QUALITATIVE PROPERTIES OF IONIC FLOWS VIA POISSON-NERNST-PLANCK SYSTEMS WITH BIKERMAN’S LOCAL HARD-SPHERE POTENTIAL: ION SIZE EFFECTS

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ABSTRACT. We study a quasi-one-dimensional steady-state Poisson-Nernst-Planck model for ionic flows through membrane channels with fixed boundary ion concentrations and electric potentials. We consider two ion species, one positively charged and one negatively charged, and assume zero permanent charge. Bikerman’s local hard-sphere potential is included in the model to account for ion size effects on the ionic flow. The model problem is treated as a boundary value problem of a singularly perturbed differential system. Our analysis is based on the geometric singular perturbation theory but, most importantly, on specific structures of this concrete model. The existence of solutions to the boundary value problem for small ion sizes is established and, treating the ion sizes as small parameters, we also derive approximations of individual fluxes and I-V (current-voltage) relations, from which qualitative properties of ionic flows related to ion sizes are studied. A detailed characterization of complicated interactions among multiple and physically crucial parameters for ionic flows, such as boundary concentrations and potentials, diffusion coefficients and ion sizes, is provided.

1. Introduction. We study the dynamics of ionic flows, the electrodiffusion of charges, through ion channels via a quasi-one-dimensional steady-state Poisson-Nernst-Planck (PNP) system. As a basic macroscopic model for electrodiffusion of charges, particularly for ionic flows through ion channels ([8, 10, 15, 16, 17, 18, 19, 26, 27, 31, 38, 39, 62, 64, 72, 73, 74], etc.), under various reasonable conditions, PNP systems can be derived as reduced models from molecular dynamic models ([80]), from Boltzmann equations ([2]), and from variational principles ([34, 36, 37]).

The simplest PNP system is the classical Poisson-Nernst-Planck (cPNP) system that includes only the ideal components of the electrochemical potentials. It has been simulated ([6, 7, 8, 9, 11, 26, 27, 30, 32, 33, 39, 40, 41, 48, 61, 77, 88]) and analyzed ([1, 3, 4, 20, 21, 24, 43, 53, 55, 56, 59, 65, 75, 76, 81, 82, 83, 84, 86, 87])

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to a great extent. However, a major weakness of the cPNP is that it treats ions as point-charges, which is reasonable only for near infinite dilute ionic mixtures. To study the ion size effect on ionic flows, in particular, for ion species with the same valence but different ion sizes, for example, Na$^+$ (sodium) and K$^+$ (potassium), one has to consider excess (beyond the ideal) components in the electrochemical potential. One way is to include hard-sphere (HS) potentials. PNP models with ion size effects have been investigated computationally with great successes ([13, 25, 27, 29, 34, 35, 36, 37, 47, 89], etc.), and have been mathematically analyzed (see, for example, [22, 42, 49, 50, 51, 58]).

In [51], the authors provided an analytical treatment of a quasi-one-dimensional version of PNP system with a HS potential. They studied the case where two oppositely charged ions are involved for the same ion channel with electroneutrality (zero net charge) boundary conditions, the permanent charge can be ignored, and a local HS potential derived from Rosenfeld’s nonlocal one is included. The authors treated ion sizes as small parameters, and derived an approximation of the I-V relation. Furthermore, the approximate I-V relation allows them to establish the following results.

(i) There is a critical potential $V_c$ so that, if $V > V_c$, then ion sizes enhance the current $I$; if $V < V_c$, then ion sizes reduce the current $I$.
(ii) There is another critical potential $V^c$ so that, if $V > V^c$, then the current $I$ increases with respect to $\lambda = d_2/d_1$ where $d_1$ and $d_2$ are, respectively, the diameters of the positively and negatively charged ions; if $V < V^c$, then the current $I$ decreases in $\lambda$.
(iii) Important scaling laws of I-V relations and critical potentials in boundary concentrations are obtained; that is,
   (a) the contribution to the I-V relation from the ideal component scales linearly in boundary concentrations;
   (b) the contribution (up to first order in ionic diameters) to the I-V relation from the HS component scales quadratically in boundary concentrations;
   (c) both $V_c$ and $V^c$ scale invariantly in boundary concentrations.

In this paper, we study a quasi-one-dimensional version of PNP type system with a local HS model proposed by Bikerman ([5]). Bikerman’s model is one of the earliest local models for HS potentials. The problem we study here has basically the same setting as that in [51] except that we take a different local model. We study the PNP system with Bikerman’s local HS potential for two purposes:

(I) To compare our results with those obtained in [51];
(II) To examine ion size effects on individual fluxes that provide detailed information on the interactions among different ion species within the channel. This is the main contribution compared to [51].

The rest of this paper is organized as follows. In Section 2, we describe the quasi-one-dimensional PNP model of ionic flows, Bikerman’s local HS potential, the boundary value problem (BVP) of the singularly perturbed PNP-HS system, and the basic assumptions.

In Section 3, the existence and (local) uniqueness result for the BVP is established in the framework of geometric singular perturbation theory. Based on the analysis in Section 3 and treating the ion sizes as small parameters, approximations of individual fluxes and the I-V (current-voltage) relations are derived, from which the ion size effect on ionic flows is analyzed in detail. This leads to our main interest
studied in Section 4, which contains four subsections. In Subsection 4.1, we examine the ion size effect on individual fluxes. We identify four critical potentials or voltages, denoted by $V_{kc}$ and $V_{kc}^k$, $k = 1, 2$, respectively. The values $V_1^c$ and $V_2^c$ are the potentials that balance the ion size effect on the individual fluxes of charge, and the values $V_1^c$ and $V_2^c$ are the potentials that separate the relative size effect on the individual fluxes of charge (see Definition 4.4, Theorem 4.7 and Theorem 4.8). More interestingly, under electroneutrality conditions, we observed that $V_{kc} = V_{kc}^k$ for $k = 1, 2$, while it is not true without electroneutrality conditions (see Corollary 4.5). Subsection 4.2 deals with the ion size effect on the total flow rate of charge (the I-V relations). Two critical potentials or voltages $V_c$ and $V_c^c$ are also identified. In particular, the two critical potential values are identical (see Definition 4.11). The roles of these critical potentials in characterizing ion size effects on ionic flows are discussed. In subsection 4.3, under electroneutrality conditions, the relationship among those critical potentials $V_{kc}$, $k = 1, 2$ for individual fluxes and $V_c$ for the I-V relations is studied in terms of multiple physical parameters such as boundary concentrations, boundary potentials and diffusion coefficients (see Lemma 4.19). The distinct effects of the nonlinear interplay between these physical parameters are characterized. In Subsection 4.4, a special case of ion size effects on ionic flows is considered.

We remark that, under electroneutrality boundary conditions, each of these critical potentials separates the potential into two regions over which the ion size effects are qualitatively opposite to each other (see Theorems 4.7, 4.8, and 4.15). Also, in the absence of electroneutrality, it is rather surprising that the roles of critical potentials on ion size effects are significant different: the opposite effects of ion sizes separated by those critical potentials depend on other quantities in terms of boundary conditions (see Proposition 4.18).

Finally, we would like to point out that, under electroneutrality conditions, as what we expect, the results related to ion size effects on the I-V relations are similar to those obtained in [51]. However, our analysis of the ion size effects on the individual fluxes provides detailed information on the interactions among different ion species. We believe our results will provide useful insights for numerical and even experimental studies of ionic flows through membrane channels.

2. Problem Setup.

2.1. A quasi-one-dimensional steady-state PNP type system. The channel is assumed to be narrow so that it can be effectively viewed as a one-dimensional channel $[0, l]$ where $l$, typically in the range of $10 - 20$ nanometers, is the length of the channel together with the baths that the channel links. A quasi-one-dimensional steady-state PNP model for ion flows of $n$ ion species though a single channel is (see [57, 61])

$$
\frac{1}{A(X)} \frac{d}{dX} \left( \varepsilon_r(X) \varepsilon_0 A(X) \frac{d\Phi}{dX} \right) = -e \left( \sum_{j=1}^{n} z_j C_j(X) + Q(X) \right), \quad (2.1)
$$

$$
\frac{dJ_i}{dX} = 0, \quad -J_i = \frac{1}{k_B T} D_i(X) A(X) C_i(X) \frac{d\mu_i}{dX}, \quad i = 1, 2, \cdots, n
$$

where $X \in [0, l]$, $e$ is the elementary charge, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature; $\Phi$ is the electric potential, $Q(X)$ is the permanent charge of the channel, $\varepsilon_r(X)$ is the relative dielectric coefficient, $\varepsilon_0$ is the vacuum permittivity;
\( A(X) \) is the area of the cross-section of the channel over the point \( X \in [0, l] \); for the \( i \)th ion species, \( C_i \) is the concentration (number of \( i \)th ions per volume), \( z_i \) is the valence (number of charges per particle) that is positive for cations and negative for anions, \( \mu_i \) is the electrochemical potential, \( J_i \) is the flux density, and \( D_i(X) \) is the diffusion coefficient. The boundary conditions are, for \( i = 1, 2, \cdots, n \),

\[
\Phi(0) = V, \quad C_i(0) = \mathcal{L}_i > 0; \quad \Phi(l) = 0, \quad C_i(l) = \mathcal{R}_i > 0. \tag{2.2}
\]

2.2. 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 \( \mu_i^{id}(X) \), the excess component \( \mu_i^{ex}(X) \) and the concentration-independent component \( \mu_i^0(X) \) (e.g. a hard-well potential):

\[
\mu_i(X) = \mu_i^0(X) + \mu_i^{id}(X) + \mu_i^{ex}(X)
\]

where

\[
\mu_i^{id}(X) = z_i e \Phi(X) + k_B T \ln \frac{C_i(X)}{C_0} \tag{2.3}
\]

with some characteristic number density \( C_0 \). As mentioned in the introduction, cPNP system takes into consideration of the ideal component \( \mu_i^{id}(X) \) only. This component reflects the collision between ion particles and water (medium) molecules. It has been accepted that cPNP system is a reasonable model in, for example, dilute cases under which ion particles can be treated as point-charges and ion-to-ion interactions can be more or less ignored. The excess electrochemical potential \( \mu_i^{ex}(X) \) accounts for finite size effects of charges (see, e.g., [69, 70]).

In this paper, we study the PNP system including a local hard-sphere (LHS) chemical potential, proposed by Bikerman ([5]) to account for the finite size effect. Bikerman’s model is, for \( i = 1, 2, \ldots, n \),

\[
\mu_i^{Bik}(X) = -k_B T \ln \left( 1 - \sum_{j=1}^{n} v_j C_j(X) \right), \tag{2.4}
\]

where \( v_j \) is the volume of a single \( j \)th ion species.

Remark 2.1. Since \( c_i \) is the number density of \( i \)th ion species, it follows that \( \sum_{j=1}^{n} v_j c_j < 1 \). In this sense, Bikerman’s LHS takes into consideration of nonzero ion sizes. It should be pointed out though Bikerman’s LHS is not ion specific since it is the same for all ion species.

2.3. The BVP and assumptions. The main focus of this paper is to examine the qualitative properties of ion size effects on ionic flows via BVP (2.1)-(2.2) with LHS model (2.4). We will take essentially the same setting as that in [51] except that we use Bikerman’s LHS (2.4). More precisely,

(i) We consider two ion species \( n = 2 \) with \( z_1 > 0 \) and \( z_2 < 0 \);
(ii) The permanent charge is set to be zero: \( Q(X) = 0 \);
(iii) For the electrochemical potential \( \mu_i \), in addition to the ideal component \( \mu_i^{id} \), we also include the LHS potential \( \mu_i^{Bik} \) in (2.4);
(iv) The relative dielectric coefficient and the diffusion coefficients are assumed to be constants, that is, \( \varepsilon_r(X) = \varepsilon_r \) and \( D_i(X) = D_i \).

We first make a dimensionless rescaling following ([24]).
Set $C_0 = \max \{ L_i, R_i : i = 1, 2 \}$ and let
\[ \varepsilon^2 = \frac{\varepsilon_r c_0 k_B T}{e^2 C_0^2}, \quad x = \frac{x}{T}, \quad h(x) = \frac{A(X)}{t^2}, \quad D_i = \frac{t C_0 D_i}{C_0} \]
\[ \phi(x) = \frac{e}{k_B T} \Phi(X), \quad c_i(x) = \frac{C_i(X)}{C_0}, \quad J_i = \frac{J_i}{D_i}; \quad (2.5) \]
\[ V = \frac{e}{k_B T} V_i, \quad L_i = \frac{L_i}{C_0}, \quad R_i = \frac{R_i}{C_0}. \]

System (2.1) becomes, with the substitution (2.3) for $\mu^{\text{bi}}_i$,
\[ \varepsilon^2 \frac{d}{h(x)} \left( \frac{d h(x)}{dx} \phi \right) = -(z_1 c_1 + z_2 c_2), \quad \frac{d J_i}{dx} = 0, \]
\[ h(x) \frac{d c_1}{dx} + h(x) z_1 c_1 \frac{d \phi}{dx} + \frac{h(x) c_1(x)}{k_B T} \frac{d}{dx} \mu^{\text{bi}}_1(x) = -J_1, \quad (2.6) \]
\[ h(x) \frac{d c_2}{dx} + h(x) z_2 c_2 \frac{d \phi}{dx} + \frac{h(x) c_2(x)}{k_B T} \frac{d}{dx} \mu^{\text{bi}}_2(x) = -J_2. \]

It follows from (2.4) that
\[ \frac{1}{k_B T} \mu^{\text{bi}}_i(x) = - \ln \left( 1 - \nu_1 c_1(x) - \nu_2 c_2(x) \right) \quad \text{where} \quad \nu_j = v_j C_0. \quad (2.7) \]

Substituting (2.7) into system (2.6), we obtain the BVP
\[ \varepsilon^2 \frac{d}{h(x)} \left( \frac{d h(x)}{dx} \phi \right) = -(z_1 c_1 + z_2 c_2), \quad \frac{d J_i}{dx} = 0, \]
\[ \frac{d c_1}{dx} = -f_1(c_1, c_2; \nu_1, \nu_2) \frac{d \phi}{dx} - \frac{1}{h(x)} g_1(c_1, J_1, J_2; \nu_1, \nu_2), \quad (2.8) \]
\[ \frac{d c_2}{dx} = f_2(c_1, c_2; \nu_1, \nu_2) \frac{d \phi}{dx} - \frac{1}{h(x)} g_2(c_2, J_1, J_2; \nu_1, \nu_2), \]

with boundary conditions, for $i = 1, 2$,
\[ \phi(0) = V, \quad c_i(0) = L_i; \quad \phi(1) = 0, \quad c_i(1) = R_i, \quad (2.9) \]

where
\[ f_1(c_1, c_2; \nu_1, \nu_2) = (z_1 - z_2 \nu_1 c_1 - z_2 \nu_2 c_2) c_1, \]
\[ f_2(c_1, c_2; \nu_1, \nu_2) = -(z_2 - z_1 \nu_1 c_1 - z_2 \nu_2 c_2) c_2, \]
\[ g_1(c_1, J_1, J_2; \nu_1, \nu_2) = J_1 - (\nu_1 J_1 + \nu_2 J_2) c_1, \]
\[ g_2(c_2, J_1, J_2; \nu_1, \nu_2) = J_2 - (\nu_1 J_1 + \nu_2 J_2) c_2. \quad (2.10) \]

For a solution of BVP (2.8)-(2.9), the total flux of charge or current $I$ is
\[ I = z_1 J_1 + z_2 J_2 = z_1 D_1 J_1 + z_2 D_2 J_2. \quad (2.11) \]

For fixed $L_i$’s and $R_i$’s, formula (2.11) provides a relation of the current $I$ on the voltage $V$. This relation is the so-called $I$-$V$ relation (current-voltage relation).

The BVP (2.8)-(2.9) will be analyzed in Section 3 based on the assumption that the dimensionless parameter $\varepsilon$ is small so that system (2.8) can be treated as a singularly perturbed system with $\varepsilon$ as the singular parameter. For typical ion channel problems, physical range for the parameter $\varepsilon$ is $10^{-2} - 10^{-6}$, which is smaller for crowded ionic mixtures (large $C_0$) and larger for less crowded ionic mixtures. It is further assumed that the dimensionless parameters $\nu_i$’s are small; typical physical range for $\nu_i = v_i C_0$ is $10^{-2} - 10^{-4}$ with $10^{-2}$ corresponding to...
crowded ionic mixtures, say, $C_0 \sim 10$ M (molar) and with $10^{-4}$ to less crowded ionic mixtures, say, $C_0 \sim 100$ mM. From the analysis of the BVP, we will obtain approximations for both $J_i$’s and I-V relations to study ion size effects on ionic flows.

3. **Geometry singular perturbation theory for (2.8)–(2.9).** We will rewrite system (2.8) into a standard form for singularly perturbed systems and convert BVP (2.8)-(2.9) to a connecting problem. Generally, there is no unique way to write a second order singular perturbed equation (the Poisson equation for $\phi$ in (2.8)) to a system of first order equations. Different choices result in different $\epsilon = 0$ limiting systems. It is the $\epsilon = 0$ limiting systems that govern the viable choices. Ideally, one would like to obtain a normally hyperbolic (NH) slow manifold, if possible. The choice used in this paper below (introduced first in [53] to the best of our knowledge) results in a NH slow manifold while the “natural” choice $\dot{\phi} = \varepsilon^2 u$ would not.

Denote the derivative with respect to $x$ by overdot and introduce $u = \varepsilon \dot{\phi}$ and $\tau = x$. System (2.8) becomes

$$
\varepsilon \dot{\phi} = u, \quad \varepsilon \dot{u} = -z_1 c_1 - z_2 c_2 - \varepsilon \frac{h(x)}{h(\tau)} \dot{u},
$$

$$
\varepsilon \dot{c}_1 = -f_1(c_1, c_2; \nu_1, \nu_2) u - \frac{\varepsilon}{h(\tau)} g_1(c_1, J_1, J_2; \nu_1, \nu_2),
$$

$$
\varepsilon \dot{c}_2 = f_2(c_1, c_2; \nu_1, \nu_2) u - \frac{\varepsilon}{h(\tau)} g_2(c_2, J_1, J_2; \nu_1, \nu_2),
$$

$$
J_1 = J_2 = 0, \quad \tau = 1.
$$

System (3.1) is the **slow system** and its phase space is $\mathbb{R}^7$ with state variables $(\phi, u, c_1, c_2, J_1, J_2, \tau)$.

For $\varepsilon > 0$, the rescaling $x = \varepsilon x$ of the independent variable $x$ gives rise to the **fast system**

$$
\phi' = u, \quad u' = -z_1 c_1 - z_2 c_2 - \varepsilon \frac{h(x)}{h(\tau)} \dot{u},
$$

$$
c_1' = -f_1(c_1, c_2; \nu_1, \nu_2) u - \frac{\varepsilon}{h(\tau)} g_1(c_1, J_1, J_2; \nu_1, \nu_2),
$$

$$
c_2' = f_2(c_1, c_2; \nu_1, \nu_2) u - \frac{\varepsilon}{h(\tau)} g_2(c_2, J_1, J_2; \nu_1, \nu_2),
$$

$$
J_1' = J_2' = 0, \quad \tau' = \varepsilon,
$$

where prime denotes the derivative with respect to the variable $\xi$.

For $\varepsilon > 0$, slow system (3.1) and fast system (3.2) have exactly the same phase portrait. But their limiting systems at $\varepsilon = 0$ are different. System of (3.1) with $\varepsilon = 0$ is called the **limiting slow system**, whose orbits are called **slow orbits** or regular layers. System of (3.2) with $\varepsilon = 0$ is the **limiting fast system**, whose orbits are called **fast orbits** or singular (boundary and/or internal) layers. In this context, a **singular orbit** of system (3.1) or (3.2) is defined to be a continuous and piecewise smooth curve in $\mathbb{R}^7$ that is a union of finitely many slow and fast orbits. Very often, limiting slow and fast systems provide complementary information on state variables. Therefore, the main task of singularly perturbed problems is to patch the limiting information together to form a solution for the entire $\varepsilon > 0$ system.
Let $B_L$ and $B_R$ be the subsets of the phase space $\mathbb{R}^7$ defined by
\[
B_L = \{(V, u, L_1, L_2, J_1, J_2, 0) \in \mathbb{R}^7 : \text{arbitrary } u, J_1, J_2\},
\]
\[
B_R = \{(0, u, R_1, R_2, J_1, J_2, 1) \in \mathbb{R}^7 : \text{arbitrary } u, J_1, J_2\}.
\]
Then the original BVP is equivalent to the connecting problem, namely, finding an orbit of (3.1) or (3.2) from $B_L$ to $B_R$ (see, for example, [44]).

In what follows, we will consider the equivalent connecting problem for system (3.1) or (3.2). The construction of a connecting orbit involves two main steps ([12, 44, 45, 46, 52, 54, 78, 79, 85]):

Step I: We construct a singular orbit to the connecting problem.

Step II: We apply geometric singular perturbation theory, particularly, the Exchange Lemmas, to show that there is a unique connecting orbit near the singular orbit for small $\varepsilon > 0$.

3.1. Geometric construction of singular orbits. Following the idea in [20, 53, 55], we will first construct a singular orbit on $[0, 1]$ that connects $B_L$ to $B_R$. Such an orbit will generally consist of two boundary layers and a regular layer.

3.1.1. Limiting fast dynamics and boundary layers. By setting $\varepsilon = 0$ in (3.1), we obtain the slow manifold
\[
Z = \{u = 0, \ z_1c_1 + z_2c_2 = 0\}.
\]
By setting $\varepsilon = 0$ in (3.2), we get the limiting fast system
\[
\phi' = u, \quad u' = -z_1c_1 - z_2c_2, \quad c_1' = -f_1(c_1, c_2; \nu_1, \nu_2)u, \quad c_2' = f_2(c_1, c_2; \nu_1, \nu_2)u, \quad J_1' = J_2' = 0, \quad \tau' = 0.
\]
(3.4)

Note that the slow manifold $Z$ is the set of equilibria of (3.4).

Lemma 3.1. For system (3.4), the slow manifold $Z$ is normally hyperbolic.

Proof. Even though the LHS models used in [51] and in this paper are different, the proof of this result is the same, word by word, as that in [51]. For convenience of the reader, we provide the key ingredients here.

The linearization of (3.4) at each point of $(\phi, 0, c_1, c_2, J_1, J_2, \tau) \in Z$ has five zero eigenvalues associated with the set of equilibria $Z$ with dim($Z$) = 5, and the other two eigenvalues are
\[
\pm \sqrt{z_1f_1 - z_2f_2} = \pm \sqrt{z_1^2c_1 + z_2^2c_2}.
\]
Note that $f_1(c_1, c_2; \nu_1, \nu_2)$ has a factor $c_1$ and $f_2(c_1, c_2; \nu_1, \nu_2)$ has a factor $c_2$. It follows from $(c_1, c_2)$-subsystem of (3.4) that $\{c_1 > 0\}$ and $\{c_2 > 0\}$ are invariant. Since $c_1$ and $c_2$ have positive boundary values, $c_1$ and $c_2$ are positive for all $x \in [0, 1]$. Therefore, $z_1f_1 - z_2f_2 > 0$. Thus $Z$ is normally hyperbolic.

We denote the stable (resp. unstable) manifold of $Z$ by $W^s(Z)$ (resp. $W^u(Z)$). Let $M_L$ be the collection of orbits from $B_L$ in forward time under the flow of system (3.4) and let $M_R$ be the collection of orbits from $B_R$ in backward time under the flow of system (3.4). Then, for a singular orbit connecting $B_L$ to $B_R$, the boundary layer at $x = 0$ must lie in $N_L = M_L \cap W^s(Z)$ and the boundary layer at $x = 1$ must lie in $N_R = M_R \cap W^u(Z)$. In this subsection, we will determine the boundary layers $N_L$ and $N_R$, and their landing points $\omega(N_L)$ and $\alpha(N_R)$ on the slow manifold.
Recall that we are interested in $\Gamma$ and connect $\omega(N_L)$ at $x = 0$ and $\alpha(N_R)$ at $x = 1$.

Recall the definitions of $\nu_1$ and $\nu_2$ from (2.7) and the discussion in the last paragraph of Section 2. We will be interested in the situation that $\nu_1$ and $\nu_2$ are small and treat (3.4) as a regular perturbation of that with $\nu_1 = \nu_2 = 0$. While $\nu_1$ and $\nu_2$ are small, their ratio is of order $O(1)$. We thus set

$$\nu_1 = \nu \quad \text{and} \quad \nu_2 = \lambda \nu$$

and look for solutions

$$\Gamma(\xi; \nu) = (\phi(\xi; \nu), u(\xi; \nu), c_1(\xi; \nu), c_2(\xi; \nu), J_1(\nu), J_2(\nu), \tau)$$

of system (3.4) of the form

$$\phi(\xi; \nu) = \phi_0(\xi) + \phi_1(\xi)\nu + o(\nu), \quad u(\xi; \nu) = u_0(\xi) + u_1(\xi)\nu + o(\nu),$$

$$c_1(\xi; \nu = c_{01}(\xi) + c_{11}(\xi)\nu + o(\nu), \quad J_i(\nu) = J_{i0} + J_{i1}\nu + o(\nu).$$

Substituting (3.6) into system (3.4), we obtain, for the zeroth order in $\nu$,

$$\phi_0 = u_0, \quad u_0' = -z_1c_{10} - z_2c_{20}, \quad c_{10}' = -z_1c_{10}u_0,$$

$$c_{20}' = -z_2c_{20}u_0, \quad J_{10}' = J_{20}' = 0, \quad \tau' = 0,$$

and, for the first order in $\nu$,

$$\phi_1 = u_1, \quad u_1' = -z_1c_{11} - z_2c_{21},$$

$$c_{11}' = -z_1u_0c_{11} - z_1c_{10}u_1 + (z_1c_{10} + \lambda z_2c_{20})c_{10}u_0,$$

$$c_{21}' = -z_2u_0c_{21} - z_2c_{20}u_1 + (z_1c_{10} + \lambda z_2c_{20})c_{20}u_0,$$

$$J_{11}' = J_{21}' = 0, \quad \tau' = 0.$$  

Recall that we are interested in $\Gamma^0(\xi; \nu) \subset N_L = M_L \cap W^s(\mathcal{Z})$ with $\Gamma^0(0; \nu) \in B_L$ and $\Gamma^1(\xi; \nu) \subset N_R = M_R \cap W^u(\mathcal{Z})$ with $\Gamma^1(0; \nu) \in B_R$.

**Proposition 3.2.** Assume $\nu \geq 0$ is small.

(i) The stable manifold $W^s(\mathcal{Z})$ intersects $B_L$ transversally at points

$$(V, u_0^L + u_1^L \nu + o(\nu), L_1, L_2, J_1(\nu), J_2(\nu), 0),$$

and the $\omega$-limit set of $N_L = M_L \cap W^s(\mathcal{Z})$ is

$$\omega(N_L) = \{ (\phi_0^L + \phi_1^L \nu + o(\nu), 0, c_{10}^L + c_{11}^\nu + o(\nu), c_{20}^L + c_{21}^L \nu + o(\nu), J_1(\nu), J_2(\nu), 0) \},$$

where $J_i(\nu) = J_{i0} + J_{i1}\nu + o(\nu), i = 1, 2$, can be arbitrary and

$$\phi_0^L = V - \frac{1}{z_1 - z_2} \ln \frac{-z_2L_2}{z_1L_1}, \quad z_1c_{10}^L = -z_2c_{20}^L = (z_1L_1)^{z_1/z_2} (-z_2L_2)^{z_2/z_1},$$

$$u_0^L = \text{sgn}(z_1L_1 + z_2L_2) \sqrt{2} \left( L_1 + L_2 + \frac{z_1 - z_2}{z_1z_2} (z_1L_1)^{z_1/z_2} (-z_2L_2)^{z_2/z_1} \right);$$

$$\phi_1^L = 0, \quad z_1c_{11}^L = -z_2c_{21}^L = z_1c_{10}^L(L_1 + \lambda L_2 - c_{10}^L - \lambda c_{20}^L),$$

$$u_1^L = \frac{1}{u_0^L} \left( \frac{\lambda}{2} (L_2 + c_{20}^L)(L_2 - c_{20}^L) + \frac{1}{2} (L_1 + c_{10}^L)(L_1 - c_{10}^L) - c_{10}^L c_{20}^L c_{11}^L - c_{11}^L c_{21}^L - \frac{z_2(1 - \lambda)}{z_1 + z_2} e^{z_1 + z_2(V - \phi_0^L)} \right).$$
(ii) The unstable manifold \( W^u(Z) \) intersects \( B_R \) transversally at points
\[
(0, u_0' + u_1' \nu + o(\nu), R_1, R_2, J_1(\nu), J_2(\nu), 1),
\]
and the \( \alpha \)-limit set of \( N_R \) is
\[
\alpha(N_R) = \{(\phi^R_0 + \phi^I_0 + o(\nu), 0, c^R_1 + c^I_1 + c^R_2 + c^I_2 + o(\nu), c^R_3 + c^R_3 + o(\nu), J_1(\nu), J_2(\nu), 1)\},
\]
where \( J_i(\nu) = J_{i0} + J_{i1} \nu + o(\nu), i = 1, 2 \), can be arbitrary and
\[
\phi^R_0 = -\frac{1}{z_1 - z_2} \ln \frac{z_2 R_2}{z_1 R_1}, \quad z_1 c^R_0 = -z_2 c^R_2 = (z_1 R_1)^{\frac{z_1}{z_1 - z_2}} (z_2 R_2)^{\frac{z_2}{z_2 - z_1}},
\]
\[
u_0' = -\text{sgn}(z_1 R_1 + z_2 R_2) \sqrt{2 \left( R_1 + R_2 + \frac{z_1}{z_2} (z_1 R_1)^{\frac{z_1}{z_1 - z_2}} (z_2 R_2)^{\frac{z_2}{z_2 - z_1}} \right)};
\]
\[
\phi^I_1 = 0, \quad z_1 c^I_1 = -z_2 c^I_2 = z_1 c^I_1(R_1 + \lambda R_2 - c^R_{10} - \lambda c^R_{20}),
\]
\[
u_1' = \frac{1}{\nu_0} \left( \frac{\lambda}{2} (R_2 + c^R_{20}) (R_2 - c^R_{20}) + \frac{1}{2} (R_1 + c^R_{10}) (R_1 - c^R_{10}) - c^R_{10} c^R_{20} - c^R_{11} - c^R_{21} \right.
\]
\[= \frac{z_2(1 - \lambda)}{z_1 + z_2} e^{-(z_1 + z_2) \nu_0'^2}.\]

Proof. The stated result for system (3.7) has been obtained in [20, 53, 55]. For system (3.8), one can check directly that it has three nontrivial first integrals:
\[
F_1 = \frac{c^I_1}{c^{10}} + z_1 \phi_1 + c^{10} + \lambda c^{20}, \quad F_2 = \frac{c^I_1}{c^{10}} + z_2 \phi_1 + c^{10} + \lambda c^{20},
\]
\[
F_3 = \nu_0 u_1' - c^{11} - c^{21} - \frac{\lambda}{2} c^{10} - \frac{1}{2} c^{10} c^{20} - \frac{z_2(1 - \lambda)}{z_1 + z_2} e^{(z_1 + z_2) \nu_0'^2}.
\]

We now establish the results for \( \phi^I_1, c^I_{11}, c^I_{21} \) and \( u_1' \) for system (3.8). Those for \( \phi^R_0, c^R_{10}, c^R_{20} \) and \( u_0' \) can be established in the similar way.

Note that \( \phi_1(0) = c_{11}(0) = \phi_1(0) = 0 \). Using the integrals \( F_1 \) and \( F_2 \), we have
\[
\frac{c^{11}}{c^{10}} + z_1 \phi_1 + c^{10} + \lambda c^{20} = L_1 + \lambda L_2, \quad \text{and} \quad \frac{c^{21}}{c^{20}} + z_2 \phi_1 + c^{10} + \lambda c^{20} = L_1 + \lambda L_2.
\]
Therefore
\[
c^{11} = c^{10}(L_1 + \lambda L_2 - c^{10} - \lambda c^{20} - z_1 \phi_1), \quad c^{21} = c^{20}(L_1 + \lambda L_2 - c^{10} - \lambda c^{20} - z_2 \phi_1).
\]

Taking the limit as \( \xi \to \infty \), we have
\[
\phi^I_1 = 0, \quad c^I_{11} = c^I_{10}(L_1 + \lambda L_2 - c^I_{10} - \lambda c^I_{20}), \quad c^I_{21} = c^I_{20}(L_1 + \lambda L_2 - c^I_{10} - \lambda c^I_{20}).
\]

In view of the relations \( z_1 c^I_{10} + z_2 c^I_{20} = z_1 c^I_{11} + z_2 c^I_{21} = 0 \), one can get the formulas for \( c^I_{11}, c^I_{21} \) and \( \phi^I_1 \). We now derive the formula for \( u_1' \) for \( u_1' = 0(1) \).

In view of \( F_3(0) = F_3(\infty) \), we have
\[
u_0' u_1' - L_1 L_2 - \frac{\lambda}{2} L_2^2 - \frac{1}{2} L_1^2 = -c^I_{11} - c^I_{21} - c^I_{10} c^I_{20} - \frac{\lambda}{2} (c^I_{10})^2 - \frac{1}{2} (c^I_{10})^2 \]
\[= \frac{z_2(1 - \lambda)}{z_1 + z_2} e^{(z_1 + z_2) \nu_0'^2}.
\]
The formula for \( u_1' \) follows directly. This completes the proof. \( \square \)

We remark that, when \( z_1 L_1 + z_2 L_2 = 0, u_0' = 0 \). In this case, \( u_1' \) is defined as the limit of its expression as \( z_1 L_1 + z_2 L_2 \to 0 \) and it is zero. Similar remark applies to \( u_1' \) when \( z_1 R_1 + z_2 R_2 = 0 \).

For later use, let \( \Gamma^0 \) denote the possible boundary layer at \( x = 0 \) and let \( \Gamma^1 \) denote the possible boundary layer at \( x = 1 \) for system (3.4).
Corollary 3.3. Under electroneutrality boundary conditions, that is,
\[ z_1L_1 = -z_2L_2 = L \quad \text{and} \quad z_1R_1 = -z_2R_2 = R, \quad (3.9) \]
one has
\[ \phi^L_0 = V, \quad z_1c^L_{10} = -z_2c^L_{20} = L; \quad \phi^R_0 = 0, \quad z_1c^R_{10} = -z_2c^R_{20} = R; \]
\[ \phi^L_1 = c^L_{11} = c^L_{21} = \phi^R_1 = c^R_{11} = c^R_{21} = 0. \]
In particular, up to \( O(\nu) \), there is no boundary layer at \( x = 0 \) and \( x = 1 \).

3.1.2. Limiting slow dynamics and regular layer. Next we construct the regular layer on \( \mathcal{Z} \) that connects \( \omega(N_L) \) and \( \alpha(N_R) \). Note that, for \( \varepsilon = 0 \), system (3.1) loses most information. To remedy this degeneracy, we follow the idea in [20, 53, 55] and make a rescaling \( u = \varepsilon p \) and \( -z_2c_2 = z_1c_1 + \varepsilon q \) in system (3.1). In term of the new variables, system (3.1) becomes
\[
\begin{align*}
\dot{\phi} &= p, \quad \dot{q} = \frac{h_\nu(t)}{h_\tau(t)} p, \quad \varepsilon \dot{q} = (z_1f_1 - z_2f_2)p + \varepsilon g_1 + z_2g_2, \\
\dot{c}_1 &= -f_1 p - \frac{g_1}{h_\tau(t)}, \quad \dot{J}_1 = \dot{J}_2 = 0, \quad \dot{\tau} = 1 
\end{align*}
\]
where, for \( i = 1, 2, \)
\[
\begin{align*}
f_i &= f_i \left( c_1, -\frac{z_1c_1 + \varepsilon q}{z_2}, \nu, \lambda \nu \right); \quad g_1 = g_1 (c_1, J_1, J_2; \nu, \lambda \nu) ; \quad \text{and} \\
g_2 &= g_2 \left( -\frac{z_1c_1 + \varepsilon q}{z_2}, J_1, J_2; \nu, \lambda \nu \right).
\end{align*}
\]
It is again a singular perturbation problem and its limiting slow system is
\[
\begin{align*}
\dot{\phi} &= p, \quad q = 0, \quad p = -\frac{z_1g_1 (c_1, J_1, J_2; \nu, \lambda \nu) + z_2g_2 \left( -\frac{z_1}{z_2}c_1, J_1, J_2; \nu, \lambda \nu \right)}{z_1(z_1 - z_2)h_\tau(t)c_1}, \\
\dot{c}_1 &= -f_1 (c_1, -\frac{z_1}{z_2}c_1; \nu, \lambda \nu) p - \frac{1}{h_\tau(t)} g_1 (c_1, J_1, J_2; \nu, \lambda \nu), \quad \dot{J}_1 = \dot{J}_2 = 0, \quad \dot{\tau} = 1.
\end{align*}
\]
For system (3.11), the slow manifold is
\[
\mathcal{S} = \left\{ q = 0, \quad p = -\frac{z_1g_1 (c_1, J_1, J_2; \nu, \lambda \nu) + z_2g_2 \left( -\frac{z_1}{z_2}c_1, J_1, J_2; \nu, \lambda \nu \right)}{z_1(z_1 - z_2)h_\tau(t)c_1} \right\}.
\]
Therefore, the limiting slow system on \( \mathcal{S} \) is
\[
\begin{align*}
\dot{\phi} &= p, \quad \dot{c}_1 = -f_1 (c_1, -\frac{z_1}{z_2}c_1; \nu, \lambda \nu) p - \frac{1}{h_\tau(t)} g_1 (c_1, J_1, J_2; \nu, \lambda \nu), \\
\dot{J}_1 = \dot{J}_2 = 0, \quad \dot{\tau} = 1,
\end{align*}
\]
where
\[
p = -\frac{z_1g_1 (c_1, J_1, J_2; \nu, \lambda \nu) + z_2g_2 \left( -\frac{z_1}{z_2}c_1, J_1, J_2; \nu, \lambda \nu \right)}{z_1(z_1 - z_2)h_\tau(t)c_1}.
\]
Similar to the layer problem, we look for solutions of (3.12) of the form
\[
\begin{align*}
\phi(x) &= \phi_0(x) + \phi_1(x)\nu + o(\nu), \quad c_1(x) = c_{10}(x) + c_{11}(x)\nu + o(\nu), \\
J_i &= J_{i0} + J_{i1}\nu + o(\nu).
\end{align*}
\]
(3.13)
Proof. We refer the readers to \cite{20, 53, 55} for a detailed proof.

There is a unique solution to connect \( \omega(N_L) \) and \( \alpha(N_R) \) given in Proposition 3.2; in particular, for \( j = 0, 1 \),

\[
(\phi_j(0), c_{1j}(0)) = (\phi_j^L, c_{1j}^L), \quad (\phi_j(1), c_{1j}(1)) = (\phi_j^R, c_{1j}^R).
\]

From system (3.12) and the definitions of \( f_j \)'s and \( g_j \)'s in (2.10), we have

\[
\begin{align*}
\dot{c}_{10} &= \frac{z_2 (J_{10} + J_{20})}{(z_1 - z_2)\tau}, \\
\dot{c}_{10} &= \frac{z_2 (J_{11} + J_{21})}{(z_1 - z_2)\tau}, \\
J_{10} &= J_{20} = 0, \quad \dot{\tau} = 1,
\end{align*}
\]

and

\[
\begin{align*}
\dot{c}_{11} &= \frac{(z_1 J_{10} + z_2 J_{20}) c_{11}}{z_1 (z_1 - z_2)\tau c_{10}}, \\
\dot{c}_{11} &= \frac{(z_1 \lambda - z_2) (J_{11} + J_{21})}{(z_1 - z_2)\tau c_{10}} + \frac{z_2 (J_{11} + J_{21})}{(z_1 - z_2)\tau c_{10}}, \\
J_{11} &= J_{21} = 0, \quad \dot{\tau} = 1.
\end{align*}
\]

We denote

\[
H(x) = \int_0^x h^{-1}(s)ds.
\]

**Lemma 3.4.** There is a unique solution \((\phi_0(x), c_{10}(x), J_{10}, J_{20}, \tau(x))\) of (3.14) such that

\[
(\phi_0(0), c_{10}(0), \tau(0)) = (\phi_0^L, c_{10}^L, 0) \quad \text{and} \quad (\phi_0(1), c_{10}(1), \tau(1)) = (\phi_0^R, c_{10}^R, 1),
\]

where \( \phi_0^L, \phi_0^R, c_{10}^L, \) and \( c_{10}^R \) are given in Proposition 3.2. It is given by

\[
\begin{align*}
\phi_0(x) &= \phi_0^L + \frac{\phi_0^R - \phi_0^L}{\ln c_{10}^L - \ln c_{10}^R} \ln \left(1 - \frac{H(x)}{H(1)} + \frac{H(x) c_{10}^R}{H(1) c_{10}^L}\right), \\
c_{10}(x) &= \left(1 - \frac{H(x)}{H(1)}\right) c_{10}^L + \frac{H(x)}{H(1)} c_{10}^R, \\
J_{10} &= \frac{c_{10}^R - c_{10}^L}{H(1)} \left(z_1 (\phi_0^L - \phi_0^R) + \ln c_{10}^L - \ln c_{10}^R\right), \\
J_{20} &= \frac{c_{20}^R - c_{20}^L}{H(1)} \left(z_2 (\phi_0^L - \phi_0^R) + \ln c_{20}^L - \ln c_{20}^R\right), \\
\tau(x) &= x.
\end{align*}
\]

**Proof.** We refer the readers to \cite{20, 53, 55} for a detailed proof. \( \square \)

We now examine system (3.15). For convenience, we define two functions

\[
M = M(L_1, L_2, R_1, R_2; \lambda), \quad N = N(L_1, L_2, R_1, R_2; \lambda)
\]

as

\[
\begin{align*}
M &= c_{11}^R - c_{11}^L + \frac{z_1 \lambda - z_2}{2z_2} (c_{10}^L + c_{10}^R)(c_{10}^L - c_{10}^R), \\
N &= \frac{\phi_0^L - \phi_0^R}{\ln c_{10}^L - \ln c_{10}^R} \left(\frac{c_{11}^R - c_{11}^L}{c_{10}^R - c_{10}^L} + \frac{z_1 \lambda - z_2}{z_2} (c_{10}^L - c_{10}^R)\right) - \frac{\phi_0^L - \phi_0^R}{c_{10}^R - c_{10}^L} M.
\end{align*}
\]

**Lemma 3.5.** There is a unique solution \((\phi_1(x), c_{11}(x), J_{11}, J_{21}, \tau(x))\) of (3.15) such that

\[
(\phi_1(0), c_{11}(0), \tau(0)) = (\phi_1^L, c_{11}^L, 0) \quad \text{and} \quad (\phi_1(1), c_{11}(1), \tau(1)) = (\phi_1^R, c_{11}^R, 1),
\]
where $\phi_1^L$, $\phi_1^R$, $c_{11}^L$, and $c_{11}^R$ are given in Proposition 3.2. It is given by

$$
\phi_1(x) = -\frac{\ln c_{10}^L - \ln c_{10}(x)}{\ln c_{10}^L - \ln c_{10}^R} N + \frac{\phi_0^L - \phi_0^R}{\ln c_{10}^L - \ln c_{10}^R} \left[ \frac{c_{10}^L - c_{10}(x)}{c_{10}^L - c_{10}^R} \left( c_{10}^L - \frac{z_1 \lambda - z_2}{2z_2} c_{10}^L \right) \right] \\
+ \frac{(z_1 \lambda - z_2)(c_{10}^L - c_{10}^R) H(x)}{2z_2} \left( \frac{H(x)}{H(1)c_{10}(x)} - \frac{\ln c_{10}^L - \ln c_{10}(x)}{c_{10}^L - c_{10}^R} \right) M, \\
$$

where $c_{11}(x) = c_{11}^L - \frac{z_1 \lambda - z_2}{2z_2} (c_{10}^L + c_{10}(x)) (c_{10}^L - c_{10}(x)) + \frac{\ln c_{10}^L - \ln c_{10}(x)}{M} M,$

$$
J_{11} = \frac{z_1(c_{10}^L - c_{10}^R)}{H(1)(\ln c_{10}^L - \ln c_{10}^R)} N - \frac{M}{H(1)}, \quad J_{21} = -\frac{z_1(c_{10}^L - c_{10}^R)}{H(1)(\ln c_{10}^L - \ln c_{10}^R)} N + \frac{z_1 M}{z_2 H(1)},
$$

where $M$ and $N$ are defined in (3.18).

Proof. It follows from (3.15) that

$$
c_{11}(x) = c_{11}^L + \frac{(z_1 \lambda - z_2) (J_{10} + J_{20})}{z_1 - z_2} \int_0^x \frac{c_{10}(s)}{h(s)} ds + \frac{z_2 (J_{11} + J_{21})}{z_1 - z_2} \int_0^x \frac{1}{h(s)} ds \\
= c_{11}^L + \frac{z_1 \lambda - z_2}{2z_2} \left( c_{10}^L (x) - (c_{10}^L)^2 \right) + \frac{z_2 (J_{11} + J_{21})}{z_1 - z_2} H(x).
$$

Thus, from Proposition 3.2,

$$
\frac{z_2 (J_{11} + J_{21})}{z_1 - z_2} H(1) = c_{11}^R - c_{11}^L + \frac{z_1 \lambda - z_2}{2z_2} \left( c_{10}^L + c_{10}(x) \right) (c_{10}^L - c_{10}(x)),
$$

which gives, by definition of $M$ in (3.18),

$$
J_{11} + J_{21} = \frac{z_1 - z_2}{z_2 H(1)} M.
$$

(3.19)

Hence,

$$
c_{11}(x) = c_{11}^L - \frac{z_1 \lambda - z_2}{2z_2} \left( c_{10}^L + c_{10}(x) \right) (c_{10}^L - c_{10}(x)) + \frac{H(x)}{H(1)} M.
$$

(3.20)

Also, from (3.15), we have

$$
\phi_1(x) = \phi_1^L + \frac{z_1 J_{10} + z_2 J_{20}}{z_1(z_1 - z_2)} \int_0^x \frac{c_{11}(s)}{h(s) c_{10}^2(s)} ds - \frac{z_1 J_{11} + z_2 J_{21}}{z(z_1 - z_2)} \int_0^x \frac{1}{h(s) c_{10}(s)} ds.
$$

Note that, from (3.14) and (3.17),

$$
\int_0^x \frac{1}{h(s) c_{10}^2(s)} ds = \frac{z_1 - z_2}{z_2 (J_{10} + J_{20})} \int_0^x \frac{c_{10}(s)}{c_{10}^2(s)} ds = \frac{H(1)(c_{10}^L - c_{10}(x))}{(c_{10}^L - c_{10}(x)) c_{10}(x)},
$$

$$
\int_0^x \frac{h^{-1}(s)}{h(s) c_{10}^2(s)} ds = -\frac{z_1 - z_2}{z_2 (J_{10} + J_{20})} \int_0^x \frac{1}{h^{-1}(s) c_{10}^2(s)} ds \frac{d}{ds} c_{10}^{-1}(s) ds \\
= \frac{H(1)}{c_{10}^L - c_{10}^R} \left( H(x) - \int_0^x h^{-1}(s) c_{10}^{-1}(s) ds \right) \\
= \frac{H(1) H(x)}{(c_{10}^L - c_{10}^R) c_{10}(x)} - \frac{H(1)^2 (\ln c_{10}^L - \ln c_{10}(x))}{(c_{10}^L - c_{10}^R)^2}.
$$
These, together with (3.20) and (3.17), yield
\[\int_0^x \frac{c_{11}(s)}{h(s)c_{10}(s)} \, ds = \left( c_{11} - \frac{z_1 \lambda - z_2}{2z_2} \right) \left( \frac{c_{10} - c_{10}(x)}{c_{10}} \right) \frac{H(1)}{c_{10}(x)} + \frac{z_1 \lambda - z_2}{2z_2} H(x) + \frac{M}{c_{10} - c_{10}^R} \left( H(x) - \ln \frac{c_{10} - c_{10}(x)}{c_{10}} \right).\]

A direct calculation then gives
\[
\phi_1(x) = -\frac{\ln c_{10}^L - \ln c_{10}(x)}{\ln c_{10}^L - \ln c_{10}^R} N + \frac{\phi_0^L - \phi_0^R}{\ln c_{10}^L - \ln c_{10}^R} \left[ \frac{c_{10} - c_{10}(x)}{c_{10}} \left( \frac{c_{11}^L - c_{10}^R}{c_{10}^L - c_{10}^R} \right) + \frac{z_1 \lambda - z_2}{2z_2} \right] M.
\]

Hence,
\[
\frac{(z_1 \lambda - z_2)(c_{10}^L - c_{10}^R)}{2z_2} = \frac{(z_1 \lambda - z_2)H(1)}{H(1)} M.
\]

which gives
\[
\frac{z_1 \lambda - z_2}{2z_2} = \frac{z_1 \lambda - z_2}{2z_2} N.
\]

Formulas for \(J_{11}, J_{21}, \) and \(\phi_1\) follow directly.

The slow orbit
\[(3.21)\]
\[
\Lambda(x; \nu) = (\phi_0(x) + \nu \phi_1(x), c_{10}(x) + \nu c_{11}(x), J_1(\nu), J_2(\nu), \tau(x)) + o(\nu)
\]
given in Lemmas 3.4 and 3.5 connects \(\omega(N_L)\) and \(\alpha(N_R)\). Let \(\bar{M}_L\) (resp., \(\bar{M}_R\)) be the forward (resp., backward) image of \(\omega(N_L)\) (resp., \(\alpha(N_R)\)) under the slow flow (3.12). One has the following result.

**Proposition 3.6.** There exists \(\nu_0 > 0\) small depending on boundary conditions so that, if \(0 \leq \nu \leq \nu_0\), then, on the five-dimensional slow manifold \(S, M_L\) and \(M_R\) intersects transversally along the unique orbit \(\Lambda(x; \nu)\) given in (3.21).

**Proof.** We will establish the transversality of the intersection by showing that \(\omega(N_L) \cdot 1\) (the image of \(\omega(N_L)\) under the time-one map of the flow of system (3.12)) is transversal to \(\alpha(N_R)\) on \(S \cap \{\tau = 1\}\). It consists of the following two steps.

**Step 1:** We will show that, for \(\nu = 0\), \(\omega(N_L) \cdot 1\) and \(\alpha(N_R)\) intersect transversally on \(S \cap \{\tau = 1\}\).

Using \((\phi, c_1, J_1, J_2)\) as a coordinate system on \(S \cap \{\tau = 1\}\), it then follows from (3.17) that, for \(\nu = 0\), \(\omega(N_L) \cdot 1\) is given by
\[
\omega(N_L) \cdot 1 = \{(\phi(J_1, J_2), c_1(J_1, J_2), J_1, J_2) : \text{ arbitrary } J_1, J_2\}
\]
with
\[
\phi(J_1, J_2) = \phi_0^L \frac{z_1 J_1 + z_2 J_2}{z_1^2 + z_2^2} \ln \frac{J_1}{J_1 + J_2} + \frac{z_2 H(1)(J_1 + J_2)}{z_1 - z_2}.
\]

Therefore, the tangent space to \(\omega(N_L) \cdot 1\) restricted on \(S \cap \{\tau = 1\}\) is spanned by the vectors
\[
(\phi_{J_1}, (c_1)_{J_1}, 1, 0) = \left( \frac{z_2 H(1)}{z_1 - z_2}, 1, 0 \right) \quad \text{and} \quad (\phi_{J_2}, (c_1)_{J_2}, 0, 1) = \left( \frac{z_2 H(1)}{z_1 - z_2}, 0, 1 \right).
\]
In view of the display in Proposition 3.2, the set $\alpha(N_R)$ is parameterized by $J_1$ and $J_2$, and hence, the tangent space to $\alpha(N_R)$ restricted on $S \cap \{\tau = 1\}$ is spanned by $(0,0,1,0)$ and $(0,0,0,1)$. Note that $S \cap \{\tau = 1\}$ is four dimensional. Thus, it suffices to show that the above four vectors are linearly independent or, equivalently, $\phi_{J_1} \neq \phi_{J_2}$ at $(J_1, J_2) = (J_{10}, J_{20})$. The latter can be verified by a direct computation as follows:

$$\phi_{J_1} - \phi_{J_2} = -\frac{z_1 - z_2}{z_1 z_2 (J_1 + J_2)} \ln \left[ 1 + \frac{z_2 (J_1 + J_2)}{(z_1 - z_2) c_{10}^0} H(1) \right] \neq 0,$$

even as $J_1 + J_2 \to 0$. This establishes the transversal intersection of $\omega(N_L) \cdot 1$ and $\alpha(N_R)$ on $S \cap \{\tau = 1\}$.

**Step 2:** We show that there exists $\nu_0 > 0$ small, so that, if $0 \leq \nu \leq \nu_0$, then $\omega(N_L) \cdot 1$ and $\alpha(N_R)$ intersect transversally on $S \cap \{\tau = 1\}$.

This can be argued directly from the smooth dependence of solutions on parameter $\nu$. We complete the proof. \hfill \Box

### 3.2. Existence of solutions near the singular orbit.
We have constructed a unique singular orbit on $[0,1]$ that connects $B_L$ to $B_R$. It consists of two boundary layer orbits $\Gamma^0$ from the point

$$(V, u_0 + u_1 \nu + o(\nu), L_1, L_2, J_{10} + J_{11} \nu + o(\nu), J_{20} + J_{21} \nu + o(\nu), 0) \in B_L$$

to the point

$$(\phi^L, 0, c_1^L, c_2^L, J_1, J_2, 0) \in \omega(N_L) \subset \mathcal{Z}$$

and $\Gamma^1$ from the point

$$(\phi^R, 0, c_1^R, c_2^R, J_1, J_2, 1) \in \alpha(N_R) \subset \mathcal{Z}$$

to the point

$$(0, u_0 + u_1 + o(\nu), R_1, R_2, J_{10} + J_{11} \nu + o(\nu), J_{20} + J_{21} \nu + o(\nu), 1) \in B_R,$$

and a regular layer $\Lambda$ on $\mathcal{Z}$ that connects the two landing points

$$(\phi^L, 0, c_1^L, c_2^L, J_1, J_2, 0) \in \omega(N_L) \quad \text{and} \quad (\phi^R, 0, c_1^R, c_2^R, J_1, J_2, 1) \in \alpha(N_R)$$
of the two boundary layers.

We now establish the existence of a solution of (2.8)-(2.9) near the singular orbit constructed above which is a union of two boundary layers and one regular layer $\Gamma^0 \cup \Lambda \cup \Gamma^1$. The proof follows the same line as that in [20, 51, 53, 55], and the main tool used is the Exchange Lemma (see, for example, [12, 44, 45, 46, 52, 54, 78, 79, 85]) of the geometric singular perturbation theory.

**Theorem 3.7.** Let $\Gamma^0 \cup \Lambda \cup \Gamma^1$ be the singular orbit of the connecting problem system (3.1) associated to $B_L$ and $B_R$ in system (3.3). Then, for $\varepsilon > 0$ small and $\nu \geq 0$ small, the boundary value problem (2.8) and (2.9) has a unique smooth solution near the singular orbit.

**Proof.** Let $\nu_0 > 0$ be as in Proposition 3.6. For $0 \leq \nu \leq \nu_0$, denote $u^\prime = u_0^\prime + u_1^\prime \nu$, $J_1(\nu) = J_{10} + J_{11} \nu$, and $J_2(\nu) = J_{20} + J_{21} \nu$. Fix $\delta > 0$ small to be determined. Let

$$B_L(\delta) = \{ (V, u, L_1, L_2, J_1, J_2, 0) \in \mathbb{R}^7 : |u - u^\prime| < \delta, |J_i - J_i(\nu)| < \delta \}.$$ 

For $\varepsilon > 0$, let $M_L(\varepsilon, \delta)$ be the forward trace of $B_L(\delta)$ under the flow of system (3.1) or equivalently of system (3.2) and let $M_R(\varepsilon)$ be the backward trace of $B_R$. To prove the existence and uniqueness statement, it suffices to show that $M_L(\varepsilon, \delta)$
intersects $M_R(\varepsilon)$ transversally in a neighborhood of the singular orbit $\Gamma^0 \cup \Lambda \cup \Gamma^1$. The latter will be established by an application of Exchange Lemmas.

Note that $\dim B_L(\delta) = 3$. It is clear that the vector field of the fast system (3.2) is not tangent to $B$ for $\varepsilon \geq 0$, and hence, $\dim M_L(\varepsilon, \delta) = 4$. We next apply Exchange Lemma to track $M_L(\varepsilon, \delta)$ in the vicinity of $\Gamma^0 \cup \Lambda \cup \Gamma^1$. First of all, the transversality of the intersection $B_L(\delta) \cap W^s(\mathcal{Z})$ along $\Gamma^0$ in Proposition 3.2 implies the transversality of intersection $M_L(0, \delta) \cap W^s(\mathcal{Z})$. Secondly, we have also established that $\dim \omega(N_L) = \dim N_L - 1 = 2$ in Proposition 3.2 and that the limiting slow flow is not tangent to $\omega(N_L)$ in Section 3.1.2. With these conditions, Exchange Lemma ([12, 44, 45, 46, 78, 85]) states that there exist $\rho > 0$ and $\varepsilon_1 > 0$ so that, if $0 < \varepsilon \leq \varepsilon_1$, then $M_L(\varepsilon, \delta)$ will first follow $\Gamma^0$ toward $\omega(N_L) \subset \mathcal{Z}$, then follow the trace of $\omega(N_L)$ in the vicinity of $\Lambda$ toward $\{\tau = 1\}$, leave the vicinity of $\mathcal{Z}$, and, upon exit, a portion of $M_L(\varepsilon, \delta)$ is $C^1 O(\varepsilon)$-close to $W^s(\omega(N_L) \times (1 - \rho, 1 + \rho))$ in the vicinity of $\Gamma^1$. Note that $\dim W^u(\omega(N_L) \times (1 - \rho, 1 + \rho)) = \dim M_L(\varepsilon, \delta) = 4$.

It remains to show that $W^u(\omega(N_L) \times (1 - \rho, 1 + \rho))$ intersects $M_R(\varepsilon)$ transversally since $M_L(\varepsilon, \delta) = C^1 O(\varepsilon)$-close to $W^u(\omega(N_L) \times (1 - \rho, 1 + \rho))$. Recall that, for $\varepsilon = 0$, $M_R$ intersects $W^u(\mathcal{Z})$ transversally along $N_R$ (Proposition 3.2); in particular, at $\gamma_1 := \alpha(\Gamma^1) \in \alpha(N_R) \subset \mathcal{Z}$, we have

$$T_{\gamma_1} M_R = T_{\gamma_1} \alpha(N_R) + T_{\gamma_1} W^u(\gamma_1) + \text{span}\{V_\tau\}$$

where, $T_{\gamma_1} W^u(\gamma_1)$ is the tangent space of the one-dimensional unstable fiber $W^u(\gamma_1)$ at $\gamma_1$ and the vector $V_\tau \notin T_{\gamma_1} W^u(\mathcal{Z})$ (the latter follows from the transversality of the intersection of $M_R$ and $W^u(\mathcal{Z})$).

Also,

$$T_{\gamma_1} W^u(\omega(N_L) \times (1 - \rho, 1 + \rho)) = T_{\gamma_1} (\omega(N_L) \cdot 1) + \text{span}\{V_\tau\} + T_{\gamma_1} W^u(\gamma_1)$$

where the vector $V_\tau$ is the tangent vector to the $\tau$-axis as the result of the interval factor $(1 - \rho, 1 + \rho)$. Recall from Proposition 3.6 that $\omega(N_L) \cdot 1$ and $\alpha(N_R)$ are transversal on $\mathcal{Z}$ and $\{\tau = 1\}$. Therefore, at $\gamma_1$, the tangent spaces $T_{\gamma_1} M_R$ and $T_{\gamma_1} W^u(\omega(N_L) \times (1 - \rho, 1 + \rho))$ contain seven linearly independent vectors: $V_s, V_\tau, T_{\gamma_1} W^u(\gamma_1)$ and the other four from $T_{\gamma_1} (\omega(N_L) \cdot 1)$ and $T_{\gamma_1} \alpha(N_R)$; that is, $M_R$ and $W^u(\omega(N_L) \times (1 - \rho, 1 + \rho))$ intersect transversally. We thus conclude that, there exists $0 < \varepsilon_0 \leq \varepsilon_1$ so that, if $0 < \varepsilon \leq \varepsilon_0$, then $M_L(\varepsilon, \delta)$ intersects $M_R(\varepsilon)$ transversally.

For uniqueness, note that the transversality of the intersection $M_L(\varepsilon, \delta) \cap M_R(\varepsilon)$ implies $\dim(M_L(\varepsilon, \delta) \cap M_R(\varepsilon)) = \dim M_L(\varepsilon, \delta) + \dim M_R(\varepsilon) = 7$. Thus, there exists $\delta_0 > 0$ such that, if $0 < \delta \leq \delta_0$, the intersection $M_L(\varepsilon, \delta) \cap M_R(\varepsilon)$ consists of precisely one solution near the singular orbit $\Gamma^0 \cup \Lambda \cup \Gamma^1$. 

4. Ion size effects on individual fluxes and on the current. The analysis in the previous sections not only establishes the existence of solutions for BVP (2.8)-(2.9) but also provides sufficiently quantitative information on the solution that allows us to extract useful approximations to the individual fluxes $J_i$’s and the total flux of charge (current) $I$ for small $\nu$.

In this section, we will study ion size effects on the individual fluxes $J_i$’s as well as the I-V relations. Contributions to $I$ from $J_{k1}$ are carefully examined, which provide detailed information on how different ion species interact within ion channels.

We express the flux $J_i$ as

$$J_i(V; \lambda, \varepsilon, \nu) = J_{10}(V; \varepsilon) + J_{11}(V; \lambda, \varepsilon, \nu) + o(\nu), \quad (4.1)$$
and the I-V relations defined in (2.11) as
\[ I(V; \lambda, \varepsilon, \nu) = I_0(V; \varepsilon) + I_1(V; \lambda, \varepsilon) \nu + o(\nu). \tag{4.2} \]

The term \( I_0(V; \varepsilon) \) (resp. \( J_{i0} \)) is the I-V relations (resp. the individual flux) without counting the ion size effect, and \( I_1(V; \lambda, \varepsilon) \) (resp. \( J_{i1} \)) is the main term providing effects on the I-V relation (resp. the individual flux) from ion sizes.

We comment that, in (4.1) and (4.2), \( J_i, J_{i0}, J_{i1}, I, I_0 \) and \( I_1 \) all depend on \( L_1, L_2, R_1 \) and \( R_2 \) too.

### 4.1 Ion size effects on individual fluxes \( J_i \)'s

We introduce two functions \( F_1 = F_1(L_1, L_2; R_1, R_2; \lambda) \) and \( F_2 = F_2(L_1, L_2; R_1, R_2; \lambda) \) as
\[
F_1 = \frac{1}{H(1)(\ln c_1^{l0} - \ln c_1^{R0})} \left( \frac{H(1)F_2 + z_1(c_1^{l0} - c_1^{R0})(R_1 - L_1 + \lambda(R_2 - L_2))}{\ln c_1^{l0} - \ln c_1^{R0}} \right),
\]
\[
F_2 = \frac{c_1^{l0}(L_1 + \lambda L_2) - c_1^{R0}(R_1 + \lambda R_2)}{H(1)} + \frac{z_1 \lambda - z_2}{2z_2 H(1)} (c_1^{l0} - c_1^{R0})(c_1^{l0} + c_1^{R0}),
\]
where \( H(1) = \int_0^1 h^{-1}(s) \, ds \) in (3.16). We have

**Corollary 4.1.** In (4.1),
\[
J_{10}(V; 0) = \frac{D_1(c_1^{l0} - c_1^{R0})}{H(1)} + \frac{z_1 D_1(c_1^{l0} - c_1^{R0})(\ln(L_1 R_2) - \ln(L_2 R_1))}{(z_1 - z_2) H(1)(\ln c_1^{l0} - \ln c_1^{R0})} + \frac{z_1 D_1(c_1^{l0} - c_1^{R0})}{z_2 H(1)} e^{k_B T V},
\]
\[
J_{20}(V; 0) = -\frac{z_1 J_1}{z_2 H(1)} - \frac{z_1 J_1}{z_2 H(1)} e^{k_B T V},
\]
\[
J_{11}(V; 0) = D_1 \left( \frac{F_1}{z_1 - z_2} + \frac{H(1)\ln(L_1 R_2) - \ln(L_2 R_1)}{z_1 - z_2} F_1 \right),
\]
\[
J_{21}(V; 0) = D_2 \left( -\frac{F_1}{z_1 - z_2} + \frac{H(1)\ln(L_1 R_2) - \ln(L_2 R_1)}{z_1 - z_2} F_1 \right),
\]
where \( c_1^{l0} \) and \( c_1^{R0} \) are given in Proposition 3.2.

Under electroneutrality boundary conditions (3.9), one has,
\[
J_{10} = \frac{D_1(L - R)}{z_1 H(1)(\ln L - \ln R)} \left( z_1 \frac{e}{k_B T} V + \ln L - \ln R \right), \quad J_{20} = \frac{D_2(L - R)}{z_2 H(1)(\ln L - \ln R)} \left( z_2 \frac{e}{k_B T} V + \ln L - \ln R \right),
\]
\[
J_{11} = \frac{D_1(z_1 \lambda - z_2)}{z_1 z_2 H(1)} e^{k_B T V} - \frac{D_1(z_1 \lambda - z_2)(L^2 - R^2)}{2z_1 z_2 H(1)},
\]
\[
J_{21} = -\frac{D_2(z_1 \lambda - z_2)}{z_1 z_2 H(1)} e^{k_B T V} + \frac{D_2(z_1 \lambda - z_2)(L^2 - R^2)}{2z_1 z_2 H(1)},
\]
where
\[
\gamma_0(L, R) = \frac{L - R}{\ln L - \ln R}, \quad \gamma_1(L, R) = \frac{L - R}{\ln L - \ln R} - \frac{L + R}{2}. \tag{4.3}
\]

**Proof.** From \( J_k = D_k J_{k0} + D_k J_{k1} \nu + o(\nu) \), one has
\[
J_{k0}(V; 0) = D_k J_{k0}(V; 0) \quad \text{and} \quad J_{k1}(V; 0) = D_k J_{k1}(V; 0).
\]
The formulas then follow directly from Lemmas 3.4 and 3.5. The conclusion under electroneutrality boundary conditions (3.9) then follows from Proposition 3.2 and Corollary 4.1.

**Remark 4.2.** We stress that the linear dependence of \( J_{i0} \)'s and \( J_{i1} \)'s on \( V \) in Corollary 4.1 is due to the fact that they are zeroth order approximations in \( \varepsilon \) of the corresponding quantities with zero permanent charge. In general, they are nonlinear when permanent charge is non-zero (see, e.g., [43]) and, even with zero permanent charge, higher order terms are not linear in \( V \) (see, e.g., [1, 87]).

For the functions defined in (4.3), we have

**Lemma 4.3.** If \( L \neq R \), then \( \gamma_0(L, R) > 0 \) and \( \gamma_1(L, R) < 0 \). As \( |L - R| \to 0 \) with \( R \) being fixed,

\[
\gamma_0(L, R) \to R \quad \text{and} \quad \gamma_1(L, R) \to 0.
\]

**Proof.** The proof is straightforward.

Based on the approximations for \( J_i \)'s in Corollary 4.1, we define four critical potentials and discuss their roles in characterizing ion size effects on individual fluxes.

**Definition 4.4.** We define four potentials \( V_{1c}, V_{2c}, V^{1c} \) and \( V^{2c} \) by

\[
J_{11}(V_{1c}; \lambda, 0) = J_{21}(V_{2c}; \lambda, 0) = \frac{d}{d \lambda} J_{11}(V^{1c}; \lambda, 0) = \frac{d}{d \lambda} J_{21}(V^{2c}; \lambda, 0) = 0.
\]

**Corollary 4.5.** Suppose \( c^{L}_{10} \neq c^{R}_{10} \). One has

\[
\begin{align*}
V_{1c} &= -\frac{k_B T}{e} \left( \frac{\ln(L_1 R_2) - \ln(L_2 R_1)}{z_1 - z_2} + \frac{\mathcal{F}_2}{\mathcal{F}_1} \right), \\
V_{2c} &= -\frac{k_B T}{e} \left( \frac{\ln(L_1 R_2) - \ln(L_2 R_1)}{z_1 - z_2} + z_1 \frac{\mathcal{F}_2}{\mathcal{F}_1} \right), \\
V^{1c} &= -\frac{k_B T}{e} \left( \frac{\ln(L_1 R_2) - \ln(L_2 R_1)}{z_1 - z_2} + \frac{\ln c^{L}_{10} - \ln c^{R}_{10}}{z_1 \left( \mathcal{G}_0 + (R_2 - L_2)(c^{L}_{10} - c^{R}_{10}) \right)} \right), \\
V^{2c} &= -\frac{k_B T}{e} \left( \frac{\ln(L_1 R_2) - \ln(L_2 R_1)}{z_1 - z_2} + \frac{\ln c^{L}_{10} - \ln c^{R}_{10}}{z_2 \left( \mathcal{G}_0 + (R_2 - L_2)(c^{L}_{10} - c^{R}_{10}) \right)} \right),
\end{align*}
\]

where

\[
\mathcal{G}_0 = (\ln c^{L}_{10} - \ln c^{R}_{10}) \left( L_2 c^{L}_{c10} - R_2 c^{R}_{10} + \frac{z_1}{2z_2} (c^{L}_{10} - c^{R}_{10})(c^{L}_{10} + c^{R}_{10}) \right).
\]

Under the electroneutrality boundary conditions (3.9) and \( L \neq R \), one has,

\[
V_{1c} = V^{1c} = \frac{k_B T}{e} \frac{L_2 - R_2}{2z_2 \gamma_0(L, R) \gamma_1(L, R)}, \quad V_{2c} = V^{2c} = \frac{k_B T}{e} \frac{L_2 - R_2}{2z_2 \gamma_0(L, R) \gamma_1(L, R)}.
\]

**Proof.** The statements follow from Corollary 4.1 and Definition 4.4.

**Remark 4.6.** It follows from Corollary 4.5 that \( V_{kc} \neq V^{kc} \) and \( V_{kc} \) depends on \( \lambda \) in general, but, under electroneutrality boundary conditions, \( V_{kc} = V^{kc} \) and \( V_{kc} \) is independent of \( \lambda \).
The significance of the four critical values \( V_{1c}, V_{2c}, V_{1c}^* \) and \( V_{2c}^* \) is apparent from their definitions. The value \( V_{1c} \) and \( V_{2c} \) are the potentials that balance the ion size effects on individual fluxes, and the values \( V_{1c}^* \) and \( V_{2c}^* \) are the potentials that separate the relative size effects on individual fluxes. More precisely,

**Theorem 4.7.** Suppose \( \frac{\partial \mathcal{J}_{k_1}}{\partial \lambda}(V; \lambda, 0) > 0 \) (resp. \( \frac{\partial \mathcal{J}_{k_1}}{\partial \lambda}(V; \lambda, 0) < 0 \)). For small \( \varepsilon > 0 \) and \( \nu > 0 \), one has

(i) if \( V > V_{k_1} \) (resp. \( V < V_{k_1} \)), then \( \mathcal{J}_{k_1}(V; \varepsilon, \nu) > \mathcal{J}_{k_1}(V; \varepsilon, 0) \) (resp. \( \mathcal{J}_{k_1}(V; \varepsilon, \nu) < \mathcal{J}_{k_1}(V; \varepsilon, 0) \));

(ii) if \( V < V_{k_1} \) (resp. \( V > V_{k_1} \)), then \( \mathcal{J}_{k_1}(V; \varepsilon, \nu) < \mathcal{J}_{k_1}(V; \varepsilon, 0) \) (resp. \( \mathcal{J}_{k_1}(V; \varepsilon, \nu) > \mathcal{J}_{k_1}(V; \varepsilon, 0) \)).

**Theorem 4.8.** Suppose \( \frac{\partial^2 \mathcal{J}_{k_1}}{\partial \lambda^2}(V; \lambda, 0) > 0 \) (resp. \( \frac{\partial^2 \mathcal{J}_{k_1}}{\partial \lambda^2}(V; \lambda, 0) < 0 \)). For small \( \varepsilon > 0 \) and \( \nu > 0 \), one has

(i) if \( V > V_{k_1}^c \) (resp. \( V < V_{k_1}^c \)), then \( \mathcal{J}_{k_1} \) is increasing (resp. decreasing) \( \lambda \);

(ii) if \( V < V_{k_1}^c \) (resp. \( V > V_{k_1}^c \)), then \( \mathcal{J}_{k_1} \) is decreasing (resp. increasing) \( \lambda \).

Concerning the conditions in Theorems 4.7 and 4.8, the following result can be easily checked.

**Lemma 4.9.** Assume electroneutrality boundary conditions (3.9) with \( L \neq R \). One has, for \( k = 1, 2 \), \( \partial \mathcal{V} \mathcal{J}_{k_1} > 0 \) and \( \partial^2 \mathcal{V} \mathcal{J}_{k_1} > 0 \). As \( L \to R \), \( \partial \mathcal{V} \mathcal{J}_{k_1} \to 0 \) and \( \partial^2 \mathcal{V} \mathcal{J}_{k_1} = O((L - R)^2) \).

4.2. **Ion size effects on the current \( I \).** We analyze ion size effects on the I-V relations following the outline as that in [51].

**Corollary 4.10.** In formulas (4.2), one has

\[
\mathcal{I}_0(V; 0) = \frac{z_1(z_1 D_1 - z_2 D_2)(c_{10}^L - c_{10}^R)(\ln(L_1 R_2) - \ln(L_2 R_1))}{H(1)(\ln c_{10}^L - \ln c_{10}^R)} + \frac{z_1(z_1 D_1 - z_2 D_2)(c_{10}^L - c_{10}^R)}{H(1)(\ln c_{10}^L - \ln c_{10}^R)} e \frac{10}{k_B T} V,
\]

\[
\mathcal{I}_1(V; 0) = \frac{z_1(z_1 \lambda - z_2)(D_1 - D_2)}{z_2 H(1)} \left( c_{10}^R R_1 - c_{10}^L L_1 + \frac{1}{2} (c_{10}^L + c_{10}^R)(c_{10}^L - c_{10}^R) \right) + \frac{z_1(z_1 \lambda - z_2)(z_1 D_1 - z_2 D_2)(c_{10}^L - c_{10}^R)}{z_2 H(1)(\ln c_{10}^L - \ln c_{10}^R)} \left( \frac{c_{10}^L R_1 - c_{10}^L L_1}{c_{10}^L - c_{10}^R} + \frac{c_{10}^L + c_{10}^R}{2} \right) \frac{10}{k_B T} V,
\]

where \( c_{10}^L \) and \( c_{10}^R \) are given in Proposition 3.2.

Under electroneutrality boundary conditions (3.9), one has

\[
\mathcal{I}_0(V; 0) = \frac{(D_1 - D_2)(L - R)}{H(1)} + \frac{z_1(z_1 D_1 - z_2 D_2)}{H(1)} e \frac{10}{k_B T} V,
\]

\[
\mathcal{I}_1(V; \lambda, 0) = - \frac{(z_1 \lambda - z_2)(D_1 - D_2)(L^2 - R^2)}{2 z_1 z_2 H(1)} + \frac{(z_1 \lambda - z_2)(z_1 D_1 - z_2 D_2)}{z_1 z_2 H(1)} e \frac{10}{k_B T} V.
\]
In particular, as $L \to R$, one has
\[
    \mathcal{I}_0(V;0) \to \frac{(z_1D_1 - z_2D_2)L}{H(1)} e V \quad \text{and} \quad \mathcal{I}_1(V;\lambda,0) \to 0.
\]

Proof. It follows from
\[
    \mathcal{I}(V;\lambda,0,\nu) = z_1J_1 + z_2J_2 = z_1D_1J_1 + z_2D_2J_2
\]
\[
    = (z_1D_1J_{10} + z_2D_2J_{20}) + (z_1D_1J_{11} + z_2D_2J_{21})\nu + o(\nu)
\]
that
\[
    \mathcal{I}_0(V;0) = z_1J_{10} + z_2J_{20}, \quad \mathcal{I}_1(V;\lambda,0) = z_1J_{11} + z_2J_{21}.
\]

The formulas for $\mathcal{I}_0(V;0)$ and $\mathcal{I}_1(V;0)$ follow directly from Lemmas 3.4 and 3.5. $\square$

Similar to Remark 4.2, the zeroth order (in $\epsilon$) approximation of I-V relation in Corollary 4.10 under the setup of this paper is linear in $V$. In general, the I-V relation is not linear in $V$.

We next define three critical potentials $V_0, V_c$ and $V^c$, which play an important role in characterizing the effect on the I-V relation from ion sizes.

**Definition 4.11.** We define three potentials $V_0$, $V_c$ and $V^c$ by
\[
    \mathcal{I}_0(V_0;0) = 0, \quad \mathcal{I}_1(V_c;\lambda,0) = 0, \quad \frac{d}{d\lambda} \mathcal{I}_1(V^c;\lambda,0) = 0.
\]

From Definition 4.11, we obtain

**Proposition 4.12.** The potentials $V_0$, $V_c$ and $V^c$ have the following expressions
\[
    V_0 = -\frac{k_B T}{e} \left( \frac{D_1 - D_2}{z_1D_1 - z_2D_2} (\ln c_1^L - \ln c_1^R) + \ln(L_1R_2) - \ln(L_2R_1) \right),
\]
\[
    V_c = V^c = -\frac{k_B T}{e} \left( \frac{D_1 - D_2}{z_1D_1 - z_2D_2} (\ln c_1^L - \ln c_1^R) \left( \frac{c_1^L - c_1^R}{c_1^L - c_1^R} \right) \right).
\]

Under electroneutrality conditions (3.9) and $L \neq R$, one has
\[
    V_0 = -\frac{k_B T}{e} \frac{D_1 - D_2}{z_1D_1 - z_2D_2} (\ln L - \ln R),
\]
\[
    V_c = k_B T \frac{(D_1 - D_2)(L^2 - R^2)}{2(z_1D_1 - z_2D_2)g_0(L,R)g_1(L,R)}.
\]

For the LHS used in [51], $V_c \neq V^c$ in general. In the following, we will use the notion $V_c$ for Bikerman’s LHS taken in this paper.

As a direct consequence of Proposition 4.12, one has

**Corollary 4.13.** Assume electroneutrality boundary conditions (3.9). Then
\(\text{(i)}\) $V_0(L,R) = -V_0(R,L)$ and $V_c(L,R;\lambda) = -V_c(R,L;\lambda)$;
\(\text{(ii)}\) for $L \geq R$, $V_0(L,R)$ is decreasing (resp. increasing) in $L$ if $D_1 > D_2$ (resp. $D_1 < D_2$), and, for fixed $R > 0$, $\lim_{L \to R} V_0(L,R) = 0$;
\(\text{(iii)}\) for fixed $R > 0$,
\[
    \lim_{L \to R} V_c(\ln L - \ln R) = -\frac{12k_B T}{e} \frac{D_1 - D_2}{z_1D_1 - z_2D_2};
\]
\[
    \lim_{L \to \infty} \frac{V_c}{\ln L - \ln R} = -\frac{k_B T}{e} \frac{D_1 - D_2}{z_1D_1 - z_2D_2}.
\]
A direct observation gives the following result:

**Theorem 4.14.** Treating $I_0$, $I_1$, $V_0$, and $V_c$ as functions of $(L_1, L_2, R_1, R_2)$, one has

(i) $I_0$ is homogeneous of degree one, that is, for any $s > 0$,

\[ I_0(V, sL_1, sL_2, sR_1, sR_2; 0) = sI_0(V, L_1, L_2, R_1, R_2; 0). \]

(ii) $I_1$ is homogeneous of degree two, that is, for any $s > 0$,

\[ I_1(V, sL_1, sL_2, sR_1, sR_2; 0) = s^2I_1(V, L_1, L_2, R_1, R_2; 0). \]

(iii) The potentials $V_0$ and $V_c$ are homogeneous of degree zero.

The potential $V_0$ is the so-called reversal potential. The value $V_c$ is the potential that balances ion size effect on I-V relations and the value $V^c$ is the potential that separates the relative size effect on I-V relations. Precise statements are provided as follows:

**Theorem 4.15.** Suppose $\partial_V I_1(V; \lambda, 0) > 0$ (resp. $\partial_V I_1(V; \lambda, 0) < 0$). For small $\varepsilon > 0$ and $\nu > 0$,

(i) If $V > V_c$ (resp. $V < V_c$), then $I(V; \varepsilon, \nu) > I(V; \varepsilon, 0)$;

(ii) If $V < V_c$ (resp. $V > V_c$), then $I(V; \varepsilon, \nu) < I(V; \varepsilon, 0)$.

Similarly,

**Theorem 4.16.** Suppose $\partial_{V}^2 I_1(V; \lambda, 0) > 0$ (resp. $\partial_{V}^2 I_1(V; \lambda, 0) < 0$). For small $\varepsilon > 0$ and $\nu > 0$,

(i) If $V > V_c$ (resp. $V < V_c$), then the current $I$ is increasing $\lambda$;

(ii) If $V < V_c$ (resp. $V > V_c$), then the current $I$ is decreasing $\lambda$.

The following result can be checked easily.

**Proposition 4.17.** Assume electroneutrality boundary conditions (3.9) with $L \neq R$. Then, $\partial_V I_1(V; \lambda, 0) > 0$. As $L \rightarrow R$, $\partial_V I_1(V; \lambda, 0) \rightarrow 0$. \[\Box\]

While $\partial_V I_1(V; \lambda, 0)$ is non-negative under electroneutrality conditions, in general, it can be negative, as shown in the following example motivated by that in [51]. We consider a special case with $z_1 = 1$ and $z_2 = -1$. Correspondingly, we have $c_{10}^l = \sqrt{L_1} L_2$ and $c_{10}^r = \sqrt{R_1} R_2$.

**Proposition 4.18.** Fix $L_2 > 0$. If either $R_2 \geq R_1 \geq L_1 > 0$ and $\sqrt{L_1L_2} > \sqrt{R_1R_2}$, or $R_1 \geq L_1$, $R_2 < R_1$ and $\sqrt{L_1L_2} > \mu^* \sqrt{R_1R_2}$, where $\mu^* > 1$ is a constant, then

\[ \partial_V I_1(V; \lambda, 0) = -\frac{e}{k_BT} \frac{(\lambda + 1)(D_1 + D_2)(\sqrt{L_1L_2} - \sqrt{R_1R_2})}{H(1)\left(\ln(L_1L_2) - \ln(R_1R_2)\right)} K(L_1, L_2, R_1, R_2) \]

is negative, where

\[ K(L_1, L_2, R_1, R_2) = \frac{L_1 - R_1}{\ln(L_1L_2) - \ln(R_1R_2)} - \frac{L_1\sqrt{L_1L_2} - R_1\sqrt{R_1R_2}}{\sqrt{L_1L_2} - \sqrt{R_1R_2}} \]

\[ + \frac{\sqrt{L_1L_2} + \sqrt{R_1R_2}}{2}. \]  

**Proof.** Note that

\[ \frac{e(D_1 + D_2)}{k_BT H(1)} > 0, \; \lambda > 0, \text{ and } \frac{\sqrt{L_1L_2} - \sqrt{R_1R_2}}{\ln(L_1L_2) - \ln(R_1R_2)} > 0, \text{ for } L_1L_2 \neq R_1R_2, \]

it is suffice to show that $K(L_1, L_2, R_1, R_2) > 0$.  

\[ \Box \]
For simplicity, we set
\[ \sqrt{L_1 L_2} = \mu \sqrt{R_1 R_2}, \tag{4.6} \]
where \( \mu > 0 \), but \( \mu \neq 1 \). Substituting (4.6) into equation (4.5), we have
\[ \mathcal{K}(L_1, L_2, R_1, R_2) = \frac{h(\mu)}{2(\mu - 1) \ln \mu}, \tag{4.7} \]
where
\[ h(\mu) = (L_1 - R_1)(\mu - 1) + 2(R_1 - L_1 \mu) \ln \mu - \sqrt{R_1 R_2}(1 - \mu^2) \ln \mu. \]
Notice that \( 2(\mu - 1) \ln \mu > 0 \), for \( \mu > 0 \), but \( \mu \neq 1 \). Now we claim that \( h(\mu) > 0 \).

To get started, a simple calculation gives
\[ h'(\mu) = R_1 \left( \frac{2}{\mu} - 1 \right) - L_1 (1 + 2 \ln \mu) + \sqrt{R_1 R_2} \left( 2\mu \ln \mu + \mu - \frac{1}{\mu} \right). \]

**Case I:** \( R_2 \geq R_1 \geq L_1 > 0 \), and \( \mu > 1 \).

Under the assumption of case 1, one has \( h'(\mu) > h_0(\mu) R_1 \), where
\[ h_0(\mu) = \frac{1}{\mu} - 2 - 2 \ln \mu + 2\mu \ln \mu + \mu. \]
A careful calculation gives
\[ h_0(1) = h'_0(1) = 0, \quad \text{and} \quad h''_0(\mu) = \frac{2}{\mu} \left( 1 + \frac{1}{\mu} + \frac{1}{\mu^2} \right) > 0, \quad \text{for} \quad \mu > 1. \]
And hence, \( h'(\mu) > 0 \) for \( \mu > 1 \). Together with \( h(1) = 0 \), we have \( h(\mu) > 0 \) for \( \mu > 1 \). Therefore, \( \mathcal{K}(L_1, L_2, R_1, R_2) > 0 \).

**Case II:** \( R_1 \geq L_1, \quad R_2 < R_1, \quad \text{and} \quad \mu > \mu^* > \mu_0 > 1 \).

For convenience, we define \( R_2 = a R_1 \), where \( 0 < a < 1 \). Then, we have
\[ h'(\mu) > g(\mu) R_1 \quad \text{with} \quad g(\mu) = \frac{2 - \sqrt{a}}{\mu} + a \mu + 2 \sqrt{a} \mu \ln \mu - 2 \ln \mu - 2. \]
Direct calculations give
\[ g'(\mu) = \frac{\sqrt{a} - 2}{\mu^2} + 2 \sqrt{a} \ln \mu - \frac{2}{\mu} + 3 \sqrt{a} \quad \text{and} \quad g''(\mu) = \frac{2 - \sqrt{a}}{2\mu^3} + \frac{2 \sqrt{a}}{\mu} + \frac{2}{\mu^2}. \]
Clearly, one has \( g''(\mu) > 0 \), for all \( \mu > 1 \). And hence, \( g'(\mu) \) is increasing for \( \mu > 1 \). Note that \( g'(1) < 0 \), and \( g'(\mu) \to \infty \) as \( \mu \to \infty \). There exists a unique \( \mu_0 > 0 \) such that \( g'(\mu_0) = 0 \). Furthermore, \( g(\mu) \) is decreasing for \( 1 < \mu < \mu_0 \) and increasing for \( \mu > \mu_0 \). Note that \( g(1) = 0 \), we have \( g(\mu_0) < 0 \), and there exists a unique \( \mu^* > \mu_0 \) such that \( g(\mu^*) = 0 \), and \( g(\mu) > 0 \) for \( \mu > \mu^* \). This completes the proof. \( \square \)

4.3. **Individual fluxes vs the current.** The critical potential \( V_c \) is directly related to \( V_{k_k} \) and \( V^{k_k}, \ k = 1, 2 \). For simplicity, from now on, we always assume the electroneutrality boundary conditions (3.9).

Recall that, under electroneutrality boundary conditions, \( V_{k_k} = V^{k_k} \). We thus use \( V_{k_k} \) in the following. The next result follows from Corollary 4.5 and Proposition 4.12.

**Lemma 4.19.** Assume electroneutrality conditions (3.9). Then
\[ V_c = \frac{z_1 D_1 V_{k_k} - z_2 D_2 V_{k_k}}{z_1 D_1 - z_2 D_2}. \]
For fixed $D_1$, $D_2$, $L$, and $R$, one can immediately characterize ion size effects on the individual fluxes $J_i$’s and the current $I$, depending on the relative locations of $V_c$, $V_{1c}$, $V_{2c}$, and where the boundary potential $V$ is located. We will provide the result only for the cases $D_1 > D_2$. The statements for other cases can be made similarly.

**Theorem 4.20.** Assume electroneutrality conditions (3.9). Suppose $\lambda \neq 1$, and $D_1 > D_2$ and $L < R$. Then,

$$V_c > V_{1c} > V_{2c}.$$

Hence, for small $\varepsilon > 0$ and $\nu > 0$,

(i) if $V > V_c$, then ion sizes enhance $J_1$, $J_2$ and $I$, that is,

$$J_1(V; \varepsilon, \nu) > J_1(V; \varepsilon, 0), \quad J_2(V; \varepsilon, \nu) > J_2(V; \varepsilon, 0), \quad I(V; \varepsilon, \nu) > I(V; \varepsilon, 0);$$

(ii) if $V_{1c} < V < V_c$, then ion sizes enhance $J_1$ and $J_2$ but reduce $I$, that is,

$$J_1(V; \varepsilon, \nu) > J_1(V; \varepsilon, 0), \quad J_2(V; \varepsilon, \nu) > J_2(V; \varepsilon, 0), \quad I(V; \varepsilon, \nu) < I(V; \varepsilon, 0);$$

(iii) if $V_2 < V < V_{1c}$, then ion sizes enhance $J_2$ but reduce $J_1$ and $I$, that is,

$$J_1(V; \varepsilon, \nu) < J_1(V; \varepsilon, 0), \quad J_2(V; \varepsilon, \nu) > J_2(V; \varepsilon, 0), \quad I(V; \varepsilon, \nu) < I(V; \varepsilon, 0);$$

(iv) if $V < V_{2c}$, then ion sizes reduce $J_1$, $J_2$ and $I$, that is,

$$J_1(V; \varepsilon, \nu) < J_1(V; \varepsilon, 0), \quad J_2(V; \varepsilon, \nu) < J_2(V; \varepsilon, 0), \quad I(V; \varepsilon, \nu) < I(V; \varepsilon, 0).$$

**Proof.** The relation among $V_c$, $V_{1c}$, and $V_{2c}$ follows from Corollary 4.5, Proposition 4.12, Lemma 4.19, and the assumption that $D_1 > D_2$ and $L < R$.

The statements (i)–(iv) then follow from Theorems 4.7 and 4.15.

**Remark 4.21.** For cases (i) and (ii) in Theorem 4.20, ion size effects on individual fluxes $J_1$ and $J_2$ are the same, but their effects on the current $I$ are opposite. For cases (iii) and (iv), ion size effects on the flux $J_2$ are opposite, but their effects on the flux $J_1$ and the current $I$ are the same.

Similarly, one has

**Theorem 4.22.** Assume electroneutrality conditions (3.9). Suppose $\lambda \neq 1$, and $D_1 > D_2$ and $L > R$. Then,

$$V_c < V_{1c} < V_{2c}.$$

Hence, for small $\varepsilon > 0$ and $\nu > 0$,

(i) if $V < V_c$, then ion sizes reduce $J_1$, $J_2$ and $I$, that is,

$$J_1(V; \varepsilon, d) < J_1(V; \varepsilon, 0), \quad J_2(V; \varepsilon, d) < J_2(V; \varepsilon, 0), \quad I(V; \varepsilon, d) < I(V; \varepsilon, 0);$$

(ii) if $V_c < V < V_{1c}$, then ion sizes reduce $J_1$ and $J_2$ but enhance $I$, that is,

$$J_1(V; \varepsilon, d) < J_1(V; \varepsilon, 0), \quad J_2(V; \varepsilon, d) < J_2(V; \varepsilon, 0), \quad I(V; \varepsilon, d) > I(V; \varepsilon, 0);$$

(iii) if $V_{1c} < V < V_{2c}$, then ion sizes reduce $J_2$ but enhance $J_1$ and $I$, that is,

$$J_1(V; \varepsilon, d) < J_1(V; \varepsilon, 0), \quad J_2(V; \varepsilon, d) > J_2(V; \varepsilon, 0), \quad I(V; \varepsilon, d) > I(V; \varepsilon, 0);$$

(iv) if $V_2 < V < V_{1c}$, then ion sizes enhance $J_1$, $J_2$ and $I$, that is,

$$J_1(V; \varepsilon, d) > J_1(V; \varepsilon, 0), \quad J_2(V; \varepsilon, d) > J_2(V; \varepsilon, 0), \quad I(V; \varepsilon, d) > I(V; \varepsilon, 0).$$

The effects of relative ion size $\lambda$ on ionic flows can also be derived directly. Recall that under electroneutrality conditions (3.9), we have $V_{ic} = V_{ie}^i$ for $i = 1, 2$. 

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Theorem 4.23. Assume electroneutrality conditions (3.9). Suppose $D_1 > D_2$ and $L < R$. Then,

$$V_c > V_{1c} > V_{2c}.$$ 

Hence, for small $\varepsilon > 0$ and $\nu > 0$, one has

(i) if $V > V_c$, then $J_1$, $J_2$ and $I$ increase in $\lambda$;
(ii) if $V_{1c} < V < V_c$, then $J_1$ and $J_2$ increase in $\lambda$ but $I$ decreases in $\lambda$;
(iii) if $V_{2c} < V < V_{1c}$, then $J_1$ and $I$ decrease in $\lambda$ but $J_2$ increases in $\lambda$;
(iv) if $V < V_{2c}$, then $J_1$, $J_2$ and $I$ decrease in $\lambda$.

Similarly,

Theorem 4.24. Assume electroneutrality conditions (3.9). Suppose $D_1 > D_2$ and $L > R$. Then,

$$V_c < V_{1c} < V_{2c}.$$ 

Hence, for small $\varepsilon > 0$ and $\nu > 0$, one has

(i) if $V < V_c$, then $J_1$, $J_2$ and $I$ decrease in $\lambda$;
(ii) if $V_c < V < V_{1c}$, then $z_1J_1$ and $J_2$ decrease in $\lambda$ but $I$ increases in $\lambda$;
(iii) if $V_{1c} < V < V_{2c}$, then $J_1$ and $I$ increase in $\lambda$ but $J_2$ decreases in $\lambda$;
(iv) if $V > V_{2c}$, then $J_1$, $J_2$ and $I$ increase in $\lambda$.

4.4. Sensitivity of ion size effects near $L = R$. We examine closely the situation for $L$ and $R$ close to each other. It turns out, in this situation, the properties of the critical potentials are extremely sensitive on whether $L > R$ or $L < R$.

Proposition 4.25. One has,

$$\lim_{L \to R^+} V_{1c} = \lim_{L \to R^-} V_{2c} = -\infty, \quad \lim_{L \to R^+} V_{1c} = \lim_{L \to R^-} V_{2c} = +\infty.$$

Proof. From Lemma 4.3, one has

$$\lim_{L \to R^+} \frac{L^2 - R^2}{\gamma_0(L,R)\gamma_1(L,R)} = -\infty \quad \text{and} \quad \lim_{L \to R^-} \frac{L^2 - R^2}{\gamma_0(L,R)\gamma_1(L,R)} = \infty.$$

Recall that $z_1 > 0 > z_2$. Our results then follow directly from Corollary 4.5. \qed

The significance of the above result is discussed in the next remark.

Remark 4.26. Combining this result with Theorems 4.20 and Theorems 4.22, one concludes that the effects of ion sizes are sensitive to whether $L > R$ or $L < R$ for $L$ and $R$ close. More precisely, on one hand, as $L \to R^-$, one has $V_{2c} < V < V_{1c}$ for any fixed potential $V$, and hence, ion sizes always reduce $J_1$ (comparing to $J_1$ from point-charge case) but enhance $J_2$ (see, (iii) in Theorem 4.20); on the other hand, as $L \to R^+$, exactly the opposite occurs, that is, one has $V_{2c} > V > V_{1c}$ for any fixed potential $V$, and hence, ion sizes always enhance $J_1$ but reduce $J_2$ (see, (iii) in Theorem 4.22).

Similar sensitivity dependence of ion sizes effects on total fluxes near $L = R$ is examined below. The result depends naturally on $D_1$ and $D_2$ as well as $z_1$ and $z_2$.

Proposition 4.27. Assume $D_1 > D_2$. One has,

$$\lim_{L \to R^+} V_c = -\infty \quad \text{and} \quad \lim_{L \to R^-} V_c = +\infty.$$
Proof. It follows from
\[ \lim_{L \to R^+} \frac{L - R}{\gamma_1(L, R)} = -\infty \quad \text{and} \quad \lim_{L \to R^-} \frac{L - R}{\gamma_1(L, R)} = \infty. \]

Remark 4.28. (a) Similar to Remark 4.26, when combining Proposition 4.27 with Theorems 4.15 and 4.16, and Proposition 4.17, one concludes sensitive dependence of ion size effects on the current \( I \) near \( L = R \). The precise dependence further involves the quantities \( D_1 \) and \( D_2 \); for example, if \( D_1 > D_2 \), on one hand, as \( L \to R^+ \), one has \( V > V_c \) for any fixed potential \( V \), and hence, ion size always 
{
\textit{enhances} \n}
the current \( I \) comparing to the current from point-charge case (see, (i) in Theorem 4.15) and the current \( I \) is always increasing in \( \lambda \) (see, (ii) in Theorem 4.16); on the other hand, as \( L \to R^- \), exactly the opposite effect occurs. For the other cases, the ion size effects as \( L \to R^- \) are always opposite to those as \( L \to R^+ \).

(b) Comparing consequences from results in Proposition 4.25 and in Proposition 4.27, we note that the qualitatively sensitive dependences of ion sizes on individual fluxes \( J_1 = D_1 J_1 \) and \( J_2 = D_2 J_2 \) do not depend on \( D_1 \) and \( D_2 \) but those on the current \( I \) do, simply because \( I = z_1 D_1 J_1 + z_2 D_2 J_2 \) with \( z_1 > 0 > z_2 \).

5. Concluding remarks. We study a quasi-one-dimensional steady-state Poisson-Nernst-Planck model for ionic flows through a single membrane channel with two ion species, one positively charged and one negatively charged. Bikerman’s local hard-sphere model is included to account for ion size effects. Under the framework of geometric singular perturbation theory, together with the specific structures of the PNP system, approximations to the individual fluxes and the I-V relations are extracted, from which the qualitative properties of ionic flows are studied. A detailed characterization of complicated interactions among multiple and physically crucial parameters (such as boundary concentrations and potentials, diffusion coefficients and ion sizes) for ionic flows is provided. Based on relatively simple biological settings, our results have demonstrated extremely rich behaviors of ionic flows and sensitive dependence of flow properties on all these parameters. We believe that this work will be useful for numerical studies and stimulate further analytical studies of ion flows through membrane channels.

We finally point out that the approximated I-V relation (zeroth order in \( \varepsilon \)) is linear in \( V \) (See Corollary 4.10) under our set-up. However, the zeroth order (in \( \varepsilon \)) approximation of the I-V relation is \textit{nonlinear} in \( V \) when permanent charge is nonzero (see, [43]) and, even with zero permanent charge, higher order terms are nonlinear in \( V \) (see [1, 87] for examples).

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