Thermodynamically consistent finite volume methods for generalized Nernst-Planck-Poisson problems

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Generalized Nernst-Planck-Poisson

- Transport of N charged species with molar concentration c_i, charge z_i in self-consistent electric field, dissolved in solvent with concentration c_0
- Driving forces for charged particle movement:
  - gradient of chemical potential of ideal dilute solvent $\mu_i^{\text{ideal}} = \mu^\circ + RT \ln \frac{c_i}{c^\circ}$
  - gradient of excess chemical potential μ_i^{ex}
  - gradient of electrostatic potential ϕ

$$-\nabla \varepsilon \nabla \phi = F \sum_{i=1}^{N} z_i c_i \qquad \text{Poisson}$$

$$\partial_t c_i + \nabla \cdot \vec{N}_i = r_i \qquad (i = 1 \dots N) \qquad \text{Continuity}$$

$$\vec{N}_i = -\frac{D_i}{RT} c_i \left(\nabla \mu_i^{\text{ideal}} + \nabla \mu_i^{\text{ex}} + z_i F \nabla \phi \right) \qquad (i = 1 \dots N) \qquad \text{Nernst-Planck}$$

Alternative formulations of Nernst-Planck flux

$$\vec{N}_i = -\frac{D_i}{RT} c_i \left(\nabla \mu_i^{\text{ideal}} + \nabla \mu_i^{\text{ex}} + z_i F \nabla \phi \right) \qquad \text{(excess chemical potential form)}$$

$$= -D_i \nabla c_i - c_i \frac{D_i}{RT} (\nabla \mu_i^{\text{ex}} + z_i \nabla \phi) \qquad \text{(drift-diffusion form)}$$

$$= -D_i c_i \left(\nabla \log \left(\gamma_i \frac{c_i}{c^\circ} \right) + z_i \frac{F}{RT} \nabla \phi \right) \qquad \text{(activity coefficent form)}$$

- Activity coefficient:

$$\gamma_i = \exp \left(\frac{\mu_i^{\text{ex}}}{RT} \right)$$

- No steric effects $\equiv$ infinitely small ions $\Rightarrow$

$$\mu_i^{\text{ex}} = 0, \quad \gamma_i = 1$$

Steric effects with equally sized ions
Ansatz: Solvent and ions fill up space

- v: solvent and ion molar volume, e.g. $v = a^3$ where a: lattice constant
- Incompressibility $\equiv$ volume filling
  - $c_0 + \sum_{i=1}^{N} c_i = \bar{c} = c^\circ = \frac{1}{v} = const$
  - Limitation if concentrations: $0 \leq c_i \leq \bar{c}$
- Chemical potentials including solvent ($i = 0 \ldots N$):

$$\mu_i = \mu_i^\circ + RT \ln \frac{c_i}{\bar{c}} = \mu_i^{\text{ideal}}$$

- Excess chemical potential $\equiv$ negative chemical potential of solvent

$$\mu_i^{\text{ex}}(c_1 \ldots c_N) = -\mu_0 = -\mu_0^\circ - RT \ln\Big(1 - \sum_{j=1}^{N} \frac{c_j}{\bar{c}}\Big)$$

$$\gamma_i = \frac{1}{v c_0} = \frac{1}{1 - v \sum_{j=1}^{N} c_j}$$

Bikerman, Phil. Mag. 1942; Freise, Z. Electrochem 1955

Generalization for solvation, varying ion sizes, molar masses
$\Rightarrow$ Chemical potential will depend on pressure p

- Varying species molar volumes v_i, molar masses M_i, relative molar masses $m_i = \frac{M_i}{M_0}$
  $\Rightarrow$ non-constant summary concentration $\bar{c} = \sum_{i=0}^{N} c_i$
- Solvation: species i ions solvated with κ_i solvent molecules
- Incompressibility using solvated molar volume $\bar{v}_i = v_i + \kappa_i v_0 \Rightarrow c_0 = \frac{1}{v_0} - \sum_{i=1}^{N} \frac{\bar{v}_i}{v_0} c_i$

$$\mathbf{N}_i = -\frac{D_i}{RT} c_i \left(\nabla \mu_i - m_i \nabla \mu_0 + z_i F \nabla \phi\right) \qquad (i = 1 \dots N)$$

$$\mu_i = \mu_i^\circ + \bar{v}_i (p - p^\circ) + RT \ln \frac{c_i}{\bar{c}} \qquad (i = 0 \dots N)$$

$$\begin{aligned} \mu_i^{\text{ex}} &= \mu_i - m_i \mu_0 - \mu_i^{\text{ideal}} \\ &= (\bar{v}_i - m_i v_0)\, p - m_i RT \log \frac{c_0}{\bar{c}} - RT \log v_0 \bar{c} \qquad (i = 1 \dots N) \end{aligned}$$

$$\gamma_i(c_1 \dots c_N, p) = \frac{1}{v_0 \bar{c}} \exp\left(\frac{\bar{v}_i - m_i v_0}{RT} p\right) \left(\frac{\bar{c}}{c_0}\right)^{m_i}$$

Dreyer/Guhlke/Müller PCCP 2013, Dreyer/Guhlke/Landstorfer, Electrochem. Comm. 2014

Constant density case

- Density $\rho = M_0 c_0 + \sum_{i=1}^{N} (M_i + \kappa_i M_0) c_i$
- ρ is constant if $m_i = \frac{M_i + \kappa_i M_0}{M_0} = \frac{\bar{v}_i}{v_0}$

$$\mu_i^{\mathrm{ex}} = -m_i RT \log \frac{c_0}{\bar{c}} - RT \log v_0 \bar{c}$$

$$\gamma_i = \frac{1}{v_0 \bar{c}} \left(\frac{\bar{c}}{c_0} \right)^{\frac{\bar{v}_i}{v_0}}$$

Useful to consider e.g. when coupling to Navier-Stokes solver wich assumes constant pressure

JF/Guhlke/Linke/Merdon/Müller, DOI 10.1007/978-3-030-33116-0_8, Springer 2020

Momentum balance in mechanical equilibrium

- Pressure needs to be calculated from Navier-Stokes equation
- Mechanical equilibrium: zero velocity $\Rightarrow$ Momentum balance with Coulomb force:

$$\nabla p = q\nabla\phi$$

- Assume $\nabla q || \nabla\phi$, take divergence:

$$\Delta p = \nabla \cdot q\nabla\phi$$

- Second order PDE which allows implementation with standard FEM/FVM methods

Thermodynamic Equilibrium

- Zero flux $\vec{N}_i = 0$
- Given (bulk) reference values $\phi^b, p^b, c_i^b, \gamma_i^b = \gamma_i(c_1^b \dots c_N^b, p^b)$
- Integration of Nernst-Planck flux $\Rightarrow$ algebraic system defining c_i:

$$c_i = c_i^b \frac{\gamma_i^b}{\gamma_i} \exp\left(z_i \frac{F}{RT}(\phi^b - \phi)\right) = c_i^b \gamma_i^b \frac{a_i}{\gamma_i}$$

  where $a_i = \frac{\gamma_i c_i}{\gamma_i^b c_i^b} = \exp\left(z_i \frac{F}{RT}(\phi^b - \phi)\right)$: activity
- Combine with Poisson equation, momentum balance:

$$-\nabla \varepsilon \nabla \phi = q = F \sum_{i=1}^{N} z_i c_i$$

$$\Delta p = \nabla \cdot q \nabla \phi$$

(Modified) Poisson-Boltzmann

- If $\gamma_i = \frac{1}{1 - v\sum_{i=1}^{N} c_j}$, one can explicitely express the activity coefficient in activities:

$$\gamma_i = 1 + \sum_{j=1}^{N} v a_j$$

- "Collapse" to Generalized Poisson Boltzmann independent of p

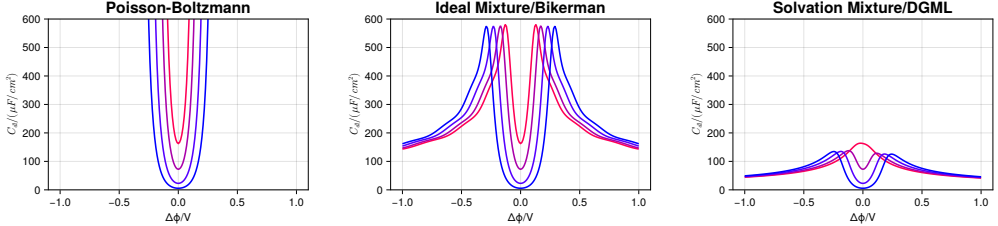
$$\begin{aligned} -\nabla\varepsilon\nabla\phi = q &= F\sum_{i=1}^{N} z_i c_i \\ &= F\sum_{i=1}^{N} z_i \frac{\exp\left(z_i \frac{F}{RT}(\phi^b - \phi)\right)}{1 + v\sum_{j=1}^{N}\exp\left(z_j \frac{F}{RT}(\phi^b - \phi)\right)} \end{aligned}$$

- $\gamma_i = 1 \Rightarrow$ original Poisson-Boltzmann/Gouy-Chapman model

Double layer capacitance of ideally polarizable electrode

- Computational domain: $\Omega = (0, L)$
- Boundary conditions:

$$\phi|_{x=0} = 0 \qquad \phi|_{x=L} = \phi^b$$
$$(\nabla p - q\nabla\phi)\cdot\vec{n}|_{x=0} = 0 \qquad p|_{x=L} = p^b$$



Boundary conditions for Faradaic reactions in electrochemical cell in domain $(0, L)$

- Solvent and metal inert with respect to reaction – only ions and electrons react
- Constant e^- concentration in electrode material (metal)
- Applied potential difference U

  $\Rightarrow$ Dirichlet BC for the electrostatic potential and bulk concentrations:

$$\begin{aligned} \phi|_{x=0} = U, \quad \phi|_{x=L} &= 0 \\ p|_{x=L} &= 0 \\ c_i|_{x=L} &= c_i^{bulk} \end{aligned}$$

- **Postulate: Reaction rates depend solely on chemical potentials at surface**

$$(N_i \cdot \mathbf{n})|_{x=0} = J_i(\mu_1^0 \dots \mu_n^0), \quad (i = 1 \dots N) \qquad \text{(PNPBC)}$$

- Fast adsorption $\Rightarrow$ equal bulk and surface chemical potentials $\mu_i^0 = \mu_i(0)$

Guhlke, PhD Thesis TU Berlin, 2015
Dreyer/Guhlke/Müller PCCP 2015

Method of matched asymptotic expansions

- Small parameter describing width of polarization boundary layer vs. width of domain

$$\lambda = \frac{\text{Debye Length}}{\text{Domain width}} = \frac{\sqrt{\frac{\varepsilon RT}{2F^2 c_\infty}}}{R-L} \sim \frac{\sqrt{\varepsilon}}{R-L}$$

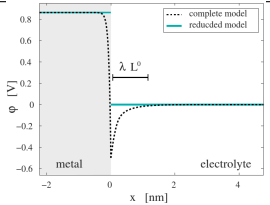
- Regard functions $h(t,x)$ ($h = \mu_i, \phi, \dots$)
- Close to $x = L$, introduce inner coordinate $\bar{x} = \frac{x-L}{\lambda}$, and define $\bar{h}(t,\bar{x};\lambda) = h(t, L+\lambda\bar{x})$
- Regard formal asymptotic expansions:

$$h(t,x;\lambda) = \sum_{j=0}^{\infty} \lambda^j h_j(t,x) \quad \text{(outer)} \qquad \bar{h}(t,\bar{x};\lambda) = \sum_{j=0}^{\infty} \lambda^j \bar{h}_j(t,\bar{x}) \quad \text{(inner)}$$

- Develop hierarchies of PDE systems for $h_j, \bar{h}_j$
- "Glue" them together by matching conditions: $\bar{h}(t,\bar{x};\lambda) \asymp h(t, L+\lambda\bar{x};\lambda)$.

Caginalp/Fife, SIAM J. Appl. Math. 1988
Dreyer/Guhlke/Müller, PCCP 2015

Zero order outer equation: PNP system with electroneutrality constraint



- Large domain ⇒ small polarization boundary layer
- Neglect its size ⇒ keep domain $(0, L)$
- Replace Poisson equation by electroneutrality constraint:

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

$$\partial_t c_i + \nabla \cdot \mathbf{N}_i = 0 \qquad \text{(NNP)}$$

$$\mathbf{N}_i = -\frac{D_i}{RT} c_i \left(\nabla \mu_i - \nabla \mu_0 + z_i F \nabla \phi\right) \quad (i = 1 \dots N)$$

- Keep (PNPBC): $(N_i \cdot \mathbf{n})|_{x=0} = J_i(\mu_1^0 \dots \mu_n^0), (i = 1 \dots N)$
- **How to calculate the surface chemical potentials μ_i^0 in this case ?**

Dreyer/Guhlke/Müller, PCCP 2015

Zero order inner equation: Equilibrium

- Local equilibrium in polarization boundary layer
- Zero order equation in polarization boundary layer: constant electrochemical potential

$$\mu_i + z_i F\phi = \text{constant}$$

- Matching $\Rightarrow$ chemical potentials at the surface:

$$\mu_i^0 = \mu_i(0) + z_i F(\phi(0) - U)$$

- $\Rightarrow$ "Butler-Volmer like" potential difference in boundary conditions for (NNP):

$$(N_i \cdot \mathbf{n})|_{x=0} = J_i(\mu_1^0 \dots \mu_n^0), (i = 1 \dots N) \qquad \text{(NNPBC)}$$

Dreyer/Guhlke/Müller, PCCP 2015

Surface reaction equation

- Let $A_0 \dots A_N$ be the reacting species, $R_1 \dots R_k$ the reactions
- Denote by A_{-1} the electrons on the metal side
- Reaction equation R_k:

$$\sum_{i=-1}^{N} a_{k,i} A_i \underset{R_k^-}{\overset{R_k^+}{\leftrightharpoons}} \sum_{i=-1}^{N} b_{k,i} A_i \tag{1}$$

- Mass and charge conservation yield for $k = 1 \dots K$, $s_{k,i} = b_{k,i} - a_{k,i}$:

$$\sum_{i=-1}^{N} M_i s_{k,i} = 0 \qquad \sum_{i=-1}^{N} z_i s_{k,i} = 0, \tag{2}$$

- With $z_{-1} = -1$ and $n = s_{k,-1}$ number of electrons: $\sum_{i=0}^{N} z_i s_{k,i} = s_{k,-1} = n$

Dreyer/Guhlke/Müller PCCP 2016, 18, 24966
R. Müller, personal communication

Rate expressions

- Affinity: $\mathcal{A}_k = \frac{1}{RT}\sum_{i=-1}^{N} s_{k,i}\mu_i$
- Rate expression:

$$R_k(\mu_0 \dots \mu_N) = R_{k,0}\Big(\exp(-\beta_k \mathcal{A}_k) - \exp((1-\beta_k)\mathcal{A}_k)\Big)$$

  - $\mu_i = \mu_i(0)$ in (PNPBC)
  - $\mu_i = \mu_i(0) + z_i F(\phi(0) - U)$ in (NNPBC)

$$\begin{aligned}
\mathcal{A}_k &= \frac{1}{RT}\left(\sum_{i=-1}^{N} s_{k,i}\mu_i + \sum_{i=0}^{N} s_{k,i} z_i F(\phi - U)\right) \\
&= \frac{1}{RT}\left(s_{-1,i}\mu_{-1} + \sum_{i=0}^{N} s_{k,i}\mu_i + nF(\phi - U)\right) \\
&= \frac{1}{RT}\left(\Delta g + \sum_{i=0}^{N} s_{k,i}\mu_i + nF(\phi - U)\right)
\end{aligned}$$

Dreyer/Guhlke/Müller PCCP 2016, 18, 24966
R. Müller, personal communication

Redox reaction

- aqeuous solution with reacting species O, R with $z_O = z_R + n$
- background electrolyte S, X with $z_S = -1$, $z_X = 1$.

The redox reaction is

$$O + ne^- \rightleftharpoons R \tag{3}$$

with affinity

- $\mathcal{A}_1 = \frac{1}{RT}(\Delta g + \mu_R - \mu_O)$ for PNP
- $\mathcal{A}_1 = \frac{1}{RT}(\Delta g + \mu_R - \mu_O + nF(\phi - U))$ for NNP

Butler-Volmer like expression

In the electroneutral case, this leads to

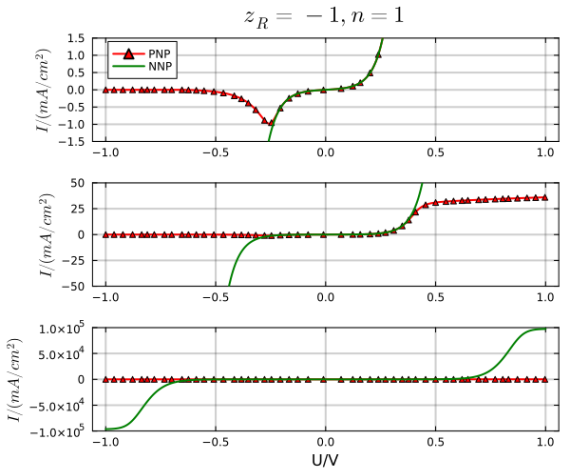
$$R(\mu_O, \mu_R, \phi) = R_0 \left(\exp\left(-\beta \frac{\mu_R - \mu_O - nF(\phi - U)}{RT} \right) - \exp\left((1-\beta) \frac{\mu_R - \mu_O - nF(\phi - U)}{RT} \right) \right)$$

Expressed in concentrations, one yields (setting $\beta = \frac{1}{2}$)

$$\begin{aligned} R(c_O, c_R, \phi) &= R_0 \left(\left(\frac{c_O}{c_R} \right)^{\frac{1}{2}} \exp\left(\frac{zF(\phi - U)}{2RT} \right) - \left(\frac{c_R}{c_O} \right)^{\frac{1}{2}} \exp\left(-\frac{zF(\phi - U)}{2RT} \right) \right) \\ &= \frac{\bar{c} R_0}{(c_O c_R)^{\frac{1}{2}}} \left(\frac{c_O}{\bar{c}} \exp\left(\frac{zF(\phi - U)}{2RT} \right) - \frac{c_R}{\bar{c}} \exp\left(\frac{-zF(\phi - U)}{2RT} \right) \right). \end{aligned}$$

Replacing $\frac{\bar{c} R_0}{(c_O c_R)^{\frac{1}{2}}}$ by $k_0 = \frac{\bar{c} R_0}{(c_O^{\text{bulk}} c_R^{\text{bulk}})^{\frac{1}{2}}}$ yields a Butler-Volmer like equation

Comparison NNP vs PNP



- Good match between results asymptotic expression and resolved boundry layer for small voltages
- “Levich exclusion” for larger negative voltages
- Displacement by X^- accumulated due to electrostatic attraction for larger positive voltages

V. Levich, Dokl. Akad. Nauk SSSR 67 (1949) 309–312

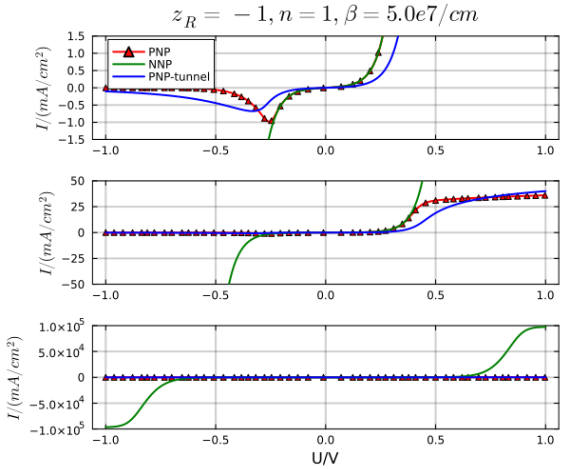
Levich exclusion vs tunneling

- Levich exclusion: decrease of conductivity of polarization boundary layer due to electrostatic repulsion
- How well is the assumption justified that the reaction takes place exactly at $x = 0$? Tunneling ?
- Tunneling assumptions:
  - The same reaction takes place in the bulk instead of the surface
  - Electrons are available in a small region close to the surface
  - Electron availability modeled by a pre-factor $a(x) = \beta \exp(-\beta x)$ such that $\int_0^\infty a(x)dx = 1$:

$$R_k^{bulk}(\mu_0 \dots \mu_N) = a(x)R_{k,0}\Big(\exp(-\beta_k \mathcal{A}_k) - \exp((1-\beta_k)\mathcal{A}_k)\Big)$$

V. Levich, Dokl. Akad. Nauk SSSR 67 (1949) 309–312
E.J.F. Dickinson, R.G. Compton / Journal of Electroanalytical Chemistry 661 (2011) 198–212

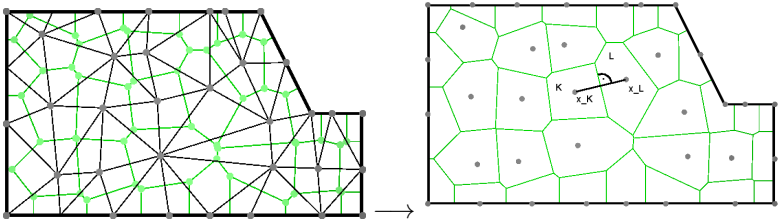
Comparison with tunneling



- Tunneling can “damp” Levich exclusion

Finite volume discretization method

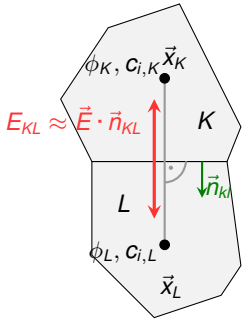
- Subdivide computational domain into control volumes aka “representative elementary volumes” (REV)
- Use Gauss theorem to derive balance laws for REV’s from PDE
- “admissible” REV generation: start with triangulation,
  create Voronoi cells by joining triangle cirumcenters as REVs



- Orthogonality between interface $\partial K \cap \partial L$ and line $x_K x_L$ between neigboring collocation points $\Rightarrow$ calculate fluxes between REVs by standard two-point finite difference formulas

Discrete Poisson equation

$$\int_K (-\nabla \cdot \varepsilon \nabla \phi - q) d\omega = 0$$



Gauss theorem:

$$\int_{\partial K} \varepsilon \nabla \phi \cdot \vec{n} d\gamma - \int_K q d\omega = 0$$

Quadrature:

$$\sum_{L \text{ neighbor of } K} |\partial K \cap \partial L| E_{KL}^n - |K| F \sum_{i=1}^{N} z_i c_{i,K} = 0$$

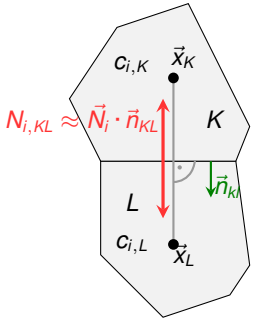
Finite difference approximation:

$$E_{KL}^n = \varepsilon \frac{\phi_K^n - \phi_L^n}{|\vec{x}_K - \vec{x}_L|}$$

Discrete Nernst-Planck

Modify implicit Euler “Scharfetter-Gummel” exponential fitting upwinding ansatz from semiconductor simulation by introducing μ^{ex} along with ϕ in the appropriate places.

$$\partial_t c_i - D_i \nabla c_i - c_i \frac{D_i}{RT}(\nabla \mu_i^{\text{ex}} + z_i \nabla \phi) = 0$$



- Subdivide time: $0 = t^0 < t^1 < \cdots < t^k = T$
- $\delta\phi_{KL}^n := \frac{F}{D_i RT}(\phi_K^n - \phi_L^n)$, $\delta\mu_{i,KL}^{\text{ex},n} := \frac{1}{D_i RT}(\mu_{i,K}^{\text{ex},n} - \mu_{i,L}^{\text{ex},n})$
- Bernoulli function: $B(x) = \frac{x}{e^x - 1}$

$$\frac{|K|}{\Delta t}(c_{i,K}^n - c_{i,K}^{n-1}) = - \sum_{L \text{ neighbor of } K} |\partial K \cap \partial L| N_{i,KL}^n$$

$$N_{i,KL}^n = D_i \frac{B(-\delta\mu_{i,KL}^{\text{ex},n} - z_i \delta\phi_{KL}^n) c_{i,K}^n - B(\delta\mu_{i,KL}^{\text{ex},n} + z_i \delta\phi_{KL}^n) c_{i,L}^n}{|\vec{x}_K - \vec{x}_L|}$$

Allen/Southwell, Quart. J. Mech. and Appl. Math. 1955; Ilin, Mat. Zametki 1969; Scharfetter/Gummel 1969; Yu/Dutton 1988; Liu/Eisenberg, J. Chem. Phys. 2014

Qualitative properties of excess chemical potential scheme
Pressure independent case

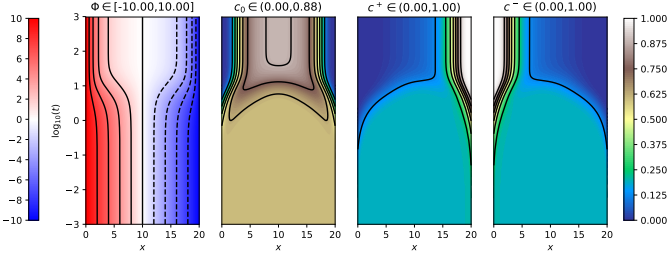
- Exact local and global **charge conservation**
- **Consistency to thermodynamic equilibrium** aka “well posedness”: Stationary solution $c_1 \dots c_N, \phi$ obtained from discrete Nernst-Planck-Poisson system coincides with the solution of the discretized generalized Poisson-Boltzmann prob
- Concentrations stay within **limits from natural constraints**
- Discrete counterpart of free energy $\int_\Omega (c_i \log c_i - \bar{c} \log \bar{c}) + (\nabla \phi)^2 \, d\omega$:

$$\sum_K |K| \sum_{i=0}^{N} c_{i,K} \log c_{i,K} - \bar{c}_{i,K} \log \bar{c}_{i,K} + \sum_{KL} |K \cap L| E_{KL}^2$$

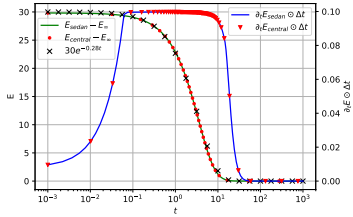
- **Decay of relative free energy** along solution trajectories on approach to equilibrium
- **Existence** of solutions of discretized system
- weak **Convergence** of discrete solution to continuous solution (proven so far for electrolyte case)

Gaudeul, Fuhrmann; Numerische Mathematik 151, 99–149 (2022)
Abdel, Chainais-Hillairet, Farrell, Herda; IMAJNA 44, 1090-1129 (2024)

Applied potential jump in closed 1D electrochemical cell with ideally polarizing electrodes
Symmetric binary electrolyte with equal sizes of solvent molecules, anions and cations.



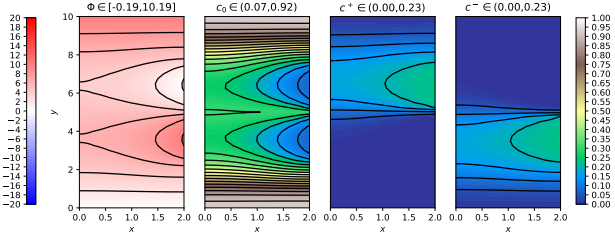
- x-t plots of potential, solvent, anion, cation concentrations
- Concentrations stay within natural bounds



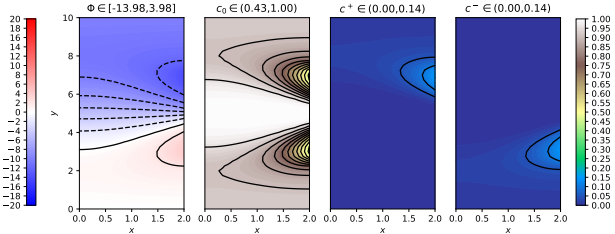
- Evolution of relative free energy and energy dissipation per time step.
- Energy dissipation per time step als step size control criterion

B. Gaudeul, JF: Numerische Mathematik 2022

Electrolytic diode, domain $\Omega = (0,2) \times (0,10)$
Rectification via surface charges of opposite signs



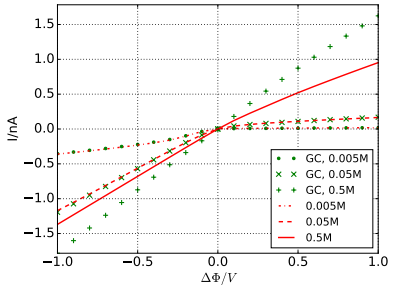
- Forward bias
- High ion concentration
- High ionic current



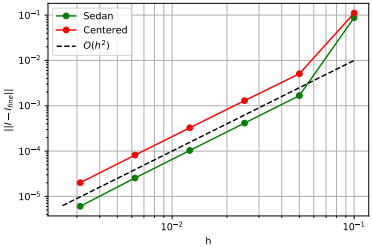
- Reverse bias
- Low ion concentration
- Low ionic current

B. Gaudeul, JF: Numerische Mathematik 2022

IV curve for electrolytic diode: convergence



IV curve for electrolytic diode



Second order grid convergence of calculated IV curve. "SEDAN" $\equiv$ excess chemical potential scheme

Deriving a software API for two-point flux finite volumes

Continuous:

n coupled PDEs in $\Omega \subset \mathbb{R}^d$:

$\partial_t s(\vec{u}) - \nabla \cdot j(\vec{u}, \nabla \vec{u}) + r(\vec{u}) = 0$

- "Storage" $s : \mathbb{R}^n \to \mathbb{R}^n$
- "Reaction" $r : \mathbb{R}^n \to \mathbb{R}^n$
- "Flux" $j : \mathbb{R}^n \times \mathbb{R}^{nd} \to \mathbb{R}^{nd}$

Problems in this class:

- Multiphase flow in porous media
- Ion transport in electrolytes
- Charge transport in semiconductors
- ...

Deriving a software API for two-point flux finite volumes

Continuous:

n coupled PDEs in $\Omega \subset \mathbb{R}^d$:

$$\partial_t s(\vec{u}) - \nabla \cdot j(\vec{u}, \nabla \vec{u}) + r(\vec{u}) = 0$$

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Problems in this class:

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- ...

Discretized:

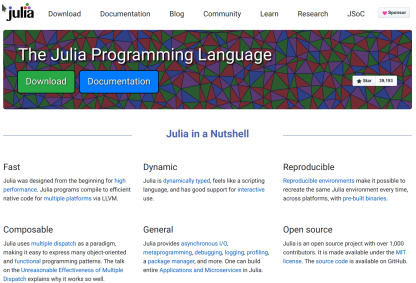
$$0 = |K| \frac{s(\vec{u}_k^n) - s(\vec{u}_k^{n-1})}{\Delta t} + \\ + \sum_{L \text{ neigbour of } K} |K \cap L| g(\vec{u}_k^n, \vec{u}_l^n) + |K| r(\vec{u}_k^n)$$

- "Storage" $s : \mathbb{R}^n \to \mathbb{R}^n$
- "Reaction" $r : \mathbb{R}^n \to \mathbb{R}^n$
- discrete edge flux $g : \mathbb{R}^n \times \mathbb{R}^n \to \mathbb{R}^n$

Solution methods:

- Delaunay mesh generation
- Implicit Euler time discretization
- Newton method with analytical Jacobians (+ damping, parameter embedding)
- Various direct and iterative linear solvers

Julia language and VoronoiFVM.jl



- Julia 1.0 (2018): new language for scientific computing & data science
- Just-in-time compilation $\Rightarrow$ C-like performance
- Syntax level like python, matlab
- Best-in-class package manager supporting reproducibility
- Open source (MIT License)
- Easy access to automatic differentiation

VoronoiFVM.jl

- Solver for coupled nonlinear partial differential equations based on the Voronoi finite volume method.
- Implements the aforementioned API
- Use automatic differentiation to assemble Jacobians for complicated nonlinear problems
- 1/2/3D

https://julialang.org
JF et al: VoronoiFVM.jl, https://github.com/WIAS-PDELib/VoronoiFVM.jl

Example code for discrete fluxes
Derivatives for Jacobian calculated automatically from this code

```
function flux(f,u,edge,data)
    iphi=data.iphi
    f[iphi]=u[iphi,1]-u[iphi,2]
    sum_c1=0.0
    sum_c2=0.0
    for ic=1:data.nc
        sum_c1+=u[ic,1]
        sum_c2+=u[ic,2]
    end
    muex1=-log(1.0-sum_c1)
    muex2=-log(1.0-sum_c2)
    for ic=1:data.nc
        arg=data.z[ic]*(u[iphi,1]-u[iphi,2])+(muex1-muex2)
        bp,bm=fbernoulli_pm(arg)
        f[ic]=bm*u[ic,1]-bp*u[ic,2]
    end
end
```

WIAS-PDELib: open source Julia packages for PDE simulation

- WIAS-PDELib: collection of Julia packages for supporting PDE simulations
  - Pre/postprocessing, mesh generation, visualization
  - finite volume solver VoronoiFVM.jl
  - finite element solver ExtendableFEM.jl
- ChargeTransport.jl: package for solid state drift-diffusion problems (semiconductors, perovskites) on top of VoronoiFVM.jl
- LiquidElectrolytes.jl: package for electrolyte calculations on top of VoronoiFVM.jl under development, implements the aforementioned discretization methods for generalized PNP problems
- Integration with Julia SciML infrastructure (ODE solvers, Linear solvers and more)

https://github.com/WIAS-PDELib
C. Rackauckas et al: https://sciml.ai/

Coupling with electro-osmotic flow

- Nernst-Planck-Poisson-Stokes system on triangular/tetrahedral meshes
- Finite ion size via pressure dependency of chemical potentials and solvent chemical potential gradient as counterforce for ion transport
- Solvation via increased effective ion volumes

Flow solver:

- Pressure robust FEM via local correction to classical FEM
- Pointwise divergence free discrete velocity
- Velocity error independent of pressure

Nernst-Planck-Poisson solver:

- Voronoi box based finite volume method
- Exponentially fitted upwind fluxes
- Consistency to thermodynamic equilibrium

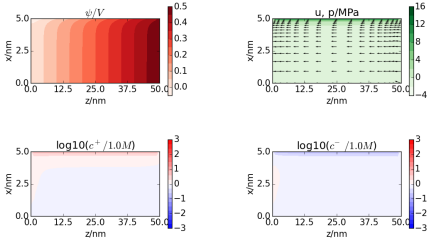
Coupling:

- Divergence free projection of FEM velocity to FVM
- Fix point iteration
- WIP: re-implementation in Julia environment

A. Linke, CMAME 2014
V. John, A. Linke, Ch. Merdon, M. Neilan, L. Rebholz, SIAM Review 2017
J. Fuhrmann, C. Guhlke, A. Linke, C. Merdon, and R. Müller, Electrochimica Acta, vol. 317, pp. 778–785, 2019

Electro-osmotic flow through straight nano pore
Velocity, concentration and electrostatic potential

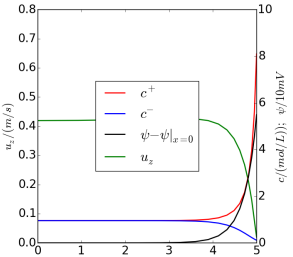
- Inlet/outlet concentrations $c_+ = c_- = 1M$
- Surface charge $\varepsilon \nabla \phi \cdot \vec{n} = \sigma = -10 \mu As/cm^2$
- Potential drop $\Delta \phi = 0.01\, V/nm$
- Simulated half channel due to symmetry

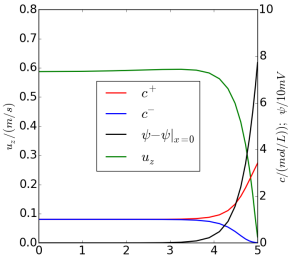


Top left: distribution of the electrostatic potential. Top right: velocity field (arrows) and pressure (color). Bottom row: positive resp. negative ion concentration.

JF/Guhlke/Linke/Merdon/Müller, DOI 10.1007/978-3-030-33116-0_8, Springer 2020

Electro-osmotic flow through straight nano pore
Velocity, concentration and electrostatic potential profiles





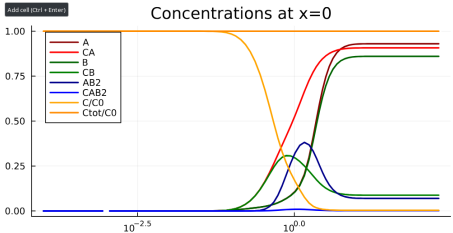
Classical Nernst-Planck (Dilute) Improved (DGML) model, $\kappa = 10$

- Body force $q\nabla\phi$ acts only in EDL
- Electro-neutral region with constant velocity $\Rightarrow$ plug flow
- Velocity, ζ-potential increase with solvation number due to wider double layer

JF/Guhlke/Linke/Merdon/Müller, DOI 10.1007/978-3-030-33116-0_8, Springer 2020

Julia tools for Reaction modeling
ModelingToolkit.jl & Catalyst.jl

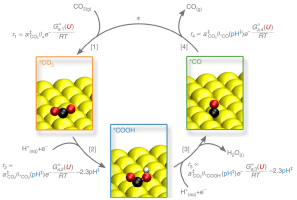
- ModelingToolkit.jl: modeling framework for symbolic-numeric computation. Automatically generate functions for model components like Jacobians and Hessians
- Catalyst.jl: symbolic modeling package for chemical reaction networks. Defines symbolic ReactionSystems, which can be created programmatically or specified using Catalyst's domain-specific language
- Reaction functions generated by Catalyst.jl can be used in bulk and boundary reaction callbacks of VoronoiFVM.jl

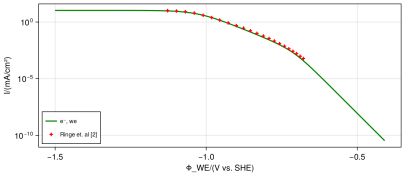


https://docs.sciml.ai/ModelingToolkit/stable/
https://docs.sciml.ai/Catalyst/stable/
https://wias-pdelib.github.io/VoronoiFVM.jl/stable/plutostatichtml_examples/heterogeneous-catalysis/

CatmapInterface
WIP, with Ringe Lab (Korea Univ.), S.Maaß (TU Berlin/AWI Bremen)

- CatMap: Python package for expressing and solving microkinetic models parametrized by relative energies of intermediate states obtained from ab-initio calculations by DFT
- CatInt: CatMAP coupled to a generalized PNP system realized in COMSOL
- CatMapInterface.jl
  - Generate electrode boundary condition functions from CatMAP data for LiquidElectrolytes.jl, leveraging ModelingToolkit.jl
  - Use ModelingToolkit.jl to describe bulk buffer reactions





CO2 electroreduction on gold (Ringe et al 2020)

S. Ringe et al (2020). Nature communications, 11(1), 33
https://catmap.readthedocs.io/en/latest/

Conclusions & outlook

- Generalized Poisson-Nernst-Planck models are able to reflect quite accurately experimental data (at least in equilibrium . . .)
- Finite volume methods provide a provably thermodynamically consistent discretization approach for coupled nonlinear systems of PDEs
- The Julia language provides an open source environment for efficient and reproducible implementations of complicated nonlinear models, leveraging among others symbolic tools and automatic differentiation
- We try to leverage these possibilities with a focus on scientific computing for (bio)electrochemistry and semiconductor modeling
- Happy give more thorough introduction to the methods/code and to try out models during this Long Program