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Roles Played by Critical Potentials in the Study of Poisson–Nernst–Planck Models with Steric Effects Under Relaxed Neutral Boundary Conditions

Xiangshuo Liu [1,†], Jie Song [2,*,†], Lijun Zhang [1] and Mingji Zhang [3,*]

[1] College of Mathematics and Systems Science, Shandong University of Science and Technology, Qingdao 266510, China; liuxiangshuo@sdust.edu.cn (X.L.); skd996000@sdust.edu.cn (L.Z.)
[2] School of Mathematics and Statistics, Linyi University, Linyi 276000, China
[3] Department of Mathematics, New Mexico Institute of Mining and Technology, Socorro, NM 87801, USA
* Correspondence: songjie@lyu.edu.cn (J.S.); mingji.zhang@nmt.edu (M.Z.)
† These authors contributed equally to this work.

Abstract: We examine the qualitative properties of ionic flows through membrane channels via Poisson–Nernst–Planck (PNP) type models with steric effects under relaxed electroneutrality boundary conditions, and more realistic setups in the study of ion channel problems. Of particular interest are the vital roles played by some critical potentials identified for both individual fluxes and current–voltage relations. These critical potentials split the whole electric potential interval into different subintervals, over which distinct dynamics of ionic flows are observed. The discussion provides an efficient way to control the boundary conditions to observe distinct dynamics of ionic flows through membrane channels. This is important for future analytical studies and critical for future numerical and even experimental studies of ion channel problems.

Keywords: PNP; ionic flows; I–V relations; perturbations; boundary layers

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1. Introduction

Ion channels, large proteins embedding in cell membranes, play a significant role in the exchange of ion species between cells and surroundings [1–5]. For example, a type of calcium channel located in the fungi's mitochondria controls the process of ATP synthesis, the transportation of calcium and apoptosis [6]. For human beings, ion channels are also crucial to cell functioning. For instance, sodium and potassium channels are widely distributed in neurons and cardiac tissues. They are responsible for the sharp switch between the action and resting potentials when the stimuli propagate through the corresponding cells. In muscle cells, a group of ion channels cooperate to trigger muscle contractions [7]. On the other hand, malfunctioning channels result in many intractable diseases such as cholera and Alzheimer's [8]. Therefore, exploring the working mechanisms of ion channels is not only promising in theoretical studies but has many practical meanings in disease treatment. The two main subjects related to ion channels, the structure of ion channels and the properties of ion flow, are the primary concerns in ion channel research. Once the structure is provided, the main research direction for open ion channels is to analyze their electric diffusion characteristics.

Ion flow follows the basic physical laws of electric diffusion. The macroscopic characteristics of ions passing through membrane channels depend on external driving forces, mainly boundary potential and concentration [9,10], as well as specific structural features [11,12]. These structural features include factors such as pore shape and size. Permeability and selectivity are two important biological properties of ion channels, which can be characterized by experimentally measuring the current–voltage (I–V) relationship under different ionic conditions.

The PNP system, as a basic macroscopic model for electrodiffusion of charges, particularly for ionic flows through ion channels ([13–17], etc.), can be derived, under various reasonable conditions, from the more fundamental models of the Langevin–Poisson system ([18–21]) and the Maxwell–Boltzmann equations ([9]and the references therein), and from variational analysis ([11,22–24]). The classical PNP system is the simplest PNP system, which has been extensively studied both numerically ([13,25–39]) and analytically ([3,10,40–70]). Particularly, in [70], the authors employed the method of matched asymptotic expansions to study the I–V relations and obtained the I–V relation up to the second order in the small singular parameter ε (see (6) for definition), which is a cubic function of the potential V that has three distinct real roots. The observation is consistent with the cubic-like feature of the average I–V relation of a population of channels in the FitzHugh–Nagumo simplification of the Hodgkin–Huxley model. In [42,48,65], the authors focused on the small permanent charge effects on ionic flows. Viewing the small permanent charge as a regular parameter, in the discussion of regular perturbation, the authors found that to optimize the effects of (small) permanent charge, the channel neck within which the permanent charge distributes should be "short" and "narrow". This observation is consistent with the typical structure of an ion channel.

However, a major weak point of the classical PNP is that it treats ions as point charges and ignores ion-to-ion interaction, which is reasonable only in near-infinite dilute situations. A lot of critical properties of ion channels rely heavily on ion sizes. The effects of finite ion size on ionic flows play key roles in the study of the selectivity of ion channels. The PNP system with finite ion size effects has been investigated computationally ([11,22–24,71–76], etc.) and analytically ([77–86]) for ion channels.

We focus on the quasi-one-dimensional PNP system first proposed by [36],

$$\begin{aligned} &\frac{1}{A(X)}\frac{d}{dX}\left(\varepsilon_r(X)\epsilon_0 A(X)\frac{d\Phi}{dX}\right) = -e\left(\sum_{j=1}^{n} z_j C_j(X) + Q(X)\right), \\ &\frac{d\mathcal{J}_i}{dX} = 0, \quad -\mathcal{J}_i = \frac{1}{k_B T}\mathcal{D}_i(X)A(X)C_i(X)\frac{d\mu_i}{dX}, \quad i = 1,2,\dots,n, \end{aligned} \tag{1}$$

where $X \in [0,1]$ is the normalized coordinate along the channel axis, and $A(X)$ denotes the cross-sectional area at point X. e is the elementary charge, k_B is the Boltzmann constant, and T is the absolute temperature. The electric potential is represented by Φ, while $Q(X)$ denotes the permanent charge of the channel. $\varepsilon_r(X)$ is the relative dielectric coefficient, and ε_0 is the vacuum permittivity. For the i-th ion species, C_i represents the concentration, z_i is the valence, μ_i is the electrochemical potential, $\mathcal{J}_i$ is the flux density, and $\mathcal{D}_i(X)$ is the diffusion coefficient.

The boundary conditions imposed on the system (1) are as follows ([44]):

$$\Phi(0) = V, \;\; c_k(0) = \mathcal{L}_k > 0; \quad \Phi(1) = 0, \;\; c_k(1) = \mathcal{R}_k > 0, \quad k = 1,2. \tag{2}$$

For a solution of the PNP system (1)–(2), the total current, $\mathcal{I}$, through a cross-section is defined as

$$\mathcal{I} = \sum_{s=1}^{n} z_s \mathcal{J}_s, \tag{3}$$

which is the well-known current–voltage (I–V) relation.

We further point out that the electrochemical potential $\mu_i(X)$ in (1) consists of two components: the ideal component $\mu_i^{\rm id}(X)$ and the excess component $\mu_i^{\rm ex}(X)$:

$$\mu_i(X) = \mu_i^{\rm id}(X) + \mu_i^{\rm ex}(X),$$

where the ideal component is defined by

$$\mu_i^{\rm id}(X) = z_i e\Phi(X) + k_B T \ln \frac{C_i(X)}{C_0}, \tag{4}$$

with C_0 being a characteristic number density. The PNP system, considering only the ideal component, is known as the classical PNP, and its major weak point in studying ionic flow properties is discussed above. To better understand the mechanism of ionic flows through membrane channels, one should consider the excess component. A strategic first step is to include hard-sphere potentials of the excess electrochemical potential in the PNP system. In this work, we consider the following Bikerman's local hard-sphere model ([87]) accounting for finite ion size effects on ionic flows

$$\mu_i^{\rm Bik}(X) = -k_B T \ln\left(1 - \sum_{j=1}^{n} \nu_j C_j(X)\right), \tag{5}$$

where ν_j is the volume of the j-th ion species.

The rest of this paper is organized as follows. In Section 2, we set up our problem, briefly recall some results from [88], which is the starting point of our study, and describe the mathematical method to be employed. Section 3 consists of four subsections. Section 3.1 provides the finite ion size effects on the individual fluxes; Section 3.2 deals with the finite ion size effects on the I–V relations; Section 3.3 provides orders of the critical potentials identified in Definition 1 while the boundary layer effects on ionic flows are characterized in Section 3.4. Concluding remarks are provided in Section 4.

2. Problem Setup, Existing Results and Mathematical Methods

The current work is an extension of the one conducted in [88]. To get started, we set up our problem and briefly introduced some existing results from [88].

2.1. Assumptions and a Rescaling of the PNP System

In our following analysis, we assume

(i) Two ion species with $z_1 > 0$ and $z_2 < 0$ included in the PNP system;
(ii) The permanent charge is zero over the whole interval: $Q(X) = 0$;
(iii) The electrochemical potential μ_i consists of the ideal component μ_i^{id} and the local hard-sphere potential μ_i^{Bik} in (5);
(iv) The relative dielectric coefficient and the diffusion coefficients are constants, that is, $\varepsilon_r(X) = \varepsilon_r$ and $\mathcal{D}_i(X) = \mathcal{D}_i$.

With the following further dimensionless rescaling,

$$\begin{aligned}
&\epsilon^2 = \frac{\varepsilon_r \varepsilon_0 k_B T}{e^2 l^2 c_0}, \quad x = \frac{X}{l}, \quad h(x) = \frac{A(x)}{l^2}, \quad D_i = l C_0 D_i;\\
&\phi(x) = \frac{e}{k_B T}\Phi(X), \quad c_i(x) = \frac{C_i(X)}{C_0}, \quad J_i = \frac{\mathcal{J}_i}{D_i};\\
&\mathcal{V} = \frac{e}{k_B T}V, \quad L_i = \frac{\mathcal{L}_i}{C_0}, \quad R_i = \frac{\mathcal{R}_i}{C_0},
\end{aligned} \tag{6}$$

the boundary value problem (1)–(2) becomes

$$\begin{aligned}
&\frac{\varepsilon^2}{h(x)}\frac{d}{dx}\left(h(x)\frac{d}{dx}\phi\right) = -z_1c_1 - z_2c_2,\\
&\frac{dc_1}{dx} = -(z_1 - z_1\nu_1c_1 - z_2\nu_2c_2)c_1\frac{d\phi}{dx} - \frac{1}{h(x)}(J_1 - (\nu_1J_1 + \nu_2J_2)c_1),\\
&\frac{dc_2}{dx} = -(z_2 - z_1\nu_1c_1 - z_2\nu_2c_2)c_2\frac{d\phi}{dx} - \frac{1}{h(x)}(J_2 - (\nu_1J_1 + \nu_2J_2)c_2),\\
&\frac{dJ_1}{dx} = \frac{dJ_2}{dx} = 0,
\end{aligned} \tag{7}$$

with the boundary conditions

$$\phi(0) = \mathcal{V}, \quad c_i(0) = L_i > 0; \quad \phi(1) = 0, \quad c_i(1) = R_i > 0. \tag{8}$$

2.2. Some Existing Results

We now introduce some existing results obtained in [88], which will be our starting point in the current work. The authors in [88] treat the system as a regular perturbation of the case with $\nu_1 = \nu_2 = 0$. With $\nu = \nu_1$ and $\nu_2 = \lambda\nu$ for the positive parameter λ, the approximations of the I–V relation are obtained and stated as follows

$$\mathcal{I}(V;\lambda,\nu) = z_1D_1J_1 + z_2D_2J_2 = I_0(V) + I_1(V;\lambda)\nu + o(\nu), \tag{9}$$

where

$$\begin{aligned}
I_0(V) &= z_1D_1J_{10} + z_2D_2J_{20},\\
I_1(V;\lambda) &= z_1D_1J_{11} + z_2D_2J_{21},
\end{aligned}$$

with $J_k = J_{k0} + \nu J_{k1} + o(\nu)$. Here,

$$\begin{aligned}
J_{10} &= \frac{c_{10}^L - c_{10}^R}{H(1)(\ln c_{10}^L - \ln c_{10}^R)}(z_1(\phi_0^L - \phi_0^R) + \ln c_{10}^L - \ln c_{10}^R),\\
J_{20} &= -\frac{z_1}{z_2}\frac{c_{10}^L - c_{10}^R}{H(1)(\ln c_{10}^L - \ln c_{10}^R)}(z_2(\phi_0^L - \phi_0^R) + \ln c_{10}^L - \ln c_{10}^R),\\
J_{11} &= \alpha_{10}(L_1, L_2, R_1, R_2, \lambda) + \alpha_{11}(L_1, L_2, R_1, R_2, \lambda)\frac{e}{k_BT}V,\\
J_{21} &= \beta_{10}(L_1, L_2, R_1, R_2, \lambda) + \beta_{11}(L_1, L_2, R_1, R_2, \lambda)\frac{e}{k_BT}V,
\end{aligned} \tag{10}$$

where

$$\begin{aligned}
&H(1) = \int_0^1 \frac{1}{h(x)}dx, \quad \alpha_{10} = \frac{\ln(L_1R_2) - \ln(L_2R_1)}{z_1 - z_2}\mathcal{F}_1 + \mathcal{F}_2, \quad \alpha_{11} = H(1)\mathcal{F}_1,\\
&\beta_{10} = -\frac{\ln(L_1R_2) - \ln(L_2R_1)}{z_1 - z_2}\mathcal{F}_1 - \frac{z_1}{z_2}\mathcal{F}_2, \quad \beta_{11} = -\alpha_{11},
\end{aligned}$$

with $\mathcal{F}_1$ and $\mathcal{F}_2$ given by

$$\begin{aligned}
\mathcal{F}_1 &= \frac{1}{\ln c_{10}^L - \ln c_{10}^R}\left(\mathcal{F}_2 + \frac{z_1(c_{10}^L - c_{10}^R)(R_1 - L_1 + \lambda(R_2 - L_2))}{\ln c_{10}^L - \ln c_{10}^R}\right),\\
\mathcal{F}_2 &= c_{10}^L(L_1 + \lambda L_2) - c_{10}^R(R_1 + \lambda R_2) + \frac{z_1\lambda - z_2}{2z_2}(c_{10}^L - c_{10}^R)(c_{10}^L + c_{10}^R),
\end{aligned}$$

where

$$\phi_0^L = \frac{e}{k_B T}V - \frac{1}{z_1 - z_2}\ln\frac{-z_2 L_2}{z_1 L_1}, \quad \phi_0^R = -\frac{1}{z_1 - z_2}\ln\frac{-z_2 R_2}{z_1 R_1},$$
$$z_1 c_{10}^L = -z_2 c_{20}^L = (z_1 L_1)^{\frac{-z_2}{z_1 - z_2}}(-z_2 L_2)^{\frac{z_1}{z_1 - z_2}}, \quad z_1 c_{10}^R = -z_2 c_{20}^R = (z_1 R_1)^{\frac{-z_2}{z_1 - z_2}}(-z_2 R_2)^{\frac{z_1}{z_1 - z_2}}.$$

Remark 1. *In our analysis, we take $h(x) = 1$ over the whole interval $[0,1]$ since it does not affect the qualitative properties of ionic flows (see [89] for a reasoning).*

2.3. Mathematical Methods

Our main focus is on the study of the dynamics of ionic flows under relaxed electroneutrality boundary concentration conditions. More specifically, we suppose

$$-z_2 L_2 = \sigma(z_1 L_1) \text{ and } -z_2 R_2 = \rho(z_1 R_1), \tag{11}$$

where $(\sigma, \rho) \to (1,1)$ are some constant parameters. Note that $(\sigma, \rho) = (1,1)$ implies electroneutrality conditions (see [49] for detailed explanation). The relaxation of the neutral conditions immediately produces boundary layers for the PNP system, which has important effects on the qualitative properties of ionic flows through membrane channels ([63,69,77,86,89]). To characterize these effects from boundary layers, we employ regular perturbation analysis, more precisely, we treat (σ, ρ) as a group of regular perturbation parameters, and expand both the individual fluxes and the I–V relations along $(\sigma, \rho) = (1,1)$ up to the first order, and ignore higher order terms. Our main interest is in the first-order terms containing boundary layer effects.

To be specific, we expand $J_{k0}(V;\sigma,\rho)$ and $J_{k1}(V;\sigma,\rho)$ at $(\sigma,\rho) = (1,1)$, from which the expansions for $I_0(V;\sigma,\rho)$ and $I_1(V;\sigma,\rho)$ follows from Equation (9). To get started, we introduce

$$f_0(L_1, R_1) = \frac{L_1 - R_1}{\ln L_1 - \ln R_1}, \quad f_1(L_1, R_1) = f_0(L_1, R_1) - \frac{L_1 + R_1}{2},$$
$$a_1 = z_1\lambda - z_2, \quad a_2 = (z_1 - z_2)\lambda, \quad a_3 = \frac{z_1}{z_2(z_1 - z_2)}, \quad a_4 = \frac{2z_1\lambda}{z_2}.$$

Then,

$$\begin{aligned}
J_{10}(V;\sigma,\rho) =& J_{10}(V;1,1) + \frac{\partial J_{10}(V;1,1)}{\partial\sigma}(\sigma - 1) + \frac{\partial J_{10}(V;1,1)}{\partial\rho}(\rho - 1),\\
J_{20}(V;\sigma,\rho) =& J_{20}(V;1,1) + \frac{\partial J_{20}(V;1,1)}{\partial\sigma}(\sigma - 1) + \frac{\partial J_{20}(V;1,1)}{\partial\rho}(\rho - 1),\\
J_{11}(V;\sigma,\rho) =& \alpha_{10}(1,1) + \frac{\partial\alpha_{10}(1,1)}{\partial\sigma}(\sigma - 1) + \frac{\partial\alpha_{10}(1,1)}{\partial\rho}(\rho - 1)\\
&+ \left(\alpha_{11}(1,1) + \frac{\partial\alpha_{11}(1,1)}{\partial\sigma}(\sigma - 1) + \frac{\partial\alpha_{11}(1,1)}{\partial\rho}(\rho - 1)\right)\frac{e}{k_B T}V,\\
J_{21}(V;\sigma,\rho) =& \beta_{10}(1,1) + \frac{\partial\beta_{10}(1,1)}{\partial\sigma}(\sigma - 1) + \frac{\partial\beta_{10}(1,1)}{\partial\rho}(\rho - 1)\\
&+ \left(\beta_{11}(1,1) + \frac{\partial\beta_{11}(1,1)}{\partial\sigma}(\sigma - 1) + \frac{\partial\beta_{11}(1,1)}{\partial\rho}(\rho - 1)\right)\frac{e}{k_B T}V,
\end{aligned} \tag{12}$$

where

$$J_{10}(V;1,1) = \frac{f_0(L_1, R_1)}{H(1)}\left(\frac{z_1 e}{k_B T}V + \ln L_1 - \ln R_1\right),$$
$$\frac{\partial J_{10}(V;1,1)}{\partial\sigma} = \frac{z_1(L_1 - f_0(L_1, R_1))}{(z_1 - z_2)H(1)(\ln L_1 - \ln R_1)}\left(\frac{z_1 e}{k_B T}V + \ln L_1 - \ln R_1\right),$$

$$
\begin{aligned}
\frac{\partial J_{10}(V;1,1)}{\partial \rho} &= -\frac{z_1(R_1 - f_0(L_1,R_1))}{(z_1-z_2)H(1)(\ln L_1 - \ln R_1)}\left(\frac{z_1 e}{k_B T}V + \ln L_1 - \ln R_1\right),\\
J_{20}(V;1,1) &= -\frac{z_1 f_0(L_1,R_1)}{z_2 H(1)}\left(\frac{z_2 e}{k_B T}V + \ln L_1 - \ln R_1\right),\\
\frac{\partial J_{20}(V;1,1)}{\partial \sigma} &= \frac{-z_1}{z_2 H(1)}\left[f_0(L_1,R_1) + \frac{z_1(L_1 - f_0(L_1,R_1))\left(\frac{z_2 e}{k_B T}V + \ln L_1 - \ln R_1\right)}{(z_1-z_2)(\ln L_1 - \ln R_1)}\right],\\
\frac{\partial J_{20}(V;1,1)}{\partial \rho} &= \frac{z_1}{z_2 H(1)}\left[f_0(L_1,R_1) - \frac{z_1(f_0(L_1,R_1) - R_1)\left(\frac{z_2 e}{k_B T}V + \ln L_1 - \ln R_1\right)}{(z_1-z_2)(\ln L_1 - \ln R_1)}\right],\\
\alpha_{10}(1,1) &= \frac{(z_2 - z_1\lambda)(L_1^2 - R_1^2)}{2z_2}, \quad \alpha_{11}(1,1) = \frac{a_1 z_1}{z_2} f_0(L_1,R_1) f_1(L_1,R_1),\\
\beta_{10}(1,1) &= -\frac{z_1(z_2 - z_1\lambda)(L_1^2 - R_1^2)}{2z_2^2}, \quad \beta_{11}(1,1) = -\alpha_{11}(1,1),\\
\frac{\partial \alpha_{10}}{\partial \sigma}(1,1) &= \frac{a_1 f_0(L_1,R_1)(L_1+R_1)}{2z_2(z_1-z_2)} - \frac{a_4}{2}L_1^2 - a_2 a_3 f_0^2(L_1,R_1),\\
\frac{\partial \alpha_{10}}{\partial \rho}(1,1) &= \frac{a_1 f_0(L_1,R_1)(L_1+R_1)}{2z_2(z_1-z_2)} + \frac{a_4}{2}R_1^2 + a_2 a_3 f_0^2(L_1,R_1),\\
\frac{\partial \beta_{10}}{\partial \sigma}(1,1) &= -\frac{a_1 f_0(L_1,R_1)(L_1+R_1)}{2z_2(z_1-z_2)} + \frac{z_1 a_4}{2z_2}L_1^2 + a_2 a_3 f_0^2(L_1,R_1),\\
\frac{\partial \beta_{10}}{\partial \rho}(1,1) &= -\frac{a_1 f_0(L_1,R_1)(L_1+R_1)}{2z_2(z_1-z_2)} - \frac{z_1 a_4}{2z_2}R_1^2 - a_2 a_3 f_0^2(L_1,R_1),\\
\frac{\partial \beta_{11}}{\partial \sigma}(1,1) &= -\frac{\partial \alpha_{11}}{\partial \sigma}(1,1), \quad \frac{\partial \beta_{11}}{\partial \rho}(1,1) = \frac{\partial \alpha_{11}}{\partial \rho}(1,1),\\
\frac{\partial \alpha_{11}}{\partial \sigma}(1,1) &= \frac{a_3 f_0(L_1,R_1)}{\ln L_1 - \ln R_1}\Big((a_1+a_2)L_1 - \frac{a_1}{2}(L_1+R_1)\Big) - \frac{a_4 L_1^2}{2(\ln L_1 - \ln R_1)},\\
\frac{\partial \alpha_{11}}{\partial \rho}(1,1) &= -\frac{a_3 f_0(L_1,R_1)}{\ln L_1 - \ln R_1}\Big((a_1+a_2)R_1 - \frac{a_1}{2}(L_1+R_1)\Big) + \frac{a_4 R_1^2}{2(\ln L_1 - \ln R_1)}.
\end{aligned}
$$

To end this section, we point out that in our analysis detailed in Section 3, we further assume that $L_1 < R_1$.

3. Results

To get started, we define six critical potentials that play significant roles in examining the impacts of boundary layers on ionic flows.

Definition 1. *We introduce six critical potentials V_{1c}, V^{1c}, V_{2c}, V^{2c}, V_c and V^c by*

$$
\begin{gathered}
J_{11}(V_{1c};\lambda) = 0, \quad \frac{\partial J_{11}}{\partial \lambda}(V^{1c};\lambda) = 0, \quad J_{21}(V_{2c};\lambda) = 0,\\
\frac{\partial J_{21}}{\partial \lambda}(V^{2c};\lambda) = 0, \quad I_1(V_c;\lambda) = 0, \quad \frac{\partial I_1}{\partial \lambda}(V^c;\lambda) = 0.
\end{gathered}
$$

Particularly,

$$
\begin{aligned}
V_{1c} &= -\frac{k_B T}{e}\frac{\alpha_{10}(L_1,R_1;\sigma,\rho)}{\alpha_{11}(L_1,R_1;\sigma,\rho)}, \quad V^{1c} = -\frac{k_B T}{e}\frac{\partial_\lambda \alpha_{10}(L_1,R_1;\sigma,\rho)}{\partial_\lambda \alpha_{11}(L_1,R_1;\sigma,\rho)},\\
V_{2c} &= \frac{k_B T}{e}\frac{\beta_{10}(L_1,R_1;\sigma,\rho)}{\alpha_{11}(L_1,R_1;\sigma,\rho)}, \quad V^{2c} = \frac{k_B T}{e}\frac{\partial_\lambda \beta_{10}(L_1,R_1;\sigma,\rho)}{\partial_\lambda \alpha_{11}(L_1,R_1;\sigma,\rho)}\\
V_c &= -\frac{k_B T}{e}\frac{z_1 D_1 \alpha_{10}(L_1,R_1;\sigma,\rho) + z_2 D_2 \beta_{10}(L_1,R_1;\sigma,\rho)}{z_1 D_1 \alpha_{11}(L_1,R_1;\sigma,\rho) + z_2 D_2 \beta_{11}(L_1,R_1;\sigma,\rho)},\\
V^c &= -\frac{k_B T}{e}\frac{z_1 D_1 \partial_\lambda \alpha_{10}(L_1,R_1;\sigma,\rho) + z_2 D_2 \partial_\lambda \beta_{10}(L_1,R_1;\sigma,\rho)}{z_1 D_1 \partial_\lambda \alpha_{11}(L_1,R_1;\sigma,\rho) + z_2 D_2 \partial_\lambda \beta_{11}(L_1,R_1;\sigma,\rho)}.
\end{aligned}
$$

3.1. Finite Ion Size Effects on the Individual Fluxes

We focus on the analysis of the effects on the individual fluxes from finite ion sizes, which consists of two directions: the sign of J_{k1} and relative ion size effects.

3.1.1. Signs of J_{k1}

As a linear function in the potential V, the sign of $\partial_V J_{k1}$, where $k = 1, 2$, plays a crucial role in characterizing the impact of finite ion size on individual fluxes. From the Equation (10), one has

$$\begin{aligned}\partial_V J_{11}(V;\sigma,\rho) &= -\partial_V J_{21}(V;\sigma,\rho)\\ &= \frac{e}{k_B T}\left(\alpha_{11}(1,1) + \frac{\partial\alpha_{11}(1,1)}{\partial\sigma}(\sigma-1) + \frac{\partial\alpha_{11}(1,1)}{\partial\rho}(\rho-1)\right).\end{aligned}$$

With $x = L_1/R_1$, from (12), we have the following:

$$\frac{\partial J_{11}}{\partial V}(x;\sigma,\rho) = \frac{e}{k_B T}\frac{R_1^2}{2\ln^2 x}F(x;\sigma,\rho).$$

Here, $F(x;\sigma,\rho) = \mathcal{A}_1(x) + \mathcal{A}_2(x;\sigma,\rho)$, where

$$\begin{aligned}\mathcal{A}_1(x) &= \frac{a_1}{z_2}(x-1)(2(x-1)-(x+1)\ln x),\\ \mathcal{A}_2(x;\sigma,\rho) &= \Big(a_3(x-1)(-a_1(x+1)+2x(a_1+a_2)) - a_4x^2\ln x\Big)(\sigma-1)\\ &\quad + (a_3(x-1)(a_1(x+1)-2(a_1+a_2)) + a_4\ln x)(\rho-1).\end{aligned} \tag{13}$$

We point out that $\mathcal{A}_1(x)$ corresponds to $\alpha_{11}(1,1)$ and $\mathcal{A}_2(x;\sigma,\rho)$ corresponds $\frac{\partial\alpha_{11}(1,1)}{\partial\sigma}(\sigma-1) + \frac{\partial\alpha_{11}(1,1)}{\partial\rho}(\rho-1)$.

Note that $0 < x < 1$. We have the following results:

Lemma 1. *For $\mathcal{A}_2(x)$, we have*

(i) *For $\rho > \max\{1,\sigma\}$:*
- (i1) *If $(\lambda-1)(\sigma+\rho-2) > 0$, then $\mathcal{A}_2(x) > 0$ for $0 < x < 1$.*
- (i2) *If $(\lambda-1)(\sigma+\rho-2) < 0$, there is a unique point $x_{1*} \in (0,1)$ so that $\mathcal{A}_2(x) > 0$ for $x \in (0,x_{1*})$ and $\mathcal{A}_2(x) < 0$ for $x \in (x_{1*},1)$.*

(ii) *For $\rho < \min\{1,\sigma\}$:*
- (ii1) *If $(\lambda-1)(\sigma+\rho-2) < 0$, then $\mathcal{A}_2(x)$ is negative for all $x \in (0,1)$.*
- (ii2) *If $(\lambda-1)(\sigma+\rho-2) > 0$, there is a unique $x_{2*} \in (0,1)$ so that $\mathcal{A}_2(x) < 0$ for $x \in (0,x_{2*})$ and $\mathcal{A}_2(x) > 0$ for $x \in (x_{2*},1)$.*

(iii) *For $1 < \rho < \sigma$ and $\lambda < 1$, there exists a unique point $x_{3*} \in (0,1)$ such that $\mathcal{A}_2(x) > 0$ for $x \in (0,x_{3*})$ and $\mathcal{A}_2(x) < 0$ for $x \in (x_{3*},1)$.*

(iv) *For $\sigma < \rho < 1$ and $\lambda < 1$, there exists a unique $x_{4*} \in (0,1)$ such that $\mathcal{A}_2(x) < 0$ for $x \in (0,x_{4*})$ and $\mathcal{A}_2(x) > 0$ for $x \in (x_{4*},1)$.*

Proof. We will just focus on the proof of the first statement. Others can be discussed in a similar way. For convenience, we further assume that $\sigma > 1$, then, $\rho > \sigma$. The case with $\sigma < 1$, which implies that $\rho > 1 > \sigma$ can be discussed similarly. Direct calculation gives

$$\begin{aligned}
\mathcal{A}_2'(x;\sigma,\rho) &= (2a_3(x(2a_2+a_1)-(a_1+a_2)) - a_4(2x\ln x + x))(\sigma-1) \\
&\quad + (2a_3x(xa_1-(a_1+a_2)) + a_4)(\rho-1)\frac{1}{x}, \\
\mathcal{A}_2''(x;\sigma,\rho) &= (2a_3(2a_2+a_1) - a_4(3+2\ln x))(\sigma-1) + \frac{1}{x^2}\Big(2a_3a_1x^2 - a_4\Big)(\rho-1), \\
\mathcal{A}_2'''(x;\sigma,\rho) &= 2a_4\Big(\rho-1-x^2(\sigma-1)\Big)\frac{1}{x^3}, \\
\mathcal{A}_2^{(4)}(x;\sigma,\rho) &= -\frac{2a_4}{x^2}\Big(5x^2(\sigma-1)+3(\rho-1)\Big).
\end{aligned} \tag{14}$$

Note that $\mathcal{A}_2'(1) = \mathcal{A}_2(1) = 0$, $\mathcal{A}_2''(1) = \frac{2z_1(\lambda-1)}{z_1-z_2}(\sigma+\rho-2)$, $\mathcal{A}_2'''(1) = 2a_4(\rho-\sigma)$ and $A^{(4)}(x) > 0$ for all $0 < x < 1$, which indicates that $A'''(x)$ is increasing in x for $0 < x < 1$.

Notice that $a_4 = \frac{2z_1\lambda}{z_2} < 0$. One has $\mathcal{A}_2'''(1) = 2a_4(\rho-\sigma) < 0$. It follows that $\mathcal{A}'''(x) < 0$ for $0 < x < 1$. Hence, one has $\mathcal{A}_2''(x)$ decreasing in x for $0 < x < 1$.

(i1) If $(\lambda-1)(\sigma+\rho-1) > 0$, one has $\mathcal{A}_2''(1) > 0$, and hence, $\mathcal{A}''(x) > 0$ for $0 < x < 1$. Taking into account $\mathcal{A}_2'(1) = \mathcal{A}_2(1) = 0$, one has $\mathcal{A}_2'(x) < 0$ and $\mathcal{A}(x) > 0$ for $x > 1$.

(i2) If $(\lambda-1)(\sigma+\rho-1) < 0$, one has $\mathcal{A}_2''(1) < 0$. Therefore, the function $\mathcal{A}_2''(x)$ has a unique zero $x_0 \in (0,1)$. Furthermore, $\mathcal{A}_2''(x) > 0$ on $(0,x_0)$ and $\mathcal{A}_2''(x) < 0$ on $(x_0,1)$. Together with $\mathcal{A}'(1) = 0$, there is a unique zero, x_1, of $\mathcal{A}_2'(x) = 0$ such that $\mathcal{A}_2'(x) < 0$ for $0 < x < x_1$ and $\mathcal{A}_2'(x) > 0$ for $x_1 < x < 1$. Hence, $\mathcal{A}_2(x)$ decreases for $0 < x < x_1$ and increases for $x_1 < x < 1$, recall that $\mathcal{A}_2(1) = 0$ and $\lim_{x\to 0^+} \mathcal{A}_2(x) = +\infty$. There exists a unique root x_{1*} such that $\mathcal{A}_2(x) > 0$ for $0 < x < x_{1*}$ and $\mathcal{A}_2(x) < 0$ for $x_{1*} < x < 1$.

This completes the proof. □

We now turn to the discussion of the sign of $F(x;\sigma,\rho) = \mathcal{A}_1(x) + \mathcal{A}_2(X;\sigma,\rho)$.

Lemma 2. *Assume that* $0 < x < 1$ *and* $(\sigma,\rho) \to (1,1)$. *One has*

(i) *For* $\rho > \sigma$,

  (i1) *If* $(\lambda-1)(\sigma+\rho-2) > 0$, *then* $F(x;\sigma,\rho) > 0$.

  (i2) *If* $(\lambda-1)(\sigma+\rho-2) < 0$, *then the equation* $F(x;\sigma,\rho) = 0$ *has a unique root* x^* *such that* $F(x;\sigma,\rho) > 0$ *for* $0 < x < x^*$ *and* $F(x;\sigma,\rho) < 0$ *for* $x^* < x < 1$.

(ii) *For* $\rho < \sigma$ *and* $(\lambda-1)(\sigma+\rho-2) < 0$, *then equation* $F(x;\sigma,\rho) = 0$ *has a unique root* x^{**} *such that* $F(x;\sigma,\rho) > 0$ *for* $0 < x < x^{**}$ *and* $F(x;\sigma,\rho) < 0$ *for* $x^{**} < x < 1$.

Proof. We will provide a proof for the cases with $\rho > \sigma$. The case with $\rho < \sigma$ can be argued similarly. From (13), direct calculation gives

$$\begin{aligned}
F'''(x) &= \frac{2}{z_2x^3}\big[(z_1\lambda(2\rho-1)-z_2) - x^2(z_1\lambda(2\sigma-1)-z_2)\big], \\
F^{(4)}(x) &= -\frac{2}{z_2x^4}\big[5x^2(z_1\lambda(2\sigma-1)-z_2) - 3(z_1\lambda(2\rho-1)-z_2)\big].
\end{aligned}$$

Note that $(\sigma,\rho) \to (1,1)$. One has $z_1\lambda(2\sigma-1)-z_2 > 0$ and $z_1\lambda(2\sigma-1)-z_2 > 0$. It is easy to check that $F'''(x) = 0$ has a unique positive root, say $\overline{x}$ given by

$$\overline{x} = \sqrt{\frac{z_1\lambda(2\rho-1)-z_2}{z_1\lambda(2\sigma-1)-z_2}}.$$

For $\rho > \sigma$, one has $\overline{x} > 1$. Therefore, $F'''(x) < 0$ for $0 < x < 1$, which implies that $F''(x)$ is decreasing for $x \in (0,1)$. Note that

$$F''(1) = \frac{2z_1(\lambda-1)}{z_1 - z_2}(\sigma+\rho-2).$$

(i1) For $(\lambda-1)(\sigma+\rho-2) > 0$, one has $F''(1) > 0$. Therefore, $F''(x) > 0$ for $0 < x < 1$. Together with the fact that $F'(1) = F(1) = 0$, one has $F'(x) < 0$ and $F(x) < 0$ for $0 < x < 1$.

(i2) For $(\lambda-1)(\sigma+\rho-1) < 0$, there exists a unique root $\overline{x}_1$ of $F''(x) = 0$, such that $F''(x) > 0$ for $0 < x < \overline{x}_1$ and $F''(x) < 0$ for $\overline{x}_1 < x < 1$. This implies that $F'(x)$ is decreasing for $0 < x < \overline{x}_1$ and increasing for $\overline{x} < x < 1$. Note that $F'(1) = 0$. There is a unique root, $\overline{x}_2$, of $F'(x) = 0$, such that $F'(x) > 0$ for $0 < x < \overline{x}_2$ and $F'(x) < 0$ for $\overline{x}_2 < x < 1$. Note also that $F(1) = 0$. A similar argument leads to the conclusion that there exists a unique root, x^*, of $F(x) = 0$, such that $F(x) < 0$ for $0 < x < x^*$ and $F(x) > 0$ for $x^* < x < 1$.

□

From Definition 1 and Lemma 2, one has

Theorem 1. *Suppose $(\sigma,\rho) \to (1,1)$, $0 < x = L_1/R_1 < 1$ and $\nu > 0$ small. Then,*

(i) *For $(\lambda-1)(\sigma+\rho-2) < 0$, $\rho < \sigma$ and $0 < x < x^{**}$, one has $\frac{\partial J_{11}}{\partial V} > 0$ while $\frac{\partial J_{21}}{\partial V} < 0$. Moreover,*

  (i1) *$\mathcal{J}_1(V;\lambda,d) < \mathcal{J}_1(V;0,0)$ if $V < V_{1c}$ (resp. $\mathcal{J}_1(V;\lambda,d) > \mathcal{J}_1(V;0,0)$ if $V > V_{1c}$), that is, the ion size reduces (resp. enhances) the individual flux $\mathcal{J}_1$ if $V < V_{1c}$ (resp. $V > V_{1c}$).*

  (i2) *$\mathcal{J}_2(V;\lambda,d) > \mathcal{J}_2(V;0,0)$ if $V < V_{2c}$ (resp. $\mathcal{J}_2(V;\lambda,d) < \mathcal{J}_2(V;0,0)$ if $V > V_{2c}$), that is, the ion size enhances (resp. reduces) the individual flux $\mathcal{J}_2$ if $V < V_{2c}$ (resp. $V > V_{2c}$).*

(ii) *For $(\lambda-1)(\sigma+\rho-2) < 0$, $\rho < \sigma$ and $x^{**} < x < 1$, one has $\frac{\partial J_{11}}{\partial V} < 0$ whlie $\frac{\partial J_{21}}{\partial V} > 0$. Furthermore,*

  (ii1) *$\mathcal{J}_1(V;\lambda,d) > \mathcal{J}_1(V;0,0)$ if $V < V_{1c}$ (resp. $\mathcal{J}_1(V;\lambda,d) < \mathcal{J}_1(V;0,0)$ if $V > V_{1c}$), that is, the ion size enhances (resp. reduces) the individual flux $\mathcal{J}_1$ if $V < V_{1c}$ (resp. $V > V_{1c}$).*

  (ii2) *$\mathcal{J}_2(V;\lambda,d) < \mathcal{J}_2(V;0,0)$ if $V < V_{2c}$ (resp. $\mathcal{J}_2(V;\lambda,d) > \mathcal{J}_2(V;0,0)$ if $V > V_{2c}$), that is, the ion size reduces (resp. enhances) the individual flux $\mathcal{J}_2$ if $V < V_{2c}$ (resp. $V > V_{2c}$).*

(iii) *For $(\lambda-1)(\sigma+\rho-2) > 0$, $\rho > \sigma$, one has $\frac{\partial J_{11}}{\partial V} > 0$ whlie $\frac{\partial J_{21}}{\partial V} < 0$. Furthermore,*

  (iii1) *$\mathcal{J}_1(V;\lambda,d) < \mathcal{J}_1(V;0,0)$ if $V < V_{1c}$ (resp. $\mathcal{J}_1(V;\lambda,d) > \mathcal{J}_1(V;0,0)$ if $V > V_{1c}$), that is, the ion size reduces (resp. enhances) the individual flux $\mathcal{J}_1$ if $V < V_{1c}$ (resp. $V > V_{1c}$).*

  (iii2) *$\mathcal{J}_2(V;\lambda,d) > \mathcal{J}_2(V;0,0)$ if $V < V_{2c}$ (resp. $\mathcal{J}_2(V;\lambda,d) < \mathcal{J}_2(V;0,0)$ if $V > V_{2c}$), that is, the ion size enhances (resp. reduces) the individual flux $\mathcal{J}_2$ if $V < V_{2c}$ (resp. $V > V_{2c}$).*

(iv) *For $(\lambda-1)(\sigma+\rho-2) < 0$, $\rho > \sigma$ and $0 < x < x^*$, one has $\frac{\partial J_{11}}{\partial V} < 0$ while $\frac{\partial J_{21}}{\partial V} > 0$. Furthermore,*

  (iv1) *$\mathcal{J}_1(V;\lambda,d) > \mathcal{J}_1(V;0,0)$ (resp. $\mathcal{J}_1(V;\lambda,d) < \mathcal{J}_1(V;0,0)$) if $V < V_{1c}$ (resp. $V > V_{1c}$), that is, the ion size enhances (resp. reduces) the individual flux $\mathcal{J}_1(V;\sigma,\rho,\lambda,d)$ if $V < V_{1c}$ (resp. $V > V_{1c}$).*

(iv2) $\mathcal{J}_2(V;\lambda,d) < \mathcal{J}_2(V;0,0)$ *(resp.* $\mathcal{J}_2(V;\lambda,d) > \mathcal{J}_2(V;0,0)$*) if* $V < V_{2c}$ *(resp.* $V > V_{2c}$*), that is, the ion size reduces (resp. enhances) the individual flux* $\mathcal{J}_2(V;\lambda,d)$ *if* $V < V_{2c}$ *(resp.* $V > V_{2c}$*).*

(v) *For* $(\lambda-1)(\sigma+\rho-2) < 0$, $\rho > \sigma$ *and* $x^* < x < 1$*, one has* $\frac{\partial J_{11}}{\partial_V} > 0$ *while* $\frac{\partial J_{21}}{\partial_V} < 0$*. Furthermore,*

(v1) $\mathcal{J}_1(V;\lambda,d) > \mathcal{J}_1(V;0,0)$ *(resp.* $\mathcal{J}_1(V;\lambda,d) < \mathcal{J}_1(V;0,0)$*) if* $V < V_{1c}$ *(resp.* $V > V_{1c}$*), that is, the ion size enhances (resp. reduces) the individual flux* $\mathcal{J}_1(V;\lambda,d)$ *if* $V < V_{1c}$ *(resp.* $V > V_{1c}$*).*

(v2) $\mathcal{J}_2(V;\lambda,d) < \mathcal{J}_2(V;0,0)$ *(resp.* $\mathcal{J}_2(V;\lambda,d) > \mathcal{J}_2(V;0,0)$*) if* $V < V_{2c}$ *(resp.* $V > V_{2c}$*), that is, the ion size reduces (resp. enhances) the individual flux* $\mathcal{J}_2(V;\lambda,d)$ *if* $V < V_{2c}$ *(resp.* $V > V_{2c}$*).*

3.1.2. Relative Ion Sizes Effects

We now characterize the relative ion size effects in terms of $\lambda = \nu_2/\nu$, on J_k. Specifically, We study the sign of $\frac{\partial^2 J_{11}}{\partial\lambda\partial V}$, which is given by, with $x = L_1/R_1$,

$$\frac{\partial J_{11}}{\partial\lambda\partial V} = -\frac{\partial J_{11}}{\partial\lambda\partial V} = \frac{e}{k_B T}\frac{R_1^2}{\ln^3 x} f(x;\sigma,\rho), \tag{15}$$

where

$$\begin{aligned} f(x;\sigma,\rho) = {} & \frac{z_1}{z_2}(x-1)(2(x-1)-(x+1)\ln x) + \Big(a_3(x-1)(-z_1(x+1)+2x(2z_1-z_2)) \\ & -2\frac{z_1}{z_2}x^2\ln x\Big)(\sigma-1) + \Big(a_3(x-1)(z_1(x+1)-2(2z_1-z_2)) + 2\frac{z_1}{z_2}\ln x\Big)(\rho-1). \end{aligned}$$

For $f(x)$, one has

Lemma 3. *Suppose* $(\sigma,\rho) \to (1,1)$*.*

(1) *For* $\rho > \sigma$ *with* $\sigma+\rho > 2$*, one has* $f(x) > 0$ *if* $0 < x < 1$*.*

(2) *For* $\sigma+\rho < 2$*,* $f(x) = 0$ *has a unique root* x_**, such that* $f(x) < 0$ *(resp.* $f(x) > 0$*) if* $0 < x < x_*$ *(resp.* $x_* < x < 1$*).*

It follows that

Theorem 2. *Assume that* $(\sigma,\rho) \to (1,1)$ *and* $0 < x < 1$*. One has*

(i) *If* $\rho > \sigma$ *with* $\sigma+\rho > 2$*, one has* $\frac{\partial^2 J_{11}}{\partial V\partial\lambda} > 0$*, and* $\frac{\partial^2 J_{21}}{\partial V\partial\lambda} < 0$*. Moreover,*

(i1) $\mathcal{J}_1$ *decreases (resp. increases) in* λ *for* $V < V^{1c}$ *(resp.* $V > V^{1c}$*).*

(i2) $\mathcal{J}_2$ *increases (resp. decreases) in* λ *for* $V < V^{2c}$ *(resp.* $V > V^{2c}$*).*

(ii) *If* $\rho > \sigma$ *with* $\sigma+\rho < 2$*, and* $0 < x < x_*$ *, one has* $\frac{\partial^2 J_{11}}{\partial V\partial\lambda} > 0$ *and* $\frac{\partial^2 J_{21}}{\partial V\partial\lambda} < 0$*. Moreover,*

(ii1) $\mathcal{J}_1$ *decreases (resp. increases) in* λ *for* $V < V^{1c}$ *(resp.* $V > V^{1c}$*).*

(ii2) $\mathcal{J}_2$ *increases (resp. decreases) in* λ *for* $V < V^{2c}$ *(resp.* $V > V^{2c}$*).*

(iii) *If* $\rho < \sigma$ *with* $\sigma+\rho < 2$*, and* $x_* < x < 1$*, one has* $\frac{\partial^2 J_{11}}{\partial V\partial\lambda} < 0$*, and* $\frac{\partial^2 J_{21}}{\partial V\partial\lambda} > 0$*. Moreover,*

(iii1) $\mathcal{J}_1$ *increases (resp. decreases) in* λ *for* $V < V^{1c}$ *(resp.* $V > V^{1c}$*).*

(iii2) $\mathcal{J}_2$ *decreases (resp. increases) in* λ *for* $V < V^{2c}$ *(resp.* $V > V^{2c}$*).*

Remark 2. *From [88], under electroneutrality boundary conditions, one always has*

- $\frac{\partial J_{11}}{\partial V} > 0$ *while* $\frac{\partial J_{21}}{\partial V} < 0$*;*
- $\frac{\partial^2 J_{11}}{\partial V\partial\lambda} > 0$ *while* $\frac{\partial^2 J_{21}}{\partial V\partial\lambda} < 0$*.*

However, with relaxed neutral boundary conditions, as stated in Theorems 1 and 2, $\frac{\partial J_{11}}{\partial V}$ and $\frac{\partial^2 J_{11}}{\partial V \partial \lambda}$ can be negative while $\frac{\partial J_{21}}{\partial V}$ and $\frac{\partial^2 J_{21}}{\partial V \partial \lambda}$ can be positive. Clearly, richer dynamics of ionic flows under relaxed neutral conditions are observed. This also demonstrates the key role played by the boundary layers in the study.

3.2. Finite Ion Size Effects on the I–V Relations

The effects on the I–V relations from finite ion sizes follow directly from Lemmas 2 and 3, and Equation (9).

Theorem 3. *Assume $(\sigma, \rho) \to (1,1)$ and $0 < x = L_1/R_1 < 1$ and $\nu > 0$ small.*

(i) *For $(\lambda - 1)(\sigma + \rho - 2) < 0$ and $\rho < \sigma$,*

- (i1) *If $0 < x < x^{**}$, then, $\frac{\partial I_1}{\partial_V} > 0$. Furthermore, $\mathcal{I}(V;\lambda,d) < \mathcal{I}(V;0,0)$ if $V < V_c$ (resp. $\mathcal{I}(V;\lambda,d) > \mathcal{I}(V;0,0)$ if $V > V_c$), that is, the ion size reduces (resp. enhances) the current $\mathcal{I}$ if $V < V_c$ (resp. $V > V_c$).*
- (i2) *If $x^{**} < x < 1$, then $\frac{\partial I_1}{\partial_V} < 0$. Furthermore, $\mathcal{I}(V;\lambda,d) > \mathcal{I}(V;0,0)$ if $V < V_c$ (resp. $\mathcal{I}(V;\lambda,d) < \mathcal{I}(V;0,0)$ if $V > V_c$), that is, the ion size enhances (resp. reduces) the current $\mathcal{I}$ if $V < V_c$ (resp. $V > V_c$).*

(ii) *For $(\lambda - 1)(\sigma + \rho - 2) > 0$, $\rho > \sigma$, one has $\frac{\partial I_1}{\partial_V} > 0$. Furthermore, $\mathcal{I}(V;\lambda,d) < \mathcal{I}(V;0,0)$ if $V < V_c$ (resp. $\mathcal{I}(V;\lambda,d) > \mathcal{I}(V;0,0)$ if $V > V_c$), that is, the ion size reduces (resp. enhances) the current $\mathcal{I}$ if $V < V_c$ (resp. $V > V_c$).*

(iii) *For $(\lambda - 1)(\sigma + \rho - 2) < 0$ and $\rho > \sigma$,*

- (iii1) *If $0 < x < x^*$, then $\frac{\partial I_1}{\partial_V} > 0$. Furthermore, $\mathcal{I}(V;\lambda,d) < \mathcal{I}(V;0,0)$ (resp. $\mathcal{I}(V;\lambda,d) > \mathcal{I}(V;0,0)$) if $V < V_{1c}$ (resp. $V > V_{1c}$), that is, the ion size reduces (resp. enhances) the current $\mathcal{I}$ if $V < V_c$ (resp. $V > V_c$).*
- (iii2) *If $x^* < x < 1$, one has $\frac{\partial I_1}{\partial_V} < 0$. Furthermore, $\mathcal{I}(V;\lambda,d) > \mathcal{I}(V;0,0)$ (resp. $\mathcal{I}(V;\lambda,d) < \mathcal{I}(V;0,0)$) if $V < V_c$ (resp. $V > V_c$), that is, the ion size enhances (resp. reduces) the current $\mathcal{I}$ if $V < V_c$ (resp. $V > V_c$).*

Theorem 4. *Assume that $(\sigma, \rho) \to (1,1)$ and $0 < x = L_1/R_1 < 1$. Then,*

(i) *If $\rho > \sigma$ with $\sigma + \rho > 2$, one has $\frac{\partial^2 I_1}{\partial V \partial \lambda} > 0$. Moreover, the current $\mathcal{I}$ decreases (resp. increases) in λ if $V < V^c$ (resp. $V > V^c$).*

(ii) *If $\sigma + \rho < 2$, one has*

- (ii1) *For either $\rho > \sigma$ and $0 < x < x_*$, or $\rho < \sigma$ and $0 < x < x_*$, one has $\frac{\partial^2 I_1}{\partial V \partial \lambda} > 0$. Furthermore, the current $\mathcal{I}$ decreases (resp. increases) in λ if $V < V^c$ (resp. $V > V^c$).*
- (ii2) *For either $\rho > \sigma$ and $x_* < x < 1$, or $\rho < \sigma$ and $x_* < x < 1$, one has $\frac{\partial^2 I_1}{\partial V \partial \lambda} < 0$. Furthermore, the current $\mathcal{I}$ increases (resp. decreases) in λ if $V < V^c$ (resp. $V > V^c$).*

3.3. Orders of Critical Potentials

Our main concern is the order of the critical potentials identified in Definition 1 under different setups of boundary conditions. For convenience, in the subsequent analysis, we use V_{kc}^{EN}, $k = 1,2$ to represent the critical potentials identified under electroneutrality conditions.

3.3.1. A Total Order of V_c, V_{1c} and V_{2c}

From Definition 1, one has

$$V_{1c} - V_{2c} = -\frac{k_B T}{e}\frac{\beta_{10} + \alpha_{10}}{\alpha_{11}}, \quad V_c - V_{1c} = -z_2 D_2 \frac{k_B T}{e}\frac{\alpha_{10} + \beta_{10}}{(z_1 D_1 - z_2 D_2)\alpha_{11}},$$

$$V_c - V_{2c} = -z_1 D_1 \frac{k_B T}{e} \frac{\alpha_{10} + \beta_{10}}{(z_1 D_1 - z_2 D_2)\alpha_{11}},$$

where $\beta_{10} + \alpha_{10} = \frac{z_2 - z_1}{2z_2}\Big(-L_1^2\Big(a_4(\sigma - 1) + \frac{a_1}{z_2}\Big) + R_1^2\Big(a_4(\rho - 1) + \frac{a_1}{z_2}\Big)\Big)$.

Letting $L_1/R_1 = x$, one has $\beta_{10} + \alpha_{10} = \frac{z_2 - z_1}{2z_2} R_1^2 p(x)$, where

$$p(x) = -x^2\left(a_4(\sigma - 1) + \frac{a_1}{z_2}\right) + \left(a_4(\rho - 1) + \frac{a_1}{z_2}\right).$$

For $p(x)$, one has

Lemma 4. *For $0 < x < 1$, one has*

(i) *If $\rho > \sigma$, then $p(x) < 0$ for $0 < x < 1$. Furthermore, one has $\beta_{10} + \alpha_{10} < 0$.*
(ii) *If $\rho < \sigma$, there is a unique root x_c of $p(x) = 0$, such that $\beta_{10} + \alpha_{10} < 0$ for $0 < x < x_c$ and $\beta_{10} + \alpha_{10} > 0$ for $x_c < x < 1$.*

From Lemmas 2 and 4, we have

Theorem 5. *Assume that $(\sigma, \rho) \to (1, 1)$ and $0 < x < 1$. One has*

(i) *For $\rho > \sigma$,*
  (i1) *$V_{1c} > V_c > V_{2c}$ when $(\lambda - 1)(\sigma + \rho - 2) > 0$.*
  (i2) *$V_{1c} > V_c > V_{2c}$ when $(\lambda - 1)(\sigma + \rho - 2) < 0$ and $0 < x < x^*$.*
  (i3) *$V_{1c} < V_c < V_{2c}$ when $(\lambda - 1)(\sigma + \rho - 2) < 0$ and $x^* < x < 1$.*
(ii) *For $\rho < \sigma$ and $(\lambda - 1)(\sigma + \rho - 2) < 0$,*
  (ii1) *$V_{1c} > V_c > V_{2c}$ when either $0 < x < \min\{x^{**}, x_c\}$ or $\max\{x^{**}, x_c\} < x < 1$.*
  (ii2) *$V_{1c} < V_c < V_{2c}$ when either $\min\{x^{**}, x_c\} < x < \max\{x^{**}, x_c\}$.*

Remark 3. *V_{1c}, V_{2c} and V_c splits the potential interval into four subintervals, over which the dynamics of ionic flows are different. Take the case $(i1)$ in Theorem 5, for example, the four subregions are $(-\infty, V_{2c})$, (V_{2c}, V_c), (V_c, V_{1c}) and (V_{1c}, ∞). From Theorems 1 and 3, one has $J_k(\lambda, d) < J_k(0, 0)$ over both the subregions (V_{2c}, V_c) and (V_c, V_{1c}), while $I(\lambda, d) < I(0, 0)$ over (V_{2c}, V_c) and $I(\lambda, d) > I(0, 0)$ over (V_c, V_{1c}). This indicates rich dynamics of ionic flows that further depend on ion valences and diffusion coefficients.*

3.3.2. A Total Order of V^c, V^{1c} and V^{2c}

From Definition 1, together with $\beta_{11} = -\alpha_{11}$, one has

$$\begin{aligned} V^{1c} - V^{2c} &= \frac{k_B T}{e} \frac{\partial_\lambda(\beta_{10} + \alpha_{10})}{\partial_\lambda \alpha_{11}}, \\ V^c - V^{1c} &= \frac{k_B T}{e} \frac{-z_2 D_2}{z_1 D_1 - z_2 D_2} \frac{\partial_\lambda(\alpha_{10} + \beta_{10})}{\partial_\lambda \alpha_{11}}, \\ V^c - V^{2c} &= \frac{k_B T}{e} \frac{-z_1 D_2}{z_1 D_1 - z_2 D_2} \frac{\partial_\lambda(\alpha_{10} + \beta_{10})}{\partial_\lambda \alpha_{11}}, \end{aligned} \tag{16}$$

where $\partial_\lambda(\beta_{10} + \alpha_{10}) = \frac{z_1(z_1 - z_2)R_1^2}{z_2^2} q(x)$ with $q(x)$ given by $q(x) = x^2\Big(\sigma - \frac{1}{2}\Big) - \Big(\rho - \frac{1}{2}\Big)$.

Lemma 5. *Assume $0 < x < 1$. For the function $q(x)$, one has*

(i) *For $\rho > \sigma$, $q(x) < 0$;*
(ii) *For $\rho < \sigma$, there is a unique zero $0 < x^c < 1$ s0 that $q(x) < 0$ for $0 < x < x^c$, and $q(x) > 0$ for $x^c < x < 1$.*

From Lemmas 3 and 5, one has

Theorem 6. *Assume that* $(\sigma,\rho) \to (1,1)$ *and* $0 < x < 1$. *Then,*

(i) *For* $\rho > \sigma$,
  (i1) $V^{1c} > V^c > V^{2c}$ *when* $(\lambda-1)(\sigma+\rho-2) > 0$.
  (i2) $V^{1c} > V^c > V^{2c}$ *when* $(\lambda-1)(\sigma+\rho-2) < 0$ *and* $0 < x < x^*$.
  (i3) $V^{1c} < V^c < V^{2c}$ *when* $(\lambda-1)(\sigma+\rho-2) < 0$ *and* $x^* < x < 1$.

(ii) *For* $\rho < \sigma$ *and* $(\lambda-1)(\sigma+\rho-2) < 0$,
  (ii1) $V^{1c} > V^c > V^{2c}$ *when* $0 < x < \min\{x^*, x^c\}$ *and* $1 > x > \max\{x^*, x^c\}$.
  (ii2) $V^{1c} < V^c < V^{2c}$ *when* $\min\{x^*, x^c\} < x < \max\{x^*, x^c\}$.

3.4. Boundary Layer Effects on Ionic Flows

We illustrate boundary layer impacts on ionic flows from two directions.

3.4.1. Direct Interplays

For convenience, in our following discussion, we use $J_{k1}^{EN}(V;\lambda)$ to denote the fluxes under electroneutrality conditions, while $J_{k1}(V;\lambda,\sigma,\rho)$ presents the flux with boundary layers. We further introduce $\mathcal{J}_{k1}^d = J_{k1}(V;\lambda,\sigma,\rho) - J_{k1}^{EN}(V;\lambda)$, which directly characterizes the boundary layer effects on the individual fluxes. One then has

$$\begin{aligned}
\mathcal{J}_{11}^d =& \frac{\partial\alpha_{10}(1,1)}{\partial\sigma}(\sigma-1) + \frac{\partial\alpha_{10}(1,1)}{\partial\rho}(\rho-1) + \Big(\frac{\partial\alpha_{11}(1,1)}{\partial\sigma}(\sigma-1) \\
&+ \frac{\partial\alpha_{11}(1,1)}{\partial\rho}(\rho-1)\Big)\frac{e}{k_BT}V, \\
\mathcal{J}_{21}^d =& \frac{\partial\beta_{10}(1,1)}{\partial\sigma}(\sigma-1) + \frac{\partial\beta_{10}(1,1)}{\partial\rho}(\rho-1) - \Big(\frac{\partial\alpha_{11}(1,1)}{\partial\sigma}(\sigma-1) \\
&+ \frac{\partial\alpha_{11}(1,1)}{\partial\rho}(\rho-1)\Big)\frac{e}{k_BT}V.
\end{aligned}$$

It follows that

$$\frac{\partial\mathcal{J}_{11}^d(V;\lambda,\sigma,\rho)}{\partial V} = -\frac{\partial\mathcal{J}_{21}^d(V;\lambda,\sigma,\rho)}{\partial V} = \frac{eR_1^2}{2k_BT\ln^2 x}\mathcal{A}_2(x,\sigma,\rho). \tag{17}$$

From Lemma 1, $\mathcal{J}_{11}^d(V;\lambda,\sigma,\rho) = 0$ has a unique root V^{1*}, and $\mathcal{J}_{21}^d(V;\lambda,\sigma,\rho) = 0$ has a unique root V^{2*}. Moreover,

$$\begin{aligned}
V^{1*} =& -\frac{\frac{\partial\alpha_{10}(1,1)}{\partial\sigma}(\sigma-1) + \frac{\partial\alpha_{10}(1,1)}{\partial\rho}(\rho-1)}{\frac{\partial\alpha_{11}(1,1)}{\partial\sigma}(\sigma-1) + \frac{\partial\alpha_{11}(1,1)}{\partial\rho}(\rho-1)}\frac{k_BT}{e}, \\
V^{2*} =& \frac{\frac{\partial\beta_{10}(1,1)}{\partial\sigma}(\sigma-1) + \frac{\partial\beta_{10}(1,1)}{\partial\rho}(\rho-1)}{\frac{\partial\alpha_{11}(1,1)}{\partial\sigma}(\sigma-1) + \frac{\partial\alpha_{11}(1,1)}{\partial\rho}(\rho-1)}\frac{k_BT}{e}.
\end{aligned}$$

Together with Lemma 1, the following result can be established.

Theorem 7. *Assume that* $0 < x = \frac{L_1}{R_1} < 1$ *and* $(\sigma,\rho) \to (1,1)$. *Then,*

(i) *For* $\mathcal{A}_2(x) > 0$, *one has* $\frac{\partial\mathcal{J}_{11}^d(V;\lambda,\sigma,\rho)}{\partial V} > 0$ *and* $\frac{\partial\mathcal{J}_{21}^d(V;\lambda,\sigma,\rho)}{\partial V} < 0$. *Furthermore,*
  (i1) $J_{11}(V;\lambda,\sigma,\rho) < J_{11}^{EN}(V,\lambda)$ *(resp.* $J_{11}(V;\lambda,\sigma,\rho) > J_{11}^{EN}(V,\lambda)$*) if* $V < V^{1*}$ *(resp.* $V > V^{1*}$*), that is, the boundary layer reduces (resp. enhances) the individual flux* $\mathcal{J}_1$ *if* $V < V^{1*}$ *(resp.* $V > V^{1*}$*).*

(i2) $J_{21}(V;\lambda,\sigma,\rho) > J_{21}^{EN}(V,\lambda)$ *(resp.* $J_{21}(V;\lambda,\sigma,\rho) < J_{21}^{EN}(V,\lambda)$*) if* $V < V^{2*}$ *(resp.* $V > V^{2*}$*), that is, the boundary layer enhances (resp. reduces) the individual flux* $\mathcal{J}_2$ *if* $V < V^{2*}$ *(resp.* $V > V^{2*}$*).*

(ii) *For* $\mathcal{A}_2(x) < 0$*, one has* $\frac{\partial \mathcal{J}_{11}^d(V;\lambda,\sigma,\rho)}{\partial V} < 0$ *while* $\frac{\partial \mathcal{J}_{21}^d(V;\lambda,\sigma,\rho)}{\partial V} > 0$*. Furthermore,*

(ii1) $J_{11}(V;\lambda,\sigma,\rho) > J_{11}^{EN}(V,\lambda)$ *(resp.* $J_{11}(V;\lambda,\sigma,\rho) < J_{11}^{EN}(V,\lambda)$*) if* $V < V^{1*}$ *(resp.* $V > V^{1*}$*), that is, the boundary layer enhances (resp. reduces) the individual flux* $\mathcal{J}_1$ *if* $V < V^{1*}$ *(resp.* $V > V^{1*}$*).*

(ii2) $J_{21}(V;\lambda,\sigma,\rho) < J_{21}^{EN}(V,\lambda)$ *(resp.* $J_{21}(V;\lambda,\sigma,\rho) > J_{21}^{EN}(V,\lambda)$*) if* $V < V^{2*}$ *(resp.* $V > V^{2*}$*), that is, the boundary layer reduces (resp. enhances) the individual flux* $\mathcal{J}_2$ *if* $V < V^{2*}$ *(resp.* $V > V^{2*}$*).*

3.4.2. Further Analysis

We further analyze the impacts on ionic flows from boundary layers in terms of a total order of $V_{1c}, V_{2c}, V_c, V_{1c}^{EN}, V_{2c}^{EN}$ and V_c^{EN}, where the critical potentials V_{1c}^{EN}, V_{2c}^{EN} and V_c^{EN} are identified under electroneutrality conditions, and from Definition 1, they are given by

$$V_{1c}^{EN} = -\frac{\alpha_{10}(1,1)}{\alpha_{11}(1,1)}\frac{k_BT}{e}, \quad V_{2c}^{EN} = -\frac{\beta_{10}(1,1)}{\beta_{11}(1,1)}\frac{k_BT}{e},$$
$$V_c^{EN} = -\frac{z_1D_1\alpha_{10}(1,1) + z_2D_2\beta_{10}(1,1)}{z_1D_1\alpha_{11}(1,1) + z_2D_2\beta_{11}(1,1)}\frac{k_BT}{e}.$$

It is easy to check that

Lemma 6. *For* $L_1 < R_1$*, one has* $V_{1c}^{EN} < V_c^{EN} < V_{2c}^{EN}$*.*

To provide a total order of the six critical potentials, we treat the critical potential V_{1c}, V_{2c} and V_c as functions of (σ,ρ) and expand them along $(\sigma,\rho) = (1,1)$ up to the first order and ignore higher order terms. For example, we write $V_{1c}(\sigma,\rho)$ as

$$V_{1c}(\sigma,\rho) = V_{1c}(1,1) + \frac{\partial V_{1c}}{\partial \sigma}\bigg|_{(\sigma=1,\rho=1)}(\sigma-1) + \frac{\partial V_{1c}}{\partial \rho}\bigg|_{(\sigma=1,\rho=1)}(\rho-1). \tag{18}$$

Note that V_{1c} is linear in σ and ρ. We first consider $V_{1c} - V_{1c}^{EN} = 0$. Note also that $V_{1c}^{EN} = V_{1c}(1,1)$. We have

$$\frac{\rho}{\sigma} := \theta_1(x) = \frac{\partial_\sigma\alpha_{10}(1,1) - V_{1c}(1,1)\partial_\sigma\alpha_{11}(1,1)}{\partial_\rho\alpha_{10}(1,1) - V_{1c}(1,1)\partial_\rho\alpha_{11}(1,1)},$$

where

$$\begin{aligned}
&\partial_\sigma\alpha_{10}(1,1) - V_{1c}(1,1)\partial_\sigma\alpha_{11}(1,1)\\
&= \frac{a_1(x^2-1)}{2z_2(z_1-z_2)\ln x} - \frac{a_4}{2}x^2 - a_2a_3\left(\frac{x-1}{\ln x}\right)^2\\
&\quad + \frac{k_BT}{z_1e}\frac{(x+1)\ln^2 x}{2(x-1)-(x+1)\ln x}\left(\frac{a_3(x-1)}{\ln^2 x}\Big(x(a_1+a_2) - \frac{a_1}{2}(x+1)\Big) - \frac{a_4x^2}{2\ln x}\right),\\
&\partial_\rho\alpha_{10}(1,1) - V_{1c}(1,1)\partial_\rho\alpha_{11}(1,1)\\
&= \frac{a_1(x^2-1)}{2z_2(z_1-z_2)\ln x} + \frac{a_4}{2} + \left(\frac{x-1}{\ln x}\right)^2 a_2a_3\\
&\quad + \frac{k_BT}{z_1e}\frac{(x+1)\ln^2 x}{2(x-1)-(x+1)\ln x}\left(-\frac{a_3(x-1)}{\ln^2 x}\Big((a_1+a_2) - \frac{a_1}{2}(x+1)\Big) + \frac{a_4}{2(\ln x)}\right).
\end{aligned}$$

Correspondingly, for a given L_1 and R_1, x and θ_1 are fixed. Note that $\sigma = \rho = 1$ satisfies the equation $V_{1c} - V_{1c}^{EN} = 0$, and we obtain the linear equation

$$\rho = \sigma\theta_1 - \theta_1 + 1,$$

which indicates that any pair of (σ, ρ) that satisfies the linear equation also satisfies $V_{1c} - V_{1c}^{EN} = 0$.

It follows that

Proposition 1. *Assume that $(\sigma, \rho) \to (1,1)$. $V_{1c}(\sigma, \rho) > V_{1c}^{EN}$ (resp. $V_{1c}(\sigma, \rho) < V_{1c}^{EN}$) for $\rho - 1 > (\sigma - 1)\theta_1$ (resp. $\rho - 1 < (\sigma - 1)\theta_1$).*

A similar discussion for $V_{2c}(\sigma, \rho)$ leads to the following result.

Proposition 2. *Assume that $(\sigma, \rho) \to (1,1)$. One has $V_{2c}(\sigma, \rho) > V_{2c}^{EN}$ (resp. $V_{2c}(\sigma, \rho) < V_{2c}^{EN}$) for $(\rho - 1) > (\sigma - 1)\theta_2$ (resp. $(\rho - 1) < (\sigma - 1)\theta_2$). Here, $\theta_2 = \frac{\partial_\sigma \beta_{10}(1,1) - V_{2c}(1,1)\partial_\sigma \beta_{11}(1,1)}{\partial_\rho \beta_{10}(1,1) - V_{2c}(1,1)\partial_\rho \beta_{11}(1,1)}$, where*

$$\begin{aligned}
&\partial_\sigma \beta_{10}(1,1) - V_{2c}(1,1)\partial_\sigma \beta_{11}(1,1) \\
&= -\frac{a_1(x^2-1)}{2z_2(z_1-z_2)\ln x} + \frac{z_1 a_4}{2z_2}x^2 + a_2 a_3 \left(\frac{x-1}{\ln x}\right)^2 \\
&\quad + \frac{k_B T}{z_2 e}\frac{(x+1)\ln^2 x}{2(x-1)-(x+1)\ln x}\left(\frac{a_3(x-1)}{\ln^2 x}\left(x(a_1+a_2) - \frac{a_1}{2}(x+1)\right) - \frac{a_4 x^2}{2(\ln x)}\right),
\end{aligned}$$

and

$$\begin{aligned}
&\partial_\rho \beta_{10}(1,1) - V_{2c}(1,1)\partial_\rho \beta_{11}(1,1) \\
&= -\frac{a_1(x^2-1)}{2z_2(z_1-z_2)\ln x} - \frac{z_1 a_4}{2z_2} - a_2 a_3 \left(\frac{x-1}{\ln x}\right)^2 \\
&\quad + \frac{k_B T}{z_2 e}\frac{(x+1)\ln^2 x}{2(x-1)-(x+1)\ln x}\left(-\frac{a_3(x-1)}{\ln^2 x}\left((a_1+a_2) - \frac{a_1}{2}(x+1)\right) + \frac{a_4}{2(\ln x)}\right).
\end{aligned}$$

As for $V_c(\sigma, \rho)$, one has

Proposition 3. *Assume that $(\sigma, \rho) \to (1,1)$. $V_c(\sigma, \rho) > V_c^{EN}$ (resp. $V_c(\sigma, \rho) < V_c^{EN}$) for $\rho > \sigma\theta_3 - \theta_3 + 1$ (resp. $\rho < \sigma\theta_3 - \theta_3 + 1$). Here,*

$$\theta_3 = \frac{z_1 D_1 \partial_\sigma \alpha_{10}(1,1) + z_2 D_2 \partial_\sigma \beta_{10}(1,1) - V_c(1,1)(z_1 D_1 - z_2 D_2)\partial_\sigma \alpha_{11}(1,1)}{z_1 D_1 \partial_\rho \alpha_{10}(1,1) + z_2 D_2 \partial_\rho \beta_{10}(1,1) - V_c(1,1)(z_1 D_1 - z_2 D_2)\partial_\rho \alpha_{11}(1,1)},$$

where

$$\begin{aligned}
&z_1 D_1 \partial_\sigma \alpha_{10}(1,1) + z_2 D_2 \partial_\sigma \beta_{10}(1,1) - V_c(1,1)(z_1 D_1 - z_2 D_2)\partial_\sigma \alpha_{11}(1,1) \\
&= (z_1 D_1 - z_2 D_2)\frac{x-1}{\ln x}\left(\frac{a_1(x+1)}{2z_2(z_1-z_2)} - a_2 a_3 \frac{x-1}{\ln x}\right) - \frac{z_1(D_1-D_2)a_4}{2}x^2 \\
&\quad + \frac{(D_1-D_2)(x+1)\ln^2 x}{2(x-1)-(x+1)\ln x}\left(\frac{a_3(x-1)}{\ln^2 x}\left(x(a_1+a_2) - \frac{a_1}{2}(x+1)\right) - \frac{a_4 x^2}{2\ln x}\right), \\
&z_1 D_1 \partial_\rho \alpha_{10}(1,1) + z_2 D_2 \partial_\rho \beta_{10}(1,1) - V_c(1,1)(z_1 D_1 - z_2 D_2)\partial_\rho \alpha_{11}(1,1) \\
&= (z_1 D_1 - z_2 D_2)\frac{x-1}{\ln x}\left(\frac{a_1(x+1)}{2z_2(z_1-z_2)} + a_2 a_3 \frac{x-1}{\ln x}\right) + \frac{z_1(D_1-D_2)a_4}{2} \\
&\quad + \frac{(D_1-D_2)(x+1)\ln^2 x}{2(x-1)-(x+1)\ln x}\left(-\frac{a_3(x-1)}{\ln^2 x}\left(x(a_1+a_2) - \frac{a_1}{2}(x+1)\right) - \frac{a_4}{2\ln x}\right).
\end{aligned}$$

Together with Lemma 6, one has

Theorem 8. *For $(\sigma, \rho) \to (1, 1)$ and $\theta_1 < \theta_2 < \theta_3$, one has*

(i) *For $\sigma \to 1^+$,*

(i1) *If $+\infty > \frac{\rho-1}{\sigma-1} > \theta_3$, then, $V_{1c}^{EN} < V_{1c} < V_c^{EN} < V_c < V_{2c}^{EN} < V_{2c}$.*
(i2) *If $\theta_3 > \frac{\rho-1}{\sigma-1} > \theta_2$, then, $V_{1c}^{EN} < V_{1c} < V_c < V_c^{EN} < V_{2c}^{EN} < V_{2c}$.*
(i3) *If $\theta_2 > \frac{\rho-1}{\sigma-1} > \theta_1$, then, $V_{1c}^{EN} < V_{1c} < V_c < V_c^{EN} < V_{2c} < V_{2c}^{EN}$.*
(i4) *If $\theta_1 > \frac{\rho-1}{\sigma-1} > -\infty$, then, $V_{1c} < V_{1c}^{EN} < V_c < V_c^{EN} < V_{2c} < V_{2c}^{EN}$.*

(ii) *For $\sigma \to 1^-$,*

(ii1) *If $+\infty > \frac{\rho-1}{\sigma-1} > \theta_3$, then, $V_{1c} < V_{1c}^{EN} < V_c < V_c^{EN} < V_{2c} < V_{2c}^{EN}$.*
(ii2) *If $\theta_3 > \frac{\rho-1}{\sigma-1} > \theta_2$, then, $V_{1c}^{EN} < V_{1c} < V_c < V_c^{EN} < V_{2c} < V_{2c}^{EN}$.*
(ii3) *If $\theta_2 > \frac{\rho-1}{\sigma-1} > \theta_1$, then, $V_{1c}^{EN} < V_{1c} < V_c < V_c^{EN} < V_{2c}^{EN} < V_{2c}$.*
(ii4) *If $\theta_1 > \frac{\rho-1}{\sigma-1} > -\infty$, then, $V_{1c}^{EN} < V_{1c} < V_c^{EN} < V_c < V_{2c}^{EN} < V_{2c}$.*

Remark 4. *The qualitative properties of ionic flows depend on the boundary layers as shown in both Theorems 7 and 8. Particularly, in Theorem 8, a total order of the critical potentials $V_{1c}, V_{2c}, V_c, V_{1c}^{EN}$, V_{2c}^{EN} and V_c^{EN} under different conditions is provided, and they split the whole potential region into seven subregions, from which the distinct dynamics of ionic flows can be observed. This further indicates the effects on ionic flows from boundary layers. More importantly, these critical potentials can be experimentally estimated. Take the potential V_c, for example, one is able to take an experimental I–V relation as $I(V; \lambda, \nu)$ and numerically compute $I_0(V)$ for the ideal case that allows one to obtain an estimate of V_c.*

4. Concluding Remarks

We study the finite ion size impacts on ionic flows under relaxed boundary conditions to better understand the dynamics of ionic flows via a one-dimensional PNP model. Ion sizes play vital roles in the characterization of the selectivity phenomena of ion channels. The detailed discussion, particularly, the argument of the relative ion size effects, could provide important insights into the selectivity phenomena of ion channels. Our study is under more realistic setups of the boundary conditions, a state that is not neutral but close to, and not surprisingly, the richer dynamics of ionic flows which are observed compared to the work conducted in [88] under the assumption of electroneutrality boundary conditions, that is, $\sigma = \rho = 1$ in current setup. The boundary layer effects on ionic flows due to the relaxation of the electroneutrality conditions are further characterized. Critical potentials are identified under different setups, which play crucial roles in our discussion of the ionic flow properties. Most importantly, those critical potentials can be experimentally identified as stated in Remark 4. The study provides an efficient way to control/adjust the boundary conditions to observe distinct dynamics of ionic flows through membrane channels. This is important for future analytical studies and critical for future numerical and even experimental studies of ion channel problems.

To end this section, we point out that the setup in this work is relatively simple, it only consisted of two oppositely charged particles and did not include nonzero permanent charges. The study in the current work is the first step for the analysis of more realistic models, such as those including multiple cations and nonzero permanent charges. The method developed in this work can be directly applied to those more realistic models and will be our future research topics.

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Abbreviations

The following abbreviations are used in this manuscript:

PNP	Poisson–Nernst–Planck
I–V	Current–voltage

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