Weierstrass Institute for
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ENERGIESPEICHER
Forschungsinitiative der Bundesregierung

Numerical Strategies for Electrolyte Simulations

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Coupled flow and ion transport without electroneutrality assumption

- Relevant in a significant number of applications:
  - PEM nanopores
  - nanofluidic devices
  - ion channels in biomembranes
  - porous electrode microstructures
  - overlimiting current in electrodialysis
- Search for numerical approach which
  - takes into account recent work on excluded volume models
  - incorporates the knowledge from semiconductor device simulation (unconditionally stable Scharfetter-Gummel scheme)
  - guarantees mass conservation due to discrete divergence condition

Problem formulation: Nernst-Planck-Poisson system

- Mixture of N species; species N: neutral solvent; diagonal Onsager coefficients
- To be closed by constitutive relationship for c_α

$$-\nabla \varepsilon_0 \varepsilon_r \nabla \phi = q$$

$$\partial_t c_\alpha + \nabla \cdot (c_\alpha \mathbf{v} + \mathbf{N}_\alpha) = 0 \qquad \alpha = 1 \ldots N-1$$

$$\mathbf{N}_\alpha = -\frac{D_\alpha}{RT} c_\alpha \left(\nabla \mu_\alpha - \frac{M_\alpha}{M_N} \nabla \mu_N + z_\alpha F \nabla \phi \right) \qquad \alpha = 1 \ldots N-1$$

$$= -\frac{D_\alpha}{RT} c_\alpha \left(\nabla \tilde{\mu}_\alpha + z_\alpha F \nabla \phi \right) \qquad \alpha = 1 \ldots N-1$$

ϕ	V	electrostatic potential
c_α	$\mathrm{mol/m^3}$	molar density (concentration)
μ_α	$\mathrm{J/mol}$	chemical potential ($\alpha = 1 \ldots N$)
$\tilde{\mu}_\alpha = \mu_\alpha - \frac{M_\alpha}{M_N} \mu_N$	$\mathrm{J/mol}$	effective chemical potential ($\alpha = 1 \ldots N-1$)
$\mathbf{N}_\alpha$	$\mathrm{mol/(m^2 \cdot s)}$	molar diffusion flux
$\mathbf{v}$	$\mathrm{m/s}$	barycentric velocity
q	$\mathrm{As/m^3}$	space charge density
z_α	1	charge number
M_α	$\mathrm{kg/mol}$	molar mass
D_α	$\mathrm{m^2/s}$	diffusion coefficient

deGroot/Mazur 1962; Dreyer/Guhlke/Müller PCCP 2013

Incompressible flow of mixture: evolution of barycentric velocity $\mathbf{v}$

$$\partial_t(\rho\mathbf{v}) + \nabla\cdot(\rho\mathbf{v}\otimes\mathbf{v}) - \eta\Delta\mathbf{v} + \nabla p = -q\nabla\phi$$

$$\partial_t\rho + \nabla\cdot(\rho\mathbf{v}) = 0$$

$$\rho = M_N c + \sum_{\alpha=1}^{N-1}(M_\alpha - M_N)c_\alpha$$

$\mathbf{v}$	$\mathrm{m/s}$	barycentric velocity
p	Pa	pressure
η	Pas	viscosity
ρ	$\mathrm{kg/m^3}$	density
$c = \sum_{\alpha=1}^{N} c_\alpha$	$\mathrm{mol/m^3}$	(constant) summary concentration

deGroot/Mazur 1962; Dreyer/Guhlke/Müller PCCP 2013

Constitutive relationship for μ: dilute solution theory

- ideal dilute solution
- ions as point charges

$$\mu_N = 0$$

$$\mu_\alpha = \tilde{\mu}_\alpha = \mu_\alpha^\circ + RT \ln \frac{c_\alpha}{c} \quad (\alpha = 1 \ldots N-1).$$

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Unphysically high concentrations in polarization boundary layer!

Constitutive relationship for μ: excluded volume models

- Account for energy needed for species to enter already crowded configuration:

$$\mu_N = 0$$

$$\mu_\alpha = \tilde{\mu}_\alpha = \mu_\alpha^\circ + RT \ln \frac{c_\alpha}{c} + \ln \frac{1}{1-\Phi} \qquad (\alpha = 1 \ldots N-1)$$

- Φ: Summary volume fraction of the dissolved species:

$$\Phi = \sum_{\alpha=1}^{N-1} v_\alpha c_\alpha,$$

- v_α: partial molar volume
- E.g. estimate from spherical packing:

$$v_\alpha = 8 N_A \frac{4}{3} \pi r_\alpha^3.$$

- E.g. all molecules share one one lattice (Bikerman model)

$$v_\alpha = v = \frac{1}{c},$$

$$1 - \Phi = \frac{c_N}{c}$$

Bikerman, Phil. Mag. 1942; Paunov, J. Coll. Interf. Sci. 1996; Biesheuvel/v.Soestbergen, J. Coll. Interf. Sci. 2007

Constitutive relationship for μ: pressure correction due to Dreyer et al.

- Derivation from nonequilibrium thermodynamics leads to a constitutive relationship which links pressure, concentrations and chemical potential:

$$\mu_\alpha = \mu_\alpha^\circ + \frac{1}{c}(p - p^\circ) + RT \ln \frac{c_\alpha}{c} \qquad (\alpha = 1 \ldots N)$$

$$\tilde{\mu}_\alpha = \mu_\alpha^\circ + RT \ln \frac{c_\alpha}{c} + \left(1 - \frac{M_\alpha}{M_N}\right) \frac{(p - p^\circ)}{c} + \frac{M_\alpha}{M_N} RT \ln \frac{1}{1 - \Phi} \qquad (\alpha = 1 \ldots N-1)$$

- Gibbs Duhem + Thermodynamic equilibrium $\Rightarrow$

$$\frac{1}{c}(p - p^\circ) = -RT \ln \frac{c_N}{c} = RT \ln \frac{1}{1 - \Phi}$$

- $\Rightarrow$ Equivalent to Bikerman model ($\nu = \frac{1}{c}$):
  - in thermodynamical equilibrium
  - for equal molar masses
- Limitations (currently under consideration in Dreyer group):
  - constant summary concentration c
  - no notation yet for different molar volumes

Dreyer/Guhlke/Müller PCCP 2013

Mechanical equilibrium

- How to use pressure correction wihtout Navier-Stokes ?

$$\partial_t \mathbf{v} = 0$$
$$\nabla \mathbf{v} = 0$$
$$\Rightarrow \nabla p = -q \nabla \phi$$

- Taking the divergence gives as second order equation for p:

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

Constitutive relationship for μ: Fermi statistics

- See semiconductor device theory:

$$c_\alpha = c\mathscr{G}\left(\frac{\mu_\alpha - \mu_\alpha^\circ}{RT}\right).$$

- $\mathscr{G}$: (approximations of) Fermi-Dirac integrals of different orders:

$$\mathscr{G}(\eta) \approx \mathscr{F}_j(\eta) = \frac{1}{\Gamma(j+1)} \int_0^\infty \frac{\xi^j}{1+\exp(\xi-\eta)} d\xi$$

- Special case: Fermi integral of order -1

$$\mathscr{F}_{-1}(\eta) = \frac{1}{1+\exp(-\eta)}$$

$\Rightarrow$

$$\tilde{\mu}_\alpha = \mu_\alpha = \mu_\alpha^\circ + RT \ln \frac{c_\alpha}{c} + RT \ln \frac{1}{1-\frac{c_\alpha}{c}} \qquad (\alpha = 1 \ldots N-1)$$

- Resembles the excluded volume expression restricted to species α.
- No interaction term between different species

Kornyshev 1981, Landstorfer 2011

Concentration based formulation

- $\mu_\alpha \to -\infty$ for small concentrations, especially in depletion regions

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$$\mathbf{N}_\alpha = D_\alpha \left(\nabla c_\alpha - c_\alpha \left(1 - \sum_{\beta=1}^{N-1} v_\beta c_\beta \right) \sum_{\beta=1}^{N-1} v_\beta \nabla c_\beta - c_\alpha z_\alpha \frac{F}{RT} \nabla \phi \right)$$

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- Pure pressure correction :

$$\mathbf{N}_\alpha = -D_\alpha \left(\nabla c_\alpha + \frac{1}{cRT} c_\alpha \nabla p + \frac{z_\alpha F}{RT} c_\alpha \nabla \phi \right)$$

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- Fermi statistics:

$$\mathbf{N}_\alpha = -D_\alpha \left(d_\alpha \nabla c_\alpha + c_\alpha z_\alpha \frac{F}{RT} \nabla \phi \right)$$

$$d_\alpha = \frac{c_\alpha}{c \mathscr{G}' \left(\mathscr{G}^{-1} \left(\frac{c_\alpha}{c} \right) \right)} \overset{\mathscr{G} = \mathscr{F}_{-1}}{=} \frac{1}{1 - \frac{c_\alpha}{c}}$$

- $\mu_\alpha \to -\infty$ for small concentrations, especially in depletion regions
- Dilute solution (Boltzmann) $\to$ classical Nernst Planck

$$\mathbf{N}_\alpha^{NP} = -D_\alpha \left(\nabla c_\alpha + \frac{z_\alpha F}{RT} c_\alpha \nabla \phi \right)$$ Wrong in boundary layer.

- Excluded volume model (Bikerman if $v_\beta = v = \frac{1}{c}$): Complicated flux coupling.

$$\mathbf{N}_\alpha = D_\alpha \left(\nabla c_\alpha - c_\alpha \left(1 - \sum_{\beta=1}^{N-1} v_\beta c_\beta \right) \sum_{\beta=1}^{N-1} v_\beta \nabla c_\beta - c_\alpha z_\alpha \frac{F}{RT} \nabla \phi \right)$$

- Pure pressure correction : Insufficient pressure regularity in Navier-Stokes.

$$\mathbf{N}_\alpha = -D_\alpha \left(\nabla c_\alpha + \frac{1}{cRT} c_\alpha \nabla p + \frac{z_\alpha F}{RT} c_\alpha \nabla \phi \right)$$

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$$d_\alpha = \frac{c_\alpha}{c \mathscr{G}' \left(\mathscr{G}^{-1} \left(\frac{c_\alpha}{c} \right) \right)} \overset{\mathscr{G} = \mathscr{F}_{-1}}{=} \frac{1}{1 - \frac{c_\alpha}{c}}$$ Degenerates for $c_\alpha \to c$.

- Expression of effective chemical potential similar to dilute solution case defines *activity*:

$$\tilde{\mu}_\alpha = \tilde{\mu}_\alpha^\circ + RT \ln a_\alpha$$

- *Activity coefficient* γ_α:

$$a_\alpha = \gamma_\alpha \frac{c_\alpha}{c} \qquad \Rightarrow c_\alpha = c \frac{a_\alpha}{\gamma_\alpha} = c \beta_\alpha a_\alpha$$

- $\beta_\alpha = \frac{1}{\gamma_\alpha}$: *inverse activity coefficient*
- Nernst-Planck-Poisson transforms to:

$$\partial_t (c\beta_\alpha a_\alpha) + \nabla \cdot (c\beta_\alpha a_\alpha \mathbf{v} + \mathbf{N}_\alpha) = 0 \qquad \alpha = 1 \ldots N-1$$

$$-\nabla \varepsilon_0 \varepsilon_r \Delta \phi = q$$

$$\mathbf{N}_\alpha = -D_\alpha c \beta_\alpha \left(\nabla a_\alpha + a_\alpha z_\alpha \frac{F}{RT} \nabla \phi \right) \qquad \alpha = 1 \ldots N-1$$

$$q = cF \sum_{\alpha=1}^{N-1} z_\alpha \beta_\alpha a_\alpha$$

Inverse activity coefficients

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$$\beta_\alpha = 1$$

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$$\beta_\alpha = \beta = \frac{1}{1 + c\sum_{i=1}^{N-1} v_i a_i} \overset{v_i = \frac{1}{c}}{=} \frac{1}{1 + \sum_{i=1}^{N-1} a_i}$$

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- Full pressure correction model (weighted with volume exclusion):

$$\beta_\alpha = \left(\exp \frac{p - p^\circ}{cRT} \right)^{1 - \frac{M_\alpha}{M_N}} \left(1 - \sum_{i=1}^{N-1} v_i \beta_i c a_i \right)^{\frac{M_\alpha}{M_N}}$$

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$$\beta_\alpha(a_\alpha) = \frac{\mathscr{G}(\ln a_\alpha)}{a_\alpha} \overset{\mathscr{G} = \mathscr{F}_{-1}}{=} \frac{1}{1 + a_\alpha}$$

Inverse activity coefficients

- Dilute solution:

$$\beta_\alpha = 1$$

- Volume exclusion models No cross-coupling of gradients.

$$\beta_\alpha = \beta = \frac{1}{1 + c\sum_{i=1}^{N-1} v_i a_i} \overset{v_i = \frac{1}{c}}{=} \frac{1}{1 + \sum_{i=1}^{N-1} a_i}$$

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No degeneration.

Equilibrium case: Nonlinear Poisson equation

- Mechanical and thermodynamical equilibrium: $\mathbf{N}_\alpha = 0$:

$$\nabla \tilde{\mu}_\alpha = -z_\alpha F \nabla \phi \quad \Rightarrow \tilde{\mu}_\alpha = z_\alpha F (\psi_\alpha - \phi)$$

- ψ_α: (constant) quasi-Fermi potential
- Nonlinear Poisson equation:

$$-\nabla \varepsilon_0 \varepsilon_r \nabla \phi = F c \sum_{\alpha=1}^{N-1} z_\alpha \beta_\alpha a_\alpha$$

$$a_\alpha = \exp\left(\frac{z_\alpha F}{RT} (\psi_\alpha - \phi) \right)$$

- “classical” Poisson-Boltzmann:

$$-\nabla \varepsilon_0 \varepsilon_r \nabla \phi = F c \sum_{\alpha=1}^{N-1} z_\alpha \exp\left(\frac{z_\alpha F}{RT}(\psi_\alpha - \phi)\right)$$

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$$-\nabla\varepsilon_0\varepsilon_r\nabla\phi = Fc\frac{\sum_{\alpha=1}^{N-1} z_\alpha \exp\left(\frac{z_\alpha F}{RT}(\psi_\alpha - \phi)\right)}{1 + c\sum_{\alpha=1}^{N-1} v_\alpha \exp\left(\frac{z_\alpha F}{RT}(\psi_\alpha - \phi)\right)}$$

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- Pure pressure correction (Dreyer et al.):

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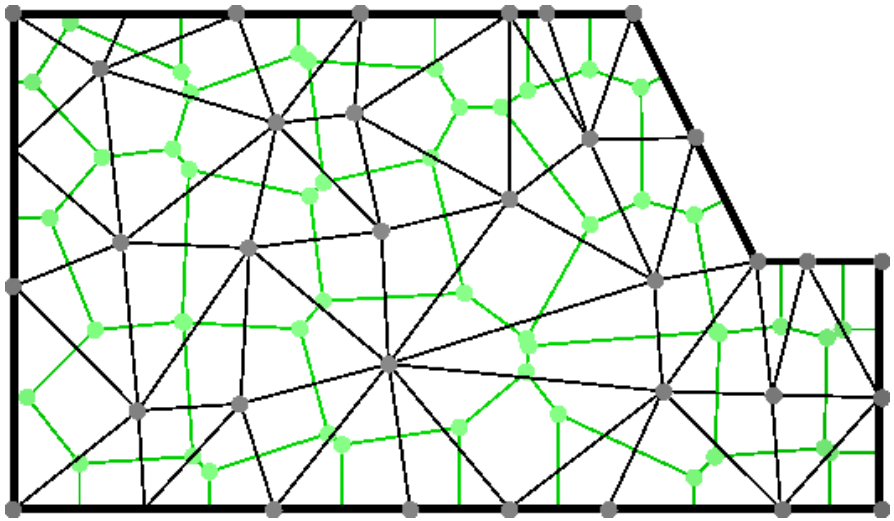
- Poisson-Fermi ($\mathscr{G} = \mathscr{F}_{-1}$):

$$-\nabla\varepsilon_0\varepsilon_r\nabla\phi = \qquad = Fc\sum_{\alpha=1}^{N-1} \frac{z_\alpha \exp\left(\frac{z_\alpha F}{RT}(\psi_\alpha - \phi)\right)}{1 + \exp\left(\frac{z_\alpha F}{RT}(\psi_\alpha - \phi)\right)}.$$



Green: Voronoï boxes

Black: Delaunay triangles.

Definition

Voronoï box K around $\mathbf{x}_K \in$ point set $\mathscr{P}$: Set of points $\mathbf{x} \in \Omega$ which are closer to $\mathbf{x}_K$ than to any other point $\mathbf{x}_L$ of $\mathscr{P}$. The set of Voronoï boxes is called *Voronoï diagram*

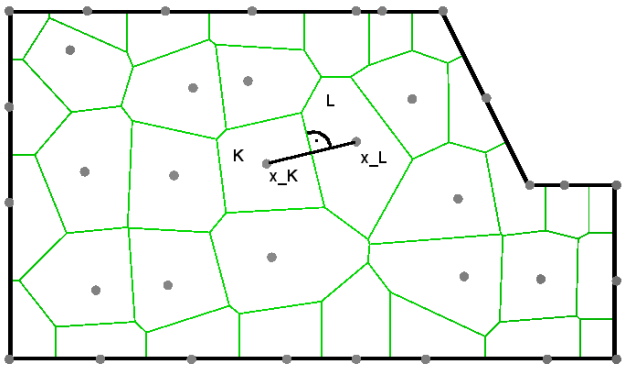
Voronoï diagram and Delaunay triangulation are dual to each other:

- Vertices of the Voronoï boxes are triangle cirumcenters.
- Voronoï box boundaries are straight line segments orthogonal to the corresponding triangle edges.
- Similar construction in 3D

Time grid in $[0,T]$:

$$0 = t_0 < t_1 < \cdots < t_{n-1} < t_n < \cdots < T$$

Flux equation:



$$0 = \int_{t^{n-1}}^{t^n} \int_K (\partial_t c + \nabla \cdot \mathbf{N})\, d\mathbf{x}\, dt$$

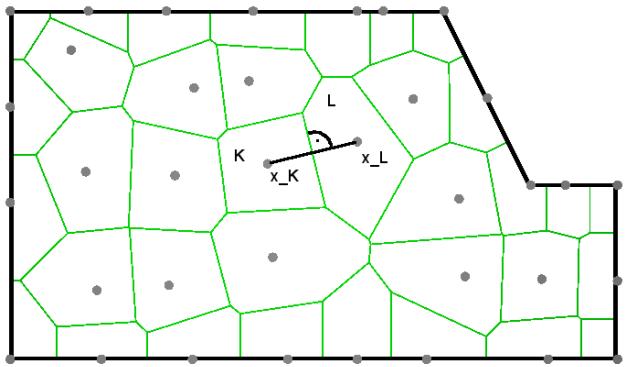
$$= \int_{t^{n-1}}^{t^n} \int_K \partial_t c\, d\mathbf{x} dt + \int_{t^{n-1}}^{t^n} \int_{\partial K} \mathbf{N} \cdot \mathbf{n}\, ds$$

$$= \int_K (c^n - c^{n-1})\, d\mathbf{x} dt + \sum_{L \text{ neighbor of } K} \int_{t^{n-1}}^{t^n} \int_{\partial K \cap \partial L} \mathbf{N} \cdot \mathbf{n}_{KL} ds$$

- Approximation step (N_{KL}: flux projection onto edge $\mathbf{x}_K \mathbf{x}_L$)

$$|K| \frac{c_K^n - c_K^{n-1}}{t^n - t^{n-1}} + \sum_{L \text{ neighbor of } K} |\partial K \cap \partial L| N_{KL}^n = 0$$

Flux equation:



$$
\begin{aligned}
0 &= \int_{t^{n-1}}^{t^n} \int_K (\partial_t c + \nabla \cdot \mathbf{N})\, d\mathbf{x}\, dt \\
&= \int_{t^{n-1}}^{t^n} \int_K \partial_t c\, d\mathbf{x} dt + \int_{t^{n-1}}^{t^n} \int_{\partial K} \mathbf{N} \cdot \mathbf{n}\, ds \\
&= \int_K (c^n - c^{n-1})\, d\mathbf{x} dt + \sum_{L \text{ neighbor of } K} \int_{t^{n-1}}^{t^n} \int_{\partial K \cap \partial L} \mathbf{N} \cdot \mathbf{n}_{KL} ds
\end{aligned}
$$

- Approximation step (N_{KL}: flux projection onto edge $\mathbf{x}_K\mathbf{x}_L$)

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|K| \frac{c_K^n - c_K^{n-1}}{t^n - t^{n-1}} + \sum_{L \text{ neighbor of } K} |\partial K \cap \partial L| N_{KL}^n = 0
$$

- Poisson equation (E_{KL}: electric field projection onto edge $\mathbf{x}_K\mathbf{x}_L$):

$$
\sum_{L \text{ neighbor of } K} |\partial K \cap \partial L| E_{KL}^n = |K| q_K^n
$$

- Electric field projection:

$$E_{KL}^n = \varepsilon\varepsilon_0 \frac{\phi_K^n - \phi_L^n}{\mathbf{x}_K - \mathbf{x}_L}.$$

- Flux field projection using ansatz from semiconductor devices ($B(\xi) = \frac{\xi}{\exp(\xi)-1}$: Bernoulli function, $Z = \frac{zF}{RT}$):

$$N_{KL}^n = \bar{\beta}_{KL} D(B(Z(\phi_L^n - \phi_K^n))a_K^n - B(Z(\phi_K^n - \phi_L^n))a_L^n)$$

- Consistent to the thermodynamic equilibrium:
  For any given constant value of ψ, assuming $N_{KL} = 0$ we arrive at

$$\begin{aligned}
\frac{a_K}{a_L} &= \frac{B(Z(\phi_K - \phi_L))}{B(Z(\phi_L - \phi_K))} = -\frac{\exp(Z(\phi_L - \phi_K)) - 1}{\exp(Z(\phi_K - \phi_L)) - 1} \\
&= -\frac{\exp(Z\phi_L)}{\exp(Z\phi_K)} \cdot \frac{\exp(-Z\phi_K) - \exp(-Z\phi_L)}{\exp(-Z\phi_L) - \exp(-Z\phi_K)} \\
&= \frac{\exp(Z\phi_L)}{\exp(Z\phi_K)} = \frac{\exp(Z(\psi - \phi_K))}{\exp(Z(\psi - \phi_L))} \\
&= \frac{a_{=,K}}{a_{=,L}}
\end{aligned}$$

Scharfetter/Gummel, IEEE Trans. Electron. Dev 1969

- $\Omega = [0, L]$.
- Boundary conditions:

$$\phi|_{x=0} = \phi_0, \qquad \phi|_{x=L} = \phi_\infty = 0,$$
$$-\nabla p \cdot \mathbf{n}|_{x=0} = q \nabla \phi \cdot \mathbf{n}|_{x=0}, \qquad p|_{x=L} = p_\infty = 0.$$

- Quasi-Fermi potentials ψ_α: obtained from given concentration values $c_\alpha|_{x=L} = c_{\alpha,\infty} << c$ such that $q|_{x=L} = F \sum_{\alpha=1}^{N-1} z_\alpha c_{\alpha,\infty} = 0$.
- Symmetric 1:1 electrolyte with bulk solution molarity $c_{\alpha,\infty} = c_\infty$ for $\alpha = 1, 2$
- Summary concentration c set to the molarity of water $c = 55.508 \cdot \mathrm{mol/dm^3}$.
- (Double layer) charge:

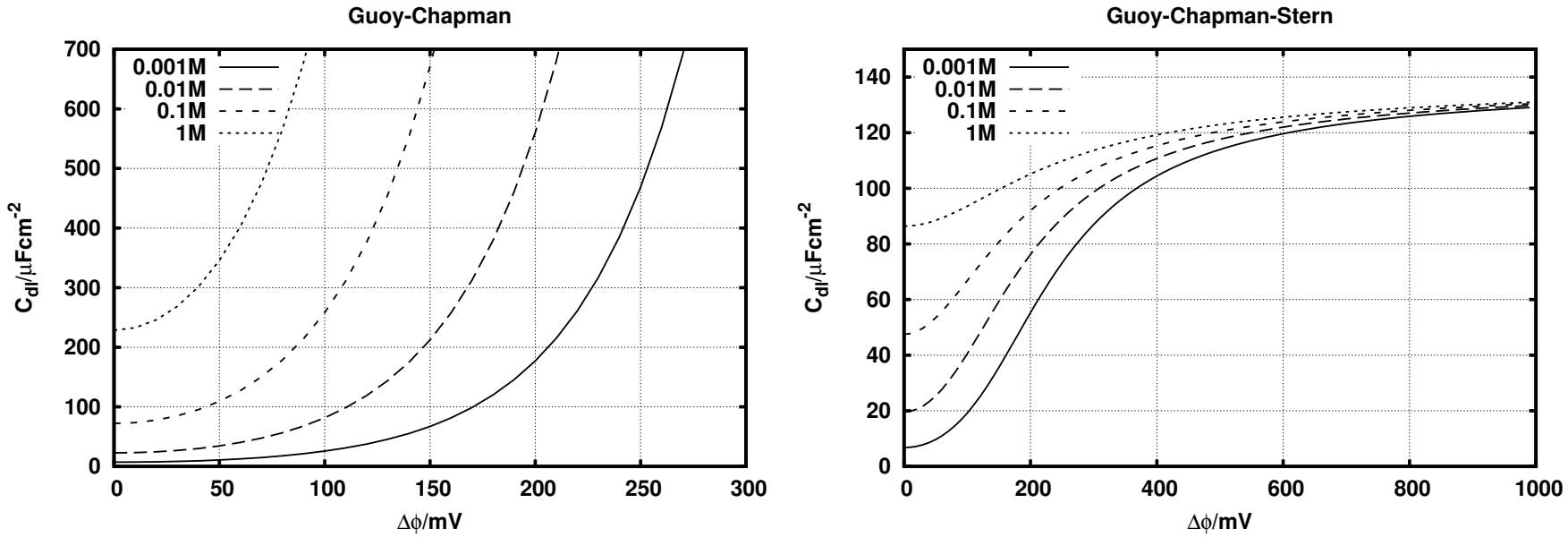
$$Q_{dl} = Q_{dl}(\phi_0) = \int_0^L q \, dx$$

- Differential (double layer) capacitance:

$$C_{dl} = \frac{dQ_{dl}}{d\phi_0} \approx \frac{Q_{dl}(\phi_0 + \delta) - Q_{dl}(\phi_0)}{\delta}, \quad \delta << \phi_0$$

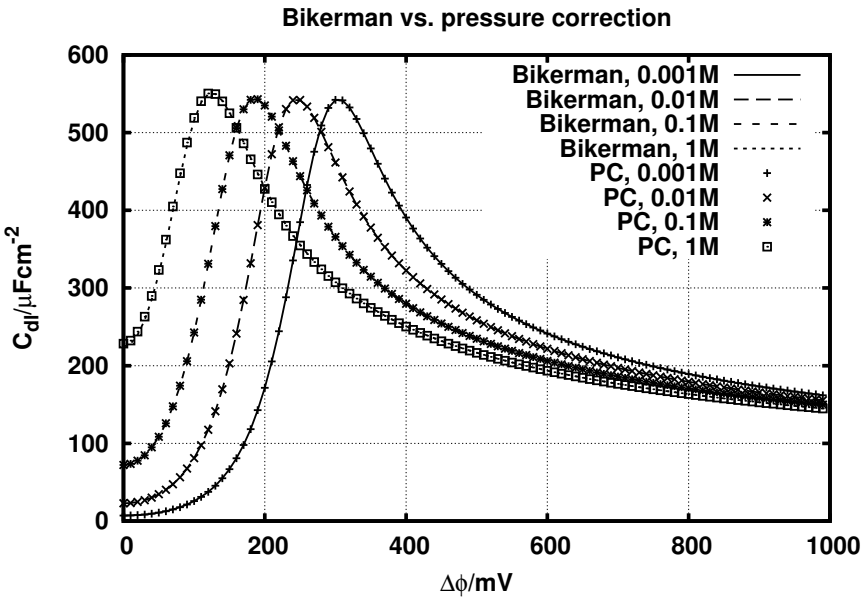
Gouy-Chapman (+Stern) differential double layer capacitance

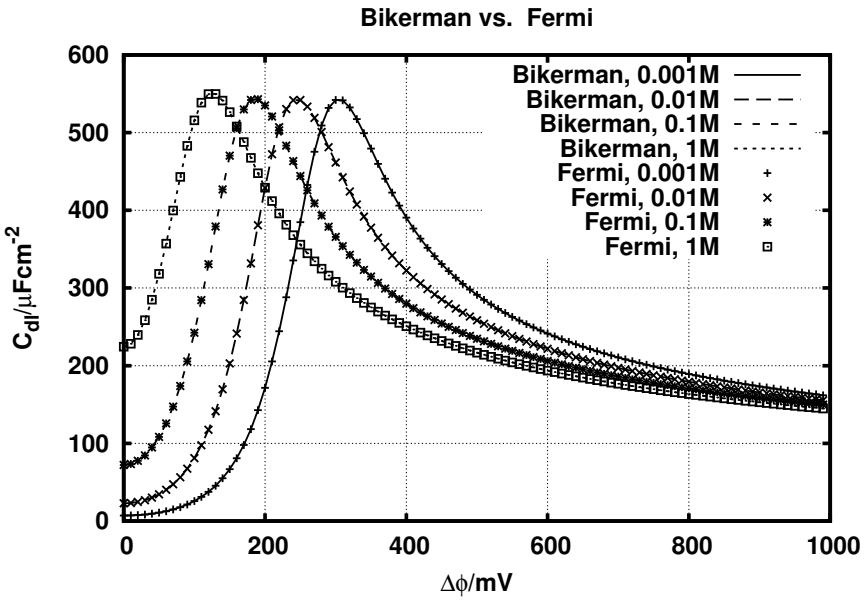
Dilute solution with uncorrected Nernst-Planck equation $\Rightarrow$ “Gouy-Chapman theory”



Numerically obtained differential double layer capacitances curves according to the Gouy-Chapman model (left) and the Gouy-Chapman-Stern model (right; OHP at $x = 0.5\text{nm}$) for aqueous 1:1 electrolytes at $25°\text{C}$ matching the classical results

Binary 1:1 electrolyte: Bikerman vs Fermi vs Pressure correction

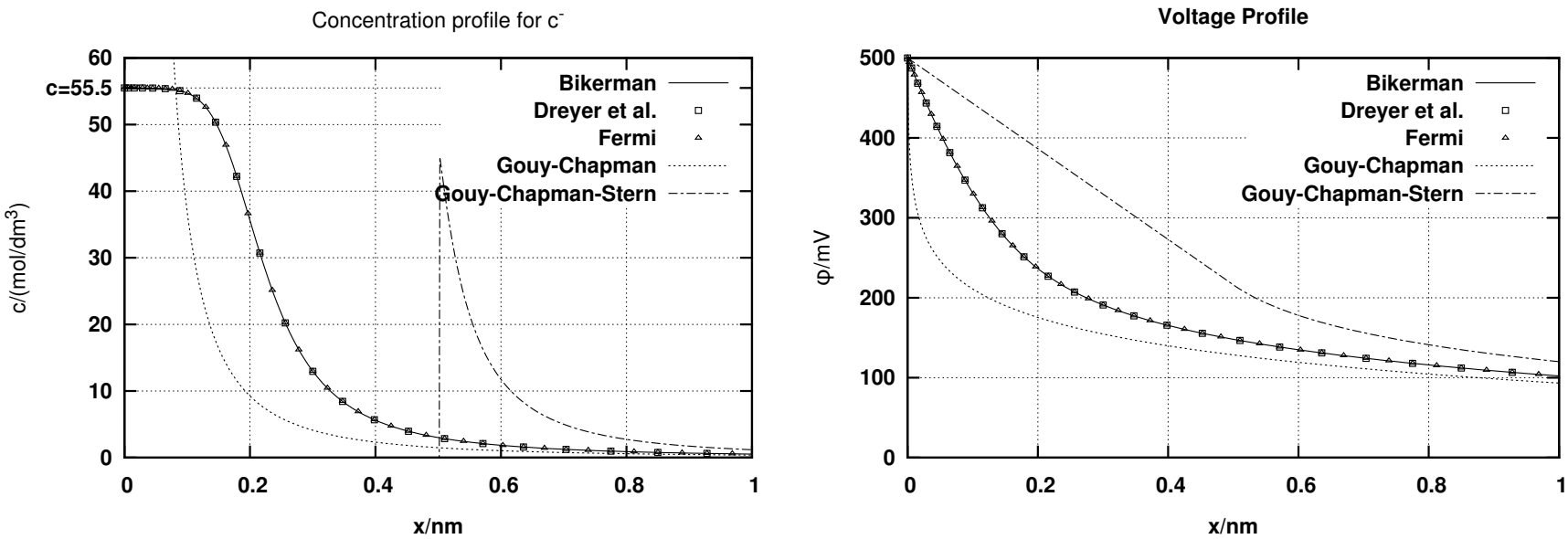




Comparison of the differential double layer capacitance curves between the Bikerman model with $\nu_\alpha = \frac{1}{c}$ and the pure pressure correction model (left) resp. the Fermi-Dirac model of index -1 (right).

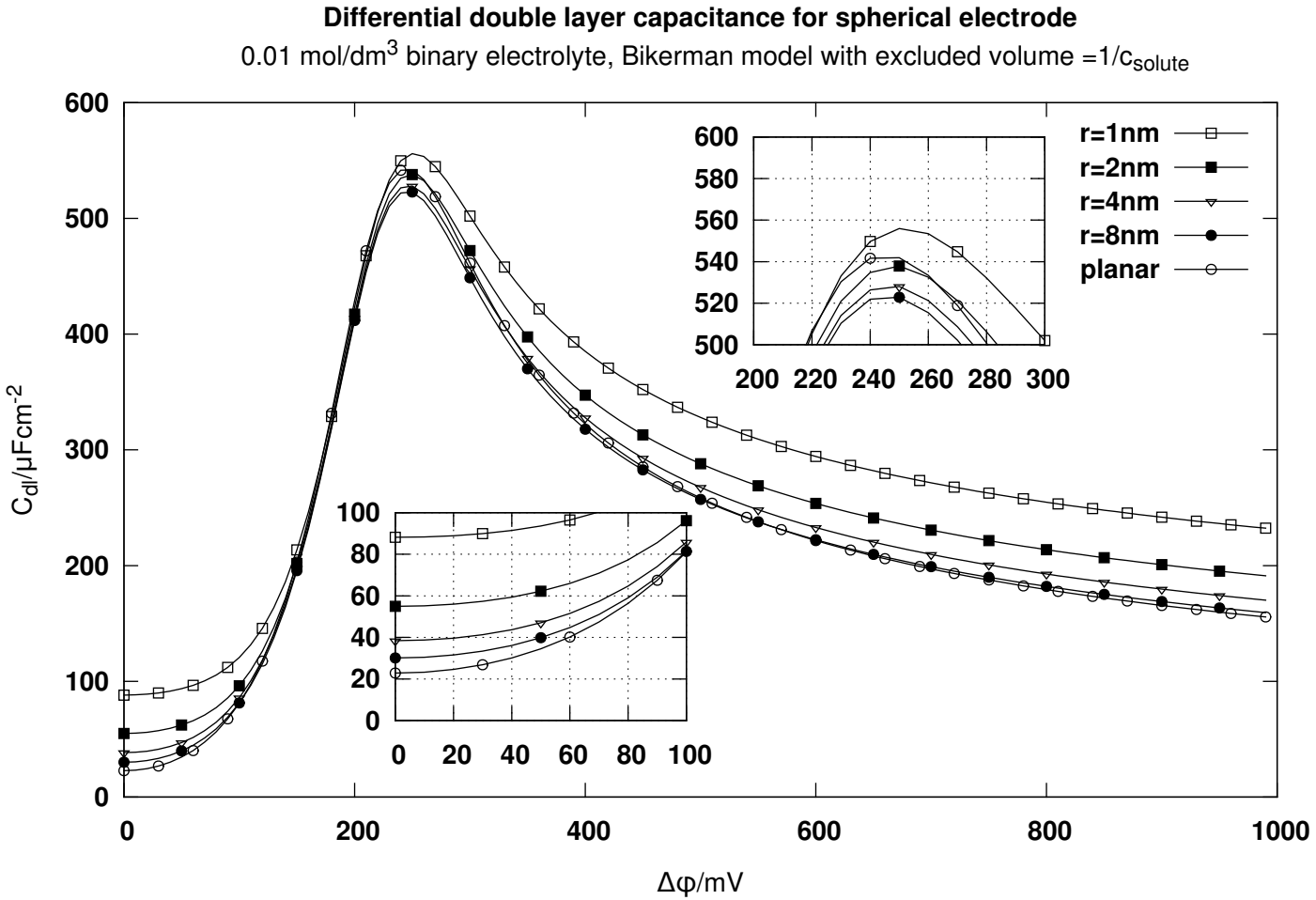
- Bikerman and pressure correction are equivalent in equilibrium due to Gibbs-Duhem
- Bikerman and Fermi (-1) are indistinguisheable as in $\beta = \frac{1}{1+a_1+a_2}$ either both activities are small or due to different charge one is large and the other is small.

Profiles



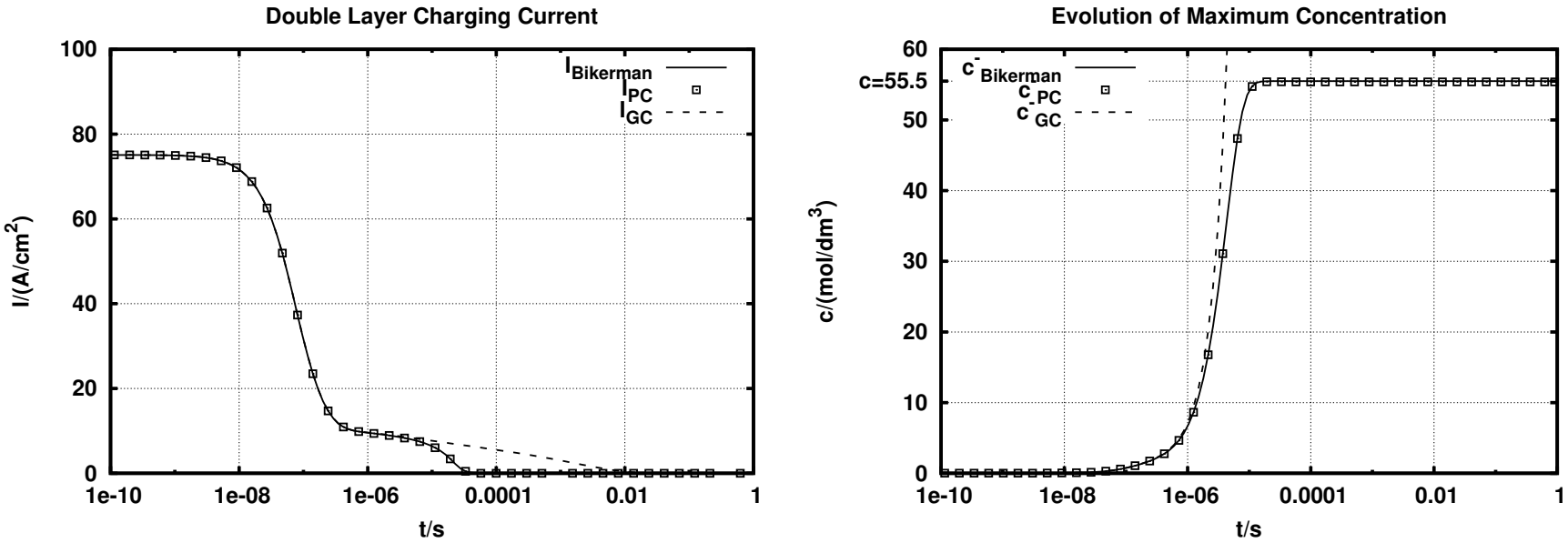
Comparison of negative ion concentration (left) and potential profile (right) for the different models. The Debye length is $\lambda_D = 3.04\text{nm}$.

Spherical coordinates



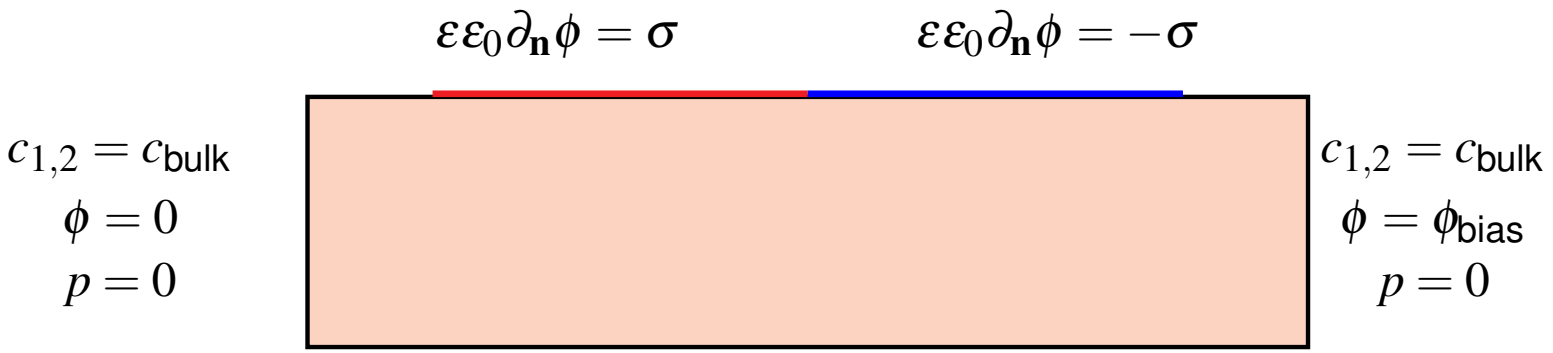
Differential double layer capacitances for different electrode radii

Dynamic calculations



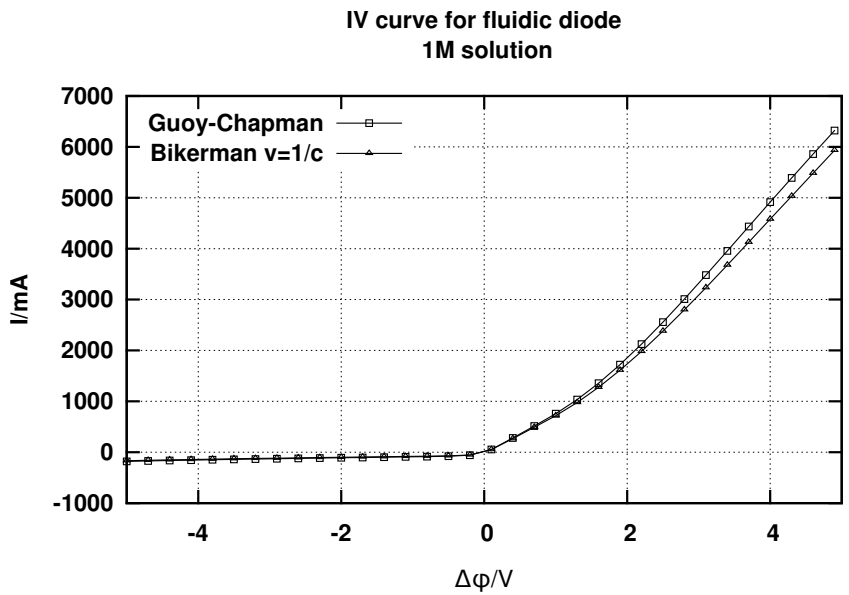
Evolution of current (left) and maximum negative ion concentration (right).

Electrolytic diode, binary 1:1 electrolyte, $\mathrm{v} = 0$

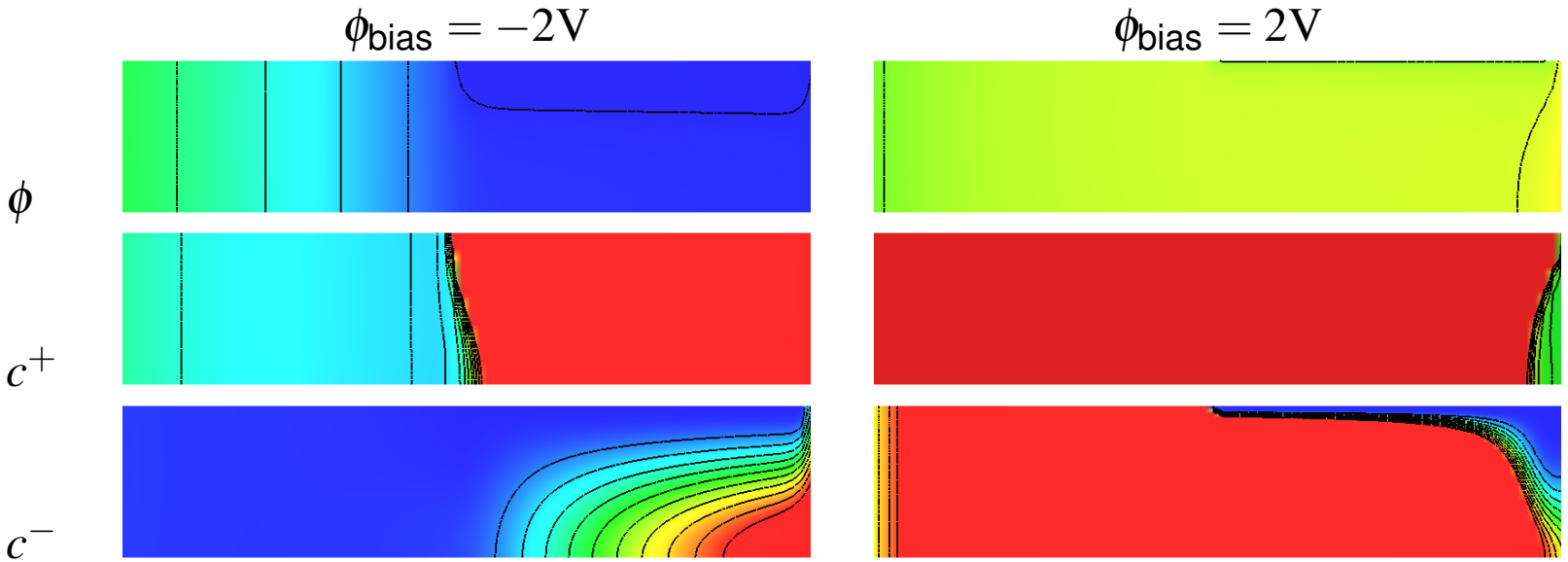


If not stated otherwise, homogeneous Neumann boundary conditions:

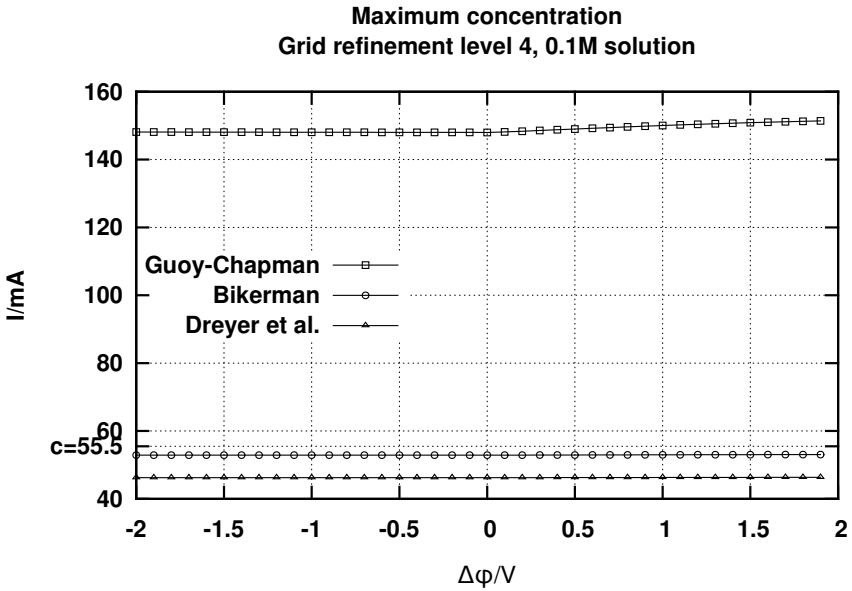
$\partial_{\mathbf{n}}\phi = 0, \quad \partial_{\mathbf{n}}p = 0, \quad \mathbf{N}_{1,2}\cdot\mathbf{n} = 0, \; \sigma = 500\mu\mathrm{As}/\mathrm{m}^2$

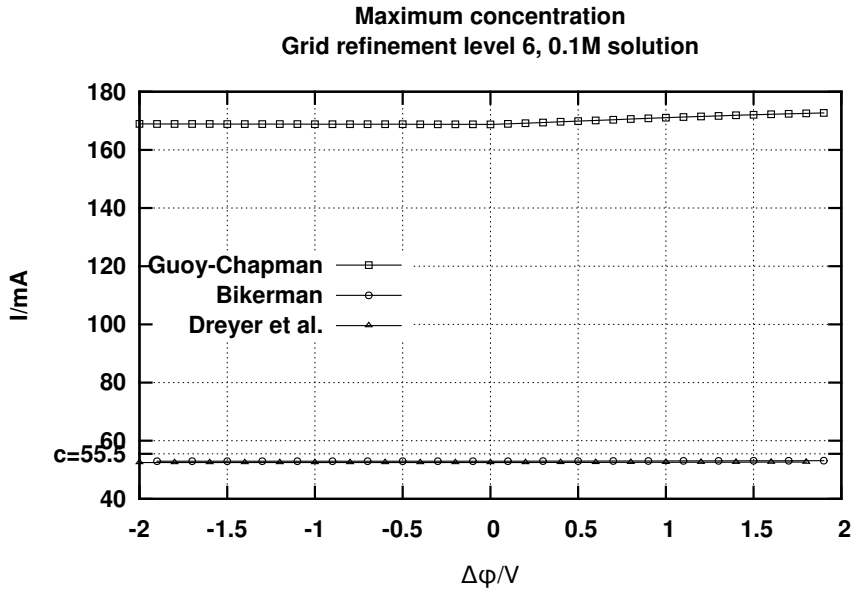


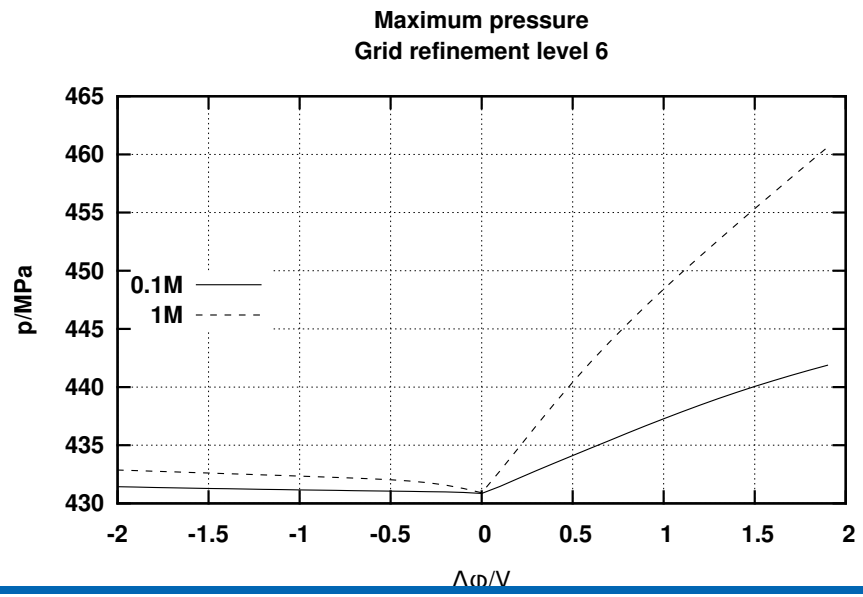
Electrolytic diode: distributions (Bikerman model, 0.01M solution, $\sigma = 150\mu\mathrm{As}/\mathrm{m}^2$)



Electrolytic diode: maximum concentrations + pressure ($\sigma = 150\mu As/m^2$)







Coupling to Navier-Stokes

Stationary distribution of single neutral species in Navier-Stokes velocity field $\mathbf{v}$

$$\nabla \cdot \mathbf{N} = 0 \qquad \text{Mass balance}$$

$$\mathbf{N} = -D\nabla c + c\mathbf{v} \qquad \text{Fick's law + convection}$$

- Problem: coupling to Navier-Stokes while maintaing concentration maximum principle.
- Stabilized finite elements do not guarantee this property!
- Voronoi finite volumes with discrete Scharfetter-Gummel (Il'in) flux:

$$N_{KL} = D\left(B\left(\frac{v_{KL}}{D}\right)c_K - B\left(-\frac{v_{KL}}{D}\right)c_L\right)$$

v_{KL}: some projection of $\mathbf{v}$ onto edge $\mathbf{x}_K\mathbf{x}_L$

Divergence free discrete flux:

$$\sum_{L\in\text{neighbors}(K)} \frac{|\partial L\cap\partial K|}{|\mathbf{x}_K-\mathbf{x}_L|}v_{KL} + \sum_{\sigma\in\text{outbound}(K)} |\sigma|v_\sigma = 0 \qquad \text{(DIV0)}$$

Fuhrmann/Linke/Langmach APNUM 2011

Divergence free discrete flux:

$$\sum_{L \in \text{neighbors}(K)} \frac{|\partial L \cap \partial K|}{|\mathbf{x}_K - \mathbf{x}_L|} v_{KL} + \sum_{\sigma \in \text{outbound}(K)} |\sigma| v_\sigma = 0 \qquad \text{(DIV0)}$$

Lemma: If (DIV0) is valid, for any solution $(c_K)_{K \in \mathscr{K}}$:

1. Global discrete minimax principle:

$$0 \le c_K \le c_{\text{inlet}} \quad \forall K \in \mathscr{K}$$

Fuhrmann/Linke/Langmach APNUM 2011

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$$\min_{L\in\text{neighbors}(K)} c_L \le c_K \le \max_{L\in\text{neighbors}(K)} c_L \quad \forall K\in\mathscr{K}^0$$

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3. The system matrix has the M-Property

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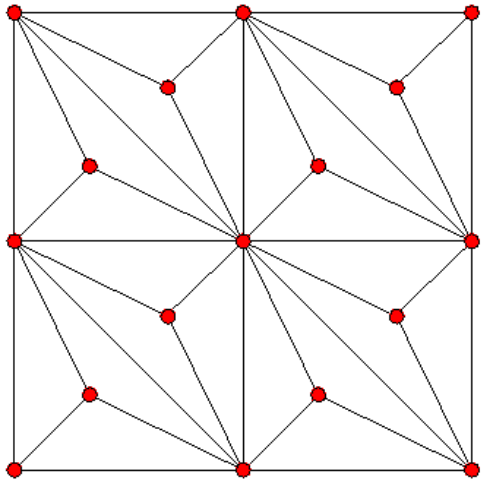
How to guarantee this condition when $\mathbf{v}$ comes from the solution of a flow problem ?

- Continuous divergence free velocity field $\mathbf{v}$:
  Exact calculation of $v_{KL} = \frac{1}{|K \cap L|} \int_{K \cap L} \mathbf{v}(s) \cdot (\mathbf{x}_K - \mathbf{x}_L) ds$:
  - Exact solutions: Hagen - Poiseuille et al
  - Pointwise divergence free finite elements (e.g. Scott Vogelius for Navier-Stokes)
    Burman/Linke, App. Num. Math 58(2008)11,1704-1719
  - Postprocessed Crouzeix-Raviart mixed finite elements (A. Linke 2013, submitted)
- Finite volume scheme for flow problem including discrete divergence free fluxes
  - Finite volume solution for Navier-Stokes (Eymard/Fuhrmann/Linke 2011, submitted) insufficient convergence properties

Divergence free Scott-Vogelius finite elements



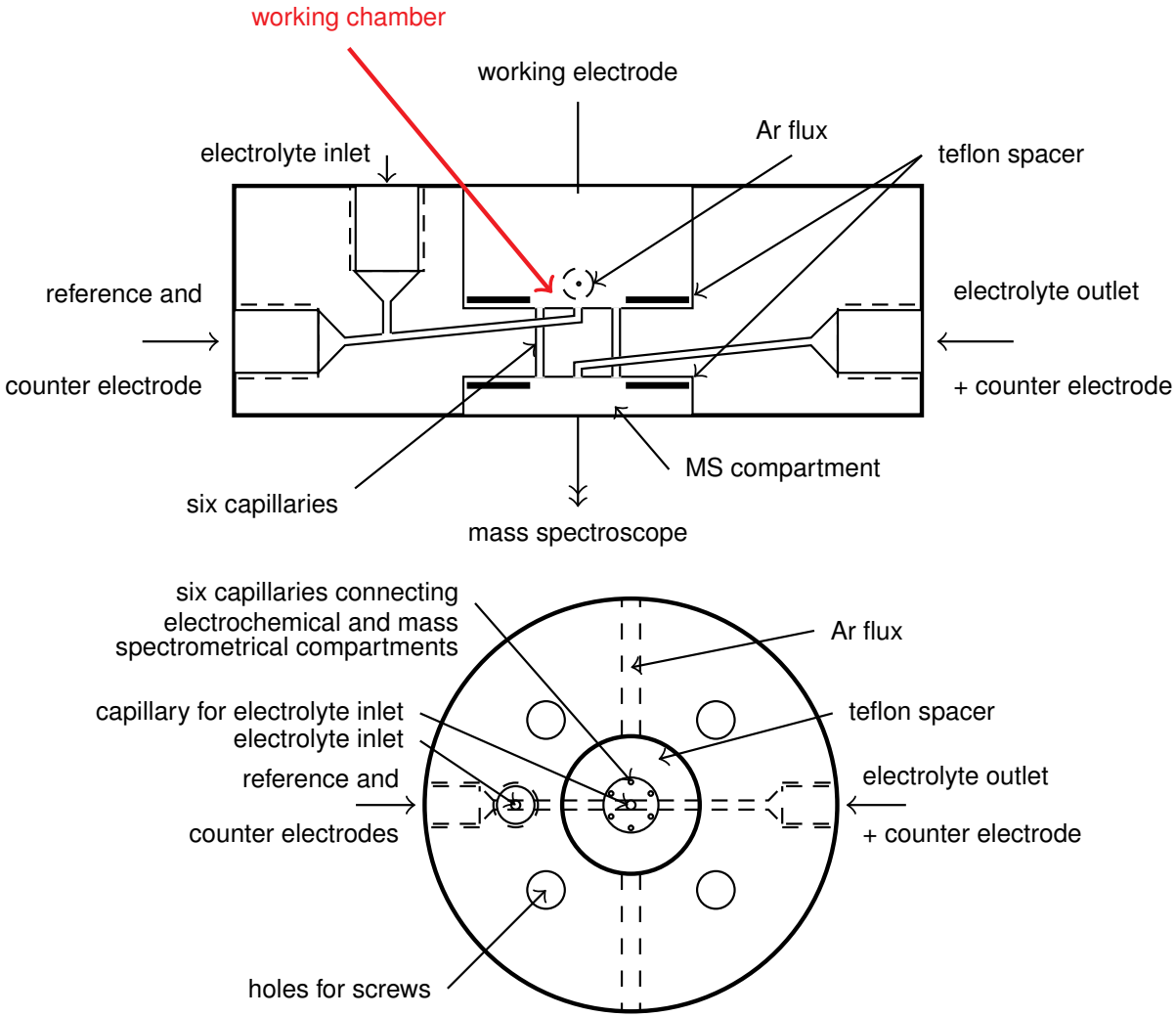
- $\mathrm{div}(\text{velocity space}) \subset \text{pressure space}$
- Lowest order Scott Vogelius elements: $(P_d, P_{-(d-1)})$ (d:space dimension)
- Stable on macro triangulations

Arnold/Qin, Proc. IMACS 1992
Burman/Linke, App. Num. Math 2008

Linke, PhD Thesis, FU Berlin 2008

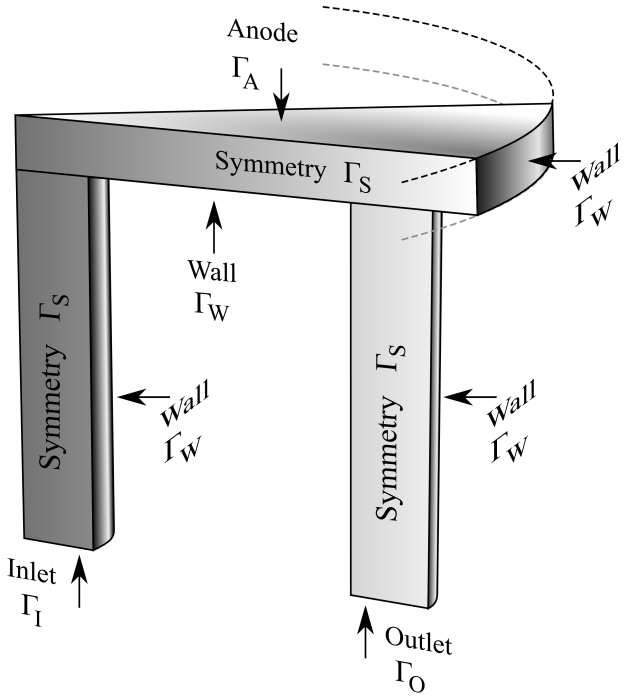
- Maintain two independent discretizations for transport (FV) and for flow (FE)
- (FV): For every simplex S, calculate simplicial contributions $\sigma_{KL;S} = \partial K \cap \partial L \cap S$ to $\partial K \cap \partial L$
- (FE): Calculate velocity projections $q_{KL;S}$ from continuous FE velocity field
- (FV): Assemble q_{KL} from $q_{KL;S}$

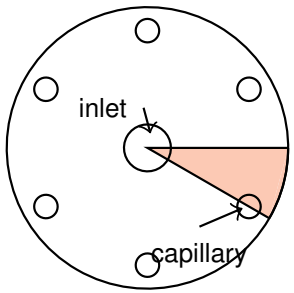
Cylindrical DEMS flow cell



Jusys/Massong/Baltruschat, J. Electrochem. Soc. 1999

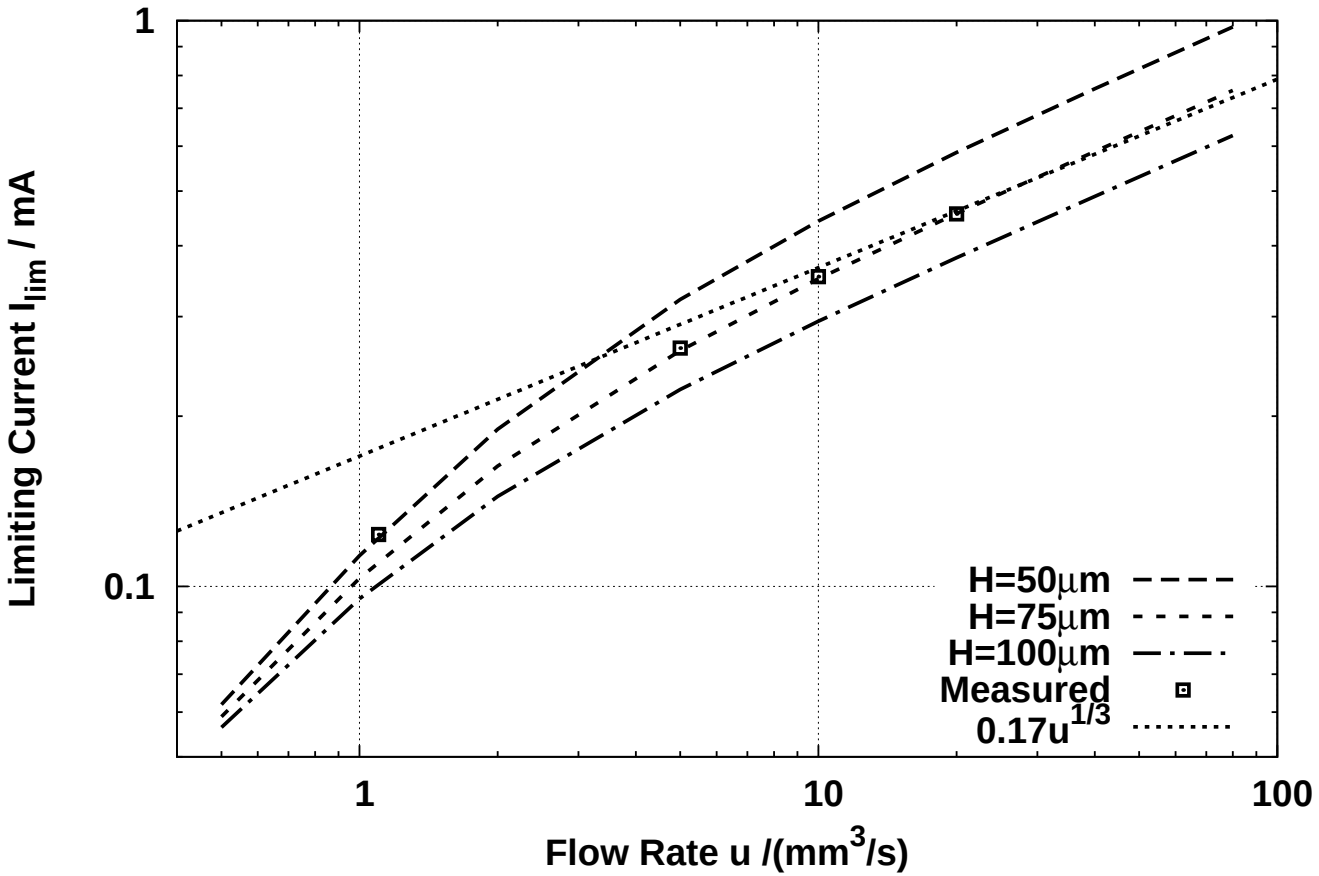
Numerical solution ansatz





- Navier-Stokes solution by Taylor-Hood or Scott Vogelius finite elements (implemented in Alberta)
- Voronoi finite volume solution implemented in pdelib (WIAS)
- Grid generation by “extrusion” of a 2D Delaunay mesh (created by triangle) in z direction in order to guarantee proper anisotropic alignment at anode
- Calculation on $\frac{1}{6}$ of the cell geometry, together with stubs of inlet and outlet channels

Comparison to experiment in a 3D cylindrical cell

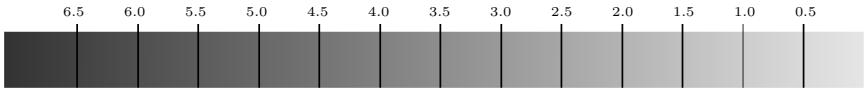


Measured and calculated values for the limiting current using fitted data from channel flow cell experiment for different values of working chamber height.

No “simple” asymptotic expression available.

Fuhrmann/Linke/Langmach/Baltruschat, Electrochim. Acta 2009

Flow regimes



$0.5mm^3/s$ $10mm^3/s$ $80mm^3/s$

Concentration isolevels for different inlet flow rates

Fuhrmann/Linke/Langmach/Baltruschat, Electrochim. Acta 2009

Scott Vogelius vs. Taylor Hood (coarse grid)

Scott Vogelius

Taylor Hood

Taylor-Hood velocity field does not guarantee discrete divergece condition $\Rightarrow$ violation of maximum principle

Main measured effects concentrated in boundary layer $\Rightarrow$ tolerable errors with Taylor Hood, if grid is fine enough.

Fuhrmann/Linke/Langmach/Baltruschat Electrochim. Acta 2009

Outlook

- Implement Nernst-Planck-Poisson-Navier-Stokes coupling using divergence free FEM ansatzes of A. Linke based on postprocessed Crouzeix-Raviart
- updated version of Nernst-Planck including different molar volumes
- nanopore calculation (model air electrode in DEMS cell, PEM)
- nanofluidic devices, electrodialysis, biomembranes etc.
- degenerate semiconductors (OLED, nitride)

Acknowledgement

German Federal Ministry of Education and Research (BMBF)

ENERGIESPEICHER
Forschungsinitiative der Bundesregierung

Research initiative on energy storage

Collaborative project “Perspectives for rechargeable magnesium air batteries”
H. Baltruschat (Bonn), Th. Bredow (Bonn), J. Behm (Ulm), M. Wachtler (Ulm)

Grant 03EK3027D