Upscaling of pore scale models for reactive flows

C.J. van Duijn, K. Kumar, T.L. van Noorden, I.S. Pop*

P. Notten, J. van Oudenhoven*

R. Helmig‡, A. Ebigbo‡

*CASA, TU Eindhoven

‡Universität Stuttgart

Outline

- A reactive flow model

  Existence and uniqueness (1D)

  Numerical results

- Pore model upscaling

- Further applications

1. The reactive flow model

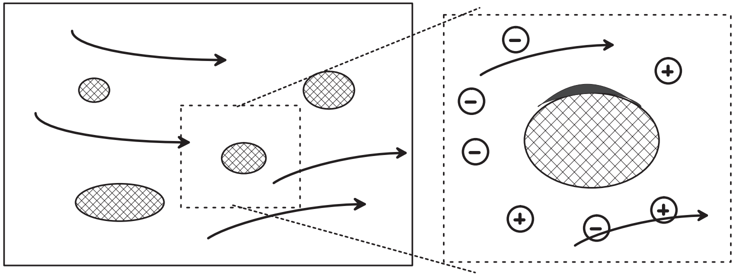
fully saturated porous medium

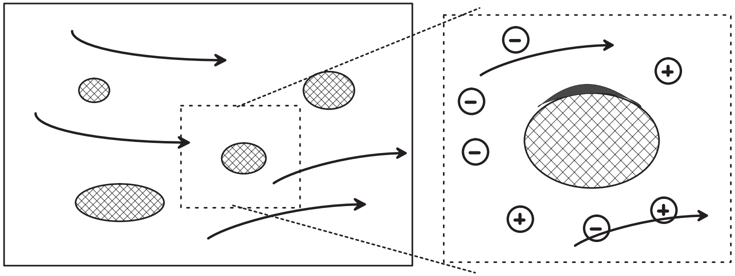
ions (Na^+, Cl^-) dissolved in the fluid *[transported by the flow]*

crystals ($NaCl$)attached to the grain surface (porous matrix)

precipitation/dissolution on the grain surface

$$M_{12} \leftrightarrows nM_1 + mM_2,$$





Chemistry:

$$M_{12} \leftrightarrows n_1 M_1 + n_2 M_2,$$

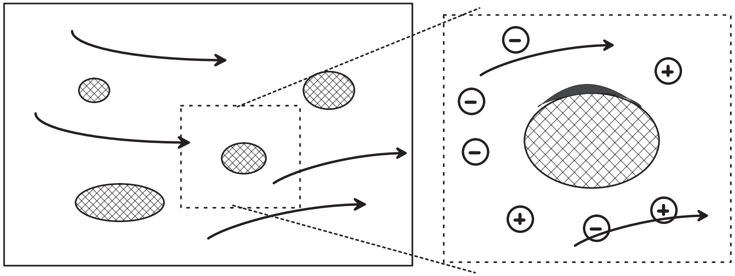
M_1, M_2 – solutes (ions: Na^+, Cl^-)

n_2, n_1 – valences $(1, 2, \ldots)$

M_{12} – immobile crystalline ($NaCl$)

c_i – volumetric molar concentration of M_i (M/m^3)

$\tilde{D} > 0$ – diffusion coefficient (m^2/s)



Crystals:

Fixed domain:
Crystal size can be neglected $\longrightarrow$ pore geometry is not affected by the chemical processes

$$c_{12} - \text{ areal molar concentration of } M_{12}(M/m^2)$$

Variable domain:
Crystals have a significant size $\longrightarrow$ change in the pore geometry

$$\text{thickness of the precipitate layer } d \longrightarrow \text{ free boundary}$$

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Results in fixed domains*

Existence and uniqueness of (weak) solutions

Uniform estimates (positivity, upper bounds, energy)

Conservation of mass

Convergent numerical scheme

Simple geometry (thin strips):

- dissolution/precipitation fronts, moving with the flow
- upscaling, including dominating transport regimes (Taylor dispersion)

Rem: Obtained for general, complex (periodic) media, including flow

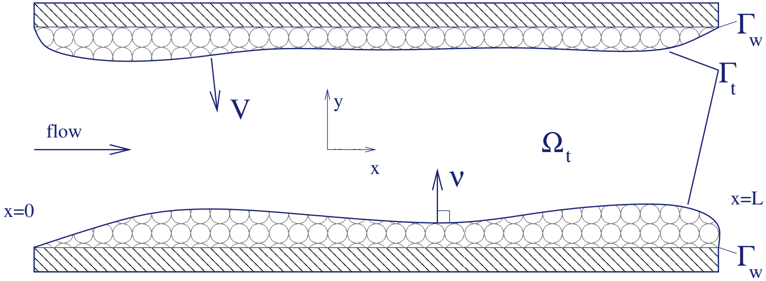
*van Duijn, P (J. Reine Angew. Math., 2004),

van Noorden, P, Röger (Discrete Contin. Dyn. Syst., 2007),

Devigne, P, van Duijn, Clopeau (SIAM J. Numer. Anal., 2008),

van Duijn, Mikelić, P, Rosier (Advances in Chemical Engineering, 2008)

Model involving a time dependent, a-priori unknown domain



Features:

The size of crystals cannot be neglected when compared to the pore size;

Variable pore size: solution dependent (thus implicitly on time);

Precipitate concentration $v \longrightarrow$ layer thickness d.

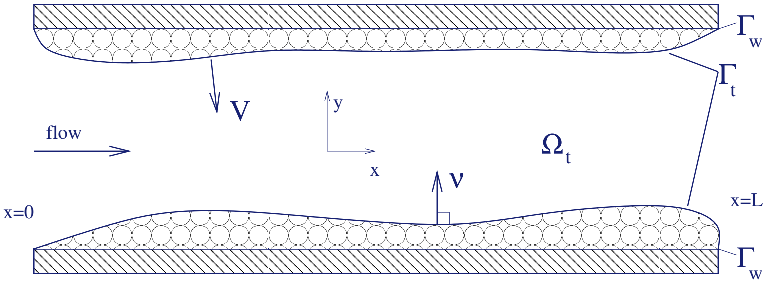
Diffusion of ions M_i, $(i = 1, 2)$ *inside the pore space* Ω_t:

$$\partial_t c_i - \tilde{D}\Delta c_i = 0$$

Note: Variable pore space Ω_t, affected by the chemical processes

Rem: Transport (Stokes flow) can be considered, correct conditions at the moving interface

At the *free interface* Γ_t:



$$(n_i \rho_c - c_i)\tilde{V} = \nu \cdot (\tilde{D} \nabla c_i),$$

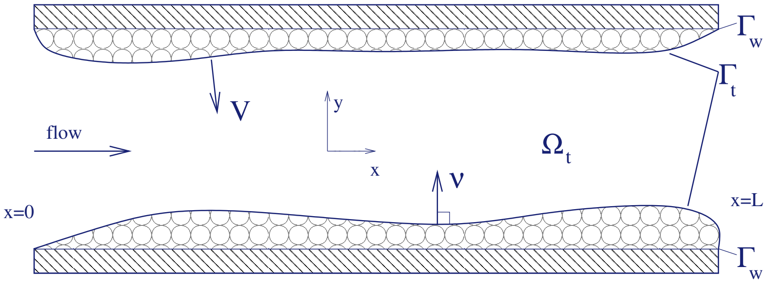
with ρ_c - molar density M/m^3, while

$$\Gamma_g(t) := \{(x,y) \mid 0 \leq x \leq L,\ y \in \{-(\ell - d(x,t)), (\ell - d(x,t))\}\},$$

and therefore $\nu = (-\partial_x d, 1)^T / \sqrt{1 + (\partial_x d)^2}$.

Rem: Mass conservation for ions $(i = 1, 2)$

At the *free interface* Γ_t:



$$\rho_c \tilde{V} = \tilde{d}(\tilde{r}_p - \tilde{r}_d)$$

Rem: $\tilde{d}$ - "typical layer thickness"

Precipitation rate:

$$r_p = k_p \bar{r}(c_1, c_2) = k_p [c_1]_+^{n_2} [c_2]_+^{n_1}$$

($\bar{r}$ – non-negative, continuous, increasing in both arguments)

Dissolution rate (van Duijn–Knabner*), $x \in \Gamma_t$:

Presence of crystal ($d(x, \Gamma_t) > 0$): *constant* dissolution rate k_d

Absence of crystal ($d(x, \Gamma_t) = 0$):

Oversaturation ($\bar{r}(c_1, c_2) > \frac{k_d}{k_p}$): effective precipitation ("switch on")

$$r_d = k_d < r_p$$

Undersaturation ($\bar{r}(c_1, c_2) \leq \frac{k_d}{k_p}$): zero overall rate ("switch off")

$$r_d = r_p = k_p \bar{r}(c_1, c_2) \qquad \text{(a.e.)}$$

Note: Undersaturation occurs at different concentrations, r_d is not fixed

$$r_d(x, c_1, c_2) = \begin{cases} 1, & \text{if } d(x, \Gamma_t) > 0 \\ [r_p - k_d]_+, & \text{if } d(x, \Gamma_t) = 0 \end{cases}$$

$$\boxed{r_d \in k_d H(d(x, \Gamma_t))}$$

*Knabner, van Duijn, Hengst (Adv. Water Res., 1995)

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Scaling

Characteristic values: c_R, L, T_D, D_R, $(T_D = L^2/D_R)$

$$u_i = \frac{c_i}{c_R}, \quad D = \frac{\tilde{D}}{D_R}, \quad \rho = \frac{\rho_c}{c_R}(> 1), \quad \varepsilon = \frac{\text{Vol}_{fluid}}{L\,\text{Area}_{grain}}$$

Characteristic velocities:

$$Q = \frac{L}{T_D} - \text{"macro scale", and } V_R := \frac{\tilde{d}}{\rho T_D} - \text{pore scale, implying } \tilde{V} = V_R V$$

Time scales: $T_D = \frac{L^2}{\tilde{D}}$, $T_C = \frac{c_R}{k_d} \longrightarrow D_a = \frac{T_D}{T_C}$

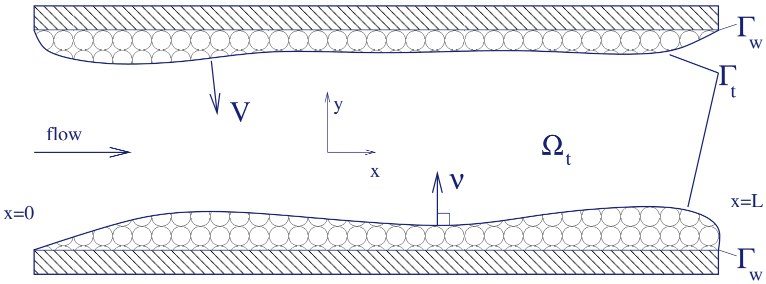
Note: ε–balance factor for solute and precipitate:

$\rho_c \times (V_R T_D)\,\text{Area}_{grain} \approx c_R \times \text{Vol}_{fluid} \longrightarrow \tilde{d} \approx \varepsilon L$

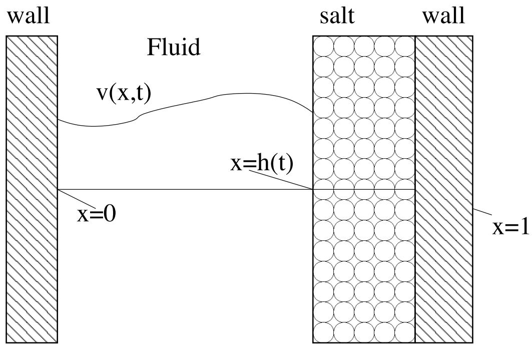
Dimensionless equations $0 < T < \infty$, $\Omega \supset \Omega_t$–time dependent

Simplified setting: no flow, equal valences (n) and ion concentrations (u), one dimensional

$$\begin{cases} \partial_t u = D\Delta u, & \text{in } \Omega_t, \\ D\nu \cdot \nabla u = \varepsilon(n\rho - u)V, & \text{at } \Gamma_t, \\ V = D_a(r(u) - w), & \text{at } \Gamma_t, \\ w \in H(d(x, \Gamma_t)). \end{cases}$$



Results in 1D*



Then Γ_t becomes $x(t)$, V becomes $h(t)$

Initial data:

Bounded: $0 < h_0 \leq 1$, $0 \leq u_0 \leq M < \rho$.

Smooth: $u_0 \in C^2([0, h_0])$.

Compatibility: $\partial_x u_0(0) = 0$, $\partial_x u_0(h_0) = D_a\big(r(u_0(h_0)) - w_0\big)(\rho - u_0(h_0))$,

with $w_0 = w(t = 0)$ defined as

$$\begin{cases} w_0 = 1, & \text{if } h_0 < 1, \\ w_0 = r(v_0(1)), & \text{if } h_0 = 1, \text{ and } v_0(1) \leq u^*, \\ w_0 = 1, & \text{if } h_0 = 1, \text{ and } v_0(1) > u^*. \end{cases}$$

Space-time domain ($h \in C([0, T])$):

$$Q_{hT} := \{(x, t) \,|\, 0 < x < h(t),\ 0 < t < T\}.$$

*van Noorden, P (IMA J Appl. Math. 2008)

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Definition: A triple (u, w, h) satisfying

1. $h \in C([0,T])$,
2. $u \in C^{2,1}(Q_{hT}) \cap C(\overline{Q_{hT}})$,
3. $\partial_x u \in C(Q_{hT} \cup \{x=0,\ 0 \le t \le T\})$,
4. $w \in L^\infty(0,T)$,

and

$$\begin{cases} \partial_t u = \partial_{xx} u, & \text{in } Q_{hT}, \\ \partial_x u = 0, & \text{on } \{x=0,\ 0 \le t \le T\}, \\ \int_0^{h(t)} (\rho - u)\, dx = h_1, & \text{for } 0 \le t \le T, \\ h(t) = D_a \int_0^t \big(w(\tau) - r(u(h(\tau),\tau))\big)\, d\tau + h_0, & \text{for } 0 \le t \le T, \\ w(t) \in H(1 - h(t)), & \text{a.e. in } [0,T], \\ u = u_0, & \text{for } 0 \le x \le h_0,\ t = 0, \end{cases}$$

with $h_1 = \int_0^{h_0} (\rho - u_0(x))\, dx$, is a solution of the 1D variable domain model.

Theorem: There is a unique solution, satisfying

$$0 \le u \le \max\{u^*, M\}, \text{ and } \frac{h_1}{\rho} \le h \le 1.$$

A. Coordinate transform

$$y = \int_x^{h(t)} (\rho - v(z,t))\, dz, \quad \tau = t.$$

Then $U(y,\tau) = u(x,t)$ satisfies:

$$\begin{cases} \partial_\tau f(U) = \partial_{yy} U, & \text{for } 0 < y < h_0 (0 < t \leq T), \\ \partial_y U = D_a(r(U) - w(t)), & \text{at } y = 0, \\ h'(t) = -D_a(r(U) - w(t)), & \text{at } y = 0, \\ w(t) \in H(1 - h(t)), & \\ \partial_y U = 0, & \text{at } y = h_0, \\ U(y,0) = v_0(x), & \text{at } t = 0. \end{cases}$$

where $f(U) = 1/(\rho - U)$.

B. Regularization

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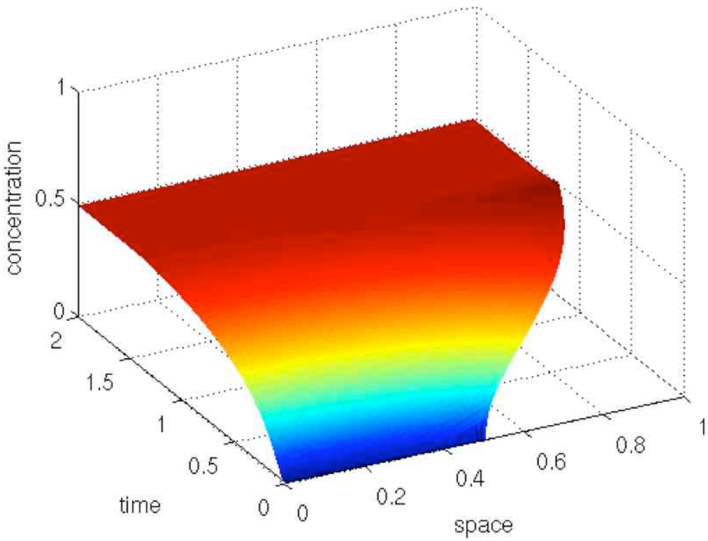
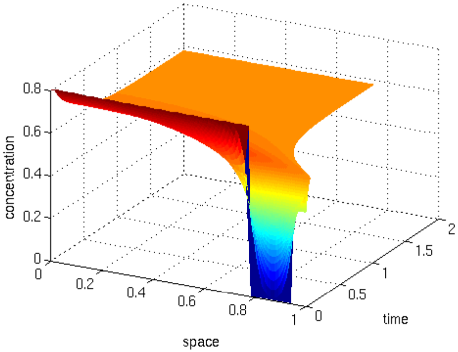
1D numerical examples

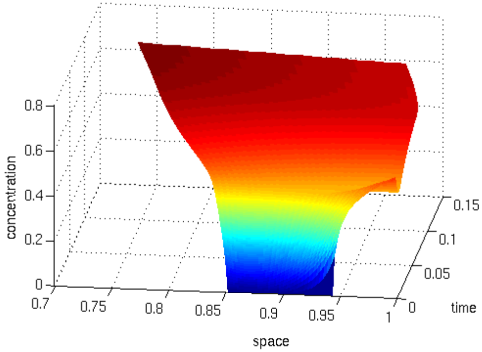
Dissolution, $\rho = 1$, $h_0 = 0.5$, $u_0 = 0$, $r(u) = 3u^2$, $D_a = 1$



1D numerical example

Dissolution and precipitation, $\rho = 1$, $h_0 = 0.95$, $u_0 = 0$, $r(u) = 3u^2$, $D_a = 20$





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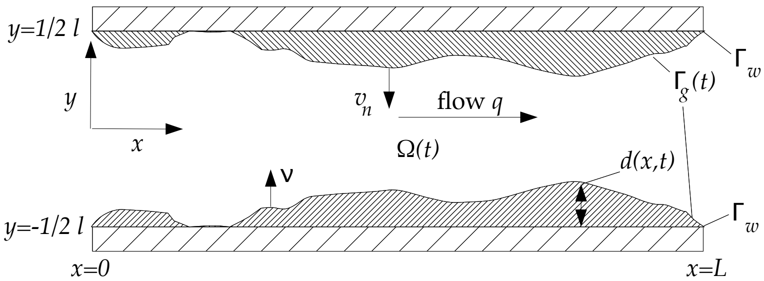
2. Pore model upscaling

General rate, $f(u, \rho d)$;

Characteristic velocity Q such that $T_Q = \frac{L}{Q}$ is in balance with $T_D = \frac{L^2}{D}$



$$
\begin{aligned}
\partial_t u - D\left(\partial_{xx} u + \tfrac{1}{\varepsilon^2}\partial_{yy} u\right) + \partial_x q^{(1)} u + \tfrac{1}{\varepsilon}\partial_y q^{(2)} u &= 0, && \text{in } \Omega(t), \\
\partial_x q^{(1)} + \tfrac{1}{\varepsilon}\partial_y q^{(2)} &= 0, && \text{in } \Omega(t), \\
\varepsilon^2 \mu \partial_{xx} q + \mu \partial_{yy} q &= \left(\partial_x P,\ \tfrac{1}{\varepsilon}\partial_y P\right)^T, && \text{in } \Omega(t), \\
\partial_t d / \sqrt{1 + (\varepsilon \partial_x d)^2} &= f(u, \rho d), && \text{on } \Gamma_g^\varepsilon(t) \\
D\left(-\varepsilon^2 \partial_x d \partial_x u + \partial_y u\right) &= \varepsilon^2 \partial_t d(\rho - u), && \text{on } \Gamma_g^\varepsilon(t).
\end{aligned}
$$

Formal asymptotic analysis*:

Assume

$$\begin{aligned} P^\varepsilon &= P_0 + \varepsilon P_1 + O(\varepsilon^2), \\ q^{\varepsilon(1)} &= q_0^{(1)} + \varepsilon q_1^{(1)} + O(\varepsilon^2), \\ q^{\varepsilon(2)} &= q_0^{(2)} + \varepsilon q_1^{(2)} + O(\varepsilon^2), \\ d^\varepsilon &= d_0 + \varepsilon d_1 + O(\varepsilon^2), \\ u^\varepsilon &= u_0 + \varepsilon u_1 + O(\varepsilon^2), \end{aligned}$$

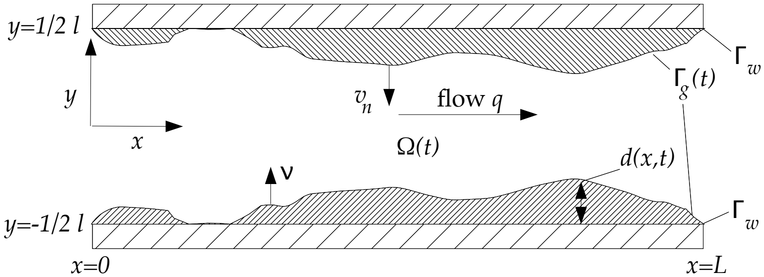
then

$$\begin{aligned} \bar{q}_0 &= -\tfrac{(1-d_0)^3}{3\mu}\partial_x P_0, \\ \partial_x \bar{q}_0 &= 0, \\ \partial_t((1-d_0)u_0 + \rho d_0) &= \partial_x \left\{(1-d_0)D\partial_x u_0 - \bar{q}_0 u_0\right\}, \\ \partial_t(\rho d_0) &= f(u_0, \rho d_0). \end{aligned}$$

*van Noorden (Eur. J. Appl. Math., 2009)

Dispersion model (Taylor)*

Transport dominated regime, characteristic velocity Q such that **Pe** $= \frac{LQ}{D} = \frac{1}{\varepsilon}$



$$
\begin{aligned}
\partial_t u - \varepsilon D \left(\partial_{xx} u + \tfrac{1}{\varepsilon^2}\partial_{yy} u\right) + \partial_x q^{(1)} u + \tfrac{1}{\varepsilon}\partial_y q^{(2)} u &= 0, && \text{in} \quad \Omega(t),\\
\partial_x q^{(1)} + \tfrac{1}{\varepsilon}\partial_y q^{(2)} &= 0, && \text{in} \quad \Omega(t),\\
\varepsilon^2 \mu \partial_{xx} q + \mu \partial_{yy} q &= \left(\partial_x P,\ \tfrac{1}{\varepsilon}\partial_y P\right)^T, && \text{in} \quad \Omega(t),\\
\partial_t d / \sqrt{1 + (\varepsilon \partial_x d)^2} &= f(u, \rho d), && \text{on} \quad \Gamma_g^\varepsilon(t)\\
D\left(-\varepsilon^2 \partial_x d \partial_x u + \partial_y u\right) &= \varepsilon \partial_t d(\rho - u), && \text{on} \quad \Gamma_g^\varepsilon(t).
\end{aligned}
$$

Kumar, van Noorden, P (Multiscale Model. Simul., accepted)

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Formal asymptotic analysis:

Define

$$d_e = d_0 + \varepsilon d_1,\ u_e = u_0 + \varepsilon \frac{1}{1-d_e}\int_{d_e-1}^{0} u_1 dy,\ \bar{q}_e = \int_{d_e-1}^{0} q_0 + \varepsilon q_1 dy, P_e = P_0 + \varepsilon P_1.$$

Then

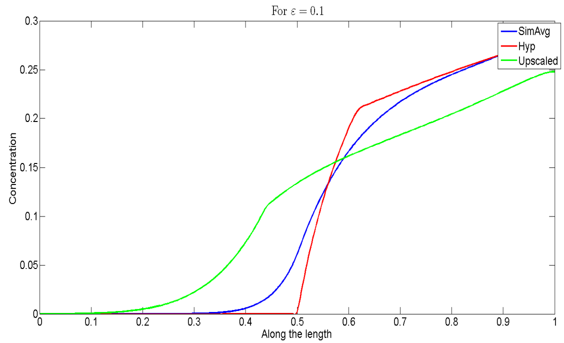
$$\begin{aligned}
\bar{q}_e &= -\tfrac{(1-d_e)^3}{3\mu}\partial_x P_e,\\
\partial_x \bar{q}_e &= 0,\\
\partial_t((1-d_e)u_e + \rho d_e) &= \partial_x\left\{\varepsilon(1-d_e)D(1+\tfrac{2\bar{q}_e^2}{105D^2})\partial_x u_e - \bar{q}_e u_e - \varepsilon\tfrac{\bar{q}_e}{15D}\partial_t d_e(\rho-u_e)(1-d_e)\right\},\\
\partial_t(\rho d_e) &= f(u_e,\rho d_e) + \varepsilon(1-d_e)\left\{-\tfrac{1}{3D}(\rho-u_e)\partial_t d_e + \tfrac{1}{15D}\bar{q}_e\partial_x u_e\right\}\partial_1 f(u_e,\rho d_e).
\end{aligned}$$

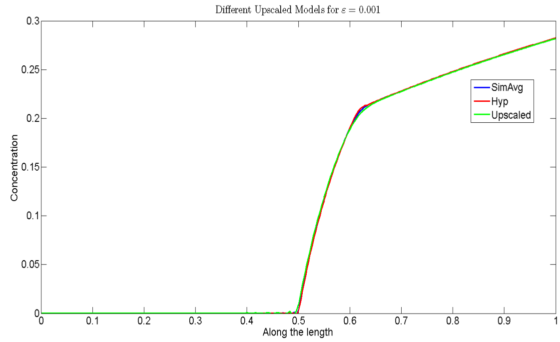
Compare to the fixed domain model (Poiseuille flow, $(\bar{q}_e, u_e, \rho d_e) \longrightarrow (\bar{q}_f, u_f, v_f)$):

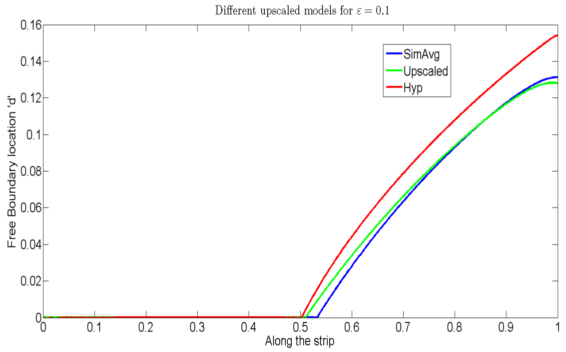
$$\partial_t(u_f + v_f) = \partial_x\left\{\varepsilon D(1+\tfrac{2\bar{q}_f^2}{105D^2})\partial_x u_f - \bar{q}_f u_f - \varepsilon\tfrac{1}{15}\tfrac{\bar{q}_f}{D} f(u_f,v_f)\right\}$$

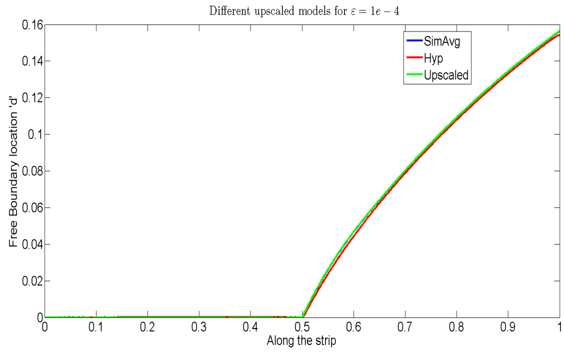
$$\partial_t v_f = f(u_f,v_f) + \varepsilon(-\tfrac{1}{3D}\partial_t v_f + \tfrac{1}{15D}\bar{q}_f\partial_x u_f)\partial_1 f(u_f,v_f).$$

Comparison between different upscaled models, $\varepsilon = 0.1$ and $\varepsilon = 0.001$









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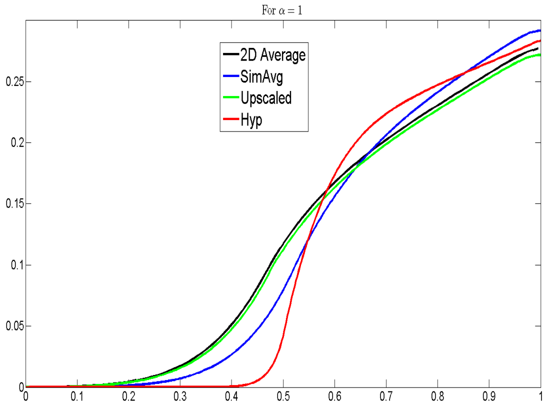
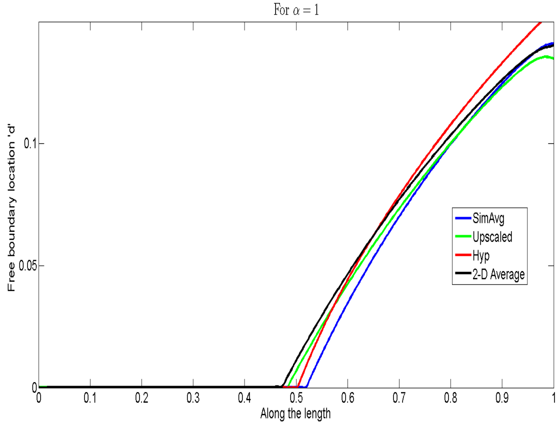
Comparison between different upscaled models, $\varepsilon = 0.1$





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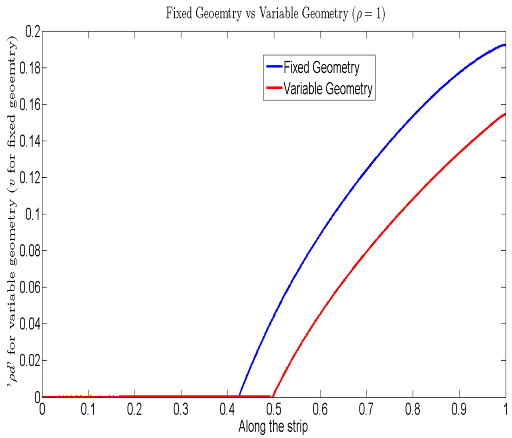
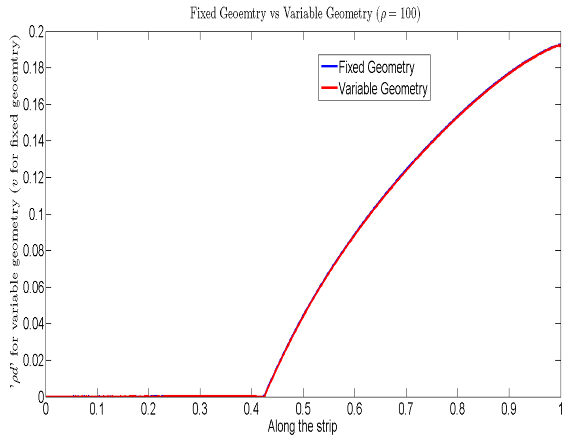
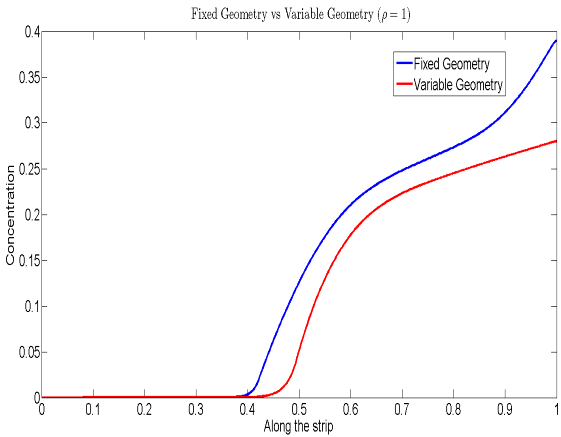
Effective precipitate, fixed vs. variable domain

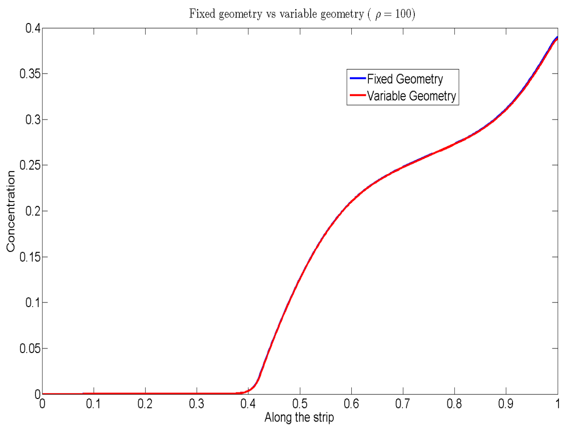




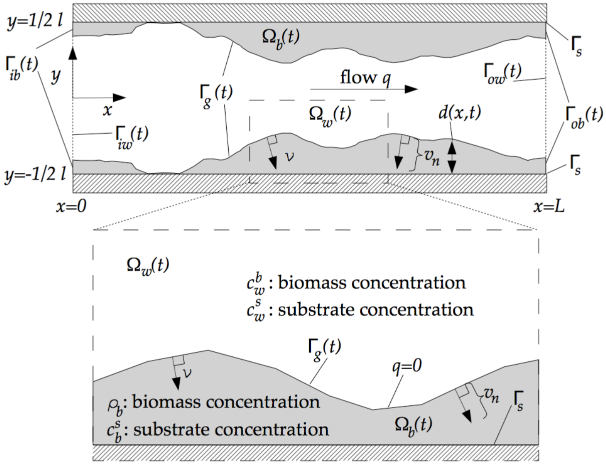
Rem: Precipitate concentration V in the *fixed* domain model becomes ρd in the *variable* domain model

Effective solute concentration, fixed vs. variable domain





3. Further application: biofilm growth*



Biomass and substrate inside the fluid:

$$\partial_t c_w^i - \nabla \cdot (D_w^i \nabla c_w^i - q c_w^i) = R_w^i, \text{ for } i = b, s,$$

Substrate in the biofilm:

$$\partial_t c_b^s - \nabla \cdot (D_b^s \nabla c_b^s) = R_b^s$$

Fluid flow (variable domain, due to biofilm)

$$\mu \Delta q = \nabla p, \text{ and } \nabla \cdot q = 0$$

Biomass displacement in the biofilm (constant density)

$$u = -\lambda \nabla p_b, \text{ and } \rho_b \nabla \cdot u = R_{prod} - R_{dec}$$

van Noorden, P, Ebigbo, Helmig (Water Resour. Res., 2010)

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At $\Gamma_g(t)$: $p_b = 0, q = 0$, $c_w^s = c_b^s$, as well as

$$\nu \cdot (D_w^s \nabla c_w^s - D_b^s \nabla c_b^s) = 0 \text{ and } \nu \cdot (D_w^b \nabla c_w^b + \rho_b u) = v_n(\rho_b - c_w^b).$$

Here $\nu = (\partial_x d, -1)/\sqrt{1 + (\partial_x d)^2}$, whereas $\rho_b v_n = \begin{cases} R_{det} - R_{att} + \nu \cdot u \rho_b & \text{if } d > 0, \\ [R_{det} - R_{att}]_- & \text{if } d = 0. \end{cases}$

Rates:

$$R_w^s = -\mu_{max}^w \tfrac{c_w^s c_w^b}{k_w^s + c_w^s}, \quad R_w^b = Y_w \mu_{max}^w \frac{c_w^s c_w^b}{k_w^s + c_w^s} - k_{res} c_w^b,$$

$$R_b^s = -\mu_{max}^b \tfrac{c_b^s \rho_b}{k_b^s + c_b^s}, \quad R_{prod} = Y_b \mu_{max}^b \frac{c_b^s \rho_b}{k_b^s + c_b^s},$$

and

$$R_{dec} = k_{res} \rho_b, \quad R_{att} = k_{att} c_w^b, \quad R_{det} = k_{det} \| \mu (I - \nu \nu^T) \nabla q \nu \|,$$

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Upscaling (thin pores)

$$
\begin{aligned}
&\partial_t\big((1-2d)c_1 + 2\rho d\big) = \partial_x\Big(\frac{D_r}{P_e}(1-2d)\partial_x c_1 - \bar{q}c_1\Big) \\
&\qquad\qquad +(1-2d)(Y_w D_{aw} f_1(c_1,c_2) - k_\dagger c_1) + 2\rho d(Y_b D_{ab} f_2(c_2) - k_\dagger), \\
&\partial_t c_2 = \partial_x\Big(\frac{1-2d+2Dd}{P_e}\partial_x c_2 - \bar{q}c_2\Big) - (1-2d)D_{aw}C_r f_1(c_1,c_2) - 2dD_{ab}C_r\rho f_2(c_2), \\
&\rho\partial_t d = \begin{cases} k_a c_1 - \mu k_d \frac{3|\bar{q}|}{2(1/2-d)^2} + \rho d(Y_b D_{ab} f_2(c_2) - k_\dagger), & d > 0, \\ \Big[k_a c_1 - \mu k_d \frac{3|\bar{q}|}{2(1/2-d)^2}\Big]_+, & d = 0, \end{cases} \\
&\bar{q} = -\frac{2\partial_x p}{3\mu}(1/2-d)^3, \\
&\partial_x \bar{q} = 0
\end{aligned}
$$

where

- d - biofilm thickness
- c_1 - biomass concentration in water
- c_2 - substrate concentration

Rem: good agreement with upscaled models in the literature

Future work

Analysis for different regimes ($D = O(\varepsilon^\gamma)$, $D_a = O(\varepsilon^\alpha)$)

Upscaling (homogenization) for general geometries

Upscaled models: appropriate numerical techniques (MFEM, FV), coupling chemistry - porous media flows, iterative solvers

Further applications: CVD, coupled porous media/free flows, pore scale two-phase flow models

Going below continuum scales

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