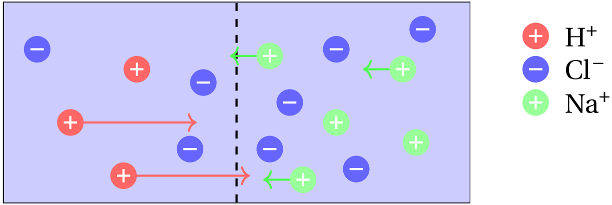
Finite volumes for a generalized Poisson–Nernst–Planck system with cross-diffusion

Clément Cancès, Maxime Herda, **Annamaria Massimini**

"Mixtures: Modeling, analysis and computing" - Prague

Introduction to the model

Aim: to describe the evolution of I ion species, immersed in a solvent like water, through long and narrow channels:



Applications: batteries, human cells, ...

The continuous model

Then, over $\Omega \times [0, +\infty)$:

$$\begin{cases} \partial_t u_i + \nabla \cdot F_i = 0, & i = 1, \ldots, I, \\ -\lambda^2 \Delta \phi = \sum_{i=1}^{I} z_i u_i, & (\lambda > 0, z_i \in \mathbb{R}) \end{cases}$$

closed with some b.c. and i.c., with the flux of the species i being given by

$(D_i > 0)$

$$F_i = -D_i \Big(u_0 \nabla u_i - u_i \nabla u_0 + u_0 u_i z_i \nabla \phi \Big).$$

where the *solvent concentration* satisfies

(size exclusion)

$$u_0 = 1 - \sum_{i=1}^{I} u_i$$

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and leads to cross-diffusion.

The continuous model[0][1]

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[0] Gerstenmayer and Jüngel 2018
[1] Burger, Schlake, and Wolfram 2012

Two numerical schemes for the modified PNP model

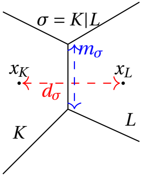
Motivations: To propose and to analyze a scheme for the model which shares the best with the approaches proposed so far [a] [b] [c]:

- positivity and bounds of the volume fractions
- decay of free energy,
- unconditional convergence,
- second order accuracy in space,
- well behaviour (even for small λ^2),
- preserve the form of the steady states.

[a] Bailo, Carrillo, and Hu 2023
[b] Cancès, C. Chainais-Hillairet, et al. 2019
[c] Gerstenmayer and Jüngel 2019

The space-time discretisation

- We introduce a mesh $(\mathcal{T}, \mathcal{E}, \{x_K\}_{K\in\mathcal{T}})$, fulfilling the *orthogonality condition* and a time discretisation $\left(t^n\right)_{n\geq 0}$ of $[0, +\infty)$.



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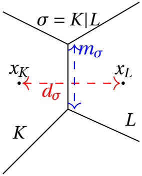

- The discretization of the Poisson equation relies on a classical two-point flux approximation:

$$\lambda^2 \sum_{\sigma\in\mathcal{E}_K} m_\sigma \frac{(\phi_K^n - \phi_{K\sigma}^n)}{d_\sigma} = m_K \sum_{i=1}^{I} z_i u_{i,K}^n, \qquad K\in\mathcal{T}, n\geq 1.$$

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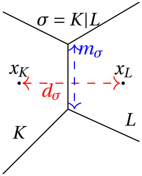

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- The conservation laws are discretized using a backward Euler method in time and finite volumes in space:

$$\frac{u_{i,K}^n - u_{i,K}^{n-1}}{\tau^n} m_K + \sum_{\sigma\in\mathcal{E}_K} F_{i,K\sigma}^n = 0, \qquad i = 1,\ldots,I,\ K \in \mathcal{T},\ n \geq 1.$$

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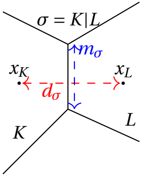

- The discretization of the Poisson equation relies on a classical two-point flux approximation:

$$\sum_{\sigma\in\mathcal{E}_K} m_\sigma \frac{(\phi_K^n - \phi_{K\sigma}^n)}{d_\sigma} = \frac{1}{\lambda^2} m_K \sum_{i=1}^{I} z_i u_{i,K}^n, \qquad K\in\mathcal{T}, n\geq 1.$$

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$$\frac{u_{i,K}^n - u_{i,K}^{n-1}}{\tau^n} m_K + \sum_{\sigma\in\mathcal{E}_K} F_{i,K\sigma}^n = 0, \qquad i=1,\ldots,I,\ K\in\mathcal{T},\ n\geq 1.$$

The SQRA scheme

The continuous model was originally derived thanks to a hopping process[a], suggesting the choice

$$F^n_{i,K\sigma} = a_\sigma D_i \left(u^n_{i,K} u^n_{0,L} e^{\frac{1}{2} z_i (\phi^n_K - \phi^n_L)} - u^n_{i,L} u^n_{0,K} e^{\frac{1}{2} z_i (\phi^n_L - \phi^n_K)} \right),$$

leading to the *square-root approximation scheme*[b].

[a] Burger, Schlake, and Wolfram 2012
[b] Cancès and Venel 2023

The SQRA scheme

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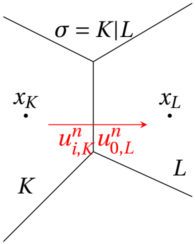

The probability that a $i-$particle jumps from K to L is proportional to:

$$u^n_{i,K} \quad = \quad \#\{\text{candidates in } K \text{ for a jump}\}$$

$$u^n_{0,L} \quad = \quad \#\{\text{available sites to host the } i- \text{ particle in the cell } L\}$$

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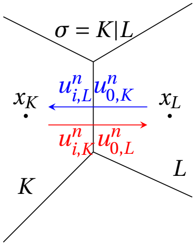

The probability that a $i-$particle jumps from L to K is proportional to:

$$u^n_{i,L} = \#\{\text{candidates in } L \text{ for a jump}\}$$

$$u^n_{0,K} = \#\{\text{available sites to host the } i- \text{ particle in the cell } K\}$$

A generalisation of the Scharfetter-Gummel scheme

Hence the scheme can be re-written using the function

$$\mathfrak{B}(y) = e^{-y/2}$$

as

$$F^n_{i,K\sigma} \quad = \quad a_\sigma D_i \left(u^n_{i,K} u^n_{0,L} \mathfrak{B}\left(z_i(\phi^n_L - \phi^n_K)\right) - u^n_{i,L} u^n_{0,K} \mathfrak{B}\left(z_i(\phi^n_K - \phi^n_L)\right) \right)$$ [2,3,4]

where

- $\mathfrak{B} \in C^1(\mathbb{R}, \mathbb{R})$;
- $\mathscr{B}(0) = 1$, $\mathscr{B}(y) > 0$;
- in general, $\mathscr{B}(y) - \mathscr{B}(-y) \neq -y$, but $\mathfrak{B}(-y) - \mathfrak{B}(y) = y + \mathcal{O}(y^2)$.

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[2] Lie, Fackeldey, and Weber 2013

[3] Heida 2018

[4] Claire Chainais-Hillairet and Droniou 2011

Behaviour for small λ^2

However, when λ^2 become small,

$$\sum_{\sigma \in \mathcal{E}_K} \frac{m_\sigma}{d_\sigma} (\phi_K^n - \phi_{K\sigma}^n) = \frac{1}{\lambda^2} m_K \sum_{i=1}^{I} z_i u_{i,K}^n,$$

the drift

$$e^{\frac{1}{2} z_i (\phi_K^n - \phi_L^n)}$$

becomes too large to evaluate its exponential.

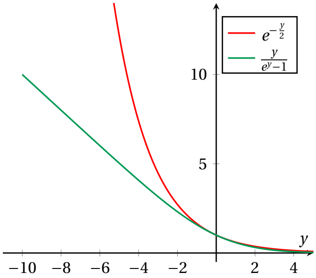
The SG scheme

Instead of using the function

(SQRA) $\mathfrak{B}(y) = e^{-y/2}$,

another natural choice for the drift term is the function

(SG) $\mathfrak{B}(y) = \dfrac{y}{e^y - 1}$,



leading to the *Scharfetter-Gummel scheme*, with fluxes:

$$F^n_{i,K\sigma} = a_\sigma D_i \left(u^n_{i,K} u^n_{0,L} \frac{z_i(\phi^n_L - \phi^n_K)}{e^{z_i(\phi^n_L - \phi^n_K)} - 1} - u^n_{i,L} u^n_{0,K} \frac{z_i(\phi^n_K - \phi^n_L)}{e^{z_i(\phi^n_K - \phi^n_L)} - 1} \right).$$

Consistency of the fluxes

By taking advantages of the entropy structure of the model the fluxes re-write as

$$F_i = -D_i\left(u_0 \nabla u_i - u_i \nabla u_0 + u_0 u_i z_i \nabla \phi\right) = -D_i u_0^2 e^{-z_i\phi} \nabla w_i$$

where $w_i := \frac{u_i}{u_0} e^{z_i \phi}$ are the *Slotboom variables*.

[5] Heida, Kantner, and Stephan 2021

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where $w_i := \frac{u_i}{u_0} e^{z_i\phi}$ are the *Slotboom variables*. Hence

$$F_{i,K\sigma}^n := a_\sigma D_i\, u_{0,K}^n\, u_{0,L}^n \mathfrak{M}(e^{-z_i\phi_K^n}, e^{-z_i\phi_L^n})\Big(w_{i,K}^n - w_{i,L}^n\Big)$$

where $\mathfrak{M}$ is a Stolarsky mean[5]:

$$\mathfrak{B}(y) = \mathfrak{M}(1, e^{-y}).$$

We used:

$(a, b > 0 \text{ with } a \neq b)$ $\qquad \mathfrak{M}^{\text{SQRA}}(a,b) := \sqrt{ab}, \qquad \mathfrak{M}^{\text{SG}}(a,b) := \dfrac{\log(1/a) - \log(1/b)}{1/a - 1/b}$

[5] Heida, Kantner, and Stephan 2021

Theorem (Existence - C. Cancès, M. Herda, A. M)

There exists (at least) one solution to the scheme which satisfies

$$0 < u_{i,K}^n < 1 \qquad \forall i = 0, \ldots, I,\ K \in \mathcal{T},\ n \geq 1.$$

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Moreover, the discrete free energy $\mathcal{H}_{\mathcal{T}}^n$ *is decaying along the time iterations*

$$\mathcal{H}_{\mathcal{T}}^n + \tau^n \mathcal{D}_{\mathcal{T}}^n \leq \mathcal{H}_{\mathcal{T}}^{n-1}, \qquad n \geq 1,$$

where $\mu_{i,K}^n = \log\left(\frac{u_{i,K}^n}{u_{0,K}^n}\right) + z_i \phi_K^n$ *is the discrete electrochemical potentials of species i, and*

$$\mathcal{D}_{\mathcal{T}}^n = \sum_{i=1}^{I} \sum_{\sigma \in \mathcal{E}_{int}} F_{i,K\sigma}^n (\mu_{i,K}^n - \mu_{i,L}^n) \geq 0.$$

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The dissipation $\mathcal{D}_{\mathcal{T}}^n$ *vanishes iff* $\left(\left(U_K^n\right)_{K\in\mathcal{T}}, \left(\phi_K^n\right)_{K\in\mathcal{T}}\right)$ *is the stationary solution.*

Theorem (Convergence of the scheme - C. Cancès, M. Herda, A. M)

There exists a weak solution (U,ϕ) *such that, up to the extraction of a subsequence,*

$$\phi_{\mathcal{T}_\ell,\tau_\ell} \underset{\ell\to+\infty}{\longrightarrow} \phi \quad \textit{and} \quad u_{0,\mathcal{T}_\ell,\tau_\ell} \underset{\ell\to+\infty}{\longrightarrow} u_0 \quad \textit{in } L^p_{loc}(\mathbb{R}_+; L^p(\Omega)) \quad \forall p \in [1,+\infty),$$

$$\textit{and} \quad U_{\mathcal{T}_\ell,\tau_\ell} \underset{\ell\to+\infty}{\longrightarrow} U \quad \textit{in the } L^\infty(\mathbb{R}_+ \times \Omega)^I \textit{ weak-}\star \textit{ sense.}$$

A simulations with $\lambda^2 = 10^{-2}$ (1D)

- $\Omega = (0,1)$
- $z_1 = 2$, $z_2 = 1$, and $D_1 = D_2 = 1$
- $\phi^D(t,0) = 10$ and $\phi^D(t,1) = 0$.
- Initial configurations: $u_1^0(x) = 0.2 + 0.1(x-1)$ and $u_2^0 \equiv 0.4$

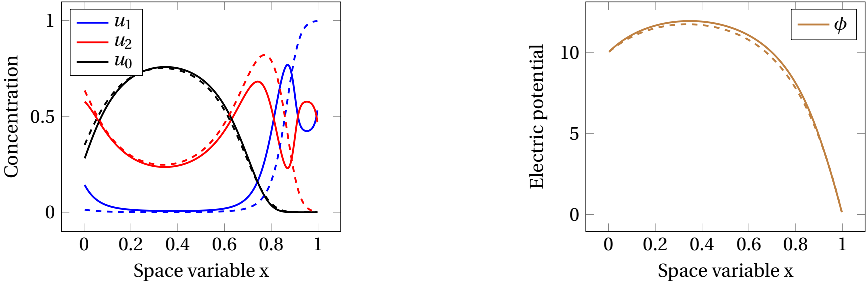
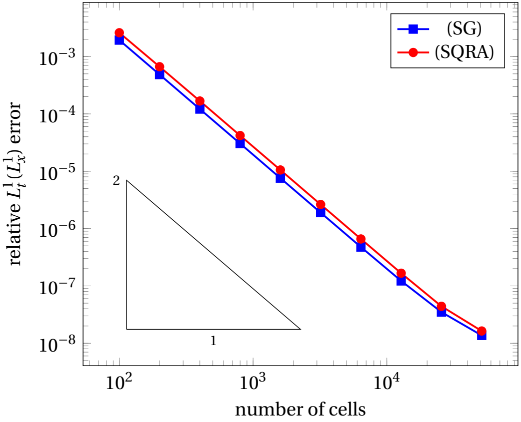


Figure 1: Solid lines: Solutions at time $T = 1$. Dashed lines: Long-time limit.

Second order convergence of the schemes



A reference solution is computed on a grid made of 1638400 cells and with a constant time step $\tau = 10^{-3}$, to which are compared solutions computed on successively refined grids but with the same constant time step.

Proposition (Existence of the (discrete) steady state)

There exists a solution to the steady scheme, with constant in space potentials in the sense that there exists $\boldsymbol{\mu}_{\mathcal{T}}^{\infty} = \left(\mu_{i,\mathcal{T}}^{\infty}\right)_{1\leq i\leq I} \in \mathbb{R}^{I}$ *such that*

$$\log \frac{u_{i,K}^{\infty}}{u_{0,K}^{\infty}} + z_i \phi_K^{\infty} = \mu_{i,\mathcal{T}}^{\infty}, \qquad K \in \mathcal{T},\ 1 \leq i \leq I,$$

such that,

$$(U_{\mathcal{T}}^{n}, \phi_{\mathcal{T}}^{n}) \underset{n\to+\infty}{\longrightarrow} (U_{\mathcal{T}}^{\infty}, \phi_{\mathcal{T}}^{\infty}).$$

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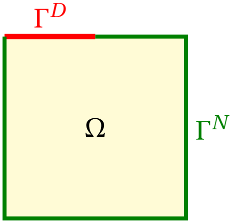
such that,

$$(U_{\mathcal{T}}^n, \phi_{\mathcal{T}}^n) \underset{n\to+\infty}{\longrightarrow} (U_{\mathcal{T}}^{\infty}, \phi_{\mathcal{T}}^{\infty}).$$

Proposition (Uniqueness)

The solution $(\phi_{\mathcal{T}}^{\infty}, \boldsymbol{\mu}_{\mathcal{T}}^{\infty})$ *minimizes the strictly convex functional* $\Psi_{\mathcal{T}} : \mathbb{R}^{\mathcal{T}} \times \mathbb{R}^I \to \mathbb{R}$ *defined by*

$$\Psi_{\mathcal{T}}(y_{\mathcal{T}}, \boldsymbol{\xi}) = \frac{\lambda^2}{2} \sum_{\sigma\in\mathcal{E}} a_\sigma (y_K - y_{K\sigma})^2 + \sum_{K\in\mathcal{T}} m_K \log\left(1 + \sum_{i=1}^{I} e^{\xi_i - z_i y_K}\right) - \sum_{K\in\mathcal{T}} m_K \left[f_K y_K + \sum_{i=1}^{I} \xi_i u_{i,K}^0 \right].$$



- $\Omega = (0,1)^2$, with $\partial\Omega = \Gamma^D \cup \Gamma^N$
- $\phi^D = 0$
- $z_1 = 2$, $z_2 = 1$, $z_3 = -1$
- $D_1 = 1$, $D_2 = 2$, $D_3 = 2$

Two initial globally neutral profiles:

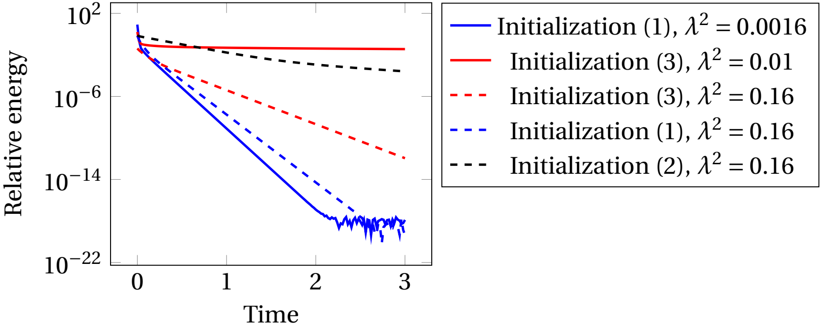
(1)
$$\begin{cases} u_1^{0,(1)}(x) = 0.3 \times 1_{(0,1/2)^2}(x), \\ u_2^{0,(1)}(x) = 0.3 \times 1_{(1/2,1)\times(0,1/2)}(x), \\ u_3^{0,(1)}(x) = 0.9 \times 1_{(1/2,1)^2}(x). \end{cases}$$

(2)
$$\begin{cases} u_1^{0,(2)}(x) = 0.1 \times u_1^{0,(1)}(x), \\ u_2^{0,(2)}(x) = 0.1 \times u_2^{0,(1)}(x) + 0.9 \times 1_{(0,1)\times(1/2,1)}(x), \\ u_3^{0,(2)}(x) = 0.1 \times u_3^{0,(1)}(x) + 0.9 \times 1_{(0,1)\times(0,1/2)}(x). \end{cases}$$

A third initial globally charged and constant in space:

(3)
$$u_1^{0,(3)}(x) = 0.2, \quad u_2^{0,(3)}(x) = 0.2, \quad u_3^{0,(3)}(x) = 0.3.$$

Convergence towards the steady long-time behavior ($\mathcal{H}_{\mathcal{T}}^n - \mathcal{H}_{\mathcal{T}}^\infty$)



We run our scheme with a constant time step $\tau = 10^{-4}$ and for two different Debye length until a final time $T = 3$, and look for the evolution of the relative energy $\mathcal{H}_{\mathcal{T}}^n - \mathcal{H}_{\mathcal{T}}^\infty$ along time. The relative energy is decaying for all the curves, but the velocity at which the decay occurs varies strongly depending on the Debye length and on the initial profile.