

Article

Additive Effects of Small Permanent Charges on Ionic Flow Using Poisson–Nernst–Planck Systems

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Abstract

We examine the effects from small, spatially localized permanent charges on ionic transport in narrow membrane channels. Our analysis is based on a one-dimensional steady-state Poisson–Nernst–Planck (PNP) model involving two oppositely charged ion species with constant diffusion coefficients under electroneutral boundary conditions. In the framework of geometric singular perturbation theory, the steady PNP system is reformulated as a fast–slow dynamical system amenable to boundary-layer analysis. In the limit of vanishing permanent charge, the solution exhibits a singular structure with sharp boundary-layer segments and smooth bulk segments across regions of piecewise constant charge. Assuming the permanent charge strength Q is small, we carry out a regular perturbation expansion about $Q = 0$ and derive explicit first-order corrections to each ion’s flux. Closed-form expressions are obtained for both the leading-order (zero-charge) fluxes and the $O(Q)$ flux corrections, revealing how even a small fixed charge can modulate the magnitude of individual ionic fluxes as a function of the applied transmembrane voltage and boundary concentration asymmetry. These results elucidate how permanent charge enhances or inhibits specific ionic flows, thereby influencing channel selectivity. Overall, our analysis provides clear asymptotic formulas and highlights the broader relevance of this perturbative approach to electro-diffusive transport modeling in biophysical systems.

Keywords: PNP; ionic flows; individual fluxes; permanent charge

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1. Introduction

Ion channels are membrane-embedded proteins forming crucial pores for rapid ion passage, enabling cellular communication, signal transduction, and coordinated functions [1–4]. Research focuses on their structure (geometry, charge distribution in narrow pore regions) and ionic flow analysis. These channels, often cylindrical with varying cross-sections, select and facilitate ion diffusion, fundamental to cell signaling and function [5–8].

A key area of physiological study is the function of ion channels. At their core, ion channels manage membrane permeability, specifically selecting certain ions and enabling or adjusting their movement across cell membranes. Currently, the most relevant properties of ion channels—permeation and selectivity—are often determined by analyzing current-voltage (I–V) relations obtained through various experiments [2,9]. These I–V

relations, which describe the ionic transport governed by fundamental physical laws of electrodiffusion, define how the channel structure functions. For practical applications, however, studying individual ion fluxes is crucial because while most experiments measure only the total current, individual fluxes offer more detailed information about channel functions [10,11]. The overall (macroscopic) behavior of these ion flows is further dependent on external forces, which are expressed mathematically as boundary conditions [12]. The standard continuum model for ionic flow is the PNP system, which views the solvent as a dielectric continuum (see [13–20] and the reference therein). Derived from various fundamental theories [21–25], it accurately represents biological ionic transport, making it widely used for analysis and simulation.

In this work, we adopt the one-dimensional steady-state PNP model analyzed in [26] first proposed by [27], which reads

$$\begin{aligned} \frac{1}{A(X)} \frac{d}{dX} \left(\epsilon_r(X) \epsilon_0 A(X) \frac{d\Phi}{dX} \right) &= -e \left(\sum_{s=1}^n z_s C_s + Q(X) \right), \\ \frac{dJ_k}{dX} &= 0, \quad -J_k = \frac{1}{k_B T} D_k(X) A(X) C_k \frac{d\mu_k}{dX}, \quad k = 1, 2, \dots, n. \end{aligned} \quad (1)$$

In this formulation, $X \in [0, l]$ denotes the axial coordinate of the channel, characterized by its cross-sectional area $A(X)$, permanent charge density $Q(X)$, and relative dielectric coefficient $\epsilon_r(X)$. Standard physical parameters include the vacuum permittivity ϵ_0 , elementary charge e , and thermal energy $k_B T$. For each ion species k , we define the concentration C_k , valence z_k , flux density J_k , and position-dependent diffusion coefficient $D_k(X)$. Finally, Φ represents the electric potential and μ_k denotes the electrochemical potential, which is a function of Φ and the concentration set $\{C_k\}$.

Equipped with system (1), we impose the following boundary conditions (see, ref. [28] for a reasoning), for $k = 1, 2, \dots, n$,

$$\Phi(0) = \mathcal{V}, \quad C_k(0) = \mathcal{L}_k > 0; \quad \Phi(l) = 0, \quad C_k(l) = \mathcal{R}_k > 0. \quad (2)$$

In many qualitative studies focused on ionic flows through membrane channels, electroneutrality boundary conditions are imposed at both ends to prevent sharp boundary layers (see, e.g., [6,8,26,29–38], and particularly those studied in the frame work of geometric singular perturbation theory [5,12,39–44]), given by

$$\sum_{k=1}^n z_k \mathcal{L}_k = \sum_{k=1}^n z_k \mathcal{R}_k = 0. \quad (3)$$

The remainder of this paper is structured as follows: Section 2 introduces the problem and the mathematical methodology used. In Section 3, we present our main result, detailing the effect of the small positive permanent charge on the magnitude of individual fluxes. Section 4 offers concluding remarks.

2. Problem Setup and Mathematical Methods

We will set up our problem with more specific assumptions and describe the mathematical method we adopted in our discussion.

2.1. Assumptions and Derivation of a Dimensionless PNP Model

To be specific, it is assumed hereinafter that

- (A1). The ionic mixture comprises two oppositely charged species, with valences denoted as $z_1 > 0$ and $z_2 < 0$.

(A2). The permanent charge is characterized by

$$Q(x) = \begin{cases} Q_1, & X_0 < X < X_1, \\ Q_2, & X_1 < X < X_2, \\ Q_3, & X_2 < X < X_3, \\ Q_4, & X_3 < X < X_4, \\ Q_5, & X_4 < X < X_5, \end{cases} \quad (4)$$

where $X_0 = 0$, $X_5 = 1$, $Q_1 = Q_3 = Q_5 = 0$, Q_2 and Q_4 are some nonzero constants with the same sign.

(A3). We limit the electrochemical potential μ_k to the ideal component μ_k^{id} , which is given by

$$\mu_k^{\text{id}}(X) = z_k e \Phi(X) + k_B T \ln \frac{C_k(X)}{C_0} \quad (5)$$

with a characteristic number density C_0 , which is defined by

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

(A4). Both the relative dielectric coefficient (ϵ_r) and the diffusion coefficient (D_k) are treated as spatially invariant constants.

For the remainder of this work, we assume conditions (A1)–(A4) hold. We then make the system dimensionless using the rescaling procedure outlined in [7]. Let

$$\begin{aligned} \varepsilon^2 &= \frac{\epsilon_r \epsilon_0 k_B T}{e^2 l^2 C_0}, \quad x = \frac{X}{l}, \quad h(x) = \frac{A(X)}{l^2}, \quad \mathcal{D}_k = l C_0 D_k; \\ \phi(x) &= \frac{e}{k_B T} \Phi(X), \quad c_k(x) = \frac{C_k(X)}{C_0}, \quad J_k = \frac{\mathcal{J}_k}{D_k}; \\ V &= \frac{e}{k_B T} \mathcal{V}, \quad L_k = \frac{\mathcal{L}_k}{C_0}, \quad R_k = \frac{\mathcal{R}_k}{C_0}. \end{aligned} \quad (6)$$

The BVP (1) and (2) then becomes

$$\begin{aligned} \frac{\varepsilon^2}{h(x)} \frac{d}{dx} \left(h(x) \frac{d\phi}{dx} \right) &= -(z_1 c_1 + z_2 c_2 + Q(x)), \\ \frac{dc_k}{dx} + z_k c_k \frac{d\phi}{dx} &= -\frac{J_k}{h(x)}, \quad \frac{dJ_k}{dx} = 0, \quad k = 1, 2, \end{aligned} \quad (7)$$

with the boundary conditions, for $k = 1, 2$,

$$\phi(0) = V, \quad c_k(0) = L_k > 0; \quad \phi(1) = 0, \quad c_k(1) = R_k > 0. \quad (8)$$

Correspondingly, the electroneutrality condition (3) now becomes

$$z_1 L_1 + z_2 L_2 = 0, \quad z_1 R_1 + z_2 R_2 = 0. \quad (9)$$

We reformulate the PNP system (7) into a standard singularly perturbed form, thereby recasting the boundary value problem as a connection problem. Under the transformation $u = \varepsilon \phi$ and $\tau = x$, the system (7) becomes

$$\begin{aligned}\varepsilon \dot{\phi} &= u, \quad \varepsilon \dot{u} = -z_1 c_1 - z_2 c_2 - Q(\tau) - \varepsilon \frac{h'(\tau)}{h(\tau)} u, \\ \varepsilon \dot{c}_1 &= -z_1 u c_1 - \varepsilon \frac{J_1}{h(\tau)}, \quad \varepsilon \dot{c}_2 = -z_2 u c_2 - \varepsilon \frac{J_2}{h(\tau)}, \\ \dot{J}_1 &= \dot{J}_2 = 0, \quad \dot{\tau} = 1,\end{aligned}\tag{10}$$

where dot denotes the derivative with respect to x . System (10) is the *slow system*, and is modeled as a dynamical system, where we consider its phase space to be $\mathbb{R}^7$ and treat the independent variable x as an evolution parameter (time). The boundary condition (8) becomes

$$\phi(0) = V, \quad c_k(0) = L_k, \quad \tau(0) = 0; \quad \phi(1) = 0, \quad c_k(1) = R_k, \quad \tau(1) = 1.$$

The rescaling $x = \varepsilon \xi$ in (10) gives rise to the *fast system*, for $k = 1, 2$,

$$\begin{aligned}\phi' &= u, \quad u' = -z_1 c_1 - z_2 c_2 - Q(\tau) - \varepsilon \frac{h_\tau(\tau)}{h(\tau)} u, \\ c'_1 &= -z_1 u c_1 - \varepsilon \frac{J_1}{h(\tau)}, \quad c'_2 = -z_2 u c_2 - \varepsilon \frac{J_2}{h(\tau)}, \\ J'_1 &= J'_2 = 0, \quad \tau' = \varepsilon,\end{aligned}\tag{11}$$

where prime denotes the derivative with respect to the variable ξ .

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

$$\begin{aligned}B_L &= \{(\phi, u, c_1, c_2, J_1, J_2, x) : \phi = V, c_1 = L_1, c_2 = L_2, x = 0\}, \\ B_R &= \{(\phi, u, c_1, c_2, J_1, J_2, x) : \phi = 0, c_1 = R_1, c_2 = R_2, x = 1\}.\end{aligned}\tag{12}$$

The boundary value problem reduces to the connection problem of determining an orbit that provides a trajectory from the left boundary layer (B_L) to the right boundary layer (B_R) within system (10).

2.2. Mathematical Methods

We will analyze Problem (10) using geometric singular perturbation theory, which establishes the existence and local uniqueness of the solution [28]. Crucially, explicit approximated expressions for individual fluxes can be derived; this allows us to employ regular perturbation analysis to examine the effects of small permanent charges on ionic flow (see [6] for a detailed discussion for a relatively simple case).

For convenience, we now outline the formation of a singular orbit, which is the union of solutions derived from the limiting slow system (obtained by setting $\varepsilon \rightarrow 0$ in (10)) and the limiting fast system (obtained by setting $\varepsilon \rightarrow 0$ in (11)). This ends up with a governing system, from which regular perturbation analysis is able to be applied.

Due to the jumps of the permanent charge $Q(x)$ in (4) at $x = x_1, x = x_2, x = x_3$ and $x = x_4$, the construction of a singular orbit on $[0, 1]$ is naturally split into five subintervals $[x_0, x_1], [x_1, x_2], [x_2, x_3], [x_3, x_4]$ and $[x_4, x_5]$. For the latter, we preassign (unknown) values of ϕ , c_1 and c_2 at $x = x_k$ for $k = 1, 2, 3, 4$:

$$\phi(x_k) = \phi^{[k]}, \quad c_1(x_k) = c_1^{[k]}, \quad c_2(x_k) = c_2^{[k]}\tag{13}$$

with given $\phi^{[0]} = V$ and $c_k^{[0]} = L_k$ at $x_0 = 0$, $\phi^{[5]} = 0$ and $c_k^{[5]} = R_k$ at $x_5 = 1$, and introduce the set, for $j = 0, 1, 2, 3, 4, 5$

$$B_j = \left\{ (\phi, u, c_1, c_2, J_1, J_2, x) : \phi = \phi^{[j]}, c_1 = c_1^{[j]}, c_2 = c_2^{[j]}, x = x_j \right\}. \quad (14)$$

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

Using these *twelve* unknowns, we can construct singular orbits within each subinterval $[x_{j-1}, x_j]$: Λ_j denotes the regular layer over the interval, while $\Gamma^{[j-1,r]}$ and $\Gamma^{[j,l]}$ represent the right and left boundary layers at $x = x_{j-1}$ and $x = x_j$, respectively.

- (i) The singular orbit on the interval $[x_0, x_1]$ is composed of three distinct segments: two boundary layers, $\Gamma^{[0,r]}$ at $x = x_0$ and $\Gamma^{[1,l]}$ at $x = x_1$, and a regular layer Λ_1 spanning (x_0, x_1) . The state (ϕ, c_1, c_2, τ) transitions from $(V, L_1, L_2, 0)$ at $x = x_0 = 0$ to $(\phi_{[1]}, c_1^{[1]}, c_2^{[1]}, x_1)$ at $x = x_1$. Specifically, given the initial condition $(\phi^{[1]}, c_1^{[1]}, c_2^{[1]})$, the scaled flux densities $J_1^{[1]}, J_2^{[1]}$ and the boundary value $u_l(x_1)$ are uniquely determined.
- (ii) The singular orbit on the interval $[x_1, x_2]$ is composed of three distinct segments: two boundary layers, $\Gamma^{[1,r]}$ at $x = x_1$ and $\Gamma^{[2,l]}$ at $x = x_2$, and a regular layer Λ_2 spanning (x_1, x_2) . The state (ϕ, c_1, c_2, τ) transitions from $(\phi^{[1]}, c_1^{[1]}, c_2^{[1]}, x_1)$ at $x = x_1$ to $(\phi_{[2]}, c_1^{[2]}, c_2^{[2]}, x_2)$ at $x = x_2$. Specifically, given the initial conditions $(\phi^{[1]}, c_1^{[1]}, c_2^{[1]})$ and the parameters $(\phi^{[2]}, c_1^{[2]}, c_2^{[2]})$, the scaled flux densities $J_1^{[2]}, J_2^{[2]}$ and the boundary values $u_r(x_1)$ and $u_l(x_2)$ are uniquely determined.
- (iii) The singular orbit on the interval $[x_2, x_3]$ is composed of three distinct segments: two boundary layers, $\Gamma^{[2,r]}$ at $x = x_2$ and $\Gamma^{[3,l]}$ at $x = x_3$, and a regular layer Λ_3 spanning (x_2, x_3) . The state (ϕ, c_1, c_2, τ) transitions from $(\phi^{[2]}, c_1^{[2]}, c_2^{[2]}, x_2)$ at $x = x_2$ to $(\phi_{[3]}, c_1^{[3]}, c_2^{[3]}, x_3)$ at $x = x_3$. Specifically, given the initial conditions $(\phi^{[2]}, c_1^{[2]}, c_2^{[2]})$ and the parameters $(\phi^{[3]}, c_1^{[3]}, c_2^{[3]})$, the scaled flux densities $J_1^{[3]}, J_2^{[3]}$ and the boundary values $u_r(x_2)$ and $u_l(x_3)$ are uniquely determined.
- (iv) The singular orbit on the interval $[x_3, x_4]$ is composed of three distinct segments: two boundary layers, $\Gamma^{[3,r]}$ at $x = x_3$ and $\Gamma^{[4,l]}$ at $x = x_4$, and a regular layer Λ_4 spanning (x_3, x_4) . The state (ϕ, c_1, c_2, τ) transitions from $(\phi^{[3]}, c_1^{[3]}, c_2^{[3]}, x_3)$ at $x = x_3$ to $(\phi_{[4]}, c_1^{[4]}, c_2^{[4]}, x_4)$ at $x = x_4$. Specifically, given the initial conditions $(\phi^{[3]}, c_1^{[3]}, c_2^{[3]})$ and the parameters $(\phi^{[4]}, c_1^{[4]}, c_2^{[4]})$, the scaled flux densities $J_1^{[4]}, J_2^{[4]}$ and the boundary values $u_r(x_3)$ and $u_l(x_4)$ are uniquely determined.
- (v) The singular orbit on the interval $[x_4, x_5]$ is composed of three distinct segments: two boundary layers, $\Gamma^{[4,r]}$ at $x = x_4$ and $\Gamma^{[5,l]}$ at $x = x_5$, and a regular layer Λ_5 spanning (x_4, x_5) . The state (ϕ, c_1, c_2, τ) transitions from $(\phi^{[4]}, c_1^{[4]}, c_2^{[4]}, x_4)$ at $x = x_4$ to $(\phi_{[5]}, c_1^{[5]}, c_2^{[5]}, x_5)$ at $x = x_5$. Specifically, given the initial conditions $(\phi^{[4]}, c_1^{[4]}, c_2^{[4]})$ and the parameters $(0, R_1, R_2)$, the scaled flux densities $J_1^{[5]}, J_2^{[5]}$ and the boundary values $u_r(x_4)$ and $u_l(x_5)$ are uniquely determined.

The following matching conditions are required for a singular orbit on $[0, 1]$. For $i = 1, 2$ and $k = 1, 2, 3, 4$,

$$J_i^{[1]} = J_i^{[2]} = J_i^{[3]} = J_i^{[4]} = J_i^{[5]}, \quad u_l(x_k) = u_r(x_k). \quad (15)$$

Consistent with the number of unknowns in (13), these twelve conditions allow the matching relations (15) to simplify the singular connection problem into the following system ($k = 0, 1$):

$$\begin{aligned}
& z_1 c_1^{[2k+1]} e^{z_1(\phi^{[2k+1]} - \phi^{[2k+1,r]})} + z_2 c_2^{[2k+1]} e^{z_2(\phi^{[2k+1]} - \phi^{[2k+1,r]})} + Q_{2k+2} = 0, \\
& z_1 c_1^{[2k+2]} e^{z_1(\phi^{[2k+2]} - \phi^{[2k+2,l]})} + z_2 c_2^{[2k+2]} e^{z_2(\phi^{[2k+2]} - \phi^{[2k+2,l]})} + Q_{2k+2} = 0, \\
& \frac{z_2 - z_1}{z_2} c_1^{[2k+1,l]} = c_1^{[2k+1]} e^{z_1(\phi^{[2k+1]} - \phi^{[2k+1,r]})} + c_2^{[2k+1]} e^{z_2(\phi^{[2k+1]} - \phi^{[2k+1,r]})} \\
& \quad + Q_{2k+2}(\phi^{[2k+1]} - \phi^{[2k+1,r]}) = 0, \\
& \frac{z_2 - z_1}{z_2} c_1^{[2k+2,r]} = c_1^{[2k+2]} e^{z_1(\phi^{[2k+2]} - \phi^{[2k+2,l]})} + c_2^{[2k+2]} e^{z_2(\phi^{[2k+2]} - \phi^{[2k+2,l]})} \\
& \quad + Q_{2k+2}(\phi^{[2k+2]} - \phi^{[2k+2,l]}) = 0, \\
& J_1 = \frac{c_1^L - c_1^{[1,l]}}{H(x_1)} \left[1 + \frac{z_1(\phi^L - \phi^{[1,l]})}{\ln c_1^L - \ln c_1^{[1,l]}} \right] = \frac{c_1^{[4,r]} - c_1^R}{H(1) - H(x_4)} \left[1 + \frac{z_1(\phi^{[4,r]} - \phi^R)}{\ln c_1^{[4,r]} - \ln c_1^R} \right], \\
& \quad = \frac{c_1^{[2,r]} - c_1^{[3,l]}}{H(x_3) - H(x_2)} \left[1 + \frac{z_1(\phi^{[2,r]} - \phi^{[3,l]})}{\ln c_1^{[2,r]} - \ln c_1^{[3,l]}} \right], \\
& J_2 = \frac{c_2^L - c_2^{[1,l]}}{H(x_1)} \left[1 + \frac{z_2(\phi^L - \phi^{[1,l]})}{\ln c_2^L - \ln c_2^{[1,l]}} \right] = \frac{c_2^{[4,r]} - c_2^R}{H(1) - H(x_4)} \left[1 + \frac{z_2(\phi^{[4,r]} - \phi^R)}{\ln c_2^{[4,r]} - \ln c_2^R} \right], \\
& \quad = \frac{c_2^{[2,r]} - c_2^{[3,l]}}{H(x_3) - H(x_2)} \left[1 + \frac{z_2(\phi^{[2,r]} - \phi^{[3,l]})}{\ln c_2^{[2,r]} - \ln c_2^{[3,l]}} \right], \\
& \phi^{[2k+2,l]} = \phi^{[2k+1,r]} - T^c y_{2k+2}, \\
& c_1^{[2k+2,l]} = e^{z_1 z_2 T^m y_{2k+2}} c_1^{[2k+1,r]} - \frac{Q_{2k+2} J_1}{z_1 T^m} \left(1 - e^{z_1 z_2 T^m y_{2k+2}} \right), \\
& T^m = - \frac{(z_1 - z_2)(c_1^{[2k+1,r]} - c_1^{[2k+2,l]}) + z_2 Q_{2k+2}(\phi^{[2k+1,r]} - \phi^{[2k+2,l]})}{z_2(H(x_{2k+2}) - H(x_{2k+1}))},
\end{aligned} \tag{16}$$

where $y_2 > 0$ and $y_4 > 0$ (see the proof of Lemma 2.4 in [5] for a detailed explanation of y_2 and y_4) are also unknowns, $H(x) = \int_0^x h^{-1}(s)ds$, and for $k = 0, 1$,

$$\begin{aligned}
& \phi^L = V - \frac{1}{z_1 - z_2} \ln \frac{-z_2 L_2}{z_1 L_1}, \quad \phi^R = - \frac{1}{z_1 - z_2} \ln \frac{-z_2 R_2}{z_1 R_1}, \\
& z_1 c_1^L = -z_2 c_2^L = (z_1 L_1)^{\frac{-z_2}{z_1 - z_2}} (-z_2 L_2)^{\frac{z_1}{z_1 - z_2}}, \\
& z_1 c_1^R = -z_2 c_2^R = (z_1 R_1)^{\frac{-z_2}{z_1 - z_2}} (-z_2 R_2)^{\frac{z_1}{z_1 - z_2}}, \\
& \phi^{[2k+1,l]} = \phi^{[2k+1]} - \frac{1}{z_1 - z_2} \ln \frac{-z_2 c_2^{[2k+1]}}{z_1 c_1^{[2k+1]}}, \\
& \phi^{[2k+2,r]} = \phi^{[2k+2]} - \frac{1}{z_1 - z_2} \ln \frac{-z_2 c_2^{[2k+2]}}{z_1 c_1^{[2k+2]}}, \\
& z_1 c_1^{[2k+1,l]} = -z_2 c_2^{[2k+1,l]} = (z_1 c_1^{[2k+1]})^{\frac{-z_2}{z_1 - z_2}} (-z_2 c_2^{[2k+1]})^{\frac{z_1}{z_1 - z_2}}, \\
& z_1 c_1^{[2k+2,r]} = -z_2 c_2^{[2k+2,r]} = (z_1 c_1^{[2k+2]})^{\frac{-z_2}{z_1 - z_2}} (-z_2 c_2^{[2k+2]})^{\frac{z_1}{z_1 - z_2}}, \\
& c_1^{[2k+1,r]} = c_1^{[2k+1]} e^{z_1(\phi^{[2k+1]} - \phi^{[2k+1,r]})}, \quad c_1^{[2k+2,l]} = c_1^{[2k+2]} e^{z_1(\phi^{[2k+2]} - \phi^{[2k+2,l]})}.
\end{aligned} \tag{17}$$

To simplify the subsequent discussion, we define $Q_2 = Q$ and $Q_4 = \mu Q$, assuming $Q > 0$ but small compared to the boundary concentrations, and $\mu > 0$. Since the governing system (16) and (17) depends regularly on the small permanent charge Q , we can apply a

regular perturbation expansion to all unknown quantities in terms of Q ; for example, we write, for $k = 1, 2, 3, 4$,

$$\begin{aligned}\phi^{[k]} &= \phi_0^{[k]} + \phi_1^{[k]} Q + \phi_2^{[k]} Q^2 + o(Q^2), \quad c_1^{[k]} = c_{10}^{[k]} + c_{11}^{[k]} Q + c_{12}^{[k]} Q^2 + o(Q^2), \\ c_2^{[k]} &= c_{20}^{[k]} + c_{21}^{[k]} Q + c_{22}^{[k]} Q^2 + o(Q^2), \quad y_2 = y_{20} + y_{21} Q + y_{22} Q^2 + o(Q^2), \\ y_4 &= y_{40} + y_{41} Q + y_{42} Q^2 + o(Q^2), \quad J_1 = J_{10} + J_{11} Q + J_{12} Q^2 + o(Q^2), \\ J_2 &= J_{20} + J_{21} Q + J_{22} Q^2 + o(Q^2).\end{aligned}\quad (18)$$

To examine the primary influence of permanent charge, we resolve the zeroth- and first-order coefficients of the ionic flux expressions. More specifically, we focus on the explicit expressions of the terms J_{k0} and J_{k1} for $k = 1, 2$.

3. Results

Using the regular perturbation analysis discussed in Section 2, we first obtain the following result.

Proposition 1. *Under the electroneutrality conditions (9), one has*

$$\begin{aligned}J_{10} &= \frac{f_0(L, R)}{z_1 H(1)} \frac{\mu_1^\delta}{k_B T}, \quad J_{20} = -\frac{f_0(L, R)}{z_2 H(1)} \frac{\mu_2^\delta}{k_B T}, \\ J_{11} &= \left(\frac{A[(1-B)z_2 V + \ln L - \ln R] + A_1[(1-B_1)z_2 V + \ln L - \ln R]\mu}{(z_1 - z_2)H(1)(\ln L - \ln R)^2} \right) \frac{\mu_1^\delta}{k_B T}, \\ J_{21} &= \left(\frac{A[(1-B)z_1 V + \ln L - \ln R] + A_1[(1-B_1)z_1 V + \ln L - \ln R]\mu}{(z_2 - z_1)H(1)(\ln L - \ln R)^2} \right) \frac{\mu_2^\delta}{k_B T}.\end{aligned}\quad (19)$$

Here

$$\begin{aligned}\frac{\mu_1^\delta}{k_B T} &= z_1 V + \ln L - \ln R, \quad \frac{\mu_2^\delta}{k_B T} = z_2 V + \ln L - \ln R, \\ A(L, R) &= -\frac{(\alpha_2 - \alpha_1)(L - R)f_0(L, R)}{\omega(\alpha_1)\omega(\alpha_2)}, \quad B(L, R) = \frac{\ln \omega(\alpha_2) - \ln \omega(\alpha_1)}{A}, \\ A_1(L, R) &= -\frac{(\alpha_4 - \alpha_3)(L - R)f_0(L, R)}{\omega(\alpha_3)\omega(\alpha_4)}, \quad B_1(L, R) = \frac{\ln \omega(\alpha_4) - \ln \omega(\alpha_3)}{A_1},\end{aligned}\quad (20)$$

where

$$f_0(L, R) = \frac{L - R}{\ln L - \ln R}, \quad \omega(x) = (1 - x)L + xR, \quad \alpha_k = \frac{H(x_k)}{H(1)}, \quad k = 1, 2, 3, 4.$$

Proof. The proof is tedious but straightforward, and we omit it here. $\square$

To streamline the analysis, we introduce the auxiliary functions $M(\mu)$, $N(\mu)$, $F_1(V)$ and $F_2(V)$ defined as follows:

$$\begin{aligned}M(\mu) &= A_1(1 - B_1)\mu + A(1 - B), \quad N(\mu) = A_1\mu + A, \\ F_1(V) &= z_2 M(\mu)V + N(\mu) \ln t, \quad F_2(V) = z_1 M(\mu)V + N(\mu) \ln t.\end{aligned}\quad (21)$$

We next identify μ_M , μ_N , V_{F1} and V_{F2} by $M(\mu_M) = N(\mu_N) = F_1(V_{F1}) = F_2(V_{F2}) = 0$. In particular,

$$\mu_M = \frac{-A(1 - B)}{A_1(1 - B_1)}, \quad \mu_N = \frac{-A}{A_1}, \quad V_{F1} = \frac{-N(\mu) \ln t}{z_2 M(\mu)}, \quad V_{F2} = \frac{-N(\mu) \ln t}{z_1 M(\mu)}.$$

Our main result then follows.

Theorem 1. Suppose that $B \neq 1$ and $B_1 \neq 1$, where B and B_1 are defined in (20). Then,

- (i) With $1 - B > 0$ and $1 - B_1 > 0$, one has $V_{F1} < V_{F2}$, and
 - (i1) $J_{10}(V)J_{11}(V) < 0$ and $J_{20}(V)J_{21}(V) > 0$ for $V \in (V_{F1}, V_{F2})$;
 - (i2) $J_{10}(V)J_{11}(V) \geq 0$ and $J_{20}(V)J_{21}(V) > 0$ for $V \leq V_{F1}$;
 - (i3) $J_{10}(V)J_{11}(V) < 0$ and $J_{20}(V)J_{21}(V) \leq 0$ for $V \geq V_{F2}$.
- (ii) With $1 - B > 0$ and $1 - B_1 < 0$, one has
 - (ii1) If $\mu = \mu_M$, then, $J_{10}(V)J_{11}(V) < 0$ and $J_{20}(V)J_{21}(V) > 0$.
 - (ii2) If $\mu \in (0, \mu_M)$, then, $V_{F1} < V_{F2}$, and
 - (2a) $J_{10}(V)J_{11}(V) < 0$ and $J_{20}(V)J_{21}(V) > 0$ for $V \in (V_{F1}, V_{F2})$;
 - (2b) $J_{10}(V)J_{11}(V) \geq 0$ and $J_{20}(V)J_{21}(V) > 0$ for $V \leq V_{F1}$;
 - (2c) $J_{10}(V)J_{11}(V) < 0$ and $J_{20}(V)J_{21}(V) \leq 0$ for $V \geq V_{F2}$.
 - (ii3) If $\mu \in (\mu_M, +\infty)$, then, $V_{F1} > V_{F2}$, and
 - (3a) $J_{10}(V)J_{11}(V) < 0$ and $J_{20}(V)J_{21}(V) > 0$ for $V \in (V_{F2}, V_{F1})$;
 - (3b) $J_{10}(V)J_{11}(V) < 0$ and $J_{20}(V)J_{21}(V) \leq 0$ for $V \leq V_{F2}$;
 - (3c) $J_{10}(V)J_{11}(V) \geq 0$ and $J_{20}(V)J_{21}(V) > 0$ for $V \geq V_{F1}$.

To end this section, we point out that in the above theorem,

- We examined how small, permanent positive charges (Q) influence individual flux magnitudes ($|J_k|$). Specifically, using the linear approximation $J_k(V) = J_{k0}(V) + QJ_{k1}(V) + o(Q)$, we observe that the effect depends on the relative directions of the zero-order flux (J_{k0}) and the first-order correction (J_{k1}):
 - For J_1 : When $V > V_{F1}$, J_{11} opposes J_{10} , so a positive Q reduces $|J_1|$. Conversely, when $V < V_{F1}$, J_{11} aligns with J_{10} , thereby increasing $|J_1|$.
 - For J_2 : Similarly, for $V > V_{F2}$, a positive Q reduces $|J_2|$, whereas for $V < V_{F2}$, it increases $|J_2|$.

In essence, a small positive charge suppresses the flux magnitude when the first-order correction opposes the base flux and enhances it when they align.

- We just studied two cases (i). $1 - B > 0$, $1 - B_1 > 0$; and (ii) $1 - B > 0$, $1 - B_1 < 0$. The cases $1 - B < 0$, $1 - B_1 < 0$; and $1 - B < 0$, $1 - B_1 > 0$ can be discussed similarly.

4. Concluding Remarks

In this work, we have employed geometric singular perturbation theory, together with a regular perturbation expansion to rigorously analyze ionic flow in a one-dimensional PNP system with small permanent charges. This allowed us to obtain explicit analytical expressions for the leading-order ionic fluxes J_{k0} and first-order ionic fluxes J_{k1} as functions of the permanent charge magnitude, the boundary concentrations L and R , and the applied voltage V . The explicit flux formulas allow one to characterize the small permanent charge effects on ionic flows in detail. More precisely, the leading-order terms recover the neutral, charge-free flux, while the first-order terms characterize the linear additive effect of the permanent charge.

Crucially, the analytical results shed light on how small permanent charges impact the current–voltage (I–V) relations (defined by $I = z_1J_1 + z_2J_2$ under our setup) and enable selective modulation of individual ion fluxes. In particular, two critical voltages V_{F1} and V_{F2} depending on other system parameters were identified that define the critical thresholds at which the permanent charge alters its effects on ionic flux. To be specific, we found that

- for $V > V_{F1}$, a small positive permanent charge reduces $|J_1|$, while for $V < V_{F1}$, the same charge enhances $|J_1|$;
- for $V > V_{F2}$, a small positive fixed charge diminishes $|J_2|$, but strengthens $|J_2|$ for $V < V_{F2}$.

These findings indicate that even the permanent charge is small compared to boundary concentrations, it is able to induce nonlinear adjustments in the I–V curve—Impeding one ion while facilitating another to create an asymmetric, tunable I–V curve. Such selective modulation of ion fluxes by permanent charge provides a mechanistic explanation for how subtle electrostatic perturbations modulate channel conductance and ionic selectivity.

The analytical insights offered in current work are significant for optimizing practical ion transport applications, spanning biological, artificial nanofluidic, and electrochemical systems. The explicit expressions of the flux obtained at the leading and the first-order terms provide a predictive framework to assess how introducing small fixed charges (e.g. due to charged residues or surface functionalization) will shift ionic currents and I–V characteristics. This is particularly important in narrow biological channels, where even minor permanent charges on the channel wall can dramatically affect permeability and selectivity, as well as in synthetic nanopores and electrochemical devices, where designers can tune surface charge to achieve desired transport or filtering properties. Our study characterizes a detailed quantitative description of the additive effects of small permanent charges on ionic flow, which bridges rigorous mathematical analysis with practical considerations in ion transport engineering. It highlights the critical roles played by small permanent charges—serving as a control mechanism for ionic selectivity and current modulation, which offers guidance for future experimental and theoretical explorations of charged nanopores and channel-based devices.

We also point out that the model analyzed in this work is relatively simple. While this simplified, quasi-one-dimensional approach trades some physical complexity for analytical tractability, it yields explicit formulas for ionic fluxes. These formulas offer clear insights into how small charge densities enforce selective ion transport-mechanisms that are often obscured in more complex models.

To end this section, we provide a table of some notation used in this work ($k = 1, 2$; $j = 1, 2, 3, 4$):

- **Spatial Domain:** $x \in [0, 1]$, where $x = 0$ and $x = 1$ represent the left and right boundaries of the channel, respectively.
- **Electric Potential:** $\phi(x)$ denotes the potential across the channel, subject to the following boundary and internal conditions:
 - $\phi(0) = V$: Applied potential at the left boundary.
 - $\phi(1) = 0$: Grounded potential at the right boundary.
 - $\phi(x_j) = \phi^{[j]}$: Preassigned potential at the discontinuity (jumping) points x_j .
- **Ionic Concentrations:** $c_k(x)$ represents the concentration of the k -th ion species, with specified values at the boundaries and jumping points:
 - $c_k(0) = L_k$ and $c_k(1) = R_k$: Concentrations at the left and right ends.
 - $c_k(x_j) = c_k^{[j]}$: Concentrations at the jumping points x_j .
- **Permanent Charge:** $Q(x)$ represents the fixed charge distribution within the channel.
- **Debye Parameter:** ϵ is a singular scaling parameter related to the Debye length.
- **Flux and Current Density:**
 - J_k : The flux density of the k -th ion species.
 - J_{k0}, J_{k1} : The zeroth and first-order approximations of J_k with respect to Q .
 - $I = \sum z_k J_k$: The total current density (specifically $I = z_1 J_1 + z_2 J_2$ for a binary system).

- **I–V Relation:** The functional dependence of current I on the potential V , given fixed boundary concentrations L_k , R_k , and permanent charge Q .

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Abbreviations

The following abbreviations are used in this manuscript:

PNP Poisson–Nernst–Planck

I–V Current–voltage

References

1. Boda, D.; Nonner, W.; Valisko, M.; Henderson, D.; Eisenberg, B.; Gillespie, D. Steric selectivity in Na channels arising from protein polarization and mobile side chains. *Biophys. J.* **2007**, *93*, 1960–1980. [\[CrossRef\]](#)
2. Eisenberg, B. Crowded charges in ion channels. In *Advances in Chemical Physics*; Rice, S.A., Ed.; John Wiley and Sons, Inc.: New York, NY, USA, 2011; pp. 77–223.
3. Hille, B. *Ion Channels of Excitable Membranes*, 3rd ed.; Sinauer Associates, Inc.: Sunderland, MA, USA, 2001.
4. Hille, B. *Transport Across Cell Membranes: Carrier Mechanisms, Chapter 2*; Textbook of Physiology; Patton, H.D., Fuchs, A.F., Hille, B., Scher, A.M., Steiner, R.D., Eds.; Saunders: Philadelphia, PA, USA, 1989; Volume 1, pp. 24–47.
5. Bates, P.W.; Wen, Z.; Zhang, M. Small permanent charge effects on individual fluxes via Poisson–Nernst–Planck models with multiple cations. *J. Nonlinear Sci.* **2021**, *31*, 55. [\[CrossRef\]](#)
6. Ji, S.; Liu, W.; Zhang, M. Effects of (small) permanent charge and channel geometry on ionic flows via classical Poisson–Nernst–Planck models. *SIAM J. Appl. Math.* **2015**, *75*, 114–135. [\[CrossRef\]](#)
7. Gillespie, D. A Singular Perturbation Analysis of the Poisson–Nernst–Planck System: Applications to Ionic Channels. Ph.D. Dissertation, Rush University, Chicago, IL, USA, 1999.
8. Wen, Z.; Bates, P.W.; Zhang, M. Effects on I–V relations from small permanent charge and channel geometry via classical Poisson–Nernst–Planck equations with multiple cations. *Nonlinearity* **2021**, *34*, 4464–4502. [\[CrossRef\]](#)
9. Gillespie, D. Energetics of divalent selectivity in a calcium channel: The Ryanodine receptor case study. *Biophys. J.* **2008**, *94*, 1169–1184. [\[CrossRef\]](#)
10. Hodgkin, A.L.; Keynes, R.D. The potassium permeability of a giant nerve fibre. *J. Physiol.* **1955**, *128*, 61–88. [\[CrossRef\]](#)
11. Ji, S.; Eisenberg, B.; Liu, W. Flux Ratios and Channel Structures. *J. Dyn. Differ. Equ.* **2019**, *31*, 1141–1183. [\[CrossRef\]](#)
12. Bates, P.W.; Jia, Y.; Lin, G.; Lu, H.; Zhang, M. Individual flux study via steady-state Poisson–Nernst–Planck systems: Effects from boundary conditions. *SIAM J. Appl. Dyn. Syst.* **2017**, *16*, 410–430. [\[CrossRef\]](#)
13. Eisenberg, B. Ion Channels as Devices. *J. Comput. Electron.* **2023**, *2*, 245–249. [\[CrossRef\]](#)
14. Eisenberg, B. Proteins, channels, and crowded ions. *Biophys. Chem.* **2003**, *100*, 507–517. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Eisenberg, R.S. Channels as enzymes. *J. Membr. Biol.* **1990**, *115*, 1–12. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Eisenberg, R.S. Atomic Biology, Electrostatics and Ionic Channels. In *New Developments and Theoretical Studies of Proteins*; Elber, R., Ed.; World Scientific: Philadelphia, PA, USA, 1996; pp. 269–357.
17. Gillespie, D.; Eisenberg, R.S. Physical descriptions of experimental selectivity measurements in ion channels. *Eur. Biophys. J.* **2002**, *31*, 454–466. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Gillespie, D.; Nonner, W.; Eisenberg, R.S. Crowded charge in biological ion channels. *Nanotech* **2003**, *3*, 435–438.
19. Im, W.; Roux, B. Ion permeation and selectivity of OmpF porin: A theoretical study based on molecular dynamics, Brownian dynamics, and continuum electrodiffusion theory. *J. Mol. Biol.* **2002**, *322*, 851–869. [\[CrossRef\]](#)
20. Roux, B.; Allen, T.W.; Berneche, S.; Im, W. Theoretical and computational models of biological ion channels. *Q. Rev. Biophys.* **2004**, *37*, 15–103. [\[CrossRef\]](#)
21. Barcilon, V. Ion flow through narrow membrane channels: Part I. *SIAM J. Appl. Math.* **1992**, *52*, 1391–1404. [\[CrossRef\]](#)
22. Hyon, Y.; Eisenberg, B.; Liu, C. A mathematical model for the hard sphere repulsion in ionic solutions. *Commun. Math. Sci.* **2010**, *9*, 459–475.

23. Hyon, Y.; Fonseca, J.; Eisenberg, B.; Liu, C. Energy variational approach to study charge inversion (layering) near charged walls. *Discret. Contin. Dyn. Syst. Ser. B* **2012**, *17*, 2725–2743. [\[CrossRef\]](#)
24. Hyon, Y.; Liu, C.; Eisenberg, B. PNP equations with steric effects: A model of ion flow through channels. *J. Phys. Chem. B* **2012**, *116*, 11422–11441. [\[CrossRef\]](#)
25. Schuss, Z.; Nadler, B.; Eisenberg, R.S. Derivation of Poisson and Nernst-Planck equations in a bath and channel from a molecular model. *Phys. Rev. E* **2001**, *64*, 036116. [\[CrossRef\]](#)
26. Abaid, N.; Eisenberg, R.S.; Liu, W. Asymptotic expansions of I–V relations via a Poisson-Nernst-Planck system. *SIAM J. Appl. Dyn. Syst.* **2008**, *7*, 1507–1526. [\[CrossRef\]](#)
27. Nonner, W.; Eisenberg, R.S. Ion permeation and glutamate residues linked by Poisson-Nernst-Planck theory in L-type Calcium channels. *Biophys. J.* **1998**, *75*, 1287–1305. [\[CrossRef\]](#)
28. Eisenberg, B.; Liu, W. Poisson-Nernst-Planck systems for ion channels with permanent charges. *SIAM J. Math. Anal.* **2007**, *38*, 1932–1966. [\[CrossRef\]](#)
29. Bates, P.W.; Liu, W.; Lu, H.; Zhang, M. Ion size and valence effects on ionic flows via Poisson-Nernst-Planck systems. *Commun. Math. Sci.* **2017**, *15*, 881–901. [\[CrossRef\]](#)
30. Fu, Y.; Liu, W.; Mofidi, H.; Zhang, M. Finite Ion Size Effects on Ionic Flows via Poisson-Nernst-Planck Systems: Higher Order Contributions. *J. Dyn. Differ. Equ.* **2023**, *35*, 1585–1609. [\[CrossRef\]](#)
31. Huang, W.; Liu, W.; Yu, Y. Permanent charge effects on ionic flows: A numerical study of flux ratios and their bifurcation. *Commun. Comput. Phys.* **2021**, *30*, 486–514. [\[CrossRef\]](#)
32. Liu, H.; Wang, Z.; Yin, P.; Yu, H. Positivity-preserving third order DG schemes for Poisson-Nernst-Planck equations. *J. Comput. Phys.* **2022**, *452*, 110777. [\[CrossRef\]](#)
33. Liu, C.; Wang, C.; Wise, S.; Yue, X.; Zhou, S. A positivity-preserving, energy stable and convergent numerical scheme for the Poisson-Nernst-Planck system. *Math. Comput.* **2021**, *90*, 2071–2106. [\[CrossRef\]](#)
34. Mofidi, H. New insights into the effects of small permanent charge on ionic flows: A higher order analysis. *Math. Biosci. Eng.* **2024**, *21*, 6042–6076. [\[CrossRef\]](#)
35. Qian, Y.; Wang, C.; Zhou, S. A positive and energy stable numerical scheme for the Poisson–Nernst–Planck–Cahn–Hilliard equations with steric interactions. *J. Comput. Phys.* **2021**, *426*, 109908. [\[CrossRef\]](#)
36. Singer, A.; Norbury, J. A Poisson-Nernst-Planck model for biological ion channels—an asymptotic analysis in a three-dimensional narrow funnel. *SIAM J. Appl. Math.* **2009**, *70*, 949–968. [\[CrossRef\]](#)
37. Wang, X.-S.; He, D.; Wylie, J.; Huang, H. Singular perturbation solutions of steady-state Poisson-Nernst-Planck systems. *Phys. Rev. E* **2014**, *89*, 022722. [\[CrossRef\]](#)
38. Yan, L.; Xu, H.; Liu, W. Poisson-Nernst-Planck models for three ion species: Monotonic profiles vs. oscillatory profiles. *J. Appl. Anal. Comput.* **2022**, *12*, 1211–1233. [\[CrossRef\]](#)
39. Zhang, M. Competition between cations via Poisson-Nernst-Planck systems with nonzero but small permanent charges. *Membranes* **2021**, *11*, 236. [\[CrossRef\]](#) [\[PubMed\]](#)
40. Zhang, L.; Liu, W. Effects of large permanent charges on ionic flows via Poisson-Nernst-Planck models. *SIAM J. Appl. Dyn. Syst.* **2020**, *19*, 1993–2029. [\[CrossRef\]](#)
41. Ji, S.; Liu, W. Poisson-Nernst-Planck systems for ion flow with density functional theory for hard-sphere potential: I–V relations and critical potentials. Part I: Analysis. *J. Dyn. Differ. Equ.* **2012**, *24*, 955–983. [\[CrossRef\]](#)
42. Liu, W.; Wang, B. Poisson-Nernst-Planck systems for narrow tubular-like membrane channels. *J. Dyn. Differ. Equ.* **2010**, *22*, 413–437. [\[CrossRef\]](#)
43. Liu, W.; Sun, N. Flux ratios for effects of permanent charges on ionic flows with three ion species: New phenomena from a case study. *J. Dyn. Differ. Equ.* **2024**, *36*, 27–62.
44. Mofidi, H.; Hadadifard, F.; Zhang, M. Analysis of critical transitions in flux ratios in ionic flows via classical Poisson-Nernst-Planck models. *Stud. Appl. Math.* **2025**, *155*, e70087. [\[CrossRef\]](#)

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