2, \beta \in (\alpha, \beta_2) \text{ and } -\frac{k_1}{k_2} < \sigma - \rho < 1; \\
\text{(i9)} \quad \alpha_1 < \alpha < \gamma(t), \beta \in (\beta_1, \beta_3) \text{ and } 0 < \sigma - \rho < -\frac{f(1.1) + g(1.1)}{s(\beta)}; \\
\text{(i10)} \quad \alpha_1 < \alpha < \gamma(t), \beta \in (\beta_1, \beta_3) \text{ and } -\frac{k_1}{k_2} < \sigma - \rho < 1; \\
\text{(i11)} \quad \alpha_1 < \alpha < \gamma(t), \beta \in (\beta_3, 1) \text{ and } 0 < \sigma - \rho < -\frac{f(1.1) + g(1.1)}{s(\beta)}; \\
\text{(i12)} \quad 0 < \alpha < \gamma(t), \beta \in (\alpha, \beta_1) \text{ and } -\frac{k_1}{k_2} < \sigma - \rho < 1.
\]

(ii) \( V_1^* < V_2^* \) under one of the following conditions

\[
\text{(ii1)} \quad \alpha_2 < \alpha < \alpha_3, \beta \in (\alpha, \beta_3) \text{ and } -\frac{k_1}{k_2} < \sigma - \rho < 1; \\
\text{(ii2)} \quad \gamma(t) < \alpha < \alpha_2, \beta \in (\beta_2, \beta_3) \text{ and } -\frac{k_1}{k_2} < \sigma - \rho < 1; \\
\text{(ii3)} \quad 0 < \alpha < \alpha_1, \beta \in (\beta_1, \beta_3) \text{ and } -\frac{k_1}{k_2} < \sigma - \rho < 1; \\
\text{(ii4)} \quad \gamma(t) < \alpha < \alpha_2, \beta \in (\alpha, \beta_2) \text{ and } -\frac{f(1.1) + g(1.1)}{s(\beta)} < \sigma - \rho < -\frac{k_1}{k_2}; \\
\text{(ii5)} \quad \alpha_1 < \alpha < \gamma(t), \beta \in (\beta_1, \beta_3) \text{ and } -\frac{f(1.1) + g(1.1)}{s(\beta)} < \sigma - \rho < -\frac{k_1}{k_2}; \\
\text{(ii6)} \quad \alpha_1 < \alpha < \gamma(t), \beta \in (\beta_3, 1) \text{ and } -\frac{f(1.1) + g(1.1)}{s(\beta)} < \sigma - \rho < 1; \\
\text{(ii7)} \quad 0 < \alpha < \gamma(t), \beta \in (\alpha, \beta_1) \text{ and } 0 < \sigma - \rho < -\frac{k_1}{k_2}.
\]

Remark 3.9. It is not difficult to see that the interactions among boundary conditions, channel geometry and boundary layers are much more rich and complicated compared with the case under electroneutrality boundary conditions studied in [33]. The observation of rich dynamics is then not a surprise for the concrete PNP model with the more realistic set-ups studied in this work.

Together with Theorem 3.5, we have

Theorem 3.10. Let \( t = L_1/R_1 > 1 \), \( \sigma > \rho \) and \( (\sigma, \rho) \to (1^+, 1^+) \). Assume \( \beta_1 < \beta_2 < \beta_3 \).

(i) Under the condition \( \gamma(t) < \alpha < \alpha_2, \beta \in (\alpha, \beta_2) \text{ and } 0 < \sigma - \rho < -\frac{f(1.1) + g(1.1)}{s(\beta)}, \) one has \( V_1^* > V_2^* \), and further, (small) positive \( Q_0 \) reduces both \( |J_1| \) and \( |J_2| \) if \( V < V_2^* \); strengthens \( |J_2| \) while reduces \( |J_1| \) if \( V_2^* < V < V_1^* \); and strengthens both \( |J_1| \) and \( |J_2| \) if \( V > V_1^* \);
(ii) Under the condition \( \gamma(t) < \alpha < \alpha_2, \beta \in (\alpha, \beta_2) \) and \( -\frac{f^{(1,1)} + g^{(1,1)}}{s^{(1)}(\beta)} < \sigma - \rho < -\frac{k_1}{k_2}, \) one has \( V_1^* < V_2^* \), and further, (small) positive \( Q_0 \) strengthens both \( |J_1| \) and \( |J_2| \) if \( V < V_1^* \); reduces \( |J_1| \) while strengthens \( |J_2| \) if \( V_1^* < V < V_2^* \); and reduces both \( |J_1| \) and \( |J_2| \) if \( V > V_2^* \).

We comment that the critical potentials \( V_1^* \) and \( V_2^* \) split the electric potential region into three subregions, over which distinct qualitative properties of the individual fluxes \( J_1 \) and \( J_2 \) are observed. This actually provides an efficient way to control ionic flows (preference of ion channel over different ion species) through ion channels by adjusting boundary conditions. Furthermore, from Theorem 3.10, one observes that, depending on the boundary conditions and channel geometry through \( (\alpha, \beta) \), (small) positive permanent charges

- can reduce the cation flux and enhance the anion flux;
- can enhance both cation and anion fluxes;
- can reduce both cation and anion fluxes;
- but cannot enhance the cation flux while reduce the anion flux.

This is consistent with the result obtained in [33] (Theorems 4.7 and 4.8) without boundary layers. However, the interplays between channel geometry and boundary conditions are much more complicated while the boundary layers present in the system. This can be seen from the existence of the critical values \( \alpha_k, \beta_k \) for \( k = 1, 2, 3 \), and \( \alpha_k \) for \( k = 1, 2 \) depending sensitively on \( t = L_1/R_1 \), which are discussed in Theorem 3.5, Lemma 3.7, Proposition 3.8, Theorem 3.10, respectively (one may also compare with the corresponding arguments, more precisely, Lemma 4.6 and Theorem 4.7 in [33]).

**Remark 3.11.** In Theorem 3.10, we just considered some cases based on the results in Theorem 3.5 and Proposition 3.8. More cases can be discussed.

### 3.3 Critical potentials: neutral conditions vs boundary layers

In this subsection, we discuss the relations among the critical potentials \( V_1^*, V_2^* \) with boundary layers and \( V_q^1, V_q^2 \) under electroneutrality boundary conditions identified in [33].

Recall from (20) that

\[
V_1^* = \frac{E}{z_2 \mathcal{N}} \quad \text{and} \quad V_2^* = -\frac{F}{z_1 \mathcal{N}},
\]

and from [33] (formula (4.8) in Theorem 4.8) that

\[
V_q^1 = -\frac{\ln L_1 - \ln R_1}{z_2 (1 - B)} \quad \text{and} \quad V_q^2 = -\frac{\ln L_1 - \ln R_1}{z_1 (1 - B)},
\]

where \( B \) is defined in (12). We comment that if \( \sigma = \rho = 1 \), then, \( V_1^* = V_q^1 \) and \( V_2^* = V_q^2 \).
3.3.1 A partial order of critical potentials

We focus on the relations among the critical potentials $V^*_{q}$ and $V^*_{q}$ and examine the effects on individual fluxes from boundary layers further characterized through those critical potentials.

**Proposition 3.12.** Let $t = L_1/R_1 > 1$. For $\sigma > \rho$ and $(\sigma, \rho) \rightarrow (1^+, 1^+)$, one has

(i) $V^*_1 > V^*_q$.

(ii) $V^*_1 < V^*_q$ (resp. $V^*_2 > V^*_q$) if $\alpha \in (\alpha^*_1, \alpha^*_2)$ (resp. $\alpha \in (0, \alpha^*_1) \cup (\alpha^*_2, 1)$).

Here $\alpha^*_1$ and $\alpha^*_2$ are two roots of

$$w^2(\alpha) \ln t + 2\omega(\alpha)(1 - t - t \ln t) - t(1 - 2(\alpha - 1) t - t) \ln t = 0$$

given by

$$\alpha^*_1 = \frac{1 - t + t \ln t - \sqrt{(1 - t)^2 - t \ln^2 t}}{(t - 1) \ln t}, \quad \alpha^*_2 = \frac{1 - t + t \ln t + \sqrt{(1 - t)^2 - t \ln^2 t}}{(t - 1) \ln t}.$$

**Proof.** We will just prove the first statement, and the second one can be discussed in a similar way. From (19) and (20), one has

$$V^*_1 = \frac{E}{z_2 N} = \frac{g_1(1, 1) + f_1(1, 1) + (\frac{\partial g_1}{\partial \sigma}(1, 1) + \frac{\partial f_1}{\partial \sigma}(1, 1)) (\sigma - \rho)}{z_2 (g(1, 1) + f(1, 1) + s(\beta)(\sigma - \rho))}.$$

Let $\tau = \sigma - \rho$, and view $V^*_1$ as a function of $\tau$, we have

$$\frac{dV^*_1}{d\tau} = -\frac{w(\beta)}{z_2 [g(1, 1) + f(1, 1) + s(\beta)\tau]^2};$$

with $w(\beta) = \frac{1}{\omega^2(\alpha)\omega^2(\beta) \ln^2 t} w_1(\beta)$, where

$$w_1(\beta) = \frac{z_2}{z_1 - z_2} \omega^2(\alpha) \omega^2(\beta) \ln^2 t \ln^2 \frac{\omega(\beta)}{\omega(\alpha)} + (t - 1)^2 (\beta - \alpha)^2 \left( \frac{z_1 \ln^2 t}{z_1 - z_2} + (t - 1)^2 \right)$$

$$- \frac{2}{z_1 - z_2} (t - 1)(\beta - \alpha) \omega(\alpha) \omega(\beta) \ln t \ln \frac{\omega(\beta)}{\omega(\alpha)} \left( z_2 (t - 1) \ln t \right)$$

$$+ \frac{2z_1}{z_1 - z_2} t(t - 1)^2 (\alpha - \beta) \ln^2 t \ln \frac{\omega(\beta)}{\omega(\alpha)} \left( t(1 - \alpha)(1 - \beta) + \frac{\alpha + \beta - 2\alpha \beta}{2} \right).$$

Obviously, $w(\beta)w_1(\beta) > 0$. Moreover,

$$\lim_{\beta \rightarrow \alpha} w_1(\beta) = 0, \quad \lim_{\beta \rightarrow \alpha} w'_1(\beta) = 0, \quad \lim_{\beta \rightarrow \alpha} w''_1(\beta) = 2(z_1 - z_2)(t - 1)^2 w_2(\alpha),$$

where

$$w_2(\alpha) = -2 z_2 \omega^2(\alpha) \ln^2 t + z_1 \ln^2 t - 2z_2 (1 - t) \omega(\alpha) \ln t - 2z_1 \omega(\alpha) t \ln^2 t$$

$$+ 2z_1 (1 - \alpha)(t^2 - t) \ln^2 t + (z_1 - z_2)(t - 1)^2.$$
It is easy to check that $w_2(\alpha)$ is a quadratic function in $\alpha$, and concave upward, whose discriminant is
\[
\Delta = 4z_1z_2(t-1)^2[(t-1)^2-t \ln t] \ln t < 0,
\]
from which one has $\lim_{\beta \to \alpha} w'_{\beta}(\beta) > 0$. It then follow that $w_1(\beta) > 0$, and so is $w(\beta) > 0$, which implies that $\frac{\partial w_1}{\partial \alpha} > 0$. Therefore, $V_1^* > V_q^1$ if $\tau > 0$.

\[\Box\]

**Remark 3.13.** Numerically, it is easy to get $\alpha_1^2 > 0.2$ and $\alpha_2^2 > 0.7$ for $t > 1$. Furthermore, one has $\alpha_1^2 < \alpha_1 < \gamma(t) < \alpha_2 < \alpha_2^*$. For convenience in our following discussion, we let $J_{k0}^E$, $J_{k1}^E$ and $J_{k2}^E$ denote the individual fluxes derived under electroneutrality boundary conditions, and $J_{k0}$, $J_{k1}$ and $J_k$ denote the individual fluxes derived with boundary layers.

From Theorem 3.5, Proposition 3.12, and the result from [33] (more precisely, for $\gamma(t) \leq \alpha$ with $t > 1$, one has $J_{10}, J_{11}^E < 0$ if $V < V_1$; $J_{10}^E J_{11}^E > 0$ and $J_{10} J_{11} < 0$ if $V < V_1^*$; $J_{10}^E J_{11}^E > 0$ and $J_{10} J_{11} > 0$ if $V > V_1^*$). Equivalently, (small) positive $Q_0$ reduces both $|J_{11}^E|$ and $|J_1|$ if $V < V_1^*$; (small) positive $Q_0$ strengthens $|J_{11}^E|$ and $|J_1|$ if $V > V_1^*$.

**Theorem 3.14.** Let $t = L_1/R_1 > 1$. Assume $\sigma > \rho$ with $(\sigma, \rho) \to (1^+, 1^+)$, and $\gamma(t) \leq \alpha < 1$. One has

(i) For $\gamma(t) \leq \alpha \leq \alpha_2$ and $\beta \in (\beta_2, 1)$, $J_{10}^E J_{11}^E < 0$ and $J_{10} J_{11} < 0$ if $V < V_1$, $J_{10}^E J_{11}^E < 0$ and $J_{10} J_{11} > 0$ if $V < V_1^*$; $J_{10}^E J_{11}^E > 0$ and $J_{10} J_{11} < 0$ if $V < V_1^*$; and $J_{10}^E J_{11}^E > 0$ and $J_{10} J_{11} > 0$ if $V > V_1^*$.

(ii) For $\gamma(t) \leq \alpha < \alpha_2$, $\beta \in (\alpha, \beta_2)$ and $\sigma - \rho > -\frac{f(1.1)+g(1.1)}{a(\beta)}$, $J_{10}^E J_{11}^E < 0$ and $J_{10} J_{11} < 0$ if $V < V_1$, $J_{10}^E J_{11}^E > 0$ and $J_{10} J_{11} > 0$ if $V < V_1^*$; $J_{10}^E J_{11}^E < 0$ and $J_{10} J_{11} < 0$ if $V > V_1^*$; and $J_{10}^E J_{11}^E > 0$ and $J_{10} J_{11} > 0$ if $V > V_1^*$.

**Theorem 3.15.** Let $t = L_1/R_1 > 1$. Assume $\sigma > \rho$ with $(\sigma, \rho) \to (1^+, 1^+)$, and $\gamma(t) \leq \alpha < 1$. One has

(i) For $\alpha_1 < \gamma(t) \leq \alpha \leq \alpha_2$ and $\beta \in (\beta_2, 1)$, $J_{10}^E J_{11}^E < 0$ and $J_{10} J_{11} < 0$ if $V < V_2^*$; $J_{10}^E J_{11}^E < 0$ and $J_{10} J_{11} > 0$ if $V < V_2^*$; and $J_{10}^E J_{11}^E > 0$ and $J_{10} J_{11} > 0$ if $V > V_2^*$.

(ii) For $\alpha_1 < \gamma(t) \leq \alpha < \alpha_2$, $\beta \in (\alpha, \beta_2)$ and $\sigma - \rho > -\frac{f(1.1)+g(1.1)}{a(\beta)}$, $J_{10}^E J_{11}^E < 0$ and $J_{10} J_{11} < 0$ if $V < V_2^*$; $J_{10}^E J_{11}^E < 0$ and $J_{10} J_{11} < 0$ if $V < V_2^*$; and $J_{10}^E J_{11}^E > 0$ and $J_{10} J_{11} > 0$ if $V > V_2^*$.
for example, in the first statement of Theorem 3.14, for \( V \)
fluxes from boundary layers are further examined. Taking the individual flux \( V \)
We provide a total order of the critical potentials
3.3.2 A total order of critical potentials
Let \( \beta \)
the potential region into subregions, from which more rich qualitative properties of
(iii) \( V \)
We would like to point out that in Theorems 3.14 and 3.15, the effects on individual
while reduces \( |J_2^E| \) and \( |J_2| \) if \( V^*_2 < V < V^*_2 \); and (small) positive \( Q_0 \) strengthens \( |J_2^E| \)
while reduces \( |J_2| \) if \( V > V^*_2 \).

We would like to point out that in Theorems 3.14 and 3.15, the effects on individual
fluxes from boundary layers are further examined. Taking the individual flux \( V_1 \)
for example, in the first statement of Theorem 3.14, for \( V^*_q < V < V^*_1 \), one has
\( J_{10}^E J_{11}^E > 0 \) while \( J_{10} J_{11} < 0 \). This once again indicates that the boundary layers
have great effects on the qualitative properties of ionic flows, and this should be
treated carefully in the future study of ion channel problems via PNP type models.

3.3.2 A total order of critical potentials
We provide a total order of the critical potentials \( V_k^* \) and \( V_q^k \) for \( k = 1, 2 \), that split
the potential region into subregions, from which more rich qualitative properties of ionic flows and effects from boundary layers can be observed.

Proposition 3.16. Let \( t = L_1/R_1 \rightarrow 1^+ \), \( \sigma > \rho \) and \( (\sigma, \rho) \rightarrow (1^+, 1^+) \). Suppose
\( \beta_1 < \beta_2 < \beta_3 \). One has
(i) \( V^*_q < V^*_2 < V^*_q < V^*_1 \) under one of the following conditions
   (i1) \( \alpha > \alpha_3 \);
   (i2) \( \alpha_2^* < \alpha < \alpha_3 \) and \( \beta \in (\beta_3, 1) \);
   (i3) \( 0 < \alpha < \alpha_1^* \) and \( \beta \in (\beta_3, 1) \);
   (i4) \( \alpha_2^* < \alpha < \alpha_3 \) and \( \beta \in (\alpha, \beta_3) \) and \( 0 < \sigma - \rho < -\frac{k_1}{k_2} \);
   (i5) \( 0 < \alpha < \alpha_1^* \) and \( \beta \in (\alpha, \beta_3) \) and \( 0 < \sigma - \rho < -\frac{k_1}{k_2} \);
(ii) \( V^*_2 < V^*_q < V^*_q < V^*_1 \) under one of the following conditions
    (ii1) \( \gamma(t) < \alpha < \alpha_2^* \) and \( \beta \in (\beta_3, 1) \);
    (ii2) \( \alpha_2^* < \alpha < \alpha_1 \) and \( \beta \in (\beta_3, 1) \);
    (ii3) \( \alpha_2 < \alpha < \alpha_2^* \), \( \beta \in (\alpha, \beta_3) \) and \( 0 < \sigma - \rho < -\frac{k_1}{k_2} \);
    (ii4) \( \gamma(t) < \alpha < \alpha_2 \), \( \beta \in (\beta_3, 1) \) and \( 0 < \sigma - \rho < -\frac{k_1}{k_2} \);
    (ii5) \( \alpha_1^* < \alpha < \alpha_1 \), \( \beta \in (\beta_3, 1) \) and \( 0 < \sigma - \rho < -\frac{k_1}{k_2} \);
    (ii6) \( \gamma(t) < \alpha < \alpha_2 \), \( \beta \in (\alpha, \beta_3) \) and \( 0 < \sigma - \rho < -\frac{f(1,1)+g(1,1)}{s(\beta)} \);
    (ii7) \( \gamma(t) < \alpha < \alpha_2 \), \( \beta \in (\alpha, \beta_3) \) and \( -\frac{k_1}{k_2} < \sigma - \rho < 1 \);
    (ii8) \( \alpha_1 < \alpha < \gamma(t) \), \( \beta \in (\beta_1, \beta_3) \) and \( 0 < \sigma - \rho < -\frac{f(1,1)+g(1,1)}{s(\beta)} \);
    (ii9) \( \alpha_1 < \alpha < \gamma(t) \), \( \beta \in (\beta_1, \beta_3) \) and \( -\frac{k_1}{k_2} < \sigma - \rho < 1 \);
    (ii10) \( \alpha_1 < \alpha < \gamma(t) \), \( \beta \in (\beta_3, 1) \) and \( -\frac{f(1,1)+g(1,1)}{s(\beta)} < \sigma - \rho < 1 \).
(iii) \( V^*_q < V^*_q < V^*_1 < V^*_2 \) under one of the following conditions
   (iii1) \( \alpha_2^* < \alpha < \alpha_3 \) and \( \beta \in (\alpha, \beta_3) \) and \( -\frac{k_1}{k_2} < \sigma - \rho < 1 \);
Table 1: Effects on individual fluxes from small positive permanent charge effects over distinct subregions split by critical potentials are examined. Boundary layers play important role in the characterization. For example, over the interval $(V_q^*, V_2^*)$, the small positive permanent charge reduces both $|J_1|$ and $|J_{EN}^2|$, enhances $|J_2|$, but reduces $|J_{EN}^2|$; while in $(V_1^*, V_q^*)$, the small positive permanent charge enhances both $|J_2|$ and $|J_{EN}^2|$, reduces $|J_1|$, but enhances $|J_{EN}^1|$.

(iii2) $0 < \alpha < \alpha_1$ and $\beta \in (\beta_1, \beta_3)$ and $-\frac{k_1}{k_2} < \sigma - \rho < 1$;

(iv) $V_q^1 < V_1^* < V_q^2 < V_2^*$ if $0 < \alpha < \alpha_1^*$, $\beta \in (\alpha, \beta_1)$ and $0 < \sigma - \rho < -\frac{k_1}{k_2}$;

(v) $V_q^1 < V_1^* < V_q^2 < V_q^2$ if $\alpha_1^* < \alpha < \gamma(t)$, $\beta \in (\alpha, \beta_1)$ and $0 < \sigma - \rho < -\frac{k_1}{k_2}$;

(vi) $V_q^1 < V_q^2 < V_2^* < V_1^*$ if $0 < \alpha < \alpha_1^*$, $\beta \in (\alpha, \beta_1)$ and $-\frac{k_1}{k_2} < \sigma - \rho < 1$;

(vii) $V_2^* < V_q^1 < V_q^2 < V_1^*$ if $\alpha_1^* < \alpha < \gamma(t)$, $\beta \in (\alpha, \beta_1)$ and $-\frac{k_1}{k_2} < \sigma - \rho < 1$.

Proof. Notice that $0 < \alpha_1^* < \alpha_1 < \gamma(t) < \alpha_2 < \alpha_2^* < \alpha_3 < 1$. The result follows directly from Propositions 3.8 and 3.12.

We take the case (iii6) in the Proposition 3.16 for example. Under the condition $\gamma(t) < \alpha < \alpha_2$, $\beta \in (\alpha, \beta_2)$ and $\sigma - \rho < -\frac{f(1,1) + g(1,1)}{s(\beta)}$ (works for both cases with and without boundary layers, respectively), we have $V_2^* < V_q^1 < V_q^2 < V_1^*$, and these four critical potentials split the potential region into five subregions, to be specific, $(-\infty, V_2^*)$, $(V_2^*, V_q^2)$, $(V_q^2, V_q^1)$, $(V_q^1, V_1^*)$ and $(V_1^*, \infty)$. Over each subregion, the effects from small positive permanent charge can be examined (see Table 1), and the effects from the boundary layers can be observed clearly, more precisely, the different dynamics of the individual fluxes over both the subregion $(V_2^*, V_q^2)$ and the subregion $(V_q^1, V_1^*)$.

3.4 Further studies on boundary layers effects

We take a closer look at the effects on individual fluxes from boundary layers. Recall that, up to the first order in small $Q_0 > 0$, one has

$$J_k(V; \sigma, \rho) = J_{k0}(V; \sigma, \rho) + Q_0 J_{k1}(V; \sigma, \rho)$$
and
\[ J_{k}^{EN}(V; 1, 1) = J_{k0}^{EN}(V; 1, 1) + Q_{0}J_{k1}^{EN}(V; 1, 1). \]

To further study the boundary layer effects on the individual flux, we consider the quantity
\[ J_{kd}(V; \sigma, \rho; Q_{0}) = J_{k}(V; \sigma, \rho) - J_{k}^{EN}(V; 1, 1) = G_{k0}(V; \sigma, \rho) + Q_{0}G_{k1}(V; \sigma, \rho), \]
where \( G_{k0} = G_{k0}(V; \sigma, \rho) = J_{k0} - J_{k}^{EN} \) and \( G_{k1} = G_{k1}(V; \sigma, \rho) = J_{k1} - J_{k}^{EN} \) given by
\[
\begin{align*}
G_{10} & = \frac{R_{1}M_{1}}{H(1)\ln^{2}t} \mu_{1}^{\delta}, & G_{20} & = \frac{z_{1}}{z_{2}} \frac{R_{1}M_{1}}{H(1)\ln^{2}t} \mu_{2}^{\delta}, \\
G_{11} & = \frac{-z_{2}N_{1}V + E_{1}}{(z_{1} - z_{2})H(1)k_{BT}}, & G_{21} & = \frac{z_{1}N_{1}V + F_{1}}{(z_{1} - z_{2})H(1)k_{BT}},
\end{align*}
\]
where \( M_{1} = M_{1}(\sigma, \rho), \ N_{1} = N_{1}(\sigma, \rho), \ E_{1} = E_{1}(\sigma, \rho) \) and \( F_{1} = F_{1}(\sigma, \rho) \) are defined as
\[
\begin{align*}
M_{1} & = \frac{z_{1}}{z_{1} - z_{2}} \left[ (\sigma - 1)t \ln t + (1 - \rho) \ln t + (\rho - \sigma)(t - 1) \right], & N_{1} & = s(\beta)(\sigma - \rho), \\
E_{1} & = \left( \frac{\partial g_{1}}{\partial \sigma}(1, 1) + \frac{\partial f_{1}}{\partial \sigma}(1, 1) \right)(\sigma - \rho), & F_{1} & = \left( \frac{\partial g_{2}}{\partial \sigma}(1, 1) - \frac{\partial f_{2}}{\partial \sigma}(1, 1) \right)(\sigma - \rho).
\end{align*}
\]

**Remark 3.17.** Both \( G_{k0}(V; \sigma, \rho) \) and \( G_{k1}(V; \sigma, \rho) \) arise from the existence of boundary layers, and provide critical information for boundary layer effects study in our work. \( G_{k0}(V; \sigma, \rho) \) does not contain permanent charges (it has been analyzed in [54]) while \( G_{k1}(V; \sigma, \rho) \) is the leading term that includes small permanent charge effects under our setups. Theorem 3.18 further characterizes the interaction among boundary layers, channel geometry and small permanent charges, and demonstrate the effects on ionic flows from boundary layers.

Note that, for \( t > 1 \) and \( \sigma > \rho \) with \((\sigma, \rho) \rightarrow (1^{+}, 1^{+})\), \( N_{1} \) has the same sign as that of \( s(\beta) \), and \( M_{1} > 0 \). The following result can be established.

**Theorem 3.18.** For \( N_{1} \neq 0 \), let \( V_{1N}^{*} \) and \( V_{2N}^{*} \) be the potentials such that \( G_{11}(V_{1N}^{*}) = 0 \) and \( G_{21}(V_{2N}^{*}) = 0 \), respectively. Then, \( V_{1N}^{*} = \frac{E_{1}}{z_{2}N_{1}}, \ V_{2N}^{*} = -\frac{F_{1}}{z_{1}N_{1}} \). Furthermore, for \( t = L_{1}/R_{1} > 1, \sigma > \rho \) and \((\sigma, \rho) \rightarrow (1^{+}, 1^{+})\), one has

(i) if \( 0 < \alpha \leq \alpha_{1}, \) then, \( N_{1} > 0 \) and

\[
\begin{align*}
& (i) \ G_{10}G_{11} > 0 \ (\text{resp. } G_{10}G_{11} < 0) \text{ if } V > V_{1N}^{*} \ (\text{resp. } V < V_{1N}^{*}), \text{ equivalently, small (positive) permanent charge strengthens (resp. reduces) } |J_{1d}| \text{ if } V > V_{1N}^{*} \ (\text{resp. } V < V_{1N}^{*}); \\
& (ii) \ G_{20}G_{21} > 0 \ (\text{resp. } G_{20}G_{21} < 0) \text{ if } V > V_{2N}^{*} \ (\text{resp. } V < V_{2N}^{*}), \text{ equivalently, small (positive) permanent charge strengthens (resp. reduces) } |J_{2d}| \text{ if } V > V_{2N}^{*} \ (\text{resp. } V < V_{2N}^{*}).
\end{align*}
\]

(ii) if \( \alpha_{1} < \alpha < \gamma(t) \), then, \( N_{1} < 0 \) and

\[
\begin{align*}
& (i) \ G_{10}G_{11} > 0 \ (\text{resp. } G_{10}G_{11} < 0) \text{ if } V < V_{1N}^{*} \ (\text{resp. } V > V_{1N}^{*}), \text{ equivalently, small (positive) permanent charge strengthens (resp. reduces) } |J_{1d}| \text{ if } V < V_{1N}^{*} \ (\text{resp. } V > V_{1N}^{*}); \\
& (ii) \ G_{20}G_{21} > 0 \ (\text{resp. } G_{20}G_{21} < 0) \text{ if } V < V_{2N}^{*} \ (\text{resp. } V > V_{2N}^{*}), \text{ equivalently, small (positive) permanent charge strengthens (resp. reduces) } |J_{2d}| \text{ if } V < V_{2N}^{*} \ (\text{resp. } V > V_{2N}^{*});
\end{align*}
\]

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(ii) $G_{20}G_{21} > 0$ (resp. $G_{20}G_{21} < 0$) if $V < V_{2N}^\ast$ (resp. $V > V_{2N}^\ast$), equivalently, small (positive) permanent charge strengthens (resp. reduces) $|J_{2d}|$ if $V < V_{2N}^\ast$ (resp. $V > V_{1N}^\ast$).

(iii) if $\gamma(t) \leq \alpha < \alpha_2$ and $\beta \in (\alpha, \beta_2)$, then, $N_1 < 0$ and

(iii1) $G_{10}G_{11} > 0$ (resp. $G_{10}G_{11} < 0$) if $V < V_{1N}^\ast$ (resp. $V > V_{1N}^\ast$), equivalently, small (positive) permanent charge strengthens (resp. reduces) $|J_{1d}|$ if $V < V_{1N}^\ast$ (resp. $V > V_{1N}^\ast$);

(iii2) $G_{20}G_{21} > 0$ (resp. $G_{20}G_{21} < 0$) if $V < V_{2N}^\ast$ (resp. $V > V_{2N}^\ast$), equivalently, small (positive) permanent charge strengthens (resp. reduces) $|J_{2d}|$ if $V < V_{2N}^\ast$ (resp. $V < V_{2N}^\ast$).

(vi) if $\alpha_2 \leq \alpha < 1$ or $\gamma(t) \leq \alpha < \alpha_2$ and $\beta \in (\beta_2, 1)$, then, $N_1 > 0$ and

(vi1) $G_{10}G_{11} > 0$ (resp. $G_{10}G_{11} < 0$) if $V > V_{1N}^\ast$ (resp. $V < V_{1N}^\ast$), equivalently, small (positive) permanent charge strengthens (resp. reduces) $|J_{1d}|$ if $V > V_{1N}^\ast$ (resp. $V < V_{1N}^\ast$);

(vi2) $G_{20}G_{21} > 0$ (resp. $G_{20}G_{21} < 0$) if $V > V_{2N}^\ast$ (resp. $V < V_{2N}^\ast$), equivalently, small (positive) permanent charge strengthens (resp. reduces) $|J_{2d}|$ if $V > V_{2N}^\ast$ (resp. $V < V_{2N}^\ast$).

### 3.5 Numerical simulations

In this part, numerical simulations are performed to provide more intuitive illustrations of some analytical results. To be specific, we numerically identify the critical potentials $V_k^\ast$ with boundary layers and $V_q^k$ under electroneutrality conditions, and further verify some analytical results stated in Theorem 3.5, Proposition 3.8, Theorem 3.10, Proposition 3.12 and Proposition 3.16 for some carefully selected system parameters. Other related results can also be numerically illustrated by choosing different parameter values, and we leave that to interested readers.

To get started, we rewrite the system (8)-(9) as a system of first order ordinary differential equations. Upon introducing $u = \varepsilon \frac{d}{dx} \phi$, one has

\[
\begin{align*}
\varepsilon \frac{d}{dx} \phi &= u, \\
\frac{\varepsilon}{h(x)} \frac{d}{dx} (h(x)u) &= -z_1c_1 - z_2c_2 - Q(x), \\
\varepsilon \frac{d}{dx} c_1 &= -z_1c_1u - \frac{J_1}{h(x)}, \\
\varepsilon \frac{d}{dx} c_2 &= -z_2c_2u - \frac{J_2}{h(x)}, \\
\frac{d}{dx} J_1 &= \frac{d}{dx} J_2 = 0,
\end{align*}
\]

with boundary conditions

\[
\phi(0) = V, \ c_k(0) = L_k; \quad \phi(1) = 0, \ c_k(1) = R_k, \quad k = 1, 2.
\]

**Remark 3.19.** We use “bvp4c” in Matlab ([35]), an adaptive mesh solver, for our BVP (22)-(23), which can efficiently take care of the jumps of $Q(x)$ and $\frac{dh}{dx}$ at the points $x = a$ and $x = b$ by adjusting the mesh points at each stage in the iterative procedure. On the other hand, we take the great advantage from our analysis and the one in [19] that provide very good initial guess for our simulation (see Section 3.2 in [39] for more detailed discussion of the BVP solver and the choice of initial guess).
In our simulations to system (22)-(23), we take \( z_1 = -z_2 = 1 \), \( L_1 = 20 \), \( R_1 = 5 \), \( \varepsilon = 0.01 \), \( Q_0 = 0.01 \), \( a = 0.76 \), \( b = 0.817 \),

\[
Q(x) = \begin{cases} 
0, & 0 < x < a, \\
Q_0, & a < x < b, \\
0, & b < x < 1,
\end{cases}
\quad \text{and} \quad h(x) = \begin{cases} 
\pi(-x + r_0 + a)^2, & 0 \leq x < a, \\
\pi r_0^2, & a \leq x < b, \\
\pi(x + r_0 - b)^2, & b \leq x < 1.
\end{cases}
\]

**Remark 3.20.** The choice of \( h(x) \) is based on the fact that the ion channel is cylindrical-like, and the variable cross-section area is chosen to reflect the fact that the channel is not uniform and much narrower in the neck \((0.76 < x < 0.817)\) than other regions ([33]). We further take \( r_0 = 0.5 \) and the function \( h(x) \) is then continuous at the jumping points \( a = 0.76 \) and \( b = 0.817 \). Different models for \( h(x) \) may be chosen, and similar numerical results should be obtained.

Under the above set-up, direct calculations gives

\[
\alpha = \frac{H(a)}{H(1)} = 0.6122915, \quad \beta = \frac{H(b)}{H(1)} = 0.7280146, \quad \gamma(t) = 0.611986 \text{ at } t = \frac{L_1}{R_1} = 4,
\]

\[
\alpha_2 = 0.834863, \quad \alpha_1^* = 0.3364903, \quad \alpha_2^* = 0.8874814, \quad \beta_2 = 0.928565
\]

and

\[
-\frac{f(1,1) + g(1,1)}{s(\beta)} = 1.391486,
\]

from which one has

\[
\gamma(t) < \alpha < \alpha_2, \quad \alpha_1^* < \alpha < \alpha_2^*, \quad \alpha < \beta < \beta_2, \quad 0 < \sigma - \rho < -\frac{f(1,1) + g(1,1)}{s(\beta)} \quad (24)
\]

for some suitable values chosen for \((\sigma,\rho)\), such as \((\sigma,\rho) = (1.008, 1.006)\) and \((\sigma,\rho) = (1.02, 1.01)\) used in our numerical simulations.

**Remark 3.21.** The relations in (24) are actually consistent with the assumption stated in Theorem 3.5 (statement (i)), Proposition 3.8 (statement (i7)), Theorem 3.10 (statement (ii)), Proposition 3.12 and Proposition 3.16 (statement (ii6)).

It turns out that our numerical simulations with nonzero but small \( \varepsilon \) are consistent with our analytical results. To be specific,

(i) We numerically identified the critical potentials \( V_1^* \) and \( V_2^* \) defined in Theorem 3.5 (first two rows in Figure 1 with different set-ups for \((\sigma,\rho)\)); and also identified the critical potentials \( V_q^1 \) and \( V_q^2 \) identified in [33] (last row in Figure 1) with \((\sigma,\rho) = (1,1)\), that is, under the electroneutrality boundary conditions, from which one can tell the effects from the existence of boundary layers. Furthermore, one can see that \( V_2^* < V_q^2 < V_q^1 < V_1^* \), which is consistent with Proposition 3.8 (statement (i) satisfying the condition (i7)), Proposition 3.12 with \( \alpha \in (\alpha_1^*,\alpha_2^*) \) and Proposition 3.16 (statement (ii) satisfying the condition (ii6)).

(ii) Our numerical results show that (see the left figure in Figure 3), with \((\sigma,\rho) = (1.008, 1.006)\),
(a) \( J_1(V; 0; \varepsilon)[J_1(V; Q_0; \varepsilon) - J_1(V; 0; \varepsilon)] < 0 \) (resp. \( J_1(V; 0; \varepsilon)[J_1(V; Q_0; \varepsilon) - J_1(V; 0; \varepsilon)] > 0 \)) if \( V < V_1^* \) (resp. \( V > V_1^* \));

(b) \( J_2(V; 0; \varepsilon)[J_2(V; Q_0; \varepsilon) - J_2(V; 0; \varepsilon)] < 0 \) (resp. \( J_2(V; 0; \varepsilon)[J_2(V; Q_0; \varepsilon) - J_2(V; 0; \varepsilon)] > 0 \)) if \( V < V_2^* \) (resp. \( V > V_2^* \)).

This is consistent with our analytical result stated in (i) of Theorem 3.5. Furthermore, it is clear that \( V_2^* < V_1^* \) and

(c) \( J_k(V; 0; \varepsilon)[J_k(V; Q_0; \varepsilon) - J_k(V; 0; \varepsilon)] < 0 \) for \( k = 1, 2 \), if \( V < V_2^* \);

(d) \( J_1(V; 0; \varepsilon)[J_1(V; Q_0; \varepsilon) - J_1(V; 0; \varepsilon)] < 0 \) while \( J_2(V; 0; \varepsilon)[J_2(V; Q_0; \varepsilon) - J_2(V; 0; \varepsilon)] > 0 \) if \( V_2^* < V < V_1^* \);

(e) \( J_k(V; 0; \varepsilon)[J_k(V; Q_0; \varepsilon) - J_k(V; 0; \varepsilon)] > 0 \) for \( k = 1, 2 \) if \( V > V_1^* \);

equivalently, (small) positive \( Q_0 \) reduces both \( |J_1| \) and \( |J_2| \) if \( V < V_2^* \); strengthens \( |J_2| \) while reduces \( |J_1| \) if \( V_2^* < V < V_1^* \); and strengthens both \( |J_1| \) and \( |J_2| \) if \( V > V_1^* \). This is consistent with our analytical result stated in (i) of Theorem 3.10. Here, we use \( J_k(V; 0; \varepsilon) \) to approximate \( J_{k0}(V; 0, 0) \), and \( J_{k}(V; Q_0; \varepsilon) - J_k(V; 0; \varepsilon) \) to approximate \( J_{k1}(V; 0, 0) \), the leading term in our analysis that contains small permanent charge effects.

(iii) Our numerical simulations also show clearly that \( J_k(V; 0) \) and \( J_k(V; Q_0) - J_k(V; 0) \) have a common zero (can be seen from Figures 1, 2 and 3), which is consistent with our analytical result (see Remark 3.6). Similar argument applies to the case under electroneutrality boundary conditions (see equations (4.4) and (4.5) in [33]).

To end this section, we would like to point out that the challenge in our simulation is the selection of the values for \( a \) and \( b \), which directly affect the interplay between the small permanent charges and the channel geometry in terms of \( (\alpha, \beta) = (H(a)/H(1), H(b)/H(1)) \). The numerical simulation not only supports our analytical results, but also provides more intuitive illustrations for our results. Interested readers can choose different values for the parameters \( a \) and \( b \) to observe other properties stated in this work.

4 Concluding Remarks

This work focuses on the boundary layer effects on individual fluxes via Poisson-Nernst-Planck models including nonzero but small permanent charges for one cation and one anion. A unique feature of this work is its capability of providing detailed information of complicated interplays among multiple system parameters, such as boundary concentrations and potentials, small permanent charges and channel geometry, for individual fluxes. Several critical potentials are identified, and those critical values split the potential region into different subregions, over which distinct qualitative properties of individual fluxes are observed. This provides important insights to further understand the mechanism of ionic flows through membrane channels, in particular, the internal dynamics of ionic flows, which cannot be discerned with current technology. Some critical potentials can be estimated experimentally. Taking the critical potential \( V_1^* \) (zero of \( J_{11}(V; \sigma, \rho) \)) for example, one can take an experimental
\( J_1(V; Q_0; \sigma, \rho) \) (although it is challenging to measure compared to the I-V relations) and numerically (or analytically) compute \( J_{10}(V; 0; \sigma, \rho) \) for ideal case, and this allows one to get an estimate of \( V_1^* \) by considering the zero of \( J_1(V; Q_0; \sigma, \rho) - J_{10}(V; 0; \sigma, \rho) \).

For the relatively simple biological setting in this work, our results have indicates complicated and rich behaviors of ionic flows, which further depend sensitively on the system parameters, in particular, the nonlinear interaction among boundary layers \((\sigma, \rho)\), channel geometry \((\alpha, \beta)\) and small permanent charge \(Q_0\). The work done in this paper might be able to provide some meaningful insights or a fundamental understanding of mechanisms for adjusting/controlling ionic flow through membrane channels.

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**References**


Figure 1: Identification of critical potentials $V^*_k$ with boundary layers and $V^q_k$ under electroneutrality boundary conditions for small $\varepsilon = 0.01$. To observe the effects from boundary layers, we take $(\sigma, \rho) = (1.008, 1.006)$ and $(\sigma, \rho) = (1.02, 1.01)$, respectively. We also point out that $V^c_{k1}$ is a common zero with $J_k(V; 0)$ with boundary layers while $V^q_{c1}$ is a common zero with $J_k(V; 0)$ under electroneutrality boundary conditions, see Figure 2. One can easily see that for $(\sigma, \rho) = (1.008, 1.006)$, $V^q_1 - V^*_1 = -0.201859$ and $V^q_2 - V^*_2 = 0.213176$, while for $(\sigma, \rho) = (1.02, 1.01)$, which indicates the existence of more sharp layers, one has $V^q_1 - V^*_1_{L} = -0.309817$ and $V^q_2 - V^*_2_{L} = 0.325381$. This shows clearly the important role played by the boundary layers in the study of ionic flows through membrane channels.
Figure 2: Numerical simulations to $J_{k0}(V)$ for both the case with boundary layers and the one under electroneutrality boundary conditions by $J_k(V;0)$ with $\varepsilon = 0.01$. Together with Figure 1, this shows that there exists a common zero for $J_{k0}(V;0) = J_k(V;Q_0) - J_{k0}(V;0)$, which is consistent with our analytical result.

Figure 3: Orders of the critical potentials $V^*_k$ with boundary layers and $V^q_k$ under electroneutrality boundary conditions, respectively for $k = 1, 2$ with $\varepsilon = 0.01$. Under our set-up, the result with boundary layers is consistent with statement (i) in Theorem 3.10, and the one under electroneutrality boundary conditions is also consistent with statement (ii) in Theorem 4.8 of [33].