Entropy and convergence analysis for two finite volume schemes for a Nernst-Planck-Poisson system with ion volume constraints

Benoît Gaudeul, Jürgen Fuhrmann

ENTROPY AND CONVERGENCE ANALYSIS FOR TWO FINITE VOLUME SCHEMES FOR A NERNST-PLANCK-POISSON SYSTEM WITH ION VOLUME CONSTRAINTS.

BENOÎT GAUDEUL AND JÜRGEN FUHRMANN

Abstract. In this paper, we consider a drift-diffusion system with cross-coupling through the chemical potentials comprising a model for the motion of finite size ions in liquid electrolytes. The drift term is due to the self-consistent electric field maintained by the ions and described by a Poisson equation. We design two finite volume schemes based on different formulations of the fluxes. We also provide a stability analysis of these schemes and an existence result for the corresponding discrete solutions. A convergence proof is proposed for non-degenerate solutions. Numerical experiments show the behavior of these schemes.

Contents

1. Introduction 2
1.1. The Nernst-Planck-Poisson system with finite ionic volumes 2
1.2. Key properties of the continuous system 4
1.3. Positioning and outline 5
2. Discretization and main Theorems 5
2.1. Discretization of $(0,T)\times\Omega$ 6
2.2. A common setting for the Finite Volume schemes 7
2.3. Numerical fluxes for the conservation equations 8
2.4. Main theorems 9
3. Fixed Mesh analysis 10
3.1. Analysis of numerical flux based functions 10
3.2. *A priori* estimates 11
3.3. Existence of solutions 14
4. Convergence 15
4.1. Reconstruction operators 15
4.2. Compactness 16
4.3. Identification 24
5. Numerical Examples 27
5.1. Species redistribution in a one-dimensional cell filled with binary electrolyte 28
5.2. 1D stationary convergence test 30
5.3. An electrolytic diode 30
Acknowledgement 30
Appendix A. Chemical free energy density and chemical potentials 32
Appendix B. Proof of Lemma 3.2 33
Appendix C. Study of a numerical scheme for $h_i = \log(c_i) - \alpha\log(c_0)$ 35
Appendix D. A simple convergence lemma 36
References 37

sec:intro

1. Introduction

Proper modeling of the motion of ions in electrolytes – mixtures of a solvent and N ionic species which can be described by their concentrations c_i – and associated simulations are crucial in the development of efficient batteries, fuel cells, and many other applications commonly considered as key technologies for the 21st century. The classical Nernst-Planck equation is a linear system which for given electrostatic potential Φ, charge number z_i and diffusion coefficient D_i describes the evolution of the ion concentration c_i via

$$\partial_t c_i - \operatorname{div}(D_i N_i) = 0, \qquad N_i = \nabla c_i + z_i c_i \nabla \Phi = c_i \nabla \left(\log(c_i) + z_i \Phi\right).$$

The self-consistent electrostatic potential is described by the Poisson equation

$$-\nabla \cdot \lambda^2 \nabla \Phi = \sum_{i=1}^{N} z_i c_i.$$

This model assumes that ions are infinitely small and that the ions of a given species i interact neither with the solvent nor with other ionic species. However, in reality, ion sizes are finite, and ion motion is only possible with a simultaneous displacement of solvent molecules. Moreover, the effective size of ions is increased by the fact that in a polar solvent like water, they are surrounded by a solvation shell consisting of a certain number of solvent molecules. The inclusion of these effects into the model is particularly important for concentrated electrolytes and in electrode boundary layers with high ion concentrations.

Historically, there have been many, often independent attempts to fix this situation, see e.g. the review in [3], the discussion in [28] or [35]. A comprehensive model of ideal mixtures of solvated ions has been derived in [21, 20]. In [28, 29], a two point flux finite volume discretization approach for these problems has been derived. Various variants of ionic flux approximations have been investigated for the unipolar case, where only one ionic species is considered, in [9], with the result that the flux approximation approach introduced in [28] has several more accurate alternatives. For two of them, we have been able to find appropriate generalizations to the case of several ionic species. These are introduced and analyzed in the present paper.

In the sequel of Section 1, the continuous problem is formulated, and several key properties of the continuous system are discussed. Among these is the decay of an entropy functional for positive solutions.

1.1. The Nernst-Planck-Poisson system with finite ionic volumes.

Consider a bounded connected polytopal domain $\Omega \subset \mathbb{R}^d$, and finite simulation horizon $T > 0$. We model the evolution of the concentration c_0 of a solvent and N dissolved species: c_i, $i \in [\![1, N]\!]$. The mixture satisfies a volume filling constraint

$$\sum_{i=0}^{N} v_i c_i = 1,$$

where v_i are the molar volumes of the species. We will use this constraint using ratios of molar volumes $k_i = \frac{v_i}{v_0}$:

$$\sum_{i=0}^{N} k_i c_i = \frac{1}{v_0}. \tag{1.1}$$

eq:VFcons

The coefficients $(k_1, \dots, k_N)$ are parameters of the problem and k_0 is by definition equal to 1. As the molar volumes are not the same, the total concentration

$$\overline{c} := \sum_{i=0}^{N} c_i \tag{1.2}$$ {eq:defcba

is not uniform. The set of positive concentrations $c_i, i \in [\![1, N]\!]$ such that c_0 is positive is denoted by

$$\mathcal{A} = \left\{ (c_1, ..., c_N) \in (0, +\infty)^N \middle| c_0 := \frac{1}{v_0} - \sum_{i=1}^{N} k_i c_i > 0 \right\}.$$

We also introduce the topological adherence of $\mathcal{A}$:

$$\bar{\mathcal{A}} = \left\{ (c_1, ..., c_N) \in [0, +\infty)^N \middle| c_0 := \frac{1}{v_0} - \sum_{i=1}^{N} k_i c_i \geq 0 \right\}.$$

For the sake of clarity, we will let $C = (c_1, ..., c_N) \in \mathcal{A}$ and often consider c_0 and $\overline{c}$ as functions of C thanks to (1.1) and (1.2) without clearly expressing the dependency. The dissolved species follow a conservation equation:

$$\partial_t c_i - \operatorname{div} D_i \mathcal{N}_i = 0, \qquad \mathcal{N}_i = c_i \nabla \left(h_i(C) + \widetilde{z}_i \Phi \right) \qquad \forall i \in [\![1, N]\!]. \tag{1.3}$$ {eq:contCo

where $\widetilde{z}_i = z_i - k_i z_0$ the reduced charge number and $D_i > 0$ the diffusion coefficient are parameters of the problem, while $h_i(C)$ the chemical potential depends on all the concentrations through:

$$h_i(C) = \log \frac{c_i}{\overline{c}} - k_i \log \frac{c_0}{\overline{c}} \qquad \forall i \in [\![1, N]\!]. \tag{1.4}$$ {eq:defh}

This system is supplemented with Poisson equation for the potential:

$$-\lambda^2 \Delta \Phi = c^{\text{dop}} + \sum_{i=0}^{N} z_i c_i. \tag{1.5}$$ {eq:contPo

To simplify the computations, we let $c^{\text{dop}} = \frac{z_0}{v_0} + \widetilde{c}^{\text{dop}}$ and see that:

$$c^{\text{dop}} + \sum_{i=0}^{N} z_i c_i = \widetilde{c}^{\text{dop}} + \sum_{i=1}^{N} \widetilde{z}_i c_i.$$

To avoid unnecessary complications of the notations, we will drop the tildas for the reduced molar charges as the real molar charges do not appear anymore. Moreover, to simplify the proofs, we will assume that the solvent carries no charge, hence $z_0 = 0$ and $\widetilde{c}^{\text{dop}} = 0$. Treatment of nonzero $\widetilde{c}^{\text{dop}}$ one can find in [9].

As in [9], we consider a Dirichlet boundary condition for the potential on a non-negligible part of the boundary $\Gamma_{\text{D}} \subset \partial\Omega$ and homogeneous Neumann boundary condition on $\Gamma_{\text{N}} = \partial\Omega \setminus \Gamma_{\text{D}}$:

$$\Phi = \Phi^D \qquad \text{on } (0,T) \times \Gamma_D, \qquad \nabla\Phi \cdot n = 0 \qquad \text{on } (0,T) \times \Gamma_N, \tag{1.6}$$ {eq:cont B

where Φ^D is assumed to be constant in time and in $H^1(\Omega) \cap L^\infty(\Omega)$.

The system is supplemented with the following no flux boundary conditions for the concentrations:

$$c_i \nabla \left(h_i(C) + z_i \Phi \right) \cdot n = 0 \qquad \text{on } (0,T) \times \partial\Omega, \text{ for all } i \in [\![1, N]\!], \tag{1.7}$$ {eq:contBC

and with an initial condition C^0 satisfying:

$$C^0 \in L^\infty(\Omega, \bar{\mathcal{A}}) \qquad \text{and} \qquad \int_\Omega c_i^0 > 0 \qquad \forall i \in [\![0, N]\!]. \tag{1.8}$$ {eq:initco

c:Key prop

1.2. **Key properties of the continuous system.** In this section, we attempt to exhibit the properties of a smooth enough solution (C, Φ) to the system (1.3)–(1.8) so that calculations are justified. The first property is the conservation of mass. In other words, thanks to (1.3), C satisfies for any $t \in [0,T], i \in [\![1,N]\!]$:

$$\int_\Omega c_i(0,x) = \int_\Omega c_i(t,x).$$

Moreover, we need the concentrations to be positive for (1.4) to have a sense. In the discrete setting, we will show that the concentrations belong to $\mathcal{A}$. In the continuous setting, it will be assumed. We hint that it might be possible to do it using the entropy method [33] and the flux formulation proposed in [28]. Indeed, another key property of the system is the dissipation of a free energy. In this case, the chemical free energy density $H(C)$ is defined as follows:

$$H(C) := \sum_{i=0}^{N} c_i \log\left(\frac{c_i}{\overline{c}}\right) = \sum_{i=0}^{N} c_i \log c_i - \overline{c}\log\overline{c}.$$

This function is convex, however, the addition of the term $-\overline{c}\log\overline{c}$ makes the proof quite intricate. This point is detailed in Appendix A along with the proof of the following equations:

$$\partial_{c_i} H(c_1,...,c_N) = h_i(C), \qquad \forall i \in [\![1,N]\!],\ C=(c_1,...,c_N) \in \mathcal{A}, \tag{1.9}$$

{eq:goodH}

$$\frac{-\log(N+1)}{v_0 \min k_i} \leq H(C) \leq 0 \qquad \forall C \in \mathcal{A}. \tag{1.10}$$

{eq:Hbound}

The total free energy is formed by the integral of the chemical free energy density and electrical terms:

$$E(C,\Phi) = \int_\Omega H(C) + \lambda^2 \frac{|\nabla\Phi|^2}{2} \mathrm{d}x - \lambda^2 \int_{\Gamma_D} \Phi_D \nabla\Phi \cdot n.$$

inuous EED

Proposition 1.1. *Let (C,Φ) be smooth solutions of (1.3)–(1.8) such that $C(t,x) \in \mathcal{A}$. For such solutions, E is a convex Lyapunov functional. Moreover, we have:*

$$\partial_t E + \int_\Omega \sum_{i=1}^{n} D_i c_i |\nabla h_i(C) + z_i \Phi|^2 = 0. \tag{1.11}$$

{eq:contin

Proof. We have using chain rules and (1.9):

$$\partial_t \int_\Omega H(c_1,...,c_N)\mathrm{d}x = \int_\Omega \sum_{i=1}^{N} h_i(C)\partial_t c_i \mathrm{d}x. \tag{1.12}$$

{eq:CEEDCh

We also have using chain rules and integrating by part:

$$\partial_t \int_\Omega \frac{|\nabla\Phi|^2}{2}\mathrm{d}x = \int_{\partial\Omega} \Phi \partial_t (\nabla\Phi \cdot n) - \int_\Omega \Phi \partial_t \Delta\Phi \mathrm{d}x.$$

Notice that we have $\nabla\Phi\cdot n = 0$ on Γ_N and $\Phi = \Phi_D$ on Γ_D. Using equation (1.5), we have:

$$\partial_t \lambda^2 \left(\int_\Omega \frac{|\nabla\Phi|^2}{2}\mathrm{d}x - \int_{\Gamma_D} \Phi_D \nabla\Phi\cdot n \right) = \int_\Omega \Phi \sum_{i=1}^{N} z_i \partial_t c_i \mathrm{d}x.$$

Using this equation and (1.12), we have:

$$\partial_t E = \sum_{i=1}^{N} \int_\Omega (h_i(C) + z_i\Phi)\partial_t c_i \mathrm{d}x.$$

Using now equation (1.3) and integration by parts, we have the desired equation (1.11). Due to the non-negativity of $D_i c_i$, E is a Lyapunov functional. Its convexity follows from the assumption $C \in \mathcal{A}$ (see Lemma A.1). □

Finally, we introduce a notion of weak solution that relies on a reformulation of the fluxes:

$$\mathcal{N}_i = \nabla c_i - k_i c_i \nabla \log c_0 + (k_i - 1) c_i \nabla \log \overline{c} + z_i c_i \nabla \Phi,$$

and the space of H^1 functions satisfying the Dirichlet boundary conditions for the potential:

$$\mathcal{H}_{\Gamma^D} = \{f \in H^1(\Omega), f_{|\Gamma_D} = 0\} \qquad \text{and} \qquad Q_T = (0,T) \times \Omega.$$

More precisely:

ef:weaksol **Definition 1.** *A couple (C, Φ) is a weak solution of (1.3)–(1.8) if*

- *$C \in L^\infty((Q_T; \overline{\mathcal{A}})$ with $\log(c_0) \in L^2((0,T); H^1(\Omega))$, and $\Phi - \Phi^D \in L^\infty((0,T), \mathcal{H}_{\Gamma^D})$;*
- *for all $\varphi \in C_c^\infty([0,T) \times \overline{\Omega})^N$, $i \in [\![1, N]\!]$*

$$\iint_{Q_T} c_i \partial_t \varphi_i \mathrm{d}x\mathrm{d}t + \int_\Omega c_i^0 \varphi_i(0,x)\mathrm{d}x - \iint_{Q_T} \big(\nabla c_i + c_i \nabla\big(-k_i \log c_0 + (k_i - 1)\log \overline{c} + z_i \Phi\big)\big) \cdot \nabla \varphi_i \mathrm{d}x\mathrm{d}t = 0; \quad (1.13)$$

{eq:weak_c

- *for all $\psi \in \mathcal{H}_{\Gamma^D}$ and almost all $t \in (0,T)$,*

$$\lambda^2 \int_\Omega \nabla \Phi(t,x) \cdot \nabla \psi(x) \mathrm{d}x = \int_\Omega \psi(x) \sum_{i=1}^N z_i c_i(t,x) \mathrm{d}x. \quad (1.14)$$

{eq:weak_P

1.3. **Positioning and outline.** The structure of cross-diffusion systems challenges the maximum principle-based methods. In this paper we aim to discretize the system (1.3)–(1.8). For $N = 1$ this system is a nonlinear drift-diffusion problem and several discretizations have been proposed in [9]. We focus on the extension of these schemes to the more general setting with $N > 1$ while adapting the proofs to tackle the challenges introduced by cross-diffusion.

More precisely, in Section 2, the two point flux based finite volume discretization with two variants of the flux approximation is introduced. The main theorems about the existence of discrete solutions and the convergence of approximate solutions are stated. Existence, free energy decay, and positivity of concentrations are proven in Section 3, whereas the convergence is proven in Section 4. Several 1D and 2D numerical examples showcasing the proven properties of the discretization scheme are discussed in Section 5.

sec:disc

2. Discretization and main Theorems

In this section, we propose two discretizations of (1.3)–(1.8) and discrete counterparts of the continuous properties. First, in Section 2.1, we state the requirements on the mesh and fix some notations. Then in Section 2.2, we describe the common setting for the two schemes to be studied in this paper. These schemes, presented in Section 2.3, rely on so-called two-point flux approximations of different formulations of $\mathcal{N}_i$. Then in Section 2.4, we state our two main results. The first one, namely Theorem 2.1, focuses on the existence of a solution to the nonlinear system corresponding to the schemes for a given mesh, and the dissipation of the energy at the discrete level. More precisely, one establishes that all the studied schemes satisfy a discrete counterpart to Proposition 1.1. Our second main result, namely Theorem 2.2, is devoted to the convergence of the schemes as the time step and the mesh size tend to 0.

ssec:mesh

2.1. **Discretization of** $(0,T)\times\Omega$**.** In this paper, we perform a parallel study of two numerical schemes based on two-point flux approximation (TPFA) finite volume schemes. As explained in [22, 26], this approach appears to be very efficient for isotropic continuous problems when one has the freedom to choose a suitable mesh fulfilling the so-called orthogonality condition [32, 27]. We recall here the definition of such a mesh, which is illustrated in Figure 1.

def:mesh

Definition 2. *An admissible mesh of* Ω *is a triplet* $\left(\mathcal{T},\mathcal{E},(x_K)_{K\in\mathcal{T}}\right)$ *such that the following conditions are fulfilled.*

(i) The set $\mathcal{T}$ *is finite and each control volume (or cell)* $K\in\mathcal{T}$ *is non-empty, open, polyhedral, and convex. We assume that*

$$K\cap L=\emptyset \quad \text{if } K,L\in\mathcal{T} \text{ with } K\neq L, \qquad \text{while} \quad \bigcup_{K\in\mathcal{T}}\overline{K}=\overline{\Omega}.$$

(ii) Each face $\sigma\in\mathcal{E}$ *is closed and is contained in a hyperplane of* $\mathbb{R}^d$*, with positive* $(d-1)$*-dimensional Hausdorff (or Lebesgue) measure denoted by* $m_\sigma=\mathcal{H}^{d-1}(\sigma)>0$*. We assume that* $\mathcal{H}^{d-1}(\sigma\cap\sigma')=0$ *for* $\sigma,\sigma'\in\mathcal{E}$ *unless* $\sigma'=\sigma$*. For all* $K\in\mathcal{T}$*, we assume that there exists a subset* $\mathcal{E}_K$ *of* $\mathcal{E}$ *such that* $\partial K=\bigcup_{\sigma\in\mathcal{E}_K}\sigma$*. Moreover, we suppose that* $\bigcup_{K\in\mathcal{T}}\mathcal{E}_K=\mathcal{E}$*. Given two distinct control volumes* $K,L\in\mathcal{T}$*, the intersection* $\overline{K}\cap\overline{L}$ *either reduces to a single face* $\sigma\in\mathcal{E}$ *denoted by* $K|L$*, or its* $(d-1)$*-dimensional Hausdorff measure is* 0*.*

(iii) The cell centers $(x_K)_{K\in\mathcal{T}}$ *belong to their cell:* $x_K\in K$*, and are such that, if* $K,L\in\mathcal{T}$ *share a face* $K|L$*, then the vector* x_L-x_K *is orthogonal to* $K|L$*.*

(iv) For the boundary faces $\sigma\subset\partial\Omega$*, we assume that either* $\sigma\subset\overline{\Gamma}_D$ *or* $\sigma\subset\overline{\Gamma}_N$*. For* $\sigma\subset\partial\Omega$ *with* $\sigma\in\mathcal{E}_K$ *for some* $K\in\mathcal{T}$*, we assume additionally that there exists* $x_\sigma\in\sigma$ *such that* $x_\sigma-x_K$ *is orthogonal to* σ*.*

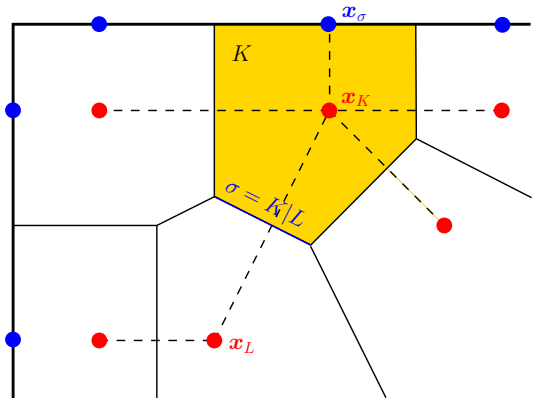

FIGURE 1. Illustration of an admissible mesh as in Definition 2. fig:mesh

We denote by m_K the d-dimensional Lebesgue measure of the control volume K. The set of the faces is partitioned into two subsets: the set $\mathcal{E}_{\rm int}$ of the interior faces defined by $\mathcal{E}_{\rm int}=\{\sigma\in\mathcal{E}\mid\sigma=K|L \text{ for some } K,L\in\mathcal{T}\}$, and the set $\mathcal{E}_{\rm ext}$ of the exterior faces defined by $\mathcal{E}_{\rm ext}=\{\sigma\in\mathcal{E}\mid\sigma\subset\partial\Omega\}$, which can also be partitioned into $\mathcal{E}^{\rm D}=\{\sigma\subset\overline{\Gamma}_{\rm D}\}$ and $\mathcal{E}^{\rm N}=\{\sigma\subset\overline{\Gamma}_{\rm N}\}$.

Given $\sigma\in\mathcal{E}$, we let

$$d_\sigma=\begin{cases}|x_K-x_L| & \text{if } \sigma=K|L\in\mathcal{E}_{\rm int},\\ |x_K-x_\sigma| & \text{if } \sigma\in\mathcal{E}_{\rm ext},\end{cases} \qquad \text{and} \quad \tau_\sigma=\frac{m_\sigma}{d_\sigma}.$$

We finally introduce the size $h_{\mathcal{T}}$ and the regularity $\zeta_{\mathcal{T}}$ (which is assumed to be positive) of a discretization $(\mathcal{T},\mathcal{E},(x_K)_{K\in\mathcal{T}})$ of Ω by setting

$$h_{\mathcal{T}} = \max_{K\in\mathcal{T}} \operatorname{diam}(K), \qquad \zeta_{\mathcal{T}} = \min_{K\in\mathcal{T}} \min_{\sigma\in\mathcal{E}_K} \frac{\mathrm{d}(x_K,\sigma)}{d_\sigma}.$$

Concerning the time discretization of $(0,T)$, we consider an increasing finite family of times $0 = t_0 < t_1 < \ldots, < t_{N_T} = T$. We denote by $\Delta t_n = t_n - t_{n-1}$ for $1 \le n \le N_T$, by $\boldsymbol{\Delta t} = (\Delta t_n)_{1\le n\le N_T}$, and by $h_{\boldsymbol{\Delta t}} = \max_{1\le n\le N_T} \Delta t_n$. We will use boldface notations for vectors whose number of components is dependent on the mesh while keeping the uppercase notation $\boldsymbol{C}$ when we also consider different species.

sec:scheme

2.2. **A common setting for the Finite Volume schemes.** The initial data C^0 which belongs to $L^\infty(\Omega,\bar{\mathcal{A}})$ thanks to (1.8) is discretized into $(C_K^0)_{K\in\mathcal{T}} \in \bar{\mathcal{A}}^{\mathcal{T}}$ by setting

$$c_{K,i}^0 = \fint_K c_i^0(x)\mathrm{d}x \qquad \forall K\in\mathcal{T}, i\in[\![1,N]\!]. \tag{2.1}$$

{eq:cK0}

Notice that previous equation also holds for $i=0$ and that this discretization satisfies:

$$\sum_{K\in\mathcal{T}} m_K c_{K,i}^0 = \int_\Omega c_i^0(x)\mathrm{d}x > 0 \qquad i\in[\![0,N]\!] \qquad \text{and} \qquad C_K^0\in\bar{\mathcal{A}} \qquad \forall K\in\mathcal{T}. \tag{2.2}$$

{eq:discin

Assume that $\boldsymbol{C}^{n-1} = \left(c_{K,i}^{n-1}\right)_{K\in\mathcal{T},i\in[\![0,N]\!]}$ is given for some $n>0$, then we have to define how to compute $(\boldsymbol{C}^n,\boldsymbol{\Phi}^n) = (C_K^n,\Phi_K^n)_{K\in\mathcal{T}}$. First, we introduce some notations. For all $K\in\mathcal{T}$ and all $\sigma\in\mathcal{E}_K$, we define the mirror values $C_{K\sigma}^n$ and $\Phi_{K\sigma}^n$ of C_K^n and Φ_K^n respectively across σ by setting

$$C_{K\sigma}^n = \begin{cases} C_L^n & \text{if } \sigma = K|L\in\mathcal{E}_{\mathrm{int}},\\ C_K^n & \text{if } \sigma\in\mathcal{E}_{\mathrm{ext}},\end{cases} \qquad \Phi_{K\sigma}^n = \begin{cases} \Phi_L^n & \text{if } \sigma = K|L\in\mathcal{E}_{\mathrm{int}},\\ \Phi_K^n & \text{if } \sigma\in\mathcal{E}^N,\\ \Phi_\sigma^D = \fint_\sigma \Phi^D\mathrm{d}\gamma & \text{if } \sigma\in\mathcal{E}^D.\end{cases} \tag{2.3}$$

{eq:mirror

Given $\boldsymbol{u} = (u_K)_{K\in\mathcal{T}}\in\mathbb{R}^{\mathcal{T}}$, we define the oriented and absolute jumps of $\boldsymbol{u}$ across any edge by

$$D_{K\sigma}\boldsymbol{u} = u_{K\sigma} - u_K, \quad D_\sigma\boldsymbol{u} = |D_{K\sigma}\boldsymbol{u}|, \qquad \forall K\in\mathcal{T},\ \forall\sigma\in\mathcal{E}_K.$$

We may now use these operators to describe our scheme. The potential is approximated using the classic TPFA scheme for the Poisson equation:

eq:scheme

$$-\lambda^2\sum_{\sigma\in\mathcal{E}_K}\tau_\sigma D_{K\sigma}\boldsymbol{\Phi}^n = m_K\sum_{i=1}^N z_i c_{K,i}^n, \qquad \forall K\in\mathcal{T}. \tag{2.4a}$$

{eq:scheme

The conservation equation is approximated using a backward-Euler scheme in time :

$$m_K\frac{c_{K,i}^n - c_{K,i}^{n-1}}{\Delta t_n} + \sum_{\sigma\in\mathcal{E}_K} F_{K\sigma,i}^n = 0, \qquad \forall K\in\mathcal{T}, i\in[\![1,N]\!], \tag{2.4b}$$

{eq:scheme

where $F_{K\sigma,i}^n$ should be a conservative and consistent approximation of $-\frac{D_i}{\Delta t_n}\int_{t_{n-1}}^{t_n}\int_\sigma \mathcal{N}_i\cdot n_{K\sigma}$ ($n_{K\sigma}$ denotes the normal to σ outward K). Finally, the concentration of the solvent is computed using a discrete version of the volume filling constraint:

$$c_{K,0}^n = \frac{1}{v_0} - \sum_{i=1}^N k_i c_{K,i}^n, \qquad \forall K\in\mathcal{T}. \tag{2.4c}$$

{eq:scheme

It remains to define the numerical fluxes $F_{K\sigma,i}^n$. Two possible choices are given in the next section.

sec:fluxes

2.3. **Numerical fluxes for the conservation equations.** To close the system (2.4), we have to define the numerical fluxes $F^n_{K\sigma,i}$. As we intend to use two point flux approximations, they should be of the form:

$$F^n_{K\sigma,i} = \begin{cases} 0 & \text{if } \sigma \in \mathcal{E}_{\text{ext}} \\ \tau_\sigma D_i \mathcal{F}_i(C_K, C_L, \Phi_K, \Phi_L) & \text{if } \sigma = K|L \in \mathcal{E}_{\text{int}} \end{cases} \tag{2.5}$$

{eq:def_fl

For the sake of readability, we have chosen to define the flux functions $\mathcal{F}_i$ for unitary D_i. Thus this constant should rarely appear in the functional inequalities of the following sections. To preserve the conservation of mass, all the flux functions $\mathcal{F}_i$ defined afterward satisfy an anti-symmetry property:

$$\mathcal{F}_i(C_K, C_L, \Phi_K, \Phi_L) = -\mathcal{F}_i(C_L, C_K, \Phi_L, \Phi_K) \qquad \forall C_K, C_L \in \mathcal{A}, \Phi_K, \Phi_L \in \mathbb{R}, \tag{2.6}$$

{eq:fluxan

so that the fluxes are locally conservative, i.e.:

$$F_{K,\sigma} + F_{L,\sigma} = 0 \qquad \forall \sigma = K|L \in \mathcal{E}_{\text{int}}.$$

2.3.1. *The centered flux.* The first numerical flux we consider is based on the original expression of the flux (1.3):

$$\mathcal{N}_i = D_i c_i \nabla \Big(h_i(c) + z_i \Phi \Big).$$

The gradient and edge concentration are independently discretized :

$$\mathcal{F}_i(C_K, C_L, \Phi_K, \Phi_L) = \frac{c_{K,i} + c_{L,i}}{2} \left(h_i(C_K) - h_i(C_L) \right) + z_i(\Phi_K - \Phi_L) \Big). \tag{C}$$

{eq:center

This flux is a straightforward generalization of the eponymous flux presented in [9]. As such it is also similar to the fluxes introduced in [15, 12, 7, 16, 11].

2.3.2. *The Sedan flux.* The other flux under study is also a generalization of the Sedan flux presented in [9]. It originates from and is named after the SEDAN III semiconductor device simulation code [41] and is used to handle the case of degenerated semiconductors in semiconductor device simulators, see [40, 39]. The scheme relies on the introduction of the excess chemical potential

$$\nu_i(C) := h_i(C) - \log(c_i) = -\log(\bar{c}) - k_i \log \frac{c_0}{\bar{c}}.$$

This excess potential characterizes the non-ideality of the electrolyte leading to the following equivalent continuous flux formulation:

$$\mathcal{N}_i = D_i \Big[\nabla c_i + c_i \nabla \left(z_i \Phi + \nu_i(C) \right) \Big].$$

The Scharfetter-Gummel-inspired discretization [38] of this expression of the flux leads to the so-called Sedan flux:

$$\begin{aligned} \mathcal{F}_i(C_K, C_L, \Phi_K, \Phi_L) = B\big(z_i\Phi_L + \nu_i(C_L) - z_i\Phi_K - \nu_i(C_K)\big)c_{K,i} \\ - B\big(z_i\Phi_K + \nu_i(C_K) - z_i\Phi_L - \nu_i(C_L)\big)c_{L,i}, \end{aligned} \tag{S}$$

{eq:sedanf

where $B(x) = \frac{x}{e^x - 1}$ for all $x \neq 0$ is the Bernoulli function. Notice that B can be extended by $B(0) = 1$ and is in C^∞.

Remark. In [9] we studied two other schemes. One was based on the diffusion enhancement and discretization ideas originating from [4]. The extension of this so-called Bessemoulin-Chatard scheme to the multi-species case appears to be not feasible due to the intrinsic use of one-dimensional chain rules. The other scheme based on activity variables and the averaging of the inverse activity coefficient was introduced for the multi-species case in [28]. Numerical analysis of such a scheme is more intricate and would likely not be satisfactory as we were not able to prove convergence in [9]. Moreover, unless more sophisticated inverse activity coefficient averaging strategies are available, this scheme is considerably less accurate compared to all the others discussed in [9].

ssec:main

2.4. **Main theorems.** We have proposed two schemes (2.4), (2.5) supplemented with either (C) or (S). Both schemes are nonlinear systems. Solutions to this nonlinear system should satisfy discrete equivalents of the properties listed in Section 1.2, namely conservation of mass and energy-dissipation. For the latter, we introduce the discrete energy functional $E_{\mathcal{T}}$ as a discrete counterpart of the continuous energy functional E. It is defined by:

$$E_{\mathcal{T}}(\boldsymbol{C}^n, \boldsymbol{\Phi}^n) = \sum_{K\in\mathcal{T}} m_K H(C_K^n) + \frac{\lambda^2}{2}\sum_{\sigma\in\mathcal{E}} \tau_\sigma \left(D_\sigma \boldsymbol{\Phi}^n\right)^2 - \lambda^2 \sum_{K\in\mathcal{T}}\sum_{\sigma\in\mathcal{E}^D\cap\mathcal{E}_K} \tau_\sigma \Phi_\sigma^D D_{K\sigma}\boldsymbol{\Phi}^n. \quad (2.7)$$

{eq:E_T}

The first theorem proven in this paper focuses on the existence of discrete solutions for a given mesh, and the preservation of the physical bounds: non negative concentrations, and the properties of Section 1.2.

:existence

Theorem 2.1. *Let $(\mathcal{T}, \mathcal{E}, (x_K)_{K\in\mathcal{T}})$ be an admissible mesh and let $\boldsymbol{C}^0$ be defined by (2.1). Then, for all $1 \le n \le N_T$, the nonlinear system of equations (2.4), (2.5) supplemented with either (C) or (S) has a solution*

$$(\boldsymbol{C}^n, \boldsymbol{\Phi}^n) \in \mathcal{A}^{\mathcal{T}} \times \mathbb{R}^{\mathcal{T}}.$$

Moreover, the solution to the scheme satisfies, for all $1 \le n \le N_T$,

$$E_{\mathcal{T}}(\boldsymbol{C}^n, \boldsymbol{\Phi}^n) - E_{\mathcal{T}}(\boldsymbol{C}^{n-1}, \boldsymbol{\Phi}^{n-1}) \le \Delta t_n \sum_{i=1}^{N}\sum_{\sigma\in\mathcal{E}} F_{K\sigma,i}^n D_{K\sigma}(h_i(\boldsymbol{C}^n) + z_i\boldsymbol{\Phi}^n), \quad (2.8)$$

{eq:EED}

and

$$\sum_{K\in\mathcal{T}} c_{K,i} m_K = \int_\Omega c_i^0(x)\mathrm{d}x \qquad \forall i \in [\![0, N]\!]. \quad (2.9)$$

{eq:MassCo

The proof of this theorem is the purpose of Section 3. Knowing a discrete solution to the scheme, $(\boldsymbol{C}^n, \boldsymbol{\Phi}^n)_{1\le n\le N}$, we can define an approximate solution $(C_{\mathcal{T},\boldsymbol{\Delta t}}, \Phi_{\mathcal{T},\boldsymbol{\Delta t}})$. It is the piecewise constant function defined almost everywhere by

$$C_{\mathcal{T},\boldsymbol{\Delta t}}(t,x) = C_K^n, \quad \Phi_{\mathcal{T},\boldsymbol{\Delta t}}(t,x) = \Phi_K^n \quad \text{if } (t,x) \in (t_{n-1}, t_n] \times K.$$

This definition will be developed in Section 4 and supplemented by other reconstruction operators.

Using this existence result, we let $(\mathcal{T}_m, \mathcal{E}_m, (x_K)_{K\in\mathcal{T}_m})_{m\ge1}$, $(\boldsymbol{C}_m^n, \boldsymbol{\Phi}_m^n) \in \mathcal{A}^{\mathcal{T}} \times \mathbb{R}^{\mathcal{T}}$, be a sequence of admissible meshes in the sense of Definition 2 and associated approximate solution. We assume that $h_{\mathcal{T}_m}, h_{\boldsymbol{\Delta t}_m} \underset{m\to\infty}{\longrightarrow} 0$ while the mesh regularity remains bounded, i.e., $\zeta_{\mathcal{T}_m} \ge \zeta^\star$ for some $\zeta^\star > 0$ not depending on m. A natural question is the convergence of $(C_{\mathcal{T}_m,\boldsymbol{\Delta t}_m}, \Phi_{\mathcal{T}_m,\boldsymbol{\Delta t}_m})$ towards a weak solution to the continuous problem. The convergence result is stated in Theorem 2.2 which will be proved in Section 4.

thm:conv **Theorem 2.2.** *For the two schemes under study, a sequence of approximate solutions* $(\boldsymbol{C}_{\mathcal{T}_m,\boldsymbol{\Delta t}_m}, \boldsymbol{\Phi}_{\mathcal{T}_m,\boldsymbol{\Delta t}_m})_{m\geq 1}$ *satisfies, up to a subsequence:*

$$C_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \underset{m\to\infty}{\longrightarrow} C \quad \text{in } L^2(Q_T)^{N+1}, \qquad \Phi_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \underset{m\to\infty}{\longrightarrow} \Phi \quad \text{in } L^2(Q_T). \tag{2.10}$$ {eq:conv}

Moreover if $\inf_{Q_T} c_0 > 0$, (C,Φ) *is a weak solution of* (1.3)–(1.8) *in the sense of Definition 1.*

:existence

3. Fixed Mesh analysis

In this section, we intend to prove Theorem 2.1. To this end, we will use a topological degree argument in Section 3.3. This topological degree relies on properties of the fluxes and *a priori* estimates detailed respectively in the following section and in Section 3.2. The methodology of this proof is very similar to the one done in [9]. The key changes and improvements are concentrated in Proposition 3.2, Lemmas 3.2 and 3.5.

xfunctions

3.1. Analysis of numerical flux based functions.

In this section, we introduce several functions derived from $\mathcal{F}_i$. As in [9], the first functions of interest models the free energy dissipation for each species $i \in [\![1,N]\!]$:

$$\mathcal{D}_i(C_K,C_L,\Phi_K,\Phi_L) := -\mathcal{F}_i(C_K,C_L,\Phi_K,\Phi_L)\left(h_i(C_K)+z_i\Phi_K - h_i(C_L) - z_i\Phi_L\right).$$

We also introduce the local free energy dissipation $\mathcal{D} := \sum_{i=1}^N \mathcal{D}_i$. In addition to this function, we can define a reconstruction of the concentration at the interfaces. This is the purpose of the following lemma:

lem:avg **Lemma 3.1.** *For a flux* $\mathcal{F}_i$ *defined either by* (C) *or* (S)*, the corresponding face concentration functions defined by*

$$\mathcal{C}_i(C_K,C_L,\Phi_K,\Phi_L) = \frac{\mathcal{F}_i(C_K,C_L,\Phi_K,\Phi_L)}{h_i(C_K)+z_i\Phi_K - h_i(C_L) - z_i\Phi_L} \qquad \forall i \in [\![1,N]\!] \tag{3.1}$$ {eq:EC}

if $h_i(C_K)+z_i\Phi_K - h_i(C_L) - z_i\Phi_L \neq 0$ *can be extended by continuity on* $\mathcal{A}\times\mathcal{A}\times\mathbb{R}\times\mathbb{R}$. *Moreover, for all* $(C_K,C_L,\Phi_K,\Phi_L) \in \mathcal{A}\times\mathcal{A}\times\mathbb{R}\times\mathbb{R}$, *and for all* $i \in [\![1,N]\!]$*:*

$$\min(c_{K,i},c_{L,i}) \leq \mathcal{C}_i(C_K,C_L,\Phi_K,\Phi_L) \leq \max(c_{K,i},c_{L,i}). \tag{3.2}$$ {eq:avg}

Proof. The proof of the extension by continuity and the average property (3.2) is highly similar to [9, Lemma 3.1]. For the centered scheme defined by (C), we have by definition:

$$\mathcal{C}_i(C_K,C_L,\Phi_K,\Phi_L) = \frac{c_{K,i}+c_{L,i}}{2},$$

hence the extension by continuity and equation (3.2).

For the Sedan scheme, defined by (S), we introduce $x_i = \log(c_{K,i}/c_{L,i})$ and $y_i = z_i\Phi_L + \nu_i(C_L) - z_i\Phi_K - \nu_i(C_K)$ and notice that:

$$\begin{aligned} h_i(C_K)+z_i\Phi_K - h_i(C_L) - z_i\Phi_L &= x_i - y_i, \\ \mathcal{F}_i(C_K,C_L,\Phi_K,\Phi_L) &= B(y_i)c_{K,i} - B(-y_i)c_{L,i}. \end{aligned} \tag{3.3}$$ {eq:h_as_x

Using the following property of the Bernoulli function:

$$B(\log(a)-\log(b))a - B(\log(b)-\log(a))b = 0, \qquad \forall (a,b)\in(0,+\infty)^2,$$

we have:

$$\mathcal{F}_i(C_K,C_L,\Phi_K,\Phi_L) = (B(y_i)-B(x_i))c_{K,i} - (B(-y_i)-B(-x_i))c_{L,i}. \tag{3.4}$$ {eq:newsed

Finally using (3.3) and the differentiability of B, we have the desired extension on $\mathcal{A}\times\mathcal{A}\times\mathbb{R}\times\mathbb{R}$. We also have equation (3.2) thanks to the monotony of B and the relation $B(x)-B(-x) = -x$ for all $x\in\mathbb{R}$. □

Thanks to this lemma, $\mathcal{D}_i$ rewrites:

$$\mathcal{D}_i(C_K, C_L, \Phi_K, \Phi_L) = \mathcal{C}_i(C_K, C_L, \Phi_K, \Phi_L)\Big(h_i(C_K) + z_i\Phi_K - h_i(C_L) - z_i\Phi_L\Big)^2. \quad (3.5)$$ {eq:Dd_ch2

This new formulation along with (3.2) grants the non-negativity of $\mathcal{D}_i$ and $\mathcal{D}$. The following lemma gives more detailed information on the behavior of $\mathcal{D}$:

m:Ddblowup **Lemma 3.2.** *Let for $\delta, \epsilon, M, c > 0$, $i \in [\![1, N]\!]$:*

$$\begin{aligned}\Psi_{\delta,\epsilon,M,i}(c) &:= \inf_{\substack{(C_K,C_L)\in\mathcal{A}^2,\ (\Phi_K,\Phi_L)\in[-M,M]^2\\ c_{K,0},c_{L,0}>\epsilon,\ c_{K,i}\geq\min(\delta,\frac{0.5}{k_i v_0}),\ c_{L,i}<c}} \mathcal{D}_i(C_K, C_L, \Phi_K, \Phi_L),\\ \Upsilon_{\delta,M}(c) &:= \inf_{\substack{(C_K,C_L)\in\mathcal{A}^2,\ (\Phi_K,\Phi_L)\in[-M,M]^2\\ c_{K,0}\geq\min(\delta,\frac{0.5}{v_0}),\ c_{L,0}<c}} \mathcal{D}(C_K, C_L, \Phi_K, \Phi_L).\end{aligned} \quad (3.6)$$ {eq:defPsi

We have, for all $\delta, \epsilon, M > 0$:

$$\lim_{c\to 0^+} \Upsilon_{\delta,M}(c) = +\infty \qquad \text{and} \qquad \lim_{c\to 0^+} \Psi_{\delta,\epsilon,M,i}(c) = +\infty \qquad \forall i \in [\![1, N]\!].$$

As the proof of this lemma is purely technical it has been relegated to appendix B.

ec:apriori 3.2. ***A priori* estimates.** In this section, we intend to establish uniform *a priori* estimates on the concentration and the potential, in order to prove the existence of solutions that satisfies the properties of Theorem 2.1.

We assume that we dispose of $(\boldsymbol{C}^n, \boldsymbol{\Phi}^n)_{n\in[\![0,N_{\max}]\!]}$ solution of (2.1), (2.4), (2.5) supplemented with either (C) or (S) in $\overline{\mathcal{A}}^{\mathcal{T}} \times \mathbb{R}^{\mathcal{T}}$. Where $\overline{\mathcal{A}}$, the adherence of $\mathcal{A}$ is the set of non-negative concentrations $c_0, ...c_N$ satisfying the volume filling constraint. The first *a priori* estimate is the conservation of mass (2.9):

m:masscons **Lemma 3.3.** *For all n in $[\![0, N_{max}]\!]$, i in $[\![0, N]\!]$ we have:*

$$\sum_{K\in\mathcal{T}} m_K c^n_{K,i} = \int_\Omega c^0_i(x)\mathrm{d}x.$$

The proof is straightforward and classical thanks to the local conservativity of the fluxes, the no flux boundary conditions, and the discretization choice for $\boldsymbol{C}^0$.

We can also build a discrete equivalent to Theorem 1.1 using $E_{\mathcal{T}}$ defined in (2.7) and the dissipation function $\mathcal{D}_i$. This is the purpose of the following proposition:

issipation **Proposition 3.1.** *For all n in $[\![0, N_{max}]\!]$, we have*

$$E_{\mathcal{T}}(\boldsymbol{C}^n, \boldsymbol{\Phi}^n) - E_{\mathcal{T}}(\boldsymbol{C}^{n-1}, \boldsymbol{\Phi}^{n-1}) \leq -\Delta t_n \sum_i D_i \sum_{\sigma=K|L\in\mathcal{E}_{int}} \tau_\sigma \mathcal{D}_i(C^n_K, C^n_L, \Phi^n_K, \Phi^n_L). \quad (3.7)$$ {eq:EEDdis

Remark 3.1. Thanks to (2.5) and the definition of $\mathcal{D}_i$, (3.7) and (2.8) are equivalents.

Proof. The proof is fairly classical once noticed that thanks to Lemma A.1, H is convex (thus $E_{\mathcal{T}}$ too). The inequality $f(a) - f(b) \leq f'(a)(a - b)$ yields:

$$\begin{aligned}E_{\mathcal{T}}(\boldsymbol{C}^n, \boldsymbol{\Phi}^n) - E_{\mathcal{T}}(\boldsymbol{C}^{n-1}, \boldsymbol{\Phi}^{n-1}) \leq \sum_{K\in\mathcal{T}}\sum_{i=1}^N m_K(c^n_{K,i} - c^{n-1}_{K,i})h_i(C^n_K) +\\ \lambda^2\sum_{\sigma\in\mathcal{E}} \tau_\sigma D_{K\sigma}\boldsymbol{\Phi}^n D_{K\sigma}(\boldsymbol{\Phi}^n - \boldsymbol{\Phi}^{n-1}) - \lambda^2\sum_{K\in\mathcal{T}}\sum_{\sigma\in\mathcal{E}^D\cap\mathcal{E}_K} \tau_\sigma\Phi^D_\sigma D_{K\sigma}(\boldsymbol{\Phi}^n - \boldsymbol{\Phi}^{n-1}).\end{aligned} \quad (3.8)$$ {eq:EED1}

Notice that the left-hand side is the term of interest, we will then focus on the reformulation of the right-hand side. We multiply equation (2.4b) by $h_i(C_K) + z_i\Phi_K$ and we sum over the cells and species in order to get the following three-terms formula:

$$\underbrace{\sum_{K\in\mathcal{T}}\sum_{i=1}^{N} m_K \frac{c_{K,i}^n - c_{K,i}^{n-1}}{\Delta t_n} h_i(C_K^n)}_{T_{\text{chem}}} + \underbrace{\sum_{K\in\mathcal{T}} \Phi_K \sum_{i=1}^{N} m_K z_i \frac{c_{K,i}^n - c_{K,i}^{n-1}}{\Delta t_n}}_{T_{\text{el}}}$$
$$+ \underbrace{\sum_{K\in\mathcal{T}}\sum_{i=1}^{N}\left(\sum_{\sigma\in\mathcal{E}_K} F_{K\sigma,i}^n\right)(h_i(C_K) + z_i\Phi_K)}_{T_{\text{diss}}} = 0. \quad (3.9)$$ {eq:EEDter

The term concerning the chemical energy, $\Delta t_n T_{\text{chem}}$, appears directly in (3.8), thus we focus on T_{el}. Using equation (2.4a), we have:

$$\Delta t_n T_{\text{el}} = \lambda^2 \sum_{\sigma\in\mathcal{E}} \tau_\sigma D_{K\sigma}\boldsymbol{\Phi}^n D_{K\sigma}(\boldsymbol{\Phi}^n - \boldsymbol{\Phi}^{n-1}) - \lambda^2 \sum_{K\in\mathcal{T}}\sum_{\sigma\in\mathcal{E}^D\cap\mathcal{E}_K} \tau_\sigma \Phi_\sigma^D D_{K\sigma}(\boldsymbol{\Phi}^n - \boldsymbol{\Phi}^{n-1}), \quad (3.10)$$ {eq:EEDTel

which is the second line of equation (3.8). For T_{diss}, an integration by parts yields:

$$T_{\text{diss}} = -\sum_{i=1}^{N}\sum_{\sigma\in\mathcal{E}} F_{K\sigma,i}^n D_{K\sigma}(h_i(\boldsymbol{C}) + z_i\boldsymbol{\Phi}).$$

Using this equation and equations (3.10), (3.9) in (3.8), we have (2.8):

$$E_{\mathcal{T}}(\boldsymbol{C}^n, \boldsymbol{\Phi}^n) - E_{\mathcal{T}}(\boldsymbol{C}^{n-1}, \boldsymbol{\Phi}^{n-1}) \le \Delta t_n \sum_{i=1}^{N}\sum_{\sigma\in\mathcal{E}} F_{K\sigma,i}^n D_{K\sigma}(h_i(\boldsymbol{C}^n) + z_i\boldsymbol{\Phi}^n),$$

which concludes the proof thanks to the preliminary remark. □

In the following lemma, we will show several bounds on the potential $\boldsymbol{\Phi}$ and then take advantage of them to get a bound on the free energy dissipation:

potential **Lemma 3.4.** *There exist M_Φ depending only on $\lambda, \Phi^D, \Omega, \frac{1}{v_0}, (k_1, \dots, k_N), (z_1, \dots, z_N)$, and another constant M_* depending also on $\zeta_{\mathcal{T}}$ such that:*

$$\|\boldsymbol{\Phi}^n\|_\infty \le M_\Phi, \qquad \forall 1 \le n \le N_{max}, \quad (3.11)$$ {eq:PhiLin

$$\sum_{\sigma\in\mathcal{E}} \tau_\sigma |D_\sigma \boldsymbol{\Phi}^n|^2 \le M_*, \qquad \forall 1 \le n \le N_{max}, \quad (3.12)$$ {est:H1dis

$$\left|\sum_{K\in\mathcal{T}}\sum_{\sigma\in\mathcal{E}^D\cap\mathcal{E}_K} \tau_\sigma \Phi_\sigma^D D_{K\sigma}\boldsymbol{\Phi}^n\right| \le M_*, \qquad \forall 1 \le n \le N_{max}, \quad (3.13)$$ {est:Phi2}

$$\sum_{n=1}^{N_{max}} \Delta t_n \sum_{i=1}^{N} D_i \sum_{\sigma=K|L\in\mathcal{E}_{int}} \tau_\sigma \mathcal{D}_i(C_K^n, C_L^n, \Phi_K^n, \Phi_L^n) \le M_*. \quad (3.14)$$ {est:diss}

Proof. The proof of (3.11) is a straightforward application of [9, Proposition A.1]. As the proof of (3.12) is detailed in [9, Lemma 3.6], we focus on the proof of (3.13), assuming (3.12).

Multiplying equation (2.4a) by Φ_K^n and summing over $K \in \mathcal{T}$ yields, using (2.3):

$$\sum_{\sigma\in\mathcal{E}} \tau_\sigma \left(D_\sigma \boldsymbol{\Phi}^n\right)^2 - \sum_{\sigma\in\mathcal{E}^D} \tau_\sigma \Phi_\sigma^D D_{K\sigma}\boldsymbol{\Phi}^n = \sum_{K\in\mathcal{T}} \Phi_K^n m_K \sum_{i=1}^{N} z_i c_{K,i}^n.$$

Using equation (3.12), (3.11), and $\boldsymbol{C}^n \in \overline{\mathcal{A}}^{\mathcal{T}}$, we have the desired result. The last result is based on (3.7). Summing that equation, we have:

$$\sum_{n=1}^{N_{\max}} \Delta t_n \sum_{i=1}^{N} D_i \sum_{\sigma=K|L\in\mathcal{E}_{\text{int}}} \tau_\sigma \mathcal{D}_i(C_K^n, C_L^n, \Phi_K^n, \Phi_L^n) \leq E_{\mathcal{T}}(\boldsymbol{C}^0, \boldsymbol{\Phi}^0) - E_{\mathcal{T}}(\boldsymbol{C}^{N_{\max}}, \boldsymbol{\Phi}^{N_{\max}}) \quad (3.15)$$

{eq:summed

We have thanks to equations (1.10), (3.12), and (3.13):

$$E_{\mathcal{T}}(\boldsymbol{C}^{N_{\max}}, \boldsymbol{\Phi}^{N_{\max}}) \geq -|\Omega| \frac{\log(N+1)}{v_0 \min k_i} - \lambda^2 M_* \qquad \text{and} \qquad E_{\mathcal{T}}(\boldsymbol{C}^0, \boldsymbol{\Phi}^0) \leq \frac{3}{2}\lambda^2 M_*,$$

so that (3.15) becomes:

$$\sum_{n=1}^{N_{\max}} \Delta t_n \sum_{i=1}^{N} D_i \sum_{\sigma=K|L\in\mathcal{E}_{\text{int}}} -\tau_\sigma \mathcal{D}_i(C_K^n, C_L^n, \Phi_K^n, \Phi_L^n) \leq \frac{5}{2}\lambda^2 M_* + |\Omega| \frac{\log(N+1)}{v_0 \min k_i}.$$

Hence the desired result, up to the choice of a bigger constant M_*. □

Finally, we use the free energy dissipation result (3.14), and the estimates on the free energy dissipation functional to improve the assumption $\boldsymbol{C}^n \in \overline{\mathcal{A}}^{\mathcal{T}}$.

tyestimate

Lemma 3.5. *There exist $\epsilon_0, \epsilon_1, ..., \epsilon_N$ positive, depending on, among other things, C^0 and decreasing with $\min \boldsymbol{\Delta t}$ and $\min_{\sigma\in\mathcal{E}} \tau_\sigma$ such that:*

$$c_{K,i}^n \geq \epsilon_i \qquad \forall K \in \mathcal{T}, n \in [\![1, N_{max}]\!], i \in [\![0, N]\!]$$

Proof. The proof follows the idea of [14, Lemma 3.10] (see also [15, Lemma 3.7], [9, Lemma 3.7]). We start with the proof for $i = 0$ and a fixed time step n using Υ_{δ,M_Φ}, then treat the case of $i \in [\![1, N]\!]$ using $\Psi_{\delta,\epsilon_0,M_\Phi,i}$ and finally notice that no assumptions were made on n.

Thanks to assumption (1.8) on the initial concentrations, and Lemma 3.3, we dispose of $K \in \mathcal{T}$ such that:

$$c_{K,0}^n \geq \fint_\Omega c_0^0 \mathrm{d}x =: \delta_0 > 0$$

We let $\delta_1 = \Upsilon^{-1}_{\delta_0,M_\Phi}(\frac{M_*}{\min \boldsymbol{\Delta t} \min_{i\in[\![1,N]\!]} D_i \min_{\sigma\in\mathcal{E}} \tau_\sigma})$ where M_* is as in Lemma 3.4. It is well defined thanks to the monotony of Υ and Lemma 3.2. Moreover, we have for every cell L sharing an edge with K:

$$c_{L,0}^n \geq \delta_1 > 0,$$

thanks to the positivity of $\mathcal{D}_i$ and equation (3.14). Similarly we recursively define:

$$\delta_{l+1} = \Upsilon^{-1}_{\delta_l,M_\Phi}(\frac{M_*}{\min \boldsymbol{\Delta t} \min_{i\in[\![1,N]\!]} D_i \min_{\sigma\in\mathcal{E}} \tau_\sigma}) \qquad \forall l \in \mathbb{N}^*, \quad (3.16)$$

{eq:defdel

and notice that thanks to the connectivity of Ω there exist l such that, for all $L \in \mathcal{T}$:

$$c_{L,0}^n \geq \delta_l.$$

Hence a possible choice for ϵ_0. As explained above, the proof is exactly the same for $i \in [\![1, N]\!]$, with the use of $\Psi_{\delta,\epsilon_0,M_\Phi,i}$ instead of Υ_{δ,M_Φ} in equation (3.16) and does not depend on the time step $n \geq 1$. □

:existence

3.3. **Existence of solutions.** Using the estimates of the previous section we can establish the existence of a solution to our numerical scheme. Thanks to Proposition 3.1 and Lemmas 3.3 and 3.5, this will conclude the proof of Theorem 2.1.

:existence

Proposition 3.2. *Let $\boldsymbol{C}^0$ be defined by (2.1). Then, for all $1 \leq n \leq N_T$, the nonlinear system of equations (2.4), (2.5) supplemented with either (C) or (S) has a solution $(\boldsymbol{C}^n, \boldsymbol{\Phi}^n) \in \mathcal{A}^{\mathcal{T}} \times \mathbb{R}^{\mathcal{T}}$.*

Proof. As in [9, Proposition 3.8], we use induction and a topological degree argument to transform continuously the non-linear system (2.4), (2.5) to a linear one. However, the path presented in [9] is no longer valid as we do not have a monotony property on h_i. The homotopy follows 3 steps. The first one is sketched in Appendix C, the second one changes the discretization while maintaining k_i, D_i to 1 and the potential to zero. The last step corresponds to the activation of the potential and the remaining nonlinearities.

Following these ideas, we follows the zeros of a homotopy $\mathcal{H}$:

$$\mathcal{H} : \begin{cases} [0,3] \times \mathcal{A}^{\mathcal{T}} \times \mathbb{R}^{\mathcal{T}} \to (\mathbb{R}^N)^{\mathcal{T}} \times \mathbb{R}^{\mathcal{T}} \\ (\alpha, \boldsymbol{C}, \boldsymbol{\Phi}) \mapsto \mathcal{H}(\alpha, \boldsymbol{C}, \boldsymbol{\Phi}), \end{cases}$$

which should be our scheme for $\alpha = 3$ and the heat equation for $\alpha = 0$.

At every step, $\boldsymbol{c}_0$ is eliminated thanks to (2.4c).

Step 1: implementation of the solvent effects using an ad hoc scheme. For $\alpha \in [0,1]$, $\mathcal{H} = 0$ means that for all $K \in \mathcal{T}$, $i \in [\![1, N]\!]$:

$$\frac{c_{K,i} - c_{K,i}^{n-1}}{\Delta t_n} m_K + \sum_{\sigma = K|L \in \mathcal{E}_{\text{int}}} \tau_\sigma \frac{c_{K,i} - c_{L,i}}{\log(c_{K,i}/c_{L,i})} \Big(\log(c_{L,i}) - \log(c_{K,i}) + \alpha \big(\log(c_{K,0}) - \log(c_{L,0}) \big) \Big) = 0,$$

$$-\lambda^2 \sum_{\sigma \in \mathcal{E}_K} \tau_\sigma D_{K\sigma} \boldsymbol{\Phi} = 0,$$

where Φ_α^D is set to zero. As expressed in Lemma C.1 we dispose of ϵ_1 such that the zeros of $\mathcal{H}$ have a concentration that is bounded away from zero by ϵ_1.

Step 2: change of scheme without potential and for identical species. We change the discretization of $c_i \nabla \log(c_i/c_0)$. For $\alpha \in [1,2]$, $\mathcal{H} = 0$ rewrites:

$$\frac{c_{K,i} - c_{K,i}^{n-1}}{\Delta t_n} m_K + (2-\alpha) \sum_{\sigma = K|L \in \mathcal{E}_{K,\text{int}}} \tau_\sigma \frac{c_{K,i} - c_{L,i}}{\log(c_{K,i}/c_{L,i})} \Big(\log(c_{L,i}) - \log(c_{K,i}) + \big(\log(c_{K,0}) - \log(c_{L,0}) \big) \Big)$$

$$+ (\alpha - 1) \sum_{\sigma = K|L \in \mathcal{E}_{K,\text{int}}} \tau_\sigma \mathcal{F}_i(C_K, C_L, 0, 0) = 0,$$

$$-\lambda^2 \sum_{\sigma \in \mathcal{E}_K} \tau_\sigma D_{K\sigma} \boldsymbol{\Phi} = 0$$

where Φ_α^D is again set to zero and $k_{i,\alpha}$ to 1. Here again we dispose of ϵ_2 such that the zeros of $\mathcal{H}$ have a concentration that is bounded away from zero by ϵ_2.

Step 3: activation of the potential and the difference between the species. For $\alpha \in [2,3]$, $\mathcal{H} = 0$ means:

$$\frac{c_{K,i} - c_{K,i}^{n-1}}{\Delta t_n} m_K + \big(3 - \alpha + (\alpha - 2)D_i\big) \sum_{\sigma = K|L \in \mathcal{E}_{K,\text{int}}} \tau_\sigma \mathcal{F}_i(C_K, C_L, (3-\alpha)\Phi_K, (3-\alpha)\Phi_L) = 0$$

$$-\lambda^2 \sum_{\sigma \in \mathcal{E}_K} \tau_\sigma D_{K\sigma} \boldsymbol{\Phi} = m_K \sum_{i=1}^{N} (3-\alpha) z_i c_i,$$

where Φ_α^D is set to $(3-\alpha)\Phi_D$ and $k_{i,\alpha}$ to $3 - \alpha + (\alpha - 2)k_i$. Thanks to Lemma 3.5, we dispose of ϵ_3 such that the zeros of $\mathcal{H}$ have a concentration that is bounded away from zero by ϵ_3.

Conclusion. Using a topological degree argument [34, 19], we can derive the existence of solutions for $\alpha = 3$ from the non zero topological degree at $\alpha = 0$ and the uniform bounds on the concentration: $\min(\epsilon_1, \epsilon_2, \epsilon_3)$ and the potential: M_Φ. □

4. Convergence

onvergence

In this section we prove Theorem 2.2, which states the convergence of our schemes towards a weak solution. We consider a sequence $\big(\mathcal{T}_m, \mathcal{E}_m, (x_K)_{K\in\mathcal{T}_m}\big)_{m\geq 1}$ of admissible meshes with $h_{\mathcal{T}_m}, h_{\boldsymbol{\Delta t}_m}$ tending to 0 as m tends to $+\infty$, while the regularity $\zeta_{\mathcal{T}_m}$ remains uniformly bounded from below by a positive constant $\zeta^\star$.

Thanks to Theorem 2.1, we have a family of discrete solutions $(\boldsymbol{C}_m, \boldsymbol{\Phi}_m)_m$. We will first propose different reconstructions of approximate solutions in Section 4.1, then we show several compactness properties in Section 4.2 in order to obtain the convergence of a subsequence of approximated solutions. Section 4.3 is then devoted to the identification of the limit as a weak solution.

To enlighten the notations, we will remove the subscript m as soon as it is not necessary for understanding.

econstruct

4.1. Reconstruction operators.

In order to carry out the analysis of convergence, we introduce some reconstruction operators following the methodology proposed in [24].

The operators $\pi_{\mathcal{T}} : \mathbb{R}^{\mathcal{T}} \to L^\infty(\Omega)$ and $\pi_{\mathcal{T},\boldsymbol{\Delta t}} : \mathbb{R}^{\mathcal{T}\times N_T} \to L^\infty((0,T)\times\Omega)$ are defined respectively by

$$\pi_{\mathcal{T}} \boldsymbol{u}(x) = u_K \quad \text{if } x \in K, \qquad \forall \boldsymbol{u} = (u_K)_{K\in\mathcal{T}},$$

and

$$\pi_{\mathcal{T},\boldsymbol{\Delta t}} \boldsymbol{u}(t,x) = u_K^n \quad \text{if } (t,x) \in (t_{n-1}, t_n] \times K, \qquad \forall \boldsymbol{u} = (u_K^n)_{K\in\mathcal{T}, 1\leq n\leq N_T}.$$

These operators allow passing from the discrete solution $(\boldsymbol{C}^n, \boldsymbol{\Phi}^n)_{1\leq n\leq N_T}$ to the approximate solution since

$$\Phi_{\mathcal{T},\boldsymbol{\Delta t}} = \pi_{\mathcal{T},\boldsymbol{\Delta t}}(\boldsymbol{\Phi}), \qquad c_{i,\mathcal{T},\boldsymbol{\Delta t}} = \pi_{\mathcal{T},\boldsymbol{\Delta t}}(\boldsymbol{c}_i), \qquad \forall i \in [\![1, N]\!].$$

To carry out the analysis, we further need to introduce an approximate gradient reconstruction. Since the boundary conditions play a crucial role in the definition of the gradient, we need to enrich the discrete solution by face values $(C_\sigma^n)_{\sigma\in\mathcal{E}_{\text{ext}}, 1\leq n\leq N}$ and $(\Phi_\sigma^n)_{\sigma\in\mathcal{E}_{\text{ext}}, 1\leq n\leq N}$ defined by $C_\sigma^n = C_{K\sigma}^n$ and $\Phi_\sigma^n = \Phi_{K\sigma}^n$ for $\sigma \in \mathcal{E}_{\text{ext}} \cap \mathcal{E}_K$. With a slight abuse of notations, we still denote by $\boldsymbol{C}^n = ((C_K^n)_{K\in\mathcal{T}}, (C_\sigma^n)_{\sigma\in\mathcal{E}_{\text{ext}}})$ and $\boldsymbol{\Phi}^n = ((\Phi_K^n)_{K\in\mathcal{T}}, (\Phi_\sigma^n)_{\sigma\in\mathcal{E}_{\text{ext}}})$ the elements of $\mathcal{A}^{\mathcal{T}\cup\mathcal{E}_{\text{ext}}}$ and $\mathbb{R}^{\mathcal{T}\cup\mathcal{E}_{\text{ext}}}$ containing both the cell values and the exterior faces values of the concentration and the potential respectively.

For $\sigma = K|L \in \mathcal{E}_{\text{int}}$, we denote by Δ_σ the diamond cell corresponding to σ, that is the interior of the convex hull of $\sigma \cup \{x_K, x_L\}$. For $\sigma \in \mathcal{E}_{\text{ext}}$, the diamond cell Δ_σ is defined as the interior of the convex hull of $\sigma \cup \{x_K\}$. The approximate gradient

$\nabla_{\mathcal{T}} : \mathbb{R}^{\mathcal{T}\cup\mathcal{E}_{\rm ext}} \to L^2(\Omega)^d$ is piecewise constant on the diamond cells Δ_σ, and it is defined as follows:

$$\nabla_{\mathcal{T}}\boldsymbol{u}(x) = d\frac{D_{K\sigma}\boldsymbol{u}}{d_\sigma}\boldsymbol{n}_{K\sigma} \quad \text{if } x \in \Delta_\sigma, \qquad \forall \boldsymbol{u} \in \mathbb{R}^{\mathcal{T}\cup\mathcal{E}_{\rm ext}}.$$

We also define $\nabla_{\mathcal{T},\boldsymbol{\Delta t}} : \mathbb{R}^{(\mathcal{T}\cup\mathcal{E}_{\rm ext})\times N} \to L^2(Q_T)^d$ by setting

$$\nabla_{\mathcal{T},\boldsymbol{\Delta t}}\boldsymbol{u}(t,\cdot) = \nabla_{\mathcal{T}}\boldsymbol{u}^n \quad \text{if } t \in (t_{n-1}, t_n], \qquad \forall \boldsymbol{u} = (\boldsymbol{u}^n)_{1\le n\le N} \in \mathbb{R}^{(\mathcal{T}\cup\mathcal{E}_{\rm ext})\times N}.$$

This reconstruction is merely weakly consistent (unless $d = 1$) and takes its source in [17, 25]. More consistent reconstruction operators will be introduced in Section 4.3. Let us recall now some key properties to be used in the analysis. First, for all $\boldsymbol{u}, \boldsymbol{v} \in \mathbb{R}^{\mathcal{T}\cup\mathcal{E}_{\rm ext}}$,

$$\sum_{\sigma\in\mathcal{E}} \tau_\sigma D_{K\sigma}\boldsymbol{u} D_{K\sigma}\boldsymbol{v} = \frac{1}{d}\int_\Omega \nabla_{\mathcal{T}}\boldsymbol{u}\cdot\nabla_{\mathcal{T}}\boldsymbol{v}\mathrm{d}x.$$

This implies in particular that

$$\sum_{\sigma\in\mathcal{E}} \tau_\sigma |D_\sigma \boldsymbol{u}|^2 = \frac{1}{d}\int_\Omega |\nabla_{\mathcal{T}}\boldsymbol{u}|^2\mathrm{d}x, \qquad \forall \boldsymbol{u} \in \mathbb{R}^{\mathcal{T}\cup\mathcal{E}_{\rm ext}}. \tag{4.1}$$ {eq:norm_L

ompactness

4.2. **Compactness.** In this section we intend to prove a discrete H^1 estimate on the concentrations using the bound on the free-energy dissipation (3.14). To that extend we will introduce a chemical dissipation $\mathcal{D}_{\rm chem}$ as a discrete equivalent to $\sum c_i|\nabla h_i(c)|^2$ and compare it both with the usual distance and the total dissipation $\mathcal{D}$.

As the identification of the limit is only possible for

$$\inf_{Q_T} c_0 > \epsilon > 0,$$

the results of this section are proved under this assumption and complemented with remarks indicating whether the hypothesis is necessary or not. In order to apply chain rules for the convergence, we need to change the face concentration $\mathcal{C}$ from the one defined by the numerical scheme through Lemma 3.1 to the logarithmic average:

$$\widetilde{\mathcal{C}}_i(C_K, C_L) = \frac{c_{K,i} - c_{L,i}}{\log(c_{K,i}) - \log(c_{L,i})} \qquad \forall i \in [\![0, N]\!]. \tag{4.2}$$ {eq:wtEC}

This choice of edge concentration will also be used in the definition of $\mathcal{D}_{\rm chem}$ to avoid a dependency on the potential. The following lemma provides an estimate the numerical-flux based averages using this logarithmic average.

conschange

Lemma 4.1. *For all $\epsilon > 0$ there exists $\alpha_\epsilon > 0$ depending only on ϵ, M_Φ such that, for all $(C_K, C_L, \Phi_K, \Phi_L) \in \mathcal{A}\times\mathcal{A}\times[-M_\Phi, M_\Phi]\times[-M_\Phi, M_\Phi]$, and for all $i \in [\![1, N]\!]$:*

$$c_{K,0}, c_{L,0} > \epsilon \implies \alpha_\epsilon\widetilde{\mathcal{C}}_i(C_K, C_L) \le \mathcal{C}_i(C_K, C_L, \Phi_K, \Phi_L). \tag{4.3}$$ {eq:edgeco

Proof. For the centered scheme, this inequality is known with $\alpha_\epsilon = 1$ without assumption on c_0 [36]. For the Sedan scheme the proof is more intricate and uses the hypothesis on c_0. Equation (4.3) is equivalent to the boundedness of

$$R_i(C_K, C_L, \Phi_K, \Phi_L) := \frac{\widetilde{\mathcal{C}}_i(C_K, C_L)}{\mathcal{C}_i(C_K, C_L, \Phi_K, \Phi_L)},$$

for $c_{K,0}, c_{L,0} > \epsilon$. Introduce $x_i = \log\frac{c_{K,i}}{c_{L,i}}$, and $y_i = z_i\Phi_L + \nu_i(C_L) - z_i\Phi_K - \nu_i(C_K)$ as in the proof of lemma 3.1. By symmetry, one can assume $x_i \ge 0$ and thanks to our assumption on the solvent and the potential, y_i is bounded by some K. Moreover, we notice that by definition of x_i, (3.4) yields:

$$\mathcal{F}_i(C_K, C_L, \Phi_K, \Phi_L) = c_{L,i}\big(B(y_i)e^{x_i} - B(-y_i)\big),$$

so that we have:

$$R_i(C_K, C_L, \Phi_K, \Phi_L) = \frac{e^{x_i} - 1}{x_i} \frac{x_i - y_i}{B(y_i)e^{x_i} - B(-y_i)}.$$

The right-hand side can be seen as a continuous function of x_i, y_i. Is is bounded on the boundary of its definition domain $[0, +\infty) \times [-K, K]$ and admits a finite limit $\frac{1}{B(\mu)}$ for $x_i \to \infty, y_i \to \mu$, thus R_i is bounded. □

Then we try to take advantage of Proposition 3.1. As Lemma 3.4 already provides satisfying estimates on $\mathbf{\Phi}$, we introduce

$$\mathcal{D}_{\text{chem,i}}(C_K, C_L) : \begin{array}{lll} \mathcal{A}^2 & \to & \mathbb{R} \\ (C_K, C_L) & \mapsto & \widetilde{\mathcal{C}}_i(C_K, C_L)(h_i(C_K) - h_i(C_L))^2, \end{array}$$

and

$$\mathcal{D}_{\text{chem}} = \sum_{i=1}^{N} \mathcal{D}_{\text{chem,i}}.$$

A first interesting result is that $\mathcal{D}_{\text{chem}}$ is a semimetric on $\mathcal{A}$. The non-negativity and symmetry properties are trivially satisfied, the last property is the subject of the following lemma.

:Ddnotzero **Lemma 4.2.** *We have $\mathcal{D}_{\text{chem}}(C_K, C_L) = 0$ if and only if $C_K = C_L$*

Proof. If $C_K = C_L$, we obviously have $\mathcal{D}_{\text{chem}}(C_K, C_L) = 0$, we will then focus on the other implication. Assume that we dispose of C_K, C_L in $\mathcal{A}$ such that $\mathcal{D}_{\text{chem}}(C_K, C_L) = 0$. We let for $i \in [\![0, N]\!]$:

$$a_{K,i} = \log \frac{c_{K,i}}{\overline{c}_K} \qquad a_{L,i} = \log \frac{c_{L,i}}{\overline{c}_L}, \tag{4.4}$$ {eq:defa}

such that $h_i(C_K) = a_{K,i} - k_i a_{K,0}$. We have $\widetilde{\mathcal{C}}_i(C_K, C_L) \geq \min(c_{K,i}, c_{L,i}) > 0$, thus $\mathcal{D}_{\text{chem}}$ is the sum of nonnegative terms. As we have $\mathcal{D}_{\text{chem}}(C_K, C_L) = 0$, we have:

$$a_{K,i} - k_i a_{K,0} = a_{L,i} - k_i a_{L,0} \qquad \forall i \in [\![1, N]\!].$$

Assume that $a_{K,0} = a_{L,0}$, then $A_K = A_L$, where $A = (a_0, ..., a_N)$. Using $\sum_{i=0}^{N} k_i e^{a_i} = \frac{1}{v_0 \overline{c}}$, $A_K = A_L$ implies $C_K = C_L$.

The other case is absurd: using the symmetry of $\mathcal{D}_{\text{chem}}$, one can freely assume that $a_{K,0} > a_{L,0}$. Using $k_i > 0$, we have $a_{K,i} > a_{L,i} \forall i \in [\![1, N]\!]$ hence:

$$1 = \sum_{i=0}^{N} e^{a_{K,i}} > \sum_{i=0}^{N} e^{a_{L,i}} = 1.$$

□

The function $\mathcal{D}_{\text{chem}}$ cannot be extended by continuity onto $\overline{\mathcal{A}}^2$. Some information for near zero concentrations is can be inferred from lemma 3.2. The following sequential result means that the semi-metric property is preserved near the boundary $\partial\mathcal{A}^2$.

semimetric **Lemma 4.3.** *Let (C_K^l, C_L^l) be a sequence of $\mathcal{A}^2$. If we have $\mathcal{D}_{\text{chem}}(C_K^l, C_L^l) \to 0$ then $C_K^l - C_L^l \to 0$*

Proof. For the sake of simplicity, as this result will only be used with a lower bound on c_0, we keep the proof to this simpler case and assume that $\inf(c_{K,0}^l, c_{L,0}^l) > 0$. To prove the limit, we will show that from any sub-sequence, we can extract a sub-sub-sequence such that $C_K^l - C_L^l \to 0$. Considering any sub-sequence, thanks to the boundedness of $\mathcal{A}$ we can extract a sub-sub-sequence such that C_K^l and C_L^l converge. If we dispose of

$i \in [\![1, N]\!]$ such that $c^l_{K,i} \to c^* > 0$ while $c^l_{L,i} \to 0$ (or the symmetric situation), then we have:

$$\widetilde{\mathcal{C}}_{\sigma,i}(C^l_K, C^l_L) \underset{l\to\infty}{\sim} \frac{c^*}{-\log(c^l_{L,i})} \qquad \text{and} \qquad \left(h_i(C^l_K) - h_i(C^l_L)\right)^2 \underset{l\to\infty}{\sim} \log(c^l_{L,i})^2$$

so that $\mathcal{D}_{\text{chem,i}}(C^l_K, C^l_L) \sim_{l\to\infty} -c^* \log(c^l_{L,i}) \to \infty$, which is absurd. Necessary, we have $c^l_{L,i} \to 0$ if and only of $c^l_{K,i} \to 0$. As we have $\mathcal{D}_{\text{chem,i}}(C^l_K, C^l_L) \to 0$, we also have:

$$a^l_{K,i} - k_i a^l_{K,0} = a^l_{L,i} - k_i a^l_{L,0} + o(1) \qquad \forall i \in [\![1, N]\!], \inf_l(c^l_{L,i}) > 0,$$

where $a_{K,i}, a_{L,i}$ are defined by (4.4). As both $c^l_{K,i}$ and $c^l_{L,i}$ are bounded away from zero, $a^l_{K,i}$ and $a^l_{L,i}$ are convergent. Using the symmetry and up to a subsequence we have either $a^l_{K,0} - a^l_{L_0}$ convergent of limit zero or bounded away from zero. We conclude using the same ideas as the proof of the previous lemma. □

This semi-metric is however not commonly used and the following lemma intends to compare it with the usual distance.

inequality **Proposition 4.1.** *For all $i \in [\![0, N]\!]$, there exist M such that:*

$$\frac{(c_{K,i} - c_{L,i})^2}{\mathcal{D}_{\text{chem}}(C_K, C_L)} \leq M, \qquad \forall\, C_K, C_L \in \mathcal{A}^2. \tag{4.5}$$ {eq:compac

Proof. We will prove the result for $i \in [\![1, N]\!]$ using *reductio ad absurdum* and case exhaustion.

Let $(C^n_K, C^n_L) \in (\mathcal{A}^2)^{\mathbb{N}}$ be such that $\frac{\left(c^n_{K,i} - c^n_{L,i}\right)^2}{\mathcal{D}_{\text{chem}}(C^n_K, C^n_L)} \to \infty$. We let $\epsilon^n := C^n_L - C^n_K$ and use the boundedness of $\mathcal{A}$ to extract a convergent sub-sequence of (C^n_K, ϵ^n) and denote (C^*, ϵ^*) its limit. As c_i is bounded, we have $\mathcal{D}_{\text{chem}}(C^n_K, C^n_L) \to 0$. Thanks to Lemma 4.3, we have $\epsilon^* = 0$ so that we will consider first order development in ϵ^n. We notice that the blow-up of the ratio implies that:

$$\mathcal{D}_{\text{chem,j}}(C^n_K, C^n_L) = o(|\epsilon^n|^2) \qquad \forall j \in [\![1, N]\!]. \tag{4.6}$$ {eq:proofk

For the sake of readability, we will drop from now on the superscript ^{n}. We have to consider three cases:

item1 (1) $c^*_j = 0$ implies $\epsilon_j = o(|\epsilon|)$;

item2 (2) we dispose of species such that $\epsilon_j \neq o(|\epsilon|)$ and $c^*_j = 0$, but for all of them $\log \frac{\epsilon_j + c_j}{c_j}$ remains bounded;

item3 (3) we dispose of a specie such that $\epsilon_j \neq o(|\epsilon|)$, $c^*_j = 0$, and up to a subsection, $\log \frac{\epsilon_j + c_j}{c_j}$ blows-up.

Preliminary remark about the solvent. We consider $j \in [\![1, N]\!]$ such that $c^*_j > 0$ and let $\overline{\epsilon}_j = \sum_{i=0}^N \epsilon_i$. We have, thanks to (4.6):

$$\log \frac{c_j + \epsilon_j}{c_j} = O(|\epsilon|) \qquad \text{and} \qquad \log \frac{\overline{c}_j + \overline{\epsilon}_j}{\overline{c}_j} = O(|\epsilon|) \qquad \text{and} \qquad h_j(C_K) - h_j(C_L) = O(|\epsilon|),$$

so that:

$$\log \frac{c_0 + \epsilon_0}{c_0} = O(|\epsilon|),$$

thus:

$$\frac{\epsilon_0}{c_0} = O(|\epsilon|) \qquad \text{and} \qquad \log \frac{c_0 + \epsilon_0}{c_0} = \frac{\epsilon_0}{c_0} + o(|\epsilon|).$$

Conclusion of the proof in case 1. The proof of this first case is by far the most intricate of the three. It is done in two step: first we use our hypothesis on $\mathcal{D}_{\text{chem}}$, c, and ϵ to obtain a estimate where the species are coupled through an ersatz of $\overline{\epsilon}$ and $\overline{c}$. Then we show an improved version of the Cauchy-Schwarz inequality to improve the estimate into decoupled estimates which are incompatible with our hypothesis.

First order development of h_j gives:

$$h_j(C_K) - h_j(C_L) = \frac{\epsilon_j}{c_j} - k_j\frac{\epsilon_0}{c_0} + (k_j-1)\frac{\overline{\epsilon}}{\overline{c}} + o(\epsilon), \qquad \forall j \in [\![1,N]\!], c_j^* > 0.$$

Thanks to (4.6) we have the estimation:

$$\frac{\epsilon_j}{c_j} - k_j\frac{\epsilon_0}{c_0} + (k_j-1)\frac{\overline{\epsilon}}{\overline{c}} = o(|\epsilon|), \qquad \forall j \in [\![1,N]\!], c_j^* > 0. \tag{4.7}$$ {eq:reform

To correct the effect of the species with negligible concentrations, we let:

$$\widetilde{\epsilon_0} = -\sum_{\substack{c_j^*>0\\ j\neq 0}} k_j\epsilon_j \qquad \widetilde{\epsilon} = \widetilde{\epsilon_0} + \sum_{\substack{c_j^*>0\\ j\neq 0}} \epsilon_j \qquad \text{and} \qquad \widetilde{c} = \sum_{c_j^*>0} c_j$$

By construction, we have $\widetilde{c} = \overline{c} + o(1)$. Using the hypothesis (1) we have $\widetilde{\epsilon} = \overline{\epsilon} + o(|\epsilon|)$ and $\widetilde{\epsilon_0} = \epsilon_0 + o(|\epsilon|)$. These three results and equation (4.7) yields:

$$\frac{\epsilon_j}{c_j} - k_j\frac{\widetilde{\epsilon_0}}{c_0} + (k_j-1)\frac{\widetilde{\epsilon}}{\widetilde{c}} = o(|\epsilon|), \qquad \forall j \in [\![1,N]\!], c_j^* > 0.$$

We let $\xi_j = \frac{\epsilon_j}{c_j} - \frac{\widetilde{\epsilon}}{\widetilde{c}}$ for $j \neq 0$ and $\xi_0 = \frac{\widetilde{\epsilon_0}}{c_0} - \frac{\widetilde{\epsilon}}{\widetilde{c}}$. Previous equation yields:

$$\xi_j = k_j\xi_0 + o(|\epsilon|), \qquad \forall j \in [\![1,N]\!], c_j^* > 0.$$

Considering $\sum_{c_j^*>0} c_j\xi_j$, we have:

$$0 = \widetilde{\epsilon} - \widetilde{\epsilon} = \sum_{c_j^*>0} c_j\xi_j = \sum c_jk_j\xi_0 + o(|\epsilon|) = \xi_0\left(\frac{1}{v_0} + o(1)\right) + o(|\epsilon|),$$

so that:

$$\xi_0 = o(|\epsilon|).$$

We conclude the first part of the proof with the following estimate that follows from (4.6):

$$\sum_{c_j^*>0\cup\{0\}} c_j\xi_j^2 = o(|\epsilon|^2). \tag{4.8}$$ {eq:case1s

For the sake of readability, we will drop the $\widetilde{}$ over ϵ_0 in the second part of the proof, use "$c_j^* > 0$" instead of "$c_j^* > 0$ or $j = 0$", and assume by symmetry that $\widetilde{\epsilon} \geq 0$. We have :

$$\sum_{c_j^*>0} c_j\xi_j^2 = \sum_{c_j^*>0} \frac{\epsilon_j^2}{c_j} - \frac{\widetilde{\epsilon}^2}{\widetilde{c}}. \tag{4.9}$$ {eq:case1s

Let $x_j = \sqrt{c_j}$, $y_j = \frac{\epsilon_j}{\sqrt{c_j}}$. We have:

$$\widetilde{\epsilon} = \sum_{c_j^*>0} x_jy_j, \qquad |x|^2 = \widetilde{c}, \qquad |y|^2 = \sum_{c_j^*>0} \frac{\epsilon_j^2}{c_j},$$

Thus the Cauchy-Schwarz inequality yields

$$\widetilde{\epsilon}^2 \leq \widetilde{c}\sum_{c_j^*>0} \frac{\epsilon_j^2}{c_j},$$

hence another proof of the non-negativity of the right-hand side of (4.9). We intend to use ideas presented in [2] to improve the estimation of $\widetilde{\epsilon}$. More precisely, the stability version of the Cauchy-Schwarz presented in [1] gives:

$$\widetilde{\epsilon} = |x||y| \left(1 - \frac{1}{2}\left|\frac{x}{|x|} - \frac{y}{|y|}\right|^2\right).$$

We intend to show that $\left|\frac{x}{|x|} - \frac{y}{|y|}\right|$ is bounded away from zero. To show this bound we let:

$$K : (C, \epsilon) \mapsto \left|\frac{x}{|x|} - \frac{y}{|y|}\right|$$

and consider a minimizing sequence of K under the conditions

$$c_j > 0, \qquad \epsilon_0 = -\sum_{\substack{c_j^* > 0 \\ j \neq 0}} k_j \epsilon_j.$$

As K is invariant by scaling, we can assume that we have a convergent minimizing sequence $C^l_{\text{inf}}, \epsilon^l_{\text{inf}}$ of limit $C^*_{\text{inf}}, \epsilon^*_{\text{inf}}$ and of norm equal to 1. Note that we do not assume $C \in \mathcal{A}$, nor $C^*_{\text{inf}} > 0$ thus we consider broader options than necessary for use in (4.9) to ensure existence of the minimum. Finally, we notice that K is non negative, its infimum is either zero or positive. We will prove the positivity by contradiction.

Assume that the limit of $K(C^l_{\text{inf}}, \epsilon^l_{\text{inf}})$ is zero, we show that $|y^l_{\text{inf}}|$ is convergent up to a subsequence. We consider j such that, up to a subsequence, $\frac{|y^l_j|}{|y^l_{\text{inf}}|}$ is bounded away from zero. If $c^*_{\text{inf},j} \neq 0$, $|y^l_j|$ is bounded thus $|y^l_{\text{inf}}|$ is too, and up to another subsequence, it is convergent. If $c^*_{\text{inf},j} = 0$ we notice that $x^l_{\text{inf},j} \to 0$ and $|x^l_{\text{inf}}|$ is bounded away from zero, so that $\frac{|y^l_j|}{|y^l_{\text{inf}}|} \to 0$, which is absurd. We let γ be the limit of $|y^l_{\text{inf}}|^2$.

As we have assumed the infimum to be zero, we have:

$$\epsilon^*_{\text{inf},j} = c^*_{\text{inf},j} \frac{\gamma}{\widetilde{c^*_{\text{inf}}}}, \qquad \forall j \text{ s.t. } c^*_j > 0.$$

This would imply that ϵ^*_{inf} is nonnegative, however, we have $\epsilon^*_{\text{inf},0} = -\sum_{j=1}^N k_j \epsilon^*_{\text{inf},j}$ and ϵ^*_{inf} is of norm 1. This is absurd, hence the infimum cannot be zero. Thus we dispose of $0 < \alpha$ depending only on $k_1, \dots k_N$ and the subset $\{c^*_j > 0\}$ of $[\![0, N]\!]$ such that:

$$\widetilde{\epsilon} \leq |x||y| \left(1 - \alpha\right).$$

As we have assumed (using symmetry) $\widetilde{\epsilon} \geq 0$, we also have $\alpha \leq 1$. So that we have:

$$\sum_{c^*_j > 0} \frac{\epsilon_j^2}{c_j} - \frac{\widetilde{\epsilon}^2}{\widetilde{c}} = |y|^2 - \frac{\widetilde{\epsilon}^2}{|x|^2} \geq |y|^2(1 - (1-\alpha)^2) = \sum_{c^*_j > 0} \frac{\epsilon_j^2}{c_j}(1 - (1-\alpha)^2).$$

Thanks to equations (4.8) and (4.9), we have:

$$\sum_{c^*_j > 0} \frac{\epsilon_j^2}{c_j} = o(|\epsilon|^2),$$

thus, thanks to (1), $\epsilon_j = o(|\epsilon|)$ for all $j \in [\![0, N]\!]$, which is absurd.

Conclusion of the proof in case 2. We dispose of j such that $c_j \to 0$ and $\epsilon_j \neq o(|\epsilon|)$, thus have up to a sub-sequence:

$$|\epsilon| = O(\epsilon_j) \qquad \text{and} \qquad \mathcal{D}_{\text{chem,j}} = \widetilde{\mathcal{C}}_{\sigma,j}\left(\log\frac{c_j+\epsilon_j}{c_j} + O(|\epsilon|)\right)^2.$$

The assumed boundedness of $\log\frac{c_j+\epsilon_j}{c_j}$ implies that $\epsilon_j = O(c_j)$ thus, $c_j \neq o(|\epsilon|)$. Moreover, we also dispose of $\alpha = \min(1, \inf_n \frac{c_j^n+\epsilon_j^n}{c_j^n}) > 0$ such that:

$$\widetilde{\mathcal{C}}_{\sigma,j} \geq \alpha c_j$$

Necessary, we have $\log\frac{c_j+\epsilon_j}{c_j} \to 0$ thus:

$$\mathcal{D}_{\text{chem,j}} \geq \alpha\frac{\epsilon_j^2}{c_j} + o(\frac{\epsilon_j^2}{c_j}),$$

which is bigger than $|\epsilon|^2$ and thus contradicts (4.6).

Conclusion of the proof in case 3. Let j be such that $\epsilon_j \neq o(|\epsilon|)$, $c_j^* = 0$, and $\log\frac{\epsilon_j+c_j}{c_j}$ blows-up.

We have:

$$h_j(C+\epsilon) - h_j(C) = \log\frac{\epsilon_j+c_j}{c_j} + o(1),$$

and:

$$\widetilde{\mathcal{C}_{\sigma,j}}(C+\epsilon, C) = \frac{\epsilon_j}{\log\frac{\epsilon_j+c_j}{c_j}},$$

so that:

$$\mathcal{D}_{\text{chem,j}} \sim \epsilon_j \log\frac{\epsilon_j+c_j}{c_j},$$

which contradicts (4.6) since $\epsilon_j \neq o(|\epsilon|)$.

Global conclusion. As each of the cases lead to a contradiction, we have the desired inequality for $i \in [\![1, N]\!]$. For the solvent, we see that:

$$c_{K,0} - c_{L,0} = -\sum_{i=1}^{N} k_i(c_{K,i} - c_{L,i}),$$

thus the announced result up to the choice of a bigger constant M. □

Using these tools, we may now prove the following necessary compactness inequality:

:L2H1bound **Proposition 4.2.** *For all $\epsilon > 0$, there exist M such that :*

$$\inf_{\substack{mesh\ m \\ n\in[\![1,N_{T,m}]\!] \\ K\in\mathcal{T}_m}} c^n_{m,K,0} > \epsilon \implies \|\nabla_{\mathcal{T}_m,\boldsymbol{\Delta t}_m}\boldsymbol{c}_i\|^2_{L^2(Q_T)} \leq M,\ \forall i \in [\![0,N]\!], \forall m.$$

Proof. We will show the result for $i \in [\![1, N]\!]$ and use the definition of $\mathcal{A}$ to extend it the solvent. For improved readability, we will drop the subscript m. By definition, we have:

$$|\nabla_{\mathcal{T},\boldsymbol{\Delta t}}\boldsymbol{c}_i|^2_{L^2(Q_T)} = \sum_{n=1}^{N_T}\Delta t_n \sum_{\sigma\in\mathcal{E}_{\text{int}}}\tau_\sigma(D_\sigma \boldsymbol{c}_i^n)^2$$

Thanks to Proposition 4.1 and Lemma 4.1, we have:

$$\sum_{\sigma\in\mathcal{E}_{\text{int}}}\tau_\sigma(D_\sigma\boldsymbol{c}_i^n)^2 \leq M\sum_{\sigma=K|L\in\mathcal{E}_{K,\text{int}}}\tau_\sigma\mathcal{D}_{\text{chem}}(C_K^n, C_L^n) \leq \frac{M}{\alpha_\epsilon}\sum_{\sigma\in\mathcal{E}_{\text{int}}}\sum_{j=1}^{N}\tau_\sigma\mathcal{C}^n_{\sigma,j}(D_\sigma h_j(\boldsymbol{C}^n))^2.$$

It is sufficient to bound $\sum_{n=1}^{N_T} \Delta t_n \sum_{\sigma\in\mathcal{E}_{\text{int}}} \tau_\sigma \mathcal{C}^n_{\sigma,j}(D_\sigma h_j(\boldsymbol{C}^n))^2$, for all $j \in [\![1, N]\!]$ to get the desired result. We have:

$$(D_\sigma h_j(\boldsymbol{C}^n))^2 \leq 2(D_\sigma(h_j(\boldsymbol{C}^n) - z_j\boldsymbol{\Phi}^n))^2 + 2(z_j D_\sigma \boldsymbol{\Phi}^n)^2$$

Thanks to equation (3.14) of Lemma 3.4, we dispose of M such that :

$$\sum_{n=1}^{N_T} \Delta t_n \sum_{\sigma\in\mathcal{E}_{\text{int}}} \tau_\sigma \mathcal{C}^n_{\sigma,j}(D_\sigma(h_j(\boldsymbol{C}^n) - z_j\boldsymbol{\Phi}^n))^2 < M.$$

Moreover, $\sum_{\sigma\in\mathcal{E}_{\text{int}}} \tau_\sigma \mathcal{C}^n_{\sigma,j}(z_j D_\sigma \boldsymbol{\Phi}^n)^2$ is also bounded thanks to (3.12) and the L^∞ bound on $\mathcal{C}_i$ and z_i. Thus we have:

$$\sum_{n=1}^{N_T} \Delta t_n \sum_{\sigma\in\mathcal{E}_{\text{int}}} \tau_\sigma \mathcal{C}^n_{\sigma,j}(D_\sigma h_j(\boldsymbol{C}^n))^2 \leq M, \tag{4.10}$$ {eq:bouded

which in turn yields the desired result.

For the solvent we notice that:

$$\nabla_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \boldsymbol{c}_0 = -\sum_{i=1}^{N} k_i \nabla_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \boldsymbol{c}_i,$$

so that the bound on all $\nabla_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \boldsymbol{c}_i$ transfers into a bound on $\nabla_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \boldsymbol{c}_0$. □

Using this discrete $L^2(H^1)$ estimate, we use a discrete Aubin-Lions lemma to get the compactness of the sequence of solutions, as stated in following proposition:

ompactness **Proposition 4.3.** *Let $(\boldsymbol{C}_m, \boldsymbol{\Phi}_m)$ be the family of discrete solutions defined either by the centered scheme or by the Sedan scheme. In both cases, there exists $\Phi \in L^\infty(Q_T;\mathbb{R}) \cap L^2((0,T);H^1(\Omega))$, $C \in L^\infty(Q_T;\overline{\mathcal{A}})$ such that, up to a subsequence,*

$$\pi_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \boldsymbol{C}_m \underset{m\to\infty}{\longrightarrow} C \quad \textit{strongly in } L^2(Q_T)^{N+1}, \tag{4.11}$$ {eq:conv_a

$$\nabla_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \boldsymbol{C}_m \underset{m\to\infty}{\longrightarrow} \nabla C \quad \textit{weakly in } L^2(Q_T), \tag{4.12}$$ {eq:conv_g

$$\pi_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \boldsymbol{\Phi}_m \underset{m\to\infty}{\longrightarrow} \Phi \quad \textit{in the } L^\infty(Q_T) \textit{ weak-}\star \textit{ sense}, \tag{4.13}$$ {eq:conv_p

$$\nabla_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \boldsymbol{\Phi}_m \underset{m\to\infty}{\longrightarrow} \nabla\Phi \quad \textit{in the } L^\infty([0,T],L^2(\Omega)^d) \textit{ weak-}\star \textit{ sense}. \tag{4.14}$$ {eq:conv_g

Proof. For improved readability we drop again the subscripts m. The proof of the first two result relies on a discrete Aubin-Lions lemma [31, Lemma 3.4]. We intend to use it in the setting described in [10, Lemma 9]. Proposition 4.2 provides a first property, but we still have to prove that there exist C independent of the mesh such that $\sum_n \|\boldsymbol{c}_i^n - \boldsymbol{c}_i^{n-1}\|_{\mathcal{T},-1} \leq C$, where $\|\cdot\|_{\mathcal{T},-1}$ is defined by duality:

$$\|\boldsymbol{c}\|_{\mathcal{T},-1} = \sup_{\boldsymbol{\varphi}} \left(\int_\Omega \pi_{\mathcal{T}}\boldsymbol{c}\pi_{\mathcal{T}}\boldsymbol{\varphi},\ \|\pi_{\mathcal{T}}\boldsymbol{\varphi}\|_{L^2}^2 + \|\nabla_{\mathcal{T}}\boldsymbol{\varphi}\|_{L^2}^2 = 1 \right).$$

Let $\boldsymbol{\varphi} \in \mathbb{R}^{\mathcal{T}}$. Tanks to (2.4b), we have:

$$\int_\Omega \pi_{\mathcal{T}}(\boldsymbol{c}_i^n - \boldsymbol{c}_i^{n-1})\pi_{\mathcal{T}}\boldsymbol{\varphi} = -\Delta t_n \sum_{K\in\mathcal{T}} \varphi_K \sum_{\sigma\in\mathcal{E}_K} F^n_{K\sigma,i}.$$

Using the definition of $F^n_{K\sigma,i}$ along with the definition of $\mathcal{C}_{\sigma,i}$ respectively equations (2.5) and (3.1), we have:

$$\int_\Omega \pi_{\mathcal{T}}(\boldsymbol{c}_i^n - \boldsymbol{c}_i^{n-1})\pi_{\mathcal{T}}\boldsymbol{\varphi} = \Delta t_n \sum_{\sigma=K|L\in\mathcal{E}_{K,\text{int}}} D_i \tau_\sigma \mathcal{C}_{\sigma,i}(C_K^n, C_L^n, \Phi_K^n, \Phi_L^n) D_{K\sigma}\left(h_i(\boldsymbol{C}^n) + z_i\boldsymbol{\Phi}^n\right) D_{K\sigma}\boldsymbol{\varphi}.$$

Thanks to the Cauchy-Schwarz inequality, we have:

$$\int_\Omega \pi_{\mathcal{T}}(\boldsymbol{c}_i^n - \boldsymbol{c}_i^{n-1})\pi_{\mathcal{T}}\boldsymbol{\varphi} \leq \Delta t_n D_i \left(\sum_{\sigma=K|L\in\mathcal{E}^{\rm int}} \tau_\sigma \mathcal{C}_{\sigma,i}(C_K^n, C_L^n, \Phi_K^n, \Phi_L^n) \left(D_{K\sigma} h_i(\boldsymbol{C}^n) + z_i \boldsymbol{\Phi}^n\right)^2 \right)^{\frac{1}{2}} \left(\sum_{\sigma=K|L\in\mathcal{E}^{\rm int}} \tau_\sigma \mathcal{C}_{\sigma,i}(C_K^n, C_L^n, \Phi_K^n, \Phi_L^n) \left(D_{K\sigma}\boldsymbol{\varphi}\right)^2 \right)^{\frac{1}{2}}.$$

Using the definition of $\mathcal{D}_{\sigma,i}$, $\mathcal{C}_{\sigma,i} \leq \frac{1}{k_i v_0}$ and $\|\nabla_{\mathcal{T}}\boldsymbol{\varphi}\|_{L^2}^2 \leq 1$, we have:

$$\|\boldsymbol{c}_i^n - \boldsymbol{c}_i^{n-1}\|_{\mathcal{T},-1} \leq \frac{\Delta t_n}{k_i D_i v_0} \left(\sum_{\sigma=K|L\in\mathcal{E}^{\rm int}} \tau_\sigma \mathcal{D}_{\sigma,i}(C_K^n, C_L^n, \Phi_K^n, \Phi_L^n) \right)^{\frac{1}{2}}.$$

Using the Cauchy-Schwarz inequality and Lemma 3.4 equation (3.14), we have :

$$\sum_n \|\boldsymbol{c}_i^n - \boldsymbol{c}_i^{n-1}\|_{\mathcal{T},-1} \leq \left(\sum_n \frac{\Delta t_n}{k_i^2 D_i^2 v_0^2} \right)^{\frac{1}{2}} \left(\sum_n \Delta t_n \sum_{\sigma=K|L\in\mathcal{E}_{K,\rm int}} \tau_\sigma \mathcal{D}_{\sigma,i}(C_K^n, C_L^n, \Phi_K^n, \Phi_L^n) \right)^{\frac{1}{2}} \leq C.$$

This concludes the proof of equations (4.11) and (4.12).

We may now focus on the convergence of the potential. The existence of Φ satisfying (4.13) is a straightforward consequence of (3.11). Similarly, (3.12) implies the existence of a vector field u such that $\nabla_{\mathcal{T}_m,\boldsymbol{\Delta t}_m}\boldsymbol{\Phi}_m \underset{m\to\infty}{\longrightarrow} u$ in the $L^\infty([0,T], L^2(\Omega)^d)$ weak-$\star$ sense.

We have to identify u with $\nabla\Phi$. We let $w \in C_c^\infty(Q_T, R^d)$ and define:

$$\boldsymbol{w}_\sigma^n = \fint_\sigma w(t_n, x)dx \qquad \forall \sigma \in \mathcal{E}, n \in [\![1, N_T]\!],$$

and the associated diamond-cell reconstruction:

$$w_{\mathcal{E},\boldsymbol{\Delta t}}(t,x) = \boldsymbol{w}_\sigma^n \qquad \text{if } x \in \Delta_\sigma \text{ and } t \in (t_{n-1}, t_n].$$

Thanks to the smoothness of w, we have convergence of $w_{\mathcal{E},\boldsymbol{\Delta t}}$ toward w and:

$$\iint_{Q_T} w_{\mathcal{E},\boldsymbol{\Delta t}} \cdot \nabla_{\mathcal{T},\boldsymbol{\Delta t}}\boldsymbol{\Phi} \to \iint_{Q_T} w \cdot u.$$

Using the geometric relation $d_\sigma m_\sigma = dm_{\Delta_\sigma}$ and the definition of $\boldsymbol{w}_\sigma^n$, we have:

$$\iint_{Q_T} w_{\mathcal{E},\boldsymbol{\Delta t}} \cdot \nabla_{\mathcal{T},\boldsymbol{\Delta t}}\boldsymbol{\Phi} = -\sum_{i=1}^{N_T} \Delta t_n \sum_{K\in\mathcal{T}} \Phi_K^n \int_K \operatorname{div}(w(t_n, x))dx.$$

Thanks to the smoothness of w and the convergence of $\boldsymbol{\Phi}$, we have:

$$\iint_{Q_T} w_{\mathcal{E},\boldsymbol{\Delta t}} \cdot \nabla_{\mathcal{T},\boldsymbol{\Delta t}}\boldsymbol{\Phi} \to -\iint_{Q_T} \Phi \operatorname{div}(w) = \iint_{Q_T} \nabla\Phi \cdot w$$

This concludes the identification of u and the proof of (4.14). □

These convergence topologies are sub-optimal and will be improved in Lemma 4.4. First, we notice that for the concentrations, we also dispose of edge values defined by $\mathcal{C}_\sigma$ and $\widetilde{\mathcal{C}_\sigma}$ in equations (3.1) and (4.2). Using these face values, we introduce another reconstruction. For i in $[\![1, N]\!]$, we let:

$$c_{\mathcal{E},\boldsymbol{\Delta t},i}(x,t) = \begin{cases} \mathcal{C}_{\sigma,i}(C_K^n, C_L^n, \Phi_K^n, \Phi_L^n) & \text{if } x \in \Delta_{K|L} \text{ and } t \in (t_{n-1}, t_n], \\ c_K^n & \text{if } x \in \Delta_\sigma, \sigma \in \mathcal{E}_K \cap \mathcal{E}^{\rm ext} \text{ and } t \in (t_{n-1}, t_n]. \end{cases}$$

Similarly, we introduce $\widetilde{c}_{\mathcal{E},\boldsymbol{\Delta t},i}$. As we expect, these reconstructions are convergent and share their limit with $\pi_{\mathcal{T},\boldsymbol{\Delta t}}\boldsymbol{c}_i$. This is the main purpose of the following lemma.

onvergence **Lemma 4.4.** *Let C be as in Proposition 4.3. We have:*

$$\pi_{\mathcal{T}_m,\boldsymbol{\Delta t}_m}\boldsymbol{c}_{m,i} \to c_i \qquad \text{strongly in } L^p, p\in[1,\infty) \qquad \forall i \in [\![0,N]\!], \tag{4.15}$$ {eq:Lpconv

$$\pi_{\mathcal{T}_m,\boldsymbol{\Delta t}_m}\boldsymbol{\Phi} \to \Phi \qquad \text{strongly in } L^p, p\in[1,\infty), \tag{4.16}$$ {eq:Lpconv

$$c_{\mathcal{E}_m,\boldsymbol{\Delta t}_m,i} \to c_i \qquad \text{strongly in } L^p, p\in[1,\infty) \qquad \forall i \in [\![1,N]\!], \tag{4.17}$$ {eq:edgeco

$$\widetilde{c}_{\mathcal{E}_m,\boldsymbol{\Delta t}_m,i} \to c_i \qquad \text{strongly in } L^p, p\in[1,\infty) \qquad \forall i \in [\![0,N]\!]. \tag{4.18}$$ {eq:altern

Proof. Equation (4.15) is a straightforward consequence of (4.11) and the boundedness of $\mathcal{A}$. The proof of (4.17) and (4.18) rely on the Lemma D.2. Thanks to Proposition 4.2, the hypothesis is satisfied with $p, \widetilde{p} = 2$, using (4.15), we have the L^1 convergence of the diamond reconstructions. Thanks to the L^∞ bound on the edge concentrations, this result translate in the desired equations. The enhanced convergence of the potential relies on the same ideas as the ones given in the previous proof ([31, Lemma 3.4] and [10, Lemma 9]) to get strong L^2 convergence. This is done following the lines of [9, Proposition 4.5]. □

Finally, we show a weak-convergence property on the gradients of the logarithms:

m:gradconv **Lemma 4.5.** *Let C be as in Proposition 4.3. We have:*

$$\nabla_{\mathcal{T}_m,\boldsymbol{\Delta t}_m}\log(\overline{\boldsymbol{c}}) \to \nabla\log(\overline{c}_m) \qquad \text{weakly in } L^2(Q_T)^d. \tag{4.19}$$ {eq:convgr

Moreover, assuming $\inf c_0 > 0$*, we have :*

$$\nabla_{\mathcal{T}_m,\boldsymbol{\Delta t}_m}\log(\boldsymbol{c}_{m,0}) \to \nabla\log(c_0) \qquad \text{weakly in } L^2(Q_T)^d. \tag{4.20}$$ {eq:convgr

Proof. Let us start with the proof on equation (4.20). By definition (4.2), we have:

$$\nabla_{\mathcal{T}_m,\boldsymbol{\Delta t}_m}\log(\boldsymbol{c}_{m,0}) = \frac{1}{\widetilde{c}_{\mathcal{E}_m,\boldsymbol{\Delta t}_m,0}}\nabla_{\mathcal{T}_m,\boldsymbol{\Delta t}_m}\boldsymbol{c}_{m,0},$$

so that, using (4.18), (4.12), and the assumed bound on c_0 we have:

$$\nabla_{\mathcal{T}_m,\boldsymbol{\Delta t}_m}\log(\boldsymbol{c}_{m,0}) \to \frac{1}{c_0}\nabla c_0.$$

We conclude using the bound on c_0 again to use the continuous chain-rule and get the announced result.

For (4.19), we proceed similarly. Notice that since $\overline{c} \geq \frac{1}{v_0 \max k_i} > 0$ the bound does not need to be assumed. we only need the strong L^2 convergence of the reconstruction using the logarithmic average on the diamond cells. This is an application of Lemma D.2, as in the proof of Lemma 4.4. □

tification

4.3. **Identification.** In this section we will identify the limits obtained in Proposition 4.3 as weak solutions in the sense of Definition 1. First we improve the convergence topology on the potential and identify it as a weak solution of the Poisson equation.

potential **Proposition 4.4.** *The function $\Phi \in L^\infty((0,T), H^1(\Omega))$ defined in Proposition 4.3 satisfies: $\Phi - \Phi^D \in L^\infty((0,T), H_{\Gamma^D})$ and for all $\psi \in \mathcal{H}_{\Gamma^D}$ and almost all $t \in (0,T)$ equation (1.14) holds:*

$$\lambda^2 \int_\Omega \nabla\Phi(t,x)\cdot\nabla\psi(x)\mathrm{d}x = \int_\Omega \psi(x)\sum_{i=1}^N z_i c_i(t,x)\mathrm{d}x.$$

Proof. Let $\psi \in C_c^\infty([0,T] \times \{\Omega \cup \Gamma^N\})$, then define $\psi_K^n = \psi(x_K, t_n)$ and $\psi_\sigma^n = \psi(x_\sigma, t_n)$ for $1 \leq n \leq N$, $K \in \mathcal{T}$ and $\sigma \in \mathcal{E}_{\text{ext}}$. As for [9, Proposition 4.5], we introduce an other reconstruction of the gradient following [23] (see [18] for a practical example). Let $\widehat{\nabla}_\mathcal{T} : \mathbb{R}^\mathcal{T} \to L^\infty(\Omega)^d$ be strongly consistent i.e.,

$$\widehat{\nabla}_\mathcal{T} \boldsymbol{\psi}^n \underset{h_\mathcal{T} \to 0}{\longrightarrow} \nabla \psi(\cdot, t_n) \text{ uniformly in } \overline{\Omega}, \quad \forall n \in \{1, \dots, N\}, \tag{4.21}$$ {eq:ov_gra

thanks to the smoothness of ψ. The operator $\widehat{\nabla}$ is also such that

$$\int_\Omega \nabla_\mathcal{T} \boldsymbol{u} \cdot \widehat{\nabla}_\mathcal{T} \boldsymbol{v} \mathrm{d}x = \sum_{\sigma \in \mathcal{E}} \tau_\sigma D_{K\sigma} \boldsymbol{u} D_{K\sigma} \boldsymbol{v}, \qquad \forall \boldsymbol{u}, \boldsymbol{v} \in \mathbb{R}^\mathcal{T}.$$

The scheme (2.4a) then reduces to

$$\lambda^2 \int_\Omega \nabla_\mathcal{T} \boldsymbol{\Phi}^n \cdot \widehat{\nabla}_\mathcal{T} \boldsymbol{\psi}^n \mathrm{d}x = \int_\Omega \pi_\mathcal{T} \boldsymbol{\psi}^n \sum_{i=1}^N z_i \pi_\mathcal{T} \boldsymbol{c}_i^n \mathrm{d}x, \quad \forall n \in \{1, \dots, N\}, \ \forall \boldsymbol{\psi} \in \mathbb{R}^{(\mathcal{T} \cup \mathcal{E}_{\text{ext}}) \times N}.$$

Integrating with respect to time over $(0,T)$ and passing to the limit $h_\mathcal{T}, h_{\boldsymbol{\Delta t}} \to 0$ thanks to Proposition 4.3 equations (4.11) and (4.14) and equation (4.21) we have:

$$\lambda^2 \iint_{Q_T} \nabla \Phi \cdot \nabla \psi \mathrm{d}x\mathrm{d}t = \iint_{Q_T} \psi \sum_{i=1}^N z_i c_i \mathrm{d}x\mathrm{d}t, \qquad \forall \psi \in C_c^\infty([0,T] \times \Omega \cup \Gamma^N).$$

By density of $C_c^\infty([0,T] \times \Omega \cup \Gamma^N)$ in $L^\infty([0,T], H_{\Gamma^D})$ and continuity of the linear application, we have:

$$\lambda^2 \iint_{Q_T} \nabla \Phi \cdot \nabla \psi \mathrm{d}x\mathrm{d}t = \iint_{Q_T} \psi \sum_{i=1}^N z_i c_i \mathrm{d}x\mathrm{d}t, \qquad \forall \psi \in L^\infty([0,T], H_{\Gamma^D}).$$

In particular, (1.14) holds for almost every $t \in (0,T)$.

Concerning the boundary conditions for Φ, the fact that $\Phi = \Phi^D$ on $(0,T) \times \Gamma^D$ can be proved for instance following the lines of [6, Section 4]. □

The following theorem focuses on the identification of C as a weak solution satisfying (1.13). As announced in Theorem 2.2 this can only be done with an assumption on the solvent. Remark C.1 is a first clue of the validity of this assumption. For positive initial condition, this assumption is valid in all the numerical test. In the 1D setting and under a CFL condition, it might be possible to prove it through improvements of Lemmas 3.2 and 3.5. This could be the topic of further research.

tification **Theorem 4.1.** *Let C and Φ be as in Propositions 4.3. If one has $\inf c_0 > 0$, they are weak solutions of (1.3)–(1.8) in the sense of Definition 1.*

Proof. Let $i \in [\![1, N]\!]$, $\varphi \in C_c^\infty([0,T) \times \overline{\Omega})$, then define $\varphi_K^n = \varphi(x_K, t_n)$ for all $n \in \{0, \dots, N_T\}$ and $K \in \mathcal{T}$. Multiplying (2.4b) by $\Delta t_n \varphi_K^{n-1}$, then summing over $K \in \mathcal{T}$ and $n \in \{1, \dots, N_T\}$ leads to

$$T_1 + T_2 + T_3 = 0, \tag{4.22}$$ {eq:T123}

where we have set

$$
\begin{aligned}
T_1 =& \sum_{n=1}^{N_T} \sum_{K\in\mathcal{T}} m_K (c_{K,i}^n - c_{K,i}^{n-1}) \varphi_K^{n-1}, \\
T_2 =& \sum_{n=1}^{N_T} \Delta t_n \sum_{\sigma\in\mathcal{E}} \tau_\sigma \mathcal{C}_{\sigma,i}^n D_{K\sigma} h_i(\boldsymbol{c}^n) D_{K\sigma} \boldsymbol{\varphi}^{n-1}, \\
T_3 =& z_i \sum_{n=1}^{N_T} \Delta t_n \sum_{\sigma\in\mathcal{E}} \tau_\sigma \mathcal{C}_{\sigma_i}^n D_{K\sigma} \boldsymbol{\Phi}^n D_{K\sigma} \boldsymbol{\varphi}^{n-1},
\end{aligned}
$$

where $\varphi_{K\sigma}^{n-1} = 0$ for $\sigma \in \mathcal{E}_{\text{ext}}$ and $\mathcal{C}_\sigma$ is defined by Lemma 3.1. The treatment of terms T_1 and T_3 is exactly the same as in [9, Proposition 4.7] and we have:

$$
T_1 \underset{m\to\infty}{\longrightarrow} -\iint_{Q_T} c_i \partial_t \varphi \mathrm{d}x\mathrm{d}t - \int_\Omega c_i^0 \varphi(0,\cdot)\mathrm{d}x, \tag{4.23}
$$

{eq:T1}

$$
T_3 \underset{m\to\infty}{\longrightarrow} \iint_{Q_T} z_i c_i \nabla\Phi\cdot\nabla\varphi \mathrm{d}x\mathrm{d}t. \tag{4.24}
$$

{eq:T3}

The treatment of the term T_2 is more intricate. First we let $\widetilde{T}_2$ be the same term with a different edge concentration:

$$
\widetilde{T}_2 = \sum_{n=1}^{N} \Delta t_n \sum_{\sigma\in\mathcal{E}} \tau_\sigma \widetilde{\mathcal{C}}_{\sigma,i}^n D_{K\sigma} h_i(\boldsymbol{c}^n) D_{K\sigma} \boldsymbol{\varphi}^{n-1},
$$

where $\widetilde{\mathcal{C}}$ is the logarithmic mean introduced in (4.2). We will first prove the convergence of $\widetilde{T}_2$ then identify its limit. To this end, we set:

$$
\begin{aligned}
\widetilde{T}_{2,1} =& \sum_{n=1}^{N} \Delta t_n \sum_{\sigma\in\mathcal{E}} \tau_\sigma \widetilde{\mathcal{C}}_{\sigma,i}^n D_{K\sigma} \log(\boldsymbol{c}_i^n) D_{K\sigma} \boldsymbol{\varphi}^{n-1}, \\
\widetilde{T}_{2,2} =& -k_i \sum_{n=1}^{N} \Delta t_n \sum_{\sigma\in\mathcal{E}} \tau_\sigma \widetilde{\mathcal{C}}_{\sigma,i}^n D_{K\sigma} \log(\boldsymbol{c}_0^n) D_{K\sigma} \boldsymbol{\varphi}^{n-1}, \\
\widetilde{T}_{2,3} =& (k_i - 1) \sum_{n=1}^{N} \Delta t_n \sum_{\sigma\in\mathcal{E}} \tau_\sigma \widetilde{\mathcal{C}}_{\sigma,i}^n D_{K\sigma} \log(\overline{\boldsymbol{c}}^n) D_{K\sigma} \boldsymbol{\varphi}^{n-1}.
\end{aligned}
$$

For term $\widetilde{T}_{2,1}$ we use the chain rule $\widetilde{\mathcal{C}}_{\sigma,i}^n D_{K\sigma} \log(\boldsymbol{c}_i^n) = D_{K\sigma} \boldsymbol{c}_i^n$ and get :

$$
\widetilde{T}_{2,1} = \sum_{n=1}^{N} \Delta t_n \sum_{\sigma\in\mathcal{E}} \tau_\sigma D_{K\sigma} \boldsymbol{c}_i^n D_{K\sigma} \boldsymbol{\varphi}^{n-1} = \iint_{Q_T} \nabla_{\mathcal{T}_m, \boldsymbol{\Delta t}_m} \cdot \boldsymbol{c}_i \widehat{\nabla}_{\mathcal{T}_m, \boldsymbol{\Delta t}_m} \boldsymbol{\varphi} \mathrm{d}c\mathrm{d}t.
$$

Thanks to the weak convergence of $\nabla_{\mathcal{T}_m, \boldsymbol{\Delta t}_m} \boldsymbol{c}_i$ and the strong convergence of $\widehat{\nabla}_{\mathcal{T}_m, \boldsymbol{\Delta t}_m} \boldsymbol{\varphi}$, we have:

$$
\widetilde{T}_{2,1} \to \iint_{Q_T} \nabla c_i \cdot \nabla \varphi \mathrm{d}x\mathrm{d}t.
$$

For the other terms, we need the enhanced convergence of gradients provided by Lemma 4.5. So that the terms $\widetilde{T}_{2,2}$ and $\widetilde{T}_{2,3}$ have the following limits:

$$\widetilde{T}_{2,2} = -k_i \iint_{Q_T} \widetilde{c}_{\mathcal{E}_m,\boldsymbol{\Delta t}_m,i} \nabla_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \log(\boldsymbol{c}_0) \widehat{\nabla}_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \boldsymbol{\varphi} \mathrm{d}x\mathrm{d}t \to -k_i \iint_{Q_T} c_i \nabla \log(c_0) \nabla \varphi \mathrm{d}x\mathrm{d}t,$$
$$\widetilde{T}_{2,3} = (k_i - 1) \iint_{Q_T} \widetilde{c}_{\mathcal{E}_m,\boldsymbol{\Delta t}_m,i} \nabla_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \log(\overline{\boldsymbol{c}}) \widehat{\nabla}_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \mathrm{d}x\mathrm{d}t \boldsymbol{\varphi} \to (k_i - 1) \iint_{Q_T} c_i \nabla \log(\overline{c}) \nabla \varphi \mathrm{d}x\mathrm{d}t.$$

Let us now establish that T_2 and $\widetilde{T}_2$ share the same limit.

Thanks to the triangle and Cauchy-Schwarz inequalities, one has

$$\begin{aligned} |T_2 - \widetilde{T}_2| &\le \sum_{n=1}^{N} \Delta t_n \sum_{\sigma\in\mathcal{E}} \tau_\sigma \left| \mathcal{C}_{\sigma,i}^n - \widetilde{\mathcal{C}}_{\sigma,i}^n \right| |D_\sigma h_i(\boldsymbol{c}^n)| \left| D_\sigma \boldsymbol{\varphi}^{n-1} \right| \\ &\le \left(\sum_{n=1}^{N} \Delta t_n \sum_{\sigma\in\mathcal{E}} \tau_\sigma \mathcal{C}_{\sigma,i}^n |D_\sigma h(\boldsymbol{c}^n)|^2 \right)^{1/2} \left(\sum_{n=1}^{N} \Delta t_n \sum_{\sigma\in\mathcal{E}} \tau_\sigma \frac{(\mathcal{C}_{\sigma,i}^n - \widetilde{\mathcal{C}}_{\sigma,i}^n)^2}{\mathcal{C}_{\sigma,i}^n} |D_\sigma \boldsymbol{\varphi}^{n-1}|^2 \right)^{1/2}. \end{aligned}$$

The first term in the right-hand side is uniformly bounded thanks to (4.10). Thus our problem amounts to show that

$$\mathcal{R} := \sum_{n=1}^{N} \Delta t_n \sum_{\sigma\in\mathcal{E}} \tau_\sigma \frac{(\mathcal{C}_{\sigma,i}^n - \widetilde{\mathcal{C}}_{\sigma,i}^n)^2}{\mathcal{C}_{\sigma,i}^n} |D_\sigma \boldsymbol{\varphi}^{n-1}|^2 \underset{m\to\infty}{\longrightarrow} 0. \tag{4.25}$$ {eq:Rto0}

Let us reformulate $\mathcal{R}$ as

$$\mathcal{R} = \sum_{n=1}^{N} \Delta t_n \sum_{\sigma\in\mathcal{E}} \tau_\sigma |\mathcal{C}_{\sigma,i}^n - \widetilde{\mathcal{C}}_{\sigma,i}^n| \left| 1 - \frac{\widetilde{\mathcal{C}}_{\sigma,i}^n}{\mathcal{C}_{\sigma,i}^n} \right| |D_\sigma \boldsymbol{\varphi}^{n-1}|^2.$$

Thanks to Lemma 4.1, the quantity $\left| 1 - \frac{\widetilde{\mathcal{C}}_{\sigma,i}^n}{\mathcal{C}_{\sigma,i}^n} \right|$ is uniformly bounded, whereas the regularity of φ implies that $D_\sigma \boldsymbol{\varphi}^{n-1} \le \|\nabla\varphi\|_\infty d_\sigma$. Putting this in the above expression of $\mathcal{R}$, we obtain that

$$0 \le \mathcal{R} \le C \|c_{\mathcal{E}_m,\boldsymbol{\Delta t}_m,i} - \widetilde{c}_{\mathcal{E}_m,\boldsymbol{\Delta t}_m,i}\|_{L^1(Q_T)} \underset{m\to\infty}{\longrightarrow} 0,$$

thanks to Lemma 4.4. Thus T_2 and $\widetilde{T}_2$ share the same limit, which gives the announced result. □

:numerical

5. Numerical Examples

The numerical examples have been implemented in the Julia language [5] based on the package `VoronoiFVM.jl` [30] which realizes the implicit Euler Voronoi finite volume method for nonlinear diffusion-convection-reaction systems on simplicial grids. The resulting nonlinear systems of equations are solved using Newton's method with optional parameter embedding. An advantage of the implementation in Julia is the availability of `ForwardDiff.jl` [37], an automatic differentiation package. This package allows the assembly of analytical Jacobians based on a generic implementation of nonlinear parameter functions without the need to write source code for derivatives.

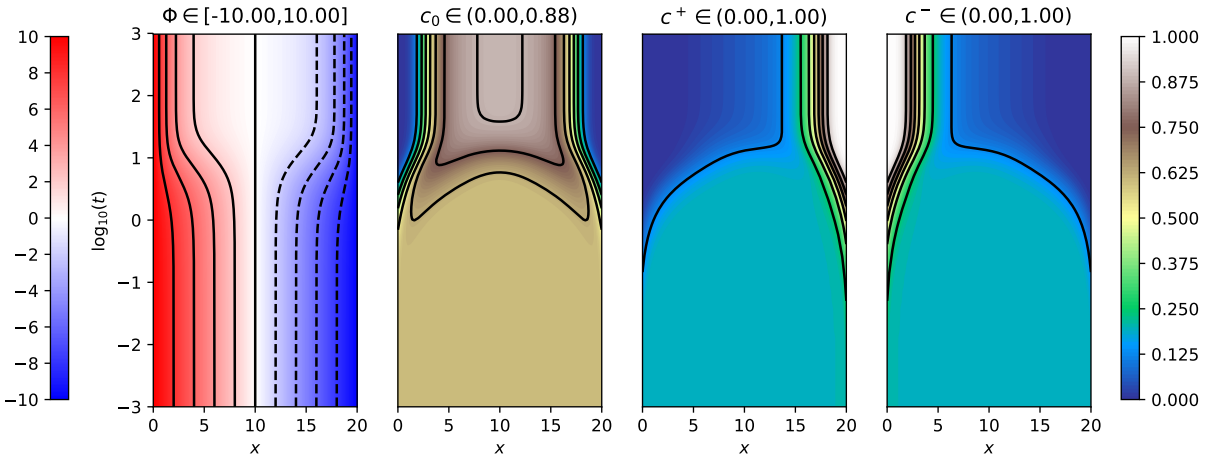

FIGURE 2. Evolution of electrostatic potential Φ, solvent concentration c_0, anion concentration c^- and cation concentration c^+ for a symmetric binary electrolyte with equal sizes of solvent molecules, anions and cations. fig:timevo

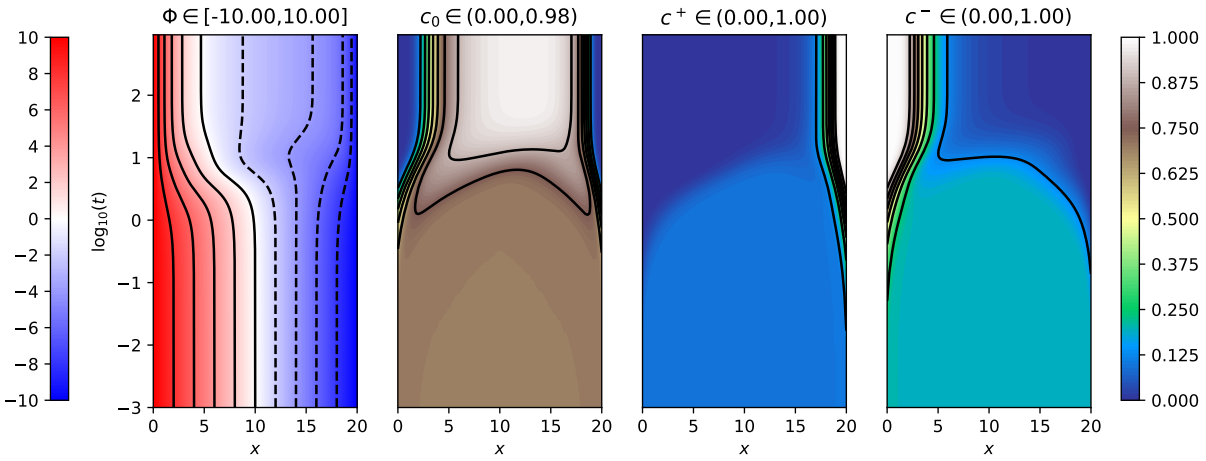

FIGURE 3. Evolution of electrostatic potential Φ, solvent concentration c_0, anion concentration c^- and cation concentration c^+ for an asymmetric binary electrolyte with equal sizes of solvent molecules, cations and anions. fig:timevo

5.1. **Species redistribution in a one-dimensional cell filled with binary electrolyte.** Let $\Omega = (0, L)$ with $L = 20$. As an initial state, assume a binary electrolyte with two ionic species with opposite charges and a solvent. At moment $t = 0$, we assume a spatially constant, electroneutral distribution of the ions. We apply a potential difference via Dirichlet boundary conditions $\Phi|_{x=0} = -10$ and $\Phi_{x=L} = 10$ and solve the Poisson equation with these data as initial value. We set homogeneous Neumann boundary conditions for both ionic species. With starting time step size $\Delta t = 10^{-3}$ we start the evolution until the species distribution reaches its equilibrium under the applied potential difference. As discussed in [8], the time step sizes are controlled such that the energy dissipation per time step is limited: $E(t_i) - E(t_{i+1}) \leq 10^{-1}$.

Fig. 2 shows the evolution in the case $v_0 = v_1 = v_2 = 1$, $z_0 = 0, z_1 = 1, z_2 = -1$. At the end of the time evolution, most of the ions are accumulated in their respective polarization boundary layers, almost completely displacing the solvent. As predicted, the ion concentration is bounded by 1. The computation used the flux (S).

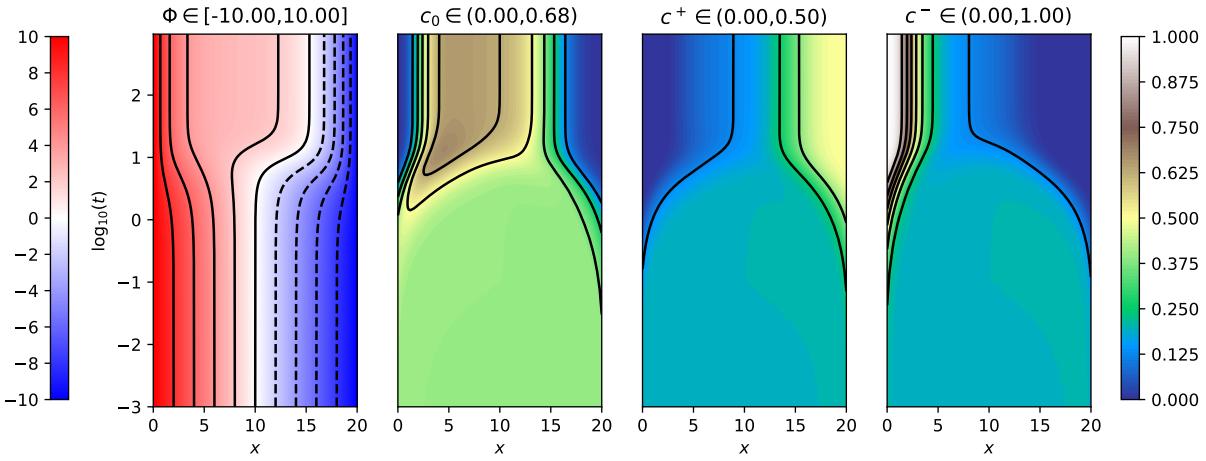

FIGURE 4. Evolution of electrostatic potential Φ, solvent concentration c_0, anion concentration c^- and cation concentration c^+ for a symmetric binary electrolyte with equal sizes of solvent molecules and anions, but larger cations.

fig:timevo

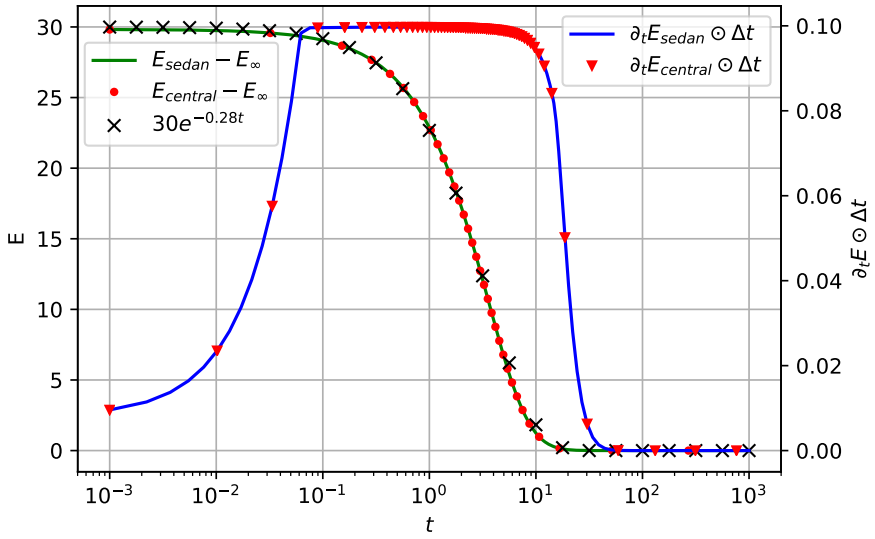

FIGURE 5. Evolution of relative free energy and energy dissipation per time step for symmetric binary electrolyte with equal sizes of solvent molecules and anions, but larger cations.

fig:relfre

Fig. 3 shows the evolution in the case $v_0 = v_1 = v_2 = 1$ and $z_0 = 0, z_1 = 2, z_2 = -1$. Once again, at the end of the evolution, anions and cations pile up in the corresponding boundary layers. Ion concentrations are bounded by 1, but due to the larger charge of the cation, the corresponding boundary layer becomes smaller.

Fig. 4 shows the evolution in the case $v_0 = v_2 = 1$, $v_1 = 2$ and $z_0 = 0, z_1 = 1, z_2 = -1$. Once again, at the end of the evolution, anions and cations pile up in the corresponding boundary layers but now, the cation concentration is bounded by $\frac{1}{2}$. The corresponding evolution of the relative free energy $E(t) - E_\infty$ is shown in Fig. 5. We observe an exponential decay and almost equal behavior for both variants of the flux approximation (S) and (C). Moreover, the time step control algorithm keeps the dissipation per timestep below the intended limit.

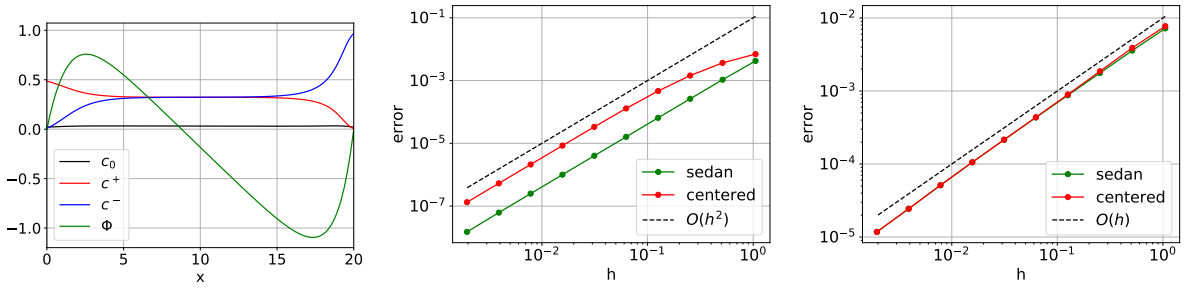

FIGURE 6. Left: stationary solution of Dirichlet problem. Center and right: results of numerical convergence test.

fig:statio

5.2. **1D stationary convergence test.** In the same domain as above, we set $v_0 = 1, v_1 = 2, v_2 = 1$, and $z_1 = 1, z_2 = -1$. This time, we look for the stationary solution with homogeneous Dirichlet boundary conditions for Φ, and Dirichlet boundary conditions for the concentrations. These boundary conditions are for $x = 0$, $c_1 v_1 = 1.0 - 3\epsilon, c_2 v_2 = \epsilon$ and for $x = L$, $c_1 v_1 = \epsilon, c_2 v_2 = 1 - 3\epsilon$, where $\epsilon = 10^{-2}$. Implicitely, this sets $c_0 = 2\epsilon$ at both boundaries. The result of the numerical convergence tests (comparison to fine grid solution with 40960 grid points) for both types of fluxes suggest $O(h^2)$ convergence in the L^2 norm and $O(h)$ convergence in the H^1 seminorm.

5.3. **An electrolytic diode.** The second example regards a domain $\Omega = (0, W) \times (0, L)$ with $W = 2$ and $L = 10$. We assume $z_0 = 0, z_1 = 1, z_2 = -1$ and $v_0 = 1, v_1 = 4, v_2 = 4$. At $y = 0$ and $y = L$ we fix concentrations to a value $c_1 = c_2 = 0.01$ We set $\Phi|_{y=0} = 0$ and apply a changing value Φ_{bias} at $y = L$. At $x = 0$ we apply symmetry (homogeneous Neumann) boundary conditions for Φ, c_1, c_2. Homogeneous Neumann boundary conditions are also applied for c_1, c_2 at $x = W$. We set Neumann boundary conditions $\lambda \nabla \Phi \cdot n = q(y)$ at $x = W$, where

$$q(y) = \begin{cases} \sigma, & y \in (\frac{1}{2}L, \frac{3}{4}L) \\ -\sigma, & y \in (\frac{1}{4}L, \frac{1}{2}L) \\ 0, & \text{else} \end{cases}$$

with $\sigma = 5$.

Fig. 7 shows three different states of the electrolytic diode. Fig. 8 (left) shows the corresponding current-voltage curve. We see a well developed rectification effect: At reverse bias, ion concentrations under the charged surface are rather low, resulting in low conductance and low ionic current. Whereas at forward bias, larger ion concentrations lead to a larger ionic current.

Fig. 8 (right) shows the estimated error of the IV curve in dependence of the grid refinement. Reference was a calculation on a grid with the quarter of the stepsize of the finest grid result shown. From this experiment, we postulate a convergence rate for the ionic current calculation of $O(h^2)$.

ACKNOWLEDGEMENT

The authors are grateful to C. Chainais-Hilliaret and C. Cances for productive discussions and careful reviewing of this manuscript. Their attention to the size-interest-readability trade-offs contributed a lot to the readability of this paper.

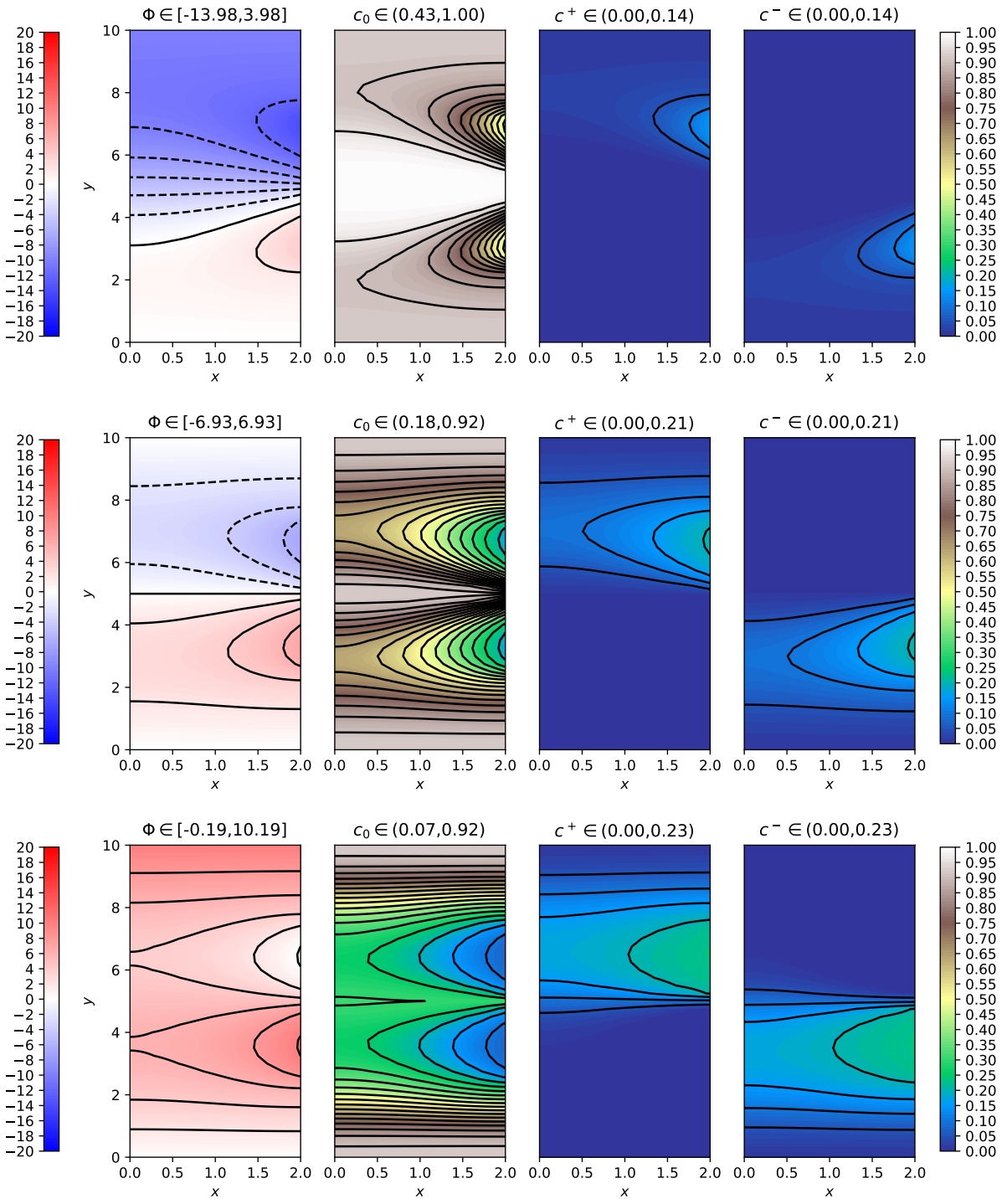

FIGURE 7. Electrostatic potential Φ, solvent concentration c_0, anion concentration c^- and cation concentration c^+ in an electrolytic diode filled with a symmetric binary electrolyte with equal sizes of solvent molecules at reverse bias $\Phi_{bias} = -10$ (top), zero bias $\Phi_{bias} = 0$ (center) and forward bias $\Phi_{bias} = 10$ (bottom)

fig:bias

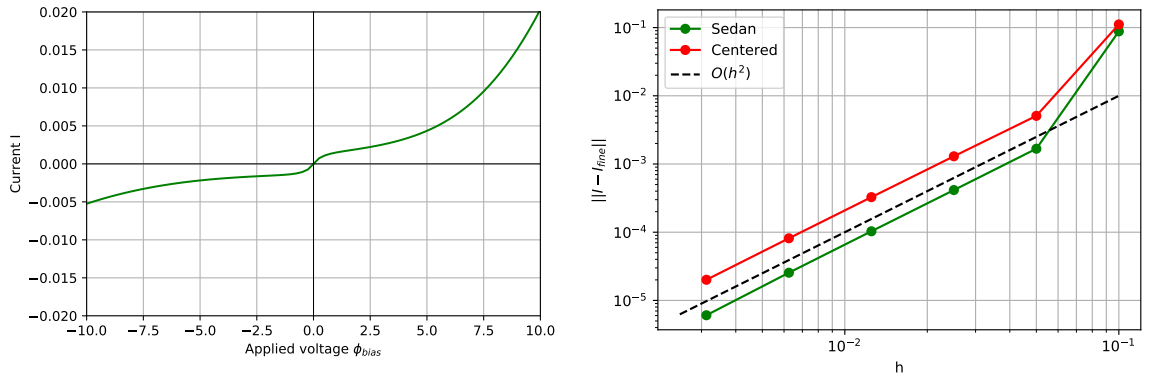

FIGURE 8. Left: Current-voltage curve for electrolytic diode, calculated using the scheme (S). Right: Convergence of calculated IV curve. fig:IV

APPENDIX A. CHEMICAL FREE ENERGY DENSITY AND CHEMICAL POTENTIALS sec:convex

In this appendix, we aim to prove (1.9), (1.10), and some convexity of:

$$H(c_1, ...c_N) = -\bar{c}\log(\bar{c}) + \sum_{i=0}^{N} c_i \log(c_i),$$

where c_0 and $\bar{c}$ are functions of $c_1, ..., c_N$. This is summarized in the following lemma:

m:H convex **Lemma A.1.** *The N-variables function H is convex, moreover we have:*

$$\partial_{c_i} H(c_1, ..., c_N) = h_i(C), \qquad \forall i \in [\![1, N]\!],\ C = (c_1, ..., c_N) \in \mathcal{A}, \tag{1.9}$$

$$\frac{-\log(N+1)}{v_0 \min k_i} \leq H(C) \leq 0 \qquad \forall C \in \mathcal{A}. \tag{1.10}$$

Elementary computation shows that :

$$\partial_{c_i} H(C) = \log \frac{c_i}{\bar{c}} - k_i \log \frac{c_0}{\bar{c}} \qquad \forall i \in [\![1, N]\!].$$

Hence the announced relation (1.9).

We now focus on the proof of the convexity of H over $\mathcal{A}$. Let $C, C^* \in \mathcal{A}$, we have:

$$(\nabla_{\mathbb{R}^N} H(C) - \nabla_{\mathbb{R}^N} H(C^*)|C - C^*) = \sum_{i=0}^{N} \left(\log \frac{c_i}{\bar{c}} - \log \frac{c_i^*}{\bar{c}^*}\right)(c_i - c_i^*). \tag{A.1}$$

eq:nulnel

To prove the convexity of H, it is sufficient to show that this is non-negative. To that extend, we introduce $\mathcal{A}_{N+1}$ the natural extension of $\mathcal{A}$ in $\mathbb{R}^{N+1}$ and consider the right-hand side of (A.1) as a function of $C_{N+1} = (c_0(c_1, ...c_N), c_1..., c_N) \in \mathcal{A}_{N+1}$ parameterized by C^*:

$$G_{C^*}(c_0, \ldots, c_N) = \sum_{i=0}^{N} \left(\log \frac{c_i}{\bar{c}} - \log \frac{c_i^*}{\bar{c}^*}\right)(c_i - c_i^*),$$

and show that $\min_{C_{N+1} \in \mathcal{A}_{N+1}}(G_{C^*}(C)) = 0$. To do so we compute the derivatives of G_{C^*} as a function of $\mathbb{R}^{N+1}$ and use the Lagrange multiplier theorem. After some simplifications, we have for all $i \in [\![0, N]\!]$:

$$\partial_{c_i} G_{C^*}(c_0, ...c_N) = \frac{\bar{c}^*}{c_i}\left(\frac{c_i}{\bar{c}} - \frac{c_i^*}{\bar{c}^*}\right) + \left(\log \frac{c_i}{\bar{c}} - \log \frac{c_i^*}{\bar{c}^*}\right)$$

Notice that both terms have the sign of $\frac{c_i}{\bar{c}} - \frac{c_i^*}{\bar{c}^*}$. The Lagrange multiplier theorem states that any extremum satisfies:

$$\exists \alpha \in \mathbb{R}, \forall i \in [\![0, N]\!], \qquad \partial_{c_i} G_{C^*} = \alpha k_i$$

Hence, all the partial derivatives of G_{C^*} should have the same sign. Moreover, we notice that the sum of $\frac{c_i}{\bar{c}} - \frac{c_i^*}{\bar{c}^*}$ is zero. This is only possible the sign of the derivatives is constantly zero, i.e. : $\frac{c_i}{\bar{c}} = \frac{c_i^*}{\bar{c}^*}$. At such a point, we have $G_{C^*} = 0$. As the coercitivity and continuity of G_{C^*} grants the existence of a minimum, we have the desired result:

$$0 \leq (\nabla_{\mathbb{R}^N} H(C) - \nabla_{\mathbb{R}^N} H(C^*) | C - C^*),$$

which yields the convexity of H.

We still have to establish the bounds (1.10). To that end, we notice that:

$$H(C) = \bar{c} \sum_{i=0}^{N} \frac{c_i}{\bar{c}} \log \frac{c_i}{\bar{c}} \qquad \forall C \in \mathcal{A}.$$

As $\bar{c}$ is non-negative and $0 \leq \frac{c_i}{\bar{c}} \leq 1$, we have $H(C) \leq 0$. For the lower bound, we notice that $-\sum_{i=0}^{N} \frac{c_i}{\bar{c}} \log \frac{c_i}{\bar{c}}$ can be interpreted as the entropy of a random variable over a set of $N+1$ elements. It is common knowledge that it is maximal for $\frac{c_i}{\bar{c}} = \frac{1}{N+1}$ thus:

$$-\bar{c} \log(N+1) \leq H(C)$$

Finally, notice that $\frac{1}{v_0 \max k_i} \leq \bar{c} \leq \frac{1}{v_0 \min k_i}$ yields

$$\frac{-\log(N+1)}{v_0 \min k_i} \leq H(C),$$

which is the desired bound.

Appendix B. Proof of Lemma 3.2

ofDdblowup

This appendix is devoted to the proof of Lemma 3.2 stating the blow-up of the diffusion for extreme concentrations. More precisely, we recall:

Lemma B.1. *Let for $\delta, \epsilon, M, c > 0$, $i \in [\![1, N]\!]$:*

$$\Psi_{\delta,\epsilon,M,i}(c) := \inf_{\substack{(C_K,C_L)\in\mathcal{A}^2,\ (\Phi_K,\Phi_L)\in[-M,M]^2 \\ c_{K,0},c_{L,0}>\epsilon,\ c_{K,i}\geq\min(\delta,\frac{0.5}{k_i v_0}),\ c_{L,i}<c}} \mathcal{D}_i(C_K, C_L, \Phi_K, \Phi_L),$$

$$\Upsilon_{\delta,M}(c) := \inf_{\substack{(C_K,C_L)\in\mathcal{A}^2,\ (\Phi_K,\Phi_L)\in[-M,M]^2 \\ c_{K,0}\geq\min(\delta,\frac{0.5}{v_0}),\ c_{L,0}<c}} \mathcal{D}(C_K, C_L, \Phi_K, \Phi_L).$$

We have, for all $\delta, \epsilon, M > 0$:

$$\lim_{c\to 0^+} \Upsilon_{\delta,M}(c) = +\infty \qquad \lim_{c\to 0^+} \Psi_{\delta,\epsilon,M,i}(c) = +\infty \qquad \forall i \in [\![1, N]\!].$$

We will prove the result for $\Psi_{\delta,\epsilon,M,i}$ first, then use this property to show the bound on the solvent.

c:limitPsi

B.1. Limit of $\Psi_{\delta,\epsilon,M,i}$.

In this section we intend to prove the limit:

$$\lim_{\substack{c\to 0 \\ c>0}} \Psi_{\delta,\epsilon,M,i}(c) = +\infty \qquad \forall i \in [\![1, N]\!],\ \delta, \epsilon, M > 0.$$

The proof for the centered scheme relies on expression (3.5):

$$\mathcal{D}_i(C_K, C_L, \Phi_K, \Phi_L) = \mathcal{C}_i(C_K, C_L, \Phi_K, \Phi_L) \left(h_i(C_K) + z_i \Phi_K - h_i(C_L) - z_i \Phi_L\right)^2.$$

We notice that $h_i(C_K) + z_i \Phi_K - h_i(C_L) - z_i \Phi_L$ blows up and that $\mathcal{C}_i \geq \frac{c_{K,i}}{2}$, hence the blow-up of the limit.

For the Sedan scheme, it is more intricate and try to bound $\mathcal{F}_i(C_K, C_L, \Phi_K, \Phi_L)$ away from zero to take advantage of the blow-up of $(h_i(C_K) + z_i\Phi_K - h_i(C_L) - z_i\Phi_L)$. The positivity of the product, ensures that the limit will have the right sign. Let $\delta, \epsilon, M > 0$, $i \in [\![1, N]\!]$. We denote by O_c the set:

$$O_c = \left\{(C_K, C_L) \in \mathcal{A}^2,\ (\Phi_K, \Phi_L) \in [-M, M]^2 \mid c_{K,0}, c_{L,0} > \epsilon,\ c_{K,i} \in [\delta, 1),\ c_{L,i} < c\right\}.$$

We notice that the hypothesis $c_0 > \epsilon$ yields a bound on ν_i. Moreover, this bound is uniform in c. We intend to use this bound to prove that the flux function defined by (S) is bounded away from zero. We let:

$$M' = \sup_{c \in \mathbb{R}_{+,*}} \left(\sup_{(C_K, C_L, \Phi_K, \Phi_L) \in O_c} z_i\Phi_L + \nu(C_{L,i}) - z_i\Phi_K - \nu(C_{K,i}) \right) < \infty.$$

We have, for all $(C_K, C_L, \Phi_K, \Phi_L) \in O_c$:

$$\mathcal{F}_i(C_K, C_L, \Phi_K, \Phi_L) \geq B(M')\delta - B(-M')c,$$

hence $\mathcal{F}_i$ is bounded away from zero for c small enough and the desired result.

B.2. **Limit of $\Upsilon_{\delta,M}$.** In this section, we prove the remaining limit:

$$\lim_{c \to 0} \Upsilon_{\delta,M}(c) = +\infty \qquad \forall \delta, M > 0$$

To reuse the ideas of previous section, we would like to dispose of a specie i such that $c_{L,i} > \epsilon$. We start by building one artificially. Let $\delta, M > 0$, and:

$$O(c) = \left\{(C_K, C_L) \in \mathcal{A}^2,\ (\Phi_K, \Phi_L) \in [-M, M]^2 \mid c_{K,0} \in [\delta, 1),\ c_{L,0} < c\right\}.$$

Notice that for all $(C_K, C_L, \Phi_K, \Phi_L) \in O_c$, we dispose of $i \in [\![1, N]\!]$ such that $c_{L,i} \geq \frac{1 - v_0 c}{N k_i v_0}$. Notice also that $\Upsilon_{\delta,M}$ is increasing, it is then sufficient to prove the limit for a given sequence. Let c^n be sequence that steadily decreases to zero such that for all $n \in \mathcal{N}$, $c^n \leq \frac{1}{2v_0}$ and there exist $i \in [\![1, N]\!]$, $(C_K^n, C_L^n, \Phi_K^n, \Phi_L^n) \in O_{c^n}$ satisfying:

$$\mathcal{D}(C_K^n, C_L^n, \Phi_K^n, \Phi_L^n) \leq \Upsilon_{\delta,M}(c^n) + \frac{1}{n} \qquad \text{and} \qquad c_{L,i}^n \geq \frac{1}{2N k_i v_0}.$$

We have, using $c_{L,0}^n \leq c^n$, $c_{K,i}^n \leq \frac{1}{k_i v_0}$, $\frac{1}{v_0 \max k_j} \leq \overline{c} \leq \frac{1}{v_0 \min k_j}$, $c_{K,0}^n \geq \delta$, the bounds on Φ, and $c_{L,i}^n \geq \frac{1}{2N k_i v_0}$:

$$h_i(C_K^n) + z_i\Phi_K^n - h_i(C_L^n) - z_i\Phi_L^n \leq k_i \log \frac{c^n}{\delta} + |k_i - 1| \log \frac{\max k_j}{\min k_j} + \log(2N) + 2M|z_i|.$$

As all the terms are bounded except $\log(c^n)$ which goes to $-\infty$, we have blow-up of $h_i(C_K^n) + z_i\Phi_K^n - h_i(C_L^n) - z_i\Phi_L^n$.

For the centered scheme, we use $\mathcal{C}_i(C_K^n, C_L^n, \Phi_K^n, \Phi_L^n) \geq \frac{1}{4N v_i}$, and we have :

$$\Upsilon_{\delta,M}(c^n) \geq \mathcal{D}_i(C_K^n, C_L^n, \Phi_K^n, \Phi_L^n) - \frac{1}{n} \geq \frac{1}{4N v_i} \left(h_i(C_K^n) + z_i\Phi_K^n - h_i(C_L^n) - z_i\Phi_L^n\right)^2 - \frac{1}{n},$$

hence the desired result.

For the Sedan scheme, we will also only consider $\mathcal{D}_i$, but we need a more precise approach : as in previous section, we bound the flux away from zero. We let:

$$M' = \sup_{c \in (0, \frac{1}{2v_0}]} \left(\sup_{(C_K, C_L, \Phi_K, \Phi_L) \in O_{c^0}, c_{L,i} \geq \frac{1}{2N v_i}} z_i\Phi_L + (k_i - 1) \log \overline{c_L} - z_i\Phi_K - \nu(C_{K,i}) \right).$$

We have:

$$\mathcal{F}_i(C_K^n, C_L^n, \Phi_K^n, \Phi_L^n) \leq B\left(-k_i \log c^n - M'\right) \frac{1}{v_i} - B\left(k_i \log c^n + M'\right) \frac{1}{2N v_i}.$$

As the right-hand side tends to $-\infty$, the left-hand side is bounded away from zero. Using the previously detailed arguments, we have the desired limit.

eirdscheme

Appendix C. Study of a numerical scheme for $h_i = \log(c_i) - \alpha \log(c_0)$

To prove the existence of solutions to the Sedan and centered scheme, we introduce this simplified cross diffusion system where the coupling occurs only through the solvent using the chemical potential defined above. This system is discretized using the ideas of the centered scheme and [13]. In detail, we use equation (2.4b), (2.4c) with $k_i, D_i = 1$, $z_i = 0$, and :

$$\mathcal{F}_i(C_K, C_L, \Phi_K, \Phi_L) = \widetilde{C}_j(C_K, C_L)\left(h_i(C_K) - h_i(C_L)\right), \quad \widetilde{C}_j(C_K, C_L) = \frac{c_{K,i} - c_{L,i}}{\log(c_{K,i}) - \log(c_{L,i})}$$

where $h_i(C)$ is: $\log(c_i) - \alpha \log(c_0)$. We want to bound the concentrations away from zero uniformly in α. This is the meaning of the following lemma, which is highly inspired by Lemma 3.5.

tyestimate

Lemma C.1. *There exist $\epsilon = \min(\epsilon_0, \epsilon_1, \dots, \epsilon_N) > 0$ depending on, among other things, C^0 and decreasing with $h_{\boldsymbol{\Delta t}}$ and $\min_{\sigma\in\mathcal{E}} \tau_\sigma$ such that for all $\boldsymbol{C}^{n-1} \in \mathcal{A}^{\mathcal{T}}$ satisfying Lemma 3.3, $\alpha \in [0,1]$, we have:*

$$c^n_{K,i} \geq \epsilon_i \qquad \forall K, i$$

The proof follows the same reasoning as for the full system and is only sketched here. Using (2.4c) we have:

$$\frac{c^n_{K,0} - c^{n-1}_{K,0}}{\Delta t_n} m_K = -\sum_{\sigma=K|L\in\mathcal{E}_{\text{int}}} \tau_\sigma \left(c^n_{K,0} - c^n_{L,0}\right) - \alpha \sum_{\sigma=K|L\in\mathcal{E}_{\text{int}}} \tau_\sigma \mathcal{R}(C^n_K, C^n_L)\left(\log(c^n_{K,0}) - \log(c^n_{L,0})\right) \tag{C.1}$$

{eq:simple

where we have set:

$$\mathcal{R}(C_K, C_L) = \sum_{i=1}^{N} \frac{c_{K,i} - c_{L,i}}{\log(c_{K,i}) - \log(c_{L,i})}.$$

assumption

Remark C.1. Noticing that $\mathcal{R}(C_K, C_L) \geq 0$ yields a maximum principle on c^0. As we did not assume that c^0_0 is uniformly positive, we have to compute further.

Multiplying (C.1) by $\log(c^n_{K,0})$ and summing over $K \in \mathcal{T}$ yields:

$$\sum_{K\in\mathcal{T}} \frac{c^n_{K,0} - c^{n-1}_{K,0}}{\Delta t_n} m_K \log(c^n_{K,0}) + \sum_{\sigma=K|L\in\mathcal{E}_K} \tau_\sigma D_{KL}\boldsymbol{c}^n_0 D_{KL} \log \boldsymbol{c}^n_0 + \alpha \sum_{\sigma=K|L\in\mathcal{E}_K} \tau_\sigma \mathcal{R}(C_K, C_L)\left(D_{KL}\log \boldsymbol{c}^n_0\right)^2 = 0$$

using the convexity of $u \log u$, we have:

$$\sum_{K\in\mathcal{T}} \frac{m_k}{\Delta t_n}(c^n_{K,0}\log(c^n_{K,0}) - c^{n-1}_{K,0}\log(c^{n-1}_{K,0})) \leq -\sum_{\sigma=K|L\in\mathcal{E}_K} \tau_\sigma D_{KL}\boldsymbol{c}^n_0 D_{KL}\log \boldsymbol{c}^n_0 - \alpha \sum_{\sigma=K|L\in\mathcal{E}_K} \mathcal{R}(C_K, C_L)\left(D_{KL}\log \boldsymbol{c}^n_0\right)^2.$$

We may now use the decay of this entropy to prove the desired result for $i = 0$. To that extent we proceed as in Lemma 3.5 and see that $D_{KL}\boldsymbol{c}^n_0 D_{KL}\log \boldsymbol{c}^n_0$ is clearly coercive in

the sense of lemma 3.2 while the part in α is non-negative. This yields the uniform bound for $\boldsymbol{c}_0$.

The bound for $\boldsymbol{c}_i$ relies on the entropy $\widetilde{H} = \sum_{j=1}^{N} c_j \log(c_j) + \alpha c_0 \log(c_0)$. As for Lemma A.1, this entropy restricted to $\mathcal{A}$ is convex and its derivatives as a function of $\mathbb{R}^N$ are the chemical potentials, Thus multiplying the conservation equation by h yields:

$$\sum_{K\in\mathcal{T}} m_K \left(\widetilde{H}(C_K^n) - \widetilde{H}(C_K^{n-1})\right) \leq \sum_{\sigma\in\mathcal{E}_{\text{int}}} \sum_{j=1}^{N} \widetilde{C}_{\sigma,j} \left(D_\sigma h_j(\boldsymbol{C}^n)\right)^2.$$

This new dissipation is also coercive in the sense of Lemma 3.2, thus we can proceed as in Lemma 3.5 to get the announced bounds.

Appendix D. A simple convergence lemma

In this section, we express the results of [9] lemma 4.2 and [13, lemma 4.2] in a more generic fashion. We let $\mathcal{T}_m$ be a sequence of admissible meshes of Ω such that $h_{\mathcal{T}_m} \to 0$, $\boldsymbol{u}_m \in \mathbb{R}^{\mathcal{T}_m}$, and $\widetilde{\boldsymbol{u}}_m \in \mathbb{R}^{\mathcal{E}_m^{\text{int}}}$ such that for all $\sigma = K|L \in \mathcal{E}_m^{\text{int}}$:

$$\min(u_K, u_L) \leq \widetilde{u}_{\sigma,m} \leq \max(u_K, u_L).$$

Lemma D.1. *If we dispose of $p \in [1,\infty)$ such that*

$$h_{\mathcal{T}_m} \|\nabla_{\mathcal{T}_m} \boldsymbol{u}_m\|_{L^p(\Omega)} \to 0$$

The L^1 convergence of the natural and diamond reconstructions are equivalent, moreover if one of them is convergent, they share the same limit.

Proof. This result is equivalent to:

$$\|\pi_{\mathcal{T}_m} \boldsymbol{u}_m - \widetilde{\boldsymbol{u}}_{m,\mathcal{E}_m}\|_{L^1(\Omega)} \to 0.$$

For the sake of simplicity, we drop the subscript m for the rest of the proof. We let $\Delta_{K\sigma}$ be the half diamond cell $\Delta_\sigma \cap K$, and notice that $m(\Delta_{K\sigma}) = \frac{1}{d} m_\sigma d(x_K, \sigma) \leq \frac{h_{\mathcal{T}} m_\sigma}{d}$. Elementary calculations yield:

$$\|\pi_{\mathcal{T}} \boldsymbol{u} - \widetilde{\boldsymbol{u}}_{\mathcal{E}}\|_{L^1(\Omega)} \leq \frac{h_{\mathcal{T}}}{d} \sum_{K\in\mathcal{T}} \sum_{\sigma\in\mathcal{E}_K} m_\sigma |u_K - u_\sigma|.$$

Thanks to our average assumption, we have $|u_K - u_\sigma| \leq D_\sigma \boldsymbol{u}$ thus:

$$\|\pi_{\mathcal{T}} \boldsymbol{u} - \widetilde{\boldsymbol{u}}_{\mathcal{E}}\|_{L^1(\Omega)} \leq \frac{2h_{\mathcal{T}}}{d} \sum_{\sigma\in\mathcal{E}^{\text{int}}} m_\sigma D_\sigma \boldsymbol{u}.$$

Let p be as in the lemma and q its Hölder conjugate. We have:

$$\sum_{\sigma\in\mathcal{E}^{\text{int}}} m_\sigma D_\sigma \boldsymbol{u} \leq \left(\sum_{\sigma\in\mathcal{E}^{\text{int}}} m_\sigma d_\sigma \left(\frac{D_\sigma \boldsymbol{u}}{d_\sigma}\right)^p\right)^{\frac{1}{p}} \left(\sum_{\sigma\in\mathcal{E}^{\text{int}}} m_\sigma d_\sigma\right)^{\frac{1}{q}} \leq d m(\Omega)^{\frac{1}{q}} \|\nabla_{\mathcal{T}} \boldsymbol{u}\|_{L^p(\Omega)},$$

hence:

$$\|\pi_{\mathcal{T}} \boldsymbol{u} - \widetilde{\boldsymbol{u}}_{\mathcal{E}}\|_{L^1(\Omega)} \leq 2m(\Omega)^{\frac{1}{q}} h_{\mathcal{T}} \|\nabla_{\mathcal{T}} \boldsymbol{u}\|_{L^p(\Omega)} \to 0. \tag{D.1}$$

{eq:shared

This concludes the proof of the lemma. □

For reconstructions in $\Omega \times [0,T]$, we consider $\boldsymbol{u}_m \in \mathbb{R}^{\mathcal{T}_m \times \boldsymbol{\Delta t}_m}$, $\widetilde{\boldsymbol{u}}_m \in \mathbb{R}^{\mathcal{E}_m^{\text{int}} \times \boldsymbol{\Delta t}_m}$ satisfying the same average property, and we have the same result.

ared limit

Lemma D.2. *If we dispose of $p \in [1,\infty)$, $\widetilde{p} \in [1,\infty)$ such that*

$$h_{\mathcal{T}_m} \|\nabla_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \boldsymbol{u}_m\|_{L^{\widetilde{p}}([0,T],L^p(\Omega))} \to 0$$

The $L^1(\Omega\times[0,T])$ convergence of the natural and diamond reconstructions are equivalent, moreover if one of them is convergent, they share the same limit.

Proof. This result is equivalent to:

$$\|\pi_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \boldsymbol{u}_m - \widetilde{\boldsymbol{u}}_{m,\mathcal{E}_m,\boldsymbol{\Delta t}_m}\|_{L^1(\Omega\times[0,T])} \to 0.$$

We make use of the computations for the previous lemma, namely (D.1) yields for all $n \in [\![1, N_{T,m}]\!]$:

$$\|\pi_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \boldsymbol{u}_m^n - \widetilde{\boldsymbol{u}}^n_{m,\mathcal{E}_m,\boldsymbol{\Delta t}_m}\|_{L^1(\Omega)} \le 2m(\Omega)^{\frac{1}{q}} h_{\mathcal{T}_m} \|\nabla_{\mathcal{T}_m} \boldsymbol{u}^n\|_{L^p(\Omega)}.$$

Thus:

$$\|\pi_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \boldsymbol{u}_m - \widetilde{\boldsymbol{u}}_{m,\mathcal{E}_m,\boldsymbol{\Delta t}_m}\|_{L^1(\Omega\times[0,T])} \le 2m(\Omega)^{\frac{1}{q}} h_{\mathcal{T}_m} \sum_{n=1}^{N_{T,m}} \Delta t_n \|\nabla_{\mathcal{T}_m} \boldsymbol{u}^n\|_{L^p(\Omega)}.$$

Hölder's inequality yields:

$$\|\pi_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \boldsymbol{u}_m - \widetilde{\boldsymbol{u}}_{m,\mathcal{E}_m,\boldsymbol{\Delta t}_m}\|_{L^1(\Omega\times[0,T])} \le 2m(\Omega)^{\frac{1}{q}} T^{\frac{1}{\widetilde{q}}} h_{\mathcal{T}_m} \|\nabla_{\mathcal{T}_m,\boldsymbol{\Delta t}_m} \boldsymbol{u}\|_{L^{\widetilde{p}}([0,T],L^p(\Omega))},$$

where $\widetilde{q}$ is the Hölder conjugate of $\widetilde{p}$. Using the assumed estimation of the gradient, we have the announced result. □

References

[1] J. M. Aldaz. A stability version of Hölder's inequality. Journal of Mathematical Analysis and Applications, 343(2):842–852, July 2008.

[2] J. M. Aldaz. Strengthened Cauchy-Schwarz and Hölder inequalities. JIPAM. Journal of Inequalities in Pure & Applied Mathematics [electronic only], 10(4):Paper No. 116, 6 p., electronic only–Paper No. 116, 6 p., electronic only, 2009.

[3] M. Z. Bazant, M. S. Kilic, B. D. Storey, and A. Ajdari. Towards an understanding of induced-charge electrokinetics at large applied voltages in concentrated solutions. Advances in colloid and interface science, 152(1-2):48–88, 2009.

[4] M. Bessemoulin-Chatard. A finite volume scheme for convection–diffusion equations with nonlinear diffusion derived from the Scharfetter–Gummel scheme. Numerische Mathematik, 121(4):637–670, Aug. 2012.

[5] J. Bezanson, A. Edelman, S. Karpinski, and V. B. Shah. Julia: A fresh approach to numerical computing. SIAM review, 59(1):65–98, 2017.

[6] K. Brenner, C. Cancès, and D. Hilhorst. Finite volume approximation for an immiscible two-phase flow in porous media with discontinuous capillary pressure. Computational Geosciences, 17(3):573–597, June 2013.

[7] C. Cancès. Energy stable numerical methods for porous media flow type problems. Oil & Gas Science and Technology - Revue d'IFP Energies nouvelles, 73:78, 2018.

[8] C. Cancès, C. Chainais-Hillairet, J. Fuhrmann, and B. Gaudeul. On four numerical schemes for a unipolar degenerate drift-diffusion model. In R. Klöfkorn, F. Radu, E. Keijgavlen, and J. Fuhrmann, editors, Finite Volumes for Complex Applications IX, Bergen (Norway), June 2020. Springer, 2020.

[9] C. Cancès, C. Chainais-Hillairet, J. Fuhrmann, and B. Gaudeul. A numerical-analysis-focused comparison of several finite volume schemes for a unipolar degenerate drift-diffusion model. IMA Journal of Numerical Analysis, 41(1):271—-314, 2021.

[10] C. Cancès, C. Chainais-Hillairet, A. Gerstenmayer, and A. Jüngel. Finite-volume scheme for a degenerate cross-diffusion model motivated from ion transport. Numerical Methods for Partial Differential Equations, 35(2):545–575, 2019.

[11] C. Cancès, C. Chainais-Hillairet, M. Herda, and S. Krell. Large time behavior of nonlinear finite volume schemes for convection-diffusion equations. SIAM Journal on Numerical Analysis, Sept. 2020.

[12] C. Cancès, C. Chainais-Hillairet, and S. Krell. Numerical Analysis of a Nonlinear Free-Energy Diminishing Discrete Duality Finite Volume Scheme for Convection Diffusion Equations. Computational Methods in Applied Mathematics, 18(3):407–432, July 2018.

[13] C. Cancès and B. Gaudeul. A convergent entropy diminishing finite volume scheme for a cross-diffusion system. 03-02-2020 submitted.
[14] C. Cancès and C. Guichard. Convergence of a nonlinear entropy diminishing Control Volume Finite Element scheme for solving anisotropic degenerate parabolic equations. Mathematics of Computation, 85(298):549–580, 2016.
[15] C. Cancès and C. Guichard. Numerical Analysis of a Robust Free Energy Diminishing Finite Volume Scheme for Parabolic Equations with Gradient Structure. Foundations of Computational Mathematics, 17(6):1525–1584, Dec. 2017.
[16] C. Cancès, F. Nabet, and M. Vohralík. Convergence and a posteriori error analysis for energy-stable finite element approximations of degenerate parabolic equations. Jan. 2019.
[17] C. Chainais-Hillairet, J.-G. Liu, and Y.-J. Peng. Finite volume scheme for multi-dimensional drift-diffusion equations and convergence analysis. ESAIM: Mathematical Modelling and Numerical Analysis, 37(2):319–338, Mar. 2003.
[18] Y. Coudière, J.-P. Vila, and P. Villedieu. Convergence rate of a finite volume scheme for a two dimensional convection-diffusion problem. ESAIM: Mathematical Modelling and Numerical Analysis, 33(3):493–516, May 1999.
[19] K. Deimling. Nonlinear Functional Analysis. Springer-Verlag, Berlin Heidelberg, 1985.
[20] W. Dreyer, C. Guhlke, and M. Landstorfer. A mixture theory of electrolytes containing solvation effects. Electrochemistry communications, 43:75–78, 2014.
[21] W. Dreyer, C. Guhlke, and R. Müller. Overcoming the shortcomings of the Nernst–Planck model. Physical Chemistry Chemical Physics, 15(19):7075–7086, Apr. 2013.
[22] J. Droniou. Finite volume schemes for diffusion equations: Introduction to and review of modern methods. Mathematical Models and Methods in Applied Sciences, 24(08):1575–1619, Jan. 2014.
[23] J. Droniou and R. Eymard. The Asymmetric Gradient Discretisation Method. In C. Cancès and P. Omnes, editors, Finite Volumes for Complex Applications VIII - Methods and Theoretical Aspects, Springer Proceedings in Mathematics & Statistics, pages 311–319, Cham, 2017. Springer International Publishing.
[24] J. Droniou, R. Eymard, T. Gallouët, C. Guichard, and R. Herbin. The Gradient Discretisation Method. Springer, July 2018.
[25] R. Eymard and T. Gallouët. H-Convergence and Numerical Schemes for Elliptic Problems. SIAM Journal on Numerical Analysis, 41(2):539–562, Jan. 2003.
[26] R. Eymard, T. Gallouët, C. Guichard, R. Herbin, and R. Masson. TP or not TP, that is the question. Computational Geosciences, 18(3):285–296, Aug. 2014.
[27] R. Eymard, T. Gallouët, and R. Herbin. Finite volume methods. In Handbook of Numerical Analysis, volume 7 of Solution of Equation in $\mathbb{R}$ (Part 3), Techniques of Scientific Computing (Part 3), pages 713–1018. Elsevier, Jan. 2000.
[28] J. Fuhrmann. Comparison and numerical treatment of generalised Nernst–Planck models. Computer Physics Communications, 196:166–178, 2015.
[29] J. Fuhrmann. A Numerical Strategy for Nernst–Planck Systems with Solvation Effect. Fuel Cells, 16(6):704–714, 2016.
[30] J. Fuhrmann. VoronoiFVM.jl: Solver for coupled nonlinear partial differential equations based on the voronoi finite volume method, 2020. DOI:10.5281/zenodo.3529808.
[31] T. Gallouët and J.-C. Latché. Compactness of discrete approximate solutions to parabolic PDEs - Application to a turbulence model. Communications on Pure & Applied Analysis, 11(6):2371, 2012.
[32] R. Herbin. An error estimate for a finite volume scheme for a diffusion–convection problem on a triangular mesh. Numerical Methods for Partial Differential Equations, 11(2):165–173, 1995.
[33] A. Jüngel. Entropy Methods for Diffusive Partial Differential Equations. Springer, 2016.
[34] J. Leray and J. Schauder. Topologie et équations fonctionnelles. Annales scientifiques de l'École Normale Supérieure, 51:45–78, 1934.
[35] J.-L. Liu and B. Eisenberg. Poisson-nernst-planck-fermi theory for modeling biological ion channels. The Journal of chemical physics, 141(22):12B640_1, 2014.
[36] B. Ostle and H. L. Terwilliger. A comparison of two means. 17:69–70, 1957.
[37] J. Revels, M. Lubin, and T. Papamarkou. Forward-mode automatic differentiation in julia. arXiv:1607.07892 [cs.MS], 2016.
[38] D. L. Scharfetter and H. K. Gummel. Large-signal analysis of a silicon Read diode oscillator. IEEE Transactions on Electron Devices, 16(1):64–77, Jan. 1969.
[39] Silvaco International. Atlas user's manual, 2016. Santa Clara, CA.
[40] Synopsys, Inc. Sentaurus device userguide, 2010. Mountain View, CA.

[41] Z. Yu and R. Dutton. SEDAN III, July 88.

Benoît Gaudeul (benoit.gaudeul@univ-lille.fr): Univ. Lille, CNRS, UMR 8524, Inria - Laboratoire Paul Painlevé, F-59000 Lille

Jürgen Fuhrmann (juergen.fuhrmann@wias-berlin.de): Weierstrass Institute (WIAS), Mohrenstr. 39, 10117 Berlin, Germany