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Research article

Effects on zero current ionic flow and reversal potential from two piecewise permanent charges in opposite signs

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Abstract: Through this work, we investigated a quasi-one-dimensional Poisson-Nernst-Planck (PNP) system containing two segments of permanent charges with opposite signs. Under a zero current condition, the internal dynamics of ionic flows inside of an open ion channel including two types of ion species, one cation and one anion, were the main focus of this work. The existence and local uniqueness solution was proved along the framework of geometric singular perturbation theory, combining with the concrete structure of this model. Furthermore, we obtained three governing equations during the construction of a connecting orbit, which played a fundamental role in subsequent investigations for the impact of permanent charges on zero current ionic flow and reversal potential. In particular, richer dynamical behaviors were demonstrated under the set-up of a multiple nonzero permanent charge distribution, which is also more realistic to the practical problem.

Keywords: PNP; ion channel; permanent charges; zero current ionic flow; reversal potential
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1. Introduction

Ion channels are large proteins with holes embedded in cell membranes, which provide a significant pathway for electrodiffusion of selected ions through biological membranes and for communications between cells and external environments [1]. The key structural features of ion channels are their pore shape and permanent charge distribution. A typical pore shape resembles a cylindrical region that is wide at both ends but is narrow in the middle [2]. Permanent charges consist of side chains of amino acids, among which negative charges are provided by acidic side chains and positive charges are contributed by positive ones. Amino acids are primarily distributed within the short and narrow sections of the channel. This distribution pattern of side chains is termed the permanent charge distribution, and the polarity of permanent charges influences the movement of ions within the channel.

Different types of ion channels only permit specific ions to pass through while blocking other particles. This phenomenon is controlled by the selectivity and permeability [3, 4] of ion channels. The selectivity and permeability of ion channels toward different types of ions are crucial for various cellular functions [5, 6]. Currently, due to limitations in existing technologies, researchers can only study related functional properties of ion channels based on experimentally measured current-voltage (I-V) relationships [7]. However, changes in current are influenced not only by intrinsic ion channel properties, but also by surrounding factors such as voltage and ion concentration or occupancy of binding sites across the channels. The I-V relationship data obtained from experiments represent merely input-output-type information, reflecting the average effects of various factors on ion flows. This makes it difficult for researchers to extract meaningful insights from large experimental datasets. Meanwhile, individual ionic flows contain more information than the current-voltage relation. Unfortunately, measuring them through current experiments is still difficult [8, 9]. Therefore, establishing appropriate mathematical models and employing suitable methods for analysis are essential for explaining the mechanisms of known biological discoveries and exploring new ones. In recent years, there have been some meaningful results in using Poisson-Nernst-Planck (PNP)-type systems to investigate ion channel problems [10].

In this paper, we will study the behaviors of zero current ionic flows with large pore diameters via a classical PNP model with two oppositely charged ion species, two piecewise constant permanent charges in opposite signs. Of particular interest are the problems of permanent charge impacts on individual fluxes and the dependence of reversal potential on permanent charge and diffusion coefficients.

1.1. Poisson-Nernst-Planck models for ionic flows

The PNP model captures the key features of the movement of ion particles through an open ion channel. The three-dimensional steady-state PNP model with n ion species is

$$\begin{aligned} &\nabla\cdot(\varepsilon_r(\mathbf{r})\varepsilon_0\nabla\Phi) = -e\left(\sum_{s=1}^{n} z_s C_s + Q(\mathbf{r})\right),\\ &\nabla\cdot\mathcal{J}_k = 0, \quad -\mathcal{J}_k = \frac{1}{k_BT}\mathcal{D}_k(\mathbf{r})C_k\nabla\mu_k, \quad k = 1, 2, ..., n. \end{aligned} \tag{1.1}$$

Most ion channels in real-world situations exhibit both elongated and narrow characteristics. Consequently, the three-dimensional PNP model can be approximated and simplified by a quasi one-dimensional PNP model [11, 12]:

$$\begin{aligned} &\frac{1}{A(X)}\frac{d}{dX}\left(\varepsilon_r(X)\varepsilon_0 A(X)\frac{d\Phi}{dX}\right) = -e\left(\sum_{s=1}^{n} z_s C_s(X) + Q(X)\right),\\ &\frac{d\mathcal{J}_k}{dX} = 0, \quad -\mathcal{J}_k = \frac{1}{k_BT}\mathcal{D}_k(X)A(X)C_k(X)\frac{d\mu_k}{dX}, \quad k = 1, 2, ..., n, \end{aligned} \tag{1.2}$$

where $X \in [0, l]$ is the coordinate along the axis of the channel, $A(X)$ is the area of the cross-section over the point X, $Q(X)$ is the permanent charge density of the channel, $\varepsilon_r(X)$ is the relative dielectric coefficient, ε_0 is the local dielectric coefficient, e is the elementary charge, k_B is the Boltzmann constant, T is the absolute temperature, and Φ is the electric potential. For the kth ion species, z_k is the valence, C_k is the concentration, $\mathcal{J}_k$ is the flux density, $\mathcal{D}_k(X)$ is the diffusion coefficient, and μ_k is the electrochemical potential, where μ_k includes the ideal component $\mu_k^{id} = z_k e\Phi(X) + k_B T \ln \frac{C_k(X)}{C_0}$ and excess component μ_k^{ex}.

For system (1.2), the boundary conditions are (see [13] for explanations), for $k = 1, 2, \cdots n$,

$$\Phi(0) = \mathcal{V}, \quad C_k(0) = \mathcal{L}_k > 0; \quad \Phi(l) = 0, \quad C_k(l) = \mathcal{R}_k > 0. \tag{1.3}$$

For the analysis of the boundary value problem (1.2)-(1.3), we will employ a dimensionless formulation. Let C_0 be a characteristic concentration, which may be taken as

$$C_0 = \max_{1\le i\le n}\left\{\mathcal{L}_i, \mathcal{R}_i, \sup_{X\in[0,l]}|\mathcal{Q}(X)|\right\}.$$

Set

$$\mathcal{D}_0 = \max_{1\le i\le n}\left\{\sup_{X\in[0,l]}\mathcal{D}_i(X)\right\} \quad \text{and} \quad \bar{\varepsilon}_r = \sup_{X\in[0,l]}\varepsilon_r(X).$$

Let

$$\begin{gathered}
\varepsilon^2 = \frac{\bar{\varepsilon}_r\varepsilon_0 k_B T}{e^2 l^2 C_0}, \quad \hat{\varepsilon}(x) = \frac{\varepsilon_r(X)}{\bar{\varepsilon}_r}, \quad x = \frac{X}{l}, \quad h(x) = \frac{A(X)}{l^2}, \quad \hat{\mu}_k = \frac{\mu_k}{k_B T}, \\
D_k(x) = \frac{\mathcal{D}_k(X)}{\mathcal{D}_0}, \quad \phi(x) = \frac{e}{k_B T}\Phi(X), \quad J_k = \frac{\mathcal{J}_k}{l C_0 \mathcal{D}_0}, \quad Q(x) = \frac{\mathcal{Q}(X)}{C_0}, \\
c_k(x) = \frac{C_k(X)}{C_0}, \quad V = \frac{e}{k_B T}\mathcal{V}, \quad L_k = \frac{\mathcal{L}_k}{C_0}, \quad R_k = \frac{\mathcal{R}_k}{C_0}.
\end{gathered}$$

In terms of the new variables, BVP (1.2)-(1.3) becomes, for $k = 1, 2, ..., n$,

$$\begin{aligned}
&\frac{\varepsilon^2}{h(x)}\frac{d}{dx}\left(\hat{\varepsilon}(x)h(x)\frac{d\phi}{dx}\right) = -\sum_{s=1}^{n} z_s c_s - Q(x), \\
&\frac{dJ_k}{dx} = 0, \quad -J_k = h(x)D_k(x)c_k\frac{d\hat{\mu}_k}{dx},
\end{aligned} \tag{1.4}$$

with the following boundary conditions:

$$\phi(0) = V, \quad c_k(0) = L_k; \quad \phi(1) = 0, \quad c_k(1) = R_k. \tag{1.5}$$

1.1.1. Permanent charge

Permanent charges are determined by the amino acids that compose ion channels. The distribution of permanent charges is extremely complex, and hence researchers in mathematical studies simplify it to investigate their impact on ion movement within the channel. In general, the permanent charge $Q(x)$ is modeled by a piecewise constant function [14–16],

$$Q(x) = \begin{cases} Q_1 = Q_m = 0, \quad x \in (x_0, x_1) \cup (x_{m-1}, x_m), \\ Q_j, \quad x \in (x_{j-1}, x_j), \quad j = 2, 3, \cdots, m-1, \end{cases} \tag{1.6}$$

where intervals (x_0, x_1) and (x_{m-1}, x_m) are regarded as the reservoirs where there is no permanent charge distribution.

1.1.2. Zero current ionic flows and reversal potentials

A zero current state is a special status of ion channels. More precisely, a zero current state is defined to be the moment when there is no net current within a channel. Reversal potential refers to the boundary potential value at the zero current state [9,17]. The reversal potential value varies for different types of ion channels. Thereby, reversal potential has been employed in biological experiments to predict the type of a given ion channel [3,4].

1.1.3. Electroneutrality boundary conditions

The following electroneutrality boundary conditions are imposed to eliminate sharp boundary layers, which influence the behaviors of ionic flows over a long distance and cause nontrivial uncertainties in experimental measurements [18].

$$\sum_{j=1}^{n} z_j L_j = \sum_{j=1}^{n} z_j R_j = 0. \tag{1.7}$$

Note that electroneutrality means that the net ion concentration among different ions on each boundary equals zero.

It is necessary to clarify that the quasi-one-dimensional PNP model is relatively simple and it has some limitations [19]. To be specific, most ion channels are selective for specific cations or anions. The PNP model in this study accommodates both cations and anions, which applies only to very large channels, nuclear pores, and bacterial pores [20]. Second, the electroneutrality conditions are conducted on the boundaries of ion channels to avoid the sharp boundary layers, which would affect the behavior of ionic flows over a long distance. However, boundary layer effects are explored in many studies [21,22], which reveal that the boundary layer would bring richer dynamics of ionic flows and the results are more practical to the biological context. Moreover, since this work mainly focuses on the permanent charge effects, the excess electrostatic component of the electrochemical potential is omitted. Properties related to ion sizes will not be discussed here.

1.2. Problem setup

Note that this is a continuation of the work of [23], therefore, we follow the same setup as in that paper.

(A1) Two oppositely charged ion particles ($n = 2$) are included in the system with $z_1 = -z_2 = z > 0$, for example, sodium (Na^+) and chloride ions (Cl^-).

(A2) The distribution of permanent charge is defined by

$$Q(x) = \begin{cases} 0, & x \in (x_0, x_1) \cup (x_2, x_3) \cup (x_4, 1), \\ Q_2, & x \in (x_1, x_2), \\ Q_4, & x \in (x_3, x_4), \end{cases} \tag{1.8}$$

where Q_2 and Q_4 are nonzero constants and $Q_2 \cdot Q_4 < 0$. It is necessary to mention that in [23], $Q_2 \cdot Q_4 > 0$ and it is the key difference between this work and that in [23].

(A3) Electroneutrality boundary condition (1.7) holds.

(A4) For electrochemical potential $\hat{\mu}_k$, the ideal component $\hat{\mu}_k^{id}$ is included.

(A5) The relative dielectric coefficient and diffusion coefficients are constants, which are $\hat{\varepsilon}_r(x) = 1$ and $D_k(X) = D_k$.

Combining assumptions (A1)–(A5), system (1.4)-(1.5) becomes

$$\begin{aligned}
&\frac{\varepsilon^2}{h(x)}\frac{d}{dx}\Big(h(x)\frac{d}{dx}\phi\Big) = -z_1c_1 - z_2c_2 - Q(x),\\
&\frac{dc_1}{dx} + z_1c_1\frac{d\phi}{dx} = -\frac{J_1}{D_1h(x)},\\
&\frac{dc_2}{dx} + z_2c_2\frac{d\phi}{dx} = -\frac{J_2}{D_2h(x)},\\
&\frac{dJ_1}{dx} = \frac{dJ_2}{dx} = 0,
\end{aligned} \tag{1.9}$$

with the following boundary conditions:

$$\phi(0) = V, \quad c_k(0) = L_k; \quad \phi(1) = 0, \quad c_k(1) = R_k, \quad k = 1,2. \tag{1.10}$$

1.3. Main results

For convenience, we briefly summarize the main results as follows, with $j = 1,2,3,4,5$:

(i) Construction of boundary layers $\Gamma^{[j-1,-]}$ and $\Gamma^{[j,+]}$, and landing points $\omega(N^{[j-1,+]})$ and $\alpha(N^{[j,-]})$ via the limiting fast system (2.6); see Propositions 2.2 and 2.3 in Section 2.1.

(ii) Characterization of regular layers Λ_j via the limiting slow system (2.9), and the transversal intersection between $\overline{M}^{[j-1,+]}$ and $\overline{N}^{[j,-]}$ on the slow manifold $\mathcal{Z}_j$, which are the forward image of $\omega(N^{[j-1,+]})$ and the backward image of $\alpha(N^{[j,-]})$, respectively; see Lemmas 2.4-2.5 and Proposition 2.6 in Section 2.2.

(iii) Establishing the existence of solution $(A,B) = (A(Q_{02},Q_{04},\theta), B(Q_{02},Q_{04},\theta))$ such that $G_2(A,B,Q_{02},\theta) = 0$ and $G_3(A,B,Q_{04},\theta) = 0$.

(iv) Analysis of permanent charge and diffusion coefficient effects on zero current ionic flows J, see Theorems 3.10–3.12 in Section 3.2.

(v) Examination on the permanent charge effects on reversal potential V_{rev}, see Theorem 3.14 in Section 3.3.

As we change the setup of permanent charges with the same sign in [23] to the one containing oppositely charged permanent charges, the behaviors of ionic flows and dynamics between related parameters are much richer than those in [23], which are also more realistic to the biological context. To be specific, one may check that:

- From Lemma 3.5 in [23], one gets that $\partial_\theta A(Q_{02},Q_{04},\theta)$ has the same sign as that of $L-R$ if $\theta > 0$. In this work, for $\theta > 0$ and $Q_{02} > 0$, we claim that $\partial_\theta A(Q_{02},Q_{04},\theta)$ has the opposite sign (resp., same sign) as that of $L-R$ if condition 2 (resp., condition 1) in Remark 3.2 holds, which is more comprehensive between the related parameters.

- The key novelty in this work is that we are capable to provide the condition to characterize the opposite role taken by permanent charges Q_{02} and Q_{04} in ionic flows. One may find the details in Theorem 3.10 and the explanation in Remark 3.5.
- From Theorem 4.5 in [23], as $\theta > 0$, one has that V_{rev} increases (resp., decreases) in Q_{02} when $L > R$ (resp., $L < R$). This relation is also valid in this work. Besides this relation, we also obtain the opposite situation. One may locate those results in Theorem 3.14 and Remark 3.6.

We organize this paper as follows. In Section 2, geometric singular perturbation theory is applied to derive the matching system of algebraic equations under a zero current condition and further reduce them to three governing equations. In Section 3, we investigate the qualitative properties of zero current ionic flow and examine the influence of the permanent charges on reversal potential. A concluding remark is provided in Section 4.

2. Geometric singular perturbation framework

To derive the solution for the quasi-one-dimensional PNP system, we first construct the orbit on each subinterval $[x_{j-1}, x_j]$ based on different permanent charge densities Q_j, $j = 1, 2, \ldots, 5$, and further match them over each jumping point x_j, $j = 1, 2, 3, 4$. The procedure contains the following steps.

Step 1. Construct singular layers using a limiting fast system on each $[x_{j-1}, x_j]$ with $Q(x) = Q_j$ in Section 2.1.
Step 2. In Section 2.2, establish regular layers on each subinterval through a limiting slow system to connect the landing points obtained in Step 1.
Step 3. In Section 2.3, match all the singular orbits $\Gamma^{[j-1,+]} \cup \Lambda_j \cup \Gamma^{[j,-]}$ constructed over each subinterval to obtain the complete orbit on $[0, 1]$.
Step 4. In Section 2.4, simplify the matching system (2.17) to a reduced form given in Proposition 2.7.
Step 5. In Section 2.5, prove that near the singular orbits of the limiting system as $\varepsilon \to 0$, there exists a unique solution for the system as $\varepsilon > 0$ by using the exchange lemma.

Introducing $u = \varepsilon\dot{\phi}$ and $\tau = x$, system (1.9) becomes

$$
\begin{aligned}
&\varepsilon\dot{\phi} = u, \quad \varepsilon\dot{u} = -z_1c_1 - z_2c_2 - \varepsilon\frac{h_\tau(\tau)}{h(\tau)}u - Q(\tau),\\
&\varepsilon\dot{c}_1 = -z_1c_1u - \varepsilon\frac{J_1}{D_1h(\tau)}, \quad \varepsilon\dot{c}_2 = -z_2c_2u - \varepsilon\frac{J_2}{D_2h(\tau)},\\
&\dot{J}_1 = \dot{J}_2 = 0, \quad \dot{\tau} = 1,
\end{aligned}
\tag{2.1}
$$

which is known as a slow system and the derivative with respect to x is denoted by an overdot.

System (2.1) will be treated as a singular perturbed system and ε is the perturbed parameter. 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 $x = \varepsilon\xi$ gives rise to

$$\begin{aligned} &\phi' = u, \quad u' = -z_1c_1 - z_2c_2 - \varepsilon\frac{h_\tau(\tau)}{h(\tau)}u - Q(\tau), \\ &c_1' = -z_1c_1u - \varepsilon\frac{J_1}{D_1h(\tau)}, \quad c_2' = -z_2c_2u - \varepsilon\frac{J_2}{D_2h(\tau)}, \\ &J_1' = J_2' = 0, \quad \tau' = \varepsilon. \end{aligned} \tag{2.2}$$

Relative to system (2.1), it is a fast system and the derivative with respect to ξ is denoted by a prime symbol.

The boundary condition (1.10) becomes

$$\phi(0) = V, \quad c_k(0) = L_k, \quad \tau(0) = 0; \quad \phi(1) = 0, \quad c_k(1) = R_k, \quad \tau(1) = 1, \quad k = 1, 2. \tag{2.3}$$

Let B_L and B_R be the subsets of the phase space $\mathbb{R}^7$ defined by

$$\begin{aligned} B_L &= \left\{(V, u, L_1, L_2, J_1, J_2, 0) \in \mathbb{R}^7 : \text{arbitrary } u, J_1, J_2\right\}, \\ B_R &= \left\{(0, u, R_1, R_2, J_1, J_2, 1) \in \mathbb{R}^7 : \text{arbitrary } u, J_1, J_2\right\}. \end{aligned} \tag{2.4}$$

Then, the boundary value problem is equivalent to a connecting problem, that is, to find an orbit of (2.1) from B_L to B_R.

Orbits on each subinterval $[x_{j-1}, x_j]$ are constructed first, where $Q(x)$ is a constant and $j = 1, 2, 3, 4, 5$. Then, we match them at jumping points $x = x_j$, $j = 1, 2, 3, 4$. To do so, we will preassign the values of ϕ and c_i at each x_j for $j = 1, 2, 3, 4$:

$$\phi(x_j) = \phi^{[j]}, \quad c_i(x_j) = c_i^{[j]}, \tag{2.5}$$

with given $\phi^{[0]} = V$ and $c_i^{[0]} = L_i$ at $x_0 = 0$, and $\phi^{[5]} = 0$ and $c_i^{[5]} = R_i$ at $x_5 = 1$. Then we introduce the set, for $j = 0, 1, 2, 3, 4, 5$:

$$B_j = \left\{(\phi, u, c_1, c_2, J_1, J_2, x) | \phi = \phi^{[j]}, c_1 = c_1^{[j]}, c_2 = c_2^{[j]}, x = x_j\right\}.$$

Notice that $B_0 = B_L$ and $B_5 = B_R$.

2.1. Fast dynamics for singular layers at $[x_{j-1}, x_j]$ with $Q(x) = Q_j$

Setting $\varepsilon = 0$ in (2.1) and (2.2), one obtains the so-called slow manifold:

$$\mathcal{Z}_j = \left\{u = 0, z_1c_1 + z_2c_2 + Q_j = 0\right\},$$

which is a five-dimensional invariant manifold in $\mathbb{R}^7$, i.e., dim $\mathcal{Z}_j = 5$, and the limiting fast system reads

$$\begin{aligned} &\phi' = u, \quad u' = -z_1c_1 - z_2c_2 - Q_j, \\ &c_1' = -z_1c_1u, \quad c_2' = -z_2c_2u, \\ &J_1' = J_2' = 0, \quad \tau' = 0. \end{aligned} \tag{2.6}$$

Since the slow manifold $\mathcal{Z}_j$ is normally hyperbolic [13], there are corresponding stable and unstable manifolds and we use $W^s(\mathcal{Z}_j)$ and $W^u(\mathcal{Z}_j)$ to represent them. We use $M^{[j-1,+]}$ to denote the collection of forward orbits from B_{j-1} and utilize $M^{[j,-]}$ to denote the collection of backward orbits from B_j. Let $N^{[j-1,+]}$ and $N^{[j,-]}$ be the set of forward orbits from B_{j-1} to $\mathcal{Z}_j$ and the set of backward orbits from B_j to $\mathcal{Z}_j$, respectively, where $N^{[j-1,+]} = M^{[j-1,+]} \cap W^s(\mathcal{Z}_j)$ and $N^{[j,-]} = M^{[j,-]} \cap W^u(\mathcal{Z}_j)$. We introduce $\Gamma^{[j-1,+]}$ and $\Gamma^{[j,-]}$ as the singular layer at x_{j-1} and at x_j, which satisfy $\Gamma^{[j-1,+]} \subset N^{[j-1,+]}$ and $\Gamma^{[j,-]} \subset N^{[j,-]}$, respectively.

Now, we are able to introduce the first integrals of (2.6), which provide a possibility to characterize the dynamics of the limiting fast system. A detailed proof can be found in [14].

Proposition 2.1. *System* (2.6) *has six first integrals:*

$$H_1 = \ln c_1 + z_1\phi, \quad H_2 = \ln c_2 + z_2\phi,$$

$$H_3 = \frac{1}{2}u^2 - c_1 - c_2 + Q_j\phi, \quad H_4 = J_1, \quad H_5 = J_2, \quad H_6 = \tau.$$

Proposition 2.2. *The stable manifold $W^s(\mathcal{Z}_j)$ intersects B_{j-1} transversally at points*

$$(\phi^{[j-1]}, u^{[j-1,+]}, c_1^{[j-1]}, c_2^{[j-1]}, J_1, J_2, x_{j-1}),$$

and the ω-limit set of $N^{[j-1,+]} = M^{[j-1,+]} \cap W^s(\mathcal{Z}_j)$ is

$$\omega(N^{[j-1,+]}) = \left\{\left(\phi^{[j-1,+]}, 0, c_1^{[j-1,+]}, c_2^{[j-1,+]}, J_1, J_2, x_{j-1}\right) : J_1, J_2 \text{ are arbitrary}\right\},$$

where $\phi^{[j-1,+]}, c_1^{[j-1,+]}, c_2^{[j-1,+]}$, and $u^{[j-1,+]}$ are determined by

$$c_1^{[j-1,+]} = c_1^{[j-1]} e^{z_1(\phi^{[j-1]} - \phi^{[j-1,+]})}, \quad c_2^{[j-1,+]} = c_2^{[j-1]} e^{z_2(\phi^{[j-1]} - \phi^{[j-1,+]})},$$

$$z_1 c_1^{[j-1]} e^{z_1(\phi^{[j-1]} - \phi^{[j-1,+]})} + z_2 c_2^{[j-1]} e^{z_2(\phi^{[j-1]} - \phi^{[j-1,+]})} + Q_j = 0,$$
$$u^{[j-1,+]} = sgn(\phi^{[j-1,+]} - \phi^{[j-1]})\sqrt{K^{[j-1,+]}},$$
$$K^{[j-1,+]} = 2\sum_{i=1}^{2} c_i^{[j-1]}(1 - e^{z_i(\phi^{[j-1]} - \phi^{[j-1,+]})}) + 2Q_j(\phi^{[j-1,+]} - \phi^{[j-1]}).$$

Proposition 2.3. *The unstable manifold $W^u(\mathcal{Z}_j)$ intersects B_j transversally at points*

$$(\phi^{[j]}, u^{[j,-]}, c_1^{[j]}, c_2^{[j]}, J_1, J_2, x_j),$$

and the α-limit set of $N^{[j,l]} = M^{[j,l]} \cap W^u(\mathcal{Z}_j)$ is

$$\alpha(N^{[j,-]}) = \left\{\left(\phi^{[j,-]}, 0, c_1^{[j,-]}, c_2^{[j,-]}, J_1, J_2, x_j\right) : J_1, J_2 \text{ are arbitrary}\right\},$$

where $\phi^{[j,-]}, c_1^{[j,-]}, c_2^{[j,-]}$, and $u^{[j,-]}$ are determined by

$$c_1^{[j,-]} = c_1^{[j]} e^{z_1(\phi^{[j]} - \phi^{[j,-]})}, \quad c_2^{[j,-]} = c_2^{[j]} e^{z_2(\phi^{[j]} - \phi^{[j,-]})},$$
$$z_1 c_1^{[j]} e^{z_1(\phi^{[j]} - \phi^{[j,-]})} + z_2 c_2^{[j]} e^{z_2(\phi^{[j]} - \phi^{[j,-]})} + Q_j = 0,$$
$$u^{[j,-]} = sgn(\phi^{[j,-]} - \phi^{[j]})\sqrt{K^{[j,-]}},$$
$$K^{[j,-]} = 2\sum_{i=1}^{2} c_i^{[j]}(1 - e^{z_i(\phi^{[j]} - \phi^{[j,-]})}) + 2Q_j(\phi^{[j,-]} - \phi^{[j]}).$$

2.2. Slow dynamics and regular layers at $[x_{j-1}, x_j]$ with $Q(x) = Q_j$

In this section, we derive regular layers Λ_j that connect $\omega(N^{[j-1,+]})$ to $\alpha(N^{[j,-]})$ in the vicinity of the slow manifold $\mathcal{Z}_j$. On $\mathcal{Z}_j$, slow system (2.1) is degenerate since all dynamical information on (ϕ, c_1, c_2) disappear. To remedy it, one can further introduce a rescaling $u = \varepsilon p$ and $-z_2c_2 = z_1c_1 + Q_j + \varepsilon q$ in system (2.1). In terms of the new variables, system (2.1) becomes

$$
\begin{aligned}
&\dot{\phi} = p, \quad \varepsilon\dot{p} = q - \varepsilon\frac{h_\tau(\tau)}{h(\tau)}p, \quad \dot{c_1} = -z_1c_1p - \frac{J_1}{D_1h(\tau)},\\
&\varepsilon\dot{q} = [z_1(z_1-z_2)c_1 - z_2Q_j - \varepsilon z_2 q]p + \frac{1}{h(\tau)}\left(\frac{z_1J_1}{D_1} + \frac{z_2J_2}{D_2}\right),\\
&\dot{J}_1 = \dot{J}_2 = 0, \quad \dot{\tau} = 1.
\end{aligned}
\tag{2.7}
$$

For $\varepsilon = 0$, one gets the limiting slow system of system (2.7):

$$
\begin{aligned}
&\dot{\phi} = p, \quad q = 0, \quad \dot{c_1} = -z_1c_1p - \frac{J_1}{D_1h(\tau)},\\
&p = -\frac{1}{h(\tau)}\frac{\frac{z_1J_1}{D_1} + \frac{z_2J_2}{D_2}}{z_1(z_1-z_2)c_1 - z_2Q_j}, \quad \dot{J}_1 = \dot{J}_2 = 0, \quad \dot{\tau} = 1.
\end{aligned}
\tag{2.8}
$$

The slow manifold of the new variables is

$$
\mathcal{S} = \left\{ q = 0, \quad p = -\frac{\frac{z_1J_1}{D_1} + \frac{z_2J_2}{D_2}}{h(\tau)\big(z_1(z_1-z_2)c_1 - z_2Q_j\big)} \right\}.
$$

The limiting slow system on $\mathcal{S}$ is

$$
\begin{aligned}
\dot{\phi} &= -\frac{\frac{z_1J_1}{D_1} + \frac{z_2J_2}{D_2}}{h(\tau)\big(z_1(z_1-z_2)c_1 - z_2Q_j\big)},\\
\dot{c_1} &= \frac{z_1c_1\left(\frac{z_1J_1}{D_1} + \frac{z_2J_2}{D_2}\right)}{h(\tau)\big(z_1(z_1-z_2)c_1 - z_2Q_j\big)} - \frac{J_1}{D_1h(\tau)},\\
\dot{J}_1 &= \dot{J}_2 = 0, \quad \dot{\tau} = 1.
\end{aligned}
\tag{2.9}
$$

Under the setup of this work, the zero current state is

$$
0 = \mathcal{I} = z_1J_1 + z_2J_2.
$$

Therefore, the limiting slow system (2.9) under zero current conditions $z_2J_2 = -z_1J_1$ becomes

$$
\begin{aligned}
\dot{\phi} &= -\frac{z_1J_1(D_2 - D_1)}{D_1D_2h(\tau)\big(z_1(z_1-z_2)c_1 - z_2Q_j\big)},\\
\dot{c_1} &= \frac{z_1c_1\,(z_2D_2 - z_1D_1) + z_2D_2Q_j}{D_1D_2h(\tau)\big(z_1(z_1-z_2)c_1 - z_2Q_j\big)}J_1,\\
\dot{J}_1 &= 0, \quad \dot{\tau} = 1.
\end{aligned}
\tag{2.10}
$$

2.2.1. $[x_{j-1}, x_j]$ with $Q_j = 0$, $j = 1, 3, 5$

System (2.10) becomes

$$\begin{aligned} \dot{\phi} &= -\frac{J_1(D_2 - D_1)}{D_1 D_2 h(\tau)(z_1 - z_2)c_1}, \\ \dot{c_1} &= \frac{(z_2 D_2 - z_1 D_1)\, J_1}{D_1 D_2 h(\tau)\,(z_1 - z_2)}, \\ \dot{J}_1 &= 0, \quad \dot{\tau} = 1. \end{aligned} \tag{2.11}$$

Lemma 2.4. *Over* $[x_{j-1}, x_j]$, *with the initial condition*

$$\Big(\phi(x_{j-1}), c_1(x_{j-1}), \tau(x_{j-1})\Big) = \Big(\phi^{[j-1,+]}, c_1^{[j-1,+]}, x_{j-1}\Big),$$

the solution of (2.11) *is*

$$\begin{aligned} \phi(x) &= \phi^{[j-1,+]} - \frac{D_2 - D_1}{z_2 D_2 - z_1 D_1} \ln \frac{c_1(x)}{c_1^{[j-1,+]}}, \\ c_1(x) &= c_1^{[j-1,+]} + \frac{(z_2 D_2 - z_1 D_1) J_1}{D_1 D_2 (z_1 - z_2)} \Big(H(x) - H(x_{j-1})\Big), \\ \tau(x) &= x, \end{aligned} \tag{2.12}$$

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

At $x = x_j$, one has

$$\begin{aligned} \phi^{[j,-]} &= \phi^{[j-1,+]} - \frac{D_2 - D_1}{z_2 D_2 - z_1 D_1} \ln \frac{c_1^{[j,-]}}{c_1^{[j-1,+]}}, \\ J_1 &= \frac{(z_1 - z_2) D_1 D_2 \Big(c_1^{[j,-]} - c_1^{[j-1,+]}\Big)}{\Big(H(x_j) - H(x_{j-1})\Big)(z_2 D_2 - z_1 D_1)}. \end{aligned} \tag{2.13}$$

2.2.2. $[x_{j-1}, x_j]$ with $Q_j \neq 0$, $j = 2, 4$

On slow manifold $\mathcal{S}$, where $q = 0$, it follows from the rescaling $-z_2 c_2 = z_1 c_1 + Q_j + \varepsilon q$ that $-z_2 c_2 = z_1 c_1 + Q_j$. Hence, $z_1(z_1 - z_2)c_1 - z_2 Q_j = z_1^2 c_1 + z_2^2 c_2 > 0$. Multiplying the right side of system (2.10) by $h(\tau)\Big(z_1(z_1 - z_2)c_1 - z_2 Q_j\Big)$, the phase portrait stays the same, and one gets

$$\begin{aligned} \frac{d\phi}{dy} &= -\frac{z_1 J_1 (D_2 - D_1)}{D_1 D_2}, \\ \frac{dc_1}{dy} &= \frac{z_1 c_1\,(z_2 D_2 - z_1 D_1) + z_2 D_2 Q_j}{D_1 D_2} J_1, \\ \frac{dJ_1}{dy} &= 0, \quad \frac{d\tau}{dy} = h(\tau)\Big(z_1(z_1 - z_2)c_1 - z_2 Q_j\Big). \end{aligned} \tag{2.14}$$

Lemma 2.5. *Over* $[x_{j-1}, x_j]$, *there is a unique solution* $(\phi(y), c_1(y), J_1, \tau(y))$ *of* (2.14) *such that* $(\phi(0), c_1(0), \tau(0)) = \Big(\phi^{[j-1,+]}, c_1^{[j-1,+]}, x_{j-1}\Big)$ *and* $\Big(\phi(y_j), c_1(y_j), \tau(y_j)\Big) = \Big(\phi^{[j,-]}, c_1^{[j,-]}, x_j\Big)$ *for some* $y_j > 0$, *where* $\phi^{[j-1,+]}$, $\phi^{[j,-]}$, $c_1^{[j-1,+]}$, *and* $c_1^{[j,-]}$ *are given in Propositions 2.2-2.3. It is given by*

$$\phi(y) = \phi^{[j-1,+]} - \frac{z_1 J_1 (D_2 - D_1)}{D_1 D_2} y,$$

$$c_1(y) = c_1^{[j-1,+]} e^{\hat{N}y} + \frac{z_2 D_2 Q_j}{z_1 (z_2 D_2 - z_1 D_1)} \left(e^{\hat{N}y} - 1 \right),$$

$$\int_{x_{j-1}}^{\tau} \frac{1}{h(s)}\, ds = \left(c_1^{[j-1,r]} + \frac{z_2 D_2 Q_j}{z_1 (z_2 D_2 - z_1 D_1)} \right) \frac{D_1 D_2 (z_1 - z_2) \left(e^{\hat{N}y} - 1 \right)}{(z_2 D_2 - z_1 D_1)\, J_1} - \frac{z_1 z_2 (D_2 - D_1) Q_j y}{z_2 D_2 - z_1 D_1},$$

where $\hat{N} = \frac{z_1(z_2D_2 - z_1D_1)J_1}{D_1D_2}$ *and* J_1, y_j *are determined by*

$$\begin{aligned} \phi^{[j,-]} &= \phi^{[j-1,+]} - \frac{z_1 J_1 (D_2 - D_1)}{D_1 D_2} y_j, \\ c_1^{[j,-]} &= c_1^{[j-1,+]} e^{\hat{N}y_j} + \frac{z_2 D_2 Q_j}{z_1 (z_2 D_2 - z_1 D_1)} \left(e^{\hat{N}y_j} - 1 \right), \\ J_1 &= \frac{D_1 D_2 \left((z_1 - z_2)(c^{[j,-]} - c^{[j-1,+]}) - z_2 Q_j (\phi^{[j-1,+]} - \phi^{[j,-]}) \right)}{(z_2 D_2 - z_1 D_1) \left(H(x_j) - H(x_{j-1}) \right)}. \end{aligned} \tag{2.15}$$

The slow orbit

$$\Lambda_j = (\phi(x), c_1(x), J_1, \tau(x)) \tag{2.16}$$

given in Lemmas 2.4 and 2.5 connects $\omega(N^{[j-1,+]})$ and $\alpha(N^{[j,-]})$. Let $\overline{M}^{[j-1,+]}$ (resp., $\overline{N}^{[j,-]}$) be the forward (resp., backward) image of $\omega(N^{[j-1,+]})$ (resp., $\alpha(N^{[j,-]})$) under the slow flow (2.10). One has the following result about the transversality between $\overline{M}^{[j-1,+]}$ and $\overline{N}^{[j,-]}$. The proof can be obtained from Section 4 in [14].

Proposition 2.6. *On the five-dimensional slow manifold* $\mathcal{Z}_j$, $\overline{M}^{[j-1,+]}$ *and* $\overline{N}^{[j,-]}$ *intersect transversally along the unique orbit* Λ_j *given in* (2.16)*.*

2.3. *Matching for zero current and singular orbits on* [0, 1]

To construct a complete singular orbit on [0, 1], one needs to match all the singular orbits $\Gamma^{[j-1,+]} \cup \Lambda_j \cup \Gamma^{[j,-]}$ established on each subinterval $[x_{j-1}, x_j]$ ($j = 1, 2, 3, 4, 5$). The matching conditions are $u^{[j,-]} = u^{[j,+]}$ at each x_j for $j = 1, 2, 3, 4$; and J_1 has to be the same on five subintervals. It follows from Lemmas 2.4 and 2.5 that

$$\begin{aligned} & z_1 c_1^{[1]} e^{z_1\left(\phi^{[1]} - \phi^{[1,+]}\right)} + z_2 c_2^{[1]} e^{z_2\left(\phi^{[1]} - \phi^{[1,+]}\right)} + Q_2 = 0, \\ & z_1 c_1^{[2]} e^{z_1\left(\phi^{[2]} - \phi^{[2,-]}\right)} + z_2 c_2^{[2]} e^{z_2\left(\phi^{[2]} - \phi^{[2,-]}\right)} + Q_2 = 0, \\ & z_1 c_1^{[3]} e^{z_1\left(\phi^{[3]} - \phi^{[3,+]}\right)} + z_2 c_2^{[3]} e^{z_2\left(\phi^{[3]} - \phi^{[3,+]}\right)} + Q_4 = 0, \\ & z_1 c_1^{[4]} e^{z_1\left(\phi^{[4]} - \phi^{[4,-]}\right)} + z_2 c_2^{[4]} e^{z_2\left(\phi^{[4]} - \phi^{[4,-]}\right)} + Q_4 = 0, \\ & c_1^{[1]} \left(e^{z_1\left(\phi^{[1]} - \phi^{[1,-]}\right)} - e^{z_1\left(\phi^{[1]} - \phi^{[1,+]}\right)} \right) + c_2^{[1]} \left(e^{z_2\left(\phi^{[1]} - \phi^{[1,-]}\right)} - e^{z_2\left(\phi^{[1]} - \phi^{[1,+]}\right)} \right) \\ & + Q_2 \left(\phi^{[1,+]} - \phi^{[1]} \right) = 0, \\ & c_1^{[2]} \left(e^{z_1\left(\phi^{[2]} - \phi^{[2,+]}\right)} - e^{z_1\left(\phi^{[2]} - \phi^{[2,-]}\right)} \right) + c_2^{[2]} \left(e^{z_2\left(\phi^{[2]} - \phi^{[2,+]}\right)} - e^{z_2\left(\phi^{[2]} - \phi^{[2,-]}\right)} \right) \\ & + Q_2 \left(\phi^{[2,-]} - \phi^{[2]} \right) = 0, \\ & c_1^{[3]} \left(e^{z_1\left(\phi^{[3]} - \phi^{[3,-]}\right)} - e^{z_1\left(\phi^{[3]} - \phi^{[3,+]}\right)} \right) + c_2^{[3]} \left(e^{z_2\left(\phi^{[3]} - \phi^{[3,-]}\right)} - e^{z_2\left(\phi^{[3]} - \phi^{[3,+]}\right)} \right) \end{aligned}$$

$$
\begin{aligned}
&+ Q_4\left(\phi^{[3,+]} - \phi^{[3]}\right) = 0,\\
&c_1^{[4]}\left(e^{z_1\left(\phi^{[4]}-\phi^{[4,+]}\right)} - e^{z_1\left(\phi^{[4]}-\phi^{[4,-]}\right)}\right) + c_2^{[4]}\left(e^{z_2\left(\phi^{[4]}-\phi^{[4,+]}\right)} - e^{z_2\left(\phi^{[4]}-\phi^{[4,-]}\right)}\right)\\
&+ Q_4\left(\phi^{[4,-]} - \phi^{[4]}\right) = 0,\\
&\frac{J_1}{D_1D_2} = \frac{\left(c_1^{[1,-]} - c_1^{[0,+]}\right)(z_1 - z_2)}{(H(x_1) - H(x_0))\,(z_2D_2 - z_1D_1)} = \frac{(z_1 - z_2)(c^{[2,-]} - c^{[1,+]}) - z_2Q_2(\phi^{[1,+]} - \phi^{[2,-]})}{(z_2D_2 - z_1D_1)\,(H(x_2) - H(x_1))}\\
&\qquad\quad = \frac{\left(c_1^{[3,-]} - c_1^{[2,+]}\right)(z_1 - z_2)}{(H(x_3) - H(x_2))\,(z_2D_2 - z_1D_1)} = \frac{(z_1 - z_2)(c^{[4,-]} - c^{[3,+]}) - z_2Q_4(\phi^{[3,+]} - \phi^{[4,-]})}{(z_2D_2 - z_1D_1)\,(H(x_4) - H(x_3))}\\
&\qquad\quad = \frac{\left(c_1^{[5,-]} - c_1^{[4,+]}\right)(z_1 - z_2)}{(H(x_5) - H(x_4))\,(z_2D_2 - z_1D_1)},\\
&\phi^{[2,-]} = \phi^{[1,+]} - \frac{z_1J_1(D_2 - D_1)}{D_1D_2}y_2, \quad \phi^{[4,-]} = \phi^{[3,+]} - \frac{z_1J_1(D_2 - D_1)}{D_1D_2}y_4,\\
&c_1^{[2,-]} = c_1^{[1,+]}e^{\hat{N}y_2} + \frac{z_2D_2Q_2}{z_1\,(z_2D_2 - z_1D_1)}\left(e^{\hat{N}y_2} - 1\right),\\
&c_1^{[4,-]} = c_1^{[3,+]}e^{\hat{N}y_4} + \frac{z_2D_2Q_4}{z_1\,(z_2D_2 - z_1D_1)}\left(e^{\hat{N}y_4} - 1\right),\\
&z_1c_1^{[1]}e^{z_1\left(\phi^{[1]}-\phi^{[1,-]}\right)} + z_2c_2^{[1]}e^{z_2\left(\phi^{[1]}-\phi^{[1,-]}\right)} = 0,\\
&z_1c_1^{[2]}e^{z_1\left(\phi^{[2]}-\phi^{[2,+]}\right)} + z_2c_2^{[2]}e^{z_2\left(\phi^{[2]}-\phi^{[2,+]}\right)} = 0,\\
&z_1c_1^{[3]}e^{z_1\left(\phi^{[3]}-\phi^{[3,-]}\right)} + z_2c_2^{[3]}e^{z_2\left(\phi^{[3]}-\phi^{[3,-]}\right)} = 0,\\
&z_1c_1^{[4]}e^{z_1\left(\phi^{[4]}-\phi^{[4,+]}\right)} + z_2c_2^{[4]}e^{z_2\left(\phi^{[4]}-\phi^{[4,+]}\right)} = 0,
\end{aligned}
\tag{2.17}
$$

where

$$
\begin{aligned}
&\phi^{[0,+]} = V - \frac{1}{z_1 - z_2}\ln\frac{-z_2L_2}{z_1L_1},\\
&c_1^{[0,+]} = L_1\left(\frac{z_1L_1}{-z_2L_2}\right)^{\frac{-z_1}{z_1-z_2}}, \quad c_2^{[0,+]} = L_2\left(\frac{z_1L_1}{-z_2L_2}\right)^{\frac{-z_2}{z_1-z_2}},\\
&\phi^{[1,-]} = \phi^{[0,+]} - \frac{D_2 - D_1}{z_2D_2 - z_1D_1}\ln\frac{c_1^{[1,-]}}{c_1^{[0,+]}},\\
&c_1^{[1,-]} = c_1^{[1]}\left(\frac{z_1c^{[1]}}{-z_2c_2^{[1]}}\right)^{-\frac{z_1}{z_1-z_2}}, \quad c_2^{[1,-]} = c_2^{[1]}\left(\frac{z_1c^{[1]}}{-z_2c_2^{[1]}}\right)^{-\frac{z_2}{z_1-z_2}},\\
&\phi^{[2,+]} = \phi^{[3,-]} + \frac{D_2 - D_1}{z_2D_2 - z_1D_1}\ln\frac{c_1^{[3,-]}}{c_1^{[2,+]}},\\
&c_1^{[2,+]} = c_1^{[2]}\left(\frac{z_1c_1^{[2]}}{-z_2c_2^{[2]}}\right)^{-\frac{z_1}{z_1-z_2}}, \quad c_2^{[2,+]} = c_2^{[2]}\left(\frac{z_1c_1^{[2]}}{-z_2c_2^{[2]}}\right)^{-\frac{z_2}{z_1-z_2}},\\
&c_1^{[3,-]} = c_1^{[3]}\left(\frac{z_1c^{[3]}}{-z_2c_2^{[3]}}\right)^{-\frac{z_1}{z_1-z_2}}, \quad c_2^{[3,-]} = c_2^{[3]}\left(\frac{z_1c^{[3]}}{-z_2c_2^{[3]}}\right)^{-\frac{z_2}{z_1-z_2}},
\end{aligned}
$$

$$\phi^{[4,+]} = \phi^{[5,-]} + \frac{D_2 - D_1}{z_2 D_2 - z_1 D_1} \ln \frac{c_1^{[5,-]}}{c_1^{[4,+]}},$$

$$c_1^{[4,+]} = c_1^{[4]} \left(\frac{z_1 c_1^{[4]}}{-z_2 c_2^{[4]}} \right)^{-\frac{z_1}{z_1 - z_2}}, \quad c_2^{[4,+]} = c_2^{[4]} \left(\frac{z_1 c_1^{[4]}}{-z_2 c_2^{[4]}} \right)^{-\frac{z_2}{z_1 - z_2}},$$

$$\phi^{[5,-]} = -\frac{1}{z_1 - z_2} \ln \frac{-z_2 R_2}{z_1 R_1},$$

$$c_1^{[5,-]} = R_1 \left(\frac{z_1 R_1}{-z_2 R_2} \right)^{\frac{-z_1}{z_1 - z_2}}, \quad c_2^{[5,-]} = R_2 \left(\frac{z_1 R_1}{-z_2 R_2} \right)^{\frac{-z_2}{z_1 - z_2}},$$

$$c_1^{[1,+]} = c_1^{[1]} e^{z_1(\phi^{[1]} - \phi^{[1,+]})}, \quad c_2^{[1,+]} = c_2^{[1]} e^{z_2(\phi^{[1]} - \phi^{[1,+]})},$$

$$c_1^{[2,-]} = c_1^{[2]} e^{z_1(\phi^{[2]} - \phi^{[2,-]})}, \quad c_2^{[2,-]} = c_2^{[2]} e^{z_2(\phi^{[2]} - \phi^{[2,-]})},$$

$$c_1^{[3,+]} = c_1^{[3]} e^{z_1(\phi^{[3]} - \phi^{[3,+]})}, \quad c_2^{[3,+]} = c_2^{[3]} e^{z_2(\phi^{[3]} - \phi^{[3,+]})},$$

$$c_1^{[4,-]} = c_1^{[4]} e^{z_1(\phi^{[4]} - \phi^{[4,-]})}, \quad c_2^{[4,-]} = c_2^{[4]} e^{z_2(\phi^{[4]} - \phi^{[4,-]})}.$$

Remark 2.1. In (2.17), the unknowns are $\phi^{[1]}$, $\phi^{[2]}$, $\phi^{[3]}$, $\phi^{[4]}$, $c_1^{[1]}$, $c_1^{[2]}$, $c_1^{[3]}$, $c_1^{[4]}$, $c_2^{[1]}$, $c_2^{[2]}$, $c_2^{[3]}$, $c_2^{[4]}$, $\phi^{[1,+]}$, $\phi^{[2,-]}$, $\phi^{[3,+]}$, $\phi^{[4,-]}$, J_1, Q_2, Q_4, y_2, and y_4. That is, there are 21 unknowns that match the total number of equations in (2.17).

2.4. Reduced system for zero current with $z_1 = -z_2 = z > 0$

Note that under electroneutrality boundary conditions

$$z_1 L_1 = -z_2 L_2 \quad \text{and} \quad z_1 R_1 = -z_2 R_2, \tag{2.18}$$

and the assumption $z_1 = -z_2 = z > 0$, one has $L_1 = L_2$ and $R_1 = R_2$.

For convenience, we further introduce

$$L_k = L, \quad R_k = R, \quad A = \sqrt{c_1^{[1]} c_2^{[1]}}, \quad B = \sqrt{c_1^{[2]} c_2^{[2]}}, \quad C = \sqrt{c_1^{[3]} c_2^{[3]}}, \quad D = \sqrt{c_1^{[4]} c_2^{[4]}},$$

$$Q_2 = 2Q_{02}, \quad Q_4 = 2Q_{04}, \quad \alpha_1 = \frac{H(x_1)}{H(1)}, \quad \alpha_2 = \frac{H(x_2)}{H(1)}, \quad \alpha_3 = \frac{H(x_3)}{H(1)}, \quad \alpha_4 = \frac{H(x_4)}{H(1)},$$

$$S_a = \sqrt{Q_{02}^2 + z^2 A^2}, \quad S_b = \sqrt{Q_{02}^2 + z^2 B^2}, \quad S_c = \sqrt{Q_{04}^2 + z^2 C^2}, \quad S_d = \sqrt{Q_{04}^2 + z^2 D^2}.$$

With the above terms, we get

$$\begin{aligned} &c_1^{[1,-]} = c_2^{[1,-]} = A, \quad c_1^{[2,+]} = c_2^{[2,+]} = B, \\ &c_1^{[3,-]} = c_2^{[3,-]} = C, \quad c_1^{[4,+]} = c_2^{[4,+]} = D, \\ &\phi^{[2,+]} = \phi^{[3,-]} + \frac{D_1 - D_2}{z(D_1 + D_2)} \ln \frac{C}{B}. \end{aligned} \tag{2.19}$$

From the first four equations in (2.17), one has

$$\phi^{[1]} - \phi^{[1,+]} = \frac{1}{z} \ln \frac{S_a - Q_{02}}{z c_1^{[1]}}, \quad \phi^{[2]} - \phi^{[2,-]} = \frac{1}{z} \ln \frac{S_b - Q_{02}}{z c_1^{[2]}}. \tag{2.20}$$

$$\phi^{[3]}-\phi^{[3,+]}=\frac{1}{z}\ln\frac{S_c-Q_{04}}{zc_1^{[3]}},\quad \phi^{[4]}-\phi^{[4,-]}=\frac{1}{z}\ln\frac{S_d-Q_{04}}{zc_1^{[4]}}. \tag{2.21}$$

From the fifth through eighth equations of (2.17), together with (2.20)–(2.21), one has

$$\begin{aligned} &S_a+Q_{02}\ln\frac{S_a-Q_{02}}{zc_1^{[1]}}=zA,\quad S_b+Q_{02}\ln\frac{S_b-Q_{02}}{zc_1^{[2]}}=zB,\\ &S_c+Q_{04}\ln\frac{S_c-Q_{04}}{zc_1^{[3]}}=zC,\quad S_d+Q_{04}\ln\frac{S_d-Q_{04}}{zc_1^{[4]}}=zD, \end{aligned} \tag{2.22}$$

i.e.,

$$\begin{aligned} &c_1^{[1]}=\frac{S_a-Q_{02}}{z}\exp\left\{\frac{S_a-zA}{Q_{02}}\right\},\quad c_1^{[2]}=\frac{S_b-Q_{02}}{z}\exp\left\{\frac{S_b-zB}{Q_{02}}\right\},\\ &c_1^{[3]}=\frac{S_c-Q_{04}}{z}\exp\left\{\frac{S_c-zC}{Q_{04}}\right\},\quad c_1^{[4]}=\frac{S_d-Q_{04}}{z}\exp\left\{\frac{S_d-zD}{Q_{04}}\right\}. \end{aligned} \tag{2.23}$$

From the fourth to last equations in (2.17), one has

$$\begin{aligned} \phi^{[1]}&=V+\frac{2D_2}{z(D_1+D_2)}\ln A-\frac{D_2-D_1}{z(D_1+D_2)}\ln L-\frac{1}{z}\ln c_1^{[1]}\\ &=V+\frac{2D_2}{z(D_1+D_2)}\ln zA-\frac{D_2-D_1}{z(D_1+D_2)}\ln zL-\frac{1}{z}\ln(S_a-Q_{02})-\frac{S_a-zA}{zQ_{02}}, \end{aligned} \tag{2.24}$$

$$\begin{aligned} \phi^{[4]}&=\frac{2D_2}{z(D_1+D_2)}\ln D-\frac{D_2-D_1}{z(D_1+D_2)}\ln R-\frac{1}{z}\ln c_1^{[4]}\\ &=\frac{2D_2}{z(D_1+D_2)}\ln zD-\frac{D_2-D_1}{z(D_1+D_2)}\ln zR-\frac{1}{z}\ln(S_d-Q_{04})-\frac{S_d-zD}{zQ_{04}}. \end{aligned} \tag{2.25}$$

Thus

$$\phi^{[1]}-\phi^{[4]}=V+\frac{2D_2}{z(D_1+D_2)}\ln\frac{A}{D}-\frac{D_2-D_1}{z(D_1+D_2)}\ln\frac{L}{R}-\frac{1}{z}\ln\frac{S_a-Q_{02}}{S_d-Q_{04}}-\frac{S_a-zA}{zQ_{02}}+\frac{S_d-zD}{zQ_{04}}. \tag{2.26}$$

From (2.20)-(2.21) and (2.23), one gets

$$\phi^{[1,+]}-\phi^{[2,-]}=\phi^{[1]}-\phi^{[2]}+\frac{S_a-zA-(S_b-zB)}{zQ_{02}}, \tag{2.27}$$

$$\phi^{[3,+]}-\phi^{[4,-]}=\phi^{[3]}-\phi^{[4]}+\frac{S_c-zC-(S_d-zD)}{zQ_{04}}. \tag{2.28}$$

The rest of the equations of (2.17) become

$$\begin{aligned} \frac{J_1}{D_1D_2}&=\frac{-2\,(A-L)}{\alpha_1H(1)(D_1+D_2)}=-2\frac{(B-A)+Q_{02}(\phi^{[1]}-\phi^{[2]})}{(D_1+D_2)\,(\alpha_2-\alpha_1)\,H(1)}\\ &=\frac{-2\,(C-B)}{(D_1+D_2)\,(\alpha_3-\alpha_2)\,H(1)}=-2\frac{(D-C)+Q_{04}(\phi^{[3]}-\phi^{[4]})}{(D_1+D_2)\,(\alpha_4-\alpha_3)\,H(1)}\\ &=\frac{-2\,(R-D)}{(1-\alpha_4)\,(D_1+D_2)H(1)}, \end{aligned} \tag{2.29}$$

$$\frac{zJ_1(D_2-D_1)}{D_1D_2}y_2=\phi^{[1]}-\phi^{[2]}+\frac{S_a-zA-(S_b-zB)}{zQ_{02}}, \tag{2.30}$$

$$\frac{zJ_1(D_2-D_1)}{D_1D_2}y_4=\phi^{[3]}-\phi^{[4]}+\frac{S_c-zC-(S_d-zD)}{zQ_{04}}, \tag{2.31}$$

$$\begin{aligned} S_b-Q_{02}&=(S_a-Q_{02})\,e^{N^*y_2}+\frac{2D_2Q_{02}}{D_1+D_2}\left(e^{N^*y_2}-1\right),\\ S_d-Q_{04}&=(S_c-Q_{04})\,e^{N^*y_4}+\frac{2D_2Q_{04}}{D_1+D_2}\left(e^{N^*y_4}-1\right), \end{aligned} \tag{2.32}$$

$$\phi^{[2,+]}=\phi^{[2]}-\frac{1}{2z}\ln\frac{c_2^{[2]}}{c_1^{[2]}},\quad \phi^{[3,-]}=\phi^{[3]}-\frac{1}{2z}\ln\frac{c_2^{[3]}}{c_1^{[3]}}, \tag{2.33}$$

where $N^*=\frac{-z^2(D_1+D_2)J_1}{D_1D_2}$.

From the equations in (2.29), one may obtain

$$\begin{aligned} &C=\frac{\alpha_3-\alpha_2}{\alpha_1}(A-L)+B,\quad D=R-\frac{1-\alpha_4}{\alpha_1}(A-L),\\ &\phi^{[1]}-\phi^{[2]}=\frac{1}{Q_{02}}\left(\frac{A-L}{\alpha_1}(\alpha_2-\alpha_1)-B+A\right),\\ &\phi^{[3]}-\phi^{[4]}=\frac{1}{Q_{04}}\left(\frac{A-L}{\alpha_1}(\alpha_4-\alpha_3)-D+C\right). \end{aligned} \tag{2.34}$$

Combining (2.29)–(2.31), one gets

$$\frac{J_1y_2}{D_1D_2}=\frac{W_2(A,B,Q_{02})}{z^2Q_{02}(D_2-D_1)},\quad \frac{J_1y_4}{D_1D_2}=\frac{W_4(A,B,Q_{04})}{z^2Q_{04}(D_2-D_1)}, \tag{2.35}$$

where

$$\begin{aligned} W_2(A,B,Q_{02})&=z\frac{A-L}{\alpha_1}(\alpha_2-\alpha_1)+S_a-S_b,\\ W_4(A,B,Q_{04})&=z\frac{A-L}{\alpha_1}(\alpha_4-\alpha_3)+S_c-S_d. \end{aligned} \tag{2.36}$$

Substituting (2.35) into (2.32), one has

$$\begin{aligned} &\frac{D_2-D_1}{D_1+D_2}Q_{02}\ln\frac{S_a+\frac{D_2-D_1}{D_1+D_2}Q_{02}}{S_b+\frac{D_2-D_1}{D_1+D_2}Q_{02}}-W_2=0,\\ &\frac{D_2-D_1}{D_1+D_2}Q_{04}\ln\frac{S_c+\frac{D_2-D_1}{D_1+D_2}Q_{04}}{S_d+\frac{D_2-D_1}{D_1+D_2}Q_{04}}-W_4=0. \end{aligned} \tag{2.37}$$

From (2.33), one obtains

$$\phi^{[2,+]}-\phi^{[3,-]}=\phi^{[2]}-\phi^{[3]}-\frac{1}{2z}\ln\frac{c_2^{[2]}c_1^{[3]}}{c_1^{[2]}c_2^{[3]}}. \tag{2.38}$$

Then together with (2.19) and (2.23), one has

$$\phi^{[2]} - \phi^{[3]} = \frac{1}{z}\left(\ln\frac{S_c - Q_{04}}{S_b - Q_{02}} + \frac{S_c - zC}{Q_{04}} - \frac{S_b - zB}{Q_{02}}\right) + \frac{2D_2}{z(D_1 + D_2)}\ln\frac{B}{C}. \tag{2.39}$$

Substituting (2.34) and (2.39) into (2.26), one has

$$\begin{aligned}\frac{D_2 - D_1}{D_1 + D_2}&\left(\ln\frac{\left(S_a + \frac{D_2-D_1}{D_1+D_2}Q_{02}\right)\left(S_c + \frac{D_2-D_1}{D_1+D_2}Q_{04}\right)}{\left(S_b + \frac{D_2-D_1}{D_1+D_2}Q_{02}\right)\left(S_d + \frac{D_2-D_1}{D_1+D_2}Q_{04}\right)} + \ln\frac{L}{R}\right) + \\ &\left(1 + \frac{D_2 - D_1}{D_1 + D_2}\right)\ln\frac{BD}{AC} + \ln\frac{(S_a - Q_{02})(S_c - Q_{04})}{(S_b - Q_{02})(S_d - Q_{04})} = zV.\end{aligned} \tag{2.40}$$

Therefore, the following conclusions can be obtained from the above analysis.

Proposition 2.7. *Let* $\theta = \frac{D_2-D_1}{D_2+D_1}$*, and the matching system* (2.17) *is reduced to*

$$G_1(A, B, Q_{02}, Q_{04}, \theta) = zV, \quad G_2(A, B, Q_{02}, \theta) = 0, \quad G_3(A, B, Q_{04}, \theta) = 0,$$

where

$$\begin{aligned}G_1(A, B, Q_{02}, Q_{04}, \theta) &= \theta\left(\ln\frac{(S_a + \theta Q_{02})(S_c + \theta Q_{04})}{(S_b + \theta Q_{02})(S_d + \theta Q_{04})} + \ln\frac{L}{R}\right) + (1 + \theta)\ln\frac{BD}{AC} \\ &\quad + \ln\frac{(S_a - Q_{02})(S_c - Q_{04})}{(S_b - Q_{02})(S_d - Q_{04})}, \\ G_2(A, B, Q_{02}, \theta) &= \theta Q_{02}\ln\frac{S_a + \theta Q_{02}}{S_b + \theta Q_{02}} - W_2, \\ G_3(A, B, Q_{04}, \theta) &= \theta Q_{04}\ln\frac{S_c + \theta Q_{04}}{S_d + \theta Q_{04}} - W_4.\end{aligned}$$

Note that the governing equation G_i ($i = 1, 2, 3$) above is equivalent to G_i ($i = 1, 2$) from Proposition 3.1 in [23]. Notations Q_{02}, Q_{04}, α_1, α_2, α_3, and α_4 in this work correspond to $Q_0, \beta Q_0$, and α_1–α_4 in [23].

2.5. Existence of solutions near the singular orbit

We have constructed a singular orbit on [0, 1] that connects B_L and B_R. It consists of fifteen pieces: two boundary layers $\Gamma^{[0,+]}$ and $\Gamma^{[5,-]}$; eight internal layers $\Gamma^{[k,-]}$ and $\Gamma^{[k,+]}$ ($k = 1, 2, 3, 4$); and five regular layers Λ_i ($i = 1, 2, 3, 4, 5$).

Next, we prove the existence of a solution of (1.9)-(1.10) in the neighborhood of the singular orbit through the exchange lemma [24, 25] of geometric singular perturbation theory (a detailed proof is in [26]).

Theorem 2.8. *Let*

$$\Gamma^{[0,+]} \cup \Lambda_1 \cup \Gamma^{[1,-]} \cup \Gamma^{[1,+]} \cup \Lambda_2 \cup \Gamma^{[2,-]} \cup \Gamma^{[2,+]} \cup \Lambda_3 \cup \Gamma^{[3,-]} \cup \Gamma^{[3,+]} \cup \Lambda_4 \cup \Gamma^{[4,-]} \cup \Gamma^{[4,+]} \cup \Lambda_5 \cup \Gamma^{[5,-]}$$

be the singular orbit of the connecting problem (2.1) *associated with* B_L *and* B_R *in system* (2.4)*. There exists* $\varepsilon_0 > 0$ *small, so that if* $0 < \varepsilon < \varepsilon_0$*, then the boundary value problem* (1.9)-(1.10) *has a unique solution near the aforementioned singular orbit.*

3. Qualitative properties of zero current ionic flow and reversal potential

We now discuss the dependence of functions G_i ($i = 1, 2, 3$) on parameters $A, B, Q_{02}, Q_{04}, and\theta$, which will be used in the subsequent analysis. Let $Q_{04} = \beta Q_{02}$. Since $Q_{02}Q_{04} < 0$, it follows that $\beta < 0$.

Lemma 3.1. *One has*

(i) $\partial_A G_2(A, B, Q_{02}, \theta) < 0$;

(ii) $\partial_B G_2(A, B, Q_{02}, \theta) > 0$;

(iii) $\partial_A G_3(A, B, Q_{04}, \theta) < 0$;

(iv) $\partial_B G_3(A, B, Q_{04}, \theta) < 0$;

(v) $\partial_B G_1$ *has the same sign as that of* Q_{04};

(vi) $\partial_A G_1$ *has the same sign as that of* Q_{04} *if* $A > \max\{C, D\}$ *and* $\beta < -\frac{\alpha_1}{\alpha_3-\alpha_2+1-\alpha_4}$; $\partial_A G_1$ *has the opposite sign as that of* Q_{04} *if* $A < \min\{C, D\}$ *and* $-\frac{\alpha_1}{\alpha_3-\alpha_2+1-\alpha_4} < \beta < 0$.

Proof. Partial derivatives of G_2 and G_3 in terms of A and B are

$$\begin{aligned}
\partial_A G_2(A, B, Q_{02}, \theta) &= \frac{-z^2 A}{S_a + \theta Q_{02}} - \frac{z(\alpha_2 - \alpha_1)}{\alpha_1},\\
\partial_B G_2(A, B, Q_{02}, \theta) &= \frac{z^2 B}{S_b + \theta Q_{02}},\\
\partial_A G_3(A, B, Q_{04}, \theta) &= \frac{z^2}{\alpha_1}\left(\frac{D(\alpha_4 - 1)}{S_d + \theta Q_{04}} - \frac{C(\alpha_3 - \alpha_2)}{S_c + \theta Q_{04}}\right) - \frac{z(\alpha_4 - \alpha_3)}{\alpha_1},\\
\partial_B G_3(A, B, Q_{04}, \theta) &= \frac{-z^2 C}{S_c + \theta Q_{04}},\\
\partial_B G_1 &= (1 - \theta^2)\left(\frac{Q_{04}}{(S_c + \theta Q_{04})C} - \frac{Q_{02}}{(S_b + \theta Q_{02})B}\right),\\
\partial_A G_1 &= \frac{1 - \theta^2}{\alpha_1}\left(\frac{\alpha_1 Q_{02}}{(S_a + \theta Q_{02})A} + \frac{(\alpha_3 - \alpha_2)Q_{04}}{(S_c + \theta Q_{04})C} + \frac{(1 - \alpha_4)Q_{04}}{(S_d + \theta Q_{04})D}\right).
\end{aligned} \tag{3.1}$$

Conclusions, except for the sign of $\partial_A G_1$, follow from (3.1) are straightforward. Note that

$$\begin{aligned}
\partial_A G_1 &= \frac{1 - \theta^2}{\alpha_1}\left(\frac{\alpha_1 Q_{02}}{(S_a + \theta Q_{02})A} + \frac{(\alpha_3 - \alpha_2)Q_{04}}{(S_c + \theta Q_{04})C} + \frac{(1 - \alpha_4)Q_{04}}{(S_d + \theta Q_{04})D}\right)\\
&= \frac{1 - \theta^2}{\alpha_1}Q_{02}\left(\frac{\alpha_1}{(S_a + \theta Q_{02})A} + \frac{(\alpha_3 - \alpha_2)\beta}{(S_c + \theta Q_{04})C} + \frac{(1 - \alpha_4)\beta}{(S_d + \theta Q_{04})D}\right).
\end{aligned} \tag{3.2}$$

For convenience, we define the following notations:

$$\overline{A} = (S_a + \theta Q_{02})A, \quad \overline{C} = (S_c + \theta Q_{04})C, \quad \overline{D} = (S_d + \theta Q_{04})D.$$

(1) For $Q_{04} < 0$ (i.e., $Q_{02} > 0$), $\partial_A G_1$ and $\frac{\alpha_1}{\overline{A}} + \frac{(\alpha_3-\alpha_2)\beta}{\overline{C}} + \frac{(1-\alpha_4)\beta}{\overline{D}}$ have the same sign. It is easy to obtain that

$$\frac{\alpha_1}{\overline{A}} + \beta\frac{\alpha_3 - \alpha_2 + 1 - \alpha_4}{\min\left\{\overline{C}, \overline{D}\right\}} \leq \frac{\alpha_1}{\overline{A}} + \beta\left(\frac{\alpha_3 - \alpha_2}{\overline{C}} + \frac{1 - \alpha_4}{\overline{D}}\right) \leq \frac{\alpha_1}{\overline{A}} + \beta\frac{\alpha_3 - \alpha_2 + 1 - \alpha_4}{\max\left\{\overline{C}, \overline{D}\right\}}. \tag{3.3}$$

Thus,

(1.1) if $\overline{A} \geq \max\left\{\overline{C}, \overline{D}\right\}$ (i.e., $A \geq \max\{C, D\}$) and $\beta < -\frac{\alpha_1}{\alpha_3-\alpha_2+1-\alpha_4}$, one has

$$\begin{aligned} \frac{\alpha_1}{\overline{A}} + \beta\left(\frac{\alpha_3 - \alpha_2}{\overline{C}} + \frac{1 - \alpha_4}{\overline{D}}\right) &\leq \frac{\alpha_1}{\overline{A}} + \beta\frac{\alpha_3 - \alpha_2 + 1 - \alpha_4}{\max\left\{\overline{C}, \overline{D}\right\}} \\ &\leq \frac{\alpha_1 + \beta(\alpha_3 - \alpha_2 + 1 - \alpha_4)}{\overline{A}} \\ &< 0, \end{aligned} \tag{3.4}$$

which means $\partial_A G_1 < 0$.

(1.2) if $\overline{A} \leq \min\left\{\overline{C}, \overline{D}\right\}$ (i.e., $A \leq \min\{C, D\}$) and $-\frac{\alpha_1}{\alpha_3-\alpha_2+1-\alpha_4} < \beta < 0$, one has

$$\begin{aligned} \frac{\alpha_1}{\overline{A}} + \beta\left(\frac{\alpha_3 - \alpha_2}{\overline{C}} + \frac{1 - \alpha_4}{\overline{D}}\right) &\geq \frac{\alpha_1}{\overline{A}} + \beta\frac{\alpha_3 - \alpha_2 + 1 - \alpha_4}{\min\left\{\overline{C}, \overline{D}\right\}} \\ &\geq \frac{\alpha_1 + \beta(\alpha_3 - \alpha_2 + 1 - \alpha_4)}{\min\left\{\overline{C}, \overline{D}\right\}} \\ &> 0, \end{aligned} \tag{3.5}$$

which implies $\partial_A G_1 > 0$.

(2) For $Q_{04} > 0$ (i.e., $Q_{02} < 0$), $\partial_A G_1$ and $\frac{\alpha_1}{\overline{A}} + \frac{(\alpha_3-\alpha_2)\beta}{\overline{C}} + \frac{(1-\alpha_4)\beta}{\overline{D}}$ have the opposite sign. The analytical process is similar to (1) and is omitted here. □

Lemma 3.2. *One has*

(i) $\partial_{Q_{02}} G_1$ *has the same sign as that of* $A - B$*;*

(ii) $\partial_{Q_{04}} G_1$ *has the opposite sign as that of* $A - B$*.*

Proof. The partial derivatives of G_1 in terms of Q_{02} and Q_{04} are

$$\begin{aligned} \partial_{Q_{02}} G_1 &= \frac{(1 - \theta^2)(S_a - S_b)}{(S_a + \theta Q_{02})(S_b + \theta Q_{02})}, \\ \partial_{Q_{04}} G_1 &= \frac{(1 - \theta^2)(S_c - S_d)}{(S_c + \theta Q_{04})(S_d + \theta Q_{04})}. \end{aligned} \tag{3.6}$$

Statement (i) follows from the first formula of (3.6). From the second formula of (3.6), we can obtain that $\partial_{Q_{04}} G_1$ and $C - D$ have the same sign, and in Theorem 3.8 will claim that $C - D$ and $A - B$ have opposite signs. The statement on the sign of $\partial_{Q_{04}} G_1$ holds then. □

Let $K(s) = \theta s + (1-\theta^2)Q_{02}$, $s \in (m, M)$, where $m = \min\{S_a + \theta Q_{02}, S_b + \theta Q_{02}\}$, $M = \max\{S_a + \theta Q_{02}, S_b + \theta Q_{02}\}$. Let $T(t) = \theta t + (1-\theta^2)Q_{04}$, $t \in (p, P)$, where $p = \min\{S_c + \theta Q_{04}, S_d + \theta Q_{04}\}$, $P = \max\{S_c + \theta Q_{04}, S_d + \theta Q_{04}\}$.

Lemma 3.3. *For* $\theta Q_{02} < 0$*, one has*

(i) $\theta K(s) > 0$ *if one of the following conditions holds:*

(i-1) $\min\{A, B\} < -\frac{Q_{02}\sqrt{1-\theta^2}}{z\theta} < \max\{A, B\}$ *for* $s \in (s_0, M)$*;*

(i-2) $\min\{A, B\} > -\frac{Q_{02}\sqrt{1-\theta^2}}{z\theta}$ *for* $s \in (m, M)$*;*

(ii) $\theta K(s) < 0$ *if one of the following conditions holds:*

(ii-1) $\min\{A, B\} < -\frac{Q_{02}\sqrt{1-\theta^2}}{z\theta} < \max\{A, B\}$ *for* $s \in (m, s_0)$*;*

(ii-2) $\max\{A, B\} < -\frac{Q_{02}\sqrt{1-\theta^2}}{z\theta}$ *for* $s \in (m, M)$*;*

where $s_0 = -\frac{(1-\theta^2)Q_{02}}{\theta}$.

Proof. For $K(s) = \theta s + (1-\theta^2)Q_{02}$, $s \in (m, M)$, the sign of $K(s)$ is consistent with that of Q_{02} if $\theta Q_{02} > 0$. Therefore, we only discuss the case when $\theta Q_{02} < 0$.

Note that as $\theta Q_{02} < 0$, the root of $K(s)$ is $s_0 = -\frac{(1-\theta^2)Q_{02}}{\theta}$.

Case I: $\theta > 0$, $Q_{02} < 0$.

(I-1) If $M < s_0$ and $A > B$, one has $S_a + \theta Q_{02} < -\frac{(1-\theta^2)Q_{02}}{\theta}$, i.e., $A < -\frac{Q_{02}\sqrt{1-\theta^2}}{z\theta}$. If $M < s_0$ and $A < B$, one has $S_b + \theta Q_{02} < -\frac{(1-\theta^2)Q_{02}}{\theta}$, i.e., $B < -\frac{Q_{02}\sqrt{1-\theta^2}}{z\theta}$. Therefore, $K(s) < 0$ for $s \in (m, M)$ and $\max\{A, B\} < -\frac{Q_{02}\sqrt{1-\theta^2}}{z\theta}$.

(I-2) If $m < s_0 < M$ and $A > B$, one has $S_b + \theta Q_{02} < -\frac{(1-\theta^2)Q_{02}}{\theta} < S_a + \theta Q_{02}$, i.e., $B < -\frac{Q_{02}\sqrt{1-\theta^2}}{z\theta} < A$. Similarly, if $m < s_0 < M$ and $A < B$, one has $A < -\frac{Q_{02}\sqrt{1-\theta^2}}{z\theta} < B$. Therefore, $K(s) < 0$ for $s \in (m, s_0)$ while $K(s) > 0$ for $s \in (s_0, M)$ and $\min\{A, B\} < -\frac{Q_{02}\sqrt{1-\theta^2}}{z\theta} < \max\{A, B\}$.

(I-3) If $m > s_0$ and $A > B$, one has $S_b + \theta Q_{02} > -\frac{(1-\theta^2)Q_{02}}{\theta}$, i.e., $B > -\frac{Q_{02}\sqrt{1-\theta^2}}{z\theta}$. Similarly, if $m > s_0$ and $A < B$, one has $A > -\frac{Q_{02}\sqrt{1-\theta^2}}{z\theta}$. Therefore, $K(s) > 0$ for $s \in (m, M)$ and $\min\{A, B\} > -\frac{Q_{02}\sqrt{1-\theta^2}}{z\theta}$.

Case II: $\theta < 0$, $Q_{02} > 0$.

(II-1) If $M < s_0$, one has $K(s) > 0$ for $s \in (m, M)$.

(II-2) If $m < s_0 < M$, one has $K(s) > 0$ for $s \in (m, s_0)$ while $K(s) < 0$ for $s \in (s_0, M)$.

(II-3) If $m > s_0$, one has $K(s) < 0$ for $s \in (m, M)$.

Combining the analysis of the above two cases leads to the statement of Lemma 3.3. □

Lemma 3.4. *For* $\theta Q_{04} < 0$*, one has*

(i) $\theta T(t) > 0$ *if one of the following conditions holds:*

(i-1) $\min\{C, D\} < -\frac{Q_{04}\sqrt{1-\theta^2}}{z\theta} < \max\{C, D\}$ *for* $t \in (t_0, P)$*;*

(i-2) $\min\{C, D\} > -\frac{Q_{04}\sqrt{1-\theta^2}}{z\theta}$ *for* $t \in (p, P)$*;*

(ii) $\theta T(t) < 0$ *if one of the following conditions holds:*

(ii-1) $\min\{C,D\} < -\frac{Q_{04}\sqrt{1-\theta^2}}{z\theta} < \max\{C,D\}$ *for* $t \in (n, t_0)$*;*

(ii-2) $\max\{C,D\} < -\frac{Q_{04}\sqrt{1-\theta^2}}{z\theta}$ *for* $t \in (p, P)$*;*

where $t_0 = -\frac{(1-\theta^2)Q_{04}}{\theta}$.

Lemma 3.5. *For* $Q_{02} \cdot Q_{04} < 0$*, one has*

(i) *if* $\theta Q_{02} > 0$ *(i.e.,* $\theta Q_{04} < 0$*), then*

(i-1) $\partial_{Q_{02}} G_2(A, B, Q_{02}, \theta)$ *has the same sign as that of* $(A - B)Q_{02}$*;*

(i-2) *when* $C > D$*,* $\partial_{Q_{04}} G_3(A, B, Q_{04}, \theta) > 0$ *for* $T(t) > 0$ *while* $\partial_{Q_{04}} G_3(A, B, Q_{04}, \theta) < 0$ *for* $T(t) < 0$*;*

(i-3) *when* $C < D$*,* $\partial_{Q_{04}} G_3(A, B, Q_{04}, \theta) > 0$ *for* $T(t) < 0$ *while* $\partial_{Q_{04}} G_3(A, B, Q_{04}, \theta) < 0$ *for* $T(t) > 0$*.*

(ii) *if* $\theta Q_{02} < 0$ *(i.e.,* $\theta Q_{04} > 0$*), then*

(ii-1) *when* $A > B$*,* $\partial_{Q_{02}} G_2(A, B, Q_{02}, \theta) > 0$ *for* $K(s) > 0$ *while* $\partial_{Q_{02}} G_2(A, B, Q_{02}, \theta) < 0$ *for* $K(s) < 0$*;*

(ii-2) *when* $A < B$*,* $\partial_{Q_{02}} G_2(A, B, Q_{02}, \theta) > 0$ *for* $K(s) < 0$ *while* $\partial_{Q_{02}} G_2(A, B, Q_{02}, \theta) < 0$ *for* $K(s) > 0$*;*

(ii-3) $\partial_{Q_{04}} G_3(A, B, Q_{04}, \theta)$ *has the same sign as that of* $(C - D)Q_{04}$*.*

Proof. The partial derivatives of G_2 and G_3 in terms of Q_{02} and Q_{04} are

$$\begin{aligned}\partial_{Q_{02}} G_2(A, B, Q_{02}, \theta) &= \theta \ln \frac{S_a + \theta Q_{02}}{S_b + \theta Q_{02}} + \frac{(1-\theta^2)(S_a - S_b)Q_{02}}{(S_a + \theta Q_{02})(S_b + \theta Q_{02})} \\ &= \frac{K(s)}{s^2}(S_a - S_b),\end{aligned} \tag{3.7}$$

$$\begin{aligned}\partial_{Q_{04}} G_3(A, B, Q_{04}, \theta) &= \theta \ln \frac{S_c + \theta Q_{04}}{S_d + \theta Q_{04}} + \frac{(1-\theta^2)(S_c - S_d)Q_{04}}{(S_c + \theta Q_{04})(S_d + \theta Q_{04})} \\ &= \frac{T(t)}{t^2}(S_c - S_d).\end{aligned} \tag{3.8}$$

The statement follows based on the above formulas and Lemmas 3.3 and 3.4. □

Lemma 3.6. *One has*

(i) $\partial_\theta G_2(A, B, Q_{02}, \theta)$ *has the same sign as that of* $(A - B)Q_{02}$*;*

(ii) $\partial_\theta G_3(A, B, Q_{04}, \theta)$ *has the same sign as that of* $(C - D)Q_{04}$*.*

Proof.

$$\partial_\theta G_2(A, B, Q_{02}, \theta) = Q_{02}\left(g_1(S_a) - g_1(S_b)\right),$$
$$\partial_\theta G_3(A, B, Q_{02}, \theta) = Q_{04}\left(g_2(S_c) - g_2(S_d)\right),$$

where $g_1(X) := \ln(X + \theta Q_{02}) + \frac{\theta Q_{02}}{X + \theta Q_{02}}$, $g_2(X) := \ln(X + \theta Q_{04}) + \frac{\theta Q_{04}}{X + \theta Q_{04}}$.

Note that $g_1'(X) = \frac{X}{(X+\theta Q_{02})^2} > 0$ and $g_2'(X) = \frac{X}{(X+\theta Q_{04})^2} > 0$ for $X > 0$. It is apparent that $S_a - S_b$ (resp., $S_c - S_d$) has the same sign as that of $A - B$ (resp., $C - D$). The statements on the signs of $\partial_\theta G_k$ follow directly. □

3.1. *The solution* $(A, B) = (A(Q_{02}, Q_{04}, \theta), B(Q_{02}, Q_{04}, \theta))$ *of* $G_2(A, B, Q_{02}, \theta) = 0$ *and* $G_3(A, B, Q_{04}, \theta) = 0$

Theorem 3.7. *For any given* (Q_{02}, Q_{04}, θ)*,* $G_2(A, B, Q_{02}, \theta) = 0$ *and* $G_3(A, B, Q_{04}, \theta) = 0$ *have a unique pair of solutions* $(A, B) = (A(Q_{02}, Q_{04}, \theta), B(Q_{02}, Q_{04}, \theta))$*.*

Proof. For any (Q_{04}, θ), let $A = L$, $B = R$, and $P_0 = (L, R)$, and from (2.34), we have $C = D = R$. One may check that

(i) $G_3(A, B, Q_{04}, \theta)$ is continuous on $(A, B) \in [0, +\infty) \times [0, +\infty)$;

(ii) $G_3(L, R, Q_{04}, \theta) = 0$;

(iii) $\partial_B G_3(A, B, Q_{04}, \theta)$ is continuous;

(iv) $\partial_B G_3(L, R, Q_{04}, \theta) \neq 0$.

With the above information and the implicit function theorem, we conclude that on the neighborhood $U(P_0)$, $G_3(A, B, Q_{04}, \theta) = 0$ uniquely determines an implicit function $B = B(A, Q_{04}, \theta)$ defined on the interval $(L-\sigma_0, L+\sigma_0)$, such that when $A \in (L-\sigma_0, L+\sigma_0)$, one has $(A, B(A, Q_{04}, \theta)) \in U(P_0)$, $G_3(A, B, Q_{04}, \theta) = 0$, and $R = B(L, Q_{04}, \theta)$.

Let $A_1 = L+\sigma_0^-$, since $A_1 \in (L-\sigma_0, L+\sigma_0)$, and there is a $B_1 = B(A_1, Q_{04}, \theta)$ and $G_3(A_1, B_1, Q_{04}, \theta) = 0$. Applying the implicit function theorem once again to $P_1 = (A_1, B_1)$ yields that, on a neighborhood $U(P_1)$, equation $G_3(A, B, Q_{04}, \theta) = 0$ uniquely determines an implicit function $B = B(A, Q_{04}, \theta)$ defined on the interval $(L+\sigma_0^- - \sigma_1, L+\sigma_0^- + \sigma_1)$. The extension from the left endpoint can be conducted in the same way. By repeatedly performing this procedure, we can expand the interval to $[0, \infty)$. Therefore, $G_3(A, B, Q_{04}, \theta) = 0$ defines a continuous and differentiable implicit function $B = B(A, Q_{04}, \theta)$ over its domain.

It follows from $G_3(A, B(A, Q_{04}, \theta), Q_{04}, \theta) = 0$ and the monotonicity of G_3 in terms of A and B in Lemma 3.1 that $\partial_A B = -\frac{\partial_A G_3}{\partial_B G_3} < 0$, i.e., B is decreasing in A strictly. Let A_M be the maximum for A (when $B = 0$), and denote B_M as the maximum for B (when $A = 0$). Since $R = B(L, Q_{04}, \theta)$, then $A_M > L$.

Substituting $B = B(A, Q_{04}, \theta)$ into $G_2(A, B, Q_{02}, \theta) = 0$ yields $G_2(A, B(A, Q_{04}, \theta), Q_{02}, \theta) = G_2(A, Q_{02}, Q_{04}, \theta) = 0$. Then $\partial_A G_2 = \frac{-z^2 A}{S_a+\theta Q_{02}} - \frac{z(\alpha_2-\alpha_1)}{\alpha_1} + \frac{z^2 B}{S_b+\theta Q_{02}} \partial_A B < 0$, i.e., G_2 is strictly decreasing in A. Set $x = \sqrt{Q_{02}^2 + z^2 B_M^2} > |Q_{02}|$ and $y = \sqrt{Q_{02}^2 + z^2 A_M^2} > |Q_{02}|$. Then

$$G_2(0^+, Q_{02}, Q_{04}, \theta) = g_1(x) := \theta Q_{02} \ln \frac{|Q_{02}| + \theta Q_{02}}{x + \theta Q_{02}} - \left(z\frac{-L}{\alpha_1}(\alpha_2 - \alpha_1) + |Q_{02}| - x \right),$$

$$G_2(A_M^-, Q_{02}, Q_{04}, \theta) = g_2(y) := \theta Q_{02} \ln \frac{y + \theta Q_{02}}{|Q_{02}| + \theta Q_{02}} - \left(z\frac{A_M - L}{\alpha_1}(\alpha_2 - \alpha_1) - |Q_{02}| + y \right).$$

One may check that $g_1'(x) = \frac{x}{x+\theta Q_{02}} > 0$, and hence $g_1(x) > g_1(|Q_{02}|) = \frac{zL}{\alpha_1}(\alpha_2 - \alpha_1) > 0$, i.e., $G_2(0^+, Q_{02}, Q_{04}, \theta) > 0$; as well as $g_2'(y) = \frac{-y}{y+\theta Q_{02}} < 0$, and hence $g_2(y) < g_2(|Q_{02}|) = \frac{-z(A_M-L)}{\alpha_1}(\alpha_2 - \alpha_1) < 0$, i.e., $G_2(A_M^-, Q_{02}, Q_{04}, \theta) < 0$.

Above all, for any (Q_{02}, Q_{04}, θ), there is a unique $A = A(Q_{02}, Q_{04}, \theta)$ such that $G_2\,(A, Q_{02}, Q_{04}, \theta) = 0$ and $B = B(A(Q_{02}, Q_{04}, \theta), Q_{04}, \theta)$. Furthermore, there is a unique pair of solutions $(A, B) = (A(Q_{02}, Q_{04}, \theta), B(Q_{02}, Q_{04}, \theta))$ such that $G_2(A, B, Q_{02}, \theta) = 0$ and $G_3(A, B, Q_{04}, \theta) = 0$. □

Next, we demonstrate some properties of the solution $(A, B) = (A(Q_{02}, Q_{04}, \theta), B(Q_{02}, Q_{04}, \theta))$ for $G_2(A, B, Q_{02}, \theta) = 0$ and $G_3(A, B, Q_{04}, \theta) = 0$.

Theorem 3.8. *$\partial_\theta A(Q_{02}, Q_{04}, \theta)$ has the same sign as that of $(A - B)Q_{02}$ or $(C - D)Q_{04}$.*

Proof. It follows from $G_2 = 0$ and $G_3 = 0$ in Proposition 2.7 that

$$\partial_\theta A(Q_{02}, Q_{04}, \theta) = -\frac{\partial_\theta G_2(A, B, Q_{02}, \theta)}{\partial_A G_2(A, B, Q_{02}, \theta)} = -\frac{\partial_\theta G_3(A, B, Q_{04}, \theta)}{\partial_A G_3(A, B, Q_{04}, \theta)}.$$

The statement is valid from (i) and (iii) in Lemma 3.1 and from Lemma 3.6. □

In [23], $\partial_\theta A(Q_{02}, Q_{04}, \theta)$ has the same sign as that of $L - R$ if $\theta > 0$. In this work, we obtain a more comprehensive relation between those parameters. Precisely, for $\theta > 0$ and $Q_{02} > 0$, $\partial_\theta A(Q_{02}, Q_{04}, \theta)$ has the opposite sign (resp., same sign) as that of $L - R$ if condition 2 (resp., condition 1) in Remark 3.2 holds.

Remark 3.1. Since $Q_{02}Q_{04} < 0$, from Theorem 3.8, one has $(A - B)(C - D) < 0$. Together with those expressions for C and D in (2.34), one may get that one of the following relations must be valid for different choices of (A, B, L, R).

(1) $A > B$

- a) $A < L$, $B < R$;
- b) $A < L$, $B > R$, and $\frac{A-L}{B-R} < \frac{-\alpha_1}{\alpha_3 - \alpha_2 + 1 - \alpha_4}$;
- c) $A > L$, $B < R$, and $\frac{A-L}{B-R} > \frac{-\alpha_1}{\alpha_3 - \alpha_2 + 1 - \alpha_4}$.

(2) $A < B$

- a) $A > L$, $B > R$;
- b) $A > L$, $B < R$, and $\frac{A-L}{B-R} < \frac{-\alpha_1}{\alpha_3 - \alpha_2 + 1 - \alpha_4}$;
- c) $A < L$, $B > R$, and $\frac{A-L}{B-R} > \frac{-\alpha_1}{\alpha_3 - \alpha_2 + 1 - \alpha_4}$.

It is worthwhile to point out that $(A - B)(C - D) > 0$ in [23], while we get $(A - B)(C - D) < 0$ under the setup of this work. This is the major difference between these two topics, which arises from the opposite signs of permanent charges Q_{02} and Q_{04}.

Lemma 3.9. *The solution $(A, B) = (A(Q_{02}, Q_{04}, \theta), B(Q_{02}, Q_{04}, \theta))$ of $G_2(A, B, Q_{02}, \theta) = 0$ and $G_3(A, B, Q_{04}, \theta) = 0$ satisfies*

(i) *for $Q_{02} = Q_{04} = 0$, one has $A(0, 0, \theta) = (1 - \alpha_1)L + \alpha_1 R$ and $B(0, 0, \theta) = (1 - \alpha_2)L + \alpha_2 R$;*

(ii) *for $Q_{02} \to \pm\infty$ and $Q_{04} \to \mp\infty$, one has $\lim_{\substack{Q_{02}\to\pm\infty \\ Q_{04}\to\mp\infty}} A(Q_{02}, Q_{04}, \theta) = L$, $\lim_{\substack{Q_{02}\to\pm\infty \\ Q_{04}\to\mp\infty}} D(Q_{02}, Q_{04}, \theta) = R$, and $\lim_{\substack{Q_{02}\to\pm\infty \\ Q_{04}\to\mp\infty}} B(Q_{02}, Q_{04}, \theta) = \lim_{\substack{Q_{02}\to\pm\infty \\ Q_{04}\to\mp\infty}} C(Q_{02}, Q_{04}, \theta)$;*

(iii) *if $L > R$, then $L > A(Q_{02}, Q_{04}, \theta) > A^* > R$;*

(iv) *if $L < R$, then $L < A(Q_{02}, Q_{04}, \theta) < A^* < R$,* *where* $A^* = \frac{\alpha_1 R + (\alpha_3-\alpha_2+1-\alpha_4)L}{\alpha_3-\alpha_2+1-\alpha_4+\alpha_1}$.

Proof. **(i)** The values $A(0,0,\theta)$ and $B(0,0,\theta)$ can be derived from the formulas of $G_2(A,B,Q_{02},\theta)=0$ and $G_3(A,B,Q_{04},\theta)=0$ in Proposition 2.7, together with the formulas of C and D in (2.34).

$$\begin{aligned}
&z\frac{A-L}{\alpha_1}(\alpha_2-\alpha_1)+zA-zB=0,\\
&z\frac{A-L}{\alpha_1}(\alpha_4-\alpha_3)+zC-zD=0,\\
&C=\frac{\alpha_3-\alpha_2}{\alpha_1}(A-L)+B,\\
&D=R-\frac{1-\alpha_4}{\alpha_1}(A-L).
\end{aligned} \tag{3.9}$$

(ii) According to $G_2(A,B,Q_{02},\theta)=0$ and $G_3(A,B,Q_{04},\theta)=0$, one has

$$\begin{aligned}
\lim_{\substack{Q_{02}\to\pm\infty\\ Q_{04}\to\mp\infty}} \theta Q_{02}\ln\frac{S_a+\theta Q_{02}}{S_b+\theta Q_{02}} &= \lim_{\substack{Q_{02}\to\pm\infty\\ Q_{04}\to\mp\infty}}\left(z\frac{A-L}{\alpha_1}(\alpha_2-\alpha_1)+S_a-S_b\right)\\
&=\frac{\alpha_2-\alpha_1}{\alpha_1}z\lim_{\substack{Q_{02}\to\pm\infty\\ Q_{04}\to\mp\infty}}(A-L),
\end{aligned} \tag{3.10}$$

$$\begin{aligned}
\lim_{\substack{Q_{02}\to\pm\infty\\ Q_{04}\to\mp\infty}} \theta Q_{04}\ln\frac{S_c+\theta Q_{04}}{S_d+\theta Q_{04}} &= \lim_{\substack{Q_{02}\to\pm\infty\\ Q_{04}\to\mp\infty}}\left(z\frac{A-L}{\alpha_1}(\alpha_4-\alpha_3)+S_c-S_d\right)\\
&=\frac{\alpha_4-\alpha_3}{\alpha_1}z\lim_{\substack{Q_{02}\to\pm\infty\\ Q_{04}\to\mp\infty}}(A-L).
\end{aligned} \tag{3.11}$$

Applying L'Hôpital's rule, we get

$$\lim_{\substack{Q_{02}\to\pm\infty\\ Q_{04}\to\mp\infty}} \theta Q_{02}\ln\frac{S_a+\theta Q_{02}}{S_b+\theta Q_{02}} = \lim_{\substack{Q_{02}\to\pm\infty\\ Q_{04}\to\mp\infty}} \theta Q_{04}\ln\frac{S_c+\theta Q_{04}}{S_d+\theta Q_{04}}=0.$$

Thus,

$$\begin{aligned}
&\lim_{\substack{Q_{02}\to\pm\infty\\ Q_{04}\to\mp\infty}} A(Q_{02},Q_{04},\theta)=L,\\
&\lim_{\substack{Q_{02}\to\pm\infty\\ Q_{04}\to\mp\infty}} D(Q_{02},Q_{04},\theta)=\lim_{\substack{Q_{02}\to\pm\infty\\ Q_{04}\to\mp\infty}}\left(R-\frac{1-\alpha_4}{\alpha_1}(A-L)\right)=R,\\
&\lim_{\substack{Q_{02}\to\pm\infty\\ Q_{04}\to\mp\infty}} C(Q_{02},Q_{04},\theta)=\lim_{\substack{Q_{02}\to\pm\infty\\ Q_{04}\to\mp\infty}}\left(\frac{\alpha_3-\alpha_2}{\alpha_1}(A-L)+B\right)=\lim_{\substack{Q_{02}\to\pm\infty\\ Q_{04}\to\mp\infty}} B(Q_{02},Q_{04},\theta).
\end{aligned} \tag{3.12}$$

(iii) One has $A=B=C=D$ if and only if $A=A^*=\frac{\alpha_1 R+(\alpha_3-\alpha_2+1-\alpha_4)L}{\alpha_3-\alpha_2+1-\alpha_4+\alpha_1}$. It is clear that $L<A^*<R$ if $L<R$ and $L>A^*>R$ if $L>R$.

For $A=B=A^*$, one has

$$G_2(A^*,A^*,Q_{02},\theta)=\frac{z(\alpha_2-\alpha_1)(L-R)}{\alpha_3-\alpha_2+1-\alpha_4+\alpha_1}. \tag{3.13}$$

If $L > R$, then $G_2(A^*, A^*, Q_{02}, \theta) > 0$. From Lemma 3.1, G_2 is monotonically decreasing with respect to A. Thus, we obtain that $A^* < A(Q_{02}, Q_{04}, \theta)$.

$$G_2(L, B, Q_{02}, \theta) = \theta Q_{02} \ln \frac{S_a + \theta Q_{02}}{S_b + \theta Q_{02}} - (S_a - S_b) = -\frac{(S_a - S_b)S_*}{S_* + \theta Q_{02}} < 0, \tag{3.14}$$

where S_* is between S_a and S_b. Thus, we obtain that $A(Q_{02}, Q_{04}, \theta) < L$.

Hence, if $L > R$, then $L > A(Q_{02}, Q_{04}, \theta) > A^* > R$.

(iv) This is similar to the proof in **(iii)**. □

Remark 3.2. According to the expression for zero current in (2.29) and cases (iii) and (iv) in Lemma 3.9, one gets that the zero current has the same sign as that of $L-R$ and of $L-A$. Furthermore, one has

(1) $A - B$ and $L - R$ have the same sign if one of the following conditions holds:

- a) $B < R < A < L$;
- b) $R < B < A < L$ and $\frac{A-L}{B-R} < \frac{-\alpha_1}{\alpha_3-\alpha_2+1-\alpha_4}$;
- c) $L < A < R < B$;
- d) $L < A < B < R$ and $\frac{A-L}{B-R} < \frac{-\alpha_1}{\alpha_3-\alpha_2+1-\alpha_4}$.

(2) $A - B$ and $L - R$ have the opposite sign if one of the following conditions holds:

- a) $R > A > \max\{B, L\}$ and $\frac{A-L}{B-R} > \frac{-\alpha_1}{\alpha_3-\alpha_2+1-\alpha_4}$;
- b) $\min\{B, L\} > A > R$ and $\frac{A-L}{B-R} > \frac{-\alpha_1}{\alpha_3-\alpha_2+1-\alpha_4}$.

Remark 3.3. $\partial_{Q_{02}} A(Q_{02}, Q_{04}, \theta)$ has the same sign as that of $\partial_{Q_{02}} G_2(A, B, Q_{02}, \theta)$ since

$$\partial_{Q_{02}} A(Q_{02}, Q_{04}, \theta) = -\frac{\partial_{Q_{02}} G_2(A, B, Q_{02}, \theta)}{\partial_A G_2(A, B, Q_{02}, \theta)}.$$

Remark 3.4. $\partial_{Q_{04}} A(Q_{02}, Q_{04}, \theta)$ has the same sign as that of $\partial_{Q_{04}} G_3(A, B, Q_{04}, \theta)$ since

$$\partial_{Q_{04}} A(Q_{02}, Q_{04}, \theta) = -\frac{\partial_{Q_{04}} G_3(A, B, Q_{04}, \theta)}{\partial_A G_3(A, B, Q_{04}, \theta)}.$$

3.2. Zero current flux J

Since $z_1 = -z_2 = z$, one has $J_1 = J_2$ under a zero current state. Flux density J is used to denote the equal fluxes and we call this a zero current flux. According to (2.29), J is given by

$$J(Q_{02}, Q_{04}, D_1, D_2) = \frac{-2D_1 D_2 (A - L)}{\alpha_1 H(1)(D_1 + D_2)} = \frac{-2D_1 D_2 (C - B)}{(D_1 + D_2)(\alpha_3 - \alpha_2) H(1)} = \frac{-2D_1 D_2 (R - D)}{(1 - \alpha_4)(D_1 + D_2) H(1)}. \tag{3.15}$$

Theorem 3.10. *The zero current flux $J = J(Q_{02}, Q_{04}, D_1, D_2)$ satisfies*

(i) *if $\theta Q_{02} > 0$ (i.e., $\theta Q_{04} < 0$), then*

(i-1) *$\partial_{Q_{02}} J$ has the opposite sign as that of $(A - B)Q_{02}$;*

(i-2) *when $C > D$ (i.e., $A < B$), $\partial_{Q_{04}} J < 0$ for $T(t) > 0$ while $\partial_{Q_{04}} J > 0$ for $T(t) < 0$;*

(i-3) *when $C < D$ (i.e., $A > B$), $\partial_{Q_{04}} J < 0$ for $T(t) < 0$ while $\partial_{Q_{04}} J > 0$ for $T(t) > 0$.*

(ii) *if $\theta Q_{02} < 0$ (i.e., $\theta Q_{04} > 0$), then*

(ii-1) *when $A > B$, $\partial_{Q_{02}} J < 0$ for $K(s) > 0$ while $\partial_{Q_{02}} J > 0$ for $K(s) < 0$;*

(ii-2) *when $A < B$, $\partial_{Q_{02}} J < 0$ for $K(s) < 0$ while $\partial_{Q_{02}} J > 0$ for $K(s) > 0$;*

(ii-3) *$\partial_{Q_{04}} J$ has the opposite sign as that of $(A - B)Q_{02}$.*

Proof. Direct calculation gives

$$\begin{aligned}\partial_{Q_{02}} J &= \frac{-2D_1D_2}{\alpha_1 H(1)(D_1 + D_2)} \partial_{Q_{02}} A \\ &= \frac{-2D_1D_2}{\alpha_1 H(1)(D_1 + D_2)} \left(-\frac{\partial_{Q_{02}} G_2}{\partial_A G_2} \right).\end{aligned} \tag{3.16}$$

$$\begin{aligned}\partial_{Q_{04}} J &= \frac{-2D_1D_2}{\alpha_1 H(1)(D_1 + D_2)} \partial_{Q_{04}} A \\ &= \frac{-2D_1D_2}{\alpha_1 H(1)(D_1 + D_2)} \left(-\frac{\partial_{Q_{04}} G_3}{\partial_A G_3} \right).\end{aligned} \tag{3.17}$$

The statement follows from Lemmas 3.1 and 3.5. □

Remark 3.5. It is worthwhile to claim that

(i) Theorem 3.10 provides the information for the effects of those two segments of oppositely charged permanent charges on zero current flow. More importantly, it contains situations where those two pieces of permanent charges take opposite roles. For example, as $\theta > 0, T(t) > 0, Q_{02} > 0$, and $Q_{04} < 0$, one has $\partial_{Q_{02}} J < 0$, while $\partial_{Q_{04}} J > 0$ if $A > B$. On the contrary, one gets $\partial_{Q_{02}} J > 0$, while $\partial_{Q_{04}} J < 0$ if $A < B$. It is necessary to clarify that $\partial_{Q_{02}} J > 0$ represents that the amount of ionic flow J gets bigger as the value of Q_{02} increases, which means that permanent charge Q_{02} enhances the ionic flux J. Oppositely, $\partial_{Q_{02}} J < 0$ stands for the inhibition role in J played by Q_{02}.

(ii) According to case (i) of Lemma 3.7 in [23], as $\theta > 0$, one gets that $\partial_{Q_{02}} J$ has an opposite sign as that of $L - R$. This relation is also valid in this study when $Q_{02} > 0$, $\theta > 0$, and condition 1 in Remark 3.2 is satisfied. Besides this, we also find that $\partial_{Q_{02}} J$ has the same sign as that of $L - R$ when $Q_{02} > 0$ and $\theta > 0$, together with condition 2 in Remark 3.2 holding. This implies that the dynamics of ion flows are much richer and the current work provides more information on the interplay between the boundary ion concentrations L and R, zero current flow J, diffusion coefficient ratio θ, permanent charge Q_{02}, and channel geometry.

Note that functions $A = A(Q_{02}, Q_{04}, \theta)$ and $B = B(Q_{02}, Q_{04}, \theta)$ depend on diffusion coefficients D_1 and D_2 through $\theta = \frac{D_2 - D_1}{D_2 + D_1}$, so A and B are homogeneous of degree zero in (D_1, D_2) but $J(Q_{02}, Q_{04}, D_1, D_2)$ is not. Therefore, it is necessary to study the effects of diffusion coefficients D_1 and D_2 on zero current flux.

A direct calculation gives

$$\partial_{D_1} J = \frac{(1+\theta)^2}{2\alpha_1 H(1)} \left(L - A + (1-\theta)\partial_\theta A \right),$$

$$\partial_{D_2} J = \frac{(1-\theta)^2}{2\alpha_1 H(1)} \left(L - A - (1+\theta)\partial_\theta A \right).$$

The following statements follow from the above formulas with Theorem 3.8 and Remark 3.2, which demonstrate the influence of diffusion coefficients D_1 and D_2 on zero current flow J.

Theorem 3.11. *$\partial_{D_1} J$ and $L - R$ have the same sign if one of the following conditions holds:*

(i) *As $Q_{02} > 0$,*

- (i-1) $B < R < A < L$;
- (i-2) $R < B < A < L$ *and* $\frac{A-L}{B-R} < \frac{-\alpha_1}{\alpha_3-\alpha_2+1-\alpha_4}$;
- (i-3) $L < A < R < B$;
- (i-4) $L < A < B < R$ *and* $\frac{A-L}{B-R} < \frac{-\alpha_1}{\alpha_3-\alpha_2+1-\alpha_4}$.

(ii) *As $Q_{02} < 0$,*

- (ii-1) $R > A > \max\{B, L\}$ *and* $\frac{A-L}{B-R} > \frac{-\alpha_1}{\alpha_3-\alpha_2+1-\alpha_4}$;
- (ii-2) $\min\{B, L\} > A > R$ *and* $\frac{A-L}{B-R} > \frac{-\alpha_1}{\alpha_3-\alpha_2+1-\alpha_4}$.

Theorem 3.12. *$\partial_{D_2} J$ and $L - R$ have the same sign if one of the following conditions holds:*

(i) *As $Q_{02} < 0$,*

- (i-1) $B < R < A < L$;
- (i-2) $R < B < A < L$ *and* $\frac{A-L}{B-R} < \frac{-\alpha_1}{\alpha_3-\alpha_2+1-\alpha_4}$;
- (i-3) $L < A < R < B$;
- (i-4) $L < A < B < R$ *and* $\frac{A-L}{B-R} < \frac{-\alpha_1}{\alpha_3-\alpha_2+1-\alpha_4}$.

(ii) *As $Q_{02} > 0$,*

- (ii-1) $R > A > \max\{B, L\}$ *and* $\frac{A-L}{B-R} > \frac{-\alpha_1}{\alpha_3-\alpha_2+1-\alpha_4}$;
- (ii-2) $\min\{B, L\} > A > R$ *and* $\frac{A-L}{B-R} > \frac{-\alpha_1}{\alpha_3-\alpha_2+1-\alpha_4}$.

Remark 3.6. In Theorems 3.11 and 3.12, we characterize effects on ionic flow J from diffusion coefficients D_1 and D_2. The interpretation for $\partial_{D_1} J > 0$ is that the amount of ionic flow J increases as the value of cation's diffusion coefficient D_1 rises, which would help one predict the behavior of ionic flow if different cations are introduced to the ion channel. $\partial_{D_2} J > 0$ can be understood in the same way.

From above two theorems, one may observe that the impact of D_1 and D_2 depends on boundary ion concentrations L and R, parameters A and B standing for intermediate ion concentrations over $x = x_1$ and $x = x_2$, the sign of permanent charge density Q_{02}, together with those parameters α_1, α_2, α_3, and α_4, which represent the ion channel geometry. Those nonlinear interplays are the reasons for the rich dynamics of ionic flows and are also nonintuitive. We hope these results would provide useful insights for numerical and even experimental research on ion channel problems regarding the controlling behaviors of ionic flows by adjusting the values of boundary ion concentrations and inner parameters.

3.3. Dependence of the reversal potential $V_{rev} = V_{rev}(Q_{02}, Q_{04}, \theta)$ on Q_{02} and Q_{04}

In this subsection, we first determine the value of transmembrane potential $V = V_{rev}$ that creates zero current I, and then investigate its dependence on permanent charges Q_{02} and Q_{04}.

V_{rev} is determined from $G_1(A, B, Q_{02}, Q_{04}, \theta) = zV_{rev}$ with the expression

$$\begin{aligned} V_{rev}(Q_{02}, Q_{04}, \theta) = &\frac{\theta}{z}\left(\ln\frac{(S_a+\theta Q_{02})\,(S_c+\theta Q_{04})}{(S_b+\theta Q_{02})\,(S_d+\theta Q_{04})} + \ln\frac{L}{R}\right) \\ &+ \frac{1+\theta}{z}\ln\frac{BD}{AC} + \frac{1}{z}\ln\frac{(S_a-Q_{02})(S_c-Q_{04})}{(S_b-Q_{02})(S_d-Q_{04})}, \end{aligned} \tag{3.18}$$

where $A = A(Q_{02}, Q_{04}, \theta)$, $B = B(Q_{02}, Q_{04}, \theta)$.

Corollary 3.1. *(i) For $Q_{02} = Q_{04} = 0$, the reversal potential is $V_{rev}(0, 0, \theta) = \frac{\theta}{z}\ln\frac{L}{R}$.*
(ii) For $Q_{02} \neq 0$ and $Q_{04} = 0$, the reversal potential is

$$V_{rev}(Q_{02}, 0, \theta) = \frac{\theta}{z}\left(\ln\frac{(S_a+\theta Q_{02})}{(S_b+\theta Q_{02})} + \ln\frac{L}{R}\right) + \frac{1+\theta}{z}\ln\frac{B}{A} + \frac{1}{z}\ln\frac{(S_a-Q_{02})}{(S_b-Q_{02})},$$

which is consistent with the results in [16]. The detailed qualitative of the reversal potential in this situation can be found in [16].

According to the expression of $V_{rev}(0, 0, \theta)$ from case (i) in Corollary 3.1, one can see that if $D_1 < D_2$ and $L > R$, then $V_{rev}(0, 0, \theta) > 0$. This complies with the electrochemical law. Note that J_k has the same sign as that of $z_kV + \ln\frac{L}{R}$ and hence if $V = 0$ and $L > R$, one has $J_1 > 0$ and $J_2 > 0$. With $D_1 < D_2$, $J_1 < J_2$, in order to promote J_1 stronger than J_2 to attain $J_1 = J_2$, one has to increase V and this is why $V(0, 0, \theta) > 0$ in this case.

Theorem 3.13. *For the reversal potential $V_{rev} = V_{rev}(Q_{02}, Q_{04}, \theta)$, one has*

(i) *if $L > R$, then $J > 0$, and hence $-\frac{1}{z}\ln\frac{L}{R} < V_{rev}(Q_{02}, Q_{04}, \theta) < \frac{1}{z}\ln\frac{L}{R}$;*

(ii) *if $L < R$, then $J < 0$, and hence $\frac{1}{z}\ln\frac{L}{R} < V_{rev}(Q_{02}, Q_{04}, \theta) < -\frac{1}{z}\ln\frac{L}{R}$;*

(iii) $\lim\limits_{\substack{Q_{02}\to+\infty\\ Q_{04}\to-\infty}} V_{rev}(Q_{02}, Q_{04}, \theta) = \frac{1}{z}\ln\frac{LR}{B^2}$, $\lim\limits_{\substack{Q_{02}\to-\infty\\ Q_{04}\to+\infty}} V_{rev}(Q_{02}, Q_{04}, \theta) = -\frac{1}{z}\ln\frac{LR}{B^2}$.

Proof. **(i)** From case (iii) in Lemma 3.9 and the expression for J in (3.15), we have that if $L > R$, then $J > 0$. The range for V_{rev} is identified based on the fact that individual flux J_k ($k = 1, 2$) has the same sign as that of $z_kV + \ln\frac{L}{R}$.

(ii) We can use the same procedure as that of **(i)**.

(iii) Since

$$\lim_{\substack{Q_{02}\to\pm\infty\\ Q_{04}\to\mp\infty}} \ln\frac{S_a+\theta Q_{02}}{S_b+\theta Q_{02}} = 0, \qquad \lim_{\substack{Q_{02}\to\pm\infty\\ Q_{04}\to\mp\infty}} \ln\frac{S_c+\theta Q_{04}}{S_d+\theta Q_{04}} = 0,$$

$$\lim_{Q_{02}\to-\infty} \ln\frac{S_a-Q_{02}}{S_b-Q_{02}} = 0, \qquad \lim_{Q_{04}\to-\infty} \ln\frac{S_c-Q_{04}}{S_d-Q_{04}} = 0,$$

$$\lim_{Q_{02}\to+\infty} \ln\frac{S_a-Q_{02}}{S_b-Q_{02}} = \lim_{Q_{02}\to+\infty} \ln\frac{A^2(S_b+Q_{02})}{B^2(S_a+Q_{02})} = 2\ln\frac{L}{B},$$

$$\lim_{Q_{04}\to+\infty} \ln \frac{S_c - Q_{04}}{S_d - Q_{04}} = \lim_{Q_{04}\to+\infty} \ln \frac{C^2(S_d + Q_{04})}{D^2(S_c + Q_{04})} = 2\ln \frac{C}{R}.$$

Using the expression for reversal potential V_{rev} in (3.18) and the limit information in Lemma 3.9, then one has

$$\lim_{\substack{Q_{02}\to+\infty\\ Q_{04}\to-\infty}} V_{rev}(Q_{02}, Q_{04}, \theta) = \frac{1}{z}\ln\frac{LR}{B^2}, \quad \lim_{\substack{Q_{02}\to-\infty\\ Q_{04}\to+\infty}} V_{rev}(Q_{02}, Q_{04}, \theta) = -\frac{1}{z}\ln\frac{LR}{B^2}.$$

□

Concerning the monotonicity of $V_{rev} = V_{rev}(Q_{02}, Q_{04}, \theta)$ in Q_{02} and Q_{04}, we have the following result.

Theorem 3.14. *For any given $\theta \in (-1, 1)$, one has*

(i) *if $\theta Q_{02} > 0$ and $-\frac{\alpha_1}{\alpha_3-\alpha_2+1-\alpha_4} < \beta < 0$, then*

  (i-1) *V_{rev} is increasing in Q_{02} for $B < A < C$;*

  (i-2) *V_{rev} is decreasing in Q_{02} for $A < \min\{B, D\}$.*

(ii) *if $\theta Q_{02} < 0$ and $\beta < -\frac{\alpha_1}{\alpha_3-\alpha_2+1-\alpha_4}$, then*

  (ii-1) *V_{rev} is increasing in Q_{04} for $B > A > C$;*

  (ii-2) *V_{rev} is decreasing in Q_{04} for $A > \max\{B, D\}$.*

Proof. We primarily prove statement (i), and (ii) can be verified similarly.

It follows from $G_1(A, B, Q_{02}, Q_{04}, \theta) = zV$, $\partial_{Q_{02}}A = -\frac{\partial_{Q_{02}}G_2}{\partial_A G_2}$, and $\partial_{Q_{02}}B = -\frac{\partial_{Q_{02}}G_2}{\partial_B G_2}$ that

$$\begin{aligned}\partial_{Q_{02}}V_{rev} &= \frac{1}{z}\left(\partial_{Q_{02}}G_1 + \partial_A G_1\partial_{Q_{02}}A + \partial_B G_1\partial_{Q_{02}}B\right)\\ &= \frac{1}{z}\left(\partial_{Q_{02}}G_1 - \frac{\partial_A G_1\partial_{Q_{02}}G_2}{\partial_A G_2} - \frac{\partial_B G_1\partial_{Q_{02}}G_2}{\partial_B G_2}\right)\\ &= \frac{1}{z}\left(\partial_{Q_{02}}G_1 - \partial_{Q_{02}}G_2\left(\frac{\partial_A G_1}{\partial_A G_2} + \frac{\partial_B G_1}{\partial_B G_2}\right)\right).\end{aligned} \tag{3.19}$$

The statements then can be received by Lemmas 3.1, 3.2, and 3.5. □

Remark 3.7. From Theorem 4.5 in [23], as $\theta > 0$, one has that V_{rev} increases (resp., decreases) in Q_{02} when $L > R$ (resp., $L < R$). This relation is also valid in this work. For example, it happens if condition (i-1) (resp., condition (i-2)) in Theorem 3.14 satisfies, combined with condition 1.1 or 1.2 (resp., condition 1.3 or 1.4) in Remark 3.2. Besides this relation, we also obtain the opposite situation. That is, for $\theta > 0$ and $Q_{02} > 0$, V_{rev} is increasing (resp., decreasing) with respect to Q_{02} as $L < R$ (resp., $L > R$) if case (i-1) (resp., case (i-2)) holds, together with condition 2.1 (resp., condition 2.2) in Remark 3.2.

4. Conclusions

In this work, we utilize the classical PNP model with two segments of permanent charges in opposite signs to investigate the internal dynamics of ionic flows under a zero current condition. We derive three crucial governing equations in Proposition 2.7 and prove the existence and local uniqueness solution to the model, upon which the effects of permanent charges and diffusion coefficients on ionic flow are characterized. We also investigate the dependence of reversal potential V_{rev} on related physical parameters, from which the nonlinear interactions are revealed.

Finally, we must point out that due to the complexity of the parameters, our discussion is not completely comprehensive, and for some results, we have only conducted analyses under specific conditions. For example, systems containing ions with general valences need to be analyzed. In addition, ion size is another critical factor and should be investigated for more practical results. However, we believe that the existing results are sufficient to provide basic insights for our further understanding of ion channels containing piecewise nonzero permanent charges.

Author contributions

Conceptualization, J.C. and Y.Q.; methodology, J.C.; formal analysis, J.C. and Y.Q.; writing—original draft J.C..; writing—review and editing, Y.Q.; funding acquisition, J.C. All authors have read and agreed to the published version of the manuscript.

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The authors didn't use any Generative-AI tools throughout the process of this article.

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Conflict of interest

All authors declare no conflicts of interest in this paper.

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