Poisson-Nernst-Planck systems for ion flow with a local hard-sphere potential for ion size effects

Guojian Lin[*], Weishi Liu[†], Yingfei Yi[‡], and Mingji Zhang[§]

Abstract

In this work, we analyze a one-dimensional steady-state Poisson-Nernst-Planck type model for ionic flow through a membrane channel with fixed boundary ion concentrations (charges) and electric potentials. We consider two ion species, one positively charged and one negatively charged, and assume zero permanent charge. A local hard-sphere potential that depends pointwise on ion concentrations is included in the model to account for ion size effects on the ionic flow. The model problem is treated as a boundary value problem of a singularly perturbed differential system. Our analysis is based on the geometric singular perturbation theory but, most importantly, on specific structures of this concrete model. The existence of solutions to the boundary value problem for small ion sizes is established and, treating the ion sizes as small parameters, we also derive an approximation of the I-V (current-voltage) relation and identify two critical potentials or voltages for ion size effects. Under electroneutrality (zero net charge) boundary conditions, each of these two critical potentials separates the potential into two regions over which the ion size effects are qualitatively opposite to each other. On the other hand, without electroneutrality boundary conditions, the qualitative effects of ion sizes will depend not only on the critical potentials but also on boundary concentrations. Important scaling laws of I-V relations and critical potentials in boundary concentrations are obtained. Similar results about ion size effects on the flow of matter are also discussed. Under electroneutrality boundary conditions, the results on the first order approximation in ion diameters of solutions, I-V relations and critical potentials agree with those with a nonlocal hard-sphere potential examined by Ji and Liu [*J. Dynam. Differential Equations* **24** (2012), 955-983].

Key Words. Ion channel, PNP, local hard-sphere potential, I-V relation, critical potentials, scaling laws

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[*]School of Information, Renmin University of China, Beijing 100872, China, E-mail: gjlin@ruc.edu.cn

[†]Department of Mathematics, University of Kansas, Lawrence, KS 66045, USA, E-mail: wliu@math.ku.edu

[‡]School of Mathematics, Georgia Institute of Technology, Atlanta, GA 30332, USA, and School of Mathematics, Jilin University, Changchun, 130012, PRC, E-mail: yi@math.gatech.edu

[§]Department of Mathematics, University of Kansas, Lawrence, KS 66045, USA, E-mail: mingjizhang@math.ku.edu, mzhang0129@yahoo.com.

1 Introduction

In this work, we study the dynamics of ionic flow, the electrodiffusion of charges, through ion channels via a one-dimensional steady-state Poisson-Nernst-Planck (PNP) type system. The *classical* PNP includes only the *ideal* component of the electrochemical potential, and hence, treats ions essentially as *point-charges*. The PNP type model studied in this paper includes an additional component, a hard-sphere (HS) potential, to account for *ion size effects* (see §2.2 for details). We are particularly interested in ion size effects on the I-V relation.

PNP system is a basic macroscopic model for electrodiffusion of charges through ion channels ([11, 14, 16, 17, 18, 19, 20, 27, 28, 32, 39, 40, 58, 60, 68, 69, 70], etc.). Under various reasonable conditions, it can be derived from the more fundamental models of the Langevin-Poisson system (see, for example, [2, 7, 8, 12, 28, 40, 56, 59, 68, 69, 74, 79]) and the Maxwell-Boltzmann equations (see, for example, [3, 39, 40, 68, 79]), and from the energy variational analysis *EnVarA* ([21, 35, 36, 37, 38, 49, 50]).

The simplest PNP system is the classical Poisson-Nernst-Planck (cPNP) system. It has been simulated ([9, 10, 11, 13, 15, 27, 28, 31, 33, 34, 40, 41, 42, 48, 57, 73, 83, 84]) and analyzed ([1, 4, 5, 22, 25, 51, 52, 55, 61, 71, 72, 75, 76, 77, 78, 82]) to a great extent. As mentioned above, a major weak point of the cPNP is that it treats ions as *point-charges*, which is reasonable only in near infinite dilute situation. Many extremely important properties of ion channels, such as *selectivity*, rely on ion sizes critically. For example, Na^+ (sodium) and K^+ (potassium), having the *same* valence (number of charges per particle), are mainly different by their ionic sizes. It is the difference in their ionic sizes that allows certain channels to prefer Na^+ over K^+ and some channels to prefer K^+ over Na^+. In order to study the ion size effects on ionic flows, one has to take into consideration of ion specific components of the electrochemical potential in the PNP models. Including hard-sphere potentials of the excess electrochemical potential is a first step toward a better modeling and is necessary to account for ion size effects in the physiology of ion flows. There are two types of models for hard-sphere potentials, *local* and *nonlocal*. Local models for hard-sphere potentials depend *pointwise* on ion concentrations, such as the model (2.6) used in this paper, while nonlocal models are proposed as *functionals* of ion concentrations (see, e.g., (5.9) in Appendix from which the local model (2.6) is derived). The PNP type models with ion sizes have been investigated computationally for ion channels and have shown great success ([21, 35, 36, 37, 38, 26, 28, 30, 47, 85], etc.). Existence and uniqueness of minimizers and saddle points of the free-energy equilibrium formulation with ionic interaction have been mathematically analyzed (see, for example, [23, 49, 50]).

In a recent paper ([43]), the authors provided an analytical treatment of a one-dimensional version of PNP type system. They studied the case where two oppositely charged ions are involved with *electroneutrality* (zero net charge) boundary conditions, the permanent charge can be ignored and a *nonlocal* hard-sphere potential of the excess component is included in addition to the ideal component. They treated the model as a singularly perturbed system and rigorously established the existence and uniqueness results of the boundary value problem for small ion sizes. Treating ion sizes as small parameters, they derived an approximation of the I-V relation. Most importantly, the approximate I-V relation allows them to establish the following results.

(i) There is a critical potential or voltage V_c so that, if the boundary potential V satisfies $V > V_c$, then ion sizes *enhance* the current I in the sense that the contribution of ion sizes to the current I is positive; if $V < V_c$, then ion sizes *reduce* the current I.

(ii) There is another critical potential V^c so that, if $V > V^c$, then the current I *increases* in $\lambda = d_2/d_1$ where d_1 and d_2 are, respectively, the diameters of the positively and negatively charged ions; if $V < V^c$, then the current I *decreases* in λ.

In [54], among other things, the authors designed an algorithm for numerically detecting these critical potentials *without using any analytical formulas for I-V relations.* They demonstrated the effectiveness of this algorithm by conducting two numerical tasks. In the first one, the authors took the model problem with the same setting as in [43] for which analytical formulas for V_c and V^c are available. The authors numerically computed I-V relations and, applying the algorithm, computed the critical potentials V_c and V^c. They found that the computed values V_c and V^c agree well with the values obtained from the analytical formulas. For the second numerical task, the authors examined a PNP type model that includes also a nonzero permanent charge Q. For this case, no analytical formulas for the I-V relations and for the critical potentials are currently available. But the authors were able to numerically identify the critical potentials by applying their algorithm.

In this paper, we study a one-dimensional version of PNP type system with a *local* model for the hard-sphere (HS) potential. The problem has basically the same setting as that in [43] except that we take a *local* model for the hard-sphere potential and allow *non-electroneutrality* boundary conditions. One of earliest local models for hard-sphere potentials was proposed by Bikerman ([6]), which contains ion size effect of mixtures but is not ion specific (i.e., the hard-sphere potential is assumed to be the same for different ion species). Local models have evolved through several stages and become very reliable; for example, the Boublík-Mansoori-Carnahan-Starling-Leland local model is ion specific and has been shown to be accurate ([66, 67], etc.). It is clear that local models have the advantage of simplicity relative to nonlocal ones. In this paper, we take a local hard-sphere model derived from the nonlocal model used in [43] for two reasons: to provide a mathematical framework for the study of the problem with local hard-sphere models; to compare the results for the local hard-sphere model with those for the nonlocal hard-sphere model in [43].

Under electroneutrality boundary conditions, we will show that the local hard-sphere model yields exactly the same results on the first order approximation (in the diameters of the ion species) I-V relation and the critical potentials V_c and V^c as those of the nonlocal hard-sphere model in [43]. This is perhaps well expected. To the contrary, in the absence of electroneutrality, it is rather surprising that the roles of critical potentials V_c and V^c on ion size effects are significantly different: the opposite effects of ion sizes separated by V_c and V^c described in (i) and (ii) above now depend on other quantities in terms of boundary concentrations (Theorems 4.5 and 4.6 and Proposition 4.8). Many important biological properties of ion channels are controlled through the boundary conditions. Our results provide a concrete situation for which the important I-V relations of ion channels can depend on boundary conditions sensitively. An observation based on the I-V relation also reveals the following scaling laws (Theorem 4.14):

(a) the contribution I_0 to the I-V relation from the ideal component scales *linearly* in boundary concentrations (that is, if one scales the boundary concentrations by a factor s, then I_0 is scaled by s);

(b) the contribution (up to the leading order) to the I-V relation from the hard-sphere component scales *quadratically* in boundary concentrations;

(c) both V_c and V^c scale *invariantly* in boundary concentrations.

Results on ion size effects to the *flow of matter* in Section 4.2 again indicate the richness of ion size effects on the electrodiffusion process.

The general framework for the analysis is the geometric singular perturbation theory–essentially the same as that for the nonlocal hard-sphere potential in [43]. A major difference is that the nonlocal hard-sphere potentials disappear in the limiting fast system but the local ones survive in this limit, and hence, more is involved in the treatment of the limiting fast dynamics for the local hard-sphere potential case. On the other hand, for the local hard-sphere potential case, we need not introduce an auxiliary problem as that for nonlocal case in [43]. A crucial ingredient for the success of our analysis is again the revealing of a set of integrals that allows us to handle the limiting fast dynamics with details as for the classical PNP cases.

The rest of this paper is organized as follows. In Section 2, we describe the one-dimensional PNP-HS model for ion flows, a local model for hard-sphere potentials, and the setup of the boundary value problem of the singularly perturbed PNP-HS system. In Section 3, the existence and (local) uniqueness result for the boundary value problem is established in the framework of the geometric singular perturbation theory. Section 4 contains two parts. In Section 4.1, we derive an approximation of the I-V relation based on the analysis in Section 3, identify three critical potentials, and examine significant roles of two of the critical potentials for ion size effects on ionic flows. Important scaling laws of I-V relations and critical potentials in boundary concentrations are obtained. In Section 4.2, we discuss ion size effects on the flow of matter. This is presented briefly due to a simple relation between the flow rate of charge and the flow rate of matter. A derivation of the local hard-sphere potential used in the work from the exact one-dimensional nonlocal model used in [43] is provided in Section 5 (the appendix).

2 Problem Setup

2.1 A one-dimensional PNP type system

We assume the channel is narrow so that it can be effectively viewed as a one-dimensional channel and normalize it as the interval $[0, 1]$ that connects the interior and the exterior of the channel. A natural one-dimensional (time-evolution) PNP type model for ion flows of n ion species is (see [53, 57])

$$
\begin{aligned}
&\frac{1}{h(x)}\frac{\partial}{\partial x}\left(\varepsilon_r(x)\varepsilon_0 h(x)\frac{\partial \Phi}{\partial x}\right) = -e\left(\sum_{j=1}^{n} z_j c_j + Q(x)\right),\\
&\frac{\partial c_i}{\partial t} + \frac{1}{h(x)}\frac{\partial \mathcal{J}_i}{\partial x} = 0, \quad -\mathcal{J}_i = \frac{1}{kT}D_i(x)h(x)c_i\frac{\partial \mu_i}{\partial x}, \quad i = 1, 2, \cdots, n
\end{aligned}
\tag{2.1}
$$

where e is the elementary charge, k is the Boltzmann constant, T is the absolute temperature; Φ is the electric potential, $Q(x)$ is the permanent charge of the channel, $\varepsilon_r(x)$ is the relative dielectric coefficient, ε_0 is the vacuum permittivity; $h(x)$ is the area of the cross-section of the channel over the point x; for the ith ion species, c_i is the concentration, z_i is the valence (the number of charges per particle), μ_i is the electrochemical potential, $\mathcal{J}_i$ is the flux density, and $D_i(x)$ is the diffusion coefficient. The boundary conditions are, for $i = 1, 2, \cdots, n$,

$$
\Phi(t,0) = V, \quad c_i(t,0) = L_i > 0; \quad \Phi(t,1) = 0, \quad c_i(t,1) = R_i > 0. \tag{2.2}
$$

For ion channels, an important characteristic is the so-called *I-V relation* (current-voltage relation). For a solution of the *steady-state* boundary value problem of (2.1) and (2.2), the *rate of flow of charge through a cross-section* or *current* $\mathcal{I}$ is

$$
\mathcal{I} = \sum_{j=1}^{n} z_j \mathcal{J}_j. \tag{2.3}
$$

For fixed boundary concentrations L_i's and R_i's, $\mathcal{J}_j$'s depend on V only and formula (2.3) provides a relation of the current $\mathcal{I}$ on the voltage V. This relation is the *I-V relation*. We will also examine ion size effects on the *flow rate of matter* through a cross-section, $\mathcal{T}$, given by

$$
\mathcal{T} = \sum_{j=1}^{n} \mathcal{J}_j. \tag{2.4}
$$

2.2 Excess potential and a local hard sphere model

The electrochemical potential $\mu_i(x)$ for the ith ion species consists of the ideal component $\mu_i^{id}(x)$, the excess component $\mu_i^{ex}(x)$ and the concentration-independent component $\mu_i^0(x)$ (e.g. a hard-well potential):

$$
\mu_i(x) = \mu_i^0(x) + \mu_i^{id}(x) + \mu_i^{ex}(x)
$$

where

$$
\mu_i^{id}(x) = z_i e\Phi(x) + kT \ln \frac{c_i(x)}{c_0} \tag{2.5}
$$

with some characteristic number density c_0. The classical PNP system takes into consideration of the ideal component $\mu_i^{id}(x)$ only. This component reflects the collision between ion particles and the water molecules. It has been accepted that the classical PNP system is a reasonable model in, for example, the dilute case under which the ion particles can be treated as point particles and the ion-to-ion interaction can be more or less ignored. The excess chemical potential $\mu_i^{ex}(x)$ accounts for the finite size effect of charges (see, e.g., [65, 66]).

In this paper, we will take the following local hard-sphere model for $\mu_i^{ex}(x)$

$$\frac{1}{kT}\mu_i^{LHS}(x) = -\ln\left(1-\sum_{j=1}^{n} d_j c_j(x)\right) + \frac{d_i \sum_{j=1}^{n} c_j(x)}{1-\sum_{j=1}^{n} d_j c_j(x)}, \tag{2.6}$$

where d_j is the diameter of the jth ion species. As mentioned in the introduction, this local model is an approximation of the well-known nonlocal model for hard-sphere (hard-rod) used in [43]. Its derivation is provided in Appendix (Section 5).

2.3 The steady-state boundary value problem and assumptions

The main goal of this paper is to examine the qualitative effect of ion sizes via the steady-state boundary value problem of (2.1) and (2.2) with the local hard-sphere (LHS) model (2.6) for the excess potential. We will examine the steady-state boundary value problem in Section 3. In Section 4, we will obtain approximations for (2.3) and (2.4) to study ion size effects on the I-V relation and on the flow rate $\mathcal{T}$.

For definiteness, we will take essentially the same setting as that in [43] but without assuming electroneutrality boundary conditions: $z_1L_1 + z_2L_2 = z_1R_1 + z_2R_2 = 0$; that is,

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

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

(A3). For the electrochemical potential μ_i, in addition to the ideal component μ_i^{id}, we also include the local hard-sphere potential μ_i^{LHS} in (2.6).

(A4). The relative dielectric coefficient and the diffusion coefficient are constants, that is, $\varepsilon_r(x) = \varepsilon_r$ and $D_i(x) = D_i$.

In the sequel, we will assume (A1)–(A4). Under the assumptions (A1)–(A4), the steady-state system of (2.1) is

$$\begin{aligned} &\frac{1}{h(x)}\frac{d}{dx}\left(\varepsilon_r(x)\varepsilon_0 h(x)\frac{d\Phi}{dx}\right) = -e\left(z_1c_1 + z_2c_2\right), \\ &\frac{d\mathcal{J}_i}{dx} = 0, \quad -\mathcal{J}_i = \frac{1}{kT}D_i(x)h(x)c_i\frac{d\mu_i}{dx}, \quad i = 1, 2. \end{aligned} \tag{2.7}$$

We now make the dimensionless re-scaling in (2.7),

$$\phi = \frac{e}{kT}\Phi, \quad \bar{V} = \frac{e}{kT}V, \quad \varepsilon^2 = \frac{\varepsilon_r\varepsilon_0 kT}{e^2}, \quad J_i = \frac{\mathcal{J}_i}{D_i}.$$

Using the expression (2.5) for the ideal component $\mu_i^{id}(x)$, we have, for $i = 1, 2$,

$$\begin{aligned} -J_i = -\frac{\mathcal{J}_i}{D_i} &= \frac{1}{kT}h(x)c_i\frac{d\mu_i^{id}}{dx} + \frac{1}{kT}h(x)c_i\frac{d\mu_i^{LHS}}{dx} \\ &= \frac{e}{kT}z_ih(x)c_i\frac{d\Phi}{dx} + h(x)\frac{dc_i}{dx} + \frac{h(x)c_i}{kT}\frac{d\mu_i^{LHS}}{dx} \\ &= z_ih(x)c_i\frac{d\phi}{dx} + h(x)\frac{dc_i}{dx} + \frac{h(x)c_i}{kT}\frac{d\mu_i^{LHS}}{dx}. \end{aligned}$$

Note also that,

$$\varepsilon_r\varepsilon_0\frac{d\Phi}{dx} = \varepsilon^2\frac{e^2}{kT}\frac{d\Phi}{dx} = \varepsilon^2\frac{e^2}{kT}\frac{kT}{e}\frac{d\phi}{dx} = \varepsilon^2 e\frac{d\phi}{dx}.$$

Therefore, the boundary value problem (2.7) and (2.2) becomes

$$\begin{aligned}
&\frac{\varepsilon^2}{h(x)}\frac{d}{dx}\left(h(x)\frac{d}{dx}\phi\right) = -z_1c_1 - z_2c_2,\ \frac{dJ_1}{dx} = \frac{dJ_2}{dx} = 0,\\
&h(x)\frac{dc_1}{dx} + z_1h(x)c_1\frac{d\phi}{dx} + \frac{h(x)c_1}{kT}\frac{d}{dx}\mu_1^{LHS}(x) = -J_1,\\
&h(x)\frac{dc_2}{dx} + z_2h(x)c_2\frac{d\phi}{dx} + \frac{h(x)c_2}{kT}\frac{d}{dx}\mu_2^{LHS}(x) = -J_2,
\end{aligned}\tag{2.8}$$

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

$$\phi(0) = \bar{V},\ c_i(0) = L_i > 0; \quad \phi(1) = 0,\ c_i(1) = R_i > 0. \tag{2.9}$$

It follows directly from (2.6) for the local hard-sphere potential μ_i^{LHS} that

$$\begin{aligned}
\frac{1}{kT}\frac{d}{dx}\mu_1^{LHS} =& \frac{d_1(2 + d_1(c_2 - c_1) - 2d_2c_2)}{(1 - d_1c_1 - d_2c_2)^2}\frac{dc_1}{dx} + \frac{d_1 + d_2 - d_1^2c_1 - d_2^2c_2}{(1 - d_1c_1 - d_2c_2)^2}\frac{dc_2}{dx},\\
\frac{1}{kT}\frac{d}{dx}\mu_2^{LHS} =& \frac{d_1 + d_2 - d_1^2c_1 - d_2^2c_2}{(1 - d_1c_1 - d_2c_2)^2}\frac{dc_1}{dx} + \frac{d_2(2 + d_2(c_1 - c_2) - 2d_1c_1)}{(1 - d_1c_1 - d_2c_2)^2}\frac{dc_2}{dx}.
\end{aligned}\tag{2.10}$$

Substituting (2.10) into system (2.8), we obtain

$$\begin{aligned}
&\frac{\varepsilon^2}{h(x)}\frac{d}{dx}\left(h(x)\frac{d}{dx}\phi\right) = -z_1c_1 - z_2c_2, \quad \frac{dJ_1}{dx} = \frac{dJ_2}{dx} = 0,\\
&\frac{dc_1}{dx} = -f_1(c_1, c_2; d_1, d_2)\frac{d\phi}{dx} - \frac{1}{h(x)}g_1(c_1, c_2, J_1, J_2; d_1, d_2),\\
&\frac{dc_2}{dx} = f_2(c_1, c_2; d_1, d_2)\frac{d\phi}{dx} - \frac{1}{h(x)}g_2(c_1, c_2, J_1, J_2; d_1, d_2)
\end{aligned}\tag{2.11}$$

where

$$\begin{aligned}
f_1(c_1, c_2; d_1, d_2) =& z_1c_1 - (d_1 + d_2 - d_1^2c_1 - d_2^2c_2)(z_1c_1 + z_2c_2)c_1\\
&- z_1(d_1 - d_2)c_1^2,\\
f_2(c_1, c_2; d_1, d_2) =& -z_2c_2 + (d_1 + d_2 - d_1^2c_1 - d_2^2c_2)(z_1c_1 + z_2c_2)c_2\\
&+ z_2(d_2 - d_1)c_2^2,\\
g_1(c_1, c_2, J_1, J_2; d_1, d_2) =& \left((1 - d_1c_1)^2 + d_2^2c_1c_2\right)J_1\\
&- c_1(d_1 + d_2 - d_1^2c_1 - d_2^2c_2)J_2,\\
g_2(c_1, c_2, J_1, J_2; d_1, d_2) =& \left((1 - d_2c_2)^2 + d_1^2c_1c_2\right)J_2\\
&- c_2(d_1 + d_2 - d_1^2c_1 - d_2^2c_2)J_1.
\end{aligned}\tag{2.12}$$

Recall the boundary conditions are

$$\phi(0) = \bar{V},\ c_i(0) = L_i > 0;\ \phi(1) = 0,\ c_i(1) = R_i > 0. \tag{2.13}$$

3 Geometric singular perturbation theory for (2.11)–(2.13)

We will rewrite system (2.11) into a standard form for singularly perturbed systems and convert the boundary value problem (2.11) and (2.13) to a connecting problem.

Denote the derivative with respect to x by overdot and introduce $u = \varepsilon\dot{\phi}$ and $\tau = x$. System (2.11) becomes

$$
\begin{aligned}
\varepsilon\dot{\phi} =& u, \quad \varepsilon\dot{u} = -z_1c_1 - z_2c_2 - \varepsilon\frac{h_\tau(\tau)}{h(\tau)}u,\\
\varepsilon\dot{c}_1 =& -f_1(c_1, c_2; d_1, d_2)u - \frac{\varepsilon}{h(\tau)}g_1(c_1, c_2, J_1, J_2; d_1, d_2),\\
\varepsilon\dot{c}_2 =& f_2(c_1, c_2; d_1, d_2)u - \frac{\varepsilon}{h(\tau)}g_2(c_1, c_2, J_1, J_2; d_1, d_2)\\
\dot{J}_1 =& \dot{J}_2 = 0, \quad \dot{\tau} = 1.
\end{aligned}
\tag{3.1}
$$

System (3.1) will be treated as a singularly perturbed system with ε as the singular parameter. Its phase space is $\mathbb{R}^7$ with state variables $(\phi, u, c_1, c_2, J_1, J_2, \tau)$. We have included constants J_1 and J_2 in the phase space. A reason for this is explained in the paragraph below that of display (3.3).

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

$$
\begin{aligned}
\phi' =& u, \quad u' = -z_1c_1 - z_2c_2 - \varepsilon\frac{h_\tau(\tau)}{h(\tau)}u,\\
c_1' =& -f_1(c_1, c_2; d_1, d_2)u - \frac{\varepsilon}{h(\tau)}g_1(c_1, c_2, J_1, J_2; d_1, d_2),\\
c_2' =& f_2(c_1, c_2; d_1, d_2)u - \frac{\varepsilon}{h(\tau)}g_2(c_1, c_2, J_1, J_2; d_1, d_2),\\
J_1' =& J_2' = 0, \quad \tau' = \varepsilon,
\end{aligned}
\tag{3.2}
$$

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

For $\varepsilon > 0$, systems (3.1) and (3.2) have exactly the same phase portrait. But their limiting systems at $\varepsilon = 0$ are different. The limiting system of (3.1) is called the *limiting slow system*, whose orbits are called *slow orbits* or regular layers. The limiting system of (3.2) is the *limiting fast system*, whose orbits are called *fast orbits* or singular (boundary and/or internal) layers. By *a singular orbit* of system (3.1) or (3.2), we mean a continuous and piecewise smooth curve in $\mathbb{R}^7$ that is a union of finitely many slow and fast orbits. Very often, limiting slow and fast systems provide complementary information on state variables. Therefore, the main task of singularly perturbed problems is to patch the limiting information together to form a solution for the entire $\varepsilon > 0$ system.

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

$$
\begin{aligned}
B_L =& \{(\bar{V}, u, L_1, L_2, J_1, J_2, 0) \in \mathbb{R}^7 : \text{arbitrary } u, J_1, J_2\},\\
B_R =& \{(0, u, R_1, R_2, J_1, J_2, 1) \in \mathbb{R}^7 : \text{arbitrary } u, J_1, J_2\},
\end{aligned}
\tag{3.3}
$$

where $\bar{V}$, L_1, L_2, R_1 and R_2 are given in (2.13). Then the original boundary value problem is equivalent to a connecting problem, namely, finding a solution of (3.1) or (3.2) from B_L to B_R (see, for example, [44]).

For $\varepsilon > 0$ small, let $M_L(\varepsilon)$ be the collection of forward orbits from B_L under the flow and let $M_R(\varepsilon)$ be that of backward orbits from B_R. Since the flow is not tangent to B_L and B_R and $\dim B_L = \dim B_R = 3$, we have $\dim M_L(\varepsilon) = \dim M_R(\varepsilon) = 4$. We will show that $M_L(\varepsilon)$ and $M_R(\varepsilon)$ intersect transversally in the phase space $\mathbb{R}^7$. Transversality of the intersection implies $\dim(M_L(\varepsilon) \cap M_R(\varepsilon)) = \dim M_L(\varepsilon) + \dim M_R(\varepsilon) - \dim \mathbb{R}^7$. It then follows that $\dim(M_L(\varepsilon) \cap M_R(\varepsilon)) = 1$ which would allow us to conclude the existence and (local) uniqueness of a solution for the connecting problem. This is the reason that we include J_1 and J_2 in the phase space. Alternatively, one can treat J_1 and J_2 as parameters and work in the phase space $\mathbb{R}^5$. Then the corresponding B_L and B_R would each be of dimension one, and hence, $M_L(\varepsilon)$ and $M_R(\varepsilon)$ would each be of dimension two. Should $M_L(\varepsilon)$ and $M_R(\varepsilon)$ intersect, the intersection cannot be transversal due to the dimension counting. To establish the existence and uniqueness result with this alternative approach, one would have to apply perturbation argument with J_1 and J_2 as perturbation parameters.

In what follows, we will consider the equivalent connecting problem for system (3.1) or (3.2) and construct its solution from B_L to B_R. The construction process 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 small $\varepsilon > 0$.

3.1 Geometric construction of singular orbits

Following the idea in [22, 51, 52], we will first construct a singular orbit on $[0, 1]$ that connects B_L to B_R. Such an orbit will generally consist of two boundary layers and a regular layer.

3.1.1 Limiting fast dynamics and boundary layers

By setting $\varepsilon = 0$ in (3.1), we obtain the so-called *slow manifold*

$$\mathcal{Z} = \{u = 0,\ z_1c_1 + z_2c_2 = 0\}. \tag{3.4}$$

By setting $\varepsilon = 0$ in (3.2), we get the *limiting fast system*

$$\begin{aligned} \phi' &= u, \quad u' = -z_1c_1 - z_2c_2, \\ c_1' &= -f_1(c_1, c_2; d_1, d_2)u, \\ c_2' &= f_2(c_1, c_2; d_1, d_2)u, \\ J_1' &= J_2' = 0, \quad \tau' = 0. \end{aligned} \tag{3.5}$$

Note that the slow manifold $\mathcal{Z}$ is the set of equilibria of (3.5).

Lemma 3.1. *For system (3.5), the slow manifold $\mathcal{Z}$ is normally hyperbolic.*

Proof. The slow manifold $\mathcal{Z}$ is precisely the set of equilibria of (3.5). The linearization of (3.5) at each point of $(\phi, 0, c_1, c_2, J_1, J_2, \tau) \in \mathcal{Z}$ has five zero eigenvalues whose generalized eigenspace is the tangent space of the five-dimensional slow manifold $\mathcal{Z}$ of equilibria, and the other two eigenvalues are $\pm\sqrt{z_1f_1 - z_2f_2}$. On the slow manifold $\mathcal{Z}$ where $z_1c_1 + z_2c_2 = 0$, one has, from (2.12),

$$z_1f_1(c_1, c_2; d_1, d_2) - z_2f_2(c_1, c_2; d_1, d_2) = z_1^2c_1 + z_2^2c_2.$$

Note that $f_1(c_1, c_2; d_1, d_2)$ has a factor c_1 and $f_2(c_1, c_2; d_1, d_2)$ has a factor c_2. It follows from (c_1, c_2)-subsystem of (3.5) that $\{c_1 > 0\}$ and $\{c_2 > 0\}$ are invariant under (3.5). Since c_1 and c_2 have positive boundary values, c_1 and c_2 are positive for all $x \in [0, 1]$. Therefore, $z_1 f_1(c_1, c_2; d_1, d_2) - z_2 f_2(c_1, c_2; d_1, d_2) > 0$. Thus $\mathcal{Z}$ is normally hyperbolic. □

We denote the stable (resp. unstable) manifold of $\mathcal{Z}$ by $W^s(\mathcal{Z})$ (resp. $W^u(\mathcal{Z})$). Let M_L be the collection of orbits from B_L in forward time under the flow of system (3.5) and M_R be the collection of orbits from B_R in backward time under the flow of system (3.5). Then, for a singular orbit connecting B_L to B_R, the boundary layer at $\tau = x = 0$ must lie in $N_L = M_L \cap W^s(\mathcal{Z})$ and the boundary layer at $\tau = x = 1$ must lie in $N_R = M_R \cap W^u(\mathcal{Z})$. In this subsection, we will determine the boundary layers N_L and N_R, and their landing points $\omega(N_L)$ and $\alpha(N_R)$ on the slow manifold $\mathcal{Z}$. The regular layer, determined by the limiting slow system in §3.1.2, will lie in $\mathcal{Z}$ and connect the landing points $\omega(N_L)$ at $\tau = 0$ and $\alpha(N_R)$ at $\tau = 1$. A singular orbit $\Gamma^0 \cup \Lambda \cup \Gamma^1$ is illustrated in Figure 1 where $\Gamma^0 \subset N_L$ is a boundary layer at $\tau = 0$ and $\Gamma^1 \subset N_R$ is a boundary layer at $\tau = 1$, and Λ is a regular layer connecting the landing points of Γ^0 and Γ^1 on the slow manifold $\mathcal{Z}$ to be constructed in Section 3.1.2. We remark that the boundary layers $\Gamma^0 \subset N_L$ and $\Gamma^1 \subset N_R$ cannot be uniquely determined untill the construction of Λ.

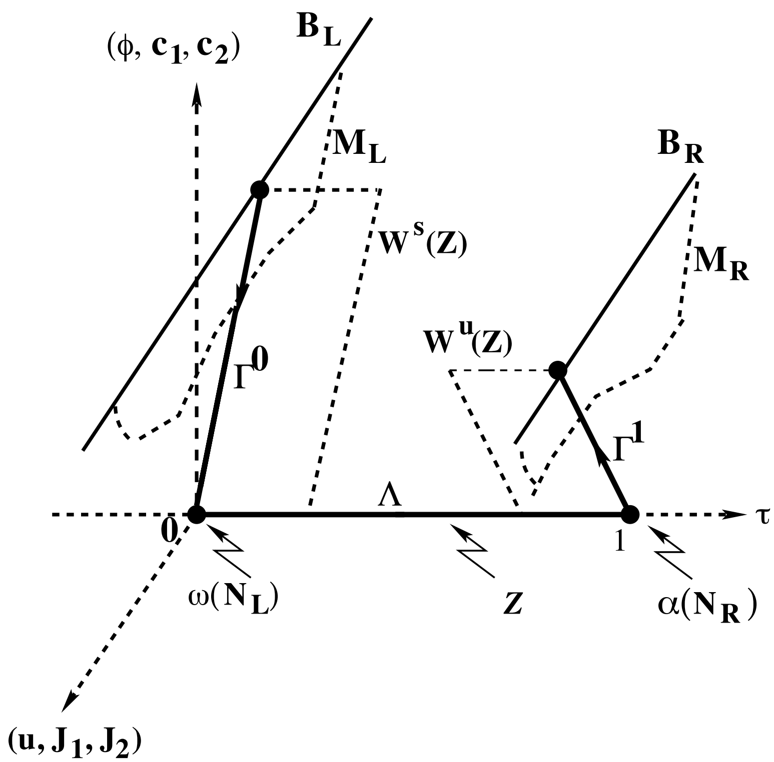

Figure 1: *A singular orbit $\Gamma^0 \cup \Lambda \cup \Gamma^1$ on $[0, 1]$: a boundary layer Γ^0 at $\tau = 0$, a regular layer Λ on $\mathcal{Z}$ from $\tau = 0$ to $\tau = 1$, and a boundary layer Γ^1 at $\tau = 1$.*

Recall that d_1 and d_2 are the diameters of the two ion species. For small $d_1 > 0$ and $d_2 > 0$, we treat (3.5) as a regular perturbation of that with $d_1 = d_2 = 0$. While

d_1 and d_2 are small, their ratio is of order $O(1)$. We thus set

$$d_1 = d \text{ and } d_2 = \lambda d \tag{3.6}$$

and look for solutions

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

of system (3.5) of the form

$$\begin{aligned}
\phi(\xi; d) &= \phi_0(\xi) + \phi_1(\xi)d + o(d), \quad u(\xi; d) = u_0(\xi) + u_1(\xi)d + o(d),\\
c_1(\xi; d) &= c_{10}(\xi) + c_{11}(\xi)d + o(d), \quad c_2(\xi) = c_{20}(\xi) + c_{21}(\xi)d + o(d),\\
J_1(d) &= J_{10} + J_{11}d + o(d), \quad J_2(d) = J_{20} + J_{21}d + o(d).
\end{aligned} \tag{3.7}$$

Substituting (3.7) into system (3.5), we obtain, for the zeroth order in d,

$$\begin{aligned}
\phi_0' &= u_0, \quad u_0' = -z_1c_{10} - z_2c_{20},\\
c_{10}' &= -z_1c_{10}u_0, \quad c_{20}' = -z_2c_{20}u_0,\\
J_{10}' &= J_{20}' = 0, \quad \tau' = 0,
\end{aligned} \tag{3.8}$$

and, for the first order in d,

$$\begin{aligned}
\phi_1' &= u_1, \quad u_1' = -z_1c_{11} - z_2c_{21},\\
c_{11}' &= -z_1u_0c_{11} - z_1c_{10}u_1 + u_0\left((\lambda+1)z_2c_{10}c_{20} + 2z_1c_{10}^2\right),\\
c_{21}' &= -z_2u_0c_{21} - z_2c_{20}u_1 + u_0\left((\lambda+1)z_1c_{10}c_{20} + 2\lambda z_2c_{20}^2\right),\\
J_{11}' &= J_{21}' = 0, \quad \tau' = 0.
\end{aligned} \tag{3.9}$$

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

Proposition 3.2. *Assume that $d \geq 0$ is small.*

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

$$\left(\bar{V}, u_0^l + u_1^l d + o(d), L_1, L_2, J_1(d), J_2(d), 0\right),$$

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

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

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

$$\begin{aligned}
\phi_0^L &= \bar{V} - \frac{1}{z_1 - z_2}\ln\frac{-z_2L_2}{z_1L_1}, \quad z_1c_{10}^L = -z_2c_{20}^L = (z_1L_1)^{\frac{-z_2}{z_1-z_2}}(-z_2L_2)^{\frac{z_1}{z_1-z_2}},\\
u_0^l &= sgn(z_1L_1 + z_2L_2)\sqrt{2\left(L_1 + L_2 + \frac{z_1 - z_2}{z_1z_2}(z_1L_1)^{\frac{-z_2}{z_1-z_2}}(-z_2L_2)^{\frac{z_1}{z_1-z_2}}\right)};\\
\phi_1^L &= \frac{1-\lambda}{z_1 - z_2}(L_1 + L_2 - c_{10}^L - c_{20}^L),\\
z_1c_{11}^L &= -z_2c_{21}^L = z_1c_{10}^L\left(L_1 + \lambda L_2 + \frac{\lambda z_1 - z_2}{z_1 - z_2}(L_1 + L_2) + \frac{2(\lambda z_1 - z_2)}{z_2}c_{10}^L\right),\\
u_1^l &= \frac{(L_1 + L_2)(L_1 + \lambda L_2) - (c_{10}^L + c_{20}^L)(c_{10}^L + \lambda c_{20}^L) - c_{11}^L - c_{21}^L}{u_0^l}.
\end{aligned}$$

(ii) The unstable manifold $W^u(\mathcal{Z})$ intersects B_R transversally at points

$$(0, u_0^r + u_1^r d + o(d), R_1, R_2, J_1(d), J_2(d), 1)\,,$$

and the α-limit set of N_R is

$$\alpha(N_R) = \left\{(\phi_0^R + \phi_1^R d + o(d), 0, c_{10}^R + c_{11}^R d + o(d), c_{20}^R + c_{21}^R d + o(d), J_1(d), J_2(d), 1)\right\},$$

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

$$\begin{aligned}
\phi_0^R =& -\frac{1}{z_1 - z_2}\ln\frac{-z_2 R_2}{z_1 R_1}, \quad z_1 c_{10}^R = -z_2 c_{20}^R = (z_1 R_1)^{\frac{-z_2}{z_1 - z_2}}(-z_2 R_2)^{\frac{z_1}{z_1 - z_2}},\\
u_0^r =& -sgn(z_1 R_1 + z_2 R_2)\sqrt{2\left(R_1 + R_2 + \frac{z_1 - z_2}{z_1 z_2}(z_1 R_1)^{\frac{-z_2}{z_1 - z_2}}(-z_2 R_2)^{\frac{z_1}{z_1 - z_2}}\right)};\\
\phi_1^R =& \frac{1-\lambda}{z_1 - z_2}(R_1 + R_2 - c_{10}^R - c_{20}^R),\\
z_1 c_{11}^R =& -z_2 c_{21}^R = z_1 c_{10}^R\left(R_1 + \lambda R_2 + \frac{\lambda z_1 - z_2}{z_1 - z_2}(R_1 + R_2) + \frac{2(\lambda z_1 - z_2)}{z_2}c_{10}^R\right),\\
u_1^r =& \frac{(R_1 + R_2)(R_1 + \lambda R_2) - (c_{10}^R + c_{20}^R)(c_{10}^R + \lambda c_{20}^R) - c_{11}^R - c_{21}^R}{u_0^r}.
\end{aligned}$$

Remark 3.3. *When $z_1 L_1 + z_2 L_2 = 0$, $u_0^l = 0$. In this case, u_1^l is defined as the limit of its expression as $z_1 L_1 + z_2 L_2 \to 0$ and it is zero. Similar remark applies to u_1^r when $z_1 R_1 + z_2 R_2 = 0$.*

Proof. The stated result for system (3.8) has been obtained in [22, 51, 52]. For system (3.9), one can check that it has three nontrivial first integrals:

$$\begin{aligned}
F_1 =& z_1\phi_1 + \frac{c_{11}}{c_{10}} + 2c_{10} + (\lambda + 1)c_{20},\\
F_2 =& z_2\phi_1 + \frac{c_{21}}{c_{20}} + 2\lambda c_{20} + (\lambda + 1)c_{10},\\
F_3 =& u_0 u_1 - c_{11} - c_{21} - (\lambda + 1)c_{10}c_{20} - c_{10}^2 - \lambda c_{20}^2.
\end{aligned}$$

We now establish the results for $\phi_1^L, c_{11}^L, c_{21}^L$ and u_1^l for system (3.9). Those for $\phi_1^R, c_{11}^R, c_{21}^R$ and u_1^r can be established in the similar way.

We note that $\phi_1(0) = c_{11}(0) = c_{21}(0) = 0$. Using the integrals F_1 and F_2, we have

$$\begin{aligned}
z_1\phi_1 + \frac{c_{11}}{c_{10}} + 2c_{10} + (\lambda + 1)c_{20} = 2L_1 + (\lambda + 1)L_2,\\
z_2\phi_1 + \frac{c_{21}}{c_{20}} + 2\lambda c_{10} + (\lambda + 1)c_{10} = 2\lambda L_2 + (\lambda + 1)L_1.
\end{aligned}$$

Therefore

$$\begin{aligned}
c_{11} =& c_{10}\left(2L_1 + (\lambda + 1)L_2 - 2c_{10} - (\lambda + 1)c_{20} - z_1\phi_1\right),\\
c_{21} =& c_{20}\left(2\lambda L_2 + (\lambda + 1)L_1 - 2\lambda c_{20} - (\lambda + 1)c_{10} - z_2\phi_1\right).
\end{aligned}$$

Taking the limit as $\xi \to \infty$, we have

$$\begin{aligned}
\phi_1^L =& \frac{1-\lambda}{z_1 - z_2}(L_1 + L_2 - c_{10}^L - c_{20}^L), \\
c_{11}^L =& c_{10}^L \left(2L_1 + (\lambda+1)L_2 - 2c_{10}^L - (\lambda+1)c_{20}^L - z_1\phi_1^L\right), \\
c_{21}^L =& c_{20}^L \left(2\lambda L_2 + (\lambda+1)L_1 - 2\lambda c_{20}^L - (\lambda+1)c_{10}^L - z_2\phi_1^L\right).
\end{aligned}$$

In view of the relations $z_1c_{10}^L + z_2c_{20}^L = z_1c_{11}^L + z_2c_{21}^L = 0$, one can get the formulas for c_{11}^L, c_{21}^L and ϕ_1^L. We now derive the formula for $u_1^l = u_1(0)$.

In view of $F_3(0) = F_3(\infty)$, we have

$$u_0^l u_1^l - (\lambda+1)L_1L_2 - L_1^2 - \lambda L_2^2 = -c_{11}^L - c_{21}^L - (\lambda+1)c_{10}^L c_{20}^L - (c_{10}^L)^2 - \lambda(c_{20}^L)^2.$$

The formula for u_1^l follows directly. □

For later use, let Γ^0 denote the potential boundary layer at $x = 0$ for system (3.5) and Let Γ^1 denote the potential boundary layer at $x = 1$ for system (3.5).

Corollary 3.4. *Under electroneutrality boundary conditions, that is, $z_1L_1 = -z_2L_2 = L$ and $z_1R_1 = -z_2R_2 = R$,*

$$\phi_0^L = \bar{V},\ z_1c_{10}^L = -z_2c_{20}^L = L;\ \phi_0^R = 0,\ z_1c_{10}^R = -z_2c_{20}^R = R,$$
$$\phi_1^L = c_{11}^L = c_{21}^L = \phi_1^R = c_{11}^R = c_{21}^R = 0.$$

In particular, up to $O(d)$, there is no boundary layer at $x = 0$ and $x = 1$.

3.1.2 Limiting slow dynamics and regular layer

Next we construct the regular layer on $\mathcal{Z}$ that connects $\omega(N_L)$ and $\alpha(N_R)$. Note that, for $\varepsilon = 0$, system (3.1) loses most information. To remedy this degeneracy, we follow the idea in [22, 51, 52] and make a rescaling $u = \varepsilon p$ and $-z_2c_2 = z_1c_1 + \varepsilon q$ in system (3.1). In term of the new variables, system (3.1) becomes

$$\begin{aligned}
\dot{\phi} =& p, \quad \varepsilon\dot{p} = q - \varepsilon\frac{h_\tau(\tau)}{h(\tau)}p, \quad \varepsilon\dot{q} = (z_1f_1 - z_2f_2)\,p + \frac{z_1g_1 + z_2g_2}{h(\tau)}, \\
\dot{c}_1 =& -f_1p - \frac{g_1}{h(\tau)}, \quad \dot{J}_1 = \dot{J}_2 = 0, \quad \dot{\tau} = 1
\end{aligned} \tag{3.10}$$

where, for $i = 1, 2$,

$$f_i = f_i\left(c_1, -\frac{z_1c_1 + \varepsilon q}{z_2}; d, \lambda d\right) \quad \text{and} \quad g_i = g_i\left(c_1, -\frac{z_1c_1 + \varepsilon q}{z_2}, J_1, J_2; d, \lambda d\right).$$

It is again a singular perturbation problem and its limiting slow system is

$$\begin{aligned}
q =& 0, \quad p = -\frac{1}{z_1(z_1 - z_2)h(\tau)c_1}\sum_{i=1}^{2} z_ig_i\big(c_1, -\frac{z_1}{z_2}c_1, J_1, J_2; d, \lambda d\big), \\
\dot{\phi} =& p, \\
\dot{c}_1 =& -f_1\big(c_1, -\frac{z_1}{z_2}c_1; d, \lambda d\big)p - \frac{1}{h(\tau)}g_1\big(c_1, -\frac{z_1}{z_2}c_1, J_1, J_2; d, \lambda d\big), \\
\dot{J}_1 =& \dot{J}_2 = 0, \quad \dot{\tau} = 1.
\end{aligned} \tag{3.11}$$

In the above, for the expression for p, we have used (2.12) to find

$$z_1 f_1\Big(c_1, -\frac{z_1 c_1}{z_2}; d, \lambda d\Big) - z_2 f_2\Big(c_1, -\frac{z_1 c_1}{z_2}; d, \lambda d\Big) = z_1(z_1 - z_2)c_1.$$

From system (3.11), the slow manifold is

$$\mathcal{S} = \left\{ q = 0,\ p = -\frac{z_1 g_1\big(c_1, -\frac{z_1}{z_2}c_1, J_1, J_2; d, \lambda d\big) + z_2 g_2\big(c_1, -\frac{z_1}{z_2}c_1, J_1, J_2; d, \lambda d\big)}{z_1(z_1 - z_2)h(\tau)c_1} \right\}.$$

Therefore, the limiting slow system on $\mathcal{S}$ is

$$\begin{aligned} \dot\phi =& p, \\ \dot c_1 =& - f_1\big(c_1, -\frac{z_1}{z_2}c_1; d, \lambda d\big)p - \frac{1}{h(\tau)} g_1\big(c_1, -\frac{z_1}{z_2}c_1, J_1, J_2; d, \lambda d\big), \\ \dot J_1 =& \dot J_2 = 0, \quad \dot\tau = 1, \end{aligned} \tag{3.12}$$

where

$$p = -\frac{z_1 g_1\big(c_1, -\frac{z_1}{z_2}c_1, J_1, J_2; d, \lambda d\big) + z_2 g_2\big(c_1, -\frac{z_1}{z_2}c_1, J_1, J_2; d, \lambda d\big)}{z_1(z_1 - z_2)h(\tau)c_1}.$$

As for the layer problem, we look for solutions of (3.12) of the form

$$\begin{aligned} \phi(x) &= \phi_0(x) + \phi_1(x)d + o(d), \\ c_1(x) &= c_{10}(x) + c_{11}(x)d + o(d), \\ J_1 &= J_{10} + J_{11}d + o(d), \quad J_2 = J_{20} + J_{21}d + o(d) \end{aligned} \tag{3.13}$$

to connect $\omega(N_L)$ and $\alpha(N_R)$ given in Proposition 3.2; in particular, for $j = 0, 1$,

$$(\phi_j(0), c_{1j}(0)) = \left(\phi_j^L, c_{1j}^L\right), \quad (\phi_j(1), c_{1j}(1)) = \left(\phi_j^R, c_{1j}^R\right).$$

From system (3.12) and the definitions of f_j's and g_j's in (2.12), we have

$$\begin{aligned} \dot\phi_0 =& -\frac{z_1 J_{10} + z_2 J_{20}}{z_1(z_1 - z_2)h(\tau)c_{10}}, \quad \dot c_{10} = \frac{z_2\left(J_{10} + J_{20}\right)}{(z_1 - z_2)h(\tau)}, \\ \dot J_{10} =& \dot J_{20} = 0, \quad \dot\tau = 1, \end{aligned} \tag{3.14}$$

and

$$\begin{aligned} \dot\phi_1 =& \frac{(z_1 J_{10} + z_2 J_{20})c_{11}}{z_1(z_1 - z_2)h(\tau)c_{10}^2} + \frac{z_1(1-\lambda)(J_{10} + J_{20})c_{10} - (z_1 J_{11} + z_2 J_{21})}{z_1(z_1 - z_2)h(\tau)c_{10}}, \\ \dot c_{11} =& \frac{2(\lambda z_1 - z_2)(J_{10} + J_{20})c_{10} + z_2(J_{11} + J_{21})}{(z_1 - z_2)h(\tau)}, \\ \dot J_{11} =& \dot J_{21} = 0, \quad \dot\tau = 1. \end{aligned} \tag{3.15}$$

For convenience, we denote

$$H(x) = \int_0^x h^{-1}(s)ds. \tag{3.16}$$

Lemma 3.5. *There is a unique solution* $(\phi_0(x), c_{10}(x), J_{10}, J_{20}, \tau(x))$ *of (3.14) such that*

$$(\phi_0(0), c_{10}(0), \tau(0)) = (\phi_0^L, c_{10}^L, 0) \quad \text{and} \quad (\phi_0(1), c_{10}(1), \tau(1)) = (\phi_0^R, c_{10}^R, 1), \tag{3.17}$$

where ϕ_0^L, ϕ_0^R, c_{10}^L, *and* c_{10}^R *are given in Proposition 3.2. It is given by*

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

Proof. The solution of system (3.14) with the initial condition $(\phi_0^L, c_{10}^L, J_{10}, J_{20}, 0)$ that corresponds to the point $(\phi_0^L, 0, c_{10}^L, c_{20}^L, J_{10}, J_{20}, 0)$ is

$$\begin{aligned}
\phi_0(x) &= \phi_0^L - \frac{z_1 J_{10} + z_2 J_{20}}{z_1(z_1 - z_2)} \int_0^x h^{-1}(s) c_{10}^{-1}(s) ds, \\
c_{10}(x) &= c_{10}^L + \frac{z_2\left(J_{10} + J_{20}\right)}{z_1 - z_2} H(x), \quad \tau(x) = x.
\end{aligned} \tag{3.18}$$

It follows from the c_{10}-equation and $c_{10}(1) = c_{10}^R$ that

$$J_{10} + J_{20} = -\frac{(z_1 - z_2)(c_{10}^L - c_{10}^R)}{z_2 H(1)}. \tag{3.19}$$

Note that, from (3.14),

$$\int_0^x h^{-1}(s) c_{10}^{-1}(s) ds = \frac{z_1 - z_2}{z_2(J_{10} + J_{20})} \int_0^x \frac{\dot{c}_{10}(s)}{c_{10}(s)} ds = H(1) \frac{\ln c_{10}^L - \ln c_{10}(x)}{c_{10}^L - c_{10}^R}.$$

Thus,

$$\phi_0(x) = \phi_0^L - H(1) \frac{z_1 J_{10} + z_2 J_{20}}{z_1(z_1 - z_2)} \frac{\ln c_{10}^L - \ln c_{10}(x)}{c_{10}^L - c_{10}^R}.$$

Applying the boundary condition $c_{10}(1) = c_{10}^R$ and $\phi_0(1) = \phi_0^R$, we have

$$\begin{aligned}
J_{10} + J_{20} =& -\frac{(z_1 - z_2)(c_{10}^L - c_{10}^R)}{z_2 H(1)}, \\
z_1 J_{10} + z_2 J_{20} =& \frac{z_1(z_1 - z_2)(c_{10}^L - c_{10}^R)(\phi_0^L - \phi_0^R)}{H(1)(\ln c_{10}^L - \ln c_{10}^R)}.
\end{aligned} \tag{3.20}$$

The expressions for J_{10} and J_{20}, and hence, for $\phi_0(x)$ and $c_{10}(x)$ follow directly. $\square$

For convenience, we define three functions

$$M = M(L_1, L_2, R_1, R_2; \lambda),\ N = N(L_1, L_2, R_1, R_2; \lambda),\ P(x) = P(x; L_1, L_2, R_1, R_2; \lambda)$$

as

$$\begin{aligned}
M =& z_1 c_{10}^L w(L_1, L_2) - z_1 c_{10}^R w(R_1, R_2) + \frac{z_1(\lambda z_1 - z_2)}{z_2} \left((c_{10}^L)^2 - (c_{10}^R)^2\right), \\
N =& \frac{z_1(c_{10}^L - c_{10}^R)}{\ln c_{10}^L - \ln c_{10}^R}(\phi_1^L - \phi_1^R) - \frac{(1-\lambda)z_1}{z_2}\frac{(c_{10}^L - c_{10}^R)^2}{\ln c_{10}^L - \ln c_{10}^R} + \frac{\phi_0^L - \phi_0^R}{\ln c_{10}^L - \ln c_{10}^R} M \\
& - \frac{z_1(c_{10}^L - c_{10}^R)(w(L_1, L_2) - w(R_1, R_2))}{(\ln c_{10}^L - \ln c_{10}^R)^2}(\phi_0^L - \phi_0^R), \\
P(x) =& \frac{\lambda z_1 - z_2}{z_2}\frac{(c_{10}^L - c_{10}^R)H(x)}{(\ln c_{10}^L - \ln c_{10}^R)H(1)} \\
& + \frac{c_{10}^L - c_{10}(x)}{\ln c_{10}^L - \ln c_{10}^R}\left(\frac{w(L_1, L_2)}{c_{10}(x)} + \frac{\lambda z_1 - z_2}{z_2}\frac{c_{10}^L}{c_{10}(x)}\right) \\
& - \frac{H(x)}{z_1(\ln c_{10}^L - \ln c_{10}^R)c_{10}(x)H(1)} M + \frac{\ln c_{10}^L - \ln c_{10}(x)}{z_1(\ln c_{10}^L - \ln c_{10}^R)(c_{10}^L - c_{10}^R)} M
\end{aligned} \tag{3.21}$$

where

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

Lemma 3.6. *There is a unique solution $(\phi_1(x), c_{11}(x), J_{11}, J_{21}, \tau(x))$ of (3.15) such that*

$$(\phi_1(0), c_{11}(0), \tau(0)) = (\phi_1^L, c_{11}^L, 0) \ \ \text{and}\ \ (\phi_1(1), c_{11}(1), \tau(1)) = (\phi_1^R, c_{11}^R, 1), \tag{3.22}$$

where ϕ_1^L, ϕ_1^R, c_{11}^L, and c_{11}^R are given in Proposition 3.2. It is given by

$$\begin{aligned}
\phi_1(x) =& \phi_1^L - \frac{(1-\lambda)(c_{10}^L - c_{10}^R)H(x)}{z_2 H(1)} + (\phi_0^L - \phi_0^R)P(x) - \frac{\ln c_{10}(x) - \ln c_{10}^L}{z_1(z_1 - z_2)(c_{10}^R - c_{10}^L)} N, \\
c_{11}(x) =& c_{11}^L + \frac{\lambda z_1 - z_2}{z_2}\left(c_{10}^2(x) - (c_{10}^L)^2\right) - \frac{H(x)}{z_1 H(1)} M, \\
J_{11} =& \frac{M}{z_1 H(1)} + \frac{N}{H(1)}, \quad J_{21} = -\frac{M}{z_2 H(1)} - \frac{N}{H(1)},
\end{aligned}$$

where M, N, and P are defined in (3.21).

Proof. It follows from (3.15) that

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

Thus, from Proposition 3.2,

$$\begin{aligned}
\frac{z_2(J_{11} + J_{21})}{z_2 - z_1} H(1) =& c_{11}^L - c_{11}^R + \frac{\lambda z_1 - z_2}{z_2}\left((c_{10}^R)^2 - (c_{10}^L)^2\right) \\
=& c_{10}^L w(L_1, L_2) - c_{10}^R w(R_1, R_2) + \frac{\lambda z_1 - z_2}{z_2}\left((c_{10}^L)^2 - (c_{10}^R)^2\right),
\end{aligned}$$

or, by the definition of M in (3.21),

$$J_{11} + J_{21} = \frac{z_2 - z_1}{z_1 z_2 H(1)} M. \tag{3.23}$$

Hence,

$$c_{11}(x) = c_{11}^L + \frac{\lambda z_1 - z_2}{z_2} \left(c_{10}^2(x) - (c_{10}^L)^2 \right) - \frac{H(x)}{z_1 H(1)} M. \tag{3.24}$$

Again, from (3.15)

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

Note that, from (3.14) and (3.19),

$$\begin{aligned}
\int_0^x \frac{c_{10}(s)}{h(s)} ds =& \frac{z_1 - z_2}{z_2(J_{10} + J_{20})} \int_0^x c_{10}(s) \dot{c}_{10}(s) ds = \frac{H(1)}{2} \frac{(c_{10}^L)^2 - c_{10}^2(x)}{c_{10}^L - c_{10}^R}, \\
\int_0^x \frac{1}{h(s) c_{10}^2(s)} ds =& \frac{z_1 - z_2}{z_2(J_{10} + J_{20})} \int_0^x \frac{\dot{c}_{10}(s)}{c_{10}^2(s)} ds = H(1) \frac{c_{10}^L - c_{10}(x)}{(c_{10}^L - c_{10}^R) c_{10}^L c_{10}(x)}, \\
\int_0^x \frac{\int_0^s h^{-1}(\sigma) d\sigma}{h(s) c_{10}^2(s)} ds =& -\frac{z_1 - z_2}{z_2(J_{10} + J_{20})} \int_0^x \int_0^s h^{-1}(\sigma) d\sigma \frac{d}{ds} c_{10}^{-1}(s) ds \\
=& \frac{H(1)}{c_{10}^L - c_{10}^R} \left(\frac{H(x)}{c_{10}(x)} - \int_0^x h^{-1}(s) c_{10}^{-1}(s) ds \right) \\
=& \frac{H(1) H(x)}{(c_{10}^L - c_{10}^R) c_{10}(x)} - H^2(1) \frac{\ln c_{10}^L - \ln c_{10}(x)}{(c_{10}^L - c_{10}^R)^2}.
\end{aligned}$$

These, together with (3.24) and (3.20), yield

$$\begin{aligned}
\int_0^x \frac{c_{11}(s)}{h(s) c_{10}^2(s)} ds =& \left(w(L_1, L_2) + \frac{\lambda z_1 - z_2}{z_2} c_{10}^L \right) \frac{H(1)(c_{10}^L - c_{10}(x))}{(c_{10}^L - c_{10}^R) c_{10}(x)} \\
& + \frac{\lambda z_1 - z_2}{z_2} H(x) - \frac{M}{z_1(c_{10}^L - c_{10}^R)} \left(\frac{H(x)}{c_{10}(x)} - \frac{\ln c_{10}^L - \ln c_{10}(x)}{c_{10}^L - c_{10}^R} H(1) \right).
\end{aligned}$$

A careful calculation then gives

$$\begin{aligned}
\phi_1(x) =& \phi_1^L - \frac{(1-\lambda)(c_{10}^L - c_{10}^R) H(x)}{z_2 H(1)} + (\phi_0^L - \phi_0^R) P(x) \\
& - \frac{z_1 J_{11} + z_2 J_{21}}{z_1(z_1 - z_2)} \frac{\ln c_{10}^L - \ln c_{10}(x)}{c_{10}^L - c_{10}^R} H(1).
\end{aligned}$$

Hence,

$$\begin{aligned}
\phi_1^R =&\phi_1^L - \frac{1-\lambda}{z_2}(c_{10}^L - c_{10}^R) + (\phi_0^L - \phi_0^R)P(1)\\
&- \frac{z_1J_{11}+z_2J_{21}}{z_1(z_1-z_2)}\frac{\ln c_{10}^L - \ln c_{10}^R}{c_{10}^L - c_{10}^R}H(1)\\
=&\phi_1^L - \frac{1-\lambda}{z_2}(c_{10}^L - c_{10}^R) - \frac{w(L_1,L_2)-w(R_1,R_2)}{\ln c_{10}^L - \ln c_{10}^R}(\phi_0^L - \phi_0^R)\\
&+ \frac{M(\phi_0^L - \phi_0^R)}{z_1(c_{10}^L - c_{10}^R)} - \frac{(z_1J_{11}+z_2J_{21})(\ln c_{10}^L - \ln c_{10}^R)}{z_1(z_1-z_2)(c_{10}^L - c_{10}^R)}H(1).
\end{aligned}$$

Thus,

$$\begin{aligned}
H(1)\frac{z_1J_{11}+z_2J_{21}}{z_1-z_2} =& z_1\frac{c_{10}^L - c_{10}^R}{\ln c_{10}^L - \ln c_{10}^R}(\phi_1^L - \phi_1^R) - \frac{(1-\lambda)z_1}{z_2}\frac{(c_{10}^L - c_{10}^R)^2}{\ln c_{10}^L - \ln c_{10}^R}\\
&+ \frac{M(\phi_0^L - \phi_0^R)}{\ln c_{10}^L - \ln c_{10}^R} - z_1\frac{(c_{10}^L - c_{10}^R)(w(L_1,L_2)-w(R_1,R_2))}{(\ln c_{10}^L - \ln c_{10}^R)^2}(\phi_0^L - \phi_0^R) = N.
\end{aligned}$$

Formulas for J_{11}, J_{21}, and ϕ_1 follow directly. □

Corollary 3.7. *Under the electroneutrality conditions at the boundaries, that is, $z_1L_1 = -z_2L_2 = L$ and $z_1R_1 = -z_2R_2 = R$, we have,*

$$\begin{aligned}
J_{10} =&\frac{L-R}{z_1H(1)}\left(1+\frac{z_1\bar{V}}{\ln L - \ln R}\right), \quad J_{20} = \frac{L-R}{z_2H(1)}\left(1+\frac{z_2\bar{V}}{\ln L - \ln R}\right);\\
J_{11} =&\frac{\lambda z_1 - z_2}{z_1z_2H(1)}\frac{R-L}{\ln R - \ln L}\left(\frac{2(R-L)}{\ln R - \ln L} - (R+L)\right)\bar{V}\\
&+ \frac{1-\lambda}{z_1z_2H(1)}\frac{(R-L)^2}{\ln R - \ln L} + \frac{\lambda z_1 - z_2}{z_1^2z_2H(1)}\left(R^2 - L^2\right),\\
J_{21} =&-\frac{\lambda z_1 - z_2}{z_1z_2H(1)}\frac{R-L}{\ln R - \ln L}\left(\frac{2(R-L)}{\ln R - \ln L} - (R+L)\right)\bar{V}\\
&- \frac{1-\lambda}{z_1z_2H(1)}\frac{(R-L)^2}{\ln R - \ln L} - \frac{\lambda z_1 - z_2}{z_1z_2^2H(1)}\left(R^2 - L^2\right).
\end{aligned}$$

Proof. This follows directly from Lemmas 3.5 and 3.6 and Proposition 3.2. □

The slow orbit, up to $O(d)$,

$$\Lambda(x;d) = (\phi_0(x)+\phi_1(x)d, c_{10}(x)+c_{11}(x)d, J_{10}+J_{11}d, J_{20}+J_{21}d, \tau(x)) \tag{3.25}$$

given in Lemmas 3.5 and 3.6 connects $\omega(N_L)$ and $\alpha(N_R)$. Let $\bar{M}_L$ (resp., $\bar{M}_R$) be the forward (resp., backward) image of $\omega(N_L)$ (resp., $\alpha(N_R)$) under the slow flow (3.12) on the five-dimensional slow manifold $\mathcal{S}$. Following the idea in [51], we have

Proposition 3.8. *There exists $d_0 > 0$ small depending on boundary conditions so that, if $0 \le d \le d_0$, then, on the five-dimensional slow manifold $\mathcal{S}$, $\bar{M}_L$ and $\bar{M}_R$ intersects transversally along the unique orbit $\Lambda(x;d)$ given in (3.25).*

Proof. To see the transversality of the intersection, it suffices to show that $\omega(N_L)\cdot 1$ (the image of $\omega(N_L)$ under the time-one map of the flow of system (3.12)) is transversal to $\alpha(N_R)$ on $\mathcal{S}\bigcap\{\tau=1\}$. We will show first that, for $d=0$, $\omega(N_L)\cdot 1$ and $\alpha(N_R)$ intersect transversally on $\mathcal{S}\bigcap\{\tau=1\}$. We will use (ϕ, c_1, J_1, J_2) as a coordinate system on $\mathcal{S}\bigcap\{\tau=1\}$. It follows from (3.18) that, for $d=0$, $\omega(N_L)\cdot 1$ is given by

$$\omega(N_L)\cdot 1=\{(\phi(J_1,J_2), c_1(J_1,J_2), J_1, J_2):\ \text{ arbitrary } J_1,\ J_2\}$$

with

$$\begin{aligned}\phi(J_1,J_2)=&\phi_0^L-\frac{z_1J_1+z_2J_2}{z_1z_2(J_1+J_2)}\ln\frac{c_1(J_1,J_2)}{c_{10}^L},\\ c_1(J_1,J_2)=&c_{10}^L+\frac{z_2H(1)(J_1+J_2)}{z_1-z_2}.\end{aligned}$$

Thus, the tangent space to $\omega(N_L)\cdot 1$ restricted on $\mathcal{S}\bigcap\{\tau=1\}$ is spanned by the vectors

$$(\phi_{J_1}, (c_1)_{J_1}, 1, 0)=\left(\phi_{J_1}, \frac{z_2}{z_1-z_2}H(1), 1, 0\right)$$

and

$$(\phi_{J_2}, (c_1)_{J_2}, 0, 1)=\left(\phi_{J_2}, \frac{z_2}{z_1-z_2}H(1), 0, 1\right).$$

In view of the display in Proposition 3.2, the set $\alpha(N_R)$ is parameterized by J_1 and J_2, and hence, the tangent space to $\alpha(N_R)$ restricted on $\mathcal{S}\bigcap\{\tau=1\}$ is spanned by (0,0,1,0) and (0,0,0,1). Note that $\mathcal{S}\bigcap\{\tau=1\}$ is four dimensional. Thus, it suffices to show that the above four vectors are linearly independent or, equivalently, $\phi_{J_1}\neq\phi_{J_2}$ at $(J_1,J_2)=(J_{10},J_{20})$. The latter can be verified by a direct computation as follows:

$$\phi_{J_1}-\phi_{J_2}=-\frac{z_1-z_2}{z_1z_2(J_1+J_2)}\ln\left[1+\frac{z_2(J_1+J_2)}{(z_1-z_2)c_{10}^L}H(1)\right]\neq 0,$$

even as $J_1+J_2\to 0$. This establishes the transversal intersection of $\omega(N_L)\cdot 1$ and $\alpha(N_R)$ on $\mathcal{S}\bigcap\{\tau=1\}$. From the smooth dependence of solutions on parameter d, we conclude that there exists $d_0>0$ small, so that, if $0\le d\le d_0$, then $\omega(N_L)\cdot 1$ and $\alpha(N_R)$ intersect transversally on $\mathcal{S}\bigcap\{\tau=1\}$. This completes the proof. $\square$

3.2 Existence of solutions near the singular orbit

We have constructed a unique singular orbit on [0,1] that connects B_L to B_R. It consists of two boundary layer orbits Γ^0 from the point

$$(\bar V, u_0^l+u_1^ld+o(d), L_1, L_2, J_{10}+J_{11}d+o(d), J_{20}+J_{21}d+o(d), 0)\in B_L$$

to the point

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

and Γ^1 from the point

$$(\phi^R, 0, c_1^R, c_2^R, J_1, J_2, 1)\in z_1(N_R)\subset\mathcal{Z}$$

to the point

$$(0, u_0^r + u_1^r + o(d), R_1, R_2, J_1, J_2, 1) \in B_R,$$

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

$$(\phi^L, 0, c_1^L, c_2^L, J_1, J_2, 0) \in \omega(N_L)$$

and

$$(\phi^R, 0, c_1^R, c_2^R, J_1, J_2, 1) \in \alpha(N_R)$$

of the two boundary layers.

We now establish the existence of a solution of (2.11) and (2.13) near the singular orbit constructed above which is a union of two boundary layers and one regular layer $\Gamma^0 \bigcup \Lambda \bigcup \Gamma^1$. The proof follows the same line as that in [22, 51, 52] and the main tool used is the Exchange Lemma (see, for example [44, 45, 46, 80]) of the geometric singular perturbation theory.

Theorem 3.9. *Let $\Gamma^0 \bigcup \Lambda \bigcup \Gamma^1$ be the singular orbit of the connecting problem system (3.1) associated to B_L and B_R in system (3.3). Let $d_0 > 0$ be as in Proposition 3.8. Then, there exists $\varepsilon_0 > 0$ small (depending on the boundary conditions and d_0) so that, if $0 \le d \le d_0$ and $0 < \varepsilon \le \varepsilon_0$, then the boundary value problem (2.11) and (2.13) has a unique smooth solution near the singular orbit $\Gamma^0 \bigcup \Lambda \bigcup \Gamma^1$.*

Proof. Let $d_0 > 0$ be as in Proposition 3.8. For $0 \le d \le d_0$, denote $u^l = u_0^l + u_1^l d$, $J_1(d) = J_{10} + J_{11}d$ and $J_2(d) = J_{20} + J_{21}d$. Fix $\delta > 0$ small to be determined. Let

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

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

Note that $\dim B_L(\delta)$=3. It is clear that the vector field of the fast system (3.2) is not tangent to $B_L(\delta)$ for $\varepsilon \ge 0$, and hence, $\dim M_L(\varepsilon, \delta)$=4. We next apply Exchange Lemma to track $M_L(\varepsilon, \delta)$ in the vicinity of $\Gamma^0 \bigcup \Lambda \bigcup \Gamma^1$. First of all, the transversality of the intersection $B_L(\delta) \bigcap W^s(\mathcal{Z})$ along Γ^0 in Proposition 3.2 implies the transversality of intersection $M_L(0, \delta) \bigcap W^s(\mathcal{Z})$. Secondly, we have also established that $\dim \omega(N_L) = \dim N_L - 1 = 2$ in Proposition 3.2 and that the limiting slow flow is not tangent to $\omega(N_L)$ in Section 3.1.2. With these conditions, Exchange Lemma ([44, 45, 46, 80]) states that there exist $\rho > 0$ and $\varepsilon_1 > 0$ so that, if $0 < \varepsilon \le \varepsilon_1$, then $M_L(\varepsilon, \delta)$ will first follow Γ^0 toward $\omega(N_L) \subset \mathcal{Z}$, then follow the trace of $\omega(N_L)$ in the vicinity of Λ toward $\{\tau = 1\}$, leave the vicinity of $\mathcal{Z}$, and, upon exit, a portion of $M_L(\varepsilon, \delta)$ is C^1 $O(\varepsilon)$-close to $W^u(\omega(N_L) \times (1-\rho, 1+\rho))$ in the vicinity of Γ^1 (see Figure 2 for an illustration). Note that $\dim W^u(\omega(N_L) \times (1-\rho, 1+\rho)) = \dim M_L(\varepsilon, \delta) = 4$.

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

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

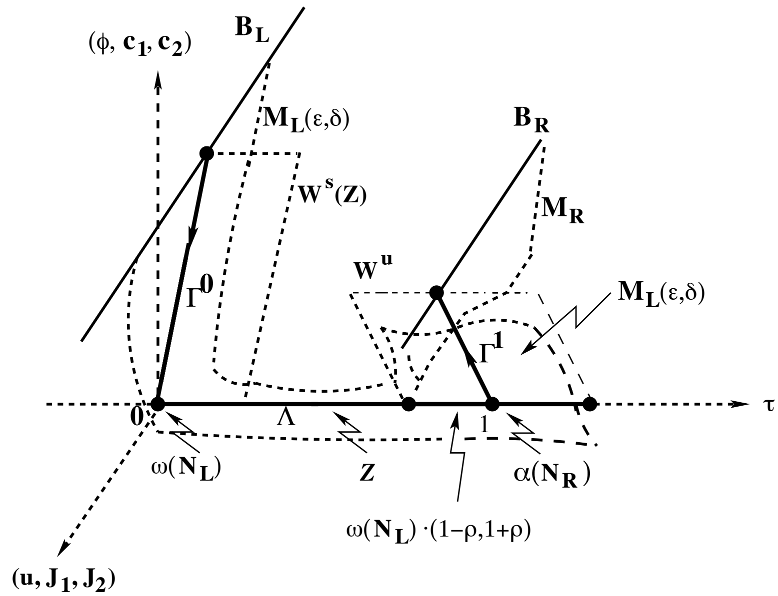

Figure 2: *Illustration of the evolution of $M_L(\varepsilon,\delta)$ from the vicinity of $\tau = 0$ to that of $\tau = 1$: On the left, $M_L(\varepsilon,\delta)$ intersects $W^s(\mathcal{Z})$ transversally and approaches $\omega(N_L)$ in the vicinity of Γ^0; It then follows the trace of $\omega(N_L)$ in the vicinity of Λ on $\mathcal{Z}$ toward the vicinity of $\omega(N_L)\cdot(1-\rho,1+\rho)$; A portion of it will leave the vicinity of $\mathcal{Z}$, and, upon exit from $\mathcal{Z}$, $M_L(\varepsilon,\delta)$ is C^1 $O(\varepsilon)$-close to $W^u(\omega(N_L)\times(1-\rho,1+\rho))$ in the vicinity of Γ^1. In the figure, $W^u(\omega(N_L)\times(1-\rho,1+\rho))$ is denoted by W^u.*

where, $T_{\gamma_1}W^u(\gamma_1)$ is the tangent space of the one-dimensional unstable fiber $W^u(\gamma_1)$ at γ_1 and the vector $V_s \notin T_{\gamma_1}W^u(\mathcal{Z})$ (the latter follows from the transversality of the intersection of M_R and $W^u(\mathcal{Z})$). Also,

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

where the vector V_τ is the tangent vector to the τ-axis as the result of the interval factor $(1-\rho,1+\rho)$. Recall from Proposition 3.8 that $\omega(N_L)\cdot 1$ and $\alpha(N_R)$ are transversal on $\mathcal{Z}\cap\{\tau=1\}$. Therefore, at γ_1, the tangent spaces $T_{\gamma_1}M_R$ and $T_{\gamma_1}W^u(\omega(N_L)\times(1-\rho,1+\rho))$ contain seven linearly independent vectors: V_s, V_τ, $T_{\gamma_1}W^u(\gamma_1)$ and the other four from $T_{\gamma_1}(\omega(N_L)\cdot 1)$ and $T_{\gamma_1}\alpha(N_R)$; that is, M_R and $W^u(\omega(N_L)\times(1-\rho,1+\rho))$ intersect transversally. We thus conclude that, there exists $0<\varepsilon_0\le\varepsilon_1$ so that, if $0<\varepsilon\le\varepsilon_0$, then $M_L(\varepsilon,\delta)$ intersects $M_R(\varepsilon)$ transversally.

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

4 Ion size effects on the flows of charge and matter

The analysis in the previous sections not only establishes the existence of solutions for the boundary value problem (2.11) and (2.13) but also provides quantitative information on the solution that allows us to extract explicit approximations to the current $\mathcal{I}$ and the flow rate of matter, $\mathcal{T}$, for small ε and d. From the explicit approximations, we are able to identify some critical values for potential V that characterize ion size effects on the ionic flow. A number of scaling laws will be also obtained. Their consequences of ion size effects are discussed.

4.1 I-V relation, critical potentials, and scaling laws

4.1.1 I-V relation and its approximation

For fixed boundary concentrations L_1, L_2, R_1 and R_2 in (2.2), we express the I-V relation in (4.1) as

$$\mathcal{I}(V;\lambda,\varepsilon,d) = I_0(V;\varepsilon) + I_1(V;\lambda,\varepsilon)d + o(d), \tag{4.1}$$

where $I_0(V;\varepsilon)$ is the I-V relation without counting the ion size effect and $I_1(V;\lambda,\varepsilon)d$ is the leading term containing ion size effect on I-V relation.

Recall that we denote $H(1) = \int_0^1 h^{-1}(s)ds$ in (3.16).

Theorem 4.1. *In formula (4.1), one has*

$$\begin{aligned}
I_0(V;0) =&\rho_{00}(L_1,L_2,R_1,R_2) + \rho_{01}(L_1,L_2,R_1,R_2)\frac{e}{kT}V,\\
I_1(V;\lambda,0) =&\rho_{10}(L_1,L_2,R_1,R_2,\lambda) + \rho_{11}(L_1,L_2,R_1,R_2;\lambda)\frac{e}{kT}V,
\end{aligned}$$

where

$$\begin{aligned}
\rho_{00} =&\frac{z_1(D_1-D_2)(c_{10}^L-c_{10}^R)}{H(1)} + \frac{z_1(z_1D_1-z_2D_2)(c_{10}^L-c_{10}^R)}{H(1)(\ln c_{10}^L - \ln c_{10}^R)}\ln\frac{L_1R_2}{L_2R_1},\\
\rho_{01} =&\frac{z_1(z_1D_1-z_2D_2)(c_{10}^L-c_{10}^R)}{H(1)(\ln c_{10}^L - \ln c_{10}^R)},
\end{aligned}$$

$$\begin{aligned}
\rho_{10} =&\frac{z_1(D_1-D_2)}{H(1)}\left[c_{10}^L w(L_1,L_2) - c_{10}^R w(R_1,R_2) + \frac{\lambda z_1 - z_2}{z_2}\left((c_{10}^L)^2 - (c_{10}^R)^2\right)\right]\\
&-\frac{z_1(z_1D_1-z_2D_2)}{H(1)}\left[\frac{1-\lambda}{z_2}\frac{(c_{10}^L-c_{10}^R)^2}{\ln c_{10}^L - \ln c_{10}^R} - \frac{c_{10}^L-c_{10}^R}{\ln c_{10}^L - \ln c_{10}^R}(\phi_1^L - \phi_1^R)\right]\\
&+\frac{z_1(z_1D_1-z_2D_2)}{(z_1-z_2)H(1)}\frac{c_{10}^L w(L_1,L_2) - c_{10}^R w(R_1,R_2)}{\ln c_{10}^L - \ln c_{10}^R}\ln\frac{L_1R_2}{L_2R_1}\\
&+\frac{z_1(\lambda z_1 - z_2)(z_1D_1-z_2D_2)}{(z_1-z_2)z_2H(1)}\frac{(c_{10}^L)^2 - (c_{10}^R)^2}{\ln c_{10}^L - \ln c_{10}^R}\ln\frac{L_1R_2}{L_2R_1}\\
&-\frac{z_1(z_1D_1-z_2D_2)}{(z_1-z_2)H(1)}\frac{(c_{10}^L-c_{10}^R)(w(L_1,L_2)-w(R_1,R_2))}{(\ln c_{10}^L - \ln c_{10}^R)^2}\ln\frac{L_1R_2}{L_2R_1},
\end{aligned}$$

$$\begin{aligned}
\rho_{11} =&\frac{z_1(z_1D_1-z_2D_2)}{H(1)}\frac{c_{10}^L w(L_1,L_2) - c_{10}^R w(R_1,R_2)}{\ln c_{10}^L - \ln c_{10}^R}\\
&+\frac{z_1(\lambda z_1 - z_2)(z_1D_1-z_2D_2)}{z_2H(1)}\frac{(c_{10}^L)^2 - (c_{10}^R)^2}{\ln c_{10}^L - \ln c_{10}^R}\\
&-\frac{z_1(z_1D_1-z_2D_2)}{H(1)}\frac{(c_{10}^L-c_{10}^R)(w(L_1,L_2)-w(R_1,R_2))}{(\ln c_{10}^L - \ln c_{10}^R)^2},
\end{aligned}$$

where c_{10}^L, c_{10}^R, ϕ_1^L and ϕ_1^R are given in Proposition 3.2 and

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

Proof. For the zeroth order in ε, it follows from

$$\begin{aligned}\mathcal{I}(V;\lambda,0,d)=&z_1\mathcal{J}_1+z_2\mathcal{J}_2=z_1D_1J_1+z_2D_2J_2\\ =&(z_1D_1J_{10}+z_2D_2J_{20})+(z_1D_1J_{11}+z_2D_2J_{21})\,d+o(d)\end{aligned}\tag{4.2}$$

that

$$I_0(V;0)=z_1D_1J_{10}+z_2D_2J_{20}\ \text{ and }\ I_1(V;\lambda,0)=z_1D_1J_{11}+z_2D_2J_{21}.$$

The formulas for $I_0(V;0)$ and $I_1(V;0)$ follow directly from Lemmas 3.5 and 3.6. □

Corollary 4.2. *Under the electroneutrality conditions $z_1L_1=-z_2L_2=L$ and $z_1R_1=-z_2R_2=R$, one has*

$$\begin{aligned}I_0(V;0)=&\frac{(D_1-D_2)(L-R)}{H(1)}+\frac{(z_1D_1-z_2D_2)(L-R)}{H(1)(\ln L-\ln R)}\frac{e}{kT}V,\\ I_1(V;\lambda,0)=&\frac{(\lambda z_1-z_2)(D_2-D_1)(L^2-R^2)}{z_1z_2H(1)}-\frac{(1-\lambda)(z_1D_1-z_2D_2)(L-R)^2}{z_1z_2H(1)(\ln L-\ln R)}\\ &-\frac{(\lambda z_1-z_2)(z_1D_1-z_2D_2)(L-R)^2}{z_1z_2H(1)(\ln L-\ln R)^2}\left(\frac{(L+R)(\ln L-\ln R)}{L-R}-2\right)\frac{e}{kT}V.\end{aligned}$$

In particular, for fixed $R>0$, one has

$$\lim_{L\to R}I_0(V;0)=\frac{(z_1D_1-z_2D_2)R}{H(1)}\frac{e}{kT}V\quad\text{and}\quad\lim_{L\to R}I_1(V;\lambda,0)=0.$$

Proof. Assume $z_1L_1=-z_2L_2=L$ and $z_1R_1=-z_2R_2=R$. It can be checked directly that

$$\begin{aligned}\rho_{00}=&\frac{(D_1-D_2)(L-R)}{H(1)},\quad\rho_{01}=\frac{(z_1D_1-z_2D_2)(L-R)}{H(1)(\ln L-\ln R)},\\ \rho_{10}=&\frac{(\lambda z_1-z_2)(D_2-D_1)(L^2-R^2)}{z_1z_2H(1)}-\frac{(1-\lambda)(z_1D_1-z_2D_2)(L-R)^2}{z_1z_2H(1)(\ln L-\ln R)},\\ \rho_{11}=&-\frac{(\lambda z_1-z_2)(z_1D_1-z_2D_2)(L-R)^2}{z_1z_2H(1)(\ln L-\ln R)^2}\left(\frac{(L+R)(\ln L-\ln R)}{L-R}-2\right).\end{aligned}\tag{4.3}$$

The formulas for $I_0(V;0)$ and $I_1(V;0)$ then follow easily. The two limits can be shown easily too. □

Remark 4.3. *The above formulas for $I_0(V;0)$ and $I_1(V;\lambda,0)$ agree with those in [43] except for a factor $2H(1)$. The factor $H(1)$ does not appear in [43] since it is assumed there that $h(x)=1$, and hence, $H(1)=1$. The factor 2 in front of $H(1)$ is due to the fact that we are expending the I-V relation in the diameter d here instead of the radius r in [43]. As we mentioned in the introduction that there is a major difference between the analysis for the local hard sphere in this paper and that for the nonlocal model in [43]. Nevertheless, the agreement on $I_0(V;0)$ and $I_1(V;\lambda,0)$ is not a surprise since we are using the local hard sphere potential which is obtained as the expansion in the variable d from the nonlocal one used in [43].*

4.1.2 Critical potentials and ion size effects on I-V relations

Based on the approximation of I-V relations in Theorem 4.1, we will identify three critical potentials and discuss their roles in characterizing ion size effects on I-V relations.

Definition 4.4. *We define three potentials V_0, V_c and V^c by*

$$I_0(V_0;0)=0, \quad I_1(V_c;\lambda,0)=0, \quad \frac{d}{d\lambda}I_1(V^c;\lambda,0)=0.$$

For ion channels, the *reversal potential* is defined to be the potential V so that $\mathcal{I}(V;\lambda,\varepsilon)=0$. Thus, the potential V_0 is simply the zeroth order approximation in ε and d of the reversal potential. The critical potentials V_c and V^c are examined for the first time in [43] for a nonlocal hard-sphere model. The significance of the two critical values V_c and V^c is apparent from their definitions. The value V_c is the potential that balances ion size effect on I-V relations and the value V^c is the potential that separates the relative size effect on I-V relations. We provide precise statements below. First of all, note that $I_1(V;\lambda,0)$ is affine in V and in λ. Thus, quantities $\partial_V I_1(V;\lambda,0)$ and V_c depend on the boundary conditions L_1, L_2, R_1, R_2 and the ratio λ of ion sizes only; $\partial^2_{V\lambda}I_1(V;\lambda,0)$ and V^c depend on the boundary conditions L_1, L_2, R_1, R_2 but not on λ.

Theorem 4.5. *Suppose $\partial_V I_1(V;\lambda,0)>0$ (resp. $\partial_V I_1(V;\lambda,0)<0$).*

If $V>V_c$ (resp. $V<V_c$), then, for small $\varepsilon>0$ and $d>0$, the ion sizes enhance the current $\mathcal{I}$; that is, $\mathcal{I}(V;\varepsilon,d)>\mathcal{I}(V;\varepsilon,0)$;

If $V<V_c$ (resp. $V>V_c$), then, for small $\varepsilon>0$ and $d>0$, the ion sizes reduce the current $\mathcal{I}$; that is, $\mathcal{I}(V;\varepsilon,d)<\mathcal{I}(V;\varepsilon,0)$.

Theorem 4.6. *Suppose $\partial^2_{V\lambda}I_1(V;\lambda,0)>0$ (resp. $\partial^2_{V\lambda}I_1(V;\lambda,0)<0$).*

If $V>V^c$ (resp. $V<V^c$), then, for small $\varepsilon>0$ and $d>0$, the larger the negatively charged ion the larger the current; that is, the current $\mathcal{I}$ is increasing in λ;

If $V<V^c$ (resp. $V>V^c$), then, for small $\varepsilon>0$ and $d>0$, the smaller the negatively charged ion the larger the current; that is, the current $\mathcal{I}$ is decreasing in λ.

The following result in [43] can be checked easily.

Proposition 4.7. *Assume electroneutrality conditions $z_1L_1=-z_2L_2=L$ and $z_1R_1=-z_2R_2=R$, and $L\neq R$. Then,*

$$\partial_V I_1(V;\lambda,0)>0 \ \text{ and } \ \partial^2_{V\lambda}I_1(V;\lambda,0)>0.$$

As $R\to L$, $\partial_V I_1(V;\lambda,0)\to 0$ and $\partial^2_{V\lambda}I_1(V;\lambda,0)=O((L-R)^2)$. □

While both $\partial_V I_1(V;\lambda,0)$ and $\partial^2_{V\lambda}I_1(V;\lambda,0)$ are non-negative under electroneutrality conditions, in general, they can be negative. We do not have a complete result for the general case but the following partial result.

Proposition 4.8. *For any $L>0$, $R_1^*>0$ and $R_2^*>0$ with $R_1^*R_2^*=L^2$, as $(R_1,R_2)\to(R_1^*,R_2^*)$,*

$$\begin{aligned}\partial_V I_1(V;\lambda,0)=&\frac{e}{kT}\rho_{11}(L,L,R_1,R_2;\lambda)\\ &\to \frac{e(D_1+D_2)L}{4kTH(1)R_1^*}\left(R_1^*-L\right)\left((3+\lambda)R_1^*-(1+3\lambda)L\right).\end{aligned}$$

The latter is negative if

$$\textit{either}\ \ L < R_1^* < \frac{1+3\lambda}{3+\lambda}L\ \ \textit{for}\ \ \lambda > 1\ \ \textit{or}\ \ \frac{1+3\lambda}{3+\lambda}L < R_1^* < L\ \ \textit{for}\ \ \lambda < 1.$$

As $(R_1, R_2) \to (R_1^*, R_2^*)$,

$$\partial_{V\lambda} I_1(V;\lambda,0) = \frac{e}{kT}\partial_\lambda \rho_{11}(L,L,R_1,R_2;\lambda) \to \frac{e(D_1+D_2)L}{4kTH(1)R_1^*}\left(R_1^*-L\right)\left(R_1^*-3L\right).$$

The latter is negative if $L < R_1^* < 3L$.

Proof. For $z_1 = -z_2 = 1$, we have

$$\begin{aligned}
\partial_V I_1(V;\lambda,0) =& \frac{e}{kT}\rho_{11}(L_1,L_2,R_1,R_2;\lambda),\\
=&\frac{2e(D_1+D_2)}{kTH(1)}\frac{R_1^{1/2}R_2^{1/2}w(R_1,R_2) - L_1^{1/2}L_2^{1/2}w(L_1,L_2)}{\ln(R_1R_2)-\ln(L_1L_2)}\\
&-\frac{2e(1+\lambda)(D_1+D_2)}{kTH(1)}\frac{R_1R_2-L_1L_2}{\ln(R_1R_2)-\ln(L_1L_2)}\\
&-\frac{4e(D_1+D_2)}{kTH(1)}\frac{R_1^{1/2}R_2^{1/2}-L_1^{1/2}L_2^{1/2}}{\ln(R_1R_2)-\ln(L_1L_2)}\frac{w(R_1,R_2)-w(L_1,L_2)}{\ln(R_1R_2)-\ln(L_1L_2)}.
\end{aligned}$$

Recall from Theorem 4.1 that, for $z_1 = -z_2 = 1$,

$$w(\alpha,\beta) = \alpha + \lambda\beta + \frac{1+\lambda}{2}(\alpha+\beta).$$

For fixed $a > 0$ and $b > 0$, we set

$$\rho(x,y;a,b) = \frac{H(1)}{D_1+D_2}\rho_{11}(a^2,b^2;x^2,y^2;\lambda).$$

Then, a direct calculation yields

$$\begin{aligned}
\rho(x,y;a,b) =& \frac{xy-ab}{\ln(xy)-\ln(ab)}w_1(x^2,y^2) - (1+\lambda)\frac{x^2y^2-a^2b^2}{\ln(xy)-\ln(ab)}\\
&-\frac{xy-ab-ab(\ln(xy)-\ln(ab))}{(\ln(xy)-\ln(ab))^2}(w_1(x^2,y^2)-w_1(a^2,b^2)).
\end{aligned}$$

Note that, as $z = xy \to ab$,

$$\frac{z-ab}{\ln z - \ln(ab)} \to ab, \quad \frac{z-ab-ab(\ln z-\ln(ab))}{(\ln z-\ln(ab))^2} \to \frac{ab}{2}, \quad \frac{z^2-a^2b^2}{\ln z-\ln(ab)} \to 2a^2b^2.$$

Thus, as $x \to x_0$ and $y \to y_0$ with $x_0y_0 = ab$,

$$\begin{aligned}
\rho(x,y;a,b) \to& abw_1(x_0^2,y_0^2) - \frac{ab}{2}\left(w_1(x_0^2,y_0^2)-w_1(a^2,b^2)\right) - 2(1+\lambda)a^2b^2\\
=&\frac{ab}{2}\left(w_1(x_0^2,y_0^2)+w_1(a^2,b^2)\right) - 2(1+\lambda)a^2b^2\\
=&\frac{ab}{2}\left(w_1(x_0^2,y_0^2)+w_1(a^2,b^2)-4(1+\lambda)ab\right)\\
=&\frac{ab}{2}\left(\frac{3+\lambda}{2}x_0^2+\frac{1+3\lambda}{2}y_0^2+\frac{3+\lambda}{2}a^2+\frac{1+3\lambda}{2}b^2-4(1+\lambda)ab\right)\\
=&\frac{ab}{2x_0^2}\left(\frac{3+\lambda}{2}x_0^4+\left(\frac{3+\lambda}{2}a^2+\frac{1+3\lambda}{2}b^2-4(1+\lambda)ab\right)x_0^2+\frac{1+3\lambda}{2}a^2b^2\right).
\end{aligned}$$

In particular, for $a=b$, as $x\to x_0$ and $y\to y_0$ with $x_0y_0=a^2$,

$$\begin{aligned}\rho(x,y;a,a)\to&\frac{a^2}{2x_0^2}\left(\frac{3+\lambda}{2}x_0^4-2(1+\lambda)a^2x_0^2+\frac{1+3\lambda}{2}a^4\right)\\=&\frac{a^2}{2x_0^2}\left(x_0^2-a^2\right)\left(\frac{3+\lambda}{2}x_0^2-\frac{1+3\lambda}{2}a^2\right).\end{aligned}$$

The latter is negative if

$$\text{either}\ \ a<x_0<\sqrt{\frac{1+3\lambda}{3+\lambda}}a\ \ \text{for}\ \ \lambda>1\ \ \text{or}\ \ \sqrt{\frac{1+3\lambda}{3+\lambda}}a<x_0<a\ \ \text{for}\ \ \lambda<1.$$

It can be directly translated to the statements for ρ_{11} and $\partial_\lambda\rho_{11}$. □

In the rest of this part, we discuss a number of properties of the critical potentials. It follows from Definition 4.4 and Theorem 4.1 that

Proposition 4.9. *The potentials V_0, V_c and V^c have the following expressions*

$$\begin{aligned}V_0:=V_0(L_1,L_2,R_1,R_2)=&-\frac{kT}{e}\frac{\rho_{00}(L_1,L_2,R_1,R_2)}{\rho_{01}(L_1,L_2,R_1,R_2)},\\V_c:=V_c(L_1,L_2,R_1,R_2;\lambda)=&-\frac{kT}{e}\frac{\rho_{10}(L_1,L_2,R_1,R_2;\lambda)}{\rho_{11}(L_1,L_2,R_1,R_2;\lambda)},\\V^c:=V^c(L_1,L_2,R_1,R_2;\lambda)=&-\frac{kT}{e}\frac{\rho_{10,\lambda}(L_1,L_2,R_1,R_2;\lambda)}{\rho_{11,\lambda}(L_1,L_2,R_1,R_2;\lambda)}.\end{aligned}$$

Remark 4.10. *The critical potentials V_0, V_c and V^c are independent of the cross-section area $h(x)$ of the channel.* □

When electroneutrality conditions $z_1L_1=-z_2L_2=L$ and $z_1R_1=-z_2R_2=R$ hold, we write

$$\begin{aligned}V_0(L,R):=&V_0(L_1,L_2,R_1,R_2),\\V_c(L,R;\lambda):=&V_c(L_1,L_2,R_1,R_2;\lambda),\\V^c(L,R;\lambda):=&V^c(L_1,L_2,R_1,R_2;\lambda).\end{aligned}$$

Corollary 4.11. *Assume the electroneutrality boundary conditions $z_1L_1=-z_2L_2=L$ and $z_1R_1=-z_2R_2=R$. Then, we have*

$$\begin{aligned}V_0(L,R)=&\frac{kT}{e}\frac{(D_1-D_2)}{z_1D_1-z_2D_2}\ln\frac{R}{L},\\V_c(L,R;\lambda)=&\frac{kT}{e}\frac{\lambda-1}{\lambda z_1-z_2}f\left(\frac{L}{R}\right)-\frac{kT}{e}\frac{D_1-D_2}{z_1D_1-z_2D_2}g\left(\frac{L}{R}\right),\quad \textit{if}\ \ L\neq R,\\V^c(L,R;\lambda)=&\frac{kT}{e}\frac{1}{z_1}f\left(\frac{L}{R}\right)-\frac{kT}{e}\frac{D_1-D_2}{z_1D_1-z_2D_2}g\left(\frac{L}{R}\right),\quad \textit{if}\ \ L\neq R,\end{aligned}$$

where, for $x>0$,

$$f(x)=\frac{(x-1)\ln x}{(1+x)\ln x-2(x-1)},\quad g(x)=\frac{(1+x)(\ln x)^2}{(1+x)\ln x-2(x-1)}.\tag{4.4}$$

Proof. The formulas follow directly from Proposition 4.9 and display (4.3). □

Lemma 4.12. *For the functions f and g defined in (4.4), one has*

(i) $f(x) = -f(1/x)$ *and* $g(x) = -g(1/x)$*;*

(ii) $\lim_{x\to 1^+} f(x)\ln x = 6$, $\lim_{x\to\infty} f(x) = 1$, *and* $f'(x) < 0$ *for* $x > 1$*;*

(iii) $\lim_{x\to 1^+} g(x)\ln x = 12$, $\lim_{x\to\infty} \frac{g(x)}{\ln x} = 1$, *and* $g(x)$ *has a unique positive minimum in* $(1,\infty)$.

Proof. The verifications of these properties are elementary. □

As a direct consequence of Corollary 4.11 and Lemma 4.12, one has

Corollary 4.13. *Assume the electroneutrality boundary conditions* $z_1L_1 = -z_2L_2 = L$ *and* $z_1R_1 = -z_2R_2 = R$*. Then,*

(i) $V_0(L,R) = -V_0(R,L)$, $V_c(L,R;\lambda) = -V_c(R,L;\lambda)$, $V^c(L,R;\lambda) = -V^c(R,L;\lambda)$*;*

(ii) for $L \geq R$, $V_0(L,R)$ *is decreasing (resp. increasing) in* L *if* $D_1 > D_2$ *(resp.* $D_1 < D_2$*), and, for fixed* $R > 0$, $\lim_{L\to R} V_0(L,R) = 0$*;*

(iii) for fixed $R > 0$,

$$\begin{aligned}
&\lim_{L\to R} V_c(L,R;\lambda)(\ln L - \ln R) = \frac{kT}{e}\left(\frac{6(\lambda-1)}{\lambda z_1 - z_2} - \frac{12(D_1-D_2)}{z_1D_1 - z_2D_2}\right),\\
&\lim_{L\to R} V^c(L,R;\lambda)(\ln L - \ln R) = \frac{kT}{e}\frac{6z_1(D_2-D_1) + 6(z_1-z_2)D_2}{z_1(z_1D_1 - z_2D_2)},\\
&\lim_{L\to\infty} \frac{V_c(L,R;\lambda)}{\ln L - \ln R} = \lim_{L\to\infty} \frac{V^c(L,R;\lambda)}{\ln L - \ln R} = -\frac{kT}{e}\frac{D_1 - D_2}{z_1D_1 - z_2D_2};
\end{aligned} \tag{4.5}$$

(iv) $V^c(L,R;\lambda) - V_c(L,R;\lambda) = \frac{kT}{e}\frac{z_1 - z_2}{z_1(\lambda z_1 - z_2)} f\left(\frac{L}{R}\right)$*, and hence, for fixed* $R > 0$,

$$\begin{aligned}
&\lim_{L\to R} \left(V^c(L,R;\lambda) - V_c(L,R;\lambda)\right)(\ln L - \ln R) = \frac{kT}{e}\frac{6(z_1 - z_2)}{z_1(\lambda z_1 - z_2)},\\
&\lim_{L\to\infty} \left(V^c(L,R;\lambda) - V_c(L,R;\lambda)\right) = 1.
\end{aligned}$$

4.1.3 Scaling laws

Next result concerns the dependences of I_0, I_1, V_0, V_c and V^c on the boundary concentrations. For this discussion, we include the boundary conditions in the arguments of I_0, I_1, V_0, V_c and V^c; for example, we write I_0 as $I_0(V;L_1,L_2,R_1,R_2)$, etc..

Theorem 4.14. *The following scaling laws hold,*

(i) I_0 *scales* linearly *in boundary concentrations, that is, for any* $s > 0$,

$$I_0(V;sL_1,sL_2,sR_1,sR_2) = sI_0(V;L_1,L_2,R_1,R_2);$$

(ii) $I_1(V; sL_1, sL_2, sR_1, sR_2)$ *scales* quadratically *in boundary concentrations, that is, for any* $s > 0$*,*

$$I_1(V; sL_1, sL_2, sR_1, sR_2) = s^2 I_1(V; L_1, L_2, R_1, R_2);$$

(iii) V_0*,* V_c *and* V^c *are* invariant *under scaling in boundary concentrations, that is, for any* $s > 0$*,*

$$\begin{aligned} V_0(sL_1, sL_2, sR_1, sR_2) =& V_0(L_1, L_2, R_1, R_2), \\ V_c(sL_1, sL_2, sR_1, sR_2) =& V_c(L_1, L_2, R_1, R_2), \\ V^c(sL_1, sL_2, sR_1, sR_2) =& V^c(L_1, L_2, R_1, R_2). \end{aligned}$$

Proof. A direct observation gives

$$\begin{aligned} \rho_{00}(sL_1, sL_2, sR_1, sR_2) =& s\rho_{00}(L_1, L_2, R_1, R_2), \\ \rho_{01}(sL_1, sL_2, sR_1, sR_2) =& s\rho_{01}(L_1, L_2, R_1, R_2), \\ \rho_{10}(sL_1, sL_2, sR_1, sR_2, \lambda) =& s^2\rho_{10}(L_1, L_2, R_1, R_2; \lambda), \\ \rho_{11}(sL_1, sL_2, sR_1, sR_2, \lambda) =& s^2\rho_{11}(L_1, L_2, R_1, R_2; \lambda). \end{aligned}$$

The above scaling laws then follow from Theorem 4.1 and Proposition 4.9. □

Remark 4.15. *(i) Note that* I_0 *and* V_0 *are* not linear *in boundary concentrations, and* I_1*,* V_c *and* V^c *are* not quadratic *in boundary concentrations.*

(ii) Recall, from (4.1), that the zeroth order in ε *and first order in* d *approximation of the I-V relation* $\mathcal{I}(V; \lambda, \varepsilon, d)$ *is* $I_0 + I_1 d$*. Since* I_0 *and* I_1 *scale differently in boundary concentrations, the approximation* $I_0 + I_1 d$ *does not have a simple scaling law.*

(iii) It follows from the scaling laws for I_0 *and* I_1 *that, at higher ion concentrations, the ion size effect becomes more significant. This is well expected. On the other hand, our scaling law results reveal a concrete way on how the ion size effect is manifested as the concentrations increase.*

4.2 The flow rate $\mathcal{T}$ of matter

In this part, we briefly discuss ion size effects on the rate $\mathcal{T}$. Recall from (2.4) that The flow rate $\mathcal{T}$ of matter is

$$\mathcal{T}(V; \lambda, \varepsilon, d) = \mathcal{J}_1 + \mathcal{J}_2 = D_1 J_1 + D_2 J_2.$$

We have the following observation. Note that J_1 and J_2 are *independent* of D_1 and D_2. We will indicate the dependence of $\mathcal{T}$ and $\mathcal{I}$ on D_1 and D_2 explicitly and omit their dependences on other variables; that is, we denote the current $\mathcal{I}(V; \lambda, \varepsilon, d)$ in Section 4.1 by $\mathcal{I}(D_1, D_2)$, and $\mathcal{T}(V; \lambda, \varepsilon, d)$ by $\mathcal{T}(D_1, D_2)$. Then,

$$\mathcal{T}(D_1, D_2) = D_1 J_1 + D_2 J_2 = z_1 \frac{D_1}{z_1} J_1 + z_2 \frac{D_2}{z_2} J_2 = \mathcal{I}\left(\frac{D_1}{z_1}, \frac{D_2}{z_2}\right). \tag{4.6}$$

Therefore, all results in Section 4.1 on the current $\mathcal{I}$ can be translated to results on $\mathcal{T}$ by replacing D_1 and D_2 in Section 4.1 with D_1/z_1 and D_2/z_2, respectively. We will thus collect the results related to $\mathcal{T}$ only.

Similar to the expression for $\mathcal{I}$ in Section 4.1, we express $\mathcal{T}$ as

$$\mathcal{T}(V; \lambda, \varepsilon, d) = T_0(V; \varepsilon) + T_1(V; \lambda, \varepsilon)d + o(d). \tag{4.7}$$

Theorem 4.16. *In the expression (4.7), one has*

$$
\begin{aligned}
T_0(V;0) =& D_1 J_{10} + D_2 J_{20} = \sigma_{00}(L_1, L_2, R_1, R_2) + \sigma_{01}(L_1, L_2, R_1, R_2)\frac{e}{kT}V,\\
T_1(V;\lambda,0) =& D_1 J_{11} + D_2 J_{21} = \sigma_{10}(L_1, L_2, R_1, R_2;\lambda) + \sigma_{11}(L_1, L_2, R_1, R_2;\lambda)\frac{e}{kT}V,
\end{aligned}
$$

where

$$
\begin{aligned}
\sigma_{00} =& \frac{(z_2D_1 - z_1D_2)(c_{10}^L - c_{10}^R)}{z_2H(1)} + \frac{z_1(D_1 - D_2)(c_{10}^L - c_{10}^R)}{H(1)(\ln c_{10}^L - \ln c_{10}^R)}(\ln(L_1R_2) - \ln(L_2R_1)),\\
\sigma_{01} =& \frac{z_1(D_1 - D_2)(c_{10}^L - c_{10}^R)}{H(1)(\ln c_{10}^L - \ln c_{10}^R)},
\end{aligned}
$$

$$
\begin{aligned}
\sigma_{10} =& \frac{z_2D_1 - z_1D_2}{z_2H(1)}\left[c_{10}^L w(L_1, L_2) - c_{10}^R w(R_1, R_2) + \frac{\lambda z_1 - z_2}{z_2}\left((c_{10}^L)^2 - (c_{10}^R)^2\right)\right]\\
&- \frac{z_1(D_1 - D_2)}{H(1)}\left[\frac{1-\lambda}{z_2}\frac{(c_{10}^L - c_{10}^R)^2}{\ln c_{10}^L - \ln c_{10}^R} - \frac{c_{10}^L - c_{10}^R}{\ln c_{10}^L - \ln c_{10}^R}(\phi_1^L - \phi_1^R)\right]\\
&+ \frac{z_1(D_1 - D_2)}{(z_1 - z_2)H(1)}\frac{c_{10}^L w(L_1, L_2) - c_{10}^R w(R_1, R_2)}{\ln c_{10}^L - \ln c_{10}^R}(\ln(L_1R_2) - \ln(L_2R_1))\\
&+ \frac{z_1(\lambda z_1 - z_2)(D_1 - D_2)}{(z_1 - z_2)z_2H(1)}\frac{(c_{10}^L)^2 - (c_{10}^R)^2}{\ln c_{10}^L - \ln c_{10}^R}(\ln(L_1R_2) - \ln(L_2R_1))\\
&- \frac{z_1(D_1 - D_2)}{(z_1 - z_2)H(1)}\frac{(c_{10}^L - c_{10}^R)(w(L_1, L_2) - w(R_1, R_2))}{(\ln c_{10}^L - \ln c_{10}^R)^2}(\ln(L_1R_2) - \ln(L_2R_1)),
\end{aligned}
$$

$$
\begin{aligned}
\sigma_{11} =& \frac{z_1(D_1 - D_2)}{H(1)}\frac{c_{10}^L w(L_1, L_2) - c_{10}^R w(R_1, R_2)}{\ln c_{10}^L - \ln c_{10}^R}\\
&+ \frac{z_1(\lambda z_1 - z_2)(D_1 - D_2)}{z_2H(1)}\frac{(c_{10}^L)^2 - (c_{10}^R)^2}{\ln c_{10}^L - \ln c_{10}^R}\\
&- \frac{z_1(D_1 - D_2)}{H(1)}\frac{(c_{10}^L - c_{10}^R)(w(L_1, L_2) - w(R_1, R_2))}{(\ln c_{10}^L - \ln c_{10}^R)^2}.
\end{aligned}
$$

Definition 4.17. *Define three potentials $\hat{V}_0$, $\hat{V}_c$ and $\hat{V}^c$ by*

$$
T_0(\hat{V}_0;0) = 0, \quad T_1(\hat{V}_c;\lambda,0) = 0, \quad \frac{d}{d\lambda}T_1(\hat{V}^c;\lambda,0) = 0.
$$

It follows from the definition that

Proposition 4.18. *The potentials $\hat{V}_0$, $\hat{V}_c$ and $\hat{V}^c$ have the following expressions*

$$
\begin{aligned}
\hat{V}_0 =& -\frac{kT}{e}\frac{\sigma_{00}(L_1, L_2, R_1, R_2)}{\sigma_{01}(L_1, L_2, R_1, R_2)},\\
\hat{V}_c =& -\frac{kT}{e}\frac{\sigma_{10}(L_1, L_2, R_1, R_2;\lambda)}{\sigma_{11}(L_1, L_2, R_1, R_2;\lambda)},\\
\hat{V}^c =& -\frac{kT}{e}\frac{\sigma_{10,\lambda}(L_1, L_2, R_1, R_2;\lambda)}{\sigma_{11,\lambda}(L_1, L_2, R_1, R_2;\lambda)}.
\end{aligned}
$$

We have the following *scaling laws*:

Theorem 4.19. *For any $s > 0$,*

$$\begin{aligned}
\sigma_{00}(sL_1, sL_2, sR_1, sR_2) =& s\sigma_{00}(L_1, L_2, R_1, R_2),\\
\sigma_{01}(sL_1, sL_2, sR_1, sR_2) =& s\sigma_{01}(L_1, L_2, R_1, R_2),\\
\sigma_{10}(sL_1, sL_2, sR_1, sR_2, \lambda) =& s^2\sigma_{10}(L_1, L_2, R_1, R_2; \lambda),\\
\sigma_{11}(sL_1, sL_2, sR_1, sR_2, \lambda) =& s^2\sigma_{11}(L_1, L_2, R_1, R_2; \lambda).
\end{aligned}$$

As a consequence, $T_0(V;0)$ scales linearly *in boundary concentrations and $T_1(V;\lambda,0)$ scales* quadratically *in boundary concentrations, and the values $\hat{V}_0$, $\hat{V}_c$ and $\hat{V}^c$ are* invariant *under scaling in boundary concentrations.* □

Theorem 4.20. *Suppose $\partial_V T_1(V;\lambda,0) > 0$ (resp. $\partial_V T_1(V;\lambda,0) < 0$).*

If $V > \hat{V}_c$ (resp. $V < \hat{V}_c$), then, for small $\varepsilon > 0$ and $d > 0$, the ion sizes enhance $\mathcal{T}$; that is, $\mathcal{T}(V;\varepsilon,d) > \mathcal{T}(V;\varepsilon,0)$;

If $V < \hat{V}_c$ (resp. $V > \hat{V}_c$), then, for small $\varepsilon > 0$ and $d > 0$, the ion sizes reduce $\mathcal{T}$; that is, $\mathcal{T}(V;\varepsilon,d) < \mathcal{T}(V;\varepsilon,0)$.

Theorem 4.21. *Suppose $\partial^2_{V\lambda} T_1(V;\lambda,0) > 0$ (resp. $\partial^2_{V\lambda} T_1(V;\lambda,0) < 0$).*

If $V > \hat{V}^c$ (resp. $V < \hat{V}^c$), then, for small $\varepsilon > 0$ and $d > 0$, the larger the negatively charged ion the larger $\mathcal{T}$; that is, $\mathcal{T}$ increases λ;

If $V < \hat{V}^c$ (resp. $V > \hat{V}^c$), then, for small $\varepsilon > 0$ and $d > 0$, the smaller the negatively charged ion the larger $\mathcal{T}$; that is, $\mathcal{T}$ decreases λ.

Corollary 4.22. *Assume the electroneutrality conditions $z_1L_1 = -z_2L_2 = L$ and $z_1R_1 = -z_2R_2 = R$, and $L \neq R$. Then*

$$\begin{aligned}
T_0(V;0) =& \frac{(z_2D_1 - z_1D_2)(L-R)}{z_1z_2H(1)} + \frac{(D_1 - D_2)(L-R)}{H(1)(\ln L - \ln R)}\frac{e}{kT}V,\\
T_1(V;\lambda,0) =& \frac{(\lambda z_1 - z_2)(z_2D_2 - z_1D_1)(L^2 - R^2)}{z_1^2z_2^2H(1)} - \frac{(1-\lambda)(D_1 - D_2)(L-R)^2}{z_1z_2H(1)(\ln L - \ln R)}\\
&- \frac{(\lambda z_1 - z_2)(D_1 - D_2)(L-R)^2}{z_1z_2H(1)(\ln L - \ln R)^2}\left(\frac{(L+R)(\ln L - \ln R)}{L-R} - 2\right)\frac{e}{kT}V.
\end{aligned}$$

and hence,

$$\begin{aligned}
\hat{V}_0 =& \frac{kT}{e}\frac{(z_2D_1 - z_1D_2)(\ln R - \ln L)}{z_1z_2(D_1 - D_2)},\\
\hat{V}_c =& \frac{kT}{e}\frac{(\lambda - 1)(\ln L - \ln R)(L-R)}{(\lambda z_1 - z_2)[(\ln L - \ln R)(L+R) - 2(L-R)]}\\
&- \frac{kT}{e}\frac{(z_2D_1 - z_1D_2)(\ln L - \ln R)^2(L+R)}{z_1z_2(D_1 - D_2)[(\ln L - \ln R)(L+R) - 2(L-R)]},\\
\hat{V}^c =& \frac{kT}{e}\frac{(\ln L - \ln R)(L-R)}{z_1[(\ln L - \ln R)(L+R) - 2(L-R)]}\\
&- \frac{kT}{e}\frac{(z_2D_1 - z_1D_2)(\ln L - \ln R)^2(L+R)}{z_1z_2(D_1 - D_2)[(\ln L - \ln R)(L+R) - 2(L-R)]}.
\end{aligned}$$

Note also that, under electroneutrality conditions,

$$\partial_V T_1(V;\lambda,0) = -\frac{e(\lambda z_1 - z_2)(D_1-D_2)(L-R)^2}{z_1 z_2 kTH(1)(\ln L - \ln R)^2}\left(\frac{(L+R)(\ln L-\ln R)}{L-R}-2\right)$$

$$\partial_{V\lambda} T_1(V;\lambda,0) = -\frac{(D_1-D_2)(L-R)^2}{z_2 H(1)(\ln L - \ln R)^2}\left(\frac{(L+R)(\ln L-\ln R)}{L-R}-2\right)\frac{e}{kT}.$$

Proposition 4.23. *Assume electroneutrality conditions $z_1L_1 = -z_2L_2 = L$ and $z_1R_1 = -z_2R_2 = R$, and $L \neq R$. If $D_1 > D_2$, then*

$$\partial_V T_1(V;\lambda,0) > 0 \ \ \text{and} \ \ \partial^2_{V\lambda} T_1(V;\lambda,0) > 0;$$

if $D_1 < D_2$, then

$$\partial_V T_1(V;\lambda,0) < 0 \ \ \text{and} \ \ \partial^2_{V\lambda} T_1(V;\lambda,0) < 0.$$

In either case, as $R \to L$,

$$\partial_V T_1(V;\lambda,0) \to 0 \ \ \text{and} \ \ \partial^2_{V\lambda} T_1(V;\lambda,0) = O((L-R)^2).$$

Proof. It can be checked directly or follows from Theorem 4.7 and the relation (4.6) between T_1 and I_1. □

In general, $\partial_V T_1(V;\lambda,0)$ and $\partial^2_{V\lambda} T_1(V;\lambda,0)$ can be negative (resp. positive) for $D_1 > D_2$ (resp. $D_1 < D_2$). In particular, we have

Proposition 4.24. *For $z_1 = -z_2 = 1$ and for any $L > 0$, $R_1^* > 0$ and $R_2^* > 0$ with $R_1^* R_2^* = L^2$, as $(R_1,R_2) \to (R_1^*, R_2^*)$,*

$$\partial_V T_1(V;\lambda,0) \to \frac{(D_1-D_2)L}{4H(1)R_1^*}\left(R_1^*-L\right)\left((3+\lambda)R_1^* - (1+3\lambda)L\right). \tag{4.8}$$

For $D_1 > D_2$ (resp. $D_1 < D_2$), the limit is negative (resp. positive) if

$$\text{either} \ \ L < R_1^* < \frac{1+3\lambda}{3+\lambda}L \ \ \text{for} \ \ \lambda > 1 \ \ \text{or} \ \ \frac{1+3\lambda}{3+\lambda}L < R_1^* < L \ \ \text{for} \ \ \lambda < 1.$$

As $(R_1,R_2) \to (R_1^*, R_2^*)$,

$$\partial_{V\lambda} T_1(V;\lambda,0) \to \frac{(D_1-D_2)L}{4H(1)R_1^*}\left(R_1^*-L\right)\left(R_1^*-3L\right).$$

For $D_1 > D_2$ (resp. $D_1 < D_2$), the limit is negative (resp. positive) if $L < R_1^* < 3L$.

Proof. It follows from Theorem 4.8 and the relation (4.6) between T_1 and I_1. □

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5 Appendix: The local hard-sphere model μ_i^{LHS} in (2.6)

We will derive the local hard-sphere model μ_i^{LHS} in (2.6) as an approximation for a well-known nonlocal hard sphere model used in [43]. Recall that, for one-dimensional space case, one has ([24, 62, 63, 64, 65, 66]) the following formula for the hard-sphere (hard-rod) potential

$$\mu_i^{HS} = \frac{\delta\Omega(\{c_j\})}{\delta c_i}, \tag{5.9}$$

where

$$\begin{aligned} &\Omega(\{c_j\}) = -\int n_0(x;\{c_j\})\ln[1-n_1(x;\{c_j\})]dx, \\ &n_l(x,\{c_j\}) = \sum_{j=1}^{n}\int c_j(x')\omega_l^j(x-x')dx', \quad (l=0,1), \\ &\omega_0^j(x) = \frac{\delta(x-r_j)+\delta(x+r_j)}{2}, \quad \omega_l^j(x) = \Theta(r_j-|x|), \end{aligned} \tag{5.10}$$

where δ is the Dirac function, Θ is the Heaviside function, and $r_j = d_j/2$ is the radius of jth ion species.

In Lemma 4.1 of [43], it is shown that

$$\begin{aligned} \mu_i^{HS}(x) = &-\frac{kT}{2}\ln\left(\left(1-\sum_j\int_{x-r_i-r_j}^{x-r_i+r_j}c_j(x')dx'\right)\left(1-\sum_j\int_{x+r_i-r_j}^{x+r_i+r_j}c_j(x')dx'\right)\right) \\ &+\frac{kT}{2}\int_{x-r_i}^{x+r_i}\frac{\sum_j(c_j(x'-r_j)+c_j(x'+r_j))}{1-\sum_j\int_{x'-r_j}^{x'+r_j}c_j(x'')dx''}dx'. \end{aligned} \tag{5.11}$$

For the first term

$$\ln\left(\left(1-\sum_j\int_{x-r_i-r_j}^{x-r_i+r_j}c_j(x')dx'\right)\left(1-\sum_j\int_{x+r_i-r_j}^{x+r_i+r_j}c_j(x')dx'\right)\right),$$

we expand $c_j(x')$ at $x'=x$

$$c_j(x') = c_j(x) + c_j'(x)(x'-x) + O((x'-x)^2).$$

This gives

$$\begin{aligned} \sum_j\int_{x-r_i-r_j}^{x-r_i+r_j}c_j(x')dx' &= \sum_j\int_{x-r_i-r_j}^{x-r_i+r_j}\left(c_j(x)+c_j'(x)(x'-x)+O((x'-x)^2)\right)dx' \\ &= \sum_j\left(2r_jc_j(x)-2r_ir_jc_j'(x)+O\left(2r_jr_i^2+\frac{2}{3}r_j^3\right)\right) \\ &= \sum_j 2r_jc_j(x)+O(r^2), \end{aligned}$$

where $r=\min\{r_1,r_2\}$. Similarly, one has

$$\sum_j\int_{x+r_i-r_j}^{x+r_i+r_j}c_j(x')dx' = \sum_j 2r_jc_j(x)+O(r^2).$$

Therefore, the first term in $\mu_i^{HS}(x)$ becomes

$$
\begin{aligned}
&-\frac{kT}{2}\ln\Big(\Big(1-\sum_j\int_{x-r_i-r_j}^{x-r_i+r_j}c_j(x')dx'\Big)\Big(1-\sum_j\int_{x+r_i-r_j}^{x+r_i+r_j}c_j(x')dx'\Big)\Big)\\
=&-\frac{kT}{2}\ln\Big(\Big(1-\sum_j 2r_jc_j(x)+O(r^2)\Big)\Big(1-\sum_j 2r_jc_j(x)+O(r^2)\Big)\Big) \qquad (5.12)\\
=&-kT\ln\Big(1-\sum_j 2r_jc_j(x)+O(r^2)\Big).
\end{aligned}
$$

For the second term

$$
\frac{kT}{2}\int_{x-r_i}^{x+r_i}\frac{\sum_j(c_j(x'-r_j)+c_j(x'+r_j))}{1-\sum_j\int_{x'-r_j}^{x'+r_j}c_j(x'')dx''}dx',
$$

we first expand the numerator of the integrand at x to get

$$
\sum_j(c_j(x'-r_j)+c_j(x'+r_j))=2\sum_j(c_j(x)+c_j'(x)(x'-x)+O((x-x')^2)).
$$

Expanding the summation term in the denominator first at x' and then at x, we have

$$
\begin{aligned}
\sum_j\int_{x'-r_j}^{x'+r_j}c_j(x'')dx'' =&\sum_j\int_{x'-r_j}^{x'+r_j}\left(c_j(x')+c_j'(x')(x''-x')+O((x''-x')^2)\right)dx'',\\
=&\sum_j\left(2r_jc_j(x')+O(r^3)\right)\\
=&\sum_j 2r_j\left(c_j(x)+c_j'(x)(x'-x)+O((x'-x)^2)+O(r^3)\right).
\end{aligned}
$$

Hence,

$$
\frac{kT}{2}\int_{x-r_i}^{x+r_i}\frac{\sum_j(c_j(x'-r_j)+c_j(x'+r_j))}{1-\sum_j\int_{x'-r_j}^{x'+r_j}c_j(x'')dx''}dx'=kT\frac{2r_i\sum_j c_j(x)}{1-\sum_j 2r_jc_j(x)}+O(r^2). \qquad (5.13)
$$

Ignoring the higher order terms, the nonlocal hard sphere model $\mu_i^{HS}(x)$ in (5.11) with (5.12) and (5.13) gives the local hard sphere model $\mu_i^{LHS}(x)$ in (2.6).

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