New upscaled charge transport equations for highly heterogeneous multiphase materials

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Outline

I) Applications and basic upscaling idea

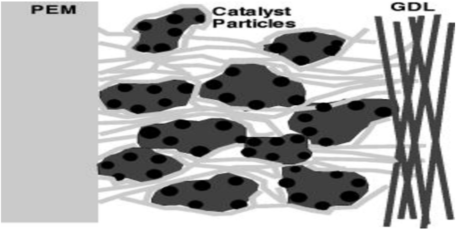
II) Upscaling of **charge transport** equations in heterogeneous media

III) Effective macroscopic **catalyst layer** formulations

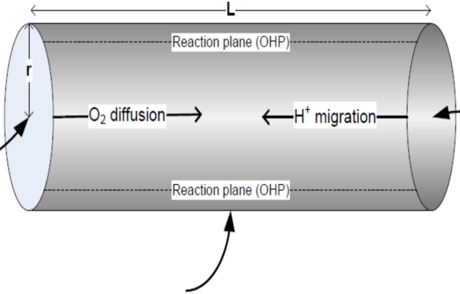
IV) **Control of Macroscopic Transport Characteristics?**

Part I): Applications and basic upscaling idea

Example I: Catalyst layer in PEM fuel cell



Smooth cylindrical Pt channel

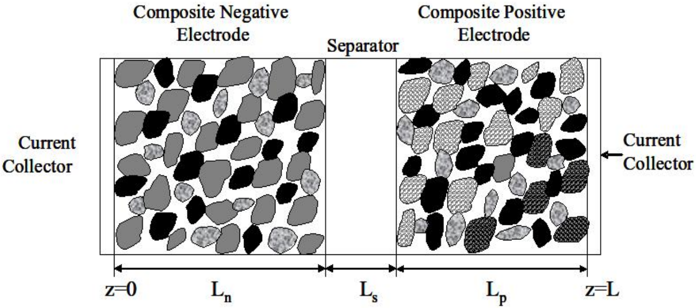


GDL boundary conditions:
Constant oxygen concentration
No proton flux

PEM boundary conditions:
Constant proton concentration
No oxygen flux

Smooth Pt **walls**
Constant metal potential

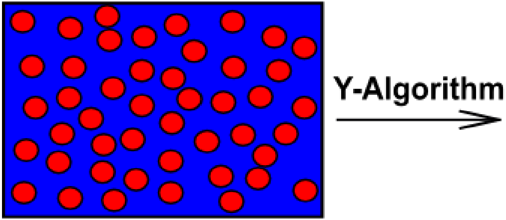
Example II: Batteries



Legend:

- Negative electrode active material (secondary particle)
- Positive electrode active material (secondary particle)
- Binder
- Carbon additive
- Pores filled by electrolyte

Effective equations for multiscale problems: Idea



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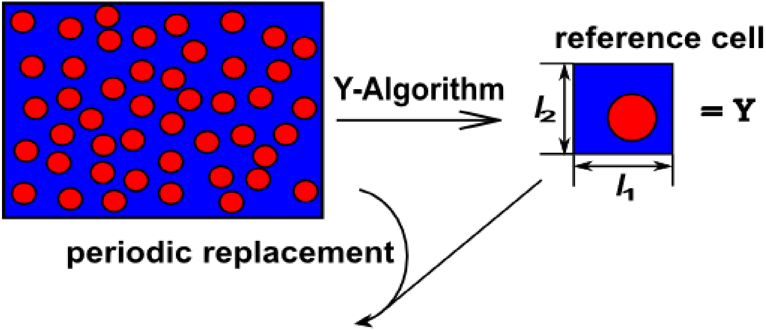

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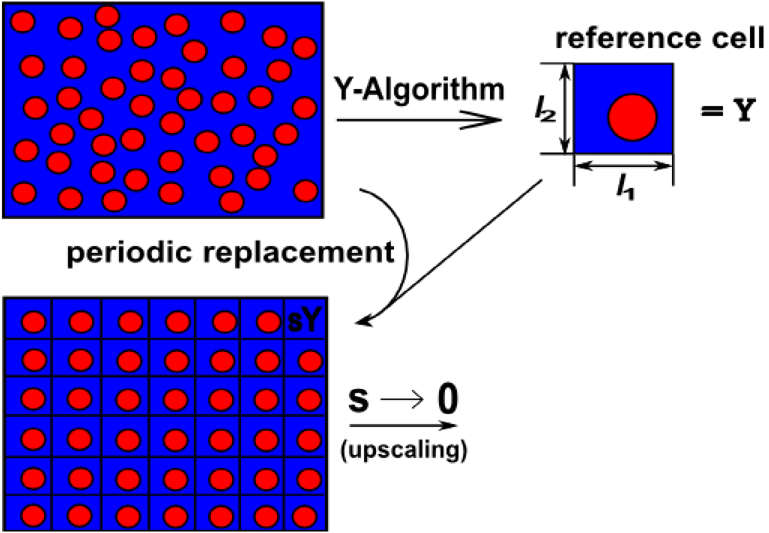

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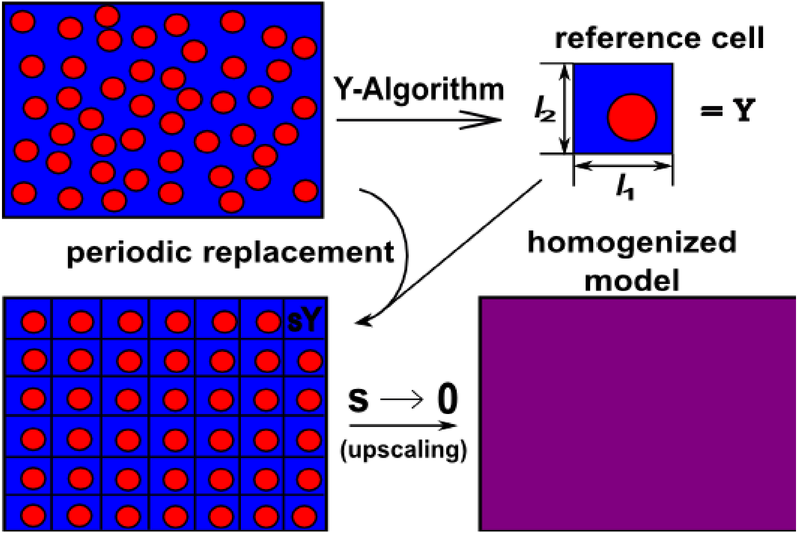

Upscaling: The asymptotic expansion method

1) **Make the Ansatz:**

$$\mathbf{u}_s(t,x) \approx \mathbf{u}_0(t,x,y) + s\mathbf{u}_1(t,x,y) + s^2\mathbf{u}_2(t,x,y) + \ldots ,$$

where $y := x/s$ is the microscale.

2) **Insert 1) in the periodic model:** (formal method by assuming differentiability)
Collect terms of the same order in s.

3) **"Take the leading order terms":**
Solvability requirements provide the upscaled system for $\mathbf{u}_0$.

References: - [Bensoussan, Lions, Papanicolaou (78)], - [Cioranescu, Donato (99)], - [Chechkin, Piatnitski, Shamaev (07)], - [G.A. Pavliotis, A.M. Stuart (08)]

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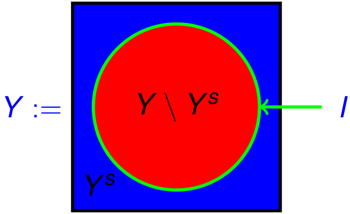
Part II): Upscaling of charge transport equations in heterogeneous media

Charged porous media

[M.S. & M.Z. Bazant, SIAM J. Appl. Math., 75(3), 1369-1401 (2015).]

Reference configuration: Solid-electrolyte composite



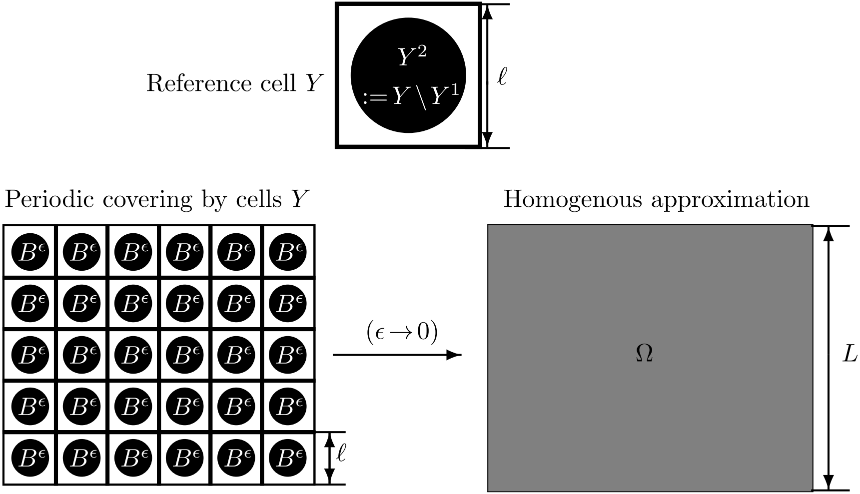
Extension: Presence of a surface charge density σ_s on I
Replace (continuity of fluxes)

$$-\lambda^2 \nabla_n \phi_s \big|_{\partial Y^s} = -\alpha \nabla_n \phi_s \big|_{\partial Y^s} \qquad \text{on } I\,,$$

by

$$-\kappa(x/s) \nabla_n \phi_s \big|_{\partial Y^s} = s \sigma_s(x/s) \big|_{\partial Y^s} \qquad \text{on } I\,,$$

for the Debey length λ and dielectric permittivity $\alpha := \frac{\epsilon_m}{\epsilon_f}$ such that $\hat{\kappa}(x) := \lambda^2 \chi_{\Omega^s}(x) + \alpha \chi_{\Omega \setminus \Omega^s}(x)$


Reference cell Y
Y^2
$:= Y \setminus Y^1$
ℓ
Periodic covering by cells Y
B^ϵ
ℓ
$(\epsilon \to 0)$
Homogenous approximation
Ω
L

Local Thermodynamic Equilibrium (LTE)

Definition: (Scale separation) *We say that the chemical potential* μ *is scale separated if and only if*

$$\frac{\partial \mu(u_0(x,t))}{\partial x_k} = \begin{cases} 0 & \text{on the reference cell } Y\,, \\ \frac{\partial \mu(u_0(x,t))}{\partial x_k} & \text{on the macroscale } \Omega\,, \end{cases}$$

where $u_0(x)$ *is the upscaled/slow variable solving the corresponding upscaled equation.*

Charged porous media

[M.S. & M.Z. Bazant, SIAM J. Appl. Math., 75(3), 1369-1401 (2015).]

Micro:

$$\begin{cases} \partial_t n_s^+ = \operatorname{div}\left(\nabla n_s^+ + n_s^+ \nabla \phi_s\right) & \text{in } \Omega^s \\ \partial_t n_s^- = \operatorname{div}\left(\nabla n_s^- - n_s^- \nabla \phi_s\right) & \text{in } \Omega^s \\ -\operatorname{div}\left(\hat{\kappa}(x/s) \nabla \phi_s\right) = n_s^+ - n_s^- & \text{in } \Omega \end{cases}$$

Micro interface:

$$\begin{cases} \nabla_n n_s^+ + n_s^+ \nabla_n \phi_s = 0 & \text{on } I_s \\ \nabla_n n_s^- - n_s^- \nabla_n \phi_s = 0 & \text{on } I_s \\ -\hat{\kappa}(x/s) \nabla_n \phi_s = s \sigma_s(x/s) & \text{on } I_s \end{cases}$$

becomes under local thermodynamic equilibrium

Macro:

$$\begin{cases} p \partial_t n_0^+ = \operatorname{div}\left(\hat{\mathrm{D}} \nabla n_0^+ + n_0^+ \hat{\mathrm{M}} \nabla \phi_0\right) & \text{in } \Omega \\ p \partial_t n_0^- = \operatorname{div}\left(\hat{\mathrm{D}} \nabla n_0^- - n_0^- \hat{\mathrm{M}} \nabla \phi_0\right) & \text{in } \Omega \\ -\operatorname{div}\left(\hat{\kappa}_{\text{eff}} \nabla \phi_0\right) = p(n_0^+ - n_0^-) + \rho_s & \text{in } \Omega \end{cases}$$

where $\rho_s := \frac{1}{|Y|} \int_I \sigma_s(x, y)\, do(y)$.

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Rigorous error bounds / Convergence rates:

Theorem: [M.S. 2012, ZAMM 92:304–319 (2012)]
Let $\partial\Omega$ be of class C^∞ and ξ^k, $\zeta^{kl} \in W^{1,\infty}(Y)$. Then, for $\mathrm{e}_s^1 := n_s^+ - \mathrm{K}_s^1 n_0^+$, $\mathrm{e}_s^2 := n_s^- - \mathrm{K}_s^1 n_0^-$, and $\mathrm{e}_s^3 := \phi_s - \mathrm{K}_s^1 \phi_0$, there holds

$$\left\| \mathrm{e}_s^1 \right\|^2 (T) \leq CTs\,,$$

$$\left\| \mathrm{e}_s^2 \right\|^2 (T) \leq CTs\,,$$

$$\left\| \mathrm{e}_s^3 \right\|^2_{H^1(\Omega)} (T) \leq C\,(T+1)\,s\,,$$

where

$$\mathrm{K}_s^1 u_0(t,x) := \left(1 - s \sum_{k=1}^{N} \xi^k(x/s)\partial_{x_k} \right) u_0(t,x)\,.$$

Related Reference: Two-scale converge result
- [M. S., COMMUN MATH SCI, 9(3):685-710 (2011)]

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2) Key ideas in the proof:

Step 1: Define error variables

$$\mathrm{e}_s^i := u_s^i - s\sum_{r=1}^{d} \xi^{i_r}(y)\frac{\partial u_0^i}{\partial x_r} \qquad \text{for } i = 1, 2, 3.$$

Step 2: Determine equations for e_s^i based on

$$\frac{\partial u(x,y)}{\partial x} = \partial_x u(x,y) + \frac{1}{s}\partial_y u(x,y)\,,$$

such that for $r = 1, 2$

$$\begin{cases} \frac{\partial \mathrm{e}_s^r}{\partial t} = \mathrm{div}\left(\nabla \mathrm{e}_s^r + z_r \mathrm{e}_s^r \nabla \mathrm{e}_s^3\right) + s\mathrm{F}_s^r & \text{in } \Omega^s \times]0, T[\,, \\ \mathrm{e}_s^r = s\mathrm{G}_s^r & \text{on } \partial\Omega^s \times]0, T[\,, \\ -\mathrm{div}\left(\kappa(x/s)\nabla \mathrm{e}_s^3\right) = \mathrm{e}_s^1 - \mathrm{e}_s^2 + s\mathrm{F}_s^3 & \text{in } \Omega_T\,, \\ \mathrm{e}_s^3 = s\mathrm{G}_s^3 & \text{on } \partial\Omega \times]0, T[\,. \end{cases}$$

3) Charged porous media

[M.S. & M.Z. Bazant, SIAM J. Appl. Math., 75(3), 1369-1401 (2015).]

Einstein relations: $\hat{\mathrm{M}} \neq \frac{\hat{\mathrm{D}}}{kT}$

Consequence:

Seem to loose Boltzmann distribution in equilibrium and Einstein relations !

But:

Introduce the mean field approximations

$$\overline{\nabla n^{\pm}} := \hat{\mathrm{D}} \nabla n^{\pm} \,,$$

$$\overline{\nabla \phi} := \hat{\mathrm{M}} \nabla \phi \,,$$

then again the Boltzmann distribution is obtained, i.e.,

$$kTn^{\pm} M_{\pm} \overline{\nabla \tilde{\mu}} = D_{\pm} \overline{\nabla n^{\pm}} + z_{\pm} n^{\pm} kTM_{\pm} \overline{\nabla \phi} \,,$$

where $\mu = \frac{\tilde{\mu}}{kT}$ and $\phi = \frac{e\Phi}{kT}$.

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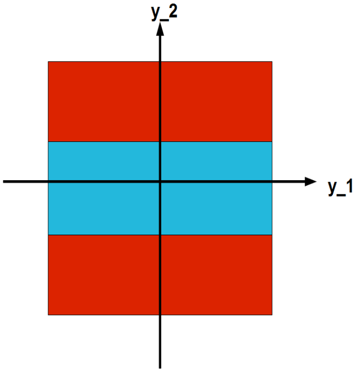
Example I: Straight channels

Assumption: Insulating porous matrix, i.e., $\alpha \to 0$
The correction tensor $\hat{\mathrm{D}} = \hat{\mathrm{M}}$ becomes

$$\hat{\mathrm{D}} := p \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} .$$



Literature: Auriault & Lewandowska 1997

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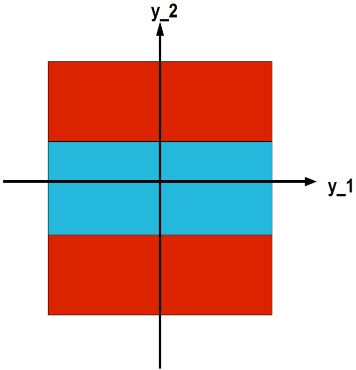

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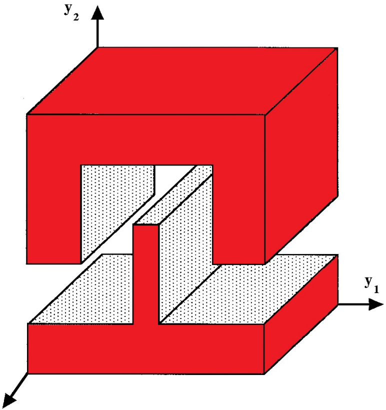
Example II: Perturbed straight channels

Assumption: Insulating porous matrix, i.e., $\alpha \to 0$
The correction tensor $\hat{\mathrm{D}} = \hat{\mathrm{M}}$ becomes

$$\hat{\mathrm{D}} := p \begin{bmatrix} 0.3833 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} .$$



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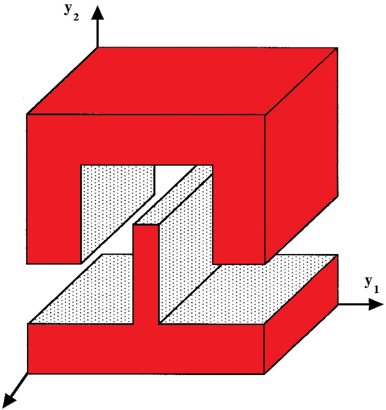

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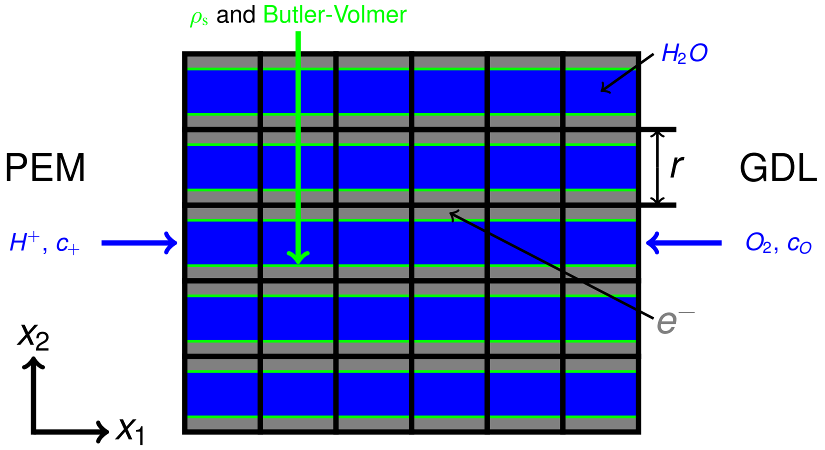
Part III): Effective Proton Transport in Catalyst Layers

1) Effective catalyst layer in PEMFC: [with P. Berg (NTNU)]

Periodic catalyst layer: Microscopic scenario



Butler-Volmer: $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$

Result:

[M.S. & P. Berg, Appl. Math. Res. Express. 2013(1):57-78 (2013)]

Under large overpotential, i.e., $\Phi^s - \Phi_{\text{eq}} \gg 0$, we have

$$\textbf{Micro bulk:} \begin{cases} -\Delta c_O^s = 0 & \text{in } \Omega^s \\ -\mathrm{div}\,(\nabla c_+^s + c_+^s \nabla \phi^s) = 0 & \text{in } \Omega^s \\ -\mathrm{div}\,(\hat{\kappa}(x/s)\nabla \phi^s) = c_+^s & \text{in } \Omega \end{cases}$$

$$\textbf{Interface:} \begin{cases} -\nabla_n c_O^s = s\beta_O (c_O^s)^{n_O}(c_+^s)^{n_+} \exp\left[-\alpha_c\left(\Phi^s - \Phi_0\right)\right] & \text{on } I \\ -\nabla_n c_+^s - c_+^s \nabla_n \Phi^s = s\beta_+ (c_O^s)^{n_O}(c_+^s)^{n_+} \exp\left[-\alpha_c\left(\Phi^s - \Phi_0\right)\right] & \text{on } I \\ -\kappa(x/s)\nabla_n \Phi^s = s\sigma_s(x, x/s) & \text{on } I \end{cases}$$

turns after upscaling under scale separation into

$$\begin{cases} -\mathrm{div}\left(\hat{\mathrm{D}}^O \nabla C_O\right) = \overline{\beta}_O (C_+)^{n_+}(C_O)^{n_O} \exp\left(-\alpha_c(\Phi - \Phi_0)\right), & \text{in } \Omega \\ -\mathrm{div}\left(\hat{\mathrm{D}}^+ \nabla C_+ + C_+ \hat{\mathrm{M}}^+ \nabla \Phi\right) = \overline{\beta}_+ (C_+)^{n_+}(C_O)^{n_O} \exp\left(-\alpha_c(\Phi - \Phi_0)\right), & \text{in } \Omega \\ -\mathrm{div}\left(\hat{\varepsilon}(\lambda^2, \gamma)\nabla \Phi\right) = pC_+ + \rho_s, & \text{in } \Omega \end{cases}$$

where $\overline{\beta}_O := \beta_O \Lambda = \frac{i_0 \Lambda}{4e\mathrm{D}_O}$ and $\overline{\beta}_+ := \beta_O \Lambda = \frac{i_0 \Lambda}{4e\mathrm{D}_+}$ with $\Lambda := |I|$.

Result:

[M.S. & P. Berg, Appl. Math. Res. Express. 2013(1):57-78 (2013)]

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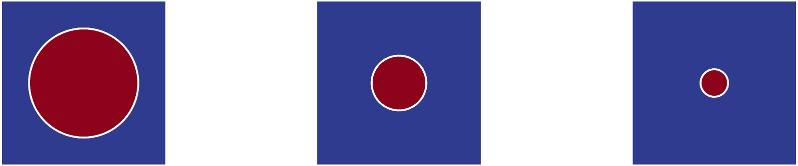
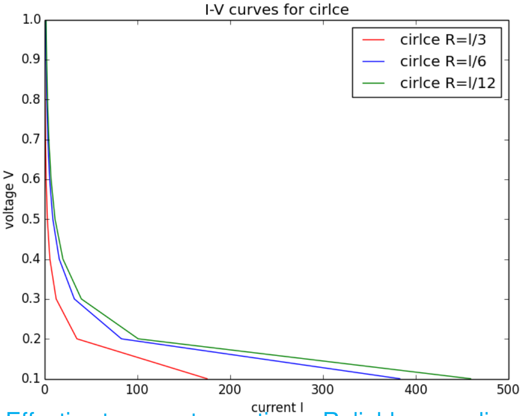
turns after upscaling under scale separation into

$$\begin{cases} -\mathrm{div}\left(\hat{\mathrm{D}}^O \nabla C_O\right) = \overline{\beta}_O (C_+)^{n_+}(C_O)^{n_O}\exp\left(-\alpha_c(\Phi - \Phi_0)\right), & \text{in } \Omega \\ -\mathrm{div}\left(\hat{\mathrm{D}}^+ \nabla C_+ + C_+ \hat{\mathrm{M}}^+ \nabla \Phi\right) = \overline{\beta}_+ (C_+)^{n_+}(C_O)^{n_O}\exp\left(-\alpha_c(\Phi - \Phi_0)\right), & \text{in } \Omega \\ -\mathrm{div}\left(\hat{\varepsilon}(\lambda^2, \gamma)\nabla \Phi\right) = pC_+ + \rho_s, & \text{in } \Omega \end{cases}$$

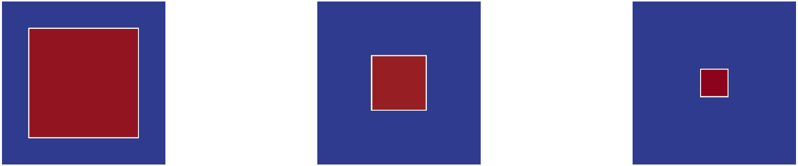
where $\overline{\beta}_O := \beta_O \Lambda = \frac{i_0 \Lambda}{4e\mathrm{D}_O}$ and $\overline{\beta}_+ := \beta_O \Lambda = \frac{i_0 \Lambda}{4e\mathrm{D}_+}$ with $\Lambda := |I|$.

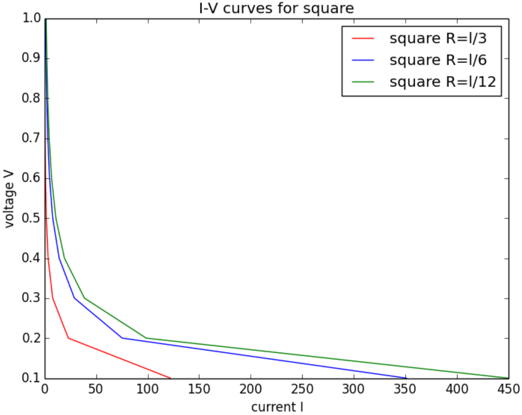
I-V curves: Circle shaped pores ($R = \ell/a$, $a = 3, 6, 12$)



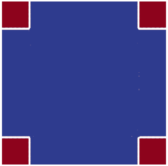


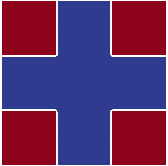
I-V curves: Square with ($R = \ell/a$, $a = 3, 6, 12$)

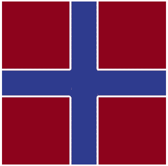


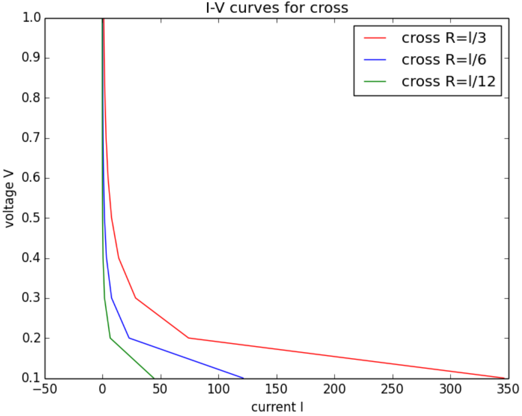


I-V curves: Cross shaped pores ($R = \ell/a$, $a = 3, 6, 12$)

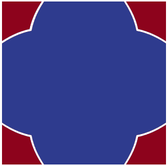
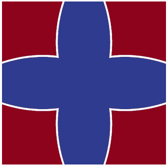
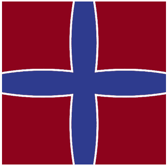


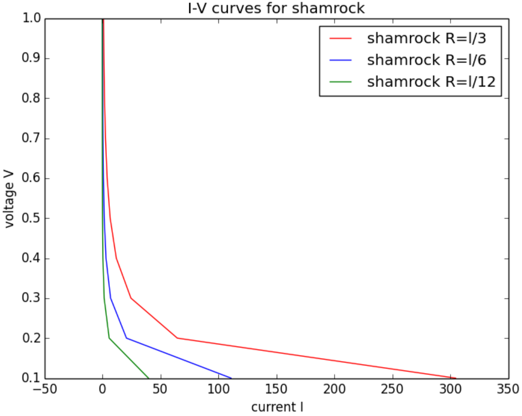






I-V curves: Shamrock ($R = \ell/a$, $h = R/2$, $a = 3, 6, 12$)



2) Extension towards fluid flow

[M. Schmuck & P. Berg, J ELECTROCHEM SOC, 161(8):E3323-E3327 (2014)]

Micro bulk:

$$\begin{cases} -\epsilon^2 \Delta \mathbf{u}^s + \nabla p^s = \kappa \mathbf{f}^s := -\kappa c_+^s \nabla \phi^s & \text{in } \Omega^s \\ \operatorname{div} \mathbf{u}^\epsilon = 0 & \text{in } \Omega^s \\ \partial_t c_O^\epsilon - \operatorname{div}\left(\mathbb{D}^O \nabla c_O^s - \mathrm{Pe}\,\mathbf{u}^\epsilon c_O^s\right) = 0 & \text{in } \Omega^s \\ \partial_t c_+^s - \operatorname{div}\left(\mathbb{D}^+ \left(\nabla c_+^s + c_+^s \nabla \phi^s\right) - \mathrm{Pe}\,\mathbf{u}^s c_+^s\right) = 0 & \text{in } \Omega^s \\ -\operatorname{div}\left(\mathbb{E}(x/s) \nabla \phi^s\right) = c_+^s & \text{in } \Omega \end{cases}$$

Interface:

$$\begin{cases} \mathbf{u}_\tau^s = 0 & \text{on } I \\ \mathbf{u}_n^s = -\frac{s}{2} R_w(c_+^s, c_O^s, \eta^s) & \text{on } I \\ -\nabla_n c_O^s = s\beta_O (c_O^s)^{n_O} (c_+^s)^{n_+} \exp\left[-\alpha_c \left(\Phi^s - \Phi_0\right)\right] & \text{on } I \\ -\nabla_n c_+^s - c_+^s \nabla_n \Phi^s = s\beta_+ (c_O^s)^{n_O} (c_+^s)^{n_+} \exp\left[-\alpha_c \left(\Phi^s - \Phi_0\right)\right] & \text{on } I \\ -\kappa(x/s) \nabla_n \Phi^s = s\sigma_s(x, x/s) & \text{on } I \end{cases}$$

where

$$R_\iota(c_+^s, c_O^s, \eta^s) := \beta_\iota \left(c_+^s\right)^{n_+} \left(c_O^s\right)^{n_O} \exp\left(-\alpha_c \eta^s\right) \; ,$$

and $\beta_\iota := \frac{i_0 L}{4e\mathrm{D}^\iota}$ for $\iota \in \{+, O\}$ and $\beta_w = \frac{i_0 M_w}{\rho_w F}$

Scale Separation: Local Equilibrium

Local Thermodynamic Equilibrium (LTE): *A system depending on a flow velocity* $\mathbf{U}$ *is in* **local thermodynamic equilibrium** *if and only if*

$$0 = \frac{\partial}{\partial x_k}\mu_\iota - \mathrm{U}_k\,, \quad \mathit{for} \quad 1 \leq k \leq N\,,$$

on the level of microscale Y, *where* $\iota \in \{O, +\}$, U_k *is the* k*-th velocity component of the upscaled fluid velocity* $\mathbf{U}$ *and* μ_ι *denotes the electrochemical potenials w.r.t. upscaled variables, i.e.,*

$$\mu_\iota := \begin{cases} \ln C_O & \mathit{if} \quad \iota = O\,, \\ \ln C_+ + z_+\Phi & \mathit{if} \quad \iota = +\,. \end{cases}$$

Result: Two-scale asymptotics

Idea: Apply **LTE** and **multiscale expansions** of the form

$$v^s(x) = v(x, x/s) \approx V(x, x/s) + s v_1(x, x/s) + \mathcal{O}(s^2)\,,$$

where V denotes the upscaled variable.

Result:

$$\begin{cases} \mathbf{U} = C_+ \overline{\mathbb{M}}^+ \nabla\Phi - \overline{\mathbb{K}}\nabla P\,, \quad \text{in } \Omega\,, \\ \text{div}\,\mathbf{U} \\ \quad = -\frac{1}{2}\overline{\beta}_w (C_+)^{n_+}(C_O)^{n_O} \exp\left(-\alpha_c(\Phi - \Phi_0)\right)\,, \quad \text{in } \Omega\,, \end{cases}$$

$$\begin{cases} \theta\partial_t C_O - \text{div}\left(\overline{\mathbb{D}}^O \nabla C_O - \text{Pe}\,\mathbf{U} C_O\right) \\ \quad = \frac{1}{4}\overline{\beta}_O (C_+)^{n_+}(C_O)^{n_O} \exp\left(-\alpha_c(\Phi - \Phi_0)\right)\,, \quad \text{in } \Omega\,, \end{cases}$$

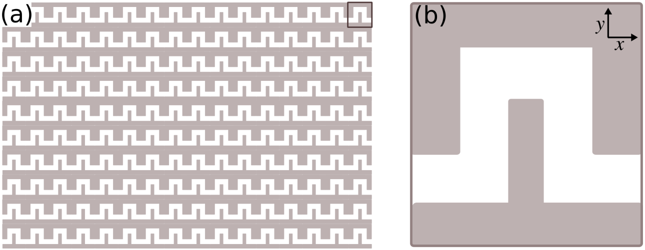
$$\begin{cases} \theta\partial_t C_+ - \text{div}\left(\overline{\mathbb{D}}^+ \nabla C_+ + C_+ \overline{\mathbb{M}}^+ \nabla\Phi - \text{Pe}\,\mathbf{U} C_+\right) \\ \quad = \overline{\beta}_+ (C_+)^{n_+}(C_O)^{n_O} \exp\left(-\alpha_c(\Phi - \Phi_0)\right)\,, \quad \text{in } \Omega\,, \end{cases}$$

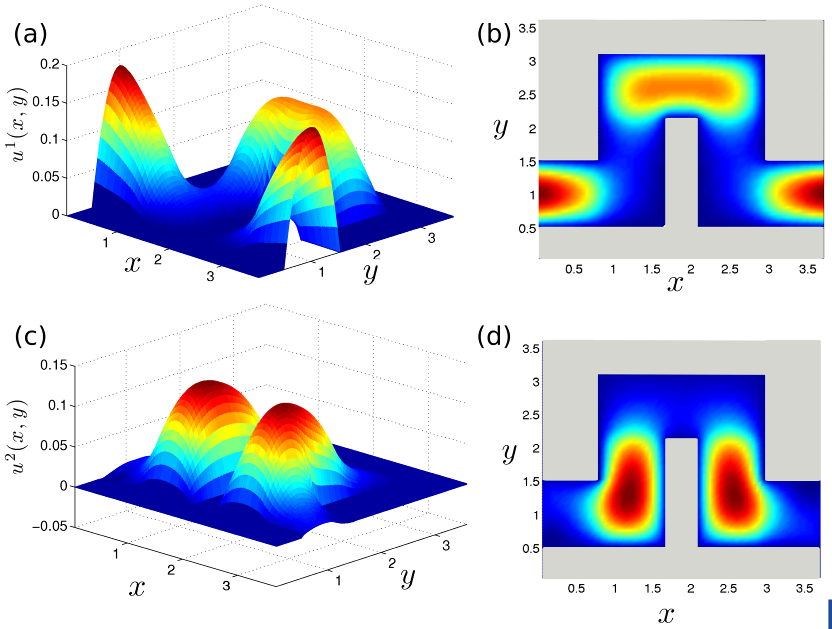
$$\left\{ -\text{div}\left(\overline{\mathbb{E}}\nabla\Phi\right) = \theta C_+ + Q_s \quad \text{in } \Omega\,, \right.$$

3) Moving frame approach: Strongly periodic fluid flow

Periodic flow problem:

$$
\begin{cases}
-\mu\Delta_{\mathbf{y}}\mathbf{u} + \nabla_{\mathbf{y}} p = \mathbf{e}_1 & \text{in } Y^1\,, \\
\mathrm{div}_{\mathbf{y}}\left(\mathbf{u}\right) = 0 & \text{in } Y^1\,, \\
\mathbf{u} = \mathbf{0} & \text{on } I_Y\,, \\
\mathbf{u} \text{ and } p \text{ are } Y\text{-periodic.} &
\end{cases}
$$




(a)
0.2
0.15
0.1
0.05
0
$u^1(x,y)$
1
2
3
x
1
2
3
y
(b)
3.5
3
2.5
2
1.5
1
0.5
y
0.5
1
1.5
2
2.5
3
3.5
x
(c)
0.15
0.1
0.05
0
−0.05
$u^2(x,y)$
1
2
3
x
1
2
3
y
(d)
3.5
3
2.5
2
1.5
1
0.5
y
0.5
1
1.5
2
2.5
3
3.5
x

Ansatz: Asymptotic expansion with drift $\mathrm{v}^j := \frac{\mathrm{Pe}_{\mathrm{loc}}}{|Y^1|} \int_{Y^1} \mathrm{u}^j(y)\, dy$

$$u^\epsilon(t,x) = u\left(t, x - \frac{\mathbf{v}}{\epsilon} t, x/\epsilon\right) \approx U(t,x) + \sum_{i=1}^{\infty} \epsilon^i u_i \left(t, x - \frac{\mathbf{v}}{\epsilon} t, x/\epsilon\right)$$

Result:

$$\begin{cases} \theta \partial_t C_O - \mathrm{div}\left(\overline{\mathbb{D}}^O(\mathbf{u}) \nabla C_O\right) \\ \qquad = \frac{1}{4} \overline{\beta}_O (C_+)^{n_+} (C_O)^{n_O} \exp\left(-\alpha_c(\Phi - \Phi_0)\right), \quad \text{in } \Omega, \end{cases}$$

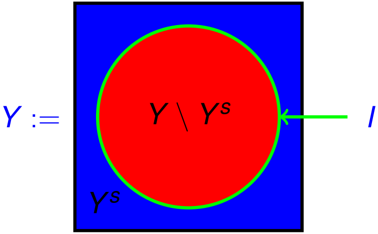
$$\begin{cases} \theta \partial_t C_+ - \mathrm{div}\left(\overline{\mathbb{D}}^+(\mathbf{u}) \nabla C_+ + C_+ \overline{\mathbb{M}}^+ \nabla \Phi\right) \\ \qquad = \overline{\beta}_+ (C_+)^{n_+} (C_O)^{n_O} \exp\left(-\alpha_c(\Phi - \Phi_0)\right), \quad \text{in } \Omega, \end{cases}$$

$$\begin{cases} -\mathrm{div}\left(\overline{\mathbb{E}} \nabla \Phi\right) = \theta C_+ + Q_s . \end{cases}$$

Part IV): Control of Macroscopic Transport Characteristics

Microscopic formulation

Material characteristic: Composite with high contrast in electric permittivity ⇒ strongly oscillating electric potential

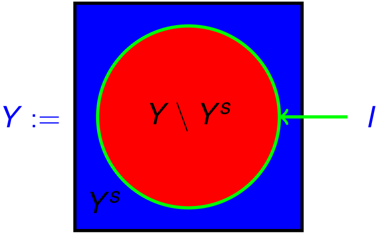


Micro:
$$\begin{cases} \partial_t n_s^+ = \mathrm{div}\left(\nabla n_s^+ + n_s^+ \nabla \phi_s\right) & \text{in } \Omega^s \\ \partial_t n_s^- = \mathrm{div}\left(\nabla n_s^- - n_s^- \nabla \phi_s\right) & \text{in } \Omega^s \\ -\mathrm{div}\left(\hat{\kappa}(x/s)\nabla \phi_s\right) = n_s^+ - n_s^- & \text{in } \Omega \end{cases}$$

Micro interface:
$$\begin{cases} \nabla_n n_s^+ + n_s^+ \nabla_n \phi_s = 0 & \text{on } I_s \\ \nabla_n n_s^- - n_s^- \nabla_n \phi_s = 0 & \text{on } I_s \\ -\hat{\kappa}(x/s)\nabla_n \phi_s & \text{continuous over } I_s \end{cases}$$

Microscopic formulation

Material characteristic: Composite with high contrast in electric permittivity $\Rightarrow$ strongly oscillating electric potential



Micro:
$$\begin{cases} \partial_t n_s^+ = \mathrm{div}\left(\nabla n_s^+ + n_s^+ \nabla \phi_s\right) & \text{in } \Omega^s \\ \partial_t n_s^- = \mathrm{div}\left(\nabla n_s^- - n_s^- \nabla \phi_s\right) & \text{in } \Omega^s \\ -\mathrm{div}\left(\hat{\kappa}(x/s)\nabla \phi_s\right) = n_s^+ - n_s^- & \text{in } \Omega \end{cases}$$

Micro interface:
$$\begin{cases} \nabla_n n_s^+ + n_s^+ \nabla_n \phi_s = 0 & \text{on } I_s \\ \nabla_n n_s^- - n_s^- \nabla_n \phi_s = 0 & \text{on } I_s \\ -\hat{\kappa}(x/s)\nabla_n \phi_s & \text{continuous over } I_s \end{cases}$$

Idea: Use **modified** expansions ($\mathrm{u}_s^1 := n_s^+$, $\mathrm{u}_s^2 := n_s^-$)

$$\mathrm{u}_s^r = \mathrm{u}_0^r - s\sum_{k=1}^{N} \xi^{r_k}(t,x,x/s)\frac{\partial \phi_0}{\partial x_k} + s^2 \sum_{k,l=1}^{N} \zeta^{r_{kl}}(t,x,x/s)\mathrm{u}_0^r + \dots \quad \text{for } r = 1,2\,,$$

$$\phi_s = \phi_0 - s\sum_{k=1}^{N} \xi_\phi^k(x/s)\frac{\partial \phi_0}{\partial x_k} + s^2 \sum_{k,l=1}^{N} \zeta_\phi^{kl}(x/s)\frac{\partial^2 \phi_0}{\partial_{x_k}\partial_{x_l}} + \dots\,,$$

where $\xi^{r_k}(\cdot,\cdot,y) \in V(\Omega_T, W_\sharp(Y^s))$, $\xi^{3_k}(y) \in W_\sharp(Y)$, $\zeta^{r_{kl}}(\cdot,\cdot,y) \in V(\Omega_T, W_\sharp(Y^s))$, and $\zeta^{3_{kl}}(y) \in W_\sharp(Y)$ solve elliptic cell problems.

Result: $\mathbf{u}_0$ is solution of the following upscaled system

$$\begin{cases} p\partial_t \mathrm{u}_0^r - p\Delta \mathrm{u}_0^r + \mathrm{div}\left(\mathbb{D}^r(t,x)\nabla\phi_0\right) - \mathrm{div}\left(z_r \mathrm{u}_0^r \mathbb{M}\nabla\phi_0\right) = 0 & \text{in } \Omega_T\,, \\ -\mathrm{div}\left(\epsilon^0\nabla\phi_0\right) = p\left(\mathrm{u}_0^1 - \mathrm{u}_0^2\right) & \text{in } \Omega_T\,, \end{cases}$$

where $p := |Y^s|/|Y|$ is the porosity and the tensors $\mathbb{D}^r(t,x) := \{\mathrm{D}_{kl}^r(t,x)\}_{1\le k,l\le N}$, $\mathbb{M} := \{\mathrm{M}_{kl}\}_{1\le k,l\le N}$, and $\epsilon^0 := \{\epsilon_{kl}^0\}_{1\le k.l\le N}$ are defined by

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$$\phi_s = \phi_0 - s\sum_{k=1}^{N} \xi_\phi^k(x/s)\frac{\partial \phi_0}{\partial x_k} + s^2 \sum_{k,l=1}^{N} \zeta_\phi^{kl}(x/s)\frac{\partial^2 \phi_0}{\partial_{x_k}\partial_{x_l}} + \dots\,,$$

where $\xi^{r_k}(\cdot,\cdot,y) \in V(\Omega_T, W_\sharp(Y^s))$, $\xi^{3_k}(y) \in W_\sharp(Y)$, $\zeta^{r_{kl}}(\cdot,\cdot,y) \in V(\Omega_T, W_\sharp(Y^s))$, and $\zeta^{3_{kl}}(y) \in W_\sharp(Y)$ solve elliptic cell problems.

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$$\mathrm{D}_{ik}^{r}(t,x) := \frac{1}{|Y|}\int_{Y^s}\sum_{j=1}^{N}\left\{\delta_{ij}\partial_{y_j}\xi^{r_k}(t,x,y)\right\}\,dy\,,$$

$$\mathrm{M}_{ik} := \frac{1}{|Y|}\int_{Y^s}\sum_{j=1}^{N}\left\{\delta_{ik}-\delta_{ij}\partial_{y_j}\xi^{3_k}(y)\right\}\,dy\,,$$

$$\epsilon_{ik}^{0} : = \frac{1}{|Y|}\int_{Y}\sum_{j=1}^{N}\hat{\kappa}(y)\left(\delta_{ik}-\delta_{ij}\partial_{y_j}\xi^{3_k}(y)\right)\,dy\,.$$

Reference:

[M. Schmuck, J MATH PHYS, 54(2):21 p.021504 (2013)]

Conclusion:

- Presented formal and rigorous upscaling/homogenization methods.
- Systematically derived upscaled charge transport equations valid for different pore geometries
- Developed a framework for deriving effective macroscopic catalyst layer equations
- **Upscaling provides means to control transport on the macroscale!**

Thank You for Your Attention!

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