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*Asymptotic Analysis
of Reaction-Diffusion-
Electromigration Systems*

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Asymptotic Analysis of Reaction-Diffusion-Electromigration Systems

Abstract

We consider a Nernst-Planck-Poisson system modelling ion migration through biological membranes, in the one dimensional case. The model includes both the effects of biochemical reaction between ions and of fixed charges. We state the existence of solutions under either an imposed potential condition or an imposed current condition. We study the asymptotical behaviour of solutions in the limit of electroneutrality. Non uniform convergence gives rise to jump in the potential, known as Donnan potential. Finally we give correctors which describe the charged boundary layers.

Analyse Asymptotique de Systèmes de Réaction-Diffusion-Electromigration

Résumé

On considère le système d'équations de Nernst-Planck et Poisson qui modélise la migration d'ions à travers une membrane biologique, dans le cas d'une dimension d'espace. Ce modèle prend en compte à la fois l'effet de réactions biochimiques entre ions et des charges fixées à la membrane. On montre l'existence de solutions pour des conditions aux limites de potentiel ou de courant imposé. On étudie le comportement asymptotique des solutions pour le passage à la limite vers l'électroneutralité. La convergence non uniforme donne lieu à un saut de potentiel connu comme le potentiel de Donnan. Enfin on fournit les correcteurs qui décrivent les couches limites chargées.

Asymptotic Analysis of Reaction-Diffusion-Electromigration Systems

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Abstract

We consider a Nernst-Planck-Poisson system modelling ion migration through biological membranes, in the one dimensional case. The model includes both the effects of biochemical reaction between ions and of fixed charges. We state the existence of solutions under either an imposed potential condition or an imposed current condition. We study the asymptotical behaviour of solutions in the limit of electroneutrality. Non uniform convergence gives rise to jump in the potential, known as Donnan potential. Finally we give correctors which describe the charged boundary layers.

1 Introduction

In this paper we consider a class of models of ion migration through biological membranes. Such migrations exist for most living cells and some biochemical processes. The movement of ions is supposed to be due to diffusion and to the effect of the electrical field. Furthermore, ions can undergo reactions. So, the ion concentrations satisfy Nernst-Planck equations, including a reaction kinetics term and the potential is given by Poisson equation; these equations, in adimensional form, read:

$$-D_i \frac{d}{dx} \left(\frac{dC_i}{dx} + z_i C_i \frac{dV}{dx} \right) = F_i, \quad x \in (0, 1), \quad i = 1, \dots, N \quad (1.1)$$

$$-\epsilon \frac{d^2 V}{dx^2} = \sum_{i=1}^N z_i C_i - f \quad (1.2)$$

x is a space direction, normal to the membrane, which fills the region $(0, 1)$. For each i , C_i is the concentration of the i species, which has mobility D_i and valency

z_i . V is the electrical potential, f is the fixed charges concentration and the F_i are reaction terms. We suppose that F_i depends continuously on the C_j s and V and that f is an $L^\infty(0, 1)$ function. We suppose that D_i is a positive constant, for each i , $\epsilon = \lambda^2/\ell^2$ where λ is the Debye length and ℓ is the membrane thickness (see, for example, Mackey [10]).

We consider boundary conditions of the Dirichlet kind for C_i :

$$C_i(0) = C_{i,0} \geq 0, \quad C_i(1) = C_{i,1} \geq 0 \quad (1.3)$$

We fix the potential at $x = 0$:

$$V(0) = V_0. \quad (1.4)$$

At the other boundary point, we consider either a fixed potential condition

$$V(1) = V_1, \quad (1.5)$$

either a current condition

$$\sum_{i=1}^N D_i z_i \left(\frac{dC_i}{dx} + z_i C_i \frac{dV}{dx} \right) (1) = I, \quad (1.6)$$

where I is the imposed total current.

These models, for passive migration (i.e., without reaction), have been deeply studied in the biophysical litterature, in order to explain the behaviour of ionic currents through biological membranes (see Lakshminarayanaiah [7], Mackey [10]). Two simplifications of these equations have been quite popular in this litterature, namely the Goldman hypothesis where the electrical field is supposed to be constant inside the membrane and the electroneutral hypothesis where the neutrality at each point of the membrane is assumed (see, for example, Mackey [10]). It has been recognized by McGillivray [12] that these models are the limit of the full equations when the ratio λ/ℓ of the Debye length to the membrane thickness goes to, respectively, infinity or zero. Only the second case is studied here.

Often, enzymes are fixed to biological membranes and ions undergo biochemical reactions when crossing the membrane. Valletton [13] did a general biophysical study of coupling of electromigration diffusion with biochemical reactions. Kernevez and Trubuil [6] and Friboulet [4] used such models to explain some oscillation phenomena.

In this paper, we present a mathematical study of such systems, in the one dimensional case, for a large class of reaction kinetics, including the usual biochemical kinetics as the Michaelis-Menten one (a previous work on the multidimensional case, not considering reaction terms, was done by Louro [9]). First, we give existence results for these equations both in the potential and the current imposed cases. In the imposed current case, the result is local (that is, it is true for a neighbourhood of zero, which is given explicitly from the boundary conditions) and it assumes that all the reactions imply only homovalent ions.

We study the limit of solutions as $\epsilon = \lambda^2/\ell^2$ goes to zero. Formally, the Poisson equation (1.2) gives, for $\epsilon = 0$

$$\sum_{i=1}^N z_i C_i = f \quad (1.7)$$

which is the electroneutrality condition. Then, we show the existence of boundary layers, that is, charged layers, due to fixed charges and/or non neutral boundary conditions. These boundary layers correspond to the well-known Donnan potentials, but we give here a mathematical proof of their existence with no other physical assumption than the electroneutrality. We derive equations for the correctors.

The mathematical development presented here is similar to previous work in the semiconductor device equations (Markowich [11], Alabau [1], Henry and Louro [5]) but it extends those in three topics: 1) it includes different reaction kinetics terms, 2) the imposed current situation, 3) it imbeds any number of ions with any valency.

In §2, we prove the existence of solutions for both cases: the imposed potential and the imposed current. We use Schauder fixed point theorem and sub and super solutions.

In §3, we study the asymptotical behaviour of the solutions as $\epsilon \rightarrow 0$, by the use of some local and some global bounds, not depending on ϵ .

In §4, by using the framework developed by Lions [8] for the linear case, we give correctors, describing the boundary layers.

2 Existence

In order to prove the existence of solution for the system (1.1)–(1.2) satisfying boundary conditions (1.3),(1.4),(1.5) or (1.3),(1.4),(1.6), we state the following assumptions:

$$f \in L^\infty(0, 1) \quad (2.1)$$

$$F_i \in C(\mathbf{R}_+^N \times \mathbf{R}, \mathbf{R}) \cap L^\infty(\mathbf{R}_+^N \times \mathbf{R}, \mathbf{R}), \quad i = 1, \dots, N \quad (2.2)$$

We consider a set of biochemical reactions with one substrate S (with concentration C_i) and some products P_l (with concentrations C_j, \dots, C_r) and suppose that the reaction kinetics are of the form:

$$F_i(C_1, \dots, C_N, V) = -C_i G_i(C_1, \dots, C_N, V), \quad F_l = -F_i, \quad l = j, \dots, r \quad (2.3)$$

with $G_i \in C(\mathbf{R}_+^N \times \mathbf{R}, \mathbf{R}_+)$

In particular, this covers the Michaelis-Menten model.

Let us remark that, by the charge conservation law, the kinetics F_i must satisfy

$$\sum_{i=1}^N z_i F_i \equiv 0 \quad (2.4)$$

By (2.4) and (1.1), if (1.6) is satisfied at $x = 1$, then it is satisfied for every $x \in (0, 1)$.

Let us consider some auxiliary sets:

$$A_0^- \cup A_0^+ \cup A_s^+ \cup A_s^- \cup A_p^+ \cup A_p^- = \{1, \dots, N\};$$

the sets A^+ relative to cations (resp. A^- relative to anions) are defined in the following way:

$$i \in A_0^+(A_0^-) \text{ if } F_i \equiv 0 \text{ and } z_i > 0 (z_i < 0), \quad (2.5)$$

for ions not involved in a reaction,

$$i \in A_s^+(A_s^-) \text{ if } F_i = -C_i G_i \text{ and } z_i > 0 (z_i < 0), \quad (2.6)$$

for substrates, and

$$i \in A_p^+(A_p^-) \text{ if } F_i = -F_k \text{ for some } k \in A_s^+ \cup A_s^- \text{ and } z_i > 0 (z_i < 0), \quad (2.7)$$

for products.

For each $i \in \{1, \dots, N\}$ let us define

$$m_i = \begin{cases} \min \{C_{i,0} e^{z_i V_0}, C_{i,1} e^{z_i V_1}\}, & i \in A_0^+ \cup A_0^- \cup A_p^+ \cup A_p^- \\ 0, & i \in A_s^+ \cup A_s^- \end{cases}$$

and

$$\mathcal{M}_i = \max \{C_{i,0} e^{z_i V_0}, C_{i,1} e^{z_i V_1}\}, \quad i = 1, 2, \dots, N$$

We suppose that there exist, at least, two species p and q such that $z_p z_q < 0$ and $m_p, m_q > 0$.

Let us consider the set

$$B = \prod_{i=1}^N [m_i, \mathcal{M}_i]$$

and define

$$\begin{aligned} d_m &= \inf_{y \in B, x \in [0,1]} \left\{ d(x, y) > 0; \sum_{i=1}^N z_i y_i d^{-z_i}(x, y) = \right. \\ &\quad \left. - \sum_{i \in A_p^-} z_i \frac{\max |F_i|}{D_i} - \sum_{i \in A_p^-} z_i (\mathcal{M}_i - m_i) \max \{e^{-z_i V_0}, e^{-z_i V_1}\} + f(x) \right\} \\ d_M &= \sup_{y \in B, x \in [0,1]} \left\{ d(x, y) > 0; \sum_{i=1}^N z_i y_i d^{-z_i}(x, y) = \right. \\ &\quad \left. - \sum_{i \in A_p^+} z_i \frac{\max |F_i|}{D_i} - \sum_{i \in A_p^+} z_i (\mathcal{M}_i - m_i) \max \{e^{-z_i V_0}, e^{-z_i V_1}\} + f(x) \right\} \end{aligned}$$

Remark that, for each (x, y) , $d(x, y)$ is well defined by the monotonicity of the function $\sum_{i=1}^N z_i y_i d^{-z_i}(x, y)$ and the fact that it maps R_+ onto R . The boundedness of d_m and d_M follows from the boundedness of f and B .

Finally, we define the quantities:

$$M_i = \begin{cases} \mathcal{M}_i, & i \in A_0^+ \cup A_0^- \cup A_s^+ \cup A_s^- \\ \mathcal{M}_i + \frac{\max |F_i|}{D_i} \left(\max\{e^{V_0}, e^{V_1}, d_M\} \right)^{z_i}, & i \in A_p^+ \\ \mathcal{M}_i + \frac{\max |F_i|}{D_i} \left(\min\{e^{V_0}, e^{V_1}, d_m\} \right)^{z_i}, & i \in A_p^- \end{cases}$$

Theorem 1 *Under hypothesis (2.1)–(2.3), if there exist, at least, two species p and q such that $z_p z_q < 0$ and $m_p, m_q > 0$, the system (1.1)–(1.2) with boundary conditions (1.3)–(1.5) has, in $(H^1(0, 1) \cap L^\infty(0, 1))^{N+1}$, at least one solution satisfying*

$$\min\{V_0, V_1, \log d_m\} \leq V \leq \max\{V_0, V_1, \log d_M\}$$

- a) $m_i e^{-z_i \max\{V_0, V_1, \log d_M\}} \leq C_i \leq M_i e^{-z_i \min\{V_0, V_1, \log d_m\}}, \quad z_i > 0$
- b) $m_i e^{-z_i \min\{V_0, V_1, \log d_m\}} \leq C_i \leq M_i e^{-z_i \max\{V_0, V_1, \log d_M\}}, \quad z_i < 0.$

Proof: If we introduce a new set of variables $(u_1, u_2, \dots, u_N, V)$ by

$$u_i = C_i e^{z_i V}, \quad (2.8)$$

the system reduces to

$$-D_i \frac{d}{dx} \left(e^{-z_i V} \frac{du_i}{dx} \right) = F_i \left(u_1 e^{-z_1 V}, \dots, u_N e^{-z_N V}, V \right), \quad (2.9)$$

$$i = 1, \dots, N$$

$$-\epsilon \frac{d^2 V}{dx^2} = \sum_{i=1}^N z_i u_i e^{-z_i V} - f \quad (2.10)$$

with u_i and V satisfying the boundary conditions

$$u_i(0) = C_{i,0} e^{z_i V_0}, u_i(1) = C_{i,1} e^{z_i V_1}, V(0) = V_0, V(1) = V_1. \quad (2.11)$$

Let K be the closed convex set of $(L^2(0, 1))^{N+1}$ given by

$$K = \left\{ (u_1, \dots, u_N, V) \in (L^2(0, 1))^{N+1}; m_i \leq u_i \leq M_i, \right. \\ \left. \min\{V_0, V_1, \log d_m\} \leq V \leq \max\{V_0, V_1, \log d_M\} \right\}$$

We define the mapping

$$T : (u_1, \dots, u_N, V) \longrightarrow (\bar{u}_1, \dots, \bar{u}_N, \bar{V})$$

by

$$\left. \begin{aligned} \text{a)} & -D_i \frac{d}{dx} \left(e^{-z_i V} \frac{d\bar{u}_i}{dx} \right) = \\ & = -\bar{u}_i e^{-z_i V} G_i \left(u_1 e^{-z_1 V}, \dots, u_N e^{-z_N V}, V \right), \quad i \in A_s^+ \cup A_s^-, \\ \text{b)} & -D_i \frac{d}{dx} \left(e^{-z_i V} \frac{d\bar{u}_i}{dx} \right) = F_i = -F_j \left(u_1 e^{-z_1 V}, \dots, u_N e^{-z_N V}, V \right), \\ & \quad (\text{for some } j \in A_s^+ \cup A_s^-), \quad i \in A_p^+ \cup A_p^-, \\ \text{c)} & -D_i \frac{d}{dx} \left(e^{-z_i V} \frac{d\bar{u}_i}{dx} \right) = 0, \quad i \in A_0^+ \cup A_0^-, \\ \text{d)} & -\epsilon \frac{d^2 \bar{V}}{dx^2} = \sum_{i=1}^N z_i u_i e^{-z_i \bar{V}} - f, \\ \text{e)} & \bar{u}_i(0) = C_{i,0} e^{z_i V_0}, \bar{u}_i(1) = C_{i,1} e^{z_i V_1}, \bar{V}(0) = V_0, \bar{V}(1) = V_1. \end{aligned} \right\} \quad (2.12)$$

We will show that $TK \subset K$. Multiplying (2.12,a,b,c) by $(\bar{u}_i - m_i)^-$ and integrating by parts, one can easily show that $\bar{u}_i \geq m_i$, $i = 1, \dots, N$.

Analogously

$$\bar{u}_i \leq M_i, \quad i \in A_0^+ \cup A_0^- \cup A_s^+ \cup A_s^-.$$

Now, let us show that $\bar{u}_i \leq M_i$ if $i \in A_p^+ \cup A_p^-$. By (2.12-b), there exists $A \in \mathbf{R}$ such that

$$-D_i e^{-z_i V} \frac{d\bar{u}_i}{dx} = A + \int_0^x F_i d\xi$$

so,

$$\bar{u}_i(x) = u_i(0) - \frac{A}{D_i} \int_0^x e^{z_i V} d\xi - \frac{1}{D_i} \int_0^x e^{z_i V} \int_0^\xi F_i ds d\xi \quad (2.13)$$

then

$$A = -D_i \frac{u_i(1) - u_i(0)}{\int_0^1 e^{z_i V} dx} - \frac{\int_0^1 e^{z_i V} \int_0^\xi F_i ds d\xi}{\int_0^1 e^{z_i V} dx}$$

Replacing in (2.13) we obtain

$$\begin{aligned} \bar{u}_i(x) &= u_i(0) + (u_i(1) - u_i(0)) \frac{\int_0^x e^{z_i V} d\xi}{\int_0^1 e^{z_i V} dx} \\ &+ \frac{1}{D_i} \frac{\int_0^x e^{z_i V} d\xi}{\int_0^1 e^{z_i V} dx} \int_0^1 e^{z_i V} \int_0^\xi F_i ds d\xi - \frac{1}{D_i} \int_0^x e^{z_i V} \int_0^\xi F_i ds d\xi \\ &\leq \max \{u_i(0), u_i(1)\} + \frac{1}{D_i} \left(\int_0^1 e^{z_i V} \int_0^\xi F_i ds d\xi - \int_0^x e^{z_i V} \int_0^\xi F_i ds d\xi \right) \\ &= \max \{u_i(0), u_i(1)\} + \frac{1}{D_i} \int_x^1 e^{z_i V} \int_0^\xi F_i ds d\xi \\ &\leq \max \{u_i(0), u_i(1)\} + \frac{1}{D_i} \max(F_i) \max(e^{z_i V}) \leq M_i \end{aligned}$$

It remains to show the condition for \bar{V} . For $(u_1, \dots, u_N, V) \in K$, let us show that $\min\{V_0, V_1, \log d_m\}$ is a sub-solution of (2.12-d)-(2.12-e).

Suppose that $\min\{V_0, V_1, \log d_m\} = \log d_m$; then

$$\begin{aligned}
 & \sum_{i=1}^N z_i u_i d_m^{-z_i} - f \geq \sum_{i \notin A_p^-} z_i u_i d_m^{-z_i} - f + \sum_{i \in A_p^-} z_i M_i d_m^{-z_i} \\
 & = \sum_{i \notin A_p^-} z_i u_i d_m^{-z_i} - f + \sum_{i \in A_p^-} z_i m_i d_m^{-z_i} + \sum_{i \in A_p^-} z_i (\mathcal{M}_i - m_i) d_m^{-z_i} \\
 & + \sum_{i \in A_p^-} z_i \frac{\max |F_i|}{D_i} \geq \sum_{i=1, y \in B}^N z_i y_i d_m^{-z_i} - f + \sum_{i \in A_p^-} z_i \frac{\max |F_i|}{D_i} \\
 & + \sum_{i \in A_p^-} z_i (\mathcal{M}_i - m_i) \max \{e^{-z_i V_0}, e^{-z_i V_1}\} \geq 0
 \end{aligned}$$

Similar calculations can be used in order to prove that $\min\{V_0, V_1, \log d_m\}$ is a sub-solution and $\max\{V_0, V_1, \log d_M\}$ is a super-solution; then, there exists a solution of (2.12-d)-(2.12-e) (see, for example, Amann [2]). The monotonicity of the right-hand side of (2.12-d) yields uniqueness.

We have shown that $TK \subset K$.

Since T is a continuous mapping, from $(L^2(0, 1))^{N+1}$ into $(H^1(0, 1))^{N+1}$, by the compactness of the imbedding $H^1(0, 1) \hookrightarrow L^2(0, 1)$, we conclude that T is compact. Hence, by Schauder fixed point theorem, T has, at least, one fixed point in K , which is clearly a solution of (2.9)-(2.11). \square

Next, we will prove the existence of a solution for the system (1.1)-(1.2) satisfying boundary conditions (1.3), (1.4), (1.6). We continue to assume (2.1)-(2.3).

Let \bar{A}_j , $j = 1, \dots, p$ be the sets of homovalent ions, that is

$$\cup_{j=1}^p \bar{A}_j = \{1, \dots, N\}, \quad \bar{A}_j \cap \bar{A}_l = \emptyset \text{ if } j \neq l \text{ and } i, k \in \bar{A}_j \Rightarrow z_j = z_k.$$

Let us make the following restrictive assumptions:

$$\sum_{i \in \bar{A}_j} F_i \equiv 0, \quad j = 1, \dots, p \quad (2.14)$$

$$\sum_{i \in \bar{A}_j} C_{i,0} > 0, \quad \sum_{i \in \bar{A}_j} C_{i,1} > 0, \quad j = 1, \dots, p \quad (2.15)$$

(2.14) means that, in each reaction, the substrate and the products have the same valency, which is not the general case. For example, the hydrolysis of ATP does not satisfy this condition. However, it is satisfied in some cases (see, for example, Kernévez and Trubuil [6]). We assume (2.14), (2.15) in order to prove the existence of a solution. They are not used for the asymptotical analysis, as we will see in sections 3 and 4.

Now, we introduce some auxiliary numbers and sets.

For $j \in \{1, \dots, p\}$ let $k \in \bar{A}_j$ and define:

$$b_j = V_0 + \frac{1}{z_k} \left[\log \left(\sum_{i \in \bar{A}_j} D_i C_{i,0} \right) - \log \left(\sum_{i \in \bar{A}_j} D_i C_{i,1} \right) \right],$$

$$\lambda_m = \min \{b_1, \dots, b_p\}, \quad \lambda_M = \max \{b_1, \dots, b_p\}.$$

Let

$$m_j(\lambda) = \min \left\{ \sum_{i \in \bar{A}_j} D_i C_{i,0} e^{z_k V_0}, \sum_{i \in \bar{A}_j} D_i C_{i,1} e^{z_k \lambda} \right\},$$

$$M_j(\lambda) = \max \left\{ \sum_{i \in \bar{A}_j} D_i C_{i,0} e^{z_k V_0}, \sum_{i \in \bar{A}_j} D_i C_{i,1} e^{z_k \lambda} \right\},$$

$$h_j = \min_{\lambda \in [\lambda_m, \lambda_M]} m_j(\lambda), \quad H_j = \max_{\lambda \in [\lambda_m, \lambda_M]} M_j(\lambda),$$

$$B_1 = \left[\min_{1 \leq j \leq p} \left(h_j \left(\max_{i \in \bar{A}_j} D_i \right)^{-1} \right), \max_{1 \leq j \leq p} \left(H_j \left(\min_{i \in \bar{A}_j} D_i \right)^{-1} \right) \right]$$

and

$$W_m = \min_{y \in B_1, x \in [0,1]} \left\{ d(x, y) > 0; \sum_{j=1}^p z_j y d^{-z_j}(x, y) = f(x) \right\},$$

$$W_M = \max_{y \in B_1, x \in [0,1]} \left\{ d(x, y) > 0; \sum_{j=1}^p z_j y d^{-z_j}(x, y) = f(x) \right\}$$

Finally, let

$$Y_i = \max \left\{ z_i \min \{V_0, \lambda_m, \log W_m\}, z_i \max \{V_0, \lambda_M, \log W_M\} \right\},$$

and

$$\underline{I} = \sum_{i=1}^N D_i z_i \frac{C_{i,1} e^{z_i \lambda_m} - C_{i,0} e^{z_i V_0}}{e^{Y_i}},$$

$$\bar{I} = \sum_{i=1}^N D_i z_i \frac{C_{i,1} e^{z_i \lambda_M} - C_{i,0} e^{z_i V_0}}{e^{Y_i}}.$$

From these definitions, it is obvious that $\underline{I} \leq 0 \leq \bar{I}$.

Theorem 2 Suppose that $I \in [\underline{I}, \bar{I}]$. Under the hypothesis (2.1)–(2.3), and (2.14)–(2.15), the system (1.1)–(1.2) with boundary conditions (1.3), (1.4), (1.6) has, at least, one solution in $(H^1(0,1) \cap L^\infty(0,1))^{N+1}$ satisfying

$$C_i \geq 0, \quad i = 1, \dots, N,$$

$$\min \{V_0, \lambda_m, \log W_m\} \leq V \leq \max \{V_0, \lambda_M, \log W_M\},$$

$$\begin{aligned}
a) \quad & h_j e^{-z_k \max\{V_0, \lambda_M, \log W_M\}} \leq \sum_{i \in \bar{A}_j} D_i C_i \leq H_j e^{-z_k \min\{V_0, \lambda_m, \log W_m\}}, \\
& \qquad \qquad \qquad z_k > 0 \ (k \in \bar{A}_j), \\
b) \quad & h_j e^{-z_k \min\{V_0, \lambda_m, \log W_m\}} \leq \sum_{i \in \bar{A}_j} D_i C_i \leq H_j e^{-z_k \max\{V_0, \lambda_M, \log W_M\}}, \\
& \qquad \qquad \qquad z_k < 0 \ (k \in \bar{A}_j).
\end{aligned}$$

Proof: Proceeding as in Theorem 1, we must show the existence of solution for the system (2.9), (2.10), satisfying

$$u_i(0) = C_{i,0} e^{z_i V_0}, \quad V(0) = V_0,$$

$$u_i(1) = C_{i,1} e^{z_i V(1)},$$

$$\sum_{i=1}^N D_i z_i e^{-z_i V(1)} \frac{du_i}{dx}(1) = I.$$

Define

$$\begin{aligned}
K_1 = \Big\{ & (u_1, \dots, u_N, V) \in (L^2(0, 1))^{N+1}; u_i \geq 0, i = 1, \dots, N, \\
& h_j \leq \sum_{i \in \bar{A}_j} D_i u_i \leq H_j, j = 1, \dots, p, \\
& \min\{V_0, \lambda_m, \log W_m\} \leq V \leq \max\{V_0, \lambda_M, \log W_M\} \Big\}
\end{aligned}$$

which is clearly a closed convex set of $(L^2(0, 1))^{N+1}$.

As in Theorem 1, we define the mapping

$$T : (u_1, \dots, u_N, V) \longrightarrow (\bar{u}_1, \dots, \bar{u}_N, \bar{V})$$

by (2.12) where we replace b) by

$$\begin{aligned}
-D_i \frac{d}{dx} \left(e^{-z_i V} \frac{d\bar{u}_i}{dx} \right) &= -\bar{u}_k e^{-z_k V} G_k(u_1 e^{-z_1 V}, \dots, u_N e^{-z_N V}, V), \\
& \text{(for some } k \text{ such that } i, k \in \bar{A}_j),
\end{aligned} \tag{2.16}$$

and

$$\bar{u}_i(0) = C_{i,0} e^{z_i V_0}, \quad \bar{V}(0) = V_0, \tag{2.17}$$

$$\bar{u}_i(1) = C_{i,1} e^{z_i \bar{V}(1)}, \tag{2.18}$$

$$\sum_{i=1}^N D_i z_i e^{-z_i \bar{V}(1)} \frac{d\bar{u}_i}{dx}(1) = I. \tag{2.19}$$

Let $\lambda \in [\lambda_m, \lambda_M]$ and consider $(u_1^\lambda, \dots, u_N^\lambda, V^\lambda)$ the solution of (2.12) (with change (2.16)), with $V^\lambda(1) = \lambda$. Looking at the proof of Theorem 1 and taking (2.14) into account, one can easily see that there exists a unique solution $(u_1^\lambda, \dots, u_N^\lambda, V^\lambda)$ that belongs to K_1 .

From (2.12) (with change (2.16)), we get

$$D_i e^{-z_i V} \frac{du_i^\lambda}{dx} = K_i + \int_0^x \omega_i ds, \quad (2.20)$$

where, by using the notations of (2.5)–(2.7),

$$\begin{aligned} \omega_i &= u_i^\lambda e^{-z_i V} G_i(u_1 e^{-z_1 V}, \dots, u_N e^{-z_N V}, V), \quad i \in A_s^+ \cup A_s^- \\ \omega_i &= u_k^\lambda e^{-z_k V} G_k(u_1 e^{-z_1 V}, \dots, u_N e^{-z_N V}, V), \quad i \in A_p^+ \cup A_p^-, \quad z_i = z_k. \end{aligned}$$

(2.19) is equivalent to

$$\sum_{i=1}^N z_i K_i = I.$$

By (2.20),

$$\begin{aligned} D_i (C_{i,1} e^{z_i \lambda} - C_{i,0} e^{z_i V_0}) &= K_i \int_0^1 e^{z_i V} dx + \int_0^1 e^{z_i V} \int_0^x \omega_i d\xi dx \\ &= (K_i + \int_0^1 \omega_i dx) \int_0^1 e^{z_i V} dx - \int_0^1 \omega_i \int_0^x e^{z_i V} d\xi dx. \end{aligned}$$

Then, we can rewrite (2.19) as

$$\sum_{i=1}^N D_i z_i \frac{C_{i,1} e^{z_i \lambda} - C_{i,0} e^{z_i V_0}}{\int_0^1 e^{z_i V} dx} = I \quad (2.21)$$

Since $I \in [\underline{I}, \bar{I}]$, by the monotonicity and continuity of the left-hand side of (2.21) with respect to λ , for each V , there exists one, and only one, $\lambda \in [\lambda_m, \lambda_M]$ such that (2.21) is satisfied. So, there exists a unique solution of (2.12) (with b) replaced by (2.16) and e) by (2.17)–(2.19)). Then T is a well defined operator from K_1 into K_1 .

The mapping $V \rightarrow \lambda$, defined by (2.21), is continuous from

$$\left\{ V \in L^2(0, 1); \min\{V_0, \lambda_m, \log W_m\} \leq V \leq \max\{V_0, \lambda_m, \log W_M\} \right\}$$

into \mathbf{R} . Since the mapping $\lambda \rightarrow (u_1^\lambda, \dots, u_N^\lambda, V^\lambda)$ is clearly continuous from \mathbf{R} into $(H^1(0, 1))^{N+1}$, T is a continuous mapping from $(L^2(0, 1))^{N+1}$ into $(H^1(0, 1))^{N+1}$. We can finish like in Theorem 1. \square

3 Asymptotical behaviour

In the following, K will always denote a constant not depending on ϵ .

We suppose that, for each $\epsilon > 0$, there exists a solution $(C_{1,\epsilon}, \dots, C_{N,\epsilon}, V_\epsilon)$ of (1.1)–(1.5) or (1.1)–(1.4), (1.6) satisfying the following assumptions:

$$C_{i,\epsilon} \geq 0, \quad \text{almost everywhere,} \quad i = 1, \dots, N \quad (3.1)$$

$$\|C_{i,\epsilon}\|_{L^\infty(0,1)} \leq K \quad , \quad i = 1, \dots, N \quad , \quad \|V_\epsilon\|_{L^\infty(0,1)} \leq K \quad , \quad (3.2)$$

$$\sum_{i=1}^N z_i^2 C_{i,\epsilon} \geq \alpha > 0 \quad \text{almost everywhere} \quad (3.3)$$

$$f \in H^1(0,1) \quad , \quad F_i \in C\left(\mathbf{R}_+^N \times \mathbf{R}, \mathbf{R}\right). \quad (3.4)$$

REMARK: If the hypothesis of Theorem 1 or Theorem 2 are satisfied, there are solutions satisfying (3.1)–(3.3). However the following analysis can be performed assuming only (3.1)–(3.3), not necessarily the hypothesis of those Theorems.

To study the convergence as ϵ goes to zero, we state some *a priori* estimates.

For local estimates, we use spaces of the kind of $L_{loc}^2(0,1)$ which is the space of locally square integrable functions in $(0,1)$.

Lemma 1 *If $(C_{1,\epsilon}, \dots, C_{N,\epsilon}, V_\epsilon)$ is a solution of (1.1)–(1.5) or (1.1)–(1.4), (1.6) satisfying (3.1)–(3.4) then:*

$$\sqrt{\epsilon} \left\| \frac{d^2 V_\epsilon}{dx^2} \right\|_{L_{loc}^2(0,1)} \leq K, \quad (3.5)$$

$$\|V_\epsilon\|_{H_{loc}^1(0,1)} \leq K, \quad (3.6)$$

$$\|C_{i,\epsilon}\|_{H_{loc}^1(0,1)} \leq K. \quad (3.7)$$

Proof: Let $T_\epsilon = \sum_{i=1}^N z_i C_{i,\epsilon}$. From (1.1), (1.2) we get

$$-\frac{d^2 T_\epsilon}{dx^2} - \frac{d}{dx} \left(\left(\sum_{i=1}^N z_i^2 C_{i,\epsilon} \right) \frac{dV_\epsilon}{dx} \right) = \sum_{i=1}^N z_i \frac{F_i}{D_i}, \quad (3.8)$$

$$-\epsilon \frac{d^2 V_\epsilon}{dx^2} = T_\epsilon - f. \quad (3.9)$$

By differentiating (3.9) twice and replacing T_ϵ in (3.8), we conclude that

$$\epsilon \frac{d^4 V_\epsilon}{dx^4} - \frac{d}{dx} \left(\left(\sum_{i=1}^N z_i^2 C_{i,\epsilon} \right) \frac{dV_\epsilon}{dx} \right) = \sum_{i=1}^N z_i \frac{F_i}{D_i} + \frac{d^2 f}{dx^2}. \quad (3.10)$$

In order to obtain local estimates for V_ϵ , we take $\phi \in \mathcal{D}(0,1)$ and from (3.10) it follows that

$$\begin{aligned} & \epsilon \frac{d^4(\phi V_\epsilon)}{dx^4} - \frac{d}{dx} \left(\left(\sum_{i=1}^N z_i^2 C_{i,\epsilon} \right) \frac{d}{dx} (\phi V_\epsilon) \right) \\ &= \phi \sum_{i=1}^N z_i \frac{F_i}{D_i} + \phi \frac{d^2 f}{dx^2} + 2\epsilon \frac{d\phi}{dx} \frac{d^3 V_\epsilon}{dx^3} + \epsilon \frac{d^2 \phi}{dx^2} \frac{d^2 V_\epsilon}{dx^2} \\ &+ 2\epsilon \frac{d^2}{dx^2} \left(\frac{d\phi}{dx} \frac{dV_\epsilon}{dx} \right) + \epsilon \frac{d^2}{dx^2} \left(V_\epsilon \frac{d^2 \phi}{dx^2} \right) - \left(\sum_{i=1}^N z_i^2 C_{i,\epsilon} \right) \frac{d\phi}{dx} \frac{dV_\epsilon}{dx} \\ &\quad - \frac{d}{dx} \left(\left(\sum_{i=1}^N z_i^2 C_{i,\epsilon} \right) V_\epsilon \frac{d\phi}{dx} \right) \end{aligned} \quad (3.11)$$

Multiplying (3.11) by ϕV_ϵ and integrating by parts, we get

$$\begin{aligned}
& \epsilon \int_0^1 \left(\frac{d^2(\phi V_\epsilon)}{dx^2} \right)^2 dx + \int_0^1 \left(\sum_{i=1}^N z_i^2 C_{i,\epsilon} \right) \left(\frac{d(\phi V_\epsilon)}{dx} \right)^2 dx \\
&= \int_0^1 \phi^2 V_\epsilon \left(\sum_{i=1}^N \frac{z_i F_i}{D_i} \right) dx - \int_0^1 \phi V_\epsilon \frac{d\phi}{dx} \frac{df}{dx} dx \\
&\quad - \int_0^1 \phi \frac{df}{dx} \frac{d}{dx}(\phi V_\epsilon) dx + 2 \int_0^1 (T_\epsilon - f)(\phi V_\epsilon) \frac{d^2\phi}{dx^2} dx \\
&\quad + 2 \int_0^1 (T_\epsilon - f) \frac{d\phi}{dx} \frac{d(\phi V_\epsilon)}{dx} dx - \int_0^1 \frac{d^2\phi}{dx^2} (\phi V_\epsilon) (T_\epsilon - f) dx \\
&\quad + 2\epsilon \int_0^1 V_\epsilon \frac{d^3\phi}{dx^3} \frac{d}{dx}(\phi V_\epsilon) dx + 2\epsilon \int_0^1 V_\epsilon \frac{d^2\phi}{dx^2} \frac{d^2(\phi V_\epsilon)}{dx^2} dx \\
&\quad + 2 \int_0^1 (T_\epsilon - f) \frac{d\phi}{dx} \frac{d(\phi V_\epsilon)}{dx} dx + \epsilon \int_0^1 V_\epsilon \frac{d^2\phi}{dx^2} \frac{d^2}{dx^2}(\phi V_\epsilon) dx \\
&\quad + \int_0^1 \left(\sum_{i=1}^N z_i^2 C_{i,\epsilon} \right) \left| \frac{d\phi}{dx} \right|^2 V_\epsilon^2 dx
\end{aligned}$$

Then

$$\begin{aligned}
& \epsilon \int_0^1 \left| \frac{d^2}{dx^2}(\phi V_\epsilon) \right|^2 dx + \alpha \int_0^1 \left| \frac{d}{dx}(\phi V_\epsilon) \right|^2 dx \leq K + K \left\| \frac{d}{dx}(\phi V_\epsilon) \right\|_{L^2(0,1)} \\
& \quad + K\epsilon \left\| \frac{d^2}{dx^2}(\phi V_\epsilon) \right\|_{L^2(0,1)},
\end{aligned}$$

which implies

$$\epsilon \int_0^1 \left| \frac{d^2}{dx^2}(\phi V_\epsilon) \right|^2 dx + \alpha \int_0^1 \left| \frac{d}{dx}(\phi V_\epsilon) \right|^2 dx \leq K$$

and (3.5), (3.6) follow.

By use of similar arguments, from (1.1) one gets (3.7). \square

Lemma 2 *The functions $u_{i,\epsilon}$, defined through (2.8) are bounded in $H^1(0,1)$ by a constant not depending on ϵ .*

Proof: Let $g_{i,\epsilon}$ be the linear function satisfying

$$g_{i,\epsilon}(0) = u_{i,\epsilon}(0) = C_{i,0} e^{z_i V_0}, \quad g_{i,\epsilon}(1) = C_{i,1} e^{z_i V_\epsilon(1)}$$

By (3.2), $\left\| \frac{dg_{i,\epsilon}}{dx} \right\|_{L^\infty(0,1)} \leq K$. Then, from (2.9),

$$\int_0^1 e^{-z_i V_\epsilon} \left(\frac{d(u_{i,\epsilon} - g_{i,\epsilon})}{dx} \right)^2 dx = \int_0^1 \frac{F_i}{D_i} (u_{i,\epsilon} - g_{i,\epsilon}) dx$$

$$- \int_0^1 e^{-z_i V_\epsilon} \frac{dg_{i,\epsilon}}{dx} (u_{i,\epsilon} - g_{i,\epsilon}) dx$$

Hence, by the uniform boundedness of V_ϵ , $u_{i,\epsilon}$ is bounded in $H^1(0, 1)$. \square

Let d_0 and d_1 be, respectively, the unique positive solution of each of the following equations

$$\sum_{i=1}^N z_i C_{i,0} d_0^{z_i} = f(0), \quad (3.12)$$

$$\sum_{i=1}^N z_i C_{i,1} d_1^{z_i} = f(1). \quad (3.13)$$

Let us consider the reduced system, derived from (1.1), (1.2) for $\epsilon = 0$,

$$- D_i \frac{d}{dx} \left(\frac{dC_i}{dx} + z_i C_i \frac{dV}{dx} \right) = F_i(C_1, \dots, C_N, V), \quad i = 1, \dots, N \quad (3.14)$$

$$\sum_{i=1}^N z_i C_i = f \quad (3.15)$$

jointly with the boundary conditions

$$C_i(0) = d_0^{z_i} C_{i,0} \quad , \quad C_i(1) = d_1^{z_i} C_{i,1} \quad , \quad V(0) = V_0 - \log d_0 \quad (3.16)$$

and the imposed potential condition

$$V(1) = V_1 - \log d_1, \quad (3.17)$$

or the current condition,

$$\sum_{i=1}^N D_i z_i \left(\frac{dC_i}{dx} + z_i C_i \frac{dV}{dx} \right) (1) = I \quad (3.18)$$

We remark that $\log d_0$ and $\log d_1$ are generalisations of Donnan potential to multi-ionic and multivalence cases. This Donnan potential, classical in biophysical litterature, gives the jump of potential at the boundary of the membrane due to the presence of fixed charges. Here, we derive it with no other physical assumption than electroneutrality. Furthermore, d_0 and d_1 only depend on the values of the concentrations and on the fixed charge density at the boundary. So, they do not depend on the kind of boundary conditions for the potential neither on the reaction rate.

Next Theorem shows that a limit of solutions of the initial system is a solution of the reduced one verifying boundary conditions of the same kind.

Theorem 3 *Under the hypothesis (3.1)–(3.4), any sequence of solutions of (1.1)–(1.2), $(C_{1,\epsilon}, \dots, C_{N,\epsilon}, V_\epsilon)$, satisfying boundary conditions (1.3)–(1.5) (respectively*

(1.3), (1.4), (1.6)) has, as a limit point when $\epsilon \rightarrow 0$, a solution (C_1, \dots, C_N, V) of (3.14)–(3.17) (respectively (3.14)–(3.16), (3.18)), in the following sense:

$$\begin{cases} C_{i,\epsilon_K} \longrightarrow C_i & , \quad \text{in } L^\infty(0,1) \text{ weak-}^* \text{ and} \\ & L^2_{loc}(0,1), \quad i = 1, \dots, N \\ V_{\epsilon_K} \longrightarrow V & , \quad \text{in } L^\infty(0,1) \text{ weak-}^* \text{ and} \\ & L^2_{loc}(0,1) \end{cases} \quad (3.19)$$

and

$$u_{i,\epsilon_k} \longrightarrow u_i = C_i e^{z_i V} \quad \text{in } H^1(0,1) \quad , \quad i = 1, \dots, N \quad , \quad (3.20)$$

where $(C_{1,\epsilon_k}, \dots, C_{N,\epsilon_k}, V_{\epsilon_k})$ is a subsequence of $(C_{1,\epsilon}, \dots, C_{N,\epsilon}, V_\epsilon)$.

Furthermore, in the case of the current condition (3.18), the condition (3.17) is asymptotically satisfied :

$$V_\epsilon(1) \rightarrow V(1) + \log d_1 \quad .$$

Proof: By (3.2), let the limit of a subsequence $(C_{1,\epsilon_k}, \dots, C_{N,\epsilon_k}, V_{\epsilon_k})$, as $\epsilon_k \rightarrow 0$, for the weak $-^*$ topology in $L^\infty(0,1)$, be (C_1, \dots, C_N, V) .

Let Ω be an open subset of $(0,1)$ such that $\bar{\Omega} \subset (0,1)$. By Lemma 1, there exists a further subsequence, still noted $(C_{1,\epsilon_k}, \dots, C_{N,\epsilon_k}, V_{\epsilon_k})$, such that

$$V_{\epsilon_k} \rightarrow V \quad \text{weakly in } H^1(\Omega) \text{ and uniformly in } \Omega \quad (3.21)$$

$$T_{\epsilon_k} = -\epsilon \frac{d^2 V_{\epsilon_k}}{dx^2} + f \longrightarrow f \quad \text{in } L^2(\Omega),$$

so

$$\sum_{i=1}^N z_i C_i = f \quad \text{in } \Omega$$

By (3.7), we conclude that

$$C_{i,\epsilon_k} \longrightarrow C_i, \quad \text{weakly in } H^1(\Omega) \text{ and uniformly in } \Omega. \quad (3.22)$$

In order to prove that (C_1, \dots, C_N, V) verifies (3.14), take any $\phi \in \mathcal{D}(\Omega)$. By (1.1) we get

$$\begin{aligned} & -D_i \int_{\Omega} C_{i,\epsilon_k} \frac{d^2 \phi}{dx^2} dx + D_i \int_{\Omega} z_i C_{i,\epsilon_k} \frac{dV_{\epsilon_k}}{dx} \frac{d\phi}{dx} dx \\ & = \int_{\Omega} F_i(C_{1,\epsilon_k}, \dots, C_{N,\epsilon_k}, V) \phi dx \end{aligned} \quad (3.23)$$

Taking the limit as ϵ_k goes to zero in (3.23), we obtain (3.14) restricted to Ω . Since this is true for any Ω , (C_1, \dots, C_N, V) is a solution of (3.14), (3.15).

By Lemma 2,

$$u_{i,\epsilon_k} \longrightarrow u \quad \text{weakly in } H^1(0,1)$$

and, by (3.21), (3.22),

$$u_{i,\epsilon_k} = C_{i,\epsilon_k} e^{z_i V_{\epsilon_k}} \longrightarrow C_i e^{z_i V}$$

uniformly in every compact of $(0,1)$, so

$$u_i = C_i e^{z_i V}.$$

On the other hand, from (1.1) we get

$$\begin{aligned} -D_i \left(\frac{dC_{i,\epsilon_k}}{dx} + z_i C_{i,\epsilon_k} \frac{dV_{\epsilon_k}}{dx} \right) &= -D_i e^{-z_i V_{\epsilon_k}} \frac{du_{i,\epsilon_k}}{dx} \\ &= k_{i,\epsilon_k} + \int_0^x F_i(C_{i,\epsilon_k}, \dots, C_{N,\epsilon_k}, V) ds, \end{aligned} \quad (3.24)$$

so

$$\begin{aligned} u_{i,\epsilon_k}(1) - C_{i,0} e^{z_i V_0} \\ = -\frac{k_{i,\epsilon_k}}{D_i} \int_0^1 e^{-z_i V_{\epsilon_k}} dx - \int_0^1 \frac{e^{-z_i V_{\epsilon_k}}}{D_i} \int_0^x F_i ds dx \end{aligned}$$

Then, by (3.2), k_{i,ϵ_k} is bounded.

By using (1.1) and (3.24) we obtain

$$\frac{dC_{i,\epsilon_k}}{dx} + z_i C_{i,\epsilon_k} \frac{dV_{\epsilon_k}}{dx} \longrightarrow g_i \text{ weakly in } H^1(0,1), \quad (3.25)$$

so, uniformly.

If $\phi \in \mathcal{D}(0,1)$,

$$\begin{aligned} - \int_0^1 C_{i,\epsilon_k} \frac{d\phi}{dx} dx + z_i \int_0^1 C_{i,\epsilon_k} \frac{dV_{\epsilon_k}}{dx} \phi dx \\ \longrightarrow \int_0^1 \left(-C_i \frac{d\phi}{dx} + z_i C_i \frac{dV}{dx} \phi \right) dx, \end{aligned}$$

therefore

$$g_i = \frac{dC_i}{dx} + z_i C_i \frac{dV}{dx} \quad (3.26)$$

and, by Lebesgue theorem, we conclude that

$$\left\| \left(\frac{dC_i}{dx} + z_i C_i \frac{dV}{dx} \right) e^{z_i V} - \left(\frac{dC_{i,\epsilon_k}}{dx} + z_i C_{i,\epsilon_k} \frac{dV_{\epsilon_k}}{dx} \right) e^{z_i V_{\epsilon_k}} \right\|^2 \longrightarrow 0$$

which proves (3.20).

For the boundary conditions we have, by use of (3.20), that

$$C_{i,\epsilon_k}^{z_j} C_{j,\epsilon_k}^{-z_i} = u_{i,\epsilon_k}^{z_j} u_{j,\epsilon_k}^{-z_i} \longrightarrow C_i^{z_j} C_j^{-z_i} \text{ uniformly in } [0,1],$$

so

$$C_i^{z_j}(0) C_j^{-z_i}(0) = C_{i,0}^{z_j} C_{j,0}^{-z_i}, \quad C_i^{z_j}(1) C_j^{-z_i}(1) = C_{i,1}^{z_j} C_{j,1}^{-z_i} \quad (3.27)$$

for any $1 \leq i, j \leq N$.

From (3.27) we get the first part of (3.16).

By (3.20),

$$u_i(0) = C_i(0) e^{z_i V(0)} = C_{i,0} e^{z_i V_0}$$

which proves (3.16).

If V_ϵ satisfies $V_\epsilon(1) = V_1$, in the same way, one shows (3.17).

If the current condition is satisfied, from (3.25), (3.26) and (1.6) we get (3.18).

Take i such that $C_{i,1} \neq 0$. Then, by (3.20),

$$C_{i,1} e^{z_i V_\epsilon(1)} \longrightarrow d_1^{z_i} C_{i,1} e^{z_i V(1)},$$

that is

$$V_\epsilon(1) - V(1) - \log d_1 \rightarrow 0 \quad \square$$

Lemma 3 *If f is Lipschitz continuous, $C_i, V \in L^\infty(0,1)$, $C_i \geq 0$, $i = 1, \dots, N$, $\sum_{i=1}^N z_i^2 C_i(x) \geq \alpha > 0$, $\forall x \in [0,1]$ and (C_1, \dots, C_N, V) is a solution of (3.14), (3.15) then C_i, V , $i = 1, \dots, N$ are Lipschitz continuous.*

Proof: From (3.14), (3.15) we get

$$\frac{d}{dx} \left(\frac{df}{dx} + \left(\sum_{i=1}^N z_i^2 C_i \right) \frac{dV}{dx} \right) = - \sum_{i=1}^N z_i \frac{F_i(C_1, \dots, C_N, V)}{D_i}$$

so

$$\frac{df}{dx} + \left(\sum_{i=1}^N z_i^2 C_i \right) \frac{dV}{dx}$$

is an $L^\infty(0,1)$ function and consequently $\frac{dV}{dx}$ is an $L^\infty(0,1)$ function.

On the same way, from (3.14) and the L^∞ boundedness of $\frac{dV}{dx}$, we can show the L^∞ boundedness of $\frac{dC_i}{dx}$. \square

4 Calculation of the Correctors

In this section, we will look for the correctors which describe the boundary layers, where the electroneutrality is not satisfied. We use the framework developed by Lions [8] for the linear case. The correctors will be defined in such a way that joining them to a solution of the initial problem, we obtain uniform convergence to a solution of the reduced problem.

Let f be Lipschitz continuous, and $\phi_\epsilon^0(x) = \Phi^0\left(\frac{x}{\sqrt{\epsilon}}\right)$ be the solution of the equation

$$-\epsilon \frac{d^2 \phi_\epsilon^0}{dx^2} = \sum_{i=1}^N z_i C_{i,0} d_0^{z_i} e^{-z_i \phi_\epsilon^0} - f(0), \quad (4.1)$$

satisfying boundary conditions

$$\phi_\epsilon^0(0) = \log d_0, \quad \phi_\epsilon^0(+\infty) = 0. \quad (4.2)$$

By a result of Fife [3] as it is presented by Markowich [11] (Lemma 4.5.1), Φ^0 is a smooth monotone function which, together with its derivative $\frac{d\Phi^0}{dy}$ decays exponentially to zero as $y \rightarrow +\infty$. So ϕ_ϵ^0 is smooth, monotone and, for each $x \neq 0$, $\phi_\epsilon^0(x)$ and $\frac{d\phi_\epsilon^0}{dx}(x)$ decay exponentially to zero as ϵ goes to zero.

Denote by $\phi_\epsilon^1(x) = \Phi^1\left(\frac{1-x}{\sqrt{\epsilon}}\right)$ the solution of the equation

$$-\epsilon \frac{d^2 \phi_\epsilon^1}{dx^2} = \sum_{i=1}^N z_i C_{i,1} d_1^{z_i} e^{-z_i \phi_\epsilon^1} - f(1), \quad (4.3)$$

satisfying

$$\phi_\epsilon^1(-\infty) = 0, \quad \phi_\epsilon^1(1) = \log d_1 \quad (4.4)$$

It is obvious that ϕ_ϵ^1 satisfies similar properties to ϕ_ϵ^0 .

Let M be a twice continuously differentiable nonnegative function such that

$$M(0) = 1, \quad M(x) = 0, \quad \forall x \geq \frac{1}{2}.$$

Taking

$$\phi_\epsilon(x) = M(x) \phi_\epsilon^0(x) + M(1-x) \phi_\epsilon^1(x), \quad (4.5)$$

ϕ_ϵ satisfies

$$-\epsilon \frac{d^2 \phi_\epsilon}{dx^2}(x) = \sum_{i=1}^N z_i C_i(x) e^{-z_i \phi_\epsilon(x)} - f(x) + g_\epsilon(x), \quad (4.6)$$

$$\phi_\epsilon(0) = \phi_\epsilon^0(0), \quad \phi_\epsilon(1) = \phi_\epsilon^1(1), \quad (4.7)$$

where

$$g_\epsilon(x) = h_\epsilon(x) + m_\epsilon(x), \quad (4.8)$$

with

$$\begin{aligned} h_\epsilon(x) = & - \sum_{i=1}^N z_i C_i(x) e^{-z_i \phi_\epsilon(x)} \\ & + f(x) + M(x) \sum_{i=1}^N z_i C_i(0) e^{-z_i \phi_\epsilon^0(x)} - M(x) f(0) \\ & + M(1-x) \sum_{i=1}^N z_i C_i(1) e^{-z_i \phi_\epsilon^1(x)} - M(1-x) f(1) \end{aligned} \quad (4.9)$$

and

$$\begin{aligned} m_\epsilon(x) = & -2\epsilon \frac{dM}{dx}(x) \frac{d\phi_\epsilon^0}{dx}(x) - \epsilon \frac{d^2 M}{dx^2}(x) \phi_\epsilon^0(x) \\ & + 2\epsilon \frac{dM}{dx}(1-x) \frac{d\phi_\epsilon^1}{dx}(x) - \epsilon \frac{d^2 M}{dx^2}(1-x) \phi_\epsilon^1(x). \end{aligned} \quad (4.10)$$

Lemma 4 Let g_ϵ be given by (4.8), (4.9), (4.10). Then

$$\|g_\epsilon\|_{L^2(0,1)} \leq k \epsilon^{\frac{3}{4}},$$

where k is a constant not depending on ϵ .

Proof: For $0 \leq x \leq \frac{1}{2}$ we have

$$\begin{aligned} h_\epsilon(x) &= - \sum_{i=1}^N z_i C_i(x) e^{-z_i M(x) \phi_\epsilon^0(x)} \\ &\quad + f(x) + M(x) \sum_{i=1}^N z_i C_i(0) e^{-z_i \phi_\epsilon^0(x)} - M(x) f(0) \\ &= - \sum_{i=1}^N z_i (C_i(x) - M(x) C_i(0)) (e^{-z_i M(x) \phi_\epsilon^0(x)} - 1) \\ &\quad - \sum_{i=1}^N z_i M(x) C_i(0) (e^{-z_i M(x) \phi_\epsilon^0(x)} - e^{-z_i \phi_\epsilon^0(x)}) \end{aligned}$$

Then, by Lemma 3, the continuous differentiability of M and the boundedness of ϕ_ϵ^0 ,

$$|h_\epsilon(x)| \leq k x \phi_\epsilon^0(x)$$

Performing the change of variable $y = \frac{x}{\sqrt{\epsilon}}$ we get, by the Fife Lemma,

$$\begin{aligned} \int_0^{\frac{1}{2}} |h_\epsilon(x)|^2 dx &\leq k \int_0^{\frac{1}{2}} (x \phi_\epsilon^0(x))^2 dx \\ &= k \epsilon^{\frac{3}{2}} \int_0^{(2\epsilon)^{-\frac{1}{2}}} (y \Phi^0(y))^2 dy \leq k \epsilon^{\frac{3}{2}} \int_0^{+\infty} (y \Phi^0(y))^2 dy \leq k \epsilon^{\frac{3}{2}}. \end{aligned}$$

In the same way, we can show

$$\int_{\frac{1}{2}}^1 |h_\epsilon(x)|^2 dx \leq k \epsilon^{\frac{3}{2}}.$$

Now, we consider the term m_ϵ . By the boundedness of $\frac{d^2 M}{dx^2} \phi_\epsilon^0$ and $\frac{d^2 M}{dx^2} \phi_\epsilon^1$, the inequality is satisfied for $\epsilon \frac{d^2 M}{dx^2} \phi_\epsilon^0$ and $\epsilon \frac{d^2 M}{dx^2} \phi_\epsilon^1$.

Again by the Fife Lemma:

$$\int_0^1 \left| \frac{d\phi_\epsilon^0}{dx} \right|^2 dx = \epsilon^{-\frac{1}{2}} \int_0^{\epsilon^{-\frac{1}{2}}} \left| \frac{d}{dy} \Phi^0(y) \right|^2 dy \leq \epsilon^{-\frac{1}{2}} \int_0^{+\infty} \left| \frac{d}{dy} \Phi^0(y) \right|^2 dy,$$

so,

$$\left\| \epsilon \frac{d\phi_\epsilon^0}{dx} \right\|_{L^2(0,1)} \leq k \epsilon^{\frac{3}{4}}.$$

The proof for the remaining term is similar. \square

As in [5], we can prove:

Lemma 5 *The following estimates for the first derivatives of ϕ_ϵ^0 and ϕ_ϵ^1 hold:*

$$\left| \frac{d\phi_\epsilon^0}{dx}(x) \right| \leq \frac{k}{x}, \quad \forall x > 0,$$

$$\left| \frac{d\phi_\epsilon^1}{dx}(x) \right| \leq \frac{k}{1-x}, \quad \forall x < 1,$$

where k is a constant not depending on ϵ .

Finally we show that the functions ϕ_ϵ , defined by (4.1)–(4.5), are correctors for the system (1.1),(1.2) with boundary conditions (1.3)–(1.5) or (1.3),(1.4),(1.6).

Theorem 4 *Let $(C_{1,\epsilon_k}, \dots, C_{N,\epsilon_k}, V_{\epsilon_k})$ be a sequence satisfying the conditions of Theorem 3. Then*

- i) $V_{\epsilon_k} - V - \phi_{\epsilon_k} \rightarrow 0$ in $H^1(0,1)$ and uniformly;
- ii) $C_{i,\epsilon_k} e^{z_i \phi_{\epsilon_k}} \rightarrow C_i$ in $H^1(0,1)$ and uniformly.

Proof: For simplicity, we use the index ϵ instead for ϵ_k .

Assertion i) implies ii). In fact, by Theorem 3, Lemma 3 and the L^∞ -boundedness of $u_{i,\epsilon}$, V_ϵ and ϕ_ϵ , we have

$$\begin{aligned} C_{i,\epsilon} e^{z_i \phi_\epsilon} &= u_{i,\epsilon} e^{-z_i(V_\epsilon - \phi_\epsilon)} \\ &\rightarrow C_i e^{z_i V} e^{-z_i V} \quad \text{in } H^1(0,1). \end{aligned}$$

So, it remains to prove i).

Let, for each ϵ , ψ_ϵ be the solution of

$$-\epsilon \frac{d^2 \psi_\epsilon}{dx^2} = \sum_{i=1}^N z_i u_{i,\epsilon} e^{-z_i(V + \psi_\epsilon)} - f \quad (4.11)$$

$$\psi_\epsilon(0) = \log d_0, \quad \psi_\epsilon(1) = V_\epsilon(1) - V(1). \quad (4.12)$$

It is easy to show that ψ_ϵ is L^∞ -bounded (the bound not depending on ϵ).

Taking $\omega_\epsilon = V_\epsilon - V - \psi_\epsilon$, we get

$$-\epsilon \frac{d^2 \omega_\epsilon}{dx^2} - \sum_{i=1}^N z_i C_{i,\epsilon} (1 - e^{z_i \omega_\epsilon}) = \epsilon \frac{d^2 V}{dx^2}, \quad (4.13)$$

$$\omega_\epsilon(0) = \omega_\epsilon(1) = 0. \quad (4.14)$$

Multiplying (4.13) by ω_ϵ and integrating by parts,

$$\epsilon \left\| \frac{d\omega_\epsilon}{dx} \right\|_{L^2(0,1)}^2 + \int_0^1 \sum_{i=1}^N z_i C_{i,\epsilon} (e^{z_i \omega_\epsilon} - 1) \omega_\epsilon dx = -\epsilon \int_0^1 \frac{dV}{dx} \frac{d\omega_\epsilon}{dx} dx.$$

Then, by the boundedness of ω_ϵ ,

$$\begin{aligned} & \epsilon \left\| \frac{d\omega_\epsilon}{dx} \right\|_{L^2(0,1)}^2 + K \int_0^1 \left(\sum_{i=1}^N z_i^2 C_{i,\epsilon} \right) \omega_\epsilon^2 dx \\ & \leq -\epsilon \int_0^1 \frac{dV}{dx} \frac{d\omega_\epsilon}{dx} dx \leq \epsilon \left\| \frac{dV}{dx} \right\|_{L^2(0,1)} \left\| \frac{d\omega_\epsilon}{dx} \right\|_{L^2(0,1)}. \end{aligned} \quad (4.15)$$

Therefore

$$\|\omega_\epsilon\|_{L^2(0,1)} \leq K \epsilon^{\frac{1}{2}} \quad \text{and} \quad \left\| \frac{d\omega_\epsilon}{dx} \right\|_{L^2(0,1)} \leq K,$$

that is

$$\omega_\epsilon \longrightarrow 0 \quad \text{weakly in } H^1(0,1). \quad (4.16)$$

By (4.15), (4.16),

$$\left\| \frac{d\omega_\epsilon}{dx} \right\|_{L^2(0,1)}^2 \leq - \int_0^1 \frac{dV}{dx} \frac{d\omega_\epsilon}{dx} dx \longrightarrow 0$$

so,

$$\omega_\epsilon \rightarrow 0 \quad \text{in } H^1(0,1). \quad (4.17)$$

Taking $\xi_\epsilon = \phi_\epsilon - \psi_\epsilon$, ξ_ϵ satisfies the equation

$$\begin{aligned} & -\epsilon \frac{d^2 \xi_\epsilon}{dx^2} + \sum_{i=1}^N z_i e^{-z_i(V+\phi_\epsilon)} u_{i,\epsilon} (e^{z_i \xi_\epsilon} - 1) \\ & = \sum_{i=1}^N z_i e^{-z_i(V+\phi_\epsilon)} (u_i - u_{i,\epsilon}) + g_\epsilon \end{aligned} \quad (4.18)$$

Define $\bar{\xi}_\epsilon$ by

$$\begin{aligned} & \sum_{i=1}^N z_i u_{i,\epsilon} e^{-z_i(V+\phi_\epsilon)} (e^{z_i \bar{\xi}_\epsilon} - 1) \\ & = \sum_{i=1}^N z_i (u_i - u_{i,\epsilon}) e^{-z_i(V+\phi_\epsilon)} \end{aligned} \quad (4.19)$$

Since the left-hand side of (4.19) is strictly monotone with respect to $\bar{\xi}_\epsilon$ and the right-hand side is uniformly bounded, $\bar{\xi}_\epsilon$ is uniformly bounded. Then

$$\bar{\xi}_\epsilon \sum_{i=1}^N z_i^2 C_{i,\epsilon} e^{z_i(V_\epsilon - V - \phi_\epsilon)} e^{z_i \bar{\xi}_\epsilon^*} = \sum_{i=1}^N z_i (u_i - u_{i,\epsilon}) e^{-z_i(V+\phi_\epsilon)}, \quad (4.20)$$

where, for each $x \in]0, 1[$, $\bar{\xi}_\epsilon^* \in]0, \bar{\xi}_\epsilon(x) \cup]\bar{\xi}_\epsilon(x), 0[$.

By Theorem 3, the right-hand side of (4.20) converges uniformly to zero, so

$$\bar{\xi}_\epsilon \rightarrow 0 \quad \text{uniformly}. \quad (4.21)$$

Differentiating (4.19), we obtain as a coefficient for $\frac{d\bar{\xi}_\epsilon}{dx}$:

$$\sum_{i=1}^N z_i^2 C_{i,\epsilon} e^{z_i(V-\phi_\epsilon+\bar{\xi}_\epsilon)}$$

which has a positive lower bound.

It is obvious that the remaining terms of that derivative converge to zero in the $L^2(0, 1)$ norm, except, eventually, those where $\frac{d\phi_\epsilon}{dx}$ appears.

First, let $0 \leq x \leq \frac{1}{2}$.

$$\begin{aligned} & z_i^2(u_i - u_{i,\epsilon}) e^{-z_i(V+\phi_\epsilon)} \frac{d\phi_\epsilon}{dx} \\ &= z_i^2(u_i - u_{i,\epsilon}) e^{-z_i(V+\phi_\epsilon)} \left(M \frac{d\phi_\epsilon^0}{dx} + \phi_\epsilon^0 \frac{dM}{dx} \right). \end{aligned} \quad (4.22)$$

It is obvious that

$$z_i^2(u_{i,\epsilon} - u_i) e^{-z_i(V+\phi_\epsilon)} \phi_\epsilon^0 \frac{dM}{dx} \longrightarrow 0 \text{ uniformly.}$$

By (3.24), $\frac{du_{i,\epsilon}}{dx}$ is uniformly bounded, so by Lemma 3, $\frac{d(u_{i,\epsilon}-u_i)}{dx}$ is also uniformly bounded.

Then, noting that $u_{i,\epsilon}(0) - u_i(0) = 0$,

$$|u_{i,\epsilon}(x) - u_i(x)| \leq kx, \quad (4.23)$$

where k is a constant not depending on ϵ .

As a consequence of Lemma 5, we get

$$\left| \frac{d\phi_\epsilon^0}{dx}(x) (u_{i,\epsilon}(x) - u_i(x)) \right| \leq k, \quad \forall x \in [0, 1/2].$$

Then, applying Lebesgue theorem

$$\int_0^{\frac{1}{2}} \left(\frac{d\phi_\epsilon^0}{dx}(u_{i,\epsilon} - u_i) \right)^2 dx \longrightarrow 0,$$

so, by (4.22),

$$\int_0^{\frac{1}{2}} \left(z_i^2(u_{i,\epsilon} - u_i) e^{-z_i(V+\phi_\epsilon)} \frac{d\phi_\epsilon}{dx} \right)^2 dx \longrightarrow 0$$

Since, for each $x \in (0, 1)$, all the summands of the left-hand side of (4.19) have the same sign, from (4.19) and (4.23) we get

$$|z_i u_{i,\epsilon} e^{-z_i(V+\phi_\epsilon)} (e^{z_i \bar{\xi}_\epsilon} - 1)| \leq kx, \quad i = 1, \dots, N$$

Then

$$\int_0^{\frac{1}{2}} \left(z_i^2 u_{i,\epsilon} e^{-z_i(V+\phi_\epsilon)} (e^{z_i \bar{\xi}_\epsilon} - 1) \frac{d\phi_\epsilon}{dx} \right)^2 dx \longrightarrow 0,$$

therefore

$$\int_0^{\frac{1}{2}} \left(\frac{d\bar{\xi}_\epsilon}{dx} \right)^2 dx \longrightarrow 0. \quad (4.24)$$

For $\frac{1}{2} \leq x \leq 1$, in the case of imposed potential (1.5) the proof is similar. In the case of current condition (1.6) let us re-write (4.19) as

$$\begin{aligned} & \sum_{i=1}^N z_i u_{i,\epsilon} e^{-z_i(V+\phi_\epsilon)} \left(e^{z_i \bar{\xi}_\epsilon} - 1 - A_{i,\epsilon} \right) \\ &= \sum_{i=1}^N z_i (u_i - u_{i,\epsilon} - A_{i,\epsilon} u_{i,\epsilon}) e^{-z_i(V+\phi_\epsilon)} \end{aligned} \quad (4.25)$$

where

$$A_{i,\epsilon} = e^{z_i(V(1)+\log d_1 - V_\epsilon(1))} - 1.$$

By Theorem 3, $A_{i,\epsilon} \rightarrow 0$ as $\epsilon \rightarrow 0$.

Remarking that $u_i(1) - u_{i,\epsilon}(1) - A_{i,\epsilon} u_{i,\epsilon}(1) = 0$ and applying the same reasoning, we can show, as before,

$$\int_{\frac{1}{2}}^1 \left(\frac{d\bar{\xi}_\epsilon}{dx} \right)^2 dx \longrightarrow 0 \quad (4.26)$$

By (4.21), (4.24) and (4.26),

$$\bar{\xi}_\epsilon \rightarrow 0 \quad \text{in } H^1(0,1). \quad (4.27)$$

By (4.18) and (4.19) we get

$$\begin{aligned} & -\epsilon \frac{d^2(\xi_\epsilon - \bar{\xi}_\epsilon)}{dx^2} + \sum_{i=1}^N z_i u_{i,\epsilon} e^{-z_i(V+\phi_\epsilon)} e^{z_i \bar{\xi}_\epsilon} \left(e^{z_i(\xi_\epsilon - \bar{\xi}_\epsilon)} - 1 \right) \\ &= \epsilon \frac{d^2 \bar{\xi}_\epsilon}{dx^2} + g_\epsilon \end{aligned} \quad (4.28)$$

From (4.2), (4.4), (4.12) and by using (4.25), we obtain

$$\xi_\epsilon(0) - \bar{\xi}_\epsilon(0) = \xi_\epsilon(1) - \bar{\xi}_\epsilon(1) = 0$$

Multiplying (4.28) by $\xi_\epsilon - \bar{\xi}_\epsilon$ and integrating by parts, we get

$$\begin{aligned} & \epsilon \left\| \frac{d(\xi_\epsilon - \bar{\xi}_\epsilon)}{dx} \right\|_{L^2(0,1)}^2 + k \|\xi_\epsilon - \bar{\xi}_\epsilon\|_{L^2(0,1)}^2 \\ & \leq \epsilon \left\| \frac{d\bar{\xi}_\epsilon}{dx} \right\|_{L^2(0,1)} \left\| \frac{d(\xi_\epsilon - \bar{\xi}_\epsilon)}{dx} \right\|_{L^2(0,1)} + C \epsilon^{\frac{3}{4}} \|\xi_\epsilon - \bar{\xi}_\epsilon\|_{L^2(0,1)}. \end{aligned}$$

Then

$$\|\xi_\epsilon - \bar{\xi}_\epsilon\|_{L^2(0,1)} \leq k \epsilon^{\frac{1}{2}}$$

and

$$\frac{d}{dx} (\xi_\epsilon - \bar{\xi}_\epsilon) \longrightarrow 0 \quad \text{in } L^2(0, 1),$$

that is

$$\xi_\epsilon - \bar{\xi}_\epsilon \longrightarrow 0 \quad \text{in } H^1(0, 1) \quad (4.29)$$

From (4.17), (4.27) and (4.29), the proof is finished. \square

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