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On generalized Poisson–Nernst–Planck equations with inhomogeneous boundary conditions: a-priori estimates and stability

V. A. Kovtunenko[a,b], **A. V. Zubkova**[a*]

In this paper we consider the strongly nonlinear Nernst–Planck equations coupled with the quasi-linear Poisson equation under inhomogeneous, moreover, nonlinear boundary conditions. This system describes joint multi-component electrokinetics in a pore phase. The system is supplemented by the force balance and by the volume and positivity constraints. We establish well-posedness of the problem in the variational setting. Namely, we prove the existence theorem supported by the energy and the entropy a-priori estimates, and we provide the Lyapunov stability of the solution as well as its uniqueness in special cases. Copyright © 2009 John Wiley & Sons, Ltd.

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1. Introduction

In this paper existence, uniqueness, and stability of a weak solution to a nonlinear time-dependent multi-component system of PDEs are investigated.

We consider the generalized Poisson–Nernst–Planck (PNP) system, which consists of $n \geqslant 2$ joint diffusion equations for n species, one electrostatic equation, and the force balance as a consequence of the Navier–Stockes equations. From physical laws, dual entropy variables (the pressure and the quasi-Fermi electro-chemical potentials) enter the governing relations, which, however, can be excluded from the mathematical formulation. The system is complemented by mixed boundary conditions. On the one part the Dirichlet conditions are given, while on the another part we set the nonlinear inhomogeneous conditions of Neumann type for the diffusion fluxes and the Robin condition for the electrostatic potential. These conditions describe electro–chemical reactions at the boundary.

Investigation of the PNP system is motivated by models of reaction–diffusion phenomena in biology and electrochemistry, see [13, 16, 20, 25], and for general thermodynamic backgrounds we refer to [6, 21]. In particular, one of important applications of such modeling to Lithium Ion batteries is described in [3, 19]. Generalizations of the classic PNP equations were suggested in [8, 9, 14]. For homogenization of reaction–diffusion models we refer to [1, 11, 24], and to [2, 14] for suitable numerical

[a] *Institute for Mathematics and Scientific Computing, Karl–Franzens University of Graz, NAWI Graz, Heinrichstraße 36, 8010 Graz, Austria*
[b] *Lavrentyev Institute of Hydrodynamics, Siberian Division of the Russian Academy of Sciences, 630090 Novosibirsk, Russia; e-mail: victor.kovtunenko@uni-graz.at*
[*] *Correspondence to: Institute for Mathematics and Scientific Computing, Karl–Franzens University of Graz, NAWI Graz, Heinrichstraße 36, 8010 Graz, Austria; e-mail: anna.zubkova@uni-graz.at*

methods. The methods used to prove existence of a weak solution of the PNP model are based on the variational theory. Existence theorems are given in [10, 16, 22] in the dynamic case, and in [5, 12] in the stationary case.

The PNP system in this paper implies several difficulties of analysis.

The first difficulty is that the diffusion equations are coupled with each other. Indeed, the constitutive law describes diffusion fluxes of charge species joined by diffusivity matrices. Due to the component coupleness, stochastic matrices of diffusion appear in our system, and no maximum principle is available for species concentrations here.

The second difficulty is inhomogeneous boundary conditions, see the related boundary phenomena in [4, 15]. We consider boundary diffusion fluxes that depend nonlinearly on the species concentrations and the electrostatic potential. To be able to work with this nonlinearity we introduce some reasonable assumptions on the boundary data.

The third difficulty is that the species concentrations should satisfy the volume and positivity constraints. These constraints appear from physical properties of concentrations, but they cannot be provided from classic existence theorems. Therefore, we investigate existence of a solution with desired properties with the help of a reduced formulation of the problem. This formulation excludes the constraints and compensates them by proper thresholding. We will discuss when these formulations are equivalent.

To prove equivalence of the reduced and the complete formulations we construct a solution of the reduced problem which satisfies the volume balance and the positivity. By this, the volume balance holds under an assumption on the positive definiteness of the sum of diffusivity matrices, which we call the weak assumption. In this case, the positivity of the solution is guaranteed by continuity only for a small time. The global non-negativeness of the solution can be provided by the weak maximum principle, and it needs a stronger assumption on the diffusivity matrices.

The main result of this article is, at first, the existence of a weak solution of the problem supported by a-priori estimates. For the proof we use the Schauder–Tikhonov fixed point theorem. In the special case of additional smoothness of an electostatic potential and small boundary fluxes we prove also the uniqueness theorem based on the technique from [16, 23]. Finally, the solution is examined for Lyapunov stability, and the dissipation inequality is established following [7].

The paper has the following structure. In Section 2 we consider two formulations of the problem: first, the complete formulation with the the volume balance and the positivity, and, second, the reduced formulation without the constraints. In Section 3 the well-posedness analysis is presented. Based on the equivalence of these two formulations under special assumptions, we show the existence theorems, the uniqueness theorem, and conclude with the stability analysis.

2. The strong and the weak formulations of the PNP problem

Further in the paper, for the given number of species $n \in \mathbb{N}$, $n \geqslant 2$, the following notations are used for physical variables and parameters:

c_i $\left(mol/m^3\right)$ concentrations of charged species (positive), $i = 1, \dots, n$,
$\mathbf{c} = (c_1, \dots, c_n)$ vector of concentrations,
C $\left(mol/m^3\right)$ summary concentration (positive),
J_i $\left(mol/(m^2 \cdot s)\right)$ diffusion fluxes, $i = 1, \dots, n$,
m_i (kg/mol) molar mass of species (positive), $i = 1, ..., n$,
μ_i (J) electro–chemical potentials of species, $i = 1, \dots, n$,
D^{ij} $\left(m^2 \cdot mol/(J \cdot s \cdot kg)\right)$ diffusivity matrices in $\mathbb{R}^{d\times d}$, $i, j = 1, \dots, n$,
D $\left(m^2 \cdot mol/(J \cdot s \cdot kg)\right)$ summary diffusivity (spd–matrix in $\mathbb{R}^{d\times d}$),
φ (V) electrostatic potential,
A (F/m) electric permittivity (spd–matrix in $\mathbb{R}^{d\times d}$),
z_i (C/mol) electric charges of species, $i = 1, \dots, n$,
$Z := \sum_{i=1}^n |z_i|$ (C/mol) summary of absolute electric charges (positive) and $\bar{Z} := \max\limits_{i=1,\dots,n} |z_i|$,
$k_B \approx 1.38e-23$ (J/K) Boltzmann constant,
$N_A \approx 6.02e+23$ $(1/mol)$ Avogadro constant,
Θ (K) absolute temperature (positive),
p (Pa) pressure,

α (F/m^2) capacitance density (positive),
β_i (m^3/mol) volume factors of species (positive), $i = 1, \dots, n$,
g_i $\big(mol/(m^2 \cdot s)\big)$ boundary fluxes of species, $i = 1, \dots, n$,
g $\big(C/m^2\big)$ electric flux through boundary.

To begin with, we describe geometry of the problem.

Let Ω be a bounded domain in $\mathbb{R}^d$, $d = \{1, 2, 3\}$, with the Lipschitz boundary $\partial\Omega = \bar{\Gamma}_N \cup \bar{\Gamma}_D$ consisted of two disjoint parts such that $\Gamma_N \cap \Gamma_D = \emptyset$, $\Gamma_D \neq \emptyset$, and the unit normal vector $\nu = (\nu_1, \dots, \nu_d)$ on Γ_N, which is outward to Ω. For an arbitrary final time $T > 0$ we denote the cylinder by $Q_T = (0, T) \times \Omega$ as illustrated in Fig. 1.

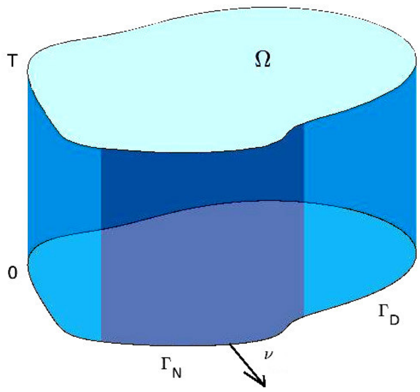

Figure 1. An example geometric domain

2.1. The strong formulation of the complete problem

For $(t, x) \in Q_T$, the unknown functions of species concentrations $\mathbf{c}(t, x) = (c_1, \dots, c_n)$ and an electrostatic potential $\varphi(t, x)$ enter the generalized Poisson–Nernst–Planck system constituted of the following time-dependent governing relations.

$$\text{The Fick's law of diffusion:} \quad \frac{\partial c_i}{\partial t} - \operatorname{div} J_i = 0, \quad i = 1, \dots, n, \quad \text{in} \quad (0, T) \times \Omega; \tag{1a}$$

$$\text{the constitutive law:} \quad J_i = m_i \sum_{j=1}^{n} c_j \nabla \mu_j^\top D^{ij}, \quad i = 1, \dots, n, \quad \text{in} \quad (0, T) \times \Omega; \tag{1b}$$

$$\text{the Gauss's flux law:} \quad -\operatorname{div}(\nabla \varphi^\top A) = \sum_{k=1}^{n} z_k c_k \quad \text{in} \quad (0, T) \times \Omega; \tag{1c}$$

$$\text{the force balance:} \quad \nabla p = -\Big(\sum_{k=1}^{n} z_k c_k\Big) \nabla \varphi \quad \text{in} \quad (0, T) \times \Omega; \tag{1d}$$

$$\text{and quasi–Fermi electro–chemical potentials:} \quad N_A \mu_i = k_B N_A \Theta \ln(\beta_i c_i) + \frac{1}{C} p + z_i \varphi, \quad i = 1, \dots, n, \quad \text{in} \quad (0, T) \times \Omega. \tag{1e}$$

After substitution of the expressions (1b) of the diffusion fluxes J_i in the Fick's law (1a) we get the nonlinear Nernst–Planck equations. These equations are coupled with the Gauss's flux law (1c) through the electro–chemical potentials μ_i from (1e).

We note that the dual entropy variables p and $\mu_1, \dots, \mu_n$ determined in the equations (1d) and (1e) come in the model from physical phenomena. They can be excluded from the system as will be shown in details further, see (16).

The system of equations (1) is endowed with the following inhomogeneous boundary conditions. At the Neumann boundary we suggest

$$\text{the nonlinear Neumann conditions:} \quad m_i \sum_{j=1}^{n} c_j \nabla \mu_j^\top D^{ij} \nu = g_i(\mathbf{c}, \varphi), \quad i = 1, \dots, n, \quad \text{on} \quad (0, T) \times \Gamma_N; \tag{2a}$$

$$\text{and the Robin condition:} \quad \nabla \varphi^\top A \nu + \alpha \varphi = g \quad \text{on} \quad (0, T) \times \Gamma_N. \tag{2b}$$

At the Dirichlet boundary we set the usual conditions:

$$c_i = c_i^D, \quad i = 1, \dots, n, \quad \text{on} \quad (0, T) \times \Gamma_D; \tag{3a}$$

$$\varphi = \varphi^D \quad \text{on} \quad (0, T) \times \Gamma_D. \tag{3b}$$

The time derivative in (1a) is endowed with the initial conditions:

$$c_i(0, \cdot) = c_i^0, \quad i = 1, \dots, n, \quad \text{as} \quad t = 0. \tag{4}$$

Moreover, we assume that feasible concentrations satisfy the following equality and inequality constraints:

$$\text{the volume constraint with the given summary volume } C > 0: \quad \sum_{i=1}^{n} c_i = C \quad \text{in} \quad (0, T) \times \Omega; \tag{5a}$$

$$\text{and the positivity constraint:} \quad c_i > 0, \quad i = 1, \dots, n, \quad \text{in} \quad (0, T) \times \Omega. \tag{5b}$$

In the next sections the boundary and initial data in (2)–(4) will be specified in function spaces.

2.1.1. Data of the problem. The Neumann data $g_i(\mathbf{c}, \varphi) \in L^2((0, T) \times \Gamma_N)$, $g \in L^\infty(0, T; L^2(\Gamma_N))$, and $\alpha \in L^\infty(\Gamma_N)$, $\alpha > 0$, the initial data $c_i^0 \in L^2(\Omega)$, the Dirichlet data $\varphi^D \in L^\infty(0, T; H^1(\Omega))$ and $c_i^D \in H^1(0, T; L^2(\Omega)) \cap L^2(0, T; H^1(\Omega))$ for $i = 1, \dots, n$ are assumed to be such that the following conditions hold.

We suggest that the boundary data satisfy:

$$\text{the volume balance:} \quad \sum_{i=1}^{n} c_i^D = C \quad \text{on} \quad (0, T) \times \Gamma_N; \tag{6a}$$

$$\text{and the positivity:} \quad c_i^D > 0 \quad \text{on} \quad (0, T) \times \Gamma_N. \tag{6b}$$

The initial data are such that the conditions in the manner of (5) hold, namely:

$$\text{the volume balance:} \quad \sum_{i=1}^{n} c_i^0 = C \quad \text{in} \quad \Omega; \tag{7a}$$

$$\text{the positivity:} \quad c_i^0 > 0, \quad i = 1, \dots, n, \quad \text{in} \quad \Omega; \tag{7b}$$

$$\text{and the compatibility conditions:} \quad c_i^D(0, \cdot) = c_i^0, \quad i = 1, \dots, n, \quad \text{in} \quad \Omega. \tag{7c}$$

For the well-posedness analysis further we will need the assumptions formulated next.

2.1.2. Assumptions. We suggest that nonlinear functions $g_i(\mathbf{c}, \varphi)$ expressing boundary reactions in (2a) satisfy the following properties for every species $i = 1, \dots, n$.

The growth conditions with the uniform bound $0 \leqslant G_i(\mathbf{c}) \leqslant 1$:

$$\int_0^T \int_{\Gamma_N} |g_i(\mathbf{c}, \varphi)|^2 \, dx \, dt \leqslant \big(\gamma_1^i + \gamma_2^i ||\varphi||^2_{L^2(0,T;H^1(\Omega))}\big) G_i(\mathbf{c}), \quad \text{where } \gamma_1^i, \gamma_2^i \geqslant 0 \text{ and depend on } T; \tag{8a}$$

$$\text{the mass balance:} \quad \sum_{k=1}^n g_k(\mathbf{c}, \varphi) = 0 \quad \text{on} \quad (0, T) \times \Gamma_N; \tag{8b}$$

$$\text{and the positive production rate:} \quad g_i(\mathbf{c}, \varphi) c_i^- = 0 \quad \text{on} \quad (0, T) \times \Gamma_N, \text{ for all admissible } c_i. \tag{8c}$$

In (8c) the partition in the positive and the negative parts is defined by

$$c_i^+ := \max\{0, c_i\}, \quad c_i^- := -\min\{0, c_i\} \tag{9a}$$

$$\text{such that} \quad c_i = c_i^+ - c_i^-, \quad c_i^+ \geqslant 0, \ c_i^- \geqslant 0, \quad c_i^+ \cdot c_i^- = 0, \quad \text{for} \quad i = 1, \dots, n. \tag{9b}$$

Example 2.1. *For example, the non trivial functions*

$$g_i(\mathbf{c}, \varphi) = \frac{c_1^+ \cdot \ldots \cdot c_n^+}{\left(\sum_{k=1}^n c_k^+\right)^n} h_i, \quad i = 1, \dots, n,$$

fulfill all the conditions (8) with $\gamma_2^i = 0$, $\gamma_1^i = T|\Gamma_N||h_i|^2$ *and* $G_i(\mathbf{c}) = 1$ *when the numbers* $h_i \in \mathbb{R}$ *are chosen such that* $\sum_{i=1}^n h_i = 0$. *In particular,* $g_1(\mathbf{c}, \varphi) = \dfrac{c_1^+ c_2^+}{(c_1^+ + c_2^+)^2}$, $g_2(\mathbf{c}, \varphi) = -g_1(\mathbf{c}, \varphi)$, *and* $g_k(\mathbf{c}, \varphi) = 0$ *for* $k = 3, \dots, n$, *are suitable.*

Let the coefficient matrices satisfy the underneath assumptions.
Symmetry and positive definiteness of $A \in \mathbb{R}^{d \times d}$: There exist $0 < \underline{a} \leqslant \bar{a}$ such that

$$\underline{a}|\xi|^2 \leqslant \xi^\top A \xi \leqslant \bar{a}|\xi|^2 \quad \text{for} \quad \xi \in \mathbb{R}^d. \tag{10a}$$

Strong ellipticity condition for $m_i D^{ij} \in \mathbb{R}^{d \times d}$: There exist $0 < \underline{d} \leqslant \bar{d}$ such that

$$\underline{d} \sum_{i=1}^n |\xi_i|^2 \leqslant \sum_{i,j=1}^n \xi_i^\top m_i D^{ij} \xi_j \leqslant \bar{d} \sum_{i=1}^n |\xi_i|^2 \quad \text{for} \quad \xi_1, \dots, \xi_n \in \mathbb{R}^d. \tag{10b}$$

Symmetry and positive definiteness of $D \in \mathbb{R}^{d \times d}$ in (12) and (13): There exist $0 < \underline{d}_1 \leqslant \bar{d}_1$ such that

$$\underline{d}_1|\xi|^2 \leqslant \xi^\top D \xi \leqslant \bar{d}_1|\xi|^2 \quad \text{for} \quad \xi \in \mathbb{R}^d; \tag{11}$$

and the following properties of the diffusivity matrices related to the respective constraints (5a) and (5b):

$$\text{either the weak assumption:} \quad \sum_{i=1}^n m_i D^{ij} = D, \quad j = 1, \dots, n, \tag{12}$$

$$\text{or the strong assumption:} \quad m_i D^{ij} = \delta_{ij} D, \quad i, j = 1, \dots, n, \tag{13}$$

where δ_{ij} is the Kronecker delta such that $\delta_{ij} = 1$ for $i = j$ and zero otherwise. The condition (13) is stronger than (12), since (12) follows straightforwardly from (13). Also we note that the bounds in (10b) and (11) coincide: $\underline{d}_1 = \underline{d}$ and $\bar{d}_1 = \bar{d}$, when the assumption (13) holds.

2.2. The weak formulation of the complete problem

We will understand a solution of the problem (1)–(5) in the sense of the following weak formulation (14) and (15) given below. It is obtained by multiplication of the equations (1a) and (1b) with suitable test functions and integrating by parts with respect to the space as well as the time variables. It is called the very weak formulation in [22].

Find $c_1,\dots,c_n$, φ, $\mu_1,\dots,\mu_n$, p such that

$$c_i \in L^\infty(0,T;L^2(\Omega))\cap L^2(0,T;H^1(\Omega)),\quad i=1,\dots,n, \tag{14a}$$

$$\varphi,\ p\in L^\infty(0,T;H^1(\Omega)), \tag{14b}$$

$$c_i\nabla\mu_i\in L^2(Q_T),\quad i=1,\dots,n, \tag{14c}$$

which satisfy the Dirichlet boundary conditions (3), the initial conditions (4), the volume and the positivity constraints (5), as well as fulfill n dynamic and one quasi-stationary variational equations for a time $\tau\in(0,T)$:

$$\int_\Omega c_i\bar c_i\,dx\Big|_0^\tau-\int_{Q_\tau} c_i\frac{\partial\bar c_i}{\partial t}\,dx\,dt+\int_{Q_\tau} m_i\sum_{j=1}^n c_j\nabla\mu_j^\top D^{ij}\nabla\bar c_i\,dx\,dt=\int_0^\tau\!\!\int_{\Gamma_N} g_i(\mathbf{c},\varphi)\bar c_i\,dS_x\,dt,\qquad i=1,\dots,n, \tag{15a}$$

$$\int_\Omega(\nabla\varphi^\top A\nabla\bar\varphi-\sum_{k=1}^n z_kc_k\bar\varphi)\,dx+\int_{\Gamma_N}\alpha\varphi\bar\varphi\,dS_x=\int_{\Gamma_N}g\bar\varphi\,dS_x, \tag{15b}$$

for all test functions $\bar c_i\in H^1(0,T;L^2(\Omega))\cap L^2(0,T;H^1(\Omega))$ and $\bar\varphi\in H^1(\Omega)$ such that $\bar c_i=0$ on $(0,T)\times\Gamma_D$ and $\bar\varphi=0$ on Γ_D, for $i=1,\dots,n$.

The system (15) is completed with $(n+1)$ identities (1d) and (1e) describing the dual entropy variables p and $\mu_1,\dots,\mu_n$ almost everywhere in $(0,T)\times\Omega$.

2.3. The reduced problem formulation

Excluding $\mu_1,\dots,\mu_n$, and p from the equations (1)–(2) and dropping the constraints (5), we arrive at the reduced problem. It will be convenient to show this calculation in details in the proof of Lemma 3.4 when studying equivalence of the problems.

At first, with the help of (1d) and (1e) we exclude the dual entropy variables from the constitutive law (1b), then substitute the result into the Fick's law (1a) and obtain:

$$\frac{\partial c_i}{\partial t}-\operatorname{div}\sum_{j=1}^n\Big[k_B\Theta\nabla c_j+\frac{c_j}{N_A}\Big(z_j-\frac{\sum_{k=1}^n z_kc_k}{C}\Big)\nabla\varphi\Big]^\top m_iD^{ij}=0,\quad i=1,\dots,n,\quad\text{in}\quad(0,T)\times\Omega. \tag{16}$$

Second, to avoid the constraints (5), we rewrite the equations (16) and (1c) as follows:

$$\frac{\partial c_i}{\partial t}-\operatorname{div}\sum_{j=1}^n\Big[k_B\Theta\nabla c_j+\Upsilon_j(\mathbf{c}^+)\nabla\varphi\Big]^\top m_iD^{ij}=0,\quad i=1,\dots,n,\quad\text{in}\quad(0,T)\times\Omega; \tag{17a}$$

$$-\operatorname{div}(\nabla\varphi^\top A)=\Upsilon(\mathbf{c}^+)\quad\text{in}\quad(0,T)\times\Omega; \tag{17b}$$

where "+" stands for the positive part as introduced in (9) and the following notations $\Upsilon_j(\mathbf{c})$ and $\Upsilon(\mathbf{c})$ are used for short:

$$\Upsilon_j(\mathbf{c}):=\frac{C}{N_A}\frac{c_j}{\sum_{k=1}^n c_k}\Big(z_j-\frac{\sum_{k=1}^n z_kc_k}{\sum_{k=1}^n c_k}\Big),\quad \Upsilon(\mathbf{c}):=C\frac{\sum_{k=1}^n z_kc_k}{\sum_{k=1}^n c_k}. \tag{18}$$

The Neumann and Robin boundary conditions (2) are rewritten according to (16) as

$$m_i\sum_{j=1}^n\Big[k_B\Theta\nabla c_j+\Upsilon_j(\mathbf{c}^+)\nabla\varphi\Big]^\top D^{ij}\nu=g_i(\mathbf{c},\varphi),\quad i=1,\dots,n,\quad\text{on}\quad(0,T)\times\Gamma_N; \tag{19a}$$

$$\nabla\varphi^\top A\nu + \alpha\varphi = g \quad \text{on} \quad (0,T)\times\Gamma_N; \tag{19b}$$

while the Dirichlet boundary conditions (3) and the initial conditions (4) are left unchanged.

For the reduced problem we set the weak formulation by analogy with (14)–(15) as follows.

Find $c_1,\dots,c_n$ and φ such that

$$c_i \in L^\infty(0,T;L^2(\Omega))\cap L^2(0,T;H^1(\Omega)), \quad i=1,\dots,n, \tag{20a}$$

$$\varphi \in L^\infty(0,T;H^1(\Omega)), \tag{20b}$$

satisfying the Dirichlet boundary conditions (3), the initial conditions (4), and the following variational equations for a time $\tau\in(0,T)$ and $i=1,\dots,n$:

$$\int_\Omega c_i\bar{c}_i\,dx\Big|_0^\tau - \int_{Q_\tau} c_i\frac{\partial\bar{c}_i}{\partial t}\,dx\,dt + \int_{Q_\tau} m_i\sum_{j=1}^n\Big[k_B\Theta\nabla c_j + \Upsilon_j(\mathbf{c}^+)\nabla\varphi\Big]^\top D^{ij}\nabla\bar{c}_i\,dx\,dt = \int_0^\tau\!\!\int_{\Gamma_N} g_i(\mathbf{c},\varphi)\bar{c}_i\,dS_x\,dt, \tag{21a}$$

$$\int_\Omega\big(\nabla\varphi^\top A\nabla\bar\varphi - \Upsilon(\mathbf{c}^+)\bar\varphi\big)\,dx + \int_{\Gamma_N}\alpha\varphi\bar\varphi\,dS_x = \int_{\Gamma_N} g\bar\varphi\,dS_x, \tag{21b}$$

for all test functions $\bar{c}_i\in H^1(0,T;L^2(\Omega))\cap L^2(0,T;H^1(\Omega))$ and $\bar\varphi\in H^1(\Omega)$ such that $\bar{c}_i=0$ on $(0,T)\times\Gamma_D$ and $\bar\varphi=0$ on Γ_D, for $i=1,\dots,n$.

With the help of the reduced formulation, in the next section we will provide well-posedness of the PNP problem.

3. Well-posedness of the generalized PNP problem

This section consists of four parts. First, we prove the existence theorem for the reduced formulation, supported by a-priori estimates. Second, three auxillary lemmas will show under which conditions the reduced and the complete formulations are equivalent. Based on these results existence of the solution of the complete problem will be proven under given assumptions. The uniqueness theorem holds in the special case of a smooth electrostatic potential and small boundary fluxes. Finally, in the last part we examine stability of the solution in the sense of Lyapunov.

3.1. Preliminaries

Before starting well-posedness analysis of the problem, some preliminaries are needed. We will use the following trace theorem and functional inequalities.

Trace theorem. Let $u\in H^1(\Omega)$. Then

$$k_0||u||^2_{H^1(\Omega)} \leqslant ||u||^2_{H^{1/2}(\partial\Omega)} \leqslant K_0||u||^2_{H^1(\Omega)}, \tag{22}$$

where $0<k_0\leqslant K_0$, and the Hölder and Sobolev norms are defined as

$$||u||^2_{H^{1/2}(\partial\Omega)} = ||u||^2_{L^2(\partial\Omega)} + \int_\Omega\int_\Omega\frac{|u(x)-u(y)|^2}{|x-y|^{1+d}}\,dx\,dy, \qquad ||u||^2_{H^1(\Omega)} = ||u||^2_{L^2(\Omega)} + ||\nabla u||^2_{L^2(\Omega)^d}.$$

Poincaré inequality. Let $u\in H^1(\Omega)$, and either $u=0$ on Γ_D or $\int_\Omega u\,dx = 0$. Then

$$||u||^2_{L^2(\Omega)} \leqslant K_P||\nabla u||^2_{L^2(\Omega)^d}, \tag{23}$$

where $K_P>0$ depends on Ω and the spatial dimension d.

From the Poincaré inequality it follows the two-sided estimate of the gradient

$$\frac{1}{1+K_P}||u||^2_{H^1(\Omega)} \leqslant ||\nabla u||^2_{L^2(\Omega)^d} \leqslant ||u||^2_{H^1(\Omega)}. \tag{24}$$

3.2. Existence theorem for the reduced problem

We start from the proof of existence of the solution for the reduced problem.

Theorem 3.1 (Existence of a weak solution of the reduced problem)**.** *Let the growth condition (8a) and the assumptions (10) on coefficient matrices hold. Then there exists a weak solution (20) of the reduced problem (21) under the boundary (3) and initial (4) conditions.*

Proof. To prove the assertion of this theorem we use the Schauder–Tikhonov fixed point theorem for a sequence of linear approximations defined iteratively.

We start with a smooth initialization $(c_1^{(0)},\dots,c_n^{(0)})$ such that

$$c_i^{(0)} = c_i^D, \quad i=1,\dots,n, \quad \text{on} \quad (0,T)\times\Gamma_D,$$

$$\sum_{i=1}^n c_i^{(0)} = C, \quad c_i^{(0)} > 0, \quad i=1,\dots,n, \quad \text{in} \quad (0,T)\times\Omega.$$

Next, we define a sequence of functions such that

$$c_1^{(m+1)},\dots,c_n^{(m+1)} \in L^\infty(0,T;L^2(\Omega))\cap L^2(0,T;H^1(\Omega)),$$

$$\varphi^{(m+1)} \in L^\infty(0,T;H^1(\Omega)) \quad \text{for} \quad m\in\mathbb{N}_0,$$

which general term is determined as an iterative solution of the following equations (25) that appear as a linearization of the nonlinear system (21) as written below.

Starting with $m=0$, we solve the linear equation for $\varphi^{(m+1)}$:

$$\int_\Omega (\nabla\varphi^{(m+1)})^\top A\nabla\bar\varphi\,dx + \int_{\Gamma_N}\alpha\varphi^{(m+1)}\bar\varphi\,dS_x = \int_{\Gamma_N} g\bar\varphi\,dS_x + \int_\Omega \Upsilon((\mathbf{c}^{(m)})^+)\bar\varphi\,dx, \tag{25a}$$

then substitute $\varphi^{(m+1)}$ in the right-hand side of the system of linear equations for $c_i^{(m+1)}$ for $\tau\in(0,T)$ and $i=1,\dots,n$:

$$\int_{Q_\tau}\frac{\partial c_i^{(m+1)}}{\partial t}\bar c_i\,dx\,dt + \int_{Q_\tau} m_i\sum_{j=1}^n k_B\Theta(\nabla c_j^{(m+1)})^\top D^{ij}\nabla\bar c_i\,dx\,dt$$
$$= \int_0^\tau\!\!\int_{\Gamma_N} g_i^{(m)}\bar c_i\,dS_x\,dt - \int_{Q_\tau} m_i\sum_{j=1}^n \Upsilon_j((\mathbf{c}^{(m)})^+)(\nabla\varphi^{(m+1)})^\top D^{ij}\nabla\bar c_i\,dx\,dt, \tag{25b}$$

for all test functions $\bar c_i\in L^\infty(0,T;L^2(\Omega))\cap L^2(0,T;H^1(\Omega))$ and $\bar\varphi\in H^1(\Omega)$ such that $\bar c_i=0$ on $(0,T)\times\Gamma_D$ and $\bar\varphi=0$ on Γ_D, for $i=1,\dots,n$. In (25b), the notation $g_i^{(m)} := g_i(\mathbf{c}^{(m)},\varphi^{(m+1)})$ was used for short.

The existence of the unique solution of this system follows from the standard linear theory of elliptic and parabolic equations [18], since the coefficient matrices A and D^{ij} are elliptic .

Estimation for $\varphi^{(m+1)}$. For fixed $t\in(0,T)$, let us choose the test function $\bar\varphi=\tilde\varphi^{(m+1)} := \varphi^{(m+1)}-\varphi^D$, which is zero at $(0,T)\times\Gamma_D$ due to (3b), and we plug it in (25a):

$$\int_\Omega (\nabla\varphi^{(m+1)})^\top A\nabla\tilde\varphi^{(m+1)}\,dx + \int_{\Gamma_N}\alpha\varphi^{(m+1)}\tilde\varphi^{(m+1)}\,dS_x = \int_{\Gamma_N} g\tilde\varphi^{(m+1)}\,dS_x + \int_\Omega \Upsilon((\mathbf{c}^{(m)})^+)\tilde\varphi^{(m+1)}\,dx.$$

After a rearrangement of terms in the left-hand side of the last equation using the identity $\varphi^{(m+1)} = \tilde{\varphi}^{(m+1)} + \varphi^D$, we will estimate the following expression:

$$I_\varphi^{(m+1)} := \int_\Omega (\nabla\tilde{\varphi}^{(m+1)})^\top A \nabla\tilde{\varphi}^{(m+1)}\, dx + \int_{\Gamma_N} \alpha(\tilde{\varphi}^{(m+1)})^2\, dS_x$$
$$= \int_\Omega \Upsilon((\mathbf{c}^{(m)})^+)\tilde{\varphi}^{(m+1)}\, dx + \int_{\Gamma_N} (g - \alpha\varphi^D)\tilde{\varphi}^{(m+1)}\, dS_x - \int_\Omega (\nabla\varphi^D)^\top A \nabla\tilde{\varphi}^{(m+1)}\, dx. \quad (26)$$

On the right-hand side of the equation (26) expressing $I_\varphi^{(m+1)}$, there are three integral terms. Estimating in (18) from above

$$\left|\Upsilon((\mathbf{c}^{(m)})^+)\right| = \left| C\frac{\sum_{k=1}^n z_k c_k}{\sum_{k=1}^n c_k}\right| \leqslant C\sum_{k=1}^n |z_k| = CZ, \quad \text{where} \quad Z := \sum_{k=1}^n |z_k|,$$

then applying Young's inequality with weights $\delta_1 > 0$ and $\delta_2 > 0$ and the Poincaré inequality (23), we obtain the following upper bounds of the first two integral terms in the right-hand side of (26):

$$\left|\int_\Omega \Upsilon((\mathbf{c}^{(m)})^+)\tilde{\varphi}^{(m+1)}\, dx\right| \leqslant \int_\Omega CZ|\tilde{\varphi}^{(m+1)}|\, dx \leqslant \frac{(CZ)^2}{2\delta_1}\int_\Omega dx + \frac{\delta_1}{2}\int_\Omega |\tilde{\varphi}^{(m+1)}|^2\, dx$$
$$\leqslant \frac{(CZ)^2}{2\delta_1}|\Omega| + \frac{\delta_1 K_P}{2}\int_\Omega |\nabla\tilde{\varphi}^{(m+1)}|^2\, dx, \quad (27)$$

where $|\Omega|$ denotes the Hausdorff measure of Ω in $\mathbb{R}^d$, and similarly

$$\left|\int_{\Gamma_N} (g - \alpha\varphi^D)\tilde{\varphi}^{(m+1)}\, dS_x\right| \leqslant \frac{1}{2\delta_2}\int_{\Gamma_N} g^2\, dS_x + \frac{\delta_2}{2}\int_{\Gamma_N} |\tilde{\varphi}^{(m+1)}|^2\, dS_x$$
$$+ \frac{||\alpha||_{L^\infty(\Omega)}}{2\delta_2}\int_{\Gamma_N} (\varphi^D)^2\, dS_x + \frac{\delta_2||\alpha||_{L^\infty(\Omega)}}{2}\int_{\Gamma_N} |\tilde{\varphi}^{(m+1)}|^2\, dS_x. \quad (28)$$

Using the upper bound of A given in (10a), from Young's inequality with a weight $\delta_3 > 0$ it follows the estimate of the third integral term in the right-hand side of (26):

$$\left|\int_\Omega (\nabla\varphi^D)^\top A \nabla\tilde{\varphi}^{(m+1)}\, dx\right| \leqslant \bar{a}\Big(\frac{1}{2\delta_3}||\nabla\varphi^D||^2_{L^2(\Omega)} + \frac{\delta_3}{2}||\nabla\tilde{\varphi}^{(m+1)}||^2_{L^2(\Omega)}\Big). \quad (29)$$

Therefore, collecting together (27)–(29), from (26) we infer the estimation for $I_\varphi^{(m+1)}$ from above:

$$I_\varphi^{(m+1)} \leqslant \Big(\frac{\delta_1 K_P}{2} + \frac{\delta_3\bar{a}}{2}\Big)||\nabla\tilde{\varphi}^{(m+1)}||^2_{L^2(\Omega)} + \frac{\delta_2}{2}(1 + ||\alpha||_{L^\infty(\Omega)})||\tilde{\varphi}^{(m+1)}||^2_{L^2(\Gamma_N)} + \bar{K}_1(t), \quad (30)$$

where $\bar{K}_1(t) := \frac{(CZ)^2}{2\delta_1}|\Omega| + \frac{1}{2\delta_2}(||g||^2_{L^2(\Gamma_N)} + ||\alpha||_{L^\infty(\Omega)}||\varphi^D||^2_{L^2(\Gamma_N)}) + \frac{\bar{a}}{2\delta_3}||\nabla\varphi^D||^2_{L^2(\Omega)}$ depends on t via g and φ^D.

On the left-hand side of the equation (26) expressing $I_\varphi^{(m+1)}$ there are two integral terms. With the help of the lower bound

$$\int_{\Gamma_N} \alpha|\tilde{\varphi}^{(m+1)}|^2\, dS_x \geqslant \min_{\alpha\in\Gamma_N}\alpha||\tilde{\varphi}^{(m+1)}||^2_{L^2(\Gamma_N)},$$

using the ellipticity of the matrix A in (10a) and the consequence from the Poincaré inequality (24), we estimate $I_\varphi^{(m+1)}$ from below:

$$\frac{\underline{a}}{1 + K_P}||\tilde{\varphi}^{(m+1)}||^2_{H^1(\Omega)} + \min_{\alpha\in\Gamma_N}\alpha||\tilde{\varphi}^{(m+1)}||^2_{L^2(\Gamma_N)} \leqslant I_\varphi^{(m+1)}. \quad (31)$$

Gathering together (30) and (31) it follows the uniform inequality for the norms of $\tilde{\varphi}^{(m+1)}$ for all $m \in \mathbb{N}_0$:

$$K_1(||\tilde{\varphi}^{(m+1)}||^2_{H^1(\Omega)} + ||\tilde{\varphi}^{(m+1)}||^2_{L^2(\Gamma_N)}) \leqslant \bar{K}_1(t),$$

where the constant $K_1 := \min\{\frac{a}{1+K_P} - \frac{\delta_1 K_P}{2} - \frac{\delta_3 \bar{a}}{2}, \min_{\alpha\in\Gamma_N} \alpha - \frac{\delta_2}{2}(1+||\alpha||_{L^\infty(\Omega)})\}$, and $K_1 > 0$ for $\delta_1, \delta_2, \delta_3$ chosen sufficiently small recalling that $\alpha > 0$. After division by K_1 this implies

$$||\tilde{\varphi}^{(m+1)}||^2_{H^1(\Omega)} + ||\tilde{\varphi}^{(m+1)}||^2_{L^2(\Gamma_N)} \leqslant K_2(t) := \frac{\bar{K}_1(t)}{K_1} \quad \text{and} \quad K_2(t) > 0. \tag{32}$$

Substituting the difference $\tilde{\varphi}^{(m+1)} = \varphi^{(m+1)} - \varphi^D$ in the expression (32) and taking the supremum over $t \in (0, T)$, we finish the estimate of $\varphi^{(m+1)}$ with respect to the induced norm $|||\varphi|||^2_\varphi := ||\varphi||^2_{L^\infty(0,T;H^1(\Omega))} + ||\varphi||^2_{L^\infty(0,T;L^2(\Gamma_N))}$ as follows:

$$|||\varphi^{(m+1)}|||^2_\varphi \leqslant 2(|||\tilde{\varphi}^{(m+1)}|||^2_\varphi + |||\varphi^D|||^2_\varphi) \leqslant 2 \sup_{t\in(0,T)} K_2(t) + 2|||\varphi^D|||^2_\varphi =: K_\varphi. \tag{33}$$

Estimation for $\mathbf{c}^{(m+1)}$. Let us choose the test functions $\bar{c}_i = \tilde{c}_i^{(m+1)} := c_i^{(m+1)} - c_i^D$, $i = 1, \dots, n$, which are zero at $(0, T) \times \Gamma_D$ due to (3a), in the linearized equations (25b) and sum them over $i = 1, \dots, n$:

$$\sum_{i=1}^n \int_{Q_\tau} \frac{\partial c_i^{(m+1)}}{\partial t} \tilde{c}_i^{(m+1)}\, dx\, dt + \sum_{i,j=1}^n \int_{Q_\tau} m_i k_B \Theta(\nabla c_j^{(m+1)})^\top D^{ij} \nabla \tilde{c}_i^{(m+1)}\, dx\, dt$$
$$= \sum_{i=1}^n \int_0^\tau\!\!\int_{\Gamma_N} g_i^{(m)} \tilde{c}_i^{(m+1)}\, dS_x\, dt - \sum_{i,j=1}^n \int_{Q_\tau} m_i \Upsilon_j((\mathbf{c}^{(m)})^+)\nabla(\varphi^{(m+1)})^\top D^{ij} \nabla \tilde{c}_i^{(m+1)}\, dx\, dt. \tag{34}$$

Inserting in the equation (34) the identity $c_i^{(m+1)} = \tilde{c}_i^{(m+1)} + c_i^D$ gets the following expression

$$I_c^{(m+1)} := \sum_{i=1}^n \int_{Q_\tau} \frac{\partial \tilde{c}_i^{(m+1)}}{\partial t} \tilde{c}_i^{(m+1)}\, dx\, dt + \sum_{i,j=1}^n \int_{Q_\tau} m_i k_B \Theta(\nabla \tilde{c}_j^{(m+1)})^\top D^{ij} \nabla \tilde{c}_i^{(m+1)}\, dx\, dt = I_1^{(m+1)} + I_2^{(m+1)} + I_3^{(m+1)} + I_4^{(m+1)}, \tag{35}$$

where $I_c^{(m+1)}$ denotes its left-hand side for short, and the four integral terms in the right-hand side of (35) are defined as follows:

$$I_1^{(m+1)} := -\sum_{i=1}^n \int_{Q_\tau} \frac{\partial c_i^D}{\partial t} \tilde{c}_i^{(m+1)}\, dx\, dt, \qquad I_2^{(m+1)} := -\sum_{i,j=1}^n \int_{Q_\tau} m_i k_B \Theta(\nabla c_j^D)^\top D^{ij} \nabla \tilde{c}_i^{(m+1)}\, dx\, dt,$$
$$I_3^{(m+1)} := \sum_{i=1}^n \int_0^\tau\!\!\int_{\Gamma_N} g_i^{(m)} \tilde{c}_i^{(m+1)}\, dS_x\, dt, \qquad I_4^{(m+1)} := -\sum_{i,j=1}^n \int_{Q_\tau} m_i \Upsilon_j((\mathbf{c}^{(m)})^+)\nabla(\varphi^{(m+1)})^\top D^{ij} \nabla \tilde{c}_i^{(m+1)}\, dx\, dt.$$

Further we will estimate these integrals. First, using Young's inequality with a weight $\delta_4 > 0$ and the Poincaré inequality (23), the absolute value of the integral $I_1^{(m+1)}$ is estimated from above:

$$\left|I_1^{(m+1)}\right| \leqslant \frac{1}{2\delta_4} \sum_{i=1}^n \int_{Q_\tau} \Big(\frac{\partial c_i^D}{\partial t}\Big)^2 dx\, dt + \frac{\delta_4}{2} \sum_{i=1}^n \int_{Q_\tau} \big(\tilde{c}_i^{(m+1)}\big)^2 dx\, dt \leqslant \sum_{i=1}^n \Big\{\frac{1}{2\delta_4} ||c_i^D||^2_{H^1(0,\tau;L^2(\Omega))} + \frac{\delta_4 K_P}{2} ||\tilde{c}_i^{(m+1)}||^2_{L^2(0,\tau;H^1(\Omega))}\Big\}.$$

Second, the upper bound of D^{ij} in (10b) provides the estimate of $\left|I_2^{(m+1)}\right|$ by Young's inequality with $\delta_5 > 0$:

$$\left|I_2^{(m+1)}\right| \leqslant \bar{d} k_B \Theta \sum_{i=1}^n \left|\int_{Q_\tau} (\nabla c_i^D)^\top \nabla \tilde{c}_i^{(m+1)}\, dx\, dt\right| \leqslant \bar{d} k_B \Theta \sum_{i=1}^n \int_{Q_\tau} \Big(\frac{1}{2\delta_5} |\nabla c_i^D|^2 + \frac{\delta_5}{2} |\nabla \tilde{c}_i^{(m+1)}|^2\Big)\, dx\, dt.$$

Third, applying Young's inequality with $\delta_6 > 0$, the trace theorem (22), the growth condition (8a), and the estimate (33) obtained before for $\varphi^{(m+1)}$, one gets

$$\left|I_3^{(m+1)}\right| \leqslant \frac{1}{2\delta_6}\sum_{i=1}^n \int_0^\tau\!\!\int_{\Gamma_N} (g_i^{(m)})^2\,dS_x\,dt + \frac{\delta_6}{2}\sum_{i=1}^n \int_0^\tau\!\!\int_{\Gamma_N} (\tilde{c}_i^{(m+1)})^2\,dS_x\,dt$$
$$\leqslant \frac{1}{2\delta_6}\sum_{i=1}^n (\gamma_1^i + \gamma_2^i ||\varphi||^2_{L^2(0,T;H^1(\Omega))})|G_i(\mathbf{c})| + \frac{\delta_6 K_0}{2}\sum_{i=1}^n ||\tilde{c}_i^{(m+1)}||^2_{L^2(0,\tau;H^1(\Omega))}$$
$$\leqslant \frac{1}{2\delta_6}\sum_{i=1}^n (\gamma_1^i + \gamma_2^i K_\varphi) + \frac{\delta_6 K_0}{2}\sum_{i=1}^n ||\tilde{c}_i^{(m+1)}||^2_{L^2(0,\tau;H^1(\Omega))}.$$

Forth, for estimation of $I_4^{(m+1)}$ we apply the auxiliary calculation holding due to (18):

$$\left|\Upsilon_j((\mathbf{c}^{(m)})^+)\right| \leqslant \frac{C}{N_A}\left|\frac{(c_j^{(m)})^+}{\sum_{k=1}^n (c_k^{(m)})^+}\right|\left|\frac{\sum_{k=1}^n z_k (c_k^{(m)})^+(\delta_{jk}-1)}{\sum_{k=1}^n (c_k^{(m)})^+}\right| \leqslant \frac{CZ}{N_A}. \tag{36}$$

With the help of (36), using the upper bound of D^{ij} in (10b), the estimate of $\varphi^{(m+1)}$ in (33), and Young's inequality with a weight $\delta_7 > 0$, we obtain

$$\left|I_4^{(m+1)}\right| \leqslant \frac{CZ}{N_A}\sum_{i,j=1}^n \left|\int_{Q_\tau} (\nabla\varphi^{(m+1)})^\top D^{ij}\nabla\tilde{c}_i^{(m+1)}\,dx\,dt\right| \leqslant \frac{\bar{d}CZ}{N_A}\sum_{i=1}^n \left|\int_{Q_\tau} (\nabla\varphi^{(m+1)})^\top \nabla\tilde{c}_i^{(m+1)}\,dx\,dt\right|$$
$$\leqslant \frac{\bar{d}CZ}{N_A}\sum_{i=1}^n \int_{Q_\tau}\Big(\frac{1}{2\delta_7}|\nabla\varphi^{(m+1)}|^2 + \frac{\delta_7}{2}|\nabla\tilde{c}_i^{(m+1)}|^2\Big)\,dx\,dt \leqslant \frac{\bar{d}CZ}{N_A}\Big(\frac{K_\varphi}{2\delta_7} + \frac{\delta_7}{2}\sum_{i=1}^n ||\tilde{c}_i^{(m+1)}||^2_{L^2(0,\tau;H^1(\Omega))}\Big).$$

Thus, summarizing the four previous relations and collecting like terms, $\left|I_c^{(m+1)}\right|$ in (35) is estimated from above:

$$\left|I_c^{(m+1)}\right| \leqslant \bar{K}_3 \sum_{i=1}^n ||\tilde{c}_i^{(m+1)}||^2_{L^2(0,\tau;H^1(\Omega))} + \bar{K}_4(\tau) + \bar{K}_5 K_\varphi, \tag{37}$$

where

$$\bar{K}_3 := \frac{\delta_4 K_P}{2} + \frac{\delta_5 \bar{d} k_B \Theta}{2} + \frac{\delta_6 K_0}{2} + \frac{\delta_7 \bar{d}CZ}{2N_A}, \quad \bar{K}_4(\tau) := \sum_{i=1}^n \Big\{\frac{1}{2\delta_4}||c_i^D||^2_{H^1(0,\tau;L^2(\Omega))} + \frac{\bar{d}k_B\Theta}{2\delta_5}||\nabla c_i^D||^2_{L^2(0,\tau;H^1(\Omega))} + \frac{\gamma_1^i}{2\delta_6}\Big\},$$
$$\bar{K}_5 := \sum_{i=1}^n \frac{\gamma_2^i}{2\delta_6} + \frac{\bar{d}CZ}{2\delta_7 N_A}.$$

In the next step, we integrate the first integral constituting $I_c^{(m+1)}$ in (35) by parts, due to the compatibility conditions (7c), and derive

$$\int_{Q_\tau} \frac{\partial\tilde{c}_i^{(m+1)}}{\partial t}\tilde{c}_i^{(m+1)}\,dx\,dt = \frac{1}{2}\frac{d}{dt}\int_{Q_\tau} (\tilde{c}_i^{(m+1)})^2\,dx\,dt = \frac{1}{2}\int_\Omega (\tilde{c}_i^{(m+1)}(\tau))^2\,dx - \frac{1}{2}\int_\Omega (\tilde{c}_i^{(m+1)}(0))^2\,dx = \frac{1}{2}\int_\Omega (\tilde{c}_i^{(m+1)}(\tau))^2\,dx.$$

The second term in $I_c^{(m+1)}$ is estimated due to (24) and the strong ellipticity of D^{ij} in (10b) as follows

$$\sum_{i,j=1}^n \int_{Q_\tau} m_i k_B \Theta (\nabla\tilde{c}_j^{(m+1)})^\top D^{ij}\nabla\tilde{c}_i^{(m+1)}\,dx\,dt \geqslant \frac{\underline{d}k_B\Theta}{1+K_P}\sum_{i=1}^n ||\tilde{c}_i^{(m+1)}||^2_{L^2(0,\tau;H^1(\Omega))}.$$

Summing the both relations above, the expression of $\left|I_c^{(m+1)}\right|$ is estimated from below:

$$\left|I_c^{(m+1)}\right| \geqslant \frac{1}{2}\sum_{i=1}^n \int_\Omega (\tilde{c}_i^{(m+1)}(\tau))^2\,dx + \frac{\underline{d}k_B\Theta}{1+K_P}\sum_{i=1}^n ||\tilde{c}_i^{(m+1)}||^2_{L^2(0,\tau;H^1(\Omega))}. \tag{38}$$

Collecting together (37) and (38) and rearranging the terms, we have

$$\sum_{i=1}^{n}\Big\{\frac{1}{2}\int_{\Omega}(\tilde{c}_i^{(m+1)}(\tau))^2\,dx+\Big(\frac{dk_B\Theta}{1+K_P}-\bar{K}_3\Big)||\tilde{c}_i^{(m+1)}||^2_{L^2(0,\tau;H^1(\Omega))}\Big\}\leqslant\bar{K}_4(\tau)+\bar{K}_5K_\varphi. \tag{39}$$

The weights δ_4, δ_5, δ_6, δ_7 in $\bar{K}_3$ can be chosen sufficiently small such that the following quantity is positive: $K_3 := \min\{\frac{1}{2}, \frac{dk_B\Theta}{1+K_P}-\bar{K}_3\}>0$. Therefore, dividing (39) by K_3 and taking the supremum over $\tau\in(0,T)$, we obtain

$$\sum_{i=1}^{n}\Big(||\tilde{c}_i^{(m+1)}||^2_{L^\infty(0,T;L^2(\Omega))}+||\tilde{c}_i^{(m+1)}||^2_{L^2(0,T;H^1(\Omega))}\Big)\leqslant K_4+K_5K_\varphi, \tag{40}$$

where $K_4 := \dfrac{1}{K_3}\sup_{\tau\in(0,T)}\bar{K}_4(\tau)$ and $K_5 := \dfrac{\bar{K}_5}{K_3}$.

To finish the estimation, according to the left-hand side of (40) we define the space $\mathcal{W}$ equipped with the norm

$$|||\mathbf{c}|||_c^2 := ||\mathbf{c}||^2_{L^\infty(0,T;L^2(\Omega))}+||\mathbf{c}||^2_{L^2(0,T;H^1(\Omega))}. \tag{41}$$

With the help of the decomposition $\tilde{\mathbf{c}}^{(m+1)}=\mathbf{c}^{(m+1)}-\mathbf{c}^D$, from (40) and (41) it follows

$$|||\mathbf{c}^{(m+1)}|||_c^2=|||\tilde{\mathbf{c}}^{(m+1)}+\mathbf{c}^D|||_c^2\leqslant K_c+\gamma_cK_\varphi,\quad\text{where}\quad K_c:=2K_4+2|||\mathbf{c}^D|||_c^2,\quad\gamma_c:=2K_5. \tag{42}$$

Consequently, the mapping $\mathfrak{M}:(\mathbf{c}^{(m)},\varphi^{(m)})\mapsto(\mathbf{c}^{(m+1)},\varphi^{(m+1)})$ transforms the set

$$S:=\{(\mathbf{c},\varphi)\in\mathcal{W}\times L^\infty(0,T;H^1(\Omega)):\quad |||\mathbf{c}|||_c^2\leqslant K_c+\gamma_cK_\varphi,\ |||\varphi|||_\varphi^2\leqslant K_\varphi\}$$

into itself. Henceforth, it follows the existence of a fixed point by the Schauder–Tikhonov theorem. □

3.3. Solution properties

In this section we prove equivalence of the complete and the reduced formulations of the problem under special assumptions.

Lemma 3.2 (Volume conservation)**.** *Under assumptions of the mass balance of the boundary fluxes (8b) and the weak assumption on the diffusivity matrices (12) it holds* $\sum_{i=1}^n c_i = C$ *a.e. on* Q_T.

Proof. For simplicity, we denote $\sigma:=\sum_{i=1}^n c_i - C$, then $\sigma=\sum_{i=1}^n c_i^0 - C = 0$ for $t=0$, and we will show that $\sigma\equiv 0$ for all $t\in[0,T]$.

By summing the reduced equations (21a) over $i=1,\dots,n$ with the test function $\bar{c}_i=\sigma$, while $\sigma=0$ at $(0,\tau)\times\Gamma_D$ for $\tau\in(0,T)$ due to (6a), after integration by parts over the time we get

$$\sum_{i=1}^{n}\int_{Q_\tau}\frac{\partial c_i}{\partial t}\sigma\,dx\,dt+\sum_{i,j=1}^{n}\int_{Q_\tau}m_i\Big[k_B\Theta\nabla c_j+\Upsilon_j(\mathbf{c}^+)\nabla\varphi\Big]^\top D^{ij}\nabla\sigma\,dx\,dt=\sum_{i=1}^{n}\int_0^\tau\!\!\int_{\Gamma_N}g_i(\mathbf{c},\varphi)\sigma\,dS_x\,dt. \tag{43}$$

Due to the mass balance (8b), the right-hand side of the equation (43) is equal to zero. Since the weak assumption (12) on D^{ij} holds, we simplify the left-hand side of (43) as

$$\int_{Q_\tau}\sum_{i=1}^{n}\frac{\partial c_i}{\partial t}\sigma\,dx\,dt+\int_{Q_\tau}\sum_{j=1}^{n}\Big[k_B\Theta\nabla c_j+\Upsilon_j(\mathbf{c}^+)\nabla\varphi\Big]^\top D\nabla\sigma\,dx\,dt=0. \tag{44}$$

We observe that after summation over $j=1,\dots,n$, the following term in (44) is trivial:

$$\sum_{j=1}^{n}\Upsilon_j(\mathbf{c}^+)=\sum_{j=1}^{n}\frac{C}{N_A}\frac{c_j^+}{\sum_{k=1}^n c_k^+}\Big(z_j-\frac{\sum_{k=1}^n z_kc_k^+}{\sum_{k=1}^n c_k^+}\Big)=0,$$

and using $\sum_{i=1}^{n} \frac{\partial c_i}{\partial t} = \frac{\partial \sigma}{\partial t}$ as well as $\sum_{j=1}^{n} \nabla c_j = \nabla \sigma$, from (44) it follows

$$\int_{Q_\tau} \frac{\partial \sigma}{\partial t} \sigma \, dx \, dt + \int_{Q_\tau} k_B \Theta \nabla \sigma^\top D \nabla \sigma \, dx \, dt = 0. \tag{45}$$

Applying to the second term in (45) the estimate of the gradient from (24) and using the positive definiteness of D given in (11), we have

$$\int_{Q_\tau} k_B \Theta \nabla \sigma^\top D \nabla \sigma \, dx \, dt \geqslant \frac{d}{1+K_P} k_B \Theta ||\sigma||^2_{L^2(0,\tau;H^1(\Omega))}. \tag{46}$$

The integration by parts of the first term of (45) over $t \in (0,\tau)$ together with (46) gives

$$\frac{1}{2} \int_\Omega \sigma^2(\tau) \, dx + \frac{d k_B \Theta}{1+K_P} ||\sigma||^2_{L^2(0,\tau;H^1(\Omega))} \leqslant \frac{1}{2} \int_\Omega \sigma^2(0) \, dx. \tag{47}$$

Finally, taking the supremum in (47) over $\tau \in (0,T)$, due to $\sigma(0) = 0$, we conclude

$$k_2 \big(||\sigma||^2_{L^\infty(0,T;L^2(\Omega))} + ||\sigma||^2_{L^2(0,T;H^1(\Omega))} \big) \leqslant 0,$$

where $k_2 := \min\Big\{ \frac{1}{2}, \frac{d k_B \Theta}{1+K_P} \Big\}$. Therefore, since $k_2 > 0$, it follows $\sigma \equiv 0$ and $\sum_{i=1}^{n} c_i \equiv C$ for all $t \in [0,T]$. □

Lemma 3.3 (Weak maximum principle)**.** *Under assumption of the positive production rate at the boundary (8c) and the strong assumption on the diffusivity matrices (13) we have* $c_i \geqslant 0$ *a.e. on* Q_T *for* $i = 1, \dots, n$ *and an arbitrary* $T > 0$. *Since* $\mathbf{c} = \mathbf{c}^D > 0$ *at* $(0,T) \times \Gamma_D$ *and* $\mathbf{c} = \mathbf{c}^0 > 0$ *at* $\{0\} \times \Omega$, *the solution* $c_i > 0$ *by continuity at least for a small* T.

Proof. Due to $c_i^- = (c_i^D)^- = 0$ on Γ_D according to (6b), we can choose the test functions $\bar{c}_i = -c_i^-$ with the negative part c_i^-, $i = 1, \dots, n$, then we use the decomposition $c_i = c_i^+ - c_i^-$, $i = 1, \dots, n$, to get from equations (21a) after integration by parts over the time that

$$\int_{Q_\tau} \frac{\partial (c_i^+ - c_i^-)}{\partial t} (-c_i^-) \, dx \, dt + \int_{Q_\tau} m_i \sum_{j=1}^{n} \Big[k_B \Theta \nabla (c_j^+ - c_j^-) + \Upsilon_j(\mathbf{c}^+) \nabla \varphi \Big]^\top D^{ij} \nabla (-c_i^-) \, dx \, dt$$
$$= \int_0^\tau \!\! \int_{\Gamma_N} g_i(\mathbf{c}, \varphi)(-c_i^-) \, dS_x \, dt, \quad i = 1, \dots, n.$$

Based on the orthogonality between $\mathbf{c}^+$ and $\mathbf{c}^-$ in (9b), we further infer

$$\int_{Q_\tau} \frac{\partial c_i^-}{\partial t} c_i^- \, dx \, dt + \int_{Q_\tau} m_i \sum_{j=1}^{n} k_B \Theta \nabla (-c_j^-)^\top D^{ij} \nabla (-c_i^-) \, dx \, dt = -\int_0^\tau \!\! \int_{\Gamma_N} g_i(\mathbf{c}, \varphi) c_i^- \, dS_x \, dt, \quad i = 1, \dots, n. \tag{48}$$

Applying to (48) the assumptions (13) and (8c) implying that $g_i(\mathbf{c}, \varphi) c_i^- = 0$, $i = 1, \dots, n$, this provides the following equations:

$$\int_{Q_\tau} \frac{\partial c_i^-}{\partial t} c_i^- \, dx \, dt + \int_{Q_\tau} \sum_{j=1}^{n} k_B \Theta (\nabla c_j^-)^\top D \delta_{ij} \nabla c_i^- \, dx \, dt = 0, \quad i = 1, \dots, n. \tag{49}$$

Due to the positivity of the initial data (7b), hence $c_i^- = 0$ as $t = 0$ and

$$\frac{1}{2} \int_{Q_\tau} \frac{\partial (c_i^-)^2}{\partial t} \, dx \, dt = \frac{1}{2} \int_\Omega (c_i^-)^2 \, dx \Big|_0^\tau = \frac{1}{2} \int_\Omega (c_i^-(\tau))^2 \, dx, \quad i = 1, \dots, n,$$

from (49) it follows the relations

$$\frac{1}{2} \int_\Omega (c_i^-(\tau))^2 \, dx + \int_{Q_\tau} k_B \Theta (\nabla c_i^-)^\top D \nabla c_i^- \, dx \, dt = 0, \quad i = 1, \dots, n. \tag{50}$$

Analogously to (46), using the properties (11) for D and (24) for ∇c_i^-, the second term in (50) admits the lower bound

$$\int_{Q_\tau} k_B\Theta(\nabla c_i^-)^\top D\nabla c_i^- \,dx\,dt \geqslant \frac{d}{1+K_P} k_B\Theta ||c_i^-||^2_{L^2(0,\tau;H^1(\Omega))}. \tag{51}$$

Therefore, taking the supremum in (50) over $\tau \in (0,T)$, due to (51) we conclude

$$k_2\big(||c_i^-||^2_{L^\infty(0,T;L^2(\Omega))} + ||c_i^-||^2_{L^2(0,T;H^1(\Omega))}\big) \leqslant 0, \quad i=1,\dots,n,$$

recalling that $k_2 = \min\Big\{\dfrac{1}{2}, \dfrac{dk_B\Theta}{1+K_P}\Big\}$. It follows $c_i^- = 0$, $i=1,\dots,n$, thus c_i are non-negative a.e. on Q_T. □

Lemma 3.4 (Equivalence of the complete and the reduced formulations)**.** *Under assumptions made in Lemmas 1 and 2, the complete (15) and the reduced (21) problems are equivalent.*

Proof. First, we show that (15) follows (21). By the positivity and volume balance (5) we have

$$c_i = c_i^+ \quad \text{and} \quad \sum_{i=1}^n c_i^+ = C \quad \text{for} \quad i=1,\dots,n,$$

which provides, in particular, according to the definition of Υ in (18), that

$$\sum_{k=1}^n z_k c_k = C\frac{\sum_{k=1}^n z_k c_k^+}{\sum_{i=1}^n c_i^+} = \Upsilon(\mathbf{c}^+). \tag{52}$$

The replacement of this factor in (15b) implies (21b). Taking the gradient of μ_j in (1e), and inserting here ∇p from (1d), this leads to the identities:

$$\nabla\mu_j = k_B\Theta\frac{\nabla(\beta_j c_j)}{\beta_j c_j} - \frac{1}{N_A C}\Big(\sum_{k=1}^n z_k c_k\Big)\nabla\varphi + \frac{1}{N_A} z_j\nabla\varphi = k_B\Theta\frac{\nabla c_j}{c_j} + \frac{1}{N_A}\Big(z_j - \frac{\sum_{k=1}^n z_k c_k}{C}\Big)\nabla\varphi, \quad j=1,\dots,n.$$

Using the expression of $\nabla\mu_j$, the volume balance and positivity (5), and the definition of Υ_j in (18), we rewrite the following factors from equations (15a):

$$c_j\nabla\mu_j^\top D^{ij} = k_B\Theta\nabla c_j^\top D^{ij} + \frac{C}{N_A}\frac{c_j^+}{\sum_{l=1}^n c_l^+}\Big(z_j - \frac{\sum_{k=1}^n z_k c_k^+}{\sum_{l=1}^n c_l^+}\Big)\nabla\varphi^\top D^{ij} = k_B\Theta\nabla c_j^\top D^{ij} + \Upsilon_j(\mathbf{c}^+)\nabla\varphi^\top D^{ij}, \quad i,j=1,\dots,n, \tag{53}$$

which after multiplication with a test function and integrating over Q_τ implies the equations (21a).

In return, (21) follows (15). Indeed, from Lemma 3.3 we have $\mathbf{c} > 0$ a.e. on Q_T, and from Lemma 3.2 we get $\sum_{k=1}^n c_k = C$ a.e. on Q_T. Thus, the conditions (5), equalities (52) and (53) hold again. This implies that (15) and (21) are equivalent. □

3.4. Well-posedness of the complete problem

Based on the results established in the previous sections, here we prove existence and uniqueness theorems for the complete formulation.

Theorem 3.5 (Existence of a weak solution of the complete problem)**.** *Let all assumptions (8) on the nonlinear boundary terms hold.*

1) *If the weak assumption on diffusivity matrices (12) holds, then there exists a weak solution of the problem (15) with the boundary (3) and initial (4) conditions subject to the constraint (5a). This solution is positive locally in a neighbourhood of $t=0$ in $\mathbb{R}_+$.*
2) *If the strong assumption on diffusivity matrices (13) holds, then the weak solution of this problem is non-negative in Q_T globally for an arbitrary time interval $(0,T)$.*

This solution satisfies the a-priori estimates

$$||\varphi||^2_{L^\infty(0,T;H^1(\Omega))} + ||\varphi||^2_{L^\infty(0,T;L^2(\Gamma_N))} \leqslant K_\varphi,$$

$$||\mathbf{c}||^2_{L^\infty(0,T;L^2(\Omega))} + ||\mathbf{c}||^2_{L^2(0,T;H^1(\Omega))} \leqslant K_c + \gamma_c K_\varphi,$$

where positive constants K_φ, γ_c and K_c are defined in (33) and (42).

Proof. By Theorem 3.1 there exists a weak solution of the reduced problem. By continuity we can guarantee the positivity of $\mathbf{c}$ in a small neighbourhood of $t = 0$ due to the positivity of the initial data (7b). Together with the volume conservation of $\mathbf{c}$ proven in Lemma 3.2, the solution of the reduced problem satisfies all constraints locally in time and, therefore, implies a local weak solution of the complete problem. It provides us the assertion 1).

If diffusivity matrices satisfy the strong assumption (13), then, due to equivalence of the problems according to Lemma 3.4, the solution of the reduced problem is non-negative by Lemma 3.3 and solves the problem (15) in the whole cylinder Q_T.

When the reduced and the complete formulations are equivalent, then estimates (33) and (42) persist for the solution of the complete formulation. The proof is complete. □

Theorem 3.6 (Uniqueness of the solution)**.** *Let the solution component φ be smooth such that*

$$\varphi \in L^\infty(Q_T),\ \nabla\varphi \in L^\infty(Q_T)^d, \tag{54}$$

and let the nonlinear boundary fluxes satisfy the following assumption: there exists $0 \leqslant \tilde{G}(\mathbf{c}^{(1)}, \mathbf{c}^{(2)}, \varphi^{(1)}, \varphi^{(2)}) \leqslant M$, where $M \in \mathbb{R}_+$, such that

$$\left|\sum_{i=1}^n \int_{\Gamma_N} \big(g_i(\mathbf{c}^{(1)}, \varphi^{(1)}) - g_i(\mathbf{c}^{(2)}, \varphi^{(2)})\big)(c_i^{(1)} - c_i^{(2)})\, dS_x\right| \leqslant \tilde{G}(\mathbf{c}^{(1)}, \mathbf{c}^{(2)}, \varphi^{(1)}, \varphi^{(2)}) \sum_{i=1}^n \int_\Omega (c_i^{(1)} - c_i^{(2)})^2\, dx, \quad i = 1, \dots, n, \tag{55}$$

for all $\varphi^{(1)}$, $\varphi^{(2)}$ and $\mathbf{c}^{(1)} \geqslant 0$, $\mathbf{c}^{(2)} \geqslant 0$, satisfying $\sum_{i=1}^n c_i^{(1)} = \sum_{i=1}^n c_i^{(2)} = C$. In this special case, a weak solution (14) of the complete problem (15) is unique.

Proof. Let us assume two different solutions $(c_1^{(1)}, \dots, c_n^{(1)}, \varphi^{(1)})$ and $(c_1^{(2)}, \dots, c_n^{(2)}, \varphi^{(2)})$ of the problem (15). For fixed $t \in (0, T)$ this problem can be written in the quasi-static version for indexes $m = 1, 2$ as:

$$\int_\Omega \frac{\partial c_i^{(m)}}{\partial t} \bar{c}_i\, dx + \int_\Omega m_i \sum_{j=1}^n \Big[k_B \Theta \nabla c_j^{(m)} + \Upsilon_j(\mathbf{c}^{(m)}) \nabla\varphi^{(m)}\Big]^\top D^{ij} \nabla\bar{c}_i\, dx = \int_{\Gamma_N} g_i(\mathbf{c}^{(m)}, \varphi^{(m)}) \bar{c}_i\, dS_x, \quad i = 1, \dots, n; \tag{56}$$

$$\int_\Omega \Big((\nabla\varphi^{(m)})^\top A \nabla\bar{\varphi} - \sum_{k=1}^n z_k c_k^{(m)} \bar{\varphi}\Big)\, dx + \int_{\Gamma_N} \alpha\varphi^{(m)} \bar{\varphi}\, dS_x = \int_{\Gamma_N} g\bar{\varphi}\, dS_x. \tag{57}$$

In order to get (56) from (15a) we have used the identities (1d) and (1e), integrated (15a) by parts over the time first and then omitted the time integral. For short, the difference between these solutions is denoted by $\tilde{\varphi} := \varphi^{(1)} - \varphi^{(2)}$ and $\tilde{c}_i := c_i^{(1)} - c_i^{(2)}$, $i = 1, \dots, n$. We note that $\tilde{\varphi} = 0$ and $\tilde{c}_i = 0$ at Γ_D, $i = 1, \dots, n$, hence it can be taken as test functions in (56) and (57).

First, we consider the difference between two equations (57) for $m = 1$ and $m = 2$ with the test function $\tilde{\varphi}$, that is

$$\int_\Omega \Big(\nabla\tilde{\varphi}^\top A \nabla\tilde{\varphi} - \sum_{k=1}^n z_k \tilde{c}_k \tilde{\varphi}\Big)\, dx + \int_{\Gamma_N} \alpha\tilde{\varphi}^2\, dS_x = 0. \tag{58}$$

Young's and the Poincaré (23) inequalities applied to the second term in (58) provide

$$\left|\int_\Omega \sum_{k=1}^n z_k \tilde{c}_k \tilde{\varphi}\, dx\right| \leqslant \max_{l=1,\dots,n} |z_l| \int_\Omega \sum_{k=1}^n |\tilde{c}_k||\tilde{\varphi}|\, dx \leqslant \bar{Z}\Big(\frac{1}{2\delta_8} \sum_{k=1}^n \int_\Omega \tilde{c}_k^2\, dx + \frac{\delta_8 K_P}{2} \int_\Omega |\nabla\tilde{\varphi}|^2\, dx\Big), \tag{59}$$

where $\bar{Z} := \max_{l=1,\dots,n} |z_l|$ and $\delta_8 \in \mathbb{R}_+$ is arbitrary. From (58), using (59) and the ellipticity (10a), by analogy with the proof of the existence Theorem 3.1 we infer

$$\Big(\underline{a} - \frac{\delta_8 K_P \bar{Z}}{2}\Big) ||\nabla\tilde{\varphi}||^2_{L^2(\Omega)} + \min_{\alpha\in\Gamma_N} \alpha ||\tilde{\varphi}||^2_{L^2(\Gamma_N)} \leqslant \frac{\bar{Z}}{2\delta_8} \sum_{k=1}^n \int_\Omega \tilde{c}_k^2\, dx,$$

which concludes with the estimate

$$||\nabla\tilde{\varphi}||^2_{L^2(\Omega)} \leqslant \tilde{K}_\varphi \sum_{k=1}^n ||\tilde{c}_k||^2_{L^2(\Omega)}, \quad \text{where} \quad \frac{1}{\tilde{K}_\varphi} := \frac{2\delta_8}{\bar{Z}} \min\Big\{\underline{a} - \frac{\delta_8 K_P \bar{Z}}{2}, \min_{\alpha\in\Gamma_N} \alpha\Big\}. \tag{60}$$

In (60) the factor $\tilde{K}_\varphi > 0$ is positive for δ_8 chosen sufficiently small.

Second, we consider the difference between two equations (56) for $m = 1$ and $m = 2$ with the test function $\tilde{c}_i$. After summation over $i = 1, \dots, n$, using the identity

$$\int_{Q_\tau} \frac{\partial \tilde{c}_i}{\partial t} \tilde{c}_i\, dx\, dt = \frac{1}{2} \frac{d}{dt} \int_\Omega \tilde{c}_i(t)^2\, dx,$$

we get the equation

$$\frac{1}{2} \sum_{i=1}^n \frac{d}{dt} \int_\Omega \tilde{c}_i(t)^2\, dx + I_1 = I_2 + I_3, \tag{61}$$

with the following three integrals, which are defined as follows:

$$I_1 := \sum_{i,j=1}^n \int_\Omega m_i k_B \Theta \nabla\tilde{c}_j^\top D^{ij} \nabla\tilde{c}_i, \quad I_2 := -\sum_{i,j=1}^n \int_\Omega m_i \Big[\Upsilon_j(\mathbf{c}^{(1)})\nabla\varphi^{(1)} - \Upsilon_j(\mathbf{c}^{(2)})\nabla\varphi^{(2)}\Big]^\top D^{ij} \nabla\tilde{c}_i\, dx,$$
$$I_3 := \sum_{i=1}^n \int_{\Gamma_N} \big(g_i(\mathbf{c}^{(1)}, \varphi^{(1)}) - g_i(\mathbf{c}^{(2)}, \varphi^{(2)})\big) \tilde{c}_i\, dS_x.$$

Based on the strong ellipticity of the diffusivity matrices in (10b), we derive the lower bound for the absolute value of the first integral I_1:

$$|I_1| \geqslant \underline{d} k_B \Theta \sum_{i=1}^n \int_\Omega |\nabla\tilde{c}_i|^2\, dx. \tag{62}$$

Inserting the expressions of Υ_j from (18), the second integral I_2 can be rewritten equivalently as

$$I_2 = \sum_{i,j=1}^n \frac{m_i}{N_A} \int_\Omega \Big(z_j \tilde{c}_j \nabla\varphi^{(1)} + z_j c_j^{(2)} \nabla\tilde{\varphi} - \frac{1}{C}\big(\tilde{c}_j \sum_{k=1}^n z_k c_k^{(1)} \nabla\varphi^{(1)} + c_j^{(2)} \sum_{k=1}^n z_k \tilde{c}_k \nabla\varphi^{(1)} + c_j^{(2)} \sum_{k=1}^n z_k c_k^{(2)} \nabla\tilde{\varphi}\big)\Big)^\top D^{ij} \nabla\tilde{c}_i\, dx.$$

Using the condition (10b) for D^{ij} and Young's inequality with $\delta_9 > 0$, further we estimate

$$|I_2| \leqslant \frac{\bar{d}}{N_A} \sum_{i,j=1}^n \int_\Omega \Big\{\frac{\delta_9}{2} |\nabla\tilde{c}_i|^2 + \frac{1}{2\delta_9}\Big(|z_j \tilde{c}_j \nabla\varphi^{(1)}|^2 + |z_j c_j^{(2)} \nabla\tilde{\varphi}|^2$$
$$+ \frac{1}{C}\Big(|\tilde{c}_j \sum_{k=1}^n z_k c_k^{(1)} \nabla\varphi^{(1)}|^2 + |c_j^{(2)} \sum_{k=1}^n z_k \tilde{c}_k \nabla\varphi^{(1)}|^2 + |c_j^{(2)} \sum_{k=1}^n z_k c_k^{(2)} \nabla\tilde{\varphi}|^2\Big)\Big)\Big\}\, dx,$$

and, applying the Caushy–Schwarz inequality and rearranging the terms, we get

$$\begin{aligned} |I_2| \leqslant \frac{\bar{d}}{N_A} \sum_{i,j=1}^n \Big\{ \frac{1}{2\delta_9} \Big[\Big(|z_j|^2 + \frac{\sum_{k=1}^n |z_k|^2 ||c_k^{(1)}||_{L^\infty(\Omega)}}{C}\Big) ||\tilde{c}_j||^2_{L^2(\Omega)} ||\nabla\varphi^{(1)}||^2_{L^\infty(\Omega)} \\ + \Big(|z_j|^2 + \frac{\sum_{k=1}^n |z_k|^2 ||c_k^{(2)}||_{L^\infty(\Omega)}}{C}\Big) ||c_j^{(2)}||^2_{L^\infty(\Omega)} ||\nabla\tilde{\varphi}||^2_{L^2(\Omega)} \\ + \frac{1}{C} ||c_j^{(2)}||^2_{L^\infty(\Omega)} \sum_{k=1}^n |z_k|^2 ||\tilde{c}_k||^2_{L^2(\Omega)} ||\nabla\varphi^{(1)}||^2_{L^\infty(\Omega)} \Big] + \frac{\delta_9}{2} \int_\Omega |\nabla\tilde{c}_i|^2\, dx \Big\}. \end{aligned} \tag{63}$$

In order to proceed the estimation of (63) we need L^∞-bounds for $\nabla\varphi^{(1)}$, $\mathbf{c}^{(1)}$ and $\mathbf{c}^{(2)}$. In fact, the assumption (54) implies that there exists $K_6>0$ such that $||\nabla\varphi^{(1)}||^2_{L^\infty(\Omega)} \leqslant K_6$. The volume balance and positivity conditions (5) provide that $||c_i^{(1)}||^2_{L^\infty(\Omega)} < C$ and $||c_i^{(2)}||^2_{L^\infty(\Omega)} < C$ for $i=1,\dots,n$. Therefore, using the estimate (60) for $\nabla\tilde\varphi$, from (63) we conclude with the expression

$$|I_2| \leqslant \frac{\bar d}{N_A}\Big(K_7\sum_{i=1}^n ||\tilde c_i||^2_{L^2(\Omega)} + \frac{\delta_9}{2}\sum_{i=1}^n ||\nabla\tilde c_i||^2_{L^2(\Omega)}\Big), \quad \text{where} \quad \bar Z = \max_{l=1,\dots,n}|z_l| \quad \text{and} \quad K_7 := \frac{\bar Z^2}{2\delta_9}(3K_6 + 2C\tilde K_\varphi). \tag{64}$$

The third integral I_3 can be estimated due to the assumption (55) as follows:

$$|I_3| = \Big|\sum_{i=1}^n \int_{\Gamma_N} \big(g_i(\mathbf{c}^{(1)},\varphi^{(1)}) - g_i(\mathbf{c}^{(2)},\varphi^{(2)})\big)\tilde c_i\, dS_x\Big| \leqslant \tilde G(\mathbf{c}^{(1)},\mathbf{c}^{(2)},\varphi^{(1)},\varphi^{(2)})\sum_{i=1}^n\int_\Omega \tilde c_i^2\,dx \leqslant M\sum_{i=1}^n\int_\Omega \tilde c_i^2\,dx. \tag{65}$$

With the help of the estimates (62), (64), and (65), introducing the positive constant $\gamma := \max\Big\{\frac{\bar d K_7}{N_A}, M\Big\} > 0$, from (61) we derive that

$$\sum_{i=1}^n \Big\{\frac{d}{dt}\Big[\int_\Omega \tilde c_i^2\,dx\Big] + \big(\underline{d}k_B\Theta - \frac{\delta_9\bar d}{2N_A}\big)||\nabla\tilde c_i||^2_{L^2(\Omega)}\Big\} \leqslant \gamma\sum_{i=1}^n ||\tilde c_i||^2_{L^2(\Omega)}. \tag{66}$$

For δ_9 chosen sufficiently small such that $\delta_9 < 2\underline{d}k_B\Theta N_A/\bar d$, the second term in the left-hand side of (66) can be omitted, that follows the differential inequality with respect to the time t:

$$\frac{d}{dt}\sum_{i=1}^n ||\tilde c_i(t)||^2_{L^2(\Omega)} \leqslant \gamma\sum_{i=1}^n ||\tilde c_i(t)||^2_{L^2(\Omega)}.$$

After integration it over $t\in(0,T)$, we conclude that

$$\sum_{i=1}^n ||\tilde c_i(t)||^2_{L^2(\Omega)} \leqslant \sum_{i=1}^n ||\tilde c_i(0)||^2_{L^2(\Omega)} e^{\gamma t} = 0,$$

since $\tilde c_i(0)=0$. Therefore, $\tilde{\mathbf{c}}\equiv 0$ for all $t\in[0,T]$, and $\tilde\varphi\equiv 0$ due to (60) in the whole cylinder Q_T. □

Remark 3.7. *The functions $g_i(\mathbf{c},\varphi)$ from Example 2.1 satisfy the assumptions (55) in Theorem 3.6. On a weak solution $\mathbf{c}$ of the complete problem (15) these functions can be simplified to the following expressions:*

$$g_1(\mathbf{c},\varphi) = \frac{c_1c_2}{C^2}, \quad g_2(\mathbf{c},\varphi) = -\frac{c_1c_2}{C^2}, \quad g_k(\mathbf{c},\varphi) = 0 \quad \text{for} \quad k=3,\dots,n,$$

due to the volume balance and the positivity (5). In this case, after summation over $i=1,\dots,n$, using (22) and coarea formula, the integral in the left-hand side of (55) can be estimated as follows:

$$\Big|\int_{\Gamma_N}\frac{1}{C^2}\Big(\big(c_1^{(1)}c_2^{(1)} - c_1^{(2)}c_2^{(2)}\big)\tilde c_1 + \big(-c_1^{(1)}c_2^{(1)} + c_1^{(2)}c_2^{(2)}\big)\tilde c_2\Big)\,dS_x\Big|$$
$$\leqslant \Big|\int_{\Gamma_N}\frac{1}{C^2}\Big(c_2^{(1)}\tilde c_1^2 + c_1^{(2)}\tilde c_1\tilde c_2 - c_2^{(1)}\tilde c_1\tilde c_2 - c_1^{(2)}\tilde c_2^2\Big)\,dS_x\Big| \leqslant \frac{2}{C}\int_{\Gamma_N}(\tilde c_1^2+\tilde c_2^2)\,dS_x \leqslant \frac{4}{C}\int_\Omega(\tilde c_1^2+\tilde c_2^2)\,dx.$$

This implies the uniform estimate (55) with $\tilde G(\mathbf{c}^{(1)},\mathbf{c}^{(2)},\varphi^{(1)},\varphi^{(2)}) = 4/C = M$.

3.5. Entropy estimate and Lyapunov stability

For functions $\mathbf{c}(t,x)$ and constant Dirichlet data $\mathbf{c}^D$ satisfying the volume balance and positivity (5) and (6), we define the Lyapunov function describing the entropy as follows:

$$S:\mathbb{R}^+\to\mathbb{R}^+, \quad S(t) := \sum_{i=1}^n\int_\Omega c_i\ln\Big(\frac{c_i}{c_i^D}\Big)\,dx.$$

This function is non-negative. Indeed, since $\xi \ln \xi \geqslant \xi - 1$ for all $\xi > 0$ and using the volume balance equalities (5a) and (6a), it follows:

$$S = \sum_{i=1}^{n} \int_{\Omega} c_i^D \frac{c_i}{c_i^D} \ln\Big(\frac{c_i}{c_i^D}\Big)\, dx \geqslant \sum_{i=1}^{n} c_i^D \Big(\frac{c_i}{c_i^D} - 1\Big) = \sum_{i=1}^{n} (c_i - c_i^D) = 0.$$

In order to provide the dynamic stability in the sense of Lyapunov for the system (15), we introduce the function of dissipation based on S and using $\sum_{i=1}^{n}(\partial c_i/\partial t) = \partial C/\partial t = 0$:

$$\mathcal{D}: \mathbb{R}^+ \to \mathbb{R}, \quad \mathcal{D}(t) := -\frac{dS}{dt} = -\sum_{i=1}^{n} \int_{\Omega} \frac{\partial c_i}{\partial t}\Big[\ln\Big(\frac{c_i}{c_i^D}\Big) + 1\Big]\, dx = -\sum_{i=1}^{n} \int_{\Omega} \frac{\partial c_i}{\partial t} \ln\Big(\frac{c_i}{c_i^D}\Big)\, dx, \tag{67}$$

which will be examined with respect to positiveness. This task needs the following assumptions:

$$\text{constant data:} \quad c_i^D = \text{const}, \tag{68a}$$

$$\text{scalar diffusivity matrices:} \quad m_i D^{ij} = \underline{d}\delta_{ij} I, \tag{68b}$$

$$\text{scalar permittivity matrix:} \quad A = \underline{a} I, \tag{68c}$$

$$\text{charge neutrality:} \quad \sum_{k=1}^{n} z_k c_k^D = 0, \tag{68d}$$

where $I \in \mathbb{R}^{d\times d}$ stands for the identity matrix. We note that the assumption (68a) was already used to compute dS/dt in (67). For the dissipation $\mathcal{D}$ we will derive the entropy estimate below.

Theorem 3.8 (Lyapunov stability)**.** *Under assumptions (68) for* $\mathbf{c}$ *and* $\mathbf{c}^D$ *satisfying (5) and (6), the entropy dissipation defined in (67) possesses the following equivalent expression:*

$$\mathcal{D} = \mathcal{D}_1 + \mathcal{D}_2, \quad \text{where} \tag{69}$$

$$\mathcal{D}_1 := \frac{\underline{d}}{\underline{a} N_A} \int_{\Omega} \Big(\sum_{k=1}^{n} z_k c_k\Big)^2 dx + 4\underline{d} k_B \Theta \sum_{i=1}^{n} \int_{\Omega} |\nabla(\sqrt{c_i})|^2\, dx,$$

$$\mathcal{D}_2 := \frac{\underline{d}}{\underline{a} N_A} \int_{\Gamma_N} (g - \alpha\varphi) \sum_{k=1}^{n} z_k c_k\, dS_x - \sum_{i=1}^{n} \int_{\Gamma_N} g_i(\mathbf{c}, \varphi) \ln\Big(\frac{c_i}{c_i^D}\Big)\, dS_x.$$

By this, $\mathcal{D}_1 \geqslant 0$ *and the dissipation inequality* $\mathcal{D} \geqslant 0$ *is ensured by non-negative* $\mathcal{D}_2$*.*

Proof. Let the time $t \in (0, T)$ be fixed. Choosing the test function $\bar{c}_i = \ln\Big(\frac{c_i}{c_i^D}\Big)$ in (56) omitting the upper index (m), since $\ln\Big(\frac{c_i}{c_i^D}\Big) = \ln 1 = 0$ at the boundary Γ_D, it follows that:

$$\int_{\Omega} \frac{\partial c_i}{\partial t} \ln\Big(\frac{c_i}{c_i^D}\Big)\, dx + \underline{d} \int_{\Omega} \Big[k_B \Theta \nabla c_i + \Upsilon_i(\mathbf{c}) \nabla\varphi\Big]^{\top} \frac{\nabla c_i}{c_i}\, dx = \int_{\Gamma_N} g_i(\mathbf{c}, \varphi) \ln\Big(\frac{c_i}{c_i^D}\Big)\, dS_x, \tag{70}$$

where the assumption (68b) on diffusivities was used. After summation of (70) over $i = 1, \dots, n$, inserting the expressions (18) for Υ_i and using here the expression of dS/dt from (67), we obtain

$$\frac{dS}{dt} + \underline{d} k_B \Theta \sum_{i=1}^{n} \int_{\Omega} \frac{|\nabla c_i|^2}{c_i}\, dx + \frac{\underline{d}}{N_A} \int_{\Omega} \Big\{\nabla\varphi^{\top} \nabla\Big(\sum_{i=1}^{n} z_i c_i\Big) - \frac{1}{C} \sum_{k=1}^{n} z_k c_k \nabla\varphi^{\top} \sum_{i=1}^{n} \nabla c_i\Big\}\, dx$$
$$= \sum_{i=1}^{n} \int_{\Gamma_N} g_i(\mathbf{c}, \varphi) \ln\Big(\frac{c_i}{c_i^D}\Big)\, dS_x. \tag{71}$$

We note that the last term in the left-hand side of (71) is zero due to $\sum_{i=1}^{n} \nabla c_i = \nabla\Big(\sum_{i=1}^{n} c_i\Big) = \nabla C = 0$.

On the other hand, from (57) omitting the upper index (m) with the test function $\bar{\varphi} = \sum_{i=1}^n z_i c_i$ which is zero at Γ_D due to the charge neutrality (68d), we have the equation

$$\underline{a} \int_\Omega \nabla\varphi^\top \nabla\Big(\sum_{i=1}^n z_i c_i\Big)\, dx - \int_\Omega \Big(\sum_{i=1}^n z_i c_i\Big)^2 dx = \int_{\Gamma_N} (g - \alpha\varphi)\Big(\sum_{i=1}^n z_i c_i\Big)\, dS_x, \tag{72}$$

where the assumption (68c) on permittivity was used. Multiplying (72) by the constant factor $\Big(-\dfrac{d}{\underline{a} N_A}\Big)$ and adding the result to the equation (71), with the help of the identity $\dfrac{|\nabla c_i|^2}{c_i} = \big(2|\nabla(\sqrt{c_i})|\big)^2$ we infer the formula (69).

It is evident that $\mathcal{D}_1 \geqslant 0$. So long as $\mathcal{D}_2$ has no definite sign, the dissipation inequality $\mathcal{D} = \mathcal{D}_1 + \mathcal{D}_2 \geqslant 0$ can be guaranteed for non-negative $\mathcal{D}_2$. $\square$

Discussion

The Poisson–Nernst–Planck system describes electro–physical phenomena in a pore space at a micro level. It is of practical importance to derive rigorously an averaged model on a micro level by homogenization with respect to the pore size. This is the subject of the forthcoming work. The a-priori estimates and techniques developed in the present work will be useful for this task.

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