WIAS
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Mathematik für Schlüsseltechnologien

NETZWERKE GRUNDLAGENFORSCHUNG
erneuerbare Energien und rationelle Energieanwendungen

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Modeling and Simulation of Coupled Species Transport, Porous Electrode Effects and Catalytic Reactions in Flow Cells

Contents

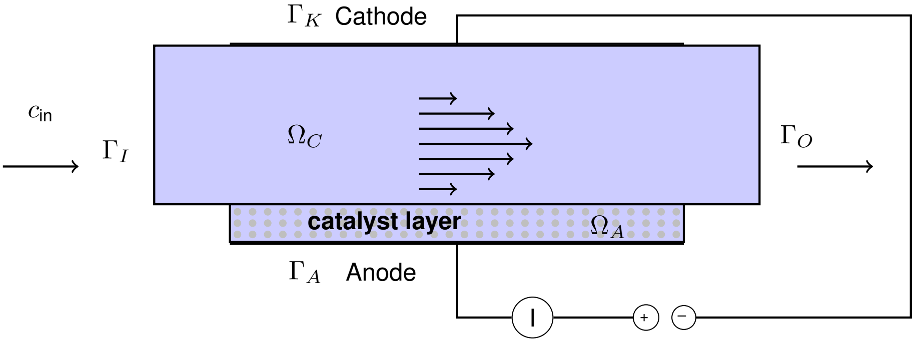
General motivation

Heterogeneous electrochemical reactions on catalyst surfaces or in porous catalyst layers are a substantial part of the working principle of fuel cells.
Flow cells are use for the experimental investigation of these processes. They allow measurements of electrode kinetics at well defined conditions.

- ▷ Modeling framework based on macro-scale kinetics (vs. DFT etc.)
- ▷ Understand interplay between solute transport, diffusion in the catalyst layer, adsorption and reaction at catalyst surface
- ▷ Ideal mixing ansatz insufficient due to possible concentration gradients at electrode
- ▷ Asymptotic theory does not work for general reaction terms and cell thickness correlating with thickness of the boundary layer

$\Rightarrow$ Use numerial models.

Principle of a Flow Cell



- ▷ Solution containing electrolyte H_2SO_4 and reactant H_2 is injected at given rate
- ▷ Oxidation reaction (creating electrons) at the anode $H_2 \to 2H^+ + 2e^-$
- ▷ Reduction reaction (consuming electrons) at cathode $2H^+ + 2e^- \to H_2$
- ▷ Reaction rate can be measured as anodic current
- ▷ Product composition can be measured at outlet

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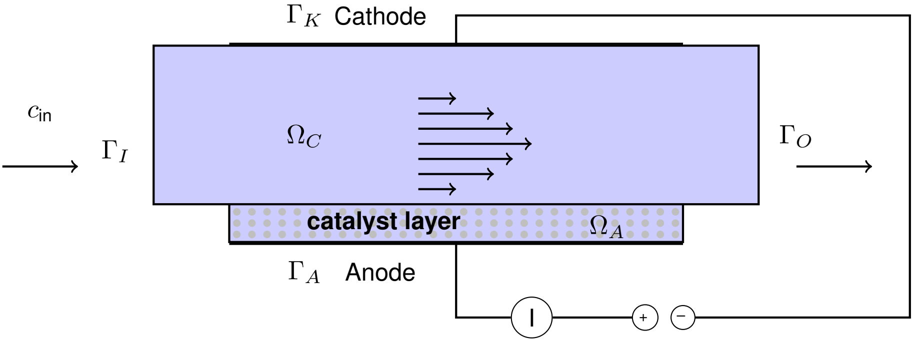

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Some measurement methods in electrochemistry

The primary measurement is that of the anodic current for a given applied voltage, which then allows different modes of exploration.

- Limiting current: fixed voltage, at which reaction is fast. Reveals transport properties.
- Transient responses to concentration change, potential steps.
- Cyclic voltammetry: response to periodic (mostly triangular) time dependent voltage.
- Impedance spectroscopy: frequency dependent amplification of a periodic applied voltage

Contents

Limiting current

- Limiting current is measured in the case where the anodic reaction is fast in comparison to diffusion processes.
- E.g. H_2 oxidation on platinum for appropriate voltage levels.
- Verification of “transport part” of a numerical flow cell model.
- Anodic reaction can be replaced by a homogeneous Dirichlet boundary condition.

Governing equations

Stationary, incompressible Navier-Stokes equations for fluid flow

$$\begin{aligned}\rho(\vec{v}\cdot\nabla)\vec{v}+\nabla p+\eta\nabla(\nabla\cdot\vec{v}+(\nabla\cdot\vec{v})^T)&=\rho\vec{f}\\ \nabla\cdot\vec{v}&=0.\end{aligned}$$

Stationary transport of species

$$\nabla\cdot\vec{q}=0,\quad \vec{q}=-(D\nabla c-c\vec{v})$$

$$\begin{array}{rclrll}
\vec{q}\cdot\vec{n} & = & 0 & \vec{v}\cdot\vec{n} & =0 & \text{(symmetry)}\\
\vec{q}\cdot\vec{n} & = & 0 & \vec{v} & =0 & \text{(impermeable wall, no slip)}\\
\vec{q}\cdot\vec{n} & = & -c\vec{v}\cdot\vec{n} & & p=0 & \text{(outflow)}\\
c & = & c_I & & \vec{v}\cdot\vec{n}=v(x) & \text{(inflow)}\\
c & = & 0 & \vec{v} & =0 & \text{(anode, no slip)}
\end{array}$$

Limiting current

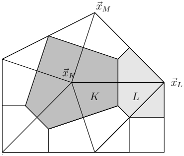
$$I_{lim}=2F\int_{anode}\vec{q}\cdot\vec{n}ds$$

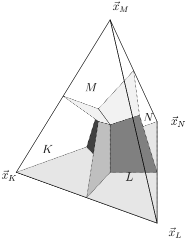
Voronoi finite volumes for transport equation

- Integrate equation over control volume K
  $\int_K \frac{c^n - c^{n-1}}{t^n - t^{n-1}} dx - \int_{\partial K} (D\nabla c^n - c^n \vec{v}) \cdot \vec{n}_K ds = 0.$
- Split surface integral into contributions from facets σ_{KL} common with the neighboring boxes L

$$|K| \frac{c_K^n - c_K^{n-1}}{t^n - t^{n-1}} + \sum_{L \in \mathcal{N}(K)} \frac{|\sigma_{KL}|}{|\vec{x}_K - \vec{x}_L|} g(c_K^n, c_L^n, v_{KL}) = 0$$

  - c_K^n: average value of c^n in K
  - v_{KL}: average normal flux through σ_{KL}
  - $g(c_K, c_L, v_{KL}) \approx (-D\nabla c + c\vec{v}) \cdot (\vec{x}_K - \vec{x}_L)$: upwind finite difference expression along $\vec{x}_K \vec{x}_L$, e.g. Il'in scheme
- $\Rightarrow$ System of linear equations to be solved for c^n.
- Upwinding + Boundary conforming Delaunay $\Rightarrow$ M-property of transition matrix $\Rightarrow$ stability + maximum principle





Delaunay Simplices and Voronoi cells

Boundary Conforming Delaunay Meshes

Definition

- A simplicial partition of a polyhedral domain Ω is *Delaunay*, if for any of it simplices, the interior of its circumball does not contain any other vertex of the partition.
- It is *boundary conforming* if all simplex circumcenters are contained in the closure $\bar{\Omega}$.

Some problems:

- Floating point errors in geometrical predicates
- Limitation of number “Steiner points” inserted for conforming property and quality improvement
- Handling of small input angles
- Avoiding slivers (skinny tetrahedra created from four nearly coplanar points)

Boundary Conforming Delaunay Mesh Generation

- triangle by J.R.Shewchuk (UC Berkeley) is able to create conforming triangulations based on *proven algorithm*
- 3D Meshes based on subdivision of prismatic meshes based on 2D boundary conforming Delaunay meshes
- TetGen by Hang Si and Klaus Gärtner (WIAS). Focused on boundary conforming Delaunay (Proven for input angles $> 90^o$, working for $> 60^o$)

Divergence free discrete fluxes

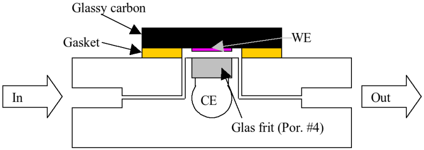
- $$\sum_{L \text{ neighbor of } K} \frac{|\sigma_{KL}|}{|\vec{x}_K - \vec{x}_L|} v_{KL} = 0$$

  $\Rightarrow$ discrete maximum principle for species concentration
- E.g. obtained from continuous divergence free velocity field by exact integration over Voronoi box faces

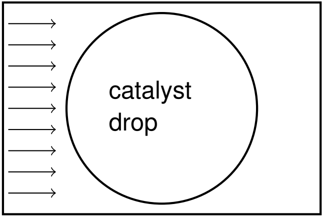
$$v_{KL} = \frac{1}{|\sigma_{KL}|} \int_{\sigma_{KL}} \vec{v} \cdot (\vec{x}_K - \vec{x}_L) ds$$

- Rectangular cell: Hagen - Poiseuille
- General case: divergence free finite elements

Flow Cell Design by Halseid/Jusys/Chojak/Behm(2006)



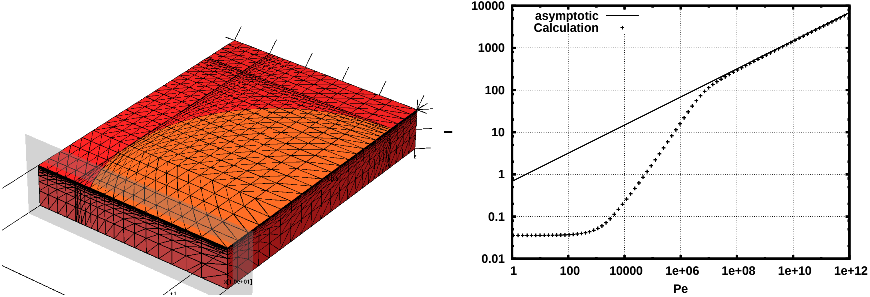
Cross section



Top view of active part

- ▷ If ignoring the elevation ($5\mu\mathrm{m}$, channel height: $50\mu\mathrm{m}$) of the catalyst spot, one can assume a channel flow regime
- ▷ Still, the transport problem is 3D due to the circular catalyst spot
- ▷ Ideal would be a cell with a rectangular catalyst spot inlay such that the surface is planar . . .

Comparison with asymptotics for 3D cell with cirular electrode

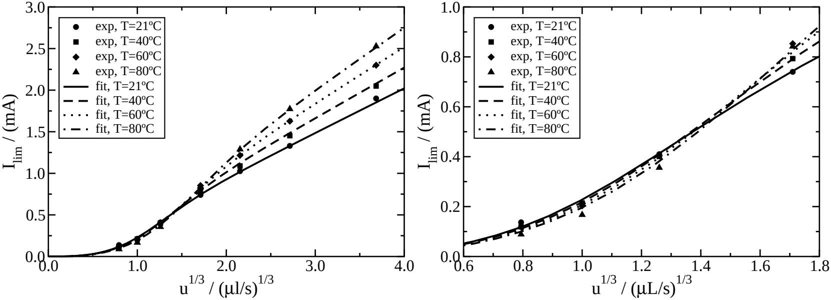


Left: flow-aligned 3D grid. Right: Sh vs. Pe: asymptotic curve and numerical result for the 3D model with circular electrode.

$$Pe = \frac{\beta R^2}{D} \qquad \beta = 6\frac{\bar{v}}{H} \qquad I = 2FD(c_I - c_0)\frac{\pi}{R}Sh$$

$$Sh = \frac{3^{\frac{4}{3}}2^{\frac{2}{3}}}{5\sqrt{\pi}\Gamma(\frac{5}{6})}Pe^{\frac{1}{3}} = \frac{2^{\frac{1}{3}}3^{\frac{4}{3}}\Gamma(\frac{1}{3})}{5\pi\Gamma(\frac{2}{3})}Pe^{\frac{1}{3}} \quad \approx 0.68658Pe^{\frac{1}{3}}$$

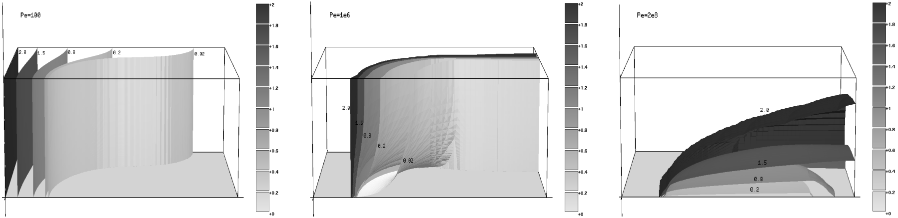
3D Cell with circular electrode: fitted data



$$c_I = \frac{k_H}{RT} p, \qquad D(T) = D_0 \exp\left(-\frac{k_D}{RT}\right)$$

Comparison of results of Levenberg-Marquardt fit for k_H, D_0, K_D to measurement
One fit for all temperatures

Limiting current: concentration isolevels



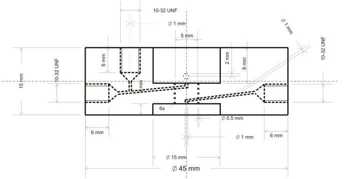
0.000283 $\mu\mathrm{L}/\mathrm{s}$ 2.83 $\mu\mathrm{L}/\mathrm{s}$ 567 $\mu\mathrm{L}/\mathrm{s}$

Concentration isolevels at different Peclet numbers. At low flow rates, the behaviour is purely diffusive. The assumptions for asymptotic theory are true only for higher flow rates.

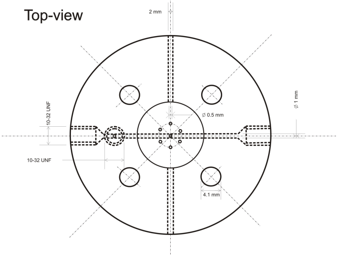
Fuhrmann, Zhao, Holzbecher, Langmach, Chojak, Jusys, Halseid, Behm PCCP 2008

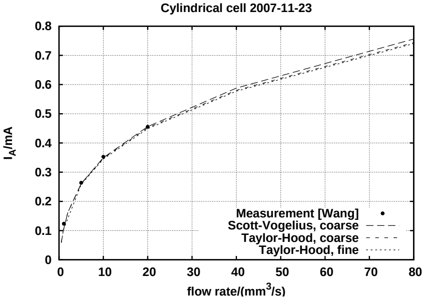
Numerical Results

Thin-Layer flow through cell (a)



Top-view

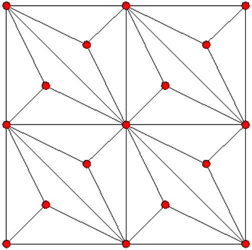




Measured (Baltruschat, Wang) and calculated values for the limiting current

Jusys/Massong/Baltruschat, 1999

Divergence free finite elements



How to obtain divergence-free discrete velocity field ?
A. Linke, Ph.D thesis (2008):

- Finite Elements:
  div(velocity space) $\subset$ pressure space
- Lowest order Scott Vogelius elements:
  $(P_d, P_{-(d-1)})$ (d:space dimension)
- stable on macro triangulations, Arnold/Qin(1992)

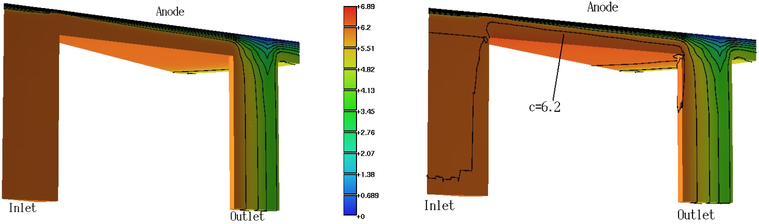
- Maintain two independent discretizations for transport (FV) and for flow (FE)
- (FV): Calculate simplicial contributions σ_S to all $\sigma \in \mathcal{F}$
- (FE): Calculate velocity projections v_{σ_S}
- (FV): Assemble v_σ from v_{σ_S}

Scott Vogelius vs. Taylor Hood

Isolines of concentration for flow rate of 20 μL/s, $c_I = 6.2$

Scott-Vogelius

Taylor-Hood



Maximum principle is preserved.

Divergence error at corner singularity triggers violation of maximum principle, error transported through domain (see $c = 6.2$ isoline)

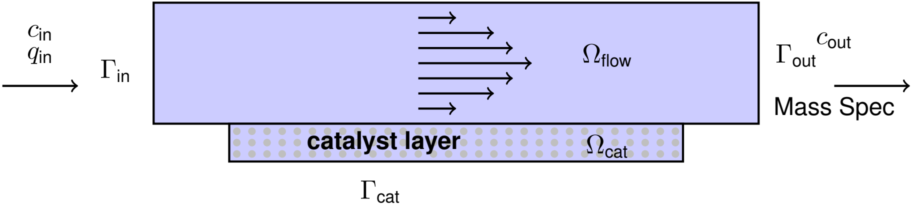
Ongoing work: Discrete divergence free finite volume scheme for Navier-Stokes

Contents

Kinetics in porous catalyst

To avoid difficulties with Navier-Stokes-Darcy coupling:

- ▷ Removal of forward facing step at catalyst edge
- ▷ Hagen-Poiseuille law in flow domain ⇒ avoid solution of Navier-Stokes
- ▷ Zero fluid velocity in porous layer ⇒ avoid solution of Darcy equation



Kinetics in porous catalyst: Volmer-Tafel Mechanism + CO Adsorption

- Reacting species H_2, CO and their concentrations: c_{H_2}, c_{CO}
- Adsorbed species H_{ad}, CO_{ad} and their normalized concentrations θ_H, θ_{CO}
- Free catalsyt sites S and their normalized concentration $\bar{\theta} = 1 - \theta_H - \theta_{CO}$
- Reaction products H^+, e^-. Ignored due to assumptions:
  - ideal conductivity for porous catalyst backing
  - ideal conductivity of electrolyte due to concentration of H^+ from dissolved H_2SO_4.

Chemical description and rate equations

$$H_2 + 2S \rightleftharpoons 2H_{ad}, \qquad r_1 = k_1^+ \frac{c_{H_2}}{c_{H_2}^{ref}} \bar{\theta}^2 - k_1^- \theta_H^2$$

$$H_{ad} \rightleftharpoons H^+ + e^- + S, \qquad r_2 = k_2^+ e^{\alpha\phi F/RT} \theta_H - k_2^- e^{(\alpha-1)\phi F/RT} a_{H^+} \bar{\theta}$$

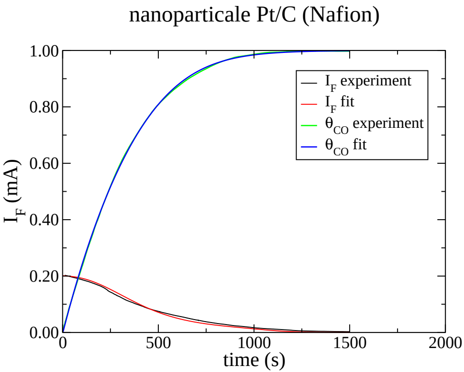
$$CO + S \rightleftharpoons CO_{ad}, \qquad r_3 = k_3^+ \frac{c_{CO}}{c_{CO}^{ref}} \bar{\theta} - k_3^- \theta_{CO}$$

$k_i^\pm$: reaction constants, ϕ: applied potential, T: temperature

- Reaction terms in transport equations $R_{H_2O} = c_{cat}^{eff} r_1 \quad R_{CO} = c_{cat}^{eff} r_3$
- Evolution of adsorbed species: $\frac{d\theta_1}{dt} = 2r_1 - r_2, \quad \frac{d\theta_2}{dt} = r_3$

Kinetics in porous catalyst: prototypical Fit of kinetic parameters

Fitted parameters: $\phi_{cat}, k_1^+, k_2^+, k_3^+, k_2^-, c_{cat}^{eff}$. Measured data from radial cell (Jusys/Kaiser/Behm 2001).



Fuhrmann, Zhao, Holzbecher, Langmach, J. Fuell Cell Sci. Tech, 2008

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Modeling Potential Distribution

- Double layer capacity enters the model
- Drop assumption of ideal conductivity
- Assume local electroneutrality, constant charge carrier concentrations in porous backing and in electrolyte
- Introduce electron and proton potentials: ϕ_{e^-}, ϕ_{H^+}
- potential ϕ in the catalytic reaction terms reads as $\phi = \phi_{e^-} - \phi_{H^+}$.
- Additional equations (Newman/Tobias 1962), “porous electrode theory”:

$$\begin{aligned} \partial_t Q_{dl} - \nabla \cdot \sigma^- \nabla \phi_{e^-} + c_{cat}^{eff} F r_2 &= 0 \quad \text{in porous layer} \\ -\partial_t Q_{dl} - \nabla \cdot \sigma^+ \nabla \phi_{H^+} - c_{cat}^{eff} F r_2 &= 0 \quad \text{in porous layer, cell} \\ Q_{dl} &= C_{\text{dl}}(\phi_{e^-} - \phi_{H^+}) \quad \text{in porous layer} \end{aligned}$$

$\sigma^{\pm}$: conductivities, C_{dl}: double layer capacity

Hydrogen oxidation with two independent adsorption sites

$$H_2 + 2S_1 \rightleftharpoons^{k_1^{\pm}} 2H_{ad1}$$ 1. H_2 adsorption

$$H_{ad1} \rightleftharpoons^{k_2^{\pm}} H^+ + e^- + S_1$$ 1. H_2 oxidation +desorption

$$H_2 + 2S_2 \rightleftharpoons^{k_3^{\pm}} 2H_{ad2}$$ 2. H_2 adsorption

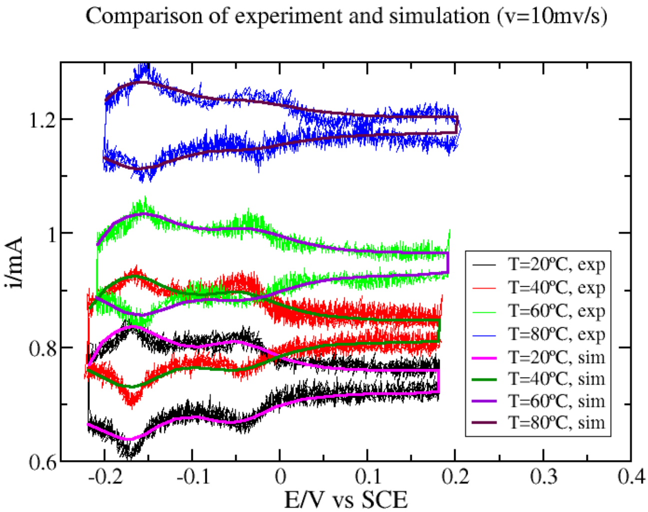
$$H_{ad2} \rightleftharpoons^{k_4^{\pm}} H^+ + e^- + S_2$$ 2. H_2 oxidation +desorption

where $k_1^{\pm}$ and $k_3^{\pm}$, $k_2^{\pm}$ and $k_4^{\pm}$ are not the same.
The reaction rate can be writen corresponding to the reactions:

$$\begin{aligned}
r_1 &= k_1^+ \frac{c_I}{c_{ref}} \theta_{Pt1}^2 - k_1^- \theta_{H1}^2 \\
r_2 &= k_2^+ \theta_{H1} e^{\alpha\phi F/RT} - k_2^- a_{H^+} \theta_{Pt1} e^{-(1-\alpha)\phi F/RT} \\
r_3 &= k_3^+ \frac{c_I}{c_{ref}} \theta_{Pt2}^2 - k_3^- \theta_{H2}^2 \\
r_4 &= k_4^+ \theta_{H2} e^{\alpha\phi F/RT} - k_4^- a_{H^+} \theta_{Pt2} e^{-(1-\alpha)\phi F/RT}
\end{aligned}$$

Cyclic voltammetry: fit results

Preliminary data from Ulm group.



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Impedance spectroscopy

- Response to a periodic (sinus- like) applied voltage with varying frequency and calculation of the complex amplification factor for each frequency.
- standard way to interpret these measurements based on equivalent electrical circuits
- Model based interpretation would allow a more comprehensive understanding
- Straightforward ansatz: transient calculations for each frequency
- Better way: small signal analysis

Small signal analysis

- Regard nonlinear evolution problem

$$\frac{dS(v(t),\lambda)}{dt} + D(v(t),\lambda) = 0$$

depending on parameter λ (e.g. voltage)
together with measurement functional $M(v)$ (e.g. current).

- Linearization around steady state v_0 + Taylor expansion in terms of $\lambda = \lambda_a \exp(i\omega t)$ yields an equation for the perturbation of the state variable

$$i\omega \left(S_v(v_0,\lambda_0)v_a + S_\lambda(v_0,\lambda_0)\right) + D_v(v_0,\lambda_0)v_a + D_\lambda(v_0,\lambda_0) = 0$$

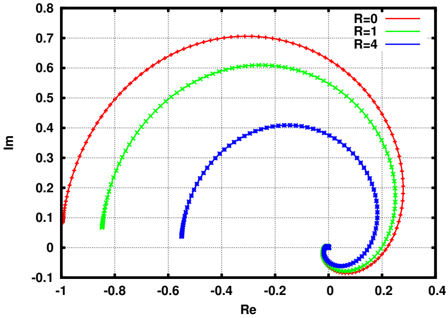
- Impedance $Z(\omega) = \frac{1}{M_v(v_0)v_a}$
- Once Jacobian of the system is given (Newton's method), impedance calculation is easily integrated into the solution strategy

Numerical experiment1

Impedance of the current response at L to voltage change in 0 of the linear reaction diffusion system in $(0, L)$

$$Cu_t - (Du_x)_x + Ru = 0, \quad u(0,t) = \lambda, \quad u(L,t) = 0 \tag{1}$$

Response function: current $I_L = Du_x(L,t)$.



Nyquist plot ($ImZ(\omega) vs. ReZ(\omega)$). Comparison of analytically (dots) and numerically (lines) obtained values for the impedance of test problem

Contents

Outlook

- ▷ Divergence free finite volumes for Navier Stokes
- ▷ Navier-Stokes Darcy coupling
- ▷ Formic acid, methanol kinetics
- ▷ Mass spectrometer compartments
- ▷ Surface diffusion