A Dynamical Study of the Poisson-Nernst-Planck System for Three Ions

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Abstract

Ionic channels and semiconductor devices use atomic scale structures to control macroscopic flows from one reservoir to another. The one-dimensional steady-state Poisson-Nernst-Planck (PNP) system is a useful representation of these devices, but experience shows that describing the reservoirs as boundary conditions is difficult. We study the PNP system for three types of ions with three regions of piecewise constant permanent charge. Reservoirs are represented by the outer regions with permanent charge zero. The PNP system can be treated as singularly perturbed system that has two limiting systems: inner and outer systems (termed fast and slow system in geometric singular perturbation theory). A complete set of integrals for the inner system is presented that provides information for boundary and internal layers. We will examine the effects of permanent charge on the fluxes of the ions through flux ratios, $\lambda(\mathrm{Q}) = J(\mathrm{Q})/J(0)$. $J(\mathrm{Q})$ is the flux associated with nonzero permanent charge, Q, and $J(0)$ will be the flux associated with zero permanent charge.

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1 Quasi-One-Dimensional Poisson-Nernst-Planck System

1.1 Introduction

Membranes are one of the most important aspects of biological cells. They provide a barrier that separates the inside of the cell from the rest of the world. Within a membrane there are pathways that allow certain molecules to enter and leave a cell. These pathways allow cells to do life sustaining activities, such as regulation of the fluxes of ions, nutrients, and molecules. Their activities underlie physiological processes as diverse as brain electrical activity, muscle contraction, water and solute transport in the kidney, hormone secretion and the immune response [7].

Substances cross membranes through proteins specialized for the task. These proteins are separated into two different classes: channels and transporters. Channels are membrane-spanning water-filled pores through which substrates passively diffuse down their electrochemical gradients whenever the regulatory gate is open. Transporters are more biological devices involving conformation changes, changes in the shape of the macromolecule. Structural biology has shown that transporters and channels have very similar structures, since transporters technically have two gates they must control through a conformational cycle, because it has been shown the processes that open and close channels ('activation' and 'inactivation') can be coupled to give properties rather like transporters.

Transporters are shown to have a much more difficult quantitative properties, particularly if the description was to be transferrable with parameters that were independent of conditions, because of this we will consider a simple model of a permanently open ion channel. Most biologists imagine that if the driving force for electrodiffusion is increased-that is to say, if the difference of the electrochemical potential across the channel is increased in magnitude - the flux through the channel should increase. It has been shown before that this is not always the case. To see this consider a channel with large permanent charge and the flux of ions with the opposite sign as the permanent charge (called counterions). The flux of counterions in a channel can decrease dramatically as the driving force increases - we call this *the declining phenomenon*. More precisely, if the

concentration of the ion is held fixed on one side of the channel, the concentration decreased on the other side ('trans') of the channel, the flux of the counter ions can decrease if the permanent charge density is large. A depletion zone which is an insulating region within a conductive, doped semiconductor material where the mobile charge carriers have been forced away by an electric field, can form that prevents flow even though the driving force increases. It is worthwhile to emphasize that if one increases the transmembrane electrochemical potential in a different manner, such as, by increasing the transmembrane electric potential or the concentration of the ion at one side of the channel, the one does not have the declining phenomenon.

The decline of flux with *trans* concentration has been considered a particular, even defining properties of transporters, involving conformation changes of state and other properties of proteins less well defined (physically) than electrodiffusion. Obligatory exchange, a cells response to physical factors, is ascribed widely to changes in the structure of transport proteins, to conformation changes in the spatial distribution of the mass of the protein, obligatory exchange is often thought to be a special property of transporters not found in channels.

The structure of many transporters can be detected thanks to advances of cryo-electron microscopy. A transporter (of one amino acid sequence and thus of a perfectly homogeneous molecular type) exists in different states. Each state is said to have a different conformation meaning, in physical language, that the spatial distribution of mass is different in different states, and the distribution of the different states form disjoint sets, with no overlap. The movement of ions is not directly controlled or driven by the conformation of mass, however. Rather, the distribution of mass produces a distribution of steric repulsion forces, and spatial distribution of electrical forces because the mass is associated with charge, mostly permanent charge of acid and base groups of the protein, but also significant polarization charge, as well. It is the conformation of these forces that determines the movement of ions. The spatial distribution of forces contributes to the potential of mean force reported in simulations of molecular dynamics.

Our model is of course oversimplified as are any models, or even simulations in apparent atomic detail, of condensed phases. More structural detail and more correlations between ions can

and should be included. Our goal is to show properties of the cell that are not always detectable experimentally.

1.2 Poisson-Nernst-Planck Model

Our study is based on a quasi-one-dimensional Poisson-Nernst-Planck (PNP) model. For a mixture of n ion species, a quasi-one-dimensional PNP model is

$$\begin{aligned} &\frac{1}{A(X)}\frac{d}{dX}\left(\varepsilon_r(X)\varepsilon_0 A(X)\frac{d\Phi}{dX}\right) = -e_0\left(\sum_{s=1}^{n} z_s C_s + Q(X)\right), \\ &\frac{d\mathscr{J}_k}{dX} = 0, \;\; -\mathscr{J}_k = \frac{1}{\kappa_B T}\mathscr{D}_k(X)A(X)C_k\frac{d\mu_k}{dX}, \;\; k = 1,2,\ldots,n \end{aligned} \tag{1}$$

where $X \in [a_0, b_0]$ is the coordinate along the axis of the channel and reservoirs, $A(X)$ is the cross-sectional area of the channel at the location X, e_0 is the elementary charge, ε_0 is the vacuum permittivity, $\varepsilon_r(X)$ is the relative dielectric coefficient, $Q(X)$ is the permanent charge density, κ_B is the Boltzmann constant, T is the absolute temperature, Φ is the electrical potential, and, for the kth ion species, C_k is the concentration, z_k is the valence, $\mathscr{D}_k(X)$ is the diffusion coefficient, μ_k is the electrochemical potential, and $\mathscr{J}_k$ is the flux density.

Equipped with system (1), a meaningful boundary condition for ionic flow through ion channels is, for $k = 1,2,\ldots,n$,

$$\Phi(a_0) = \mathscr{V}, \;\; C_k(a_0) = \mathscr{L}_k > 0; \;\; \Phi(b_0) = 0, \;\; C_k(b_0) = \mathscr{R}_k > 0. \tag{2}$$

Mathematically, we will be interested in solutions of the boundary value problem (BVP) given by (1) and (2). An important measurement for properties of ion channels is the $\mathscr{I} - \mathscr{V}$ (*current - voltage*) *relation* where the current $\mathscr{I}$ depends on the transmembrane potential (voltage) $\mathscr{V}$ and is given by

$$\mathscr{I} = \sum_{s=1}^{n} z_s \mathscr{J}_s(\mathscr{V}) \tag{3}$$

where $\mathscr{J}_k(\mathscr{V})$'s are determined by the BVP (1) and (2) for fixed $\mathscr{L}_k$'s and $\mathscr{R}_k$'s. Of course, the

relations of individual fluxes $\mathscr{J}_k's$ to $\mathscr{V}$ contain more information, but biologically it is harder to find the individual fluxes, only the total current. Our model, though, can help us find certain fluxes.

The positions $X = a_0$ and $X = b_0$ are located in the reservoir separated by the channel. They are the locations of two electrodes that are applied to control or drive the ionic flow through the ion channel. Ideally, the experimental designs should not affect the intrinsic ionic flow properties so one would like to design the boundary conditions to meet the so-called electroneutrality

$$\sum_{s=1}^{n} z_s \mathscr{L}_s = 0 = \sum_{s=1}^{n} z_s \mathscr{R}_s, \tag{4}$$

so that sharp boundary layers, which might cause significant changes in the electrical potential and concentrations near the boundaries, do not occur (see Remark 2.2).

The electrochemical potential μ_k consists of the ideal component, u_k^{id}, and the excess component, μ_k^{ex}, where the ideal component,

$$\mu_k^{id}(X) = z_k e_0 \Phi(X) + \kappa_B T \ln \frac{C_k(X)}{C_0}, \tag{5}$$

is the point charge contribution where C_0 is a characteristic concentration, and the excess component μ_k^{ex} accounts for ion size effects. For our purposes we will only consider the ideal component. The interested reader may refer to [1] for more results with the consideration of ion size effect.

The permanent charge $Q(X)$ is a simplified mathematical model for ion channel (protein) structure. It is determined by the spatial distribution of amino acids in the channel wall, the acid (negative) and base (positive) side chains, more than anything else. We will assume $Q(X)$ is known and take an oversimplified description to capture some essence of its effects. For the majority of this paper, we take it to be for some A, B with $a_0 < A < B < b_0$,

$$Q(X) = \begin{cases} 0, & X \in [a_0, A) \cup (B, b_0] \\ 2Q_0, & X \in (A, B) \end{cases},$$

but will also discuss theoretical results when $Q(X)$ is more robust. The reader might note though that work has been done to see the effect of refining the permanent charge over the neck of the channel to better reflect the actual geometry to the channel.

The cross-sectional area $A(X)$ typically has the property that $A(X)$ is much smaller for $X \in (A,B)$ (the neck region) than that for $X \notin (A,B)$. It is interesting to note that it has been shown before the neck of the channel should be "narrow" and "short" to optimize the effect of permanent charge.

We will assume that $\varepsilon_r(X) = \varepsilon_r$, $\mathscr{D}_k(X) = \mathscr{D}(X)\mathscr{D}_k$ where ε_r is a constant and $\mathscr{D}(X)$ is some dimensionless function and a dimensional constant $\mathscr{D}_k$.

Note that the assumption $\mathscr{D}_k(X) = \mathscr{D}(X)\mathscr{D}_k$ is equivalent to the statement that $\mathscr{D}_k(X)/\mathscr{D}_j(X)$ is a constant for $k \neq j$ since $\mathscr{D}_k$ is a dimensional constant. Roughly speaking, the assumption says that, as the environment varies from location to location, its influences on the two diffusion coefficients vary from one common environment to another common environment in a way so that their ratio is independent of locations.

The following rescaling or its variations have been widely used for convenience of mathematical analysis. Let C_0 be a characteristic concentration of the ionic solution. We now make a dimensionless re-scaling of the variables in system (1) as follows,

$$\begin{aligned} \varepsilon^2 = \frac{\varepsilon_r \varepsilon_0 \kappa_B T}{e_0^2 (b_0 - a_0)^2 C_0}, \;\; x = \frac{X - a_0}{b_0 - a_0}, \;\; h(x) = \frac{A(X)}{(b_0 - a_0)^2}, \;\; \mathrm{Q}(x) = \frac{Q(X)}{C_0}, \\ D(x) = \mathscr{D}(X), \;\; \phi(x) = \frac{e_0}{\kappa_B T}\Phi(X), \;\; c_k(x) = \frac{C_k(X)}{C_0}, \;\; J_k = \frac{\mathscr{J}_k}{(b_0 - a_0) C_0 \mathscr{D}_k}, \\ \overline{\mu}_k(x) = \frac{1}{\kappa_B T}\mu_k(X) = z_k \phi(x) + \ln c_k(x). \end{aligned} \tag{6}$$

The dimensionless quantity $\mathrm{Q}(x)$ from the permanent charge Q becomes

$$\mathrm{Q}(x) = \begin{cases} 0, & x \in [0,a) \cup (b,1] \\ 2\mathrm{Q}_0, & x \in (a,b), \end{cases}$$

where

$$\mathrm{Q}_0 = \frac{Q_0}{C_0}, \text{ and } 0 < a = \frac{A-a_0}{b_0-a_0} < b = \frac{B-a_0}{b_0-a_0} < 1.$$

In terms of the dimensionless quantities, the subinterval $(a,b) \subset (0,1)$ corresponds to the neck region $[A,B]$. We will make the key assumption that the parameter $\varepsilon > 0$ is small. This assumption allows us to treat the PNP system as a singularly perturbed problem. For general electrodiffusion problems, this may not be the case. But for ion channel problems, this assumption is reasonable.

In terms of the new variables in (6), the BVP (1) and (2) becomes

$$\begin{aligned} \frac{\varepsilon^2}{h(x)}\frac{d}{dx}\left(h(x)\frac{d\phi}{dx}\right) &= -\sum_{s=1}^{n} z_s c_s - \mathrm{Q}(x), \\ \frac{dJ_k}{dx} = 0, \quad -J_k &= D(x)h(x)c_k\frac{d\overline{\mu}_k}{dx} \end{aligned} \tag{7}$$

with boundary conditions at $x = 0$ and $x = 1$

$$\phi(0) = V, \;\; c_k(0) = L_k; \;\; \phi(1) = 0, \;\; c_k(1) = R_k, \tag{8}$$

where

$$V := \frac{e_0}{\kappa_B T}\mathscr{V}, \;\; L_k := \frac{\mathscr{L}_k}{C_0}, \;\; R_k := \frac{\mathscr{R}_k}{C_0}.$$

2 A Dynamical System Study with Three Ions

For the purposes of this section we will consider only three ion species, two cations (positive charge) and one anion (negative charge). We will also consider the case where the outer regions are reservoirs together with the two regions of the channel near the ends and the permanent charge is constant in the middle of the channel. We will rewrite the PNP system into a standard form for singularly perturbed systems of first order ordinary differential equations and convert the boundary value problem to a connecting problem.

Denote the derivative with respect to x by overdot and introduce $u = \varepsilon\dot{\phi}$ and $\tau = x$. Then our system becomes,

$$\begin{aligned} \varepsilon\dot{\phi} = u,\ \ \varepsilon\dot{u} &= -z_1c_1 - z_2c_2 - z_3c_3 - \mathrm{Q}(\tau) - \varepsilon\frac{h'(\tau)}{h(\tau)}u, \\ \varepsilon\dot{c_1} &= -z_1c_1u - \varepsilon h^{-1}(\tau)J_1, \\ \varepsilon\dot{c_2} &= -z_2c_2u - \varepsilon h^{-1}(\tau)J_2, \\ \varepsilon\dot{c_3} &= -z_3c_3u - \varepsilon h^{-1}(\tau)J_3, \\ \dot{J}_1 = \dot{J}_2 = \dot{J}_3 = 0,\ \ \dot{\tau} &= 1. \end{aligned} \tag{9}$$

We will treat this system as a dynamical system of phase space $\mathbb{R}^9$ with state variables $(\phi, u, c_1, c_2, c_3, J_1, J_2, J_3, \tau)$. The introduction of the extra state variable $\tau = x$ and the τ-equation seems to add complications to the problem, but this has a great advantage that we will explain shortly. This introduction also makes (9) autonomous, so that dynamical system theory can be applied directly.

For $\varepsilon > 0$, the rescaling $x = \varepsilon\xi$ of the independent variable x gives rise to an equivalent (with

the same phase space portrait) system

$$\begin{aligned}
\phi' = u,\ \ u' = -z_1c_1 - z_2c_2 - z_3c_3 - \mathrm{Q}(\tau) - \varepsilon\frac{h'(\tau)}{h(\tau)}u, \\
c_1' = -z_1c_1u - \varepsilon h^{-1}(\tau)J_1, \\
c_2' = -z_2c_2u - \varepsilon h^{-1}(\tau)J_2, \\
c_3' = -z_3c_3u - \varepsilon h^{-1}(\tau)J_3, \\
J_1' = J_2' = J_3' = 0,\ \ \tau' = \varepsilon
\end{aligned} \tag{10}$$

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

For $\varepsilon > 0$, (9) and (10) have exactly the same phase portrait since they differ by a rescaling only. The limiting systems ($\varepsilon = 0$) though provide vastly different, but often times complementary information about the state variables. Singular perturbation theories help us patch this limiting information together to form the solution for the system for $\varepsilon > 0$. In terms of the asymptotic expansions, system (9) and its limit at $\varepsilon = 0$ will be used to study *regular layer* solutions. We will call this system the *outer system* and its limit at $\varepsilon = 0$ the *outer limit system*. System (10) and its limit at $\varepsilon = 0$ will be used to study *inner or singular layer* solutions, and we call the system the *inner system* and its limit at $\varepsilon = 0$ the *inner limit system*. By a *singular orbit*, we mean a continuous and piecewise smooth curve in $\mathbb{R}^9$ that is a union of finitely many orbits of outer limit system or inner limit system. In the theory of geometric singular perturbations, viewing the independent variables x and ξ as slow and fast time variables, the outer system is called the *slow system*, the inner system is called the *fast system*, and a singular orbit is a union of *slow* and *fast* orbits.

Please note that we will call the *inner or singular layers* as *boundary layers* since they lie on the boundary of each section ($[0,a]$, $[a,b]$, or $[b,1]$). In reference to the whole interval, $[0,1]$, they may be seen as interior layers.

Let B_L and B_R be the subsets of the phase space $\mathbb{R}^9$ defined by,

$$B_L = \{(v_0,u,L_1,L_2,L_3,J_1,J_2,J_3,0) \in \mathbb{R}^9 \ :\ \text{arbitrary } u,J_1,J_2,J_3\}$$

$$B_R = \{(0,u,R_1,R_2,R_3,J_1,J_2,J_3,1) \in \mathbb{R}^9 \ : \ \text{arbitrary } u,J_1,J_2,J_3\}$$

Then the boundary value problem is equivalent to a *connecting problem*, namely, finding an orbit of system (9) or system (10) from B_L to B_R. To see this, suppose that $(\phi,u,c_1,c_2,c_3,J_1,J_2,J_3,\tau)$ is an orbit starting at a point on B_L and ending at a point on B_R. Due to the definitions of B_L and B_R, the starting point automatically has $x = \tau = 0$ with the assigned values for ϕ, c_1, c_2, and c_3 at $x = 0$, and the ending point has $x = \tau = 1$ with the assigned values for ϕ, c_1, c_2, and c_3 at $x = 1$. This solution $(\phi,u,c_1,c_2,c_3,J_1,J_2,J_3,\tau)$ satisfies the boundary condition automatically. Most importantly, when we *arbitrarily* rescale the independent variable x, the phase portrait will remain the same. Therefore, in searching for a solution from B_L to B_R, we can apply any rescaling of the independent variable x, even a rescaling that depends on each individual solution, this may include multiplying by any positive scalar function that could depend on the state variables. This is the significant advantage of introducing $\tau = x$ and $\dot{\tau} = 1$ promised earlier (see treatments of outer dynamics).

We will be interested in solutions of the connecting problem of the slow or fast system from B_L to B_R. In view of the jump of $\mathrm{Q}(x)$ at $x = a$ and $x = b$, the best one can hope is that the solution is continuous and piecewise differentiable. We therefore require our solutions to be *continuous and piecewise differentiable*. The continuity of u implies that ϕ, c_1, c_2, and c_3 are differentiable.

Orbits of the $\varepsilon = 0$ limiting systems are called singular orbits. Our construction of a solution involves two main steps: the first step is to construct a singular orbit to the connecting problem, and the second step is to apply geometric singular perturbation theory to show that there is a unique solution near the singular orbit for $\varepsilon > 0$ small. This requires several transversality conditions for limiting systems. The curious reader may reference [3] to learn more about the application of geometric singular perturbation theory for this system.

To construct a singular orbit to the connecting problem, we first construct a singular orbit on each subinterval $[0,a]$, $[a,b]$, and $[b,1]$. The reason to split the interval $[0,1]$ into three subintervals is simply because the permanent charge $\mathrm{Q}(x)$ has jumps at $x = a$ and $x = b$. To be able to construct a singular orbit on each subinterval, we need to preassign the values of ϕ, c_1, c_2, and c_3 at $x = a$

and $x = b$. Suppose, for the moment, that $\phi = \phi^a$, $c_1 = c_1^a$, $c_2 = c_2^a$ and $c_3 = c_3^a$ at $x = a$, and that $\phi = \phi^b$, $c_1 = c_1^b$, $c_2 = c_2^b$, and $c_3 = c_3^b$ at $x = b$. Those eight unknown values,

$$\phi^a, c_1^a, c_2^a, c_3^a;\ \phi^b, c_1^b, c_2^b, c_3^b \tag{11}$$

will be determined along our construction of a singular orbit on the whole interval $[0,1]$.

1. On the left subinterval $[0,a]$ where $\mathrm{Q} = 0$ or there is no permanent charge, we construct a singular orbit for the boundary value problem with $(\phi, c_1, c_2, c_3, \tau)$ being

   $$(v_0, L_1, L_2, L_3, 0) \ \text{ at } \ x = 0 \ \text{ and } \ (\phi^a, c_1^a, c_2^a, c_3^a, a) \ \text{ at } \ x = a.$$

   The orbit consists of two boundary layers Γ_ℓ^0 and Γ_ℓ^a and one regular layer Λ_ℓ. In particular, given $(\phi^a, c_1^a, c_2^a, c_3^a)$, the flux densities $J_1^\ell, J_2^\ell, J_3^\ell$ and the value $u_\ell(a)$ are uniquely determined. The label ℓ indicates the quantities from the construction over the *left* subinterval $[0,a]$. Similar remarks apply to the labels m and r over the middle and right subintervals.

2. On the middle subinterval $[a,b]$, we construct a singular orbit for the boundary value problem with $(\phi, c_1, c_2, c_3, \tau)$ being

   $$(\phi^a, c_1^a, c_2^a, c_3^a, a) \ \text{ at } \ x = a \ \text{ and } \ (\phi^b, c_1^b, c_2^b, c_3^b, b) \ \text{ at } \ x = b.$$

   The orbit consists of two boundary layers Γ_m^a and Γ_m^b and one regular layer Λ_m. In particular, given $(\phi^a, c_1^a, c_2^a, c_3^a)$ and $(\phi^b, c_1^b, c_2^b, c_3^b)$, the flux densities J_1^m, J_2^m, J_3^m and the values $u_m(a)$ and $u_m(b)$ are uniquely determined.

3. On the right subinterval $[b,1]$, we construct a singular orbit for the boundary value problem with $(\phi, c_1, c_2, c_3, \tau)$ being

   $$(\phi^b, c_1^b, c_2^b, c_3^b, b) \ \text{ at } \ x = b \ \text{ and } \ (0, R_1, R_2, R_3, 1) \ \text{ at } \ x = 1.$$

The orbit again consists of two boundary layers Γ_r^b and Γ_r^1 and one regular layer Λ_r. In particular, given $(\phi^b, c_1^b, c_2^b, c_3^b)$, the flux densities J_1^r, J_2^r, J_3^r and the value $u_r(b)$ are uniquely determined.

4. Finally, for a singular orbit on the whole interval $[0,1]$, we require that

$$J_1^\ell = J_1^m = J_1^r,\ \ J_2^\ell = J_2^m = J_2^r,\ \ J_3^\ell = J_3^m = J_3^r,\ \ u_\ell(a) = u_m(a),\ \ u_m(b) = u_r(b).$$

This consists of eight conditions. The number of conditions is exactly the same as the number of values in (11).

Remark 2.1. We call Γ_ℓ^a, Γ_m^a, Γ_m^b, and Γ_r^b boundary layers because, relative to each subinterval, they are boundary layers. But, relative to the whole interval $[0,1]$, they should be termed *interal layers*.

2.1 Singular orbit on $[0,a]$ where $\mathrm{Q}(x) = 0$.

We consider the case with zero permanent charge on the subinterval $[0,a]$ because $[0,a]$ is viewed as one of the reservoirs. The nonzero Q over the subinterval $[a,b]$ will affect the solution on $[0,a]$ and on $[b,1]$. This effect will show up when matching conditions are imposed on ϕ^a, c_1^a, c_2^a, and c_3^a to construct the singular orbit over the whole interval $[0,1]$.

Recall that we have set $\phi(a) = \phi^a$, $c_1(a) = c_1^a$, $c_2(a) = c_2^a$, and $c_3(a) = c_3^a$, where ϕ^a, c_i^a are unknown values to be determined later on. Now let

$$B_a = \{(\phi^a, u, c_1^a, c_2^a, c_3^a, J_1, J_2, J_3, a) \in \mathbb{R}^9 \ :\ u, J_i \text{ arbitrary}\}.$$

In this part, we will construct a singular orbit that connects B_L to B_a. Two boundary layers and one singular layer will be constructed.

If we set $\varepsilon = 0$ in (9) with $\mathrm{Q}(x) = 0$, we get the outer limit system and, in particular, $u = 0$ and

$z_1c_1 + z_2c_2 + z_3c_3 = 0$. The set

$$Z_\ell = \{u = 0,\ \ z_1c_1 + z_2c_2 + z_3c_3 = 0\} \tag{12}$$

will be called *the outer manifold*. In the theory of geometric singular perturbations, Z_ℓ is called *the slow manifold* because if x and ξ are viewed as time variables, the evolution on Z_ℓ is characterized by the time variable ξ, which is slow.

The geometric method for a construction of singular orbits on each of the subintervals $[0,a]$, $[a,b]$, and $[b,1]$ is the same. Let us explain the approach for constructing the singular orbit that connects B_L to B_a on $[0,a]$. Generally, the outer manifold Z_ℓ will not intersect B_L and B_a. Since the regular layer orbit lies entirely on the outer manifold Z_ℓ it will not intersect B_L and B_a; that is, it cannot satisfy the boundary conditions. Two boundary layers need to be introduced to connect boundaries B_L and B_a with the regular layer solution on Z_ℓ. These boundary layers should satisfy the inner limit system. The boundary layer orbit Γ_ℓ^0 at $x = 0$ will connect B_L to Z_ℓ. It must lie on the stable manifold $W^s(Z_\ell)$; that is, it belongs to the intersection $M_L \cap W^s(Z_\ell)$, where M_L is the collection of orbits starting from points on B_L and proceeding in forward time. Similarly, the boundary layer Γ_ℓ^a at $x = a$ will connect Z_ℓ to B_a and it must lie on the unstable manifold $W^u(Z_\ell)$; that is, it belongs to the intersection $M_\ell^a \cap W^u(Z_\ell)$, where M_ℓ^a is the collection of orbits starting from points on B_ℓ^a proceeding in backwards time.

The first step in the construction examines the stability of the outer manifold Z_ℓ by linearizing along Z_ℓ. (Z_ℓ is the set of equilibria of the inner limit system.) It turns out that the outer manifold Z_ℓ has a stable manifold $W^s(Z_\ell)$ and a unstable manifold $W^u(Z_\ell)$. The next step is to check whether $W^s(Z_\ell)$ intersects B_L. This requires knowledge of the global behavior of $W^s(Z_\ell)$ and $W^u(Z_\ell)$, and the information from the linearization is not enough. Neither is abstract dynamical systems theory (since the inner limit system is *nonlinear*). Luckily, there was discovered a complete set of integrals for the inner limit system.

It is this set of integrals that allows us to give a complete, global description of the inner

limit dynamics; in particular, we are able to establish the required intersections $M_L \cap W^s(Z_\ell)$ and $M_\ell^a \cap W^u(Z_\ell)$ and are also able to identify the so-called ω-limit set (set of limit points in forward time on Z_ℓ) $\omega(M_L \cap W^s(Z_\ell))$ and the α-limit set (set of limit points in backward time on Z_ℓ) $\alpha(M_\ell^a \cap W^u(Z_\ell))$ of the intersections. The intersections give the set of candidates for the boundary layers (consisting of three parameter families of inner orbits parameterized by J_1, J_2, and J_3). The foot point $\omega(M_L \cap W^s(Z_\ell))$ and $\alpha(M_\ell^a \cap W^u(Z_\ell))$ (each parameterized by J_1, J_2, and J_3 also) on Z_ℓ provide the (reduced) boundary conditions for the regular solutions. We also are able to identify one regular orbit Λ_ℓ that connects $\omega(M_L \cap W^s(Z_\ell))$ to $\alpha(M_\ell^a \cap W^u(Z_\ell))$ and also determined the triple (J_1, J_2, J_3) uniquely. The desired singular orbit connecting B_L to B_a on $[0,a]$ is formed by this regular orbit Λ_ℓ together with the two boundary layers Γ_ℓ^0 and Γ_ℓ^a that are uniquely determined by the triple (J_1, J_2, J_3).

2.1.1 Inner dynamics on $[0,a]$: boundary layers.

We start with the examination of boundary layers on the interval $[0,a]$ where $\mathrm{Q} = 0$. These will be studied using the inner limit system obtained by setting $\varepsilon = 0$ in (10):

$$\begin{aligned} \phi' = u, \;\; u' &= -z_1 c_1 - z_2 c_2 - z_3 c_3, \\ c_1' &= -z_1 c_1 u, \\ c_2' &= -z_2 c_2 u, \\ c_3' &= -z_3 c_3 u, \\ J_1' = J_2' = J_3' &= 0, \;\; \tau' = 0. \end{aligned} \tag{13}$$

The set of equilibria of (13), that is, the set of points at which the vector field of (13) vanishes, is precisely $Z_\ell = \{u = 0, z_1 c_1 + z_2 c_2 + z_3 c_3 = 0\}$. The linearization at the point $(\phi, 0, c_1, c_2, c_3, J_1, J_2, J_3, \tau) \in$

Z_ℓ is

$$\begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -z_1 & -z_2 & -z_3 & 0 & 0 & 0 & 0 \\ 0 & -z_1c_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -z_2c_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -z_3c_3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

The linearized system has seven zero eigenvalue whose generalized eigenspace is the tangent space of the seven-dimensional outer manifold Z_ℓ of equilibria. The two other eigenvalues are $\pm\sqrt{z_1^2c_1+z_2^2c_2+z_3^2c_3} \neq 0$ whose eigenvectors are not tangent to Z_ℓ. In this sense, Z_ℓ is called *normally hyperbolic*. The theory of normally hyperbolic invariant manifolds states [8] that

1. there is an eight-dimensional stable manifold $W^s(Z_\ell)$ of Z_ℓ that consists of points approaching Z_ℓ in forward time;

2. there is an eight-dimensional unstable manifold $W^u(Z_\ell)$ of Z_ℓ that consists of points approaching Z_ℓ in backward time;

3. Z_ℓ as well as $W^s(Z_\ell)$ and $W^u(Z_\ell)$ persists for $\varepsilon > 0$ small; that is, for $\varepsilon > 0$ small, there exist invariant manifolds Z_ℓ^ε, $W^s(Z_\ell^\varepsilon)$, and $W^u(Z_\ell^\varepsilon)$, close to their counterparts.

What this result suggests is that, for a singular orbit connecting B_L to B_a, the boundary layer at $x = 0$ must lie in $M_L \cap W^s(Z_\ell)$ and the boundary layer at $x = a$ must lie in $M_\ell^a \cap W^u(Z_\ell)$, where M_L and M_ℓ^a are the collection of fowards and backward orbits, respectively, under the flow of (13).

Definition 2.1. A *smooth function* $H : \mathbb{R}^n \to \mathbb{R}$ is called an integral of system $\dfrac{d}{dt}z = f(z)$, $z \in \mathbb{R}^n$, if $\dfrac{d}{dt}[H(z(t))] = 0$ whenever $z(t)$ is a solution.

For a system on $\mathbb{R}^n$, if there are $(n-1)$ (independent) integrals, then any orbits can be theoretically determined by the intersection of $(n-1)$ level sets of the integrals.

Proposition 2.1. *System* (13) *has the following eight integrals:*

$$\begin{aligned} H_1 = e^{z_1\phi}c_1,\ \ H_2 = e^{z_2\phi}c_2,\ \ H_3 = e^{z_3\phi}c_3\ \ H_4 = c_1+c_2+c_3-\frac{1}{2}u^2, \\ H_5 = J_1,\ \ H_6 = J_2,\ \ H_7 = J_3,\ \ H_8 = \tau. \end{aligned} \tag{14}$$

Proof. We can verify our first integrals by taking the derivative with respect to x and applying system (13).

$$H_1' = z_1\phi' e^{z_1\phi}c_1 + c_1' e^{z_1\phi} = z_1 u c_1 e^{z_1\phi} - z_1 c_1 u e^{z_1\phi} = 0$$

$$H_4' = c_1' + c_2' + c_3' - \frac{1}{2}\cdot 2uu' = -z_1c_1u - z_2c_2u - z_3c_3u - (-z_1c_1 - z_2c_2 - z_3c_3)u = 0$$

H_5, H_6, H_7, H_8 can be proved trivially, and H_2, H_3 follow from the proof of H_1. □

These integrals allow one to completely understand the boundary layers (at $x = 0,\ a$) and characterize landing points of boundary layers on the outer manifold Z_ℓ. The information on landing points is crucial because it provides the boundary conditions that allow the regular layer to connect boundary layers.

Corollary 1. *i Let $\phi = \phi^L$ be the unique solution of*

$$z_1L_1e^{z_1(v_0-\phi^L)} + z_2L_2e^{z_2(v_0-\phi^L)} + z_3L_3e^{z_3(v_0-\phi^L)} = 0,$$

$$\textit{that is, } \ \phi^L = v_0 + \frac{1}{z_3-z_2}\left(\ln\left(\frac{-z_3L_3}{z_1L_1}\right) - \ln\left(\frac{z_2L_2}{z_1L_1}\right)\right)$$

and let

$$c_1^L = L_1(-z_3L_3)^{\frac{z_1}{z_3-z_2}}(z_2L_2)^{\frac{-z_1}{z_3-z_2}},\ \ c_2^L = L_2(-z_3L_3)^{\frac{z_2}{z_3-z_2}}(z_2L_2)^{\frac{-z_2}{z_3-z_2}},$$

$$c_3^L = L_3(-z_3L_3)^{\frac{z_3}{z_3-z_2}}(z_2L_2)^{\frac{-z_3}{z_3-z_2}}$$

The stable manifold $W^s(Z_\ell)$ intersects B_L transversally at points with

$$u_0 = [sgn(\phi^L - v_0)]\sqrt{2(L_1+L_2+L_3) - 2(L_1e^{z_1(v_0-\phi^L)} + L_2e^{z_2(v_0-\phi^L)} + L_3e^{z_3(v_0-\phi^L))})} \quad (15)$$

and arbitrary J_i's, where sgn is the sign function.

Let $\phi = \phi^{a,\ell}$ be the unique solution of

$$z_1c_1^ae^{z_1(\phi^a-\phi)} + z_2c_2^ae^{z_2(\phi^a-\phi)} + z_3c_3^ae^{z_3(\phi^a-\phi)} = 0,$$

$$\textit{that is, } \phi^{a,\ell} = \phi^a - \frac{1}{z_3-z_2}\left(\ln\left(\frac{-z_3c_3^a}{z_1c_1^a}\right) - \ln\left(\frac{z_2c_2^a}{z_1c_1^a}\right)\right),$$

and let

$$c_1^{a,\ell} = L_1(-z_3L_3)^{\frac{z_1}{z_3-z_2}}(z_2L_2)^{\frac{-z_1}{z_3-z_2}}, \;\; c_2^{a,\ell} = L_2(-z_3L_3)^{\frac{z_2}{z_3-z_2}}(z_2L_2)^{\frac{-z_2}{z_3-z_2}},$$

$$c_3^{a,\ell} = L_3(-z_3L_3)^{\frac{z_3}{z_3-z_2}}(z_2L_2)^{\frac{-z_3}{z_3-z_2}}$$

The unstable manifold $W^u(Z_\ell)$ intersects B_a transversally at points with

$$u_\ell(z) = [sgn(\phi^a - \phi^{a,\ell})]\sqrt{2(c_1^a+c_2^a+c_3^a) - 2(c_1^ae^{z_1(\phi^a-\phi^{a,\ell})} + c_2^ae^{z_2(\phi^a-\phi^{a,\ell})} + c_3^ae^{z_3(\phi^a-\phi^{a,\ell})})}$$

arbitrary J_i's.

ii Potential boundary layers Γ_ℓ^0 at $x = 0$ are determined up to (J_1, J_2, J_3) as follows: the ϕ-component satisfies the Hamiltonian system

$$\phi'' + z_1L_1e^{z_1(v_0-\phi)} + z_2L_2e^{z_2(v_0-\phi)} + z_3L_3e^{z_3(v_0-\phi)} = 0,$$

together with $\phi(0) = v_0$ *and* $\phi(\xi) \to \phi^L$ *as* $\xi \to \infty$, $u(\xi) = \phi'(\xi)$, *and*

$$c_1(\xi) = L_1 e^{z_1(v_0-\phi(\xi))}, \;\; c_2(\xi) = L_2 e^{z_2(v_0-\phi(\xi))}, \;\; c_3(\xi) = L_3 e^{z_3(v_0-\phi(\xi))}.$$

Similarly, potential boundary layers Γ_ℓ^a *at* $x = a$ *are determined in the following way: the* ϕ*-component satisfies the Hamiltonian system*

$$\phi'' + z_1 c_1^a e^{z_1(\phi^a-\phi)} + z_2 c_2^a e^{z_2(\phi^a-\phi)} + z_3 c_2^a e^{z_3(\phi^a-\phi)} = 0,$$

together with $\phi(0) = \phi^a$ *and* $\phi(\xi) \to \phi^{a,\ell}$ *as* $\xi \to -\infty$, $u(\xi) = \phi'(\xi)$, *and*

$$c_1(\xi) = c_1^a e^{z_1(\phi^a-\phi(\xi))}, \;\; c_2(\xi) = c_2^a e^{z_2(\phi^a-\phi(\xi))}, \;\; c_3(\xi) = c_3^a e^{z_3(\phi^a-\phi(\xi))}.$$

iii Let $N_L = M_L \cap W^s(Z_\ell)$ *and* $N_\ell^a = M_\ell^a \cap W^u(Z_\ell)$. *Then,*

$$\omega(N_L) = \{(\phi^L, 0, c_1^L, c_2^L, c_3^L, J_1, J_2, J_3, 0) : \;\; all \;\; J_1, J_2, J_3\},$$

$$\alpha(N_\ell^a) = \{(\phi^{a,\ell}, 0, c_1^{a,\ell}, c_2^{a,\ell}, c_2^{a,\ell}, J_1, J_2, J_3 a) : \;\; all \;\; J_1, J_2, J_3\},$$

where $\phi^L, c_1^L, c_2^L, c_3^L, \phi^{a,\ell}, c_1^{a,\ell}$, $c_2^{a,\ell}$, *and* $c_3^{a,\ell}$ *are given explicitly as in part (i),*

Proof. We provide a proof for the first part that is related to the boundary layer on the left in each statement.

Let $z(\xi) = (\phi(\xi), u(\xi), c_1(\xi), c_2(\xi), c_3(\xi), J_1(\xi), J_2(\xi), J_3(\xi), \tau(\xi))$ be a solution to system (13) with $z(0) \in B_L$ and $z(\xi) \in W^s(Z_\ell)$. Then, $J_i(\xi) = J_i$, $\tau(\xi) = 0$ for all ξ,and

$$z(\xi) \to z(\infty) = (\phi^L, 0, c_1^L, c_2^L, c_3^L, J_1, J_2, J_3, 0) \in Z_\ell$$

for some ϕ^L and c_i^L with $0 = z_1c_1^L + z_2c_2^L + z_3c_3^L$ and

$$\phi(0) = v_0,\ \ c_1(0) = L_1,\ \ c_2(0) = L_2.\ \ c_3(0) = L_3.$$

Using our first integrals H_1, H_2 and H_3, we have,

$$H_1 = e^{z_1\phi}c_1 = e^{z_1v_0}L_1,\ \ H_2 = e^{z_1\phi}c_2 = e^{z_2v_0}L_2,\ \ H_3 = e^{z_3\phi}c_3 = e^{z_3v_0}L_3$$

at our boundary conditions. Therefore, we can solve for c_1, c_2, and c_3

$$c_1 = L_1e^{z_1(v_0-\phi)},\ \ c_2 = L_2e^{z_2(v_0-\phi)},\ \ c_3 = L_3e^{z_3(v_0-\phi)}.$$

And when we take the limit as $\xi \to \infty$, we have,

$$c_1^L = L_1e^{z_1(v_0-\phi^L)},\ \ c_2^L = L_2e^{z_2(v_0-\phi^L)},\ \ c_3^L = L_3e^{z_3(v_0-\phi^L)}.$$

Then we have,

$$z_1L_1e^{z_1(v_0-\phi^L)} + z_2L_2e^{z_2(v_0-\phi^L)} + z_3L_3e^{z_3(v_0-\phi^L)} = 0,$$

$$\text{that is,}\ \ \phi^L = v_0 + \frac{1}{z_3 - z_2}\left(\ln\left(\frac{-z_3L_3}{z_1L_1}\right) - \ln\left(\frac{z_2L_2}{z_1L_1}\right)\right)$$

Hence we have,

$$c_1^L = L_1e^{z_1(v_0-\phi^L)} = L_1e^{z_1\left(v_0 - v_0 + \frac{1}{z_3-z_2}\left(\ln\left(\frac{-z_3L_3}{z_1L_1}\right) - \ln\left(\frac{z_2L_2}{z_1L_1}\right)\right)\right)}$$

$$= L_1e^{\frac{z_1}{z_3-z_2}\left(\ln\left(\frac{-z_3L_3}{z_1L_1}\right) - \ln\left(\frac{z_2L_2}{z_1L_1}\right)\right)}$$

$$= L_1e^{\ln(-z_3L_3)^{\frac{z_1}{z_3-z_2}}}e^{\ln(z_2L_2)^{\frac{-z_1}{z_3-z_2}}}$$

$$= L_1(-z_3L_3)^{\frac{z_1}{z_3-z_2}}(z_2L_2)^{\frac{-z_1}{z_3-z_2}}$$

A similar calculation can be used to show that

$$c_2^L = L_2(-z_3L_3)^{\frac{z_2}{z_3-z_2}}(z_2L_2)^{\frac{-z_2}{z_3-z_2}}, \;\; c_3^L = L_3(-z_3L_3)^{\frac{z_3}{z_3-z_2}}(z_2L_2)^{\frac{-z_3}{z_3-z_2}}$$

Since $\phi' = u$ we have that $\phi'' = -z_1c_1 - z_2c_2 - z_3c_3$, so then our expressions for c_1, c_2, and c_3 implies that ϕ satisfies the Hamiltonian equation,

$$\phi'' + z_1L_1e^{z_1(v_0-\phi)} + z_2L_2e^{z_2(v_0-\phi)} + z_3L_3e^{z_3(v_0-\phi)} = 0$$

with $\phi(0) = v_0$ and $\phi(\xi) \to \phi^L$ as $\xi \to \infty$. The Hamiltonian is

$$H(\phi,u) = \frac{u^2}{2} - L_1e^{z_1(v_0-\phi)} - L_2e^{z_2(v_0-\phi)} - L_3e^{z_3(v_0-\phi)}.$$

In terms of ϕ and $u = \phi'$, the equation becomes,

$$\phi' = u, \;\; u' = -z_1L_1e^{z_1(v_0-\phi)} - z_2L_2e^{z_2(v_0-\phi)} - z_3L_3e^{z_3(v_0-\phi)}.$$

The Hamiltonian system has a unique equilibrium $(\phi^L, 0)$ with ϕ^L given above. If $W^s(\phi^L)$ is the stable manifold of $(\phi^L,0)$, then it is the restriction of $W^s(Z_\ell)$ to the (ϕ,u)-plane. In order to have $(v_0,u_0) \in W^s(\phi^L)$, $H(\phi^L,0) = H(v_0,u_0)$ and one can explicitly solve for u_0. To determine the sign of u_0, note that the left branch of the stable manifold $W^s(\phi^L)$ lies above the ϕ-axis and hence that $v_0 < \phi^L$ implies $u_0 > 0$; similarly, if $v_0 > \phi^L$, then $u_0 < 0$. □

Remark 2.2. Note that, with the electroneutrality boundary conditons (4), one finds that

$$(\phi^L, c_1^L, c_2^L, c_3^L) = (v_0, L_1, L_2, L_3).$$

Thus, under the electroneutrality boundary conditions, there is no boundary layers at $x = 0$. Like-

wise, with the electroneutrality boundary conditions (4), one finds, in Proposition 2.3, that

$$(\phi^R, c_1^R, c_2^R, c_3^R) = (0, R_1, R_2, R_3),$$

so that there is no boundary layers at $x = 1$. On the other hand, there must be internal layers at $x = a$, and $x = b$ due to the jumps of the permanent charge.

2.1.2 Outer dynamics on $[0,a]$: Regular layers.

We now construct regular layers on Z_ℓ that connect $\omega(N_L)$ to $\alpha(N_\ell^a)$. We find that the outer flow on Z_ℓ is itself a singular perturbation problem. To see this, we zoom in on an $O(\varepsilon)$-neighborhood of Z_ℓ by blowing up the u and $z_1c_1 + z_2c_2 + z_3c_3$ coordinates. Let us introduce $\hat{q} = -z_1c_1 - z_2c_2 - z_3c_3$. In terms of the variables $(\phi, u, \hat{q}, c_i, J_i, \tau)$, system (10) (with Q = 0)) becomes

$$\begin{aligned}
\phi' = u, \;\; u' &= \hat{q} - \varepsilon \frac{h'(\tau)}{h(\tau)} u, \\
\hat{q}' &= (z_1(z_1 - z_3)c_1 + z_2(z_2 - z_3)c_2 - z_3\hat{q})u - \varepsilon h^{-1}(\tau)(-z_1J_1 - z_2J_2 - z_3J_3), \\
c_1' &= -z_1c_1u - \varepsilon h^{-1}(\tau)J_1, \\
c_2' &= -z_2c_2u - \varepsilon h^{-1}(\tau)J_2 \\
J_i' = 0, \;\; \tau' &= \varepsilon
\end{aligned} \tag{16}$$

For $\varepsilon = 0$, the set $\{u = \hat{q} = 0\}$ is normally hyperbolic invariant manifold consisting of equilibria. By Fenichel's theory, the manifold persists for $\varepsilon > 0$ small and is given by

$$u = \varepsilon A(\phi, c_i, J_i, \tau) + O(\varepsilon^2), \;\; \hat{q} = \varepsilon B(\phi, c_i, J_i, \tau) + O(\varepsilon^2).$$

Using the invariance of the manifold we will preform a center manifold reduction. The procedure is as follows, find u' and $\hat{q}'$ and substitute the expressions for those as well for u and $\hat{q}$ into system

(16). One then obtains,

$$B = O(\varepsilon),\ \ A = \frac{-z_1J_1 - z_2J_2 - z_3J_3}{(z_1(z_1-z_3)c_1 + z_2(z_2-z_3)c_2)h(\tau)} + O(\varepsilon).$$

System (16) on the perturbed invariant manifold can be obtained by substituting the expression of u and $\hat{q}$ with the approximations of A and B above. It reads as follows:

$$\begin{aligned}
\phi' &= \varepsilon \frac{-z_1J_1 - z_2J_2 - z_3J_3}{(z_1(z_1-z_3)c_1 + z_2(z_2-z_3)c_2)h(\tau)} + O(\varepsilon^2),\\
c_1' &= -z_1c_1\left(\frac{-z_1J_1 - z_2J_2 - z_3J_3}{(z_1(z_1-z_3)c_1 + z_2(z_2-z_3)c_2)h(\tau)}\right) - \varepsilon h^{-1}(\tau)J_1 + O(\varepsilon^2),\\
c_2' &= -z_2c_2\left(\frac{-z_1J_1 - z_2J_2 - z_3J_3}{(z_1(z_1-z_3)c_1 + z_2(z_2-z_3)c_2)h(\tau)}\right) - \varepsilon h^{-1}(\tau)J_2 + O(\varepsilon^2),\\
J_i' &= 0,\ \ \tau' = \varepsilon.
\end{aligned} \tag{17}$$

The corresponding outer dynamics is

$$\begin{aligned}
\dot{\phi} &= \frac{-z_1J_1 - z_2J_2 - z_3J_3}{(z_1(z_1-z_3)c_1 + z_2(z_2-z_3)c_2)h(\tau)},\\
\dot{c_1} &= -z_1c_1\left(\frac{-z_1J_1 - z_2J_2 - z_3J_3}{(z_1(z_1-z_3)c_1 + z_2(z_2-z_3)c_2)h(\tau)}\right) - h^{-1}(\tau)J_1,\\
\dot{c_2} &= -z_2c_2\left(\frac{-z_1J_1 - z_2J_2 - z_3J_3}{(z_1(z_1-z_3)c_1 + z_2(z_2-z_3)c_2)h(\tau)}\right) - h^{-1}(\tau)J_2,\\
\dot{J}_i &= 0,\ \ \dot{\tau} = 1.
\end{aligned} \tag{18}$$

Notice that the denominators in the equations for ϕ and the concentrations are the same and we can verify that,

$$z_1(z_1-z_3)c_1 + z_2(z_2-z_3)c_2 = z_1^2c_1 + z_2^2c_2 + z_3^2c_3$$

since $\hat{q} = 0$ on the slow manifold Z_ℓ and consequentially $z_1c_1 + z_2c_2 + z_3c_3 = 0$. Since we are only interested in solutions where $c_k > 0$ then the above quantity is positive.

If we multiply the right hand side of the system by $(z_1(z_1-z_3)c_1 + z_2(z_2-z_3)c_2)h(\tau)$ the phase portrait will remain the same. In doing so our system becomes in terms of a new variable that we

will call y,

$$\begin{aligned}
\frac{d}{dy}\phi &= -z_1J_1 - z_2J_2 - z_3J_3,\\
\frac{d}{dy}c_1 &= z_1c_1(z_1c_1 + z_2c_2 + z_3c_3) - J_1(z_1(z_1 - z_3)c_1 + z_2(z_2 - z_3)c_2)\\
\frac{d}{dy}c_2 &= z_2c_2(z_1c_1 + z_2c_2 + z_3c_3) - J_2(z_1(z_1 - z_3)c_1 + z_2(z_2 - z_3)c_2)\\
\frac{d}{dy}J_i &= 0,\ \ \frac{d}{dy}\tau = h(\tau)(z_1c_1(z_1(z_1 - z_3)c_1 + z_2(z_2 - z_3)c_2)
\end{aligned} \tag{19}$$

The equations for c_1, c_2 for a linear system of the form,

$$\frac{d}{dy}\hat{C} = D\hat{C}$$

where $\hat{C} = (c_1, c_2)^T$, and D is a matrix with constant (independent of y) entries given by,

$$D = \begin{bmatrix} z_1(z_1J_1 + z_2J_2 + z_3J_3) + z_1(z_3 - z_1)J_1 & z_2(z_3 - z_2)J_1 \\ z_1(z_3 - z_1)J_2 & z_2(z_1J_1 + z_2J_2 + z_3J_3) + z_2(z_3 - z_2)J_2 \end{bmatrix}.$$

Then the solution of (19) with the initial condition $(\phi^L, 0, c_1^L, c_2^L, c_3^L, J_1, J_2, J_3, 0) \in \omega(N_L)$ is

$$\begin{aligned}
\phi(y) &= \phi^L + (-z_1J_1 - z_2J_2 - z_3J_3)y,\\
\hat{C}(y) &= e^{Dy}\hat{C}^L,\\
\int_0^y h^{-1}(s)ds &= (z_1 - z_3)z_1\int_0^y c_1(s)ds + (z_2 - z_3)z_2\int_0^y c_2(s)ds,
\end{aligned} \tag{20}$$

where $\hat{C}^L = (c_1^L, c_2^L)^T$.

Now we are trying to find solutions that are in $\alpha(N_\ell^a)$ when $\tau = x = a$, say at $y = y_a$. We get,

$$\begin{aligned}
\phi_\ell^a &= \phi^L + (-z_1J_1 - z_2J_2 - z_3J_3)y_a,\\
\hat{C}^{\ell,a} &= e^{Dy_a}\hat{C}^L,\\
\int_0^a h^{-1}(t)dt &= \Omega\int_0^{y_a}\hat{C}(t),
\end{aligned} \tag{21}$$

where $\Omega = (z_1(z_1 - z_3), z_2(z_2 - z_3))$. Note that, the unknowns for the above system of the four (4) equations are J_1, J_2, J_3 and y_a. This system gives us the implicit forms of J_1, J_2 and J_3.

The regular layer Λ_ℓ is given by (20) for $y \in [0, y_a]$, where J_1, J_2, and J_3 are determined by (21) together with $u = 0 = z_1c_1 + z_2c_2 + z_3c_3$.

In figure 1 we can see the complete singular orbit on $[0, a]$. The singular orbit for $[b, 1]$ can be derived the exact same way.

2.2 Singular orbits on $[a, b]$ with $\mathrm{Q}(x) = \mathrm{Q}$.

We now construct a singular orbit on the subinterval $[a, b]$ viewed as the channel where the permanent charge $\mathrm{Q}(x) = \mathrm{Q}$ is a nonzero constant. The construction is nearly the same as that for singular orbits on $[0, a]$.

We set $\phi(b) = \phi^b$, $c_1(b) = c_1^b$, $c_2(b) = c_2^b$ and $c_3(b) = c_3^b$, where ϕ^b, $c_i(b)$ are unknowns to be

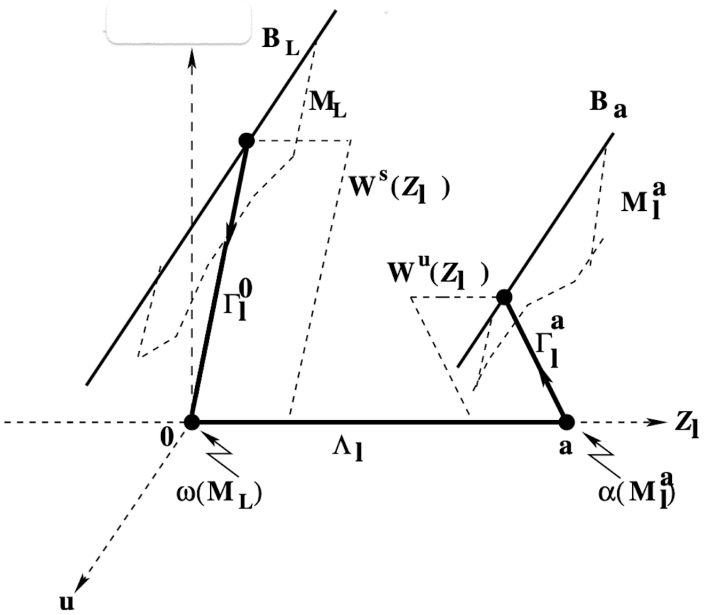


Figure 1: The Singular Orbit on $[0, a]$

determined later. Let

$$B_b = \{(\phi^b, u, c_1^b, c_2^b, c_3^b, J_1, J_2, J_3, b) \in \mathbb{R}^9 \ : \ \text{arbitrary } u, J_1, J_2, J_3\}.$$

The singular orbit to be constructed will be a connecting orbit from B_a to B_b over $[a,b]$.

2.2.1 Inner dynamics on $[a,b]$: Boundary layers.

By setting $\varepsilon = 0$ in system (9) with $\mathrm{Q}(x) = \mathrm{Q}$, we get $u = 0$ and $z_1c_1 + z_2c_2 + z_3c_3 + \mathrm{Q} = 0$. The outer manifold is

$$Z_m = \{u = 0, \ \ z_1c_1 + z_2c_2 + z_3c_3 + \mathrm{Q} = 0\}.$$

In terms of ξ, we obtain the inner system of (9):

$$\begin{aligned}
\phi' = u, \ \ u' &= -z_1c_1 - z_2c_2 - z_3c_3 - \mathrm{Q} - \varepsilon\frac{h'(\tau)}{h(\tau)}u, \\
c_1' &= -z_1c_1u - \varepsilon h^{-1}(\tau)J_1, \\
c_2' &= -z_2c_2u - \varepsilon h^{-1}(\tau)J_2, \\
c_3' &= -z_3c_3u - \varepsilon h^{-1}(\tau)J_3, \\
J_1' = J_2' = J_3' &= 0, \ \ \tau' = \varepsilon.
\end{aligned} \tag{22}$$

The limiting system at $\varepsilon = 0$ is

$$\begin{aligned}
\phi' = u, \ \ u' &= -z_1c_1 - z_2c_2 - z_3c_3 - \mathrm{Q}, \\
c_1' &= -z_1c_1u, \\
c_2' &= -z_2c_2u, \\
c_3' &= -z_3c_3u, \\
J_1' = J_2' = J_3' &= 0, \ \ \tau' = 0.
\end{aligned} \tag{23}$$

The set of equilibria of (23) is precisely Z_m, and Z_m is normally hyperbolic with an eight-dimensional stable manifold, $W^s(Z_m)$, and an eight dimensional unstable manifold, $W^u(Z_m)$, just like for Z_ℓ on $[0,a]$. The manifolds Z_m, $W^s(Z_m)$, and $W^u(Z_m)$ persist for $\varepsilon > 0$ small.

Proposition 2.2. *i System* (23) *has the following eight integrals:*

$$H_1 = e^{z_1\phi}c_1,\ \ H_2 = e^{z_2\phi}c_2,\ \ H_3 = e^{z_3\phi}c_3\ \ H_4 = c_1+c_2+c_3-\frac{1}{2}u^2-\mathrm{Q}\phi,$$
$$H_5 = J_1,\ \ H_6 = J_2, H_7 = J_3,\ \ H_8 = \tau.$$

ii Let $\phi = \phi^{a,m}$ be the unique solution of

$$z_1c_1^a e^{z_1(\phi^a-\phi)} + z_2c_2^a e^{z_2(\phi^a-\phi)} + z_3c_3^a e^{z_3(\phi^a-\phi)} + \mathrm{Q} = 0,$$

and let

$$c_1^{a,m} = e^{z_1(\phi^a-\phi^{a,m})}c_1^a,\ \ c_2^{a,m} = e^{z_2(\phi^a-\phi^{a,m})}c_2^a,\ \ c_3^{a,m} = e^{z_3(\phi^a-\phi^{a,m})}c_3^a.$$

The stable manifold $W^s(Z_m)$ intersects B_a transversally at point with

$$u_m(a) =$$
$$[sgn(\phi^{a,m}-\phi^a)]\sqrt{2c_1^a(1-e^{z_1(\phi^a-\phi^{a,m})})+2c_2^a(1-e^{z_2(\phi^a-\phi^{a,m})})+2c_3^a(1-e^{z_3(\phi^a-\phi^{a,m})}-2\mathrm{Q}(\phi^a-\phi^{a,m})}.$$

are arbitrary J_i's.

Let $\phi = \phi^{b,m}$ be the unique solution of

$$z_1c_1^b e^{z_1(\phi^b-\phi)} + z_2c_2^b e^{z_2(\phi^b-\phi)} + z_3c_3^b e^{z_3(\phi^b-\phi)} + \mathrm{Q} = 0,$$

and let

$$c_1^{b,m} = e^{z_1(\phi^b-\phi^{b,m})}c_1^b,\ \ c_2^{b,m} = e^{z_2(\phi^b-\phi^{b,m})}c_2^b,\ \ c_3^{b,m} = e^{z_3(\phi^b-\phi^{b,m})}c_3^b.$$

The unstable manifold $W^u(Z_m)$ intersects B_b transversally at points with

$$u_m(b) =$$
$$[sgn(\phi^b - \phi^{b,m})]\sqrt{2c_1^b(1-e^{z_1(\phi^b-\phi^{b,m})})+2c_2^b(1-e^{z_2(\phi^b-\phi^{b,m})})+2c_3^b(1-e^{z_3(\phi^b-\phi^{b,m})}-2Q(\phi^b-\phi^{b,m})}.$$

are arbitrary J_i's.

iii Potential boundary layers Γ_m^a at $x=a$ can be determined in the following way: the ϕ-component satisfies the Hamiltonian system

$$\phi'' + z_1 c_1^a e^{z_1(\phi^a-\phi)} + z_2 c_2^a e^{z_2(\phi^a-\phi)} + z_3 c_3^a e^{z_3(\phi^a-\phi)} + Q = 0,$$

together with $\phi(0)=\phi^a$ and $\phi(\xi)\to\phi^{a,m}$ as $\xi\to\infty$, $u(\xi)=\phi'(\xi)$, and

$$c_1(\xi) = c_1^a e^{z_1(\phi^a-\phi(\xi))},\ \ c_2(\xi) = c_2^a e^{z_2(\phi^a-\phi(\xi))},\ \ c_3(\xi) = c_3^a e^{z_3(\phi^a-\phi(\xi))}.$$

Similarly, potential boundary layers Γ_m^b at $x=b$ can be determined in the following way: the ϕ-component satisfies the Hamiltonian system

$$\phi'' + z_1 c_1^b e^{z_1(\phi^b-\phi)} + z_2 c_2^b e^{z_2(\phi^b-\phi)} + z_3 c_3^b e^{z_3(\phi^b-\phi)} + Q = 0,$$

together with $\phi(0)=\phi^b$ and $\phi(\xi)\to\phi^{b,m}$ as $\xi\to-\infty$, $u(\xi)=\phi'(\xi)$, and

$$c_1(\xi) = c_1^b e^{z_1(\phi^b-\phi(\xi))},\ \ c_2(\xi) = c_2^b e^{z_2(\phi^b-\phi(\xi))}\ \ c_3(\xi) = c_3(\xi) = c_3^b e^{z_3(\phi^b-\phi(\xi))}.$$

iv Let $N_m^a = M_m^a \cap W^s(Z_m)$ and $N_m^b = M_m^b \cap W^u(Z_m)$, where M_m^a is the collection of orbits from B_a in forward time under the flow (23) *and M_m^b is the collection of orbits from B_b in backward time under the flow* (23)*. Then,*

$$\omega(N_m^a) = \{(\phi^{a,m}, 0, c_1^{a,m}, c_2^{a,m}, c_3^{a,m}, J_1, J_2, J_3, a)\ :\ all\ J_i\},$$

$$\alpha(N_m^b) = \{(\phi^{b,m}, 0, c_1^{b,m}, c_2^{b.m}, c_3^{b,m}, J_1, J_2, J_3, b) \ : \ all\ J_i\}.$$

Remark 2.3. To show that the quantity under the square root is nonnegative, we assume $c_1^a > 0$, $c_2^a > 0$, and $c_3^a > 0$ for the moment and let

$$f(x) = c_1^a + c_2^a + c_3^a - c_1^a e^{z_1(\phi^a - x)} - c_2^a e^{z_2(\phi^a - x)} - c_3^a e^{z_3(\phi^a - x)} - Q(\phi^a - x).$$

Then,

$$f'(x) = z_1 c_1^a e^{z_1(\phi^a - x)} + z_2 c_2^a e^{z_2(\phi^a - x)} + z_3 c_3^a e^{z_3(\phi^a - x)} + Q$$

and

$$f''(x) = -z_1^2 c_1^a e^{z_1(\phi^a - x)} - z_2^2 c_2^a e^{z_2(\phi^a - x)} - z_3^2 c_3^a e^{z_3(\phi^a - x)} < 0.$$

Therefore $f(x)$ is concave downward. Note that $f'(x) \to +\infty$ as $x \to -\infty$ and $f'(x) \to -\infty$ as $x \to +\infty$. Hence, $f(x)$ has a unique criticial point and it must have a global maximum at this critical point. Since $x = \phi_m^a$ is the critical point, we have

$$f(\phi_m^a) \geq f(\phi^a) = 0.$$

By continuity, we have $f(\phi_m^a) \geq 0$ even if $c_1^a = 0$, $c_2^a = 0$, and/or $c_3^a = 0$.

2.2.2 Outer dynamics on $[a,b]$: Regular layers.

We now study the flow in the vicinity of the outer manifold Z_m. Similarly to on $[0,a]$ we will now construct regular layers on Z_m. Let us introduce $\hat{q} = -z_1 c_1 - z_2 c_2 - z_3 c_3 - \mathrm{Q}$. In terms of the

variables $(\phi, u, \hat{q}, c_1, c_2, J_i, \tau)$, system (10) (with Q being nonzero) becomes

$$\begin{aligned}
\phi' = u, \;\; u' = \hat{q} - \varepsilon \frac{h'(\tau)}{h(\tau)} u, \\
\hat{q}' = (z_1(z_1 - z_3)c_1 + z_2(z_2 - z_3)c_2 - z_3\hat{q} - z_3\mathrm{Q})u - \varepsilon h^{-1}(\tau)(-z_1 J_1 - z_2 J_2 - z_3 J_3), \\
c_1' = -z_1 c_1 u - \varepsilon h^{-1}(\tau) J_1, \\
c_2' = -z_2 c_2 u - \varepsilon h^{-1}(\tau) J_2, \\
J_i' = 0, \;\; \tau' = \varepsilon
\end{aligned} \tag{24}$$

For $\varepsilon = 0$, the set $\{u = \hat{q} = 0\}$ is normally hyperbolic invariant manifold consisting of equilibria. By Fenichel's theory, the manifold persists for $\varepsilon > 0$ small and is given by

$$u = \varepsilon A(\phi, c_1, c_2, J_i, \tau) + O(\varepsilon^2), \;\; \hat{q} = \varepsilon B(\phi, c_1, c_2, J_i, \tau) + O(\varepsilon^2).$$

Using the invariance of the manifold we will preform a center manifold reduction, just like on $[0, a]$ One then obtains,

$$B = O(\varepsilon), \;\; A = \frac{-z_1 J_1 - z_2 J_2 - z_3 J_3}{(z_1(z_1 - z_3)c_1 + z_2(z_2 - z_3)c_2 - z_3\mathrm{Q})h(\tau)} + O(\varepsilon).$$

System (24) on the perturbed invariant manifold can be obtained by substituting the expression of u and $\hat{q}$ with the approximations of A and B above. The corresponding outer dynamics is

$$\begin{aligned}
\dot{\phi} = \frac{-z_1 J_1 - z_2 J_2 - z_3 J_3}{(z_1(z_1 - z_3)c_1 + z_2(z_2 - z_3)c_2 - z_3\mathrm{Q})h(\tau)}, \\
\dot{c_1} = -z_1 c_1 \frac{-z_1 J_1 - z_2 J_2 - z_3 J_3}{(z_1(z_1 - z_3)c_1 + z_2(z_2 - z_3)c_2 - z_3\mathrm{Q})h(\tau)} - h^{-1}(\tau) J_1, \\
\dot{c_2} = -z_2 c_2 \frac{-z_1 J_1 - z_2 J_2 - z_3 J_3}{(z_1(z_1 - z_3)c_1 + z_2(z_2 - z_3)c_2 - z_3\mathrm{Q})h(\tau)} - h^{-1}(\tau) J_2, \\
\dot{J_i} = 0, \;\; \dot{\tau} = 1.
\end{aligned} \tag{25}$$

Again, we see that the first three equations have the same denominator. Since $\hat{q} = 0$ and similarly $z_1c_1 + z_2c_2 + z_3c_3 + \mathrm{Q} = 0$ then by some manipulation we see,

$$(z_1c_1(z_1 - z_3) + z_2c_2(z_2 - z_3) - z_3\mathrm{Q}) = z_1^2c_1 + z_2^2c_2 + z_3^2c_3.$$

Since we want our concentration to be positive then our denominator is positive. Multiplying through by the common denominator on the right hand side of the system we get,

$$\begin{aligned} \frac{d}{dy}\phi &= -z_1J_1 - z_2J_2 - z_3J_3, \\ \frac{d}{dy}\hat{C} &= D\hat{C} + z_3\mathrm{Q}\hat{J}, \\ \frac{d}{dy}J_i = 0, \quad \frac{d}{dy}\tau &= (z_1c_1(z_1 - z_3) + z_2c_2(z_2 - z_3) - z_3\mathrm{Q}), \end{aligned} \tag{26}$$

where $\hat{C}$, and D are the same as for $[0,a]$ and $\hat{J} = (J_1, J_2)^T$.

Our solution with the initial condition $(\phi^{a,m}, 0, c_1^{a,m}, c_2^{a,m}, c_3^{a,m}, J_1, J_2, J_3, a) \in \omega(N_m^a)$ is

$$\begin{aligned} \phi(y) &= \phi^{a,m} + (-z_1J_1 - z_2J_2 - z_3J_3)y, \\ \hat{C}(y) &= e^{Dy}\hat{C}^{a,m} + z_3\mathrm{Q}\int_0^y e^{D(y-t)}dt\hat{J}, \\ \int_a^b h^{-1}(t)dt &= (z_1 - z_3)z_1\int_0^y c_1(t)dt + (z_2 - z_3)z_2\int_0^y c_2(t)dt - z_3\mathrm{Q}y. \end{aligned} \tag{27}$$

Now since we are trying to find solutions that connect our orbit from $\omega(N_m^a)$ to $\alpha(N_m^b)$ we also want to evaluate for where (27) is a $\tau = x = b$ for some $y = y_b$.

$$\begin{aligned} \phi^{b,m} &= \phi^{a,m} + (-z_1J_1 - z_2J_2 - z_3J_3)y_b, \\ \hat{C}^{b,m} &= e^{Dy_b}\hat{C}^{a,m} + z_3\mathrm{Q}\int_0^y e^{D(y_b-t)}dt\hat{J}, \\ \int_a^b h^{-1}(t)dt &= \Omega\int_0^{y_b}\hat{C}(t)dt - z_3\mathrm{Q}y_b, \end{aligned} \tag{28}$$

where Ω is like it was described for $[0,a]$.

It has been shown in [6] that system (28) is equivalent to,

$$\begin{aligned}
\phi^{b,m} &= \phi^{a,m} + (-z_1J_1 - z_2J_2 - z_3J_3)y_b, \\
\hat{C}^{b,m} &= e^{Dy_b}\hat{C}^{a,m} + z_3QD^{-1}(e^{Dy_b} - I)\hat{J}, \\
\int_a^b h^{-1}(t)dt &= \Omega\int_0^{y_b}\hat{C}(t)dt - z_3\mathrm{Q}y_b.
\end{aligned} \tag{29}$$

Systems (29) helps us determine our unknown variables.

Our regular orbit, Λ_m is given by (27) where J_1, J_2 and J_3 are determined by (29) together with $u = 0$ and $z_1c_1 + z_2c_2 + z_3c_3 + \mathrm{Q} = 0$.

2.3 Singular orbits on $[b,1]$ with $\mathrm{Q}(x) = 0$.

The construction of singular orbits on $[b,1]$ is virtually identical to the construction of singular orbits on $[0,a]$, We will state only the results.

2.3.1 Inner dynamics on $[b,1]$: Boundary layers.

The inner limit system is

$$\begin{aligned}
\phi' = u,\ \ u' &= -z_1c_1 - z_2c_2 - z_3c_3, \\
c_1' &= -z_1c_1u, \\
c_2' &= -z_2c_2u, \\
c_3' &= -z_3c_3u, \\
J_1' = J_2' = J_3' = 0, &\quad \tau' = 0.
\end{aligned} \tag{30}$$

The outer manifold is

$$Z_r = \{u = 0,\ \ z_1c_1 + z_2c_2 + z_3c_3 = 0\}.$$

It consists of the equilibria of system (30) and is normally hyperbolic with an eight-dimensional stable manifold $W^s(Z_r)$ and an eight dimensional unstable manifold $W^u(Z_r)$, similarly to Z_ℓ. Concerning the boundary layers we have the following proposition.

Proposition 2.3. *i System* (30) *has the following eight integrals:*

$$H_1 = e^{z_1\phi}c_1,\ \ H_2 = e^{z_2\phi}c_2,\ \ H_3 = e^{z_3\phi}c_3\ \ H_4 = c_1+c_2+c_3-\frac{1}{2}u^2,$$
$$H_5 = J_1,\ \ H_6 = J_2,\ \ H_7 = J_3\ \ H_8 = \tau.$$

ii Let $\phi = \phi^{b,r}$ be the unique solution of

$$z_1c_1^be^{z_1(\phi^b-\phi)} + z_2c_2^be^{z_2(\phi^b-\phi)} + z_3c_3^be^{z_3(\phi^b-\phi)} = 0,$$

$$\textit{that is, }\ \phi^{b,r} = \phi^b + \frac{1}{z_3-z_2}\left(\ln\left(\frac{-z_3c_3^b}{z_1c_1^b}\right) - \ln\left(\frac{z_2c_2^b}{z_1c_1^b}\right)\right)$$

and let

$$c_1^{b,r} = c_1^b(-z_3c_3^b)^{\frac{z_1}{z_3-z_2}}(z_2c_2^b)^{\frac{-z_1}{z_3-z_2}}\ \ c_2^{b,r} = c_2^b(-z_3c_3^b)^{\frac{z_2}{z_3-z_2}}(z_2c_2^b)^{\frac{-z_2}{z_3-z_2}},$$

$$c_3^{b,r} = c_3^b(-z_3c_3^b)^{\frac{z_3}{z_3-z_2}}(z_2c_2^b)^{\frac{-z_3}{z_3-z_2}}$$

The stable manifold $W^s(Z_\ell)$ intersects B_L transversally at points with

$$u_0 = [sgn(\phi^b-\phi)]\sqrt{2(c_1^b+c_2^b+c_3^b) - 2(c_1^be^{z_1(\phi^b-\phi)} + c_2^be^{z_2(\phi^b-\phi)} + c_3^be^{z_3(\phi^b-\phi))})} \quad (31)$$

and arbitrary J_i's, where sgn is the sign function.

Let $\phi = \phi^R$ be the unique solution of

$$z_1R_1e^{z_1\phi} + z_2R_2e^{z_2\phi} + z_3R_3e^{z_3\phi} = 0,$$

$$\textit{that is, }\ \phi^R = -\frac{1}{z_3-z_2}\left(\ln\left(\frac{-z_3R_3}{z_1R_1}\right) - \ln\left(\frac{z_2R_2}{z_1R_1}\right)\right),$$

and let

$$c_1^R = R_1(-z_3R_3)^{\frac{z_1}{z_3-z_2}}(z_2R_2)^{\frac{-z_1}{z_3-z_2}} \quad c_2^R = R_2(-z_3R_3)^{\frac{z_2}{z_3-z_2}}(z_2R_2)^{\frac{-z_2}{z_3-z_2}},$$

$$c_3^R = R_3(-z_3R_3)^{\frac{z_3}{z_3-z_2}}(z_2R_2)^{\frac{-z_3}{z_3-z_2}}$$

The unstable manifold $W^u(Z_\ell)$ intersects B_a transversally at points with

$$u_r(z) = [sgn(\phi)]\sqrt{2(R_1+R_2+R_3) - 2(R_1e^{z_1\phi} + R_2e^{z_2\phi} + R_3e^{z_3\phi})}$$

arbitrary J_i's.

iii Potential boundary layers Γ_r^b at $x = b$ are determined in the following way: the ϕ-component satisfies the Hamiltonian system

$$\phi'' + z_1c_1^be^{z_1(\phi^b-\phi)} + z_2c_2^be^{z_2(\phi^b-\phi)} + z_2c_3^be^{z_3(\phi^b-\phi)} = 0,$$

together with $\phi(0) = \phi^b$ and $\phi(\xi) \to \phi^{b,r}$ as $\xi \to \infty$, $u(\xi) = \phi'(\xi)$, and

$$c_1(\xi) = c_1^be^{z_1(\phi^b-\phi(\xi))}, \quad c_2(\xi) = c_2^be^{z_2(\phi^b-\phi(\xi))} \quad c_3(\xi) = c_3^be^{z_3(\phi^b-\phi(\xi))}.$$

Similarly, potential boundary layers Γ_r^1 at $x = 1$ are determined in the following way: the ϕ-component satisfies the Hamiltonian system

$$\phi'' + z_1R_1e^{-z_1\phi} + z_2R_2e^{-z_2\phi} + z_3R_3e^{-z_3\phi} = 0,$$

together with $\phi(0) = 0$ and $\phi(\xi) \to \phi^R$ as $\xi \to -\infty$, $u(\xi) = \phi'(\xi)$, and

$$c_1(\xi) = R_1e^{-z_1\phi(\xi)}, \quad c_2(\xi) = R_2e^{-z_2\phi(\xi)}, \quad c_3(\xi) = R_3e^{-z_3\phi(\xi)}.$$

iv Let $N_r^b = M_r^b \cap W^s(Z_r)$ and $N_R = M_R \cap W^u(Z_r)$, where M_r^b is the collection of orbits from B_b

in forward time under the flow (30) *and M_R is the collection for orbits from B_R in backward time under the flow of* (30)*. Then,*

$$\omega(N_r^b) = \{(\phi^{b,r}, 0, c_1^{b,r}, c_2^{b,r} c_3^{b,r}, J_1, J_2, J_3, b) : \ \textit{all} \ \ J_1, J_2, J_3\},$$

$$\alpha(N_R) = \{(\phi^R, 0, c_1^R, c_2^R, c_3^R, J_1, J_2, J_3, 1) : \ \textit{all} \ \ J_1, J_2, J_3\}.$$

2.3.2 Outer dynamics on $[b,1]$: Regular layers.

We now examine the existence of regular layers or outer solutions that connect $\omega(N_r^b)$ to $\alpha(N_R)$. Following exactly the same analysis as for $[0,a]$, we find that the outer limit dynamics is

$$\begin{aligned}
\dot{\phi} &= \frac{-z_1 J_1 - z_2 J_2 - z_3 J_3}{(z_1(z_1-z_3)c_1 + z_2(z_2-z_3)c_2)h(\tau)}, \\
\dot{c_1} &= -z_1 c_1 \left(\frac{-z_1 J_1 - z_2 J_2 - z_3 J_3}{(z_1(z_1-z_3)c_1 + z_2(z_2-z_3)c_2)h(\tau)} \right) - h^{-1}(\tau) J_1, \\
\dot{c_2} &= -z_2 c_2 \left(\frac{-z_1 J_1 - z_2 J_2 - z_3 J_3}{(z_1(z_1-z_3)c_1 + z_2(z_2-z_3)c_2)h(\tau)} \right) - h^{-1}(\tau) J_2, \\
\dot{J}_i &= 0, \ \ \dot{\tau} = 1.
\end{aligned} \tag{32}$$

The regular layer Λ_R, following the same analysis as for $[0,a]$, is given by,

$$\begin{aligned}
\phi &= \phi^{b,r} + (-z_1 J_1 - z_2 J_2 - z_3 J_3) y, \\
\hat{C}(y) &= e^{Dy} \hat{C}^{b,r}, \\
u &= 0, \ \ 0 = z_1 c_1 + z_2 c_2 + z_3 c_3, \\
\tau &= 1,
\end{aligned} \tag{33}$$

where J_1, J_2 and J_3 are determined by,

$$\begin{aligned} \phi^R &= \phi^{b,r} + (-z_1 J_1 - z_2 J_2 - z_3 J_3) y, \\ \hat{C}^R &= e^{Dy} \hat{C}^{b,r}, \\ \int_b^1 h^{-1}(t) dt &= \Omega \int_0^y \hat{C}(t), \end{aligned} \tag{34}$$

where $\tau = x = 1$.

The outer solution Λ_r together with the inner solutions Γ_r^b and Γ_r^1 in statement (iii) of proposition 2.3 gives the singular orbit on $[b, 1]$.

2.4 Singular Orbit over $[0, 1]$

Like was stated previously, there has been extensive work done to show the connection of these orbits which will altogether form the singular orbit by geometric singular perturbation theory [3]. To construct the singular orbit over $[0, 1]$ we need to match our orbits by making sure the following are satisfied,

$$J_1^\ell = J_1^m = J_1^r, \;\; J_2^\ell = J_2^m = J_2^r, \;\; J_3^\ell = J_3^m = J_3^r, \;\; u_\ell(a) = u_m(a), \;\; u_m(b) = u_r(b).$$

Over each of our intervals we say that we had 4 unknowns, u_i, J_1^i, J_2^i, J_3^i where $i = \ell, m, r$. We also observed that for each interval we had three systems of 4 equations, (21),(29),(34), which would help us determine these unknowns. Since our number of unknowns match our number equations we can find an appropriate solution.

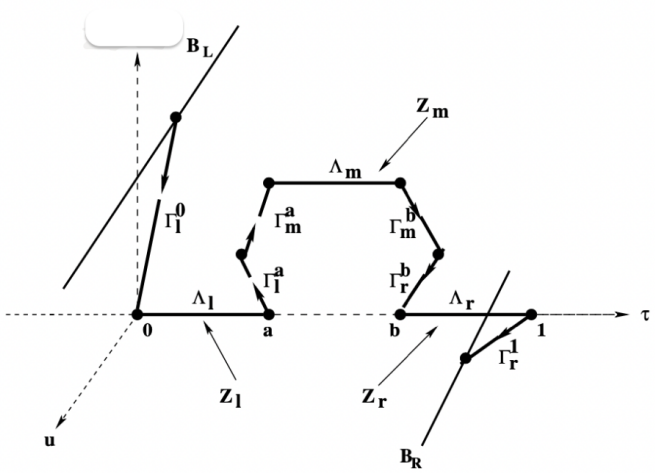


Figure 2: Singular Orbit over $[0,1]$

For our work we will only state that the singular orbit will consist of,

$$(\Gamma_\ell^0 \cup \Lambda_\ell \cup \Gamma_\ell^a) \cup (\Gamma_m^a \cup \Lambda_m \cup \Gamma_m^b) \cup (\Gamma_r^b \cup \Lambda_r \cup \Gamma_r^1).$$

It should be known that studies have been conducted for a more robust Q where, that is, we assume, for a partition $x_0 = 0 < x_1 < \ldots < x_{m-1} < x_m = 1$ of $[0,1]$ into m sub-intervals, $\mathrm{Q}(x) = \mathrm{Q}_j$ for $x \in (x_{j-1}, x_j)$ where Q_j's are constants with $\mathrm{Q}_1 = \mathrm{Q}_m = 0$ similar results hold by the Exchange Lemma [6].

3 Numerical Study on Flux Ratios

To study the PNP system we will consider two cations with corresponding valences,$z_1 = 2, z_2 = 1$, and one anion with valence $z_3 = -1$. We will also be considering a smooth channel geometry function, $A(x)$, and our permanent charge as a piecewise constant function with the form

$$\mathrm{Q}(x) = \begin{cases} 0, & x \in [0,a] \cup b,1] \\ 2\mathrm{Q}_0 & x \in [a,b] \end{cases}.$$

3.1 Numerical Method

To study our PNP system we will use an adaptive moving mesh finite element method. under the effects of the permanent charge and the shape of the channel, the solution to the BVP is known to have discontinuous second order derivatives at the jumps in permanent charge. For better resolution and improvements of the accuracy of the numerical simulation, we adopt the so-called moving mesh PDE (MMPDE) method to dynamically relocate the concentrate more mesh nodes around these jump points. Remember that for the electrochemical potential we will only consider the ideal component.

It should be pointed out that other moving mesh strategies or refinement-based mesh adaptation methods can also be used for the numerical solution. The interested reader is referred to [1]. The main reason for choosing the MMPDE method is that the method has also been shown analytically and numerically to produce a nonsingular dynamically varying mesh. These features are important since our long-term goal is to study time-dependent three-dimensional PNP models.

Within our interval we have large jumps in permanent charge at $x = a$ and $x = b$. These are the points at which we will concentrate more mesh points since finding a smooth solution along these jumps will be trickier to calculate than for constant Q_0.

3.1.1 Finite element discretization

We first describe the finite element approximation to PNP for a given mesh. Denote the mesh nodes by

$$0 = x_1 < x_2 < \ldots < x_{N_v-1} < x_{N_v} = 1,$$

where N_v is the number of mesh nodes. Define

$$V_h = span\{\psi_1, \ldots, \psi_{N_v}\}, \;\; V_h^0 = span\{\psi_2, \ldots, \psi_{N_v-1}\},$$

where $\Psi_j = \Psi_j(x)$ denotes the piecewise linear basis function corresponding to the node x_j. A linear finite element discretization of our BVP is to find $\phi_h, c_{1,h}, c_{2,h}, c_{3,h} \in V_h$ such that

$$\begin{aligned} \int_0^1 \varepsilon^2 h(x) \frac{d\phi_h}{dx}\frac{dv}{dx}dx - \int_0^1 h(x)\left(\sum_{j=1}^{3} z_j c_{j,h} + Q(x)\right) v dx = 0, \;\; \forall v \in V_h^0 \\ \int_0^1 D_k h(x)\left(z_k c_{k,h}\frac{d\phi_h}{dx} + \frac{dc_{k,h}}{dx}\right)\frac{dv}{dx}dx = 0, \;\; k = 1,2,3 \;\; \forall v \in V_h^0. \end{aligned} \tag{35}$$

Here, the subscript "h" used in $\phi_h, c_{1,h}, c_{2,h}$, and $c_{3,h}$ is different from the function $h(x)$. It is used to distinguish these discrete functions from their continuous counterparts. Express $\phi_h, c_{1,h}, c_{2,h}$ and $c_{3,h}$ as

$$\phi_h = \sum_{j=1}^{N_v} \phi_h^{(j)} \psi_j(x), \;\; c_{k,h} = \sum_{j=1}^{N_v} c_{k,h}^{(j)} \psi_j(x), \;\; k = 1,2,3.$$

Using these and the boundary conditions and taking $v = \psi_2, \ldots, \psi_{N_v-1}$ in (35) sequentially, we obtain a system of nonlinear algebraic equations for the unknown variables $\phi_h^{(j)}$, $c_{1,h}^{(j)}, c_{2,h}^{(j)}$, and $c_{3,h}^{(j)}$, $j = 1, \ldots, N_v$. This system is solved by the MATLAB® function *fsolve*, a nonlinear system solver based on the trust-region-Dogleg algorithm.

The computation alternates between the mesh generation and the solution of BVP. More specifically, at the nth iteration, we assume that the physical mesh $\mathscr{T}_h^n$ and the solution there on are known. Then, a new mesh $\mathscr{T}_h^{n+1}$ is generated based on the solution of $\mathscr{T}_h^n$. The new solution on the new mesh are then obtain by solving (35). This procedure is repeated until convergence is

reached. In practice, we have found that the convergence is reached very quickly and the solution changes very little after a few iterations [1].

Note that the analytical solution to BVP is not available for any set of boundary values. Nevertheless, since the fluxes J_1, J_2, and J_3 should be consistent throughout the domain, we can check the accuracy of the computation by examining if the fluxes stay constant.

3.2 Internal Dynamics

In figure 3 we see the internal dynamics for when the electroneutrality boundary conditions are and are not satisfied. In figure 3b we see that there is a slight boundary layer along $x = 0$ in the images of the conentrations and the electrical potiential, ϕ.

One of the interesting things we do observe is the electrochemical potentials cross over each other. Each of the electrochemical potentials is monotonic. This can be seen from the third equation of (7). The expression $D(x)h(x)c_k > 0$ so the sign of $\frac{d\overline{\mu}_k}{dx}$ is determined solely by $-J_k$.

In figure 3 we see that even though the voltage and permanent charge are the same the internal dynamics do slightly. Therefore the boundary conditions do effect the internal dynamics more than we might expect.

Lastly, over the interval $[0,1]$ all fluxes, J_1, J_2, and J_3 seem to stay constant. This is one of the ways that we can verify our numerical method.

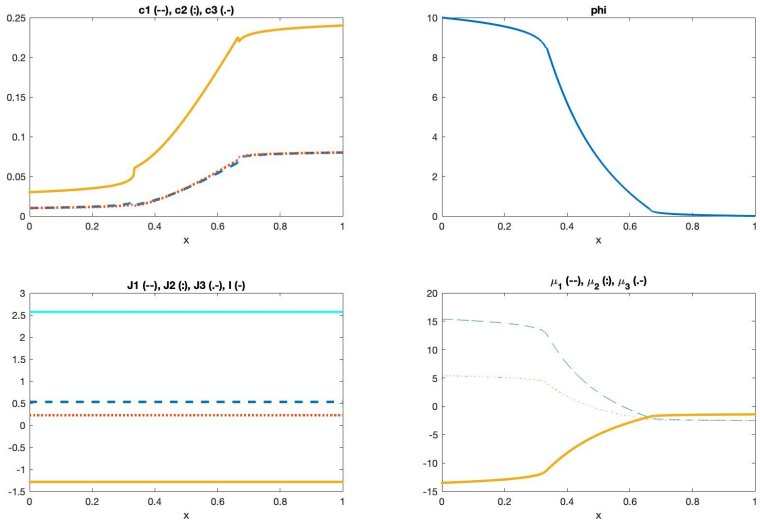
3.3 Flux Ratios

We want to introduce the flux ratio,

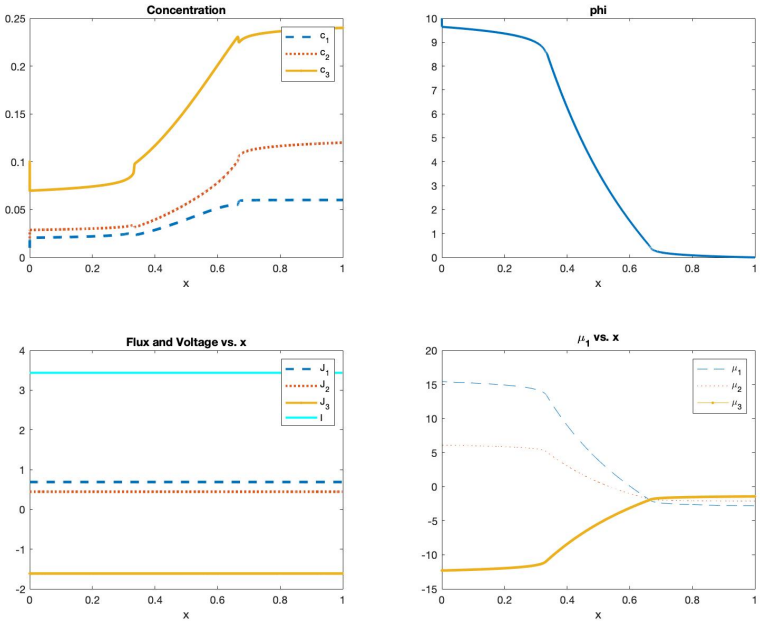
$$\lambda_k(\mathrm{Q},\varepsilon) := \frac{J_k(\mathrm{Q},\varepsilon)}{J_k(0,\varepsilon)}. \tag{36}$$

It is important to note that from our BVP, (7) and (8), gives us,

$$J_k(\mathrm{Q},\varepsilon)F_k(\mathrm{Q},\varepsilon) = \mu_k(0) - \mu_k(1). \tag{37}$$



(a) Electroneutrality boundary conditions are satisfied.



(b) Electroneutrality boundary conditions are not satisfied.

Figure 3: Internal Dynamics for $V = 10$, $Q_0 = 0.01$. Starting in the top left and continuing in a counter-clockwise rotation we have the graphs of concentrations, electrical potential, electrochemical potential, and flux and current vs. x.

where

$$F_k(\mathrm{Q},\varepsilon) = \int_0^1 \frac{1}{D_k(x;\mathrm{Q})h(x)c_k(x,\mathrm{Q},\varepsilon)}dx > 0.$$

This means that the sign of $J_k(\mathrm{Q},\varepsilon)$ is determined solely by the transmembrane electrochemical potential $\mu_k(0) - \mu_k(1)$, this is under the same boundary conditions independent of permanent charge. This means that (36) is always greater than 0. However the permanent charge, $\mathrm{Q}(x)$, influences the magnitude of $J_k(\mathrm{Q},\varepsilon)$. In particular, if $\lambda_k(\mathrm{Q},\varepsilon) > 1$, then $\mid J_k(\mathrm{Q},\varepsilon) \mid > \mid J_k(0,\varepsilon) \mid$; that is the magnitude of the flux $J_k(\mathrm{Q},\varepsilon)$, relative to that of the flux $J_k(0,\varepsilon)$, is *enhanced* by the permanent charge Q, and if $\lambda_k(\mathrm{Q},\varepsilon) < 1$, then the magnitude of the flux $J_k(\mathrm{Q},\varepsilon)$, relative to that of the flux $J_k(0,\varepsilon)$, is *reduced* by the permanent charge Q.

For experiments with 2 ion species, one cation with valence z_1, and one anion with valence z_2, it has been shown that the flux ratios might be one of three cases,

$$(i)\ \ \lambda_1 < 1 < \lambda_2;\ \ (ii)\ \ 1 < \lambda_1 < \lambda_2;\ \ (iii)\ \ \lambda_1 < \lambda_2 < 1. \tag{38}$$

for $Q > 0$. So we see that the fluxes of both ions might be *enhanced* or *reduced* [5]. For $n = 2$ we actually see that the flux ratios are symmetric around 0, again we will see that for $n = 3$ this will not happen.

Though mathematically it has not been shown it can be expect that permanent charge will greater enhance the flux of the couterions. We will see, though, that nonzero voltage can cause areas where the co-ions have a larger flux ratio than that of the same sign.

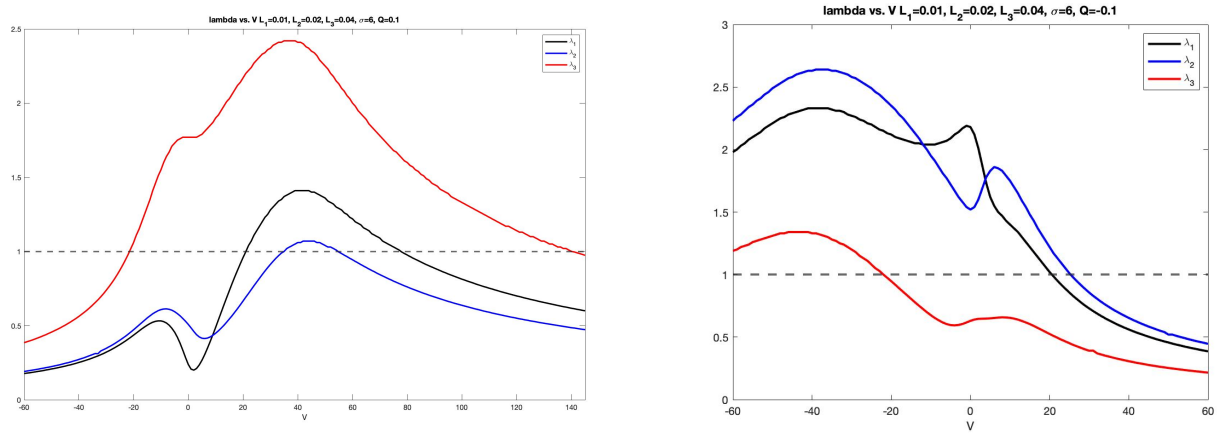
3.4 Numerical Results

When $n = 3$ we will see that the flux ratios do not necessarily follow the nice rules as for $n = 2$. We will consider the valences $z_1 = 2, z_2 = 1$ and $z_3 = -1$. Each λ_k will be associated with the corresponding valence, z_k. For our study we will consider separately fixed V and Q_0 when the other is constant, along with constant L and R. For our boundary conditions on c_k we think about the ratio of the concentrations as being constant, $\sigma = \dfrac{L_k}{R_k}$. When $\sigma \ll 1$ and $\sigma \gg 1$ we will observe

different phenomena.

3.4.1 Fixed Q_0

We will consider positive and negative Q_0, and in each case will have $\sigma \ll 1$ and $\sigma \gg 1$.



(a) $Q_0 = 0.1$.

(b) $Q_0 = -0.1$.

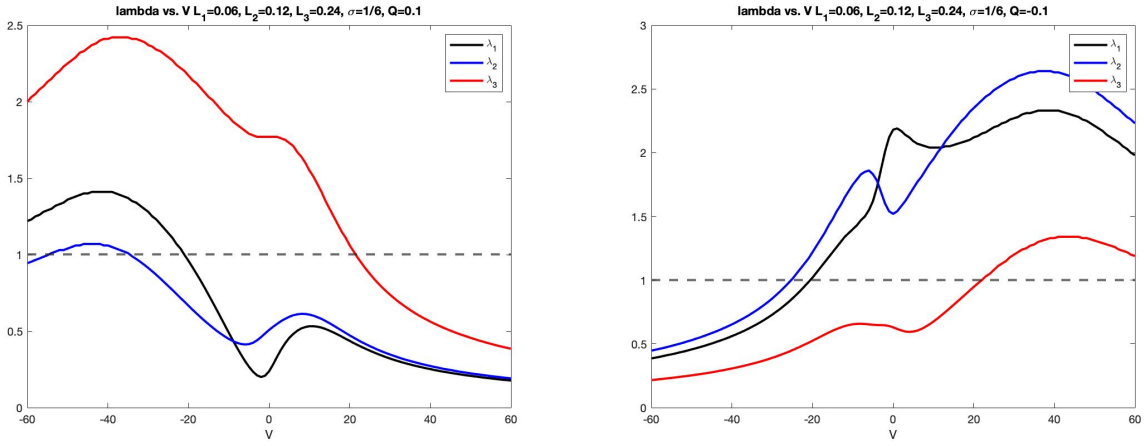
Figure 4: $L_1 = 0.01, L_2 = 0.02, L_3 = 0.04, \sigma = 6$

In figure (4) we will consider $\sigma = 6$ and the boundary conditions on c_k to be, $L_1 = 0.01, L_2 = 0.02, L_3 = 0.04, R_1 = 0.06, R_2 = 0.12$, and $R_3 = 0.24$. With these boundary conditions our problem satisfies the electroneutrality conditions, (4). We see that these figures show that the the effect of Q_0 is not symmetric.

For both positive and negative Q_0 we see that there are ranges of V that in which the flux ratios switch from $\lambda_2 > \lambda_1$ to $\lambda_2 < \lambda_1$. This is a characteristic that is unseen with flux ratios for the $n = 2$ case. When this happens it can be seen as one ion "sacrificing" itself for the other.

Remember, for $\lambda_k > 1$ we say that the permanent charge *enhances* the flux while for $\lambda_k < 1$ the flux is *reduced* by the permanent charge. In figure (4a) we see that λ_3 is enhanced for $-20 \leq V \leq 140$ while λ_2 only enhanced for a short range of V around $V = 40$, and λ_1 is only enhanced for $20 \leq V \leq 80$. This is consistent with our assumption that negative permanent charge will help the counterion.

In figure (4b) we see almost the opposite effect. For positive valence, λ_1, λ_2, the negative permanent charge *enhances* the flux of each ion, while the ion with negative charge is reduce, except large negative V. Again, this is consistent with our hypothesis that permanent charge will enhance the flux of the a couterion more than that of a co-ion.



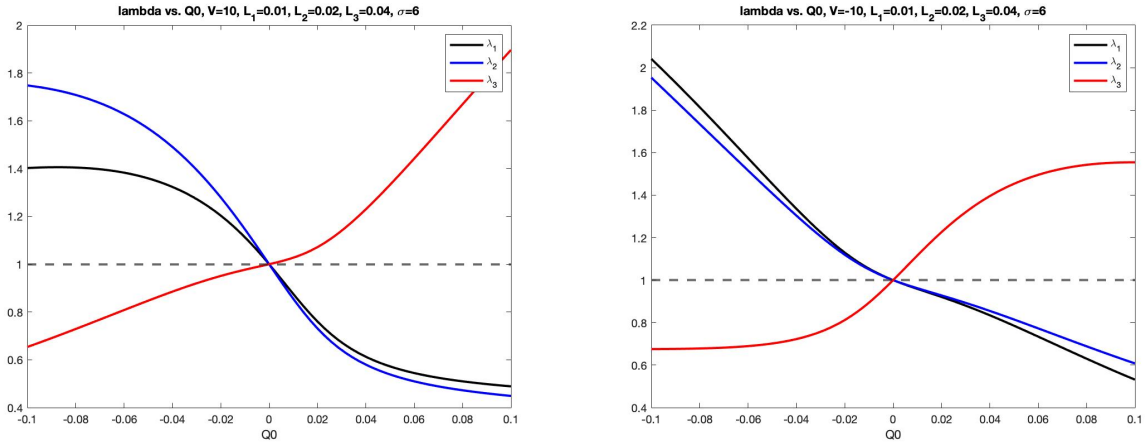
(a) $Q_0 = 0.1$.

(b) $Q_0 = -0.1$.

Figure 5: $L_1 = 0.06, L_2 = 0.12, L_3 = 0.24, \sigma = 1/6$

For both (4a), (4b), (5a), and (5b) at least once λ_1 and λ_2 cross. For negative Q_0, (4b) and (5b), this we actually see this phenomena occur twice, both for V near 0. Whenever $V = 0$ the only driving force is Q_0. Since $Q_0 = -0.1$ we expect that it will enhance the most positive charge the most, which is associated with λ_1.

We would assume that for all values of V that the flux ratio of the ion associated with z_1 would be larger than both that associated with z_2 and z_3 for $Q_0 < 0$. We see that is not the case though since for V away from 0 $\lambda_2 > \lambda_1$ in both (4b) and (5b). This implies that for nonzero V the voltage may enhance the flux of z_2 more than that for z_1 even though it is not the most positively charged ion.



(a) $V = 10$. (b) $V = -10$.

Figure 6: $L_1 = 0.01, L_2 = 0.02, L_3 = 0.04, \sigma = 6$

3.4.2 Fixed V

Just like for fixed Q_0 we will consider $\sigma \ll 1$ and $\sigma \gg 1$

In figure (6) we again make our boundary conditions on c_k such that they satisfy the electroneutrality condition. For both positive and negative V we see similar phenomena, negative Q_0 enhances the flux of cations and reduces that of anions while positive Q_0 enhances the flux of anions and reduces the flux of cations.

In experiments done with a large magnitude of V produced similar results.

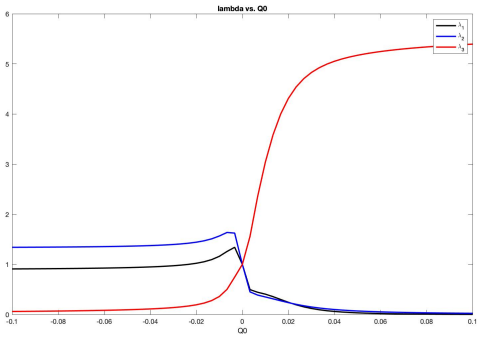


Figure 7: $L_k = 0.01, R_k = 0.08$ for $k = 1, 2, 3$

In figure 7 we see that the flux ratios of λ_1 and λ_2 cross. In figure 8 we see that in fact they do

cross twice, once at $Q_0 = 0$ and again around $Q_0 = 0.02$. While not proven it could be thought that this is attributed to our boundary conditions do not satisfy electroneutrality (4).

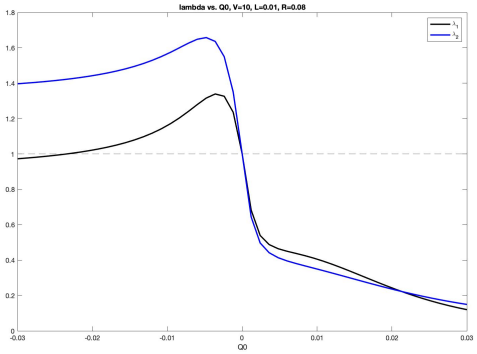


Figure 8: A closer look at the crossing of λ_1 and λ_2 in figure 7

4 Conclusions

With three ions we see that the dynamical systems study of the Poisson-Nernst-Planck system is more intricate than it is for two ions, both analytically and numerically. We also see that numerically the flux ratios have more robust variations. We observed that λ_1 and λ_2 may cross over each other multiple times whenever we fix Q_0 and vary V. While for fixed V they only cross over each other (away from $Q_0 = 0$) when the elecroneutrality conditions are not satisfied. More work should be done to prove analytically why the flux ratios behave in this manner.

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