BOUNDARY LAYER EFFECTS ON IONIC FLOWS VIA POISSON-NERNST-PLANCK SYSTEMS WITH NONUNIFORM ION SIZES

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Abstract. We study a one-dimensional Poisson-Nernst-Planck model with two oppositely charged particles, zero permanent charges and nonuniform finite ion sizes through a local hard-sphere model. Of particular interest is to examine the boundary layer effects on ionic flows systematically in terms of individual fluxes, the total flow rate of charges (current-voltage relations) and the total flow rate of matter. This is particularly important because boundary layers of charge are particularly likely to create artifacts over long distances, and this could dramatically affect the behavior of ionic flows. Several critical potentials are identified, which play unique and critical roles in examining the dynamics of ionic flows. Some can be estimated experimentally. Numerical simulations are performed for a better understanding and further illustrating our analytical results. We believe the analysis can provide complementary information of the qualitative properties of ionic flows and help one better understand the mechanism of ionic flow through membrane channels.

1. Introduction. The study of electrodiffusion is an extremely rich area for multi-disciplinary research with diverse applications in many research fields, particularly in chemistry, physiology and biology. More specifically, semiconductor technology controls the migration and diffusion of quasi-particles of charge in transistors and integrated circuits ([51, 55]), chemical science deals with charged molecules in water ([7, 12, 13]), and biology occurs in plasma of ions and charged organic molecules in water ([3, 15, 29, 57]). 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

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move in semiconductors ([17, 18, 19]). 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.

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, 11, 16, 21, 22, 34, 36, 39, 40, 43, 48, 58, 59, 62]) 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 PNP models with nonuniform finite ion sizes. Of particular interest is to characterize the nonlinear interplays among system parameters, such as finite ion size, 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. One-dimensional Poisson-Nernst-Planck models. PNP system is a basic macroscopic model for electrodiffusion of charges through ion channels ([15, 17, 26, 29, 33, 52, 53], etc.). Under various reasonable conditions, the PNP system can be derived as a reduced model from molecular dynamics, Boltzmann equations, and variational principles ([4, 30, 31, 54]).

Based on the fact that the channel is narrow and one can effectively view it as a one-dimensional channel $[0, l]$, where $l (= l \times 10^{-9}$ m) is the length of the channel together with the baths that the channel links. A quasi-one-dimensional steady-state PNP model for a mixtures of $n$ ion species though a single channel reads (first proposed in [47])

$$
\begin{align*}
\frac{1}{A(X)} \frac{d}{dX} \left( \varepsilon_r(X) \varepsilon_0 A(X) \frac{d\Phi(X)}{dX} \right) &= -e \left( \sum_{j=1}^{n} z_j C_j(X) + Q(X) \right), \\
\frac{dJ_i}{dX} &= 0, \quad -J_i = \frac{1}{k_B T} D_i(X) A(X) C_i(X) \frac{d\mu_i(X)}{dX}, \quad i = 1, 2, \ldots, n,
\end{align*}
$$

(1)

where

- $e \approx 1.60217666 \times 10^{-19}$ (C=coulomb) is the elementary charge,
- $k_B = 1.380648813 \times 10^{-23}$ (JK$^{-1}$) is the Boltzmann constant,
- $T$ is the absolute temperature (unit K (kelvin)), it is $T \approx 273.16$ (K),
- $\Phi(X)$ is the electric potential with the unit V=Volt=JC$^{-1}$,
- $Q(X)$ is the permanent charge density of the channel (with unit 1/m$^3$),
- $\varepsilon_0$ is the local dielectric coefficient (with unit Fm$^{-1}$),
- $\varepsilon_r(X)$ is the relative dielectric coefficient (with unit 1),
- $A(X)$ represents the area of the cross-section over the point $X$ (with unit m$^2$),
- $n$ is the number of distinct types of ion species (with unit 1),
- for the $j$th ion species,
  - $C_j(X)$ is the number density (with unit 1/m$^3$),
  - $z_j$ is the valence (the number of charges per particle with unit 1),
– $\mu_j(X)$ is the electrochemical potential (with unit J=CV),
– $J_j$ is the number flux density (with unit 1/s) – the number of particles across each cross-section per unit time;
– $D_j(X)$ is the diffusion coefficient (with unit m$^2$/s).

The boundary conditions are, for $i = 1, 2, \cdots, n$,

$$\Phi(0) = V, \quad C_i(0) = L_i > 0; \quad \Phi(l) = 0, \quad C_i(l) = R_i > 0. \quad (2)$$

For a solution of the steady-state boundary value problem of (1)-(2), the rate of flow of charge through a cross-section or current $I$ is

$$I = \sum_{j=1}^{n} z_j J_j \quad (3)$$
and the flow rate of matter through a cross-section is defined by

$$T = \sum_{j=1}^{n} J_j. \quad (4)$$

Particularly, for fixed boundary concentrations $L_i$ and $R_i$, $J_i$ depends on $V$ only, and formula (3) provides a relation of the current $I$ to the voltage $V$, which is the so-called I-V relation.

1.2. Excess potential and a local hard-sphere model. The electrochemical potential $\mu_i(X)$ for the $i$th ion species consists of the ideal component $\mu_i^{id}(X)$, and the excess component $\mu_i^{ex}(X)$:

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

where

$$\mu_i^{id}(X) = z_i e \Phi(X) + k_B T \ln \frac{C_i(X)}{C_0}, \quad (5)$$

with some characteristic number density $C_0$. The ideal component $\mu_i^{id}(X)$ reflects the collision between ion particles and the water molecules. The PNP system including the ideal component only is the so-called classical PNP (cPNP). It has been well accepted that the cPNP system is a reasonable model in, for example, the dilute case under which the ion particles can be treated as point-particles and the ion-to-ion interaction can be more or less ignored. The cPNP is the simplest PNP model, which has been extensively studied ([4, 5, 6, 15, 21, 27, 33, 43, 44, 47, 59, 61, 63, 64] and the reference therein). However, many extremely important properties of ion channels, such as selectivity, rely on finite ion sizes critically, especially for those that have the same ion valence but distinct ion size like Na$^+$ (sodium) and K$^+$ (potassium). To analyze the finite ion size effects on ionic flows, one need to consider ion-specific components of the electrochemical potential in the PNP models. One reasonable way is to include Hard-Sphere (HS) potential models of the excess electrochemical potential. There are two types of models for HS potentials: local and nonlocal. Local HS potential models depends pointwise on ion concentrations while nonlocal HS models are proposed as functionals of ion concentrations (see [39, 49, 50] for more discussions). The PNP type models with ion sizes have been investigated computationally and analytically for ion channels and have shown great success ([8, 10, 20, 27, 30, 32, 37, 38, 39, 46, 56, 65], etc.).
In this work, we will take the following local hard-sphere model for $\mu^{c^r}_i(X)$ (derived from some nonlocal model in [39])

$$\frac{1}{k_B T} \mu^{\text{HS}}_i(X) = -\ln \left( 1 - \sum_{j=1}^n d_j C_j(X) \right) + \frac{d_i \sum_{j=1}^n C_j(X)}{1 - \sum_{j=1}^n d_j C_j(X)},$$

(6)

where $d_i$ is the diameter of the $i$th ion species.

1.3. Electroneutrality boundary conditions vs boundary layers. To describe the actual behavior of channels or useful transistors, macroscopic reservoirs linked by ion channels must be included ([14, 24, 27, 28]). 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. However, 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, 35, 36, 37, 39, 46, 60]), which are defined as

$$\sum_{k=1}^n z_k \mathcal{L}_k = \sum_{k=1}^n z_k \mathcal{R}_k = 0$$

(7)

Under the condition (7), the difficulty in analyzing the dynamics of ionic flows is reduced to a great extent, but 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 [61] 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

$$-z_2 \mathcal{L}_2 = \sigma (z_1 \mathcal{L}_1) \text{ and } -z_2 \mathcal{R}_2 = \rho (z_1 \mathcal{R}_1),$$

(8)

where $\sigma$ and $\rho$ are some positive constants close to but not equal to 1 simultaneously ($\sigma = 1 = \rho$ in (8) implies neutral state). More rich qualitative properties of ionic flows were observed compared to the one with electroneutrality conditions. More recently, the authors in [59] 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, 45]. 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 nonuniform finite ion size is included in the PNP model.

1.4. Main interests. Under the framework of geometric singular perturbation theory, the authors in [39] studied the PNP system with the local HS model (6) accounting for the finite ion size effects. Their analysis was under the assumption
of electroneutrality boundary conditions (7) for two oppositely charged ion species. The existence of solution to the boundary value problem for small ion sizes is established, and furthermore, treating the ion sizes as small parameters, the author also derived approximations of the I-V relation of the form with 

\[ I = I_0(V) + I_1(V; \lambda)d + o(d), \]

and the flow rate of matter of the form 

\[ T = T_0(V) + T_1(V; \lambda)d + o(d) \]

from which the finite ion size effects on ionic flows were characterized through the leading terms \( I_1(V; \lambda) \) and \( T_1(V; \lambda) \) in great detail. Later, in [10], the individual fluxes \( J_k \) of the form 

\[ J_k = D_k J_{k0}(V) + D_k J_{k1}(V; \lambda)d + o(d) \]

was further studied. It turns out that the leading terms \( I_1(V; \lambda), T_1(V; \lambda) \) and \( J_{k1}(V; \lambda) \) that contains finite ion size effects are all linear functions of the potential \( V \), and thus the signs of \( \frac{\partial I_1}{\partial V}, \frac{\partial T_1}{\partial V} \) and \( \frac{\partial J_{k1}}{\partial V} \) are critical in the study of ion size effects on ionic flows. Under the electroneutrality boundary conditions, they are all positive, while in general they could be negative. A special case was observed in [39], which showed the negativeness of \( \frac{\partial I_1}{\partial V} \) and \( \frac{\partial T_1}{\partial V} \), but it is too degenerate.

Our main interest in this work is to provide a systematic study of the boundary layer effects on ionic flows with nonuniform ion sizes in terms of \( I_1(V; \lambda), T_1(V; \lambda) \) and \( J_{k1}(V; \lambda) \), in particular, the signs of \( \frac{\partial I_1}{\partial V}, \frac{\partial T_1}{\partial V} \) and \( \frac{\partial J_{k1}}{\partial V} \). To be specific, we will analyze these terms without assuming the electroneutrality boundary conditions (7), but under the state which is close to the neutral one (see (1)). For this more general and more realistic setting, much more rich qualitative properties of ionic flows are observed due to the existence of the boundary layers (arising from the violation of the electroneutrality boundary conditions) in the PNP system.

The rest of the work is organized as follows. In Section 2, we set up the problem and recall some results obtained in [10] and [39], which are critical for our discussion. Our main results are stated in Section 3, which deals with the boundary layer effects on individual fluxes, I-V relations and the flow rate of matter with nonuniform ion sizes, respectively. Numerical simulations are also performed to help better understand our analytical results. A concluding remark is provided in Section 4.

2. Problem setup and some previous results. We set up our problem and recall some existing results from [10, 39] to be used frequently in our following discussions.

2.1. Assumptions and a dimensionless PNP type system. For consistency, we take essentially the same assumptions as those in [39]. More precisely, we assume the following

(A1) We consider two ion species \((n = 2)\) with \(z_1 > 0, z_2 < 0\).

(A2) The permanent charge is set to be zero: \(Q(x) = 0\).

(A3) For the electrochemical potential \(\mu_i\), we include both the ideal component \(\mu_i^d\) in (5) and the LHS potential \(\mu_i^{LHS}\) in (6).

(A4) \(\varepsilon_r(x) = \varepsilon_r\) and \(D_i(x) = D_i\), where \(\varepsilon_r\) and \(D_i\) are some constants.
In the sequel, we will assume (A1)–(A4). First of all, we need to make a dimensionless rescaling following ([25]). Set \( C_0 = \max \{ \mathcal{L}_i, \mathcal{R}_i : i = 1, 2 \} \) and let

\[
\varepsilon^2 = \frac{\varepsilon r_0 k_B T}{e^2 I^2 C_0}, \quad x = \frac{X}{I}, \quad h(x) = \frac{A(X)}{I^2}, \quad D_i = l C_0 D_i;
\]

\[
\phi(x) = \frac{e}{k_B T} \Phi(X), \quad c_i(x) = \frac{C_i(X)}{C_0}, \quad J_i = \frac{J_i}{D_i};
\]

\[
\bar{V} = \frac{e}{k_B T} V, \quad L_i = \frac{\mathcal{L}_i}{C_0}, \quad R_i = \frac{\mathcal{R}_i}{C_0}.
\]

The boundary value problem (1)-(2) now becomes

\[
\frac{\varepsilon^2}{h(x)} \frac{d}{dx} \left( h(x) \frac{d}{dx} \phi \right) = -z_1 c_1 - z_2 c_2, \quad \frac{dJ_1}{dx} = \frac{dJ_2}{dx} = 0,
\]

\[
\frac{dc_1}{dx} = -f_1(c_1, c_2; d_1, d_2) \frac{d\phi}{dx} - \frac{1}{h(x)} g_1(c_1, c_2, J_1, J_2; d_1, d_2),
\]

\[
\frac{dc_2}{dx} = f_2(c_1, c_2; d_1, d_2) \frac{d\phi}{dx} - \frac{1}{h(x)} g_2(c_1, c_2, J_1, J_2; d_1, d_2)
\]

with the boundary conditions

\[
\phi(0) = \bar{V}, \quad c_i(0) = L_i > 0; \quad \phi(1) = 0, \quad c_i(1) = R_i > 0.
\]

where

\[
f_1(c_1, c_2; d_1, d_2) = z_1 c_1 - (d_1 + d_2 - d_1^2 c_1 - d_2^2 c_2)(z_1 c_1 + z_2 c_2)c_1 - z_1(d_1 - d_2)c_1^2,
\]

\[
f_2(c_1, c_2; d_1, d_2) = -z_2 c_2 + (d_1 + d_2 - d_1^2 c_1 - d_2^2 c_2)(z_1 c_1 + z_2 c_2)c_2 + z_2(d_2 - d_1)c_2^2,
\]

\[
g_1(c_1, c_2, J_1, J_2; d_1, d_2) = ((1 - d_1 c_1^2 + d_2^2 c_1 c_2) J_1 - c_1(d_1 + d_2 - d_1^2 c_1 - d_2^2 c_2) J_2,
\]

\[
g_2(c_1, c_2, J_1, J_2; d_1, d_2) = ((1 - d_2 c_2^2 + d_1^2 c_1 c_2) J_2 - c_2(d_1 + d_2 - d_1^2 c_1 - d_2^2 c_2) J_1.
\]

We take \( h(x) = 1 \) over the whole interval \([0, 1]\) in our analysis. This is because for ion channels with zero permanent charge, it turns out that the variable \( h(x) \) contributes through an average, explicitly through the factor \( \frac{1}{L^2(I(x)dx)} \) (for example, the individual flux will be \( \frac{dJ_0}{L^2 h^{-1}(x)dx} \), see [39]), which does not affect the qualitative properties of ionic flows.

2.2. Some existing results. We now recall some results from [39] and [10] and summarize them in the following lemma, which are fundamental for our study and will be frequently used.

**Lemma 2.1.** With \( \mathcal{F} = \frac{\phi^R - \phi^L}{\ln c_{10}^R - \ln c_{10}^L} \), one has

\[
J_{10}(V) = (c_0^L - c_0^R)(1 + z_1 \mathcal{F}), \quad J_{20}(V) = \frac{z_1(c_0^L - c_0^R)}{-z_2} (1 + z_2 \mathcal{F}),
\]

\[
J_{11}(V; \lambda) = \alpha_{11}(L_1, L_2, R_1, R_2, \lambda) + \alpha_{11}(L_1, L_2, R_1, R_2, \lambda) \frac{e}{k_B T} V,
\]

\[
J_{21}(V; \lambda) = \beta_{11}(L_1, L_2, R_1, R_2, \lambda) + \beta_{11}(L_1, L_2, R_1, R_2, \lambda) \frac{e}{k_B T} V,
\]
where,

$$\alpha_{10} = \frac{(z_1 - z_2)(\ln c_{10}^F - \ln c_{10}^R) + z_1 \ln \frac{R_2 L_1}{R_1 L_2}}{(z_1 - z_2)(\ln c_{10}^F - \ln c_{10}^R)} \left( c_{10}^F w(L_1, L_2) - c_{10}^R w(R_1, R_2) + (z_1 \lambda - z_2)\frac{[(c_{10}^F)^2 - (c_{10}^R)^2]}{z_2} \right) + \frac{z_1(1 - \lambda)(c_{10}^F - c_{10}^R)(L_1 - R_1 + L_2 - R_2)}{(z_1 - z_2)(\ln c_{10}^F - \ln c_{10}^R)}$$

$$\alpha_{11} = \frac{z_1 c_{10}^F w(L_1, L_2) - z_1 c_{10}^R w(R_1, R_2)}{\ln c_{10}^F - \ln c_{10}^R} + \frac{z_1(1 - \lambda)(c_{10}^F - c_{10}^R)}{z_2(\ln c_{10}^F - \ln c_{10}^R)}$$

$$\beta_{10} = -\frac{z_1(1 - \lambda)(c_{10}^F - c_{10}^R)}{z_2(\ln c_{10}^F - \ln c_{10}^R)} + \frac{z_1 z_2 \ln \frac{R_1 L_2}{R_2 L_1}}{z_1 L_1} \left( c_{10}^F w(L_1, L_2) - c_{10}^R w(R_1, R_2) \right) + \frac{(z_1 \lambda - z_2)\frac{[(c_{10}^F)^2 - (c_{10}^R)^2]}{z_2}}{(z_1 - z_2)(\ln c_{10}^F - \ln c_{10}^R)} \left( c_{10}^F w(L_1, L_2) - c_{10}^R w(R_1, R_2) \right) + \frac{z_1(1 - \lambda)(c_{10}^F - c_{10}^R)}{z_2(\ln c_{10}^F - \ln c_{10}^R)}$$

$$\beta_{11} = -\alpha_{11},$$

where

$$\phi_{10}^V = \tilde{V} - \frac{1}{z_1 - z_2} \ln \frac{-z_2 L_2}{z_1 L_1}, \quad \phi_{10}^F = -\frac{z_2 c_{10}^F}{z_1 - z_2} = (z_1 L_1)^{\frac{-z_2}{z_1 - z_2}} (z_2 L_2)^{\frac{z_1}{z_1 - z_2}},$$

$$w(x, y) = x + \lambda y + \frac{z_1 \lambda - z_2}{z_1 - z_2} (x + y).$$

In particular,

$$I_0(V) = z_1 D_1 J_{10} + z_2 D_2 J_{20} = z_1 (c_{10}^F - c_{10}^R)(D_1 - D_2 + (z_1 D_1 - z_2 D_2)\mathcal{F}),$$

$$I_1(V; \lambda) = z_1 D_1 J_{11} + z_2 D_2 J_{21} = z_1 D_1 \alpha_{10}(L_1, L_2, R_1, R_2, \lambda) + z_2 D_2 \beta_{10}(L_1, L_2, R_1, R_2, \lambda)$$

$$+ (z_1 D_1 - z_2 D_2)\alpha_{11}(L_1, L_2, R_1, R_2, \lambda) \frac{e}{k_B T} V$$

and

$$T_0(V) = D_1 J_{10} + D_2 J_{20} = (c_{10}^F - c_{10}^R) \left( \frac{z_2 D_1 - z_1 D_2}{z_2} + z_1 (D_1 - D_2)\mathcal{F} \right),$$

$$T_1(V; \lambda) = D_1 J_{11} + D_2 J_{21} = D_1 \alpha_{10}(L_1, L_2, R_1, R_2, \lambda) + D_2 \beta_{10}(L_1, L_2, R_1, R_2, \lambda)$$

$$+ (D_1 - D_2)\alpha_{11}(L_1, L_2, R_1, R_2, \lambda) \frac{e}{k_B T} V.$$
3. **Boundary layer effects on ionic flows.** In order to better understand the ionic flow properties of interest, we consider a more general and more realistic (compare with the study in [39]) case with

\[-z_2L_2 = \sigma(z_1L_1), \quad -z_2R_2 = \rho(z_1R_1)\]

for some positive constant \(\sigma\) and \(\rho\), which are close to but not equal to 1 simultaneously since \((\sigma, \rho) = (1, 1)\) implies electroneutrality conditions on boundary concentrations. Notice that assumption (1) implies that \(c_{f0} = \sigma^{\frac{1}{1-k}}L_1\) and \(c_{r0} = \rho^{\frac{1}{1-k}}R_1\).

Based on the approximations of the individual fluxes, the I-V relations and the flow rate of matter in Lemma 2.1, we identify eight critical potentials and discuss their roles played in characterizing boundary layer effects on ionic flows with nonuniform ion sizes.

**Definition 3.1.** We define the critical potentials \(V_{Ik}, V^{1c}, V^{2c}, V_c, V^c, V_c, \bar{V}_c\) and \(\bar{V}^c\) by

\[
J_{11}(V_{1c}; \lambda) = 0, \quad \frac{\partial J_{11}}{\partial \lambda}(V_{1c}; \lambda) = 0, \quad J_{21}(V_{2c}; \lambda) = 0, \quad \frac{\partial J_{21}}{\partial \lambda}(V_{2c}; \lambda) = 0,
\]

\[
I_1(V_c; \lambda) = 0, \quad \frac{\partial I_1}{\partial \lambda}(V_c; \lambda) = 0, \quad T_1(\bar{V}_c; \lambda) = 0, \quad \frac{\partial T_1}{\partial \lambda}(\bar{V}_c; \lambda) = 0.
\]

To examine the boundary layer effects on ionic flows, we expand \(\alpha_{11}(\sigma, \rho)\), for fixed boundary concentrations \(L_k\) and \(R_k\), at \((\sigma, \rho) = (1, 1)\) up to the first order (neglecting higher order terms) and get

\[
\alpha_{11}(\sigma, \rho) = \alpha_{11}(1, 1) + \frac{\partial \alpha_{11}}{\partial \sigma}(1, 1)(\sigma - 1) + \frac{\partial \alpha_{11}}{\partial \rho}(1, 1)(\rho - 1),
\]

where

\[
\alpha_{11}(1, 1) = a_4f_0(L_1, R_1)f_1(L_1, R_1),
\]

\[
\frac{\partial \alpha_{11}}{\partial \sigma}(1, 1) = \frac{a_1f_0(L_1, R_1)f_2(L_1, R_1) - a_2L_1(f_0(L_1, R_1) - a_3L_1)}{\ln L_1 - \ln R_1},
\]

\[
\frac{\partial \alpha_{11}}{\partial \rho}(1, 1) = \frac{a_2R_1(f_0(L_1, R_1) - a_3R_1) - a_1f_0(L_1, R_1)f_2(L_1, R_1)}{\ln L_1 - \ln R_1},
\]

with

\[
a_1 = \frac{4z_1^2(z_2 - z_1\lambda)}{z_2(z_1 - z_2)}, \quad a_2 = \frac{z_2^2[2z(3 + \lambda) - 4z_1\lambda]}{z_2(z_1 - z_2)}, \quad a_3 = \frac{z_2(1 + \lambda) - 2z_1\lambda}{z_2(3 + \lambda) - 4z_1\lambda},
\]

\[
a_4 = \frac{2z_1(z_1\lambda - z_2)}{z_2}, \quad f_0(L_1, R_1) = \frac{L_1 - R_1}{\ln L_1 - \ln R_1},
\]

\[
f_1(L_1, R_1) = f_0(L_1, R_1) - \frac{L_1 + R_1}{2}, \quad f_2(L_1, R_1) = f_0(L_1, R_1) - \frac{L_1 + R_1}{4}.
\]

3.1. **Boundary layer effects on individual fluxes with nonuniform ion sizes.** Notice that, for fixed boundary concentrations, \(J_{k1}\) is linear in boundary potential, and hence, the sign of \(\partial VJ_{k1}\), \(k = 1, 2\) plays a critical role in characterizing finite ion size effects on individual fluxes.

From Lemma 2.1, one has

\[
\partial VJ_{11} = -\partial VJ_{21}.
\]
Therefore, we will mainly focus on the study of the sign for $\partial V J_{11}$. From Lemma 2.1, with $x = L_1/R_1 > 1$, one has

$$\frac{\partial J_{11}}{\partial V}(x; \sigma, \rho) = \frac{e}{k_B T} \frac{R_1^2}{4(\ln x)^3} F(x; \sigma, \rho),$$

where

$$F(x; \sigma, \rho) = 4a_4(x - 1)^2 \ln x - 2a_4(x^2 - 1)(\ln x)^2 + \left( 4a_1(x - 1)^2 - a_1(x^2 - 1) \ln x 
- 4a_2(x - 1) \ln x + 4a_2a_3x^2(\ln x)^2 \right)(\sigma - 1) + \left( - 4a_1(x - 1)^2 
+ a_1(x^2 - 1) \ln x + 4a_2(x - 1) \ln x - 4a_2a_3(\ln x)^2 \right)(\rho - 1).$$

For $F(x; \sigma, \rho)$ with fixed $(\sigma, \rho)$, we have the following result, which is crucial to analyze finite ion size effects on individual fluxes.

**Lemma 3.2.** Assume $x = L_1/R_1 > 1$. Then,

(i) For $0 < \lambda < \frac{3z^2}{11z^2 - 8z_i}$ and $(\sigma, \rho) \to (1^+, 1^+)$, one has $F(x; \sigma, \rho) < 0$ (resp. $F(x; \sigma, \rho) > 0$) for $1 < x < x_1^*$ (resp. $x > x_1^*$), where $x_1^*$ is the unique root of $F(x; \sigma, \rho)$ with $x > 1$;

(ii) For $\lambda > 1$ and $(\sigma, \rho) \to (1^+, 1^-)$ with $\sigma + \rho < 2$, one has $F(x; \sigma, \rho) < 0$ (resp. $F(x; \sigma, \rho) > 0$) for $1 < x < x_2^*$ (resp. $x > x_2^*$), where $x_2^*$ is the unique root of $F(x; \sigma, \rho)$ with $x > 1$.

**Proof.** We will provide a detailed proof for the first statement. The second one can be argued similarly. Direct calculation gives $F(1; \sigma, \rho) = F'(1; \sigma, \rho) = F''(1, \sigma, \rho) = 0$, where

$$F'(x; \sigma, \rho) = 8a_4(x - 1) \ln x + 4a_4(x - 1)^2 \frac{1}{x} - 4a_4x(\ln x)^2 - 4a_4 \left( x - \frac{1}{x} \right) \ln x 
+ \left( 8a_1(x - 1) - 2a_1 \ln x - a_1 \left( x - \frac{1}{x} \right) - 4a_2(x - 1) \ln x - 4a_2x \ln x - 4a_2(x - 1) 
+ 8a_2a_3x(\ln x)^2 + 8a_2a_3x \ln x \right)(\sigma - 1) + \left( - 8a_1(x - 1) + 2a_1 \ln x + a_1 \left( x - \frac{1}{x} \right) 
+ 4a_2 \ln x + 4a_2 \left( 1 - \frac{1}{x} \right) - 8a_2a_3 \ln x \right)(\rho - 1),$$

$$F''(x; \sigma, \rho) = 16a_4(x - 1) \frac{1}{x} - 4a_4(x - 1)^2 \frac{2}{x^2} - 4a_4(\ln x)^2 - 4a_4 \left( 1 + \frac{1}{x^2} \right) \ln x 
- 4a_4 \left( 1 - \frac{1}{x^2} \right) + \left( 6a_1 - 2a_1 \ln x - a_1 \left( 1 + \frac{1}{x^2} \right) - 4a_2 \ln x - 4a_2 \left( 1 - \frac{1}{x} \right) 
- 4a_2 \ln x - 8a_2a_3(\ln x)^2 + 24a_2a_3 \ln x + 8a_2a_3 \right)(\sigma - 1) 
+ \left( - 6a_1 + 2a_1 \ln x + a_1 \left( 1 + \frac{1}{x^2} \right) + 4a_2 \frac{2}{x} + \frac{4a_2}{x^2} - \frac{8a_2a_3(1 - \ln x)}{x^2} \right)(\rho - 1),$$
and \( F'''(x; \sigma, \rho) = \frac{G(x; \sigma, \rho)}{x^3} \), where

\[
G(x; \sigma, \rho) = 4a_4(2 \ln x - 2x^2 \ln x - (x - 1)^2) \\
+ \left(-2a_1x^2 + 2a_1 - 8a_2x^2 - 4a_2x + 16a_2a_3x^2 \ln x + 24a_2a_3x^2 \right)(\sigma - 1) \\
+ \left(2a_1x^2 - 2a_1 - 4a_2x - 8a_2 + 8a_2a_3 + 16a_2a_3(1 - \ln x) \right)(\rho - 1).
\]

It follows that

\[
G'(x; \sigma, \rho) = 4a_4\left(\frac{2}{x} - 4x \ln x - 2x - 2(x - 1) \right) + \left(4a_1x - 4a_2 - \frac{16a_2a_3}{x} \right)(\rho - 1) \\
+ \left(-4a_1x - 16a_2 - 4a_3 + 32a_2a_3x \ln x + 64a_2a_3x \right)(\sigma - 1),
\]

\[
G''(x; \sigma, \rho) = 4a_4\left(-\frac{2}{x^2} - 4 \ln x - 8 \right) + \left(4a_1 + \frac{16a_2a_3}{x^2} \right)(\rho - 1) \\
+ \left(-4a_1 - 16a_2 + 32a_2a_3 \ln x + 96a_2a_3 \right)(\sigma - 1).
\]

We now consider the sign of \( G''(x; \sigma, \rho) \) for \( x > 1 \). Note that \( a_4 < 0 \), one has

\[-32a_4 - 16a_4 \ln x - \frac{32a_4}{x^2} > 0 \text{ for } x > 1.\]

It follows from \( a_1 > 0, a_2 > 0, a_3 > 0 \) and

\[-4a_1 - 16a_2 + 96a_2a_3 = 16 \frac{2z_2z_1(\lambda + 5z_2^2z_2\lambda)}{z_2(z_1z_2)} > 0\]

that \( G''(x; \sigma, \rho) > 0 \) under the condition \( \sigma > 1 \) and \( \rho > 1 \), which implies that \( G'(x; \sigma, \rho) \) is increasing for \( x > 1 \).

Notice that

\[
G'(1; \sigma, \rho) = 4(-a_1 - 5a_2 + 16a_2a_3)(\sigma - 1) + 4(a_1 - a_2 - 4a_2a_3)(\rho - 1) < 0,
\]

since with \( 0 < \lambda < \frac{3z_2}{11z_2 - 8z_1} \), one has

\[-a_1 - 5a_2 + 16a_2a_3 = \frac{z_2^2(-3z_2 - 8z_1\lambda + 11z_2\lambda)}{z_2(z_1z_2)} < 0, \]

\[a_1 - a_2 - 4a_2a_3 = \frac{-5z_2^2z_2\lambda + 8z_2^3\lambda}{z_2(z_1z_2)} < 0.\]

Note also that \( \lim_{x \to \infty} G'(x; \sigma, \rho) = +\infty \). Thus, there exists a unique zero, say \( x_1 > 1 \), of \( G'(x; \sigma, \rho) = 0 \) such that \( G'(x; \sigma, \rho) > 0 \) if \( x > x_1 \), and \( G'(x; \sigma, \rho) < 0 \) if \( 1 < x < x_1 \). This also indicates that \( G(x; \sigma, \rho) \) is increasing if \( x > x_1 \), and \( G(x; \sigma, \rho) \) is decreasing if \( 1 < x < x_1 \).

Note that \( G(1; \sigma, \rho) = 12a_2(2a_3 - 1)(\sigma - \rho - 2) \), where \( 2a_3 - 1 = \frac{z_2(\lambda - 1)}{z_2(3\lambda - z_2) - 4z_2\lambda^2} \).

It is easy to see that \( 2a_3 - 1 < 0 \) if \( \lambda < 1 \). Together with \( a_2 > 0, \sigma \to 1^+ \) and \( \rho \to 1^+ \), one has \( G(1; \sigma, \rho) < 0 \) if \( \lambda < 1 \). Together with \( \lim_{x \to \infty} G(x; \sigma, \rho) = +\infty \), one has \( G(x; \sigma, \rho) < 0 \) (resp. \( G(x; \sigma, \rho) > 0 \)) as \( 1 < x < x_2 \) (resp. \( x > x_2 \)), where \( x_2 \) is the unique root of \( G(x; \sigma, \rho) = 0 \) for \( x > 1 \).

Recall that \( F''''(x; \sigma, \rho) = G(x; \sigma, \rho)/x^3 \). Hence, \( F''''(x; \sigma, \rho) \) have the same sign as that of \( G(x; \sigma, \rho) \) for \( x > 1 \). That is, \( F''''(x; \sigma, \rho) < 0 \) (resp. \( F''''(x; \sigma, \rho) > 0 \)) as \( 1 < x < x_2 \) (resp. \( x > x_2 \)). This implies that \( F''''(x; \sigma, \rho) \) is decreasing for \( 1 < x < x_2 \) and is increasing for \( x > x_2 \). Since we have already got \( F''''(1; \sigma, \rho) = 0 \) and \( \lim_{x \to \infty} F''''(x; \sigma, \rho) = +\infty \), we have \( F''''(x; \sigma, \rho) < 0 \) (resp. \( F''''(x; \sigma, \rho) > 0 \)) for \( 1 < x < x_3 \) (resp. \( x > x_3 \)), where \( x_3 > x_2 \) is the unique root of \( F''''(x) = 0 \). Similar argument gives \( F''''(x; \sigma, \rho) > 0 \) (resp. \( F''''(x; \sigma, \rho) > 0 \)) if \( 1 < x < x_4 \) (resp. \( x > x_4 \)), where \( x_4 > x_3 \) is the unique root of \( F''''(x; \sigma, \rho) = 0 \). It follows that \( F(x; \sigma, \rho) \) is decreasing for \( 1 < x < x_4 \) and increasing for \( x > x_4 \). Since \( F(1) = 0 \).
and \( \lim_{x \to +\infty} F(x; \sigma, \rho) = +\infty \), there exists a unique root \( x_1^* > x_4 \) of \( F(x; \sigma, \rho) = 0 \) such that \( F(x; \sigma, \rho) < 0 \) (resp. \( F(x; \sigma, \rho) > 0 \)) as \( 1 < x < x_1^* \) (resp. \( x > x_1^* \)). \( \square \)

It then follows

**Theorem 3.3.** Assume \( x = L_1/R_1 > 1, \epsilon > 0 \) small and \( d > 0 \) small.

(i) For \( 0 < \lambda < \frac{3d^2}{11z_2^2 R_1^2} \) and \( (\sigma, \rho) \to (1^+, 1^+) \), one has

\[ \frac{\partial J_{11}}{\partial \lambda} < 0 \text{ and } \frac{\partial J_{11}}{\partial \rho} > 0. \]

Furthermore,

(i) For \( 1 < x < x_1^* \), one has \( \frac{\partial J_{11}}{\partial \rho} < 0 \) while \( \frac{\partial J_{11}}{\partial \lambda} > 0 \). Furthermore,

(ii) The ion size enhances (resp. reduces) the individual flux \( J_{11} \) if \( V < V_{1c} \) (resp. \( V > V_{1c} \)), that is, \( J_{11}(V; \sigma, \rho; \lambda, d) > J_{11}(V; \sigma, \rho; 0, 0) \) (resp. \( J_{11}(V; \sigma, \rho; \lambda, d) < J_{11}(V; \sigma, \rho; 0, 0) \) if \( V < V_{1c} \) (resp. \( V > V_{1c} \));

(ii) The ion size enhances (resp. reduces) the individual flux \( J_{21} \) if \( V < V_{2c} \) (resp. \( V > V_{2c} \)), that is, \( J_{21}(V; \sigma, \rho; \lambda, d) < J_{21}(V; \sigma, \rho; 0, 0) \) (resp. \( J_{21}(V; \sigma, \rho; \lambda, d) > J_{21}(V; \sigma, \rho; 0, 0) \) if \( V < V_{2c} \) (resp. \( V > V_{2c} \)).

(ii) For \( x > x_2^* \), one has \( \frac{\partial J_{11}}{\partial \rho} > 0 \) while \( \frac{\partial J_{11}}{\partial \lambda} < 0 \). Furthermore,

(iii) The ion size enhances (resp. reduces) the individual flux \( J_{11} \) if \( V < V_{1c} \) (resp. \( V > V_{1c} \)), that is, \( J_{11}(V; \sigma, \rho; \lambda, d) > J_{11}(V; \sigma, \rho; 0, 0) \) (resp. \( J_{11}(V; \sigma, \rho; \lambda, d) < J_{11}(V; \sigma, \rho; 0, 0) \) if \( V < V_{1c} \) (resp. \( V > V_{1c} \));

(iii) The ion size enhances (resp. reduces) the individual flux \( J_{21} \) if \( V < V_{2c} \) (resp. \( V > V_{2c} \)), that is, \( J_{21}(V; \sigma, \rho; \lambda, d) < J_{21}(V; \sigma, \rho; 0, 0) \) (resp. \( J_{21}(V; \sigma, \rho; \lambda, d) > J_{21}(V; \sigma, \rho; 0, 0) \) if \( V < V_{2c} \) (resp. \( V > V_{2c} \)).

We now turn to the relative ion size effects on individual fluxes in terms of \( \lambda = d_2/d_1 \), where \( d_1 \) is the diameter of the cation while \( d_2 \) is the diameter of the anion. More precisely, we consider the quantity \( \frac{\partial^2 J_{11}}{\partial \lambda \partial \rho} \), which depends on other system parameters, such as boundary concentrations \((L_1, R_1)\), ion valences \((z_1, z_2)\) and \( \lambda \).

Direct calculation gives, with \( x = L_1/R_1 \),

\[
\frac{\partial^2 J_{11}}{\partial \lambda \partial \rho} = \frac{e}{k_B T} \frac{R_1^2}{(\ln x)^3} f(x),
\]
where
\[ f(x) = 2b_4(x - 1)^2 \ln x - b_4(x^2 - 1)(\ln x)^2 \]
\[ + [4b_1(x - 1)^2 - b_1(x^2 - 1) \ln x - b_2(x - 1) \ln x + b_3x^2(\ln x)^2](\sigma - 1) \]
\[ + [-4b_1(x - 1)^2 + b_1(x^2 - 1) \ln x + b_2(x - 1) \ln x - b_3(\ln x)^2](\rho - 1) \]
with
\[ b_1 = \frac{z_1^2}{z_2(z_2 - z_1)} > 0, \quad b_2 = \frac{z_1^2(z_2 - 4z_1)}{z_2(z_1 - z_2)} > 0, \]
\[ b_3 = \frac{z_1^2(3z_2^2 + z_2^2\lambda - 6z_1z_2\lambda - 6z_1z_2 + 8z_1^2\lambda)}{z_2(z_1 - z_2)[z_2(3 + \lambda) - 4z_1\lambda]} > 0, \quad b_4 = \frac{z_1^2}{z_2^2} < 0. \]

**Lemma 3.4.** Assume \((\sigma, \rho) \to (1^+, 1^-)\) with \(\sigma + \rho < 2\) and \(x = L_1/R_1 > 1\). One has \(f(x) < 0\) (resp. \(f(x) > 0\)) as \(1 < x < x_*\) (resp. \(x > x_*\)), where \(x_*\) is the unique root of \(f(x)\) with \(x > 1\).

**Proof.** The argument is similar as the one in Lemma 3.2, and we omit it here. \(\square\)

It follows that

**Theorem 3.5.** Assume \((\sigma, \rho) \to (1^+, 1^-)\) with \(\sigma + \rho < 2\) and \(x = L_1/R_1 > 1\). Assume also that \(0 > \epsilon > 0\) small and \(d > 0\) small.

(i) For \(1 < x < x_*\), one has \(\frac{\partial^2 J_1}{\partial \lambda^2} < 0\) while \(\frac{\partial^2 J_2}{\partial \lambda^2} > 0\). Furthermore,

(i1) The individual flux \(J_1\) is increasing (resp. decreasing) in \(\lambda\) if \(V < V^{1c}\) (resp. \(V > V^{1c}\)).

(ii) The individual flux \(J_2\) is decreasing (resp. increasing) in \(\lambda\) if \(V < V^{2c}\) (resp. \(V > V^{2c}\)).

(ii) For \(x > x_*\), one has \(\frac{\partial^2 J_1}{\partial \lambda^2} > 0\) while \(\frac{\partial^2 J_2}{\partial \lambda^2} < 0\). Furthermore,

(iii) The individual flux \(J_1\) is increasing (resp. decreasing) in \(\lambda\) if \(V > V^{1c}\) (resp. \(V < V^{1c}\)).

(iii) The individual flux \(J_2\) is decreasing (resp. increasing) in \(\lambda\) if \(V > V^{2c}\) (resp. \(V < V^{2c}\)).

3.2. Boundary layer effects on the I-V relations with nonuniform ion sizes. From (11) and Lemmas 3.2 and 3.4, we have the following results, which characterize the boundary layer effects on I-V relations with ion sizes.

**Theorem 3.6.** Assume \(x = L_1/R_1 > 1, \epsilon > 0\) small and \(d > 0\) small.

(i) For \(0 < \lambda < \frac{3z_2}{11z_2 - 8z_1}\) and \((\sigma, \rho) \to (1^+, 1^+),\) one has

(i1) For \(1 < x < x_1^*, \frac{\partial I}{\partial \lambda} < 0\). Furthermore, the ion size enhances (resp. reduces) the current \(I\) if \(V < V_c\) (resp. \(V > V_c\)), that is, \(I(V; \sigma, \rho; \lambda, d) > I(V; \sigma, \rho; 0, 0)\) (resp. \(I(V; \sigma, \rho; 0, 0) > I(V; \sigma, \rho; \lambda, d)\)) if \(V < V_c\) (resp. \(V > V_c\)).

(ii) For \(x > x_1^*, \frac{\partial I}{\partial \lambda} > 0\). Furthermore, the ion size enhances (resp. reduces) the current \(I\) if \(V > V_c\) (resp. \(V < V_c\)), that is, \(I(V; \sigma, \rho; 0, 0) > I(V; \sigma, \rho; \lambda, d)\) (resp. \(I(V; \sigma, \rho; \lambda, d) < I(V; \sigma, \rho; 0, 0)\)) if \(V > V_c\) (resp. \(V < V_c\)).

(ii) For \(\lambda > 1\) and \((\sigma, \rho) \to (1^+, 1^-)\) with \(\sigma + \rho < 2\), one has

(iii) For \(1 < x < x_2^*, \frac{\partial I}{\partial \sigma} < 0\). Furthermore, the ion size enhances (resp. reduces) the current \(I\) if \(V < V_c\) (resp. \(V > V_c\)), that is, \(I(V; \sigma, \rho; \lambda, d) > I(V; \sigma, \rho; 0, 0)\) (resp. \(I(V; \sigma, \rho; 0, 0) < I(V; \sigma, \rho; \lambda, d)\)) if \(V < V_c\) (resp. \(V > V_c\)).
in terms of the critical potentials identified in Definition 3.1 with boundary layers. The ionic flow properties of interest observed due to the existence of boundary layers under-define the effects on ionic flows from boundary layers, we take a further look at these phenomena.

Assume \( \sigma, \rho \rightarrow (1^+, 1^-) \) with \( \sigma + \rho < 2 \) and \( x = L_1/R_1 > 1 \). For \( \epsilon > 0 \) small and \( d > 0 \) small, one has

(i) For \( 1 < x < x_1^* \), \( \partial I/\partial \lambda < 0 \). Furthermore, the current \( I \) is increasing (resp. decreasing) in \( \lambda \) if \( V > V_c \) (resp. \( V < V_c \)).

(ii) For \( x > x_1^* \), \( \partial^2 I/\partial V \partial \lambda > 0 \). Furthermore, the current \( I \) is increasing (resp. decreasing) in \( \lambda \) if \( V > V_c \) (resp. \( V < V_c \)).

3.3. Boundary layer effects on the flow rate of matter with nonuniform ion sizes. From (12) and Lemmas 3.2 and 3.4, we have the following results, which characterize the boundary layer effects on the flow rate of matter with ion sizes.

**Theorem 3.8.** Assume \( x = L_1/R_1 > 1 \) and \( D_1 < D_2 \). For \( \epsilon > 0 \) small and \( d > 0 \) small, one has

(i) If \( 0 < \lambda < 3 \sigma - 3 \rho \) and \( \sigma, \rho \rightarrow (1^+, 1^-) \), then

\( i_1 \): For \( 1 < x < x_1^* \), \( \partial I/\partial \lambda > 0 \). Furthermore, the ion size enhances (resp. reduces) the flow rate of matter \( \mathcal{T} \) if \( V > V_c \) (resp. \( V < V_c \)), that is, \( \mathcal{T}(V; \sigma, \rho; \lambda, d) > \mathcal{T}(V; \sigma, \rho; 0, 0) \) (resp. \( \mathcal{T}(V; \sigma, \rho; \lambda, d) < \mathcal{T}(V; \sigma, \rho; 0, 0) \)) if \( V > V_c \) (resp. \( V < V_c \)).

(ii) For \( x > x_1^* \), \( \partial I/\partial \lambda < 0 \). Furthermore, the ion size enhances (resp. reduces) the flow rate of matter \( \mathcal{T} \) if \( V < V_c \) (resp. \( V > V_c \)), that is, \( \mathcal{T}(V; \sigma, \rho; \lambda, d) > \mathcal{T}(V; \sigma, \rho; 0, 0) \) (resp. \( \mathcal{T}(V; \sigma, \rho; \lambda, d) < \mathcal{T}(V; \sigma, \rho; 0, 0) \)) if \( V < V_c \) (resp. \( V > V_c \)).

(ii1) For \( 1 < x < x_2^* \), \( \partial I/\partial \lambda > 0 \). Furthermore, the ion size enhances (resp. reduces) the flow rate of matter \( \mathcal{I} \) if \( V > V_c \) (resp. \( V < V_c \)), that is, \( \mathcal{I}(V; \sigma, \rho; \lambda, d) > \mathcal{I}(V; \sigma, \rho; 0, 0) \) (resp. \( \mathcal{I}(V; \sigma, \rho; \lambda, d) < \mathcal{I}(V; \sigma, \rho; 0, 0) \)) if \( V > V_c \) (resp. \( V < V_c \)).

(ii2) For \( x > x_2^* \), \( \partial I/\partial \lambda < 0 \). Furthermore, the ion size enhances (resp. reduces) the flow rate of matter \( \mathcal{I} \) if \( V < V_c \) (resp. \( V > V_c \)), that is, \( \mathcal{I}(V; \sigma, \rho; \lambda, d) > \mathcal{I}(V; \sigma, \rho; 0, 0) \) (resp. \( \mathcal{I}(V; \sigma, \rho; \lambda, d) < \mathcal{I}(V; \sigma, \rho; 0, 0) \)) if \( V < V_c \) (resp. \( V > V_c \)).

**Theorem 3.9.** Assume \( \sigma, \rho \rightarrow (1^+, 1^-) \) with \( \sigma + \rho < 2 \), \( D_1 < D_2 \) and \( x = L_1/R_1 > 1 \). For \( \epsilon > 0 \) small and \( d > 0 \) small, one has

(i) For \( 1 < x < x_1^* \), \( \partial^2 I/\partial \lambda^2 > 0 \). Furthermore, the flow rate of matter \( \mathcal{T} \) is increasing (resp. decreasing) in \( \lambda \) if \( V > V_c \) (resp. \( V < V_c \)).

(ii) For \( x > x_1^* \), \( \partial^2 I/\partial \lambda^2 < 0 \). Furthermore, the flow rate of matter \( \mathcal{I} \) is increasing (resp. decreasing) in \( \lambda \) if \( V < V_c \) (resp. \( V > V_c \)).

**Remark 3.10.** Similar arguments can be applied to the case with \( D_1 > D_2 \).

3.4. Further comparison: electroneutrality vs boundary layers. To better understand the effects on ionic flows from boundary layers, we take a further look at the ionic flow properties of interest observed due to the existence of boundary layers in terms of the critical potentials identified in Definition 3.1 with boundary layers...
and the ones identified in \[10, 39\] under electroneutrality boundary concentration conditions.

For convenience, in our following discussion, we use \(V_{ic}^{EN}\) to denote the critical potential identified in \[10\] and \(\mathcal{J}_i^{EN}\) to denote the individual flux under electroneutrality boundary conditions. Together with \(\frac{\partial J_1^{EN}}{\partial V} > 0\), the leading term containing finite ion size effects, under the electroneutrality boundary conditions \((10)\), the following result can be established.

**Proposition 3.11.** Assume \(L_1 > R_1\), \((\sigma, \rho) \rightarrow (1, 1)\) and \(V_{ic}^{EN} < V_{ic}\). For small \(\varepsilon > 0\) and small \(d > 0\), one has

(i) If \(\frac{\partial J_1}{\partial V}(V; \sigma, \rho) < 0\), then,

(i1) for \(V < V_{ic}^{EN}\), the ion size reduces the individual flux \(\mathcal{J}_1^{EN}(V)\), the one under electroneutrality boundary conditions, while enhances the individual flux \(\mathcal{J}_i(V)\), the one with boundary layers, equivalently, \(\mathcal{J}_i^{EN}(V; d) < \mathcal{J}_i^{EN}(V; 0)\), while \(\mathcal{J}_1(V; \sigma, \rho; d) > \mathcal{J}_1(V; \sigma, \rho; 0)\);

(ii) for \(V_{ic}^{EN} < V < V_{ic}\), the ion size enhances both \(\mathcal{J}_1^{EN}(V)\) and \(\mathcal{J}_i(V)\), equivalently, \(\mathcal{J}_i^{EN}(V; d) > \mathcal{J}_i^{EN}(V; 0)\) and \(\mathcal{J}_1(V; \sigma, \rho; d) > \mathcal{J}_1(V; \sigma, \rho; 0)\);

(iii) for \(V > V_{ic}\), the ion size enhances the individual flux \(\mathcal{J}_i^{EN}(V)\) while reduces the individual flux \(\mathcal{J}_1(V)\), equivalently, \(\mathcal{J}_i^{EN}(V; d) > \mathcal{J}_i^{EN}(V; 0)\), while \(\mathcal{J}_1(V; \sigma, \rho; d) < \mathcal{J}_1(V; \sigma, \rho; 0)\).

(ii) If \(\frac{\partial J_1}{\partial V}(V; \sigma, \rho) > 0\), then,

(iii) for \(V < V_{ic}^{EN}\), the ion size reduces both \(\mathcal{J}_1^{EN}(V)\) and \(\mathcal{J}_i(V)\), equivalently, \(\mathcal{J}_i^{EN}(V; d) < \mathcal{J}_i^{EN}(V; 0)\) and \(\mathcal{J}_1(V; \sigma, \rho; d) < \mathcal{J}_1(V; \sigma, \rho; 0)\);

(ii2) for \(V_{ic}^{EN} < V < V_{ic}\), the ion size enhances the individual flux \(\mathcal{J}_i^{EN}(V)\) while reduces the individual flux \(\mathcal{J}_1(V)\), equivalently, \(\mathcal{J}_i^{EN}(V; d) > \mathcal{J}_i^{EN}(V; 0)\), while \(\mathcal{J}_1(V; \sigma, \rho; d) < \mathcal{J}_1(V; \sigma, \rho; 0)\);

(iii) for \(V > V_{ic}\), the ion size enhances both \(\mathcal{J}_1^{EN}(V)\) and \(\mathcal{J}_i(V)\), equivalently, \(\mathcal{J}_i^{EN}(V; d) > \mathcal{J}_i^{EN}(V; 0)\) and \(\mathcal{J}_1(V; \sigma, \rho; d) > \mathcal{J}_1(V; \sigma, \rho; 0)\).

**Remark 3.12.** Similar arguments can be applied to the case with \(V_{ic}^{EN} > V_{ic}\), the individual flux \(\mathcal{J}_2\), the I-V relation \(\mathcal{I}\), and the flow rate of matter \(\mathcal{T}\) in terms of the corresponding identified critical potentials. We would like to further point out that due to the existence of boundary layers, the qualitative properties of ionic flows are significantly different from those observed under electroneutrality boundary conditions over some specific potential subregions. Take the discussion in the statement (i1) and (i3) in the Proposition 3.11 for example. In the statement (i1), under the electroneutrality boundary conditions, the finite ion size reduces the individual flux \(J_1^{EN}(V)\) for \(V < V_{ic}^{EN}\), but enhances the individual flux \(J_1(V)\) with boundary layers, more precisely, a state that is very close to the neutral condition; while in the statement (i3), opposite situation occurs for \(V > V_{ic}\). The qualitative properties for these two set-ups over specific potential subregions are quite different, and this observations should be carefully considered in the future study of ion channel problems.

To provide more intuitive illustration of the effects on ionic flows from boundary layers, we perform the following numerical simulations to the PNP system with dimensions. To be specific, we consider the cation to be Na\(^+\) and the anion to be Cl\(^-\), and \(\lambda\) is the ratio of the volume of Na\(^+\) to Cl\(^-\). Then, we may take \((42)\)

\[
D_{Na} = 1.334 \times 10^{-9} \text{m}^2/\text{s}, \quad D_{Cl} = 2.032 \times 10^{-9} \text{m}^2/\text{s}, \quad k_B = 1.381 \times 10^{-23} \text{JK}^{-1}, \\
T = 273.16 \text{K}, \quad e = 1.602 \times 10^{-19} \text{C}, \quad z_1 = -z_2 = 1 \text{ and } \lambda = 1.885.
\]
(i) Identify $x^*$, the root of $F(x) = 0$ introduced in Lemma 3.2, which further helps understand the result, particularly, the proof (see Figure 1);
(ii) Identify the critical potentials $V_{kc}^{EN}$ and $V_c$ defined in Definition 3.1, and observe the monotonicity of $J_{k1}^{EN}$ and $J_{k1}$, respectively, viewed as functions of the potential $V$ (see Figures 2 and 3);
(iii) Identify the critical potentials $V_c^{EN}$ and $V_c$ defined in Definition 3.1, and observe the monotonicity of $I_{k1}^{EN}$ and $I_{k1}$, respectively, viewed as functions of the potential $V$ (see Figure 4).
(vi) Identify the critical potentials $\bar{V}_{c}^{EN}$ and $\bar{V}_c$ defined in Definition 3.1, and observe the monotonicity of $T_{1}^{EN}$ and $T_{1}$, respectively, viewed as functions of the potential $V$ (see Figure 5).

To end this section, we demonstrate that the numerical results shown in Figures 2-5 further illustrate the boundary layer effects on ionic flows with nonuniform ion size (numerically explain the results stated in Theorems 3.3, 3.6 and 3.8 with $\lambda > 1$). To be specific, we take Figure 2 for example, which shows the graphs of $J_{11}(V)$ under

\begin{align*}
\text{Figure 1. Graph of function } F(x) \text{ as } (\sigma, \rho) \to (1^+, 1^-) \text{ with } \sigma + \rho < 2 \text{ helps understand the result stated in Lemma 3.2. To be specific, the graph corresponds to the statement (ii) of the lemma with } \lambda > 1.
\end{align*}

\begin{align*}
\text{Figure 2. Function } J_{11}(V) \text{ (solid line) for } x > x_2^* \text{ (left figure) and } 1 < x < x_2^* \text{ (right figure) with } \sigma = 1.001 \text{ and } \rho = 0.998, \text{ where } x_2^* = 1.01978; \\
\text{and function } J_{11}^{EN}(V) \text{ (dashed line with star) with } \sigma = \rho = 1. \text{ In the left figure, the slope of } J_{11} \text{ is } 0.291 \text{ while the one of } J_{11}^{EN} \text{ is } 0.29.
\end{align*}
different set-ups. For the left figure in Figure 2 corresponding to the case with $x > x_2^*$, which shows both $\partial V J_{11}$ and $\partial V J_{11}^{EN}$ are positive but with different slopes ($\partial V J_{11} = 0.291$ while $\partial V J_{11}^{EN} = 0.29$), and for this case, the qualitative properties of ionic flows are similar; however, for the right one in Figure 2 corresponding to the case with $1 < x < x_2^*$, which shows $\partial V J_{11} < 0$ while $\partial V J_{11}^{EN} > 0$, and this indicates quite different qualitative properties of ionic flows. In particular, the negativeness of $\partial V J_{11}$ cannot be observed under the condition of electroneutrality. This should be carefully considered in the future study of ion channel problems. The critical potentials identified in Definition 3.1 and further detected numerically in Figures 2-5 are critical in our discussion and their significance is apparent from the definition. Furthermore, they can be estimated experimentally. Take the critical potential $V_c$ for example, one can take an experimental I-V relation as $I(V; \lambda, d; \sigma, \rho)$ and numerically (or analytically) compute $I_0(V; \sigma, \rho)$ for ideal case that allows one to get an estimate of $V_c$. 

Figure 3. Function $J_{21}(V)$ (solid line) for $x > x_2^*$ (left figure) and $1 < x < x_2^*$ (right figure) with $\sigma = 1.001$ and $\rho = 0.998$, where $x_2^* = 1.01978$; and function $J_{21}^{EN}(V)$ (dashed line with star) with $\sigma = \rho = 1$. In the left figure, the slope of $J_{21}$ is $-0.291$ while the one of $J_{21}^{EN}$ is $-0.29$.

Figure 4. Function $I_1(V)$ (solid line) for $x > x_2^*$ (left figure) and $1 < x < x_2^*$ (right figure) with $\sigma = 1.001$ and $\rho = 0.998$, where $x_2^* = 1.01978$; and function $I_1^{EN}(V)$ (dashed line with star) with $\sigma = \rho = 1$. In the left figure, the slope of $I_1$ is $9.7945 \times 10^{-10}$ while the one of $I_1^{EN}$ is $9.7617 \times 10^{-10}$. 
4. Concluding remarks. We study the one-dimensional PNP system with nonuniform ion sizes, of particular interest is to examine the boundary layer effects on ionic flows systematically and to provide better understandings of the mechanism of ionic flows through membrane channels. This is particularly important because boundary layers of charge are particularly likely to create artifacts over long distances and this could dramatically affects the behavior of ionic flows. In terms of the individual fluxes, the I-V relations and the total flow rate of matter, the boundary layer effects are carefully analyzed. On one hand, similar results to those from [10, 39] under electroneutrality conditions are obtained (see each left figure in Figures 2-5 for an intuitive comparison, and corresponding analytical results stated in Theorems 3.3, 3.6 and 3.8), on the other hand, much more rich qualitative properties of ionic flows are observed due to the existence of the boundary layers, which further depend on nonlinear interplays of system parameters. Among others, we find

- as linear functions of the potential $V$ (fixing other system parameters)
  - $\partial V J_{11}$ and $\partial V I_1$ (resp. $\partial V J_{21}$) can be negative (resp. positive) while they are always positive (resp. negative) under the electroneutrality boundary conditions (characterized in Theorems 3.3 and 3.6);
  - $\partial V J_{11}$ and $\partial V J_1$ (resp. $\partial V J_{21}$) can be negative (resp. positive) while they are always positive (negative) under the electroneutrality boundary conditions (characterized in Theorems 3.5 and 3.7);
  - $\partial V T_1$ and $\partial V T_1$ further depends on the order of $D_1$ and $D_2$, more precisely, they are always both positive (resp. negative) with $D_1 > D_2$ (resp. $D_1 < D_2$) under electroneutrality conditions, while they generally can have opposite signs (characterized in Theorems 3.8 and 3.9 with $D_1 < D_2$);
- Critical potentials that either balance the ion size effects (such as $V_{1c}$, $V_{2c}$, $V_c$ and $\bar{V}_c$) or separate the relative ion size effects (such as $V^{1c}$, $V^{2c}$, $V^c$ and $\bar{V}^c$) on individual fluxes, I-V relations and the total flow rate of matter, respectively, are identified (Definition 3.1), which play critical roles in studying ionic flow properties of interest and characterizing the effects from boundary layers (discussed in Section 3).
We point out that, recently, to better understand the boundary layer effects on ionic flows, the authors considered the classical PNP system with nonzero but small permanent charges ([16] and the classical PNP system with multiple cations ([59]). Much more complicated and rich dynamics of ionic flows are observed.

Finally, for this relatively simple setting of the PNP problem in this work, our analysis is rigorous. It is an extension of the work done in [10] and [39], which provides complementary information of the qualitative properties of ionic flows and helps people better understand the mechanism of ionic flow through a single ion channel. We believe the analysis in this work, together with the ones done in [16, 59], could provide some deep insights for future studies of ion channel problems both numerically and analytically, and even experimentally.

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