Crystal dissolution and precipitation in porous media: formal homogenization and numerical experiments

T.L. van Noorden, I.S. Pop

technische universiteit eindhoven

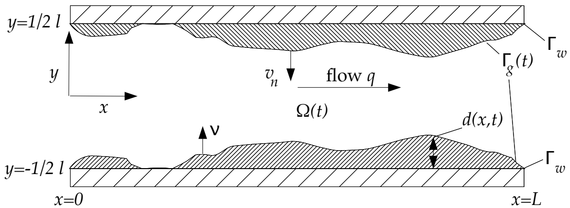
Centre for Analysis, Scientific Computing and Applications
Department of Mathematics, Technische Universiteit Eindhoven
Part of this research has been funded by the Dutch BSIK/BRICKS project

Dubrovnik, 15-10-2008

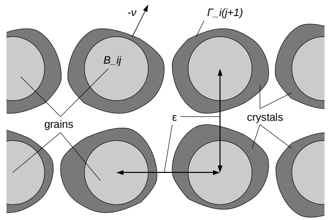
.

Outline

- Introduction: crystals in porous media
- Model: free boundary problem
- Thin strip



- Perforated domain



- Open Problems / Future Directions

Flow through porous medium

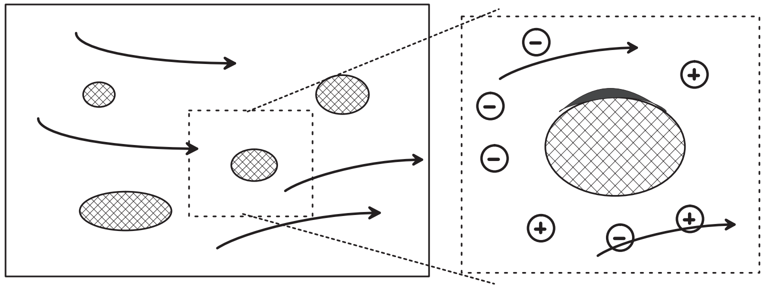
porous medium, fully saturated

dissolved ions transported by the flow, e.g. sodium (Na^+) and chlorine (Cl^-) ions

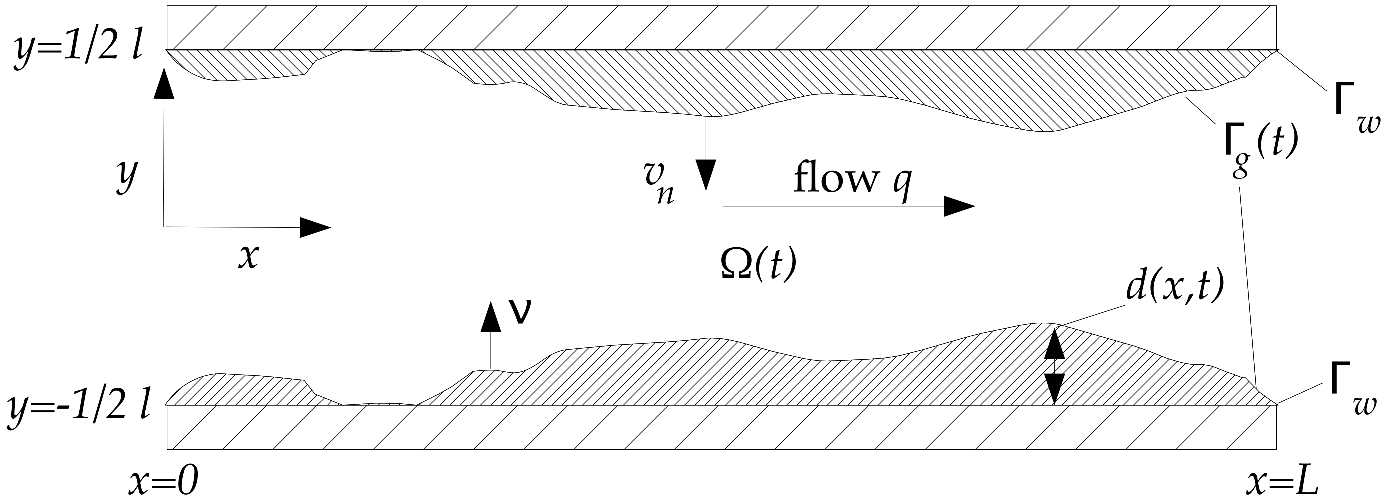
crystals attached to the grain surface (porous matrix), e.g. sodium chloride ($NaCl$)

precipitation/dissolution reaction on the grain surface

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



Model equations



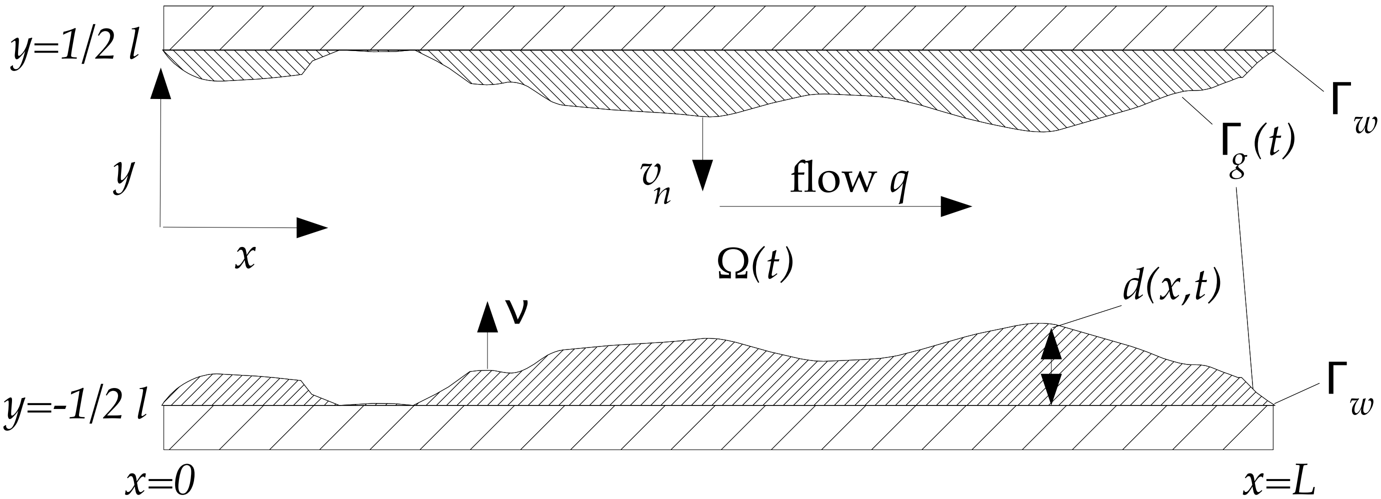
Flow:

q – fluid velocity (m/s)
p – pressure inside fluid (Pa)
μ – dynamic viscosity (kg/(ms))

Stokes flow: $$\left.\begin{array}{rcl}\mu\,\Delta q &=& \nabla p, \\ \nabla\cdot q &=& 0.\end{array}\right\}$$ in Ω_t and $q = K v_n \nu$, on Γ_t,

with $K = \frac{\rho_f - (n_1+n_2)\rho_c}{\rho_f}$. (Using the assumption $c_f + c_1 + c_2 \equiv \rho_f$)

Model equations



Ion concentration:

Precipitation, dissolution reaction:

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

Mass conservation for ion concentrations c_i (mol/m^3) ($i = 1, 2$):
in fluid

$$\partial_t c_i + \nabla \cdot (q c_i - D \nabla c_i) = 0 \quad \text{for} \quad x \in \Omega_t$$
$$(n_i \rho - c_i) v_n = D \nu \cdot \nabla c_i \quad \text{for} \quad x \in \Gamma_t$$

Dissolution and precipitation rate

Thickness of crystalline layer:
normal velocity of interface between cristals and fluid

$$v_n = r_p - r_d,$$

1) Precipitation rate r_p (mol/m^{2}s):

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

2) Dissolution rate r_d (mol/m^{2}s)

$$r_d \in k_d H(d(x, \Gamma_w))$$

where H denotes the set-valued Heaviside graph

$$H(u) = \begin{cases} \{0\}, & \text{if } u < 0, \\ [0,1], & \text{if } u = 0, \\ \{1\}, & \text{if } u > 0. \end{cases}$$

2D Model: dimensionless equations

Denote $\epsilon := \frac{l}{L}$, ...
Assumptions: symmetry w.r.t. y-axis, $c_1 = c_2 = c_{ref} u^\epsilon$

$$\begin{cases} u_t^\epsilon = \nabla \cdot (D \nabla u^\epsilon - q^\epsilon u^\epsilon), \\ \epsilon^2 \mu \Delta q^\epsilon = \nabla p^\epsilon, \\ \nabla \cdot q^\epsilon = 0, \\ u^\epsilon,\ q^\epsilon \text{ and } p^\epsilon \text{ symmetric around } y = 0, \end{cases} \quad \text{in } \Omega^\epsilon(t),$$

$$\begin{cases} d_t^\epsilon = k(r(u^\epsilon) - w)\sqrt{1 + (\epsilon d_x^\epsilon)^2}, \\ w \in H(d^\epsilon), \\ \nu^\epsilon \cdot (D \nabla u^\epsilon - q^\epsilon u^\epsilon) = -\epsilon k(r(u^\epsilon) - w)(\rho - u^\epsilon), \\ q^\epsilon = -\epsilon K k(r(u^\epsilon) - w)\nu^\epsilon, \end{cases} \quad \text{on } \Gamma^\epsilon(t)$$

where

$$\Omega^\epsilon(t) := \{(x, y) \,|\, 0 \le x \le 1,\ -\epsilon(1/2 - d^\epsilon(x,t)) \le y \le \epsilon(1/2 - d^\epsilon(x,t))\},$$

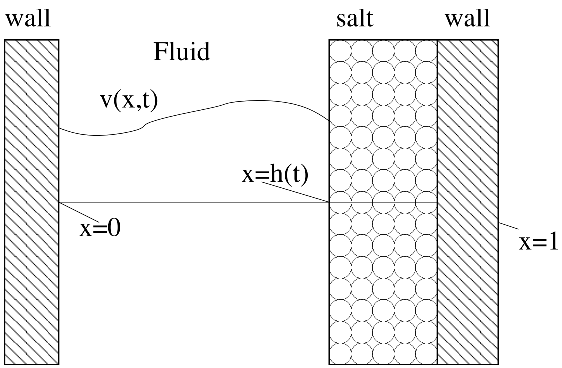
and where

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

1D model

Assumptions:

- no flow: $q = 0$
- 1D



$$\begin{cases} \partial_t v = \partial_x^2 v, & \text{for } x \in (0, h(t)), \\ \partial_x v = 0, & \text{for } x = 0, \\ \partial_x v = (\rho - v)h'(t), & \text{for } x = h(t), \\ h'(t) = D_a(w(t) - r(v)), & \text{for } x = h(t), \\ w(t) \in H(1 - h(t)). \end{cases}$$

Theorem: *There exists a unique, positive and bounded solution.* (Pop, v.N. *IMA J. Appl. Math.* 2008) ,

2D/3D: existence and uniqueness are open

2D Simulation: dissolution in strip

(Movie)

Thin strip: upscaling

Formal assymptotics for $\epsilon \to 0$

Assume

$$
\begin{aligned}
u^\epsilon(x,y,t) &= u_0(x,\frac{y}{\epsilon},t) + \epsilon u_1(x,\frac{y}{\epsilon},t) + \epsilon^2(\ldots), \\
q^\epsilon(x,y,t) &= q_0(x,\frac{y}{\epsilon},t) + \epsilon q_1(x,\frac{y}{\epsilon},t) + \epsilon^2(\ldots), \\
p^\epsilon(x,y,t) &= p_0(x,\frac{y}{\epsilon},t) + \epsilon p_1(x,\frac{y}{\epsilon},t) + \epsilon^2(\ldots), \\
d^\epsilon(x,t) &= d_0(x,t) + \epsilon d_1(x,t) + \epsilon^2(\ldots).
\end{aligned}
$$

The vertical coordinate of the variables $u_i(x,z,t)$, $q_i(x,z,t)$ and $p^\epsilon(x,z,t)$ are rescaled. They are defined on

$$\Omega(t) := \{(x,z) | 0 \le x \le 1, \, -1/2 + d^\epsilon \le z \le 1/2 - d^\epsilon\}.$$

Formal asymptotics

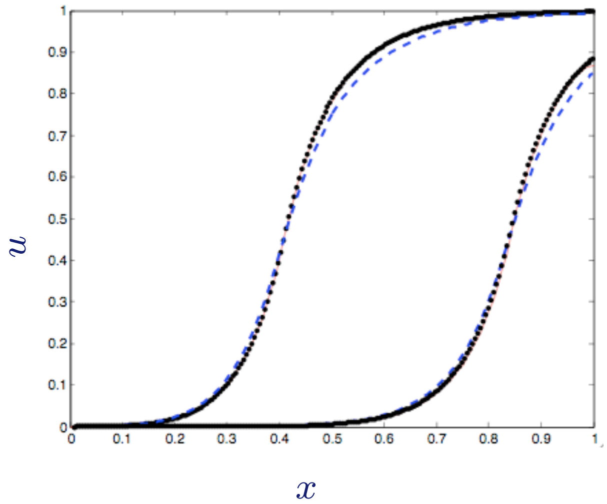
Substituting the asymptotic expansions, integrating along the z-coordinate, and retaining only terms independent of ϵ, yields

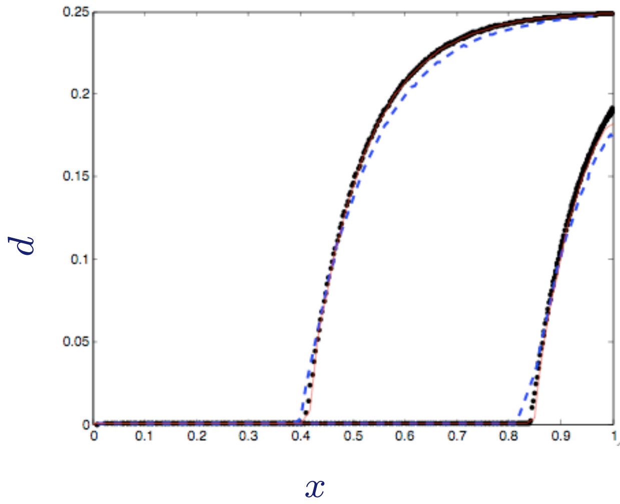
$$\begin{cases} \partial_t((1-2d_0)u_0 + 2\rho d_0) = \partial_x(D(1-2d_0)\partial_x u_0 - \bar{q}u_0), \\ \partial_x \bar{q} - 2K\partial_t d_0 = 0, \\ \partial_t d_0 \in k(r(u_0) - H(d_0)), \end{cases}$$

where

$$\bar{q}(x,t) = \int_{-1/2+d_0(x,t)}^{1/2-d^0(x,t)} q_0^{(1)}(x,z,t)\, dz.$$

Thin strip: upscaled vs. original equations





Profiles of both 2-D and effective model, for $t = 20$ and $t = 40$.

Thin line: solution of the effective model

Dashed line: 2-D model with $\epsilon = 0.1$

Dots: 2-D model with $\epsilon = 0.01$

Thin strip: traveling wave

Non-negative traveling wave solutions:
$u = u(\eta)$, $d = d(\eta)$ and $q = q(\eta)$ with $\eta = x - at$, and $d < 1/2$, satisfying

$$\left.\begin{array}{l} -a((1-2d)u + 2\rho d)' - ((1-2d)Du' - qu)' = 0, \\ -ad' \in k(r(u) - H(d)), \\ q' + 2aKd' = 0, \end{array}\right\} \text{ in } \mathbb{R}.$$

and boundary conditions

$$\begin{aligned} u(-\infty) &= u^*,\ u(\infty) = u_*, \\ d(-\infty) &= d^*,\ d(\infty) = d_*, \\ q(-\infty) &= q^*, \end{aligned}$$

where $0 \le u^*, u_*, q^*$ and $0 \le d^*, d_* < 1/2$.

Thin strip: traveling wave (2)

$$I \begin{cases} d_* > 0, & d^* = 0 \\ u_* = u_s, & 0 \le u^* < u_s \end{cases} \quad \text{(dissolution wave)}$$

$$II \begin{cases} d^* > 0, & d_* = 0 \\ u^* = u_s, & 0 \le u_* < u_s \end{cases} \quad \text{(precipitation wave)}$$

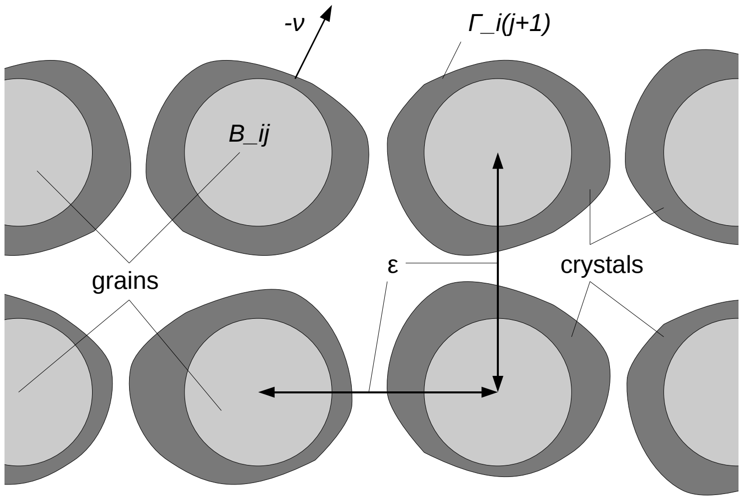
Theorem. *No traveling wave exists with boundary conditions from class II.*

Theorem. *For any set of boundary conditions from class I, there exists a traveling wave (unique up to a shift).*

(v.N. *EJAM* 2008)

(Compare to results in Knabner, Van Duijn, *EJAM* 1997: crystal layer has infinitesimal thickness, can be obtained as formal limit $\rho \to \infty$)

Perforated Domain



Level set function S such that $\Gamma = \{S = 0\}$.
Evolution of Γ given by

$$S_t + |\nabla S| v_n = S_t - \frac{1}{\rho_c}(k_p r(c_1, c_2) - k_d w(x))|\nabla S| = 0$$

Expand S^ϵ

Perforated Domain: homogenization

Formal assymptotics for $\epsilon \longrightarrow 0$

Assume

$$
\begin{aligned}
u^\epsilon(x,t) &= u_0(x,\frac{x}{\epsilon},t) + \epsilon u_1(x,\frac{x}{\epsilon},t) + \epsilon^2(\ldots),\\
q^\epsilon(x,t) &= q_0(x,\frac{x}{\epsilon},t) + \epsilon q_1(x,\frac{x}{\epsilon},t) + \epsilon^2(\ldots),\\
p^\epsilon(x,t) &= p_0(x,\frac{x}{\epsilon},t) + \epsilon p_1(x,\frac{x}{\epsilon},t) + \epsilon^2(\ldots),\\
S^\epsilon(x,t) &= S_0(x,\frac{x}{\epsilon},t) + \epsilon S_1(x,\frac{x}{\epsilon},t) + \epsilon^2(\ldots).
\end{aligned}
$$

Where $u_k(\cdot,y,\cdot)$, $q_k(\cdot,y,\cdot)$, $p_k(\cdot,y,\cdot)$ and $S_k(\cdot,y,\cdot)$ are 1-periodic in y.

Upscaled equations

$$\begin{cases} \partial_t S_0(x,y,t) - f(u_0(x,t),y)|\nabla_y S_0(x,y,t)| = 0 & y \in [0,1]^2 \\ \partial_t(|Y_0(x,t)|u_0) = \nabla_x \cdot (D\mathcal{A}(x,t)\nabla_x u_0 - \bar{q}u_0) + |\Gamma_0(x,t)|f(u_0)\rho & x \in \Omega \\ \bar{q} = -\frac{1}{\mu}\mathcal{K}(x,t)\nabla_x p_0 & x \in \Omega \\ \nabla_x \cdot \bar{q} = |\Gamma_0(x,t)|K f(u_0) & x \in \Omega \end{cases}$$

where

$$f(u_0(x,t),y) = k(u_0^2 - H_\delta(dist(y,\Gamma)))$$
$$Y_0(x,t) = \{S_0 < 0\}$$
$$\Gamma_0 = \{S_0 = 0\}$$

(Hard step: interchange ∇_x and integration

$$\begin{aligned} |Y_0(x,t)|\partial_t u_0 &= \int_{Y_0(x,t)} \nabla_y \cdot (\nabla_y u_2 + \nabla_x u_1 - q_1 u_0 - q_0 u_1)\, dy \\ &+ \int_{Y_0(x,t)} \nabla_x \cdot (\nabla_y u_1 + \nabla_x u_0 - q_0 u_0)\, dy \end{aligned}$$

(v.N. *MSS* 2008))

where the tensors $\mathcal{A} = (a_{ij})_{i,j}$ and $\mathcal{K} = (k_{ij})_{i,j}$ are given by

$$a_{ij} = \int_{Y_0(x,t)} \delta_{ij} + \partial_{y_i} v_j \, dy,$$

where v_j solves the cell-problem

$$\begin{cases} \Delta_y v_j = 0 & y \in Y_0(x,t) \\ \nu_0 \nabla_y v_j = -e_j & y \in \Gamma_0(x,t) \\ \text{periodicity in } y, \end{cases}$$

and

$$k_{ij} = \int_{Y_0(x,t)} w_{ji} \, dy,$$

where the vector w_j with components w_{ji} solves the cell-problem

$$\begin{cases} \Delta_y w_j = \nabla_y \pi_j + e_j & y \in Y_0(x,t) \\ \nabla_y \cdot w_j = 0 & y \in Y_0(x,t) \\ w_j = 0 & y \in \Gamma_0(x,t) \\ \text{periodicity in } y, \end{cases}$$

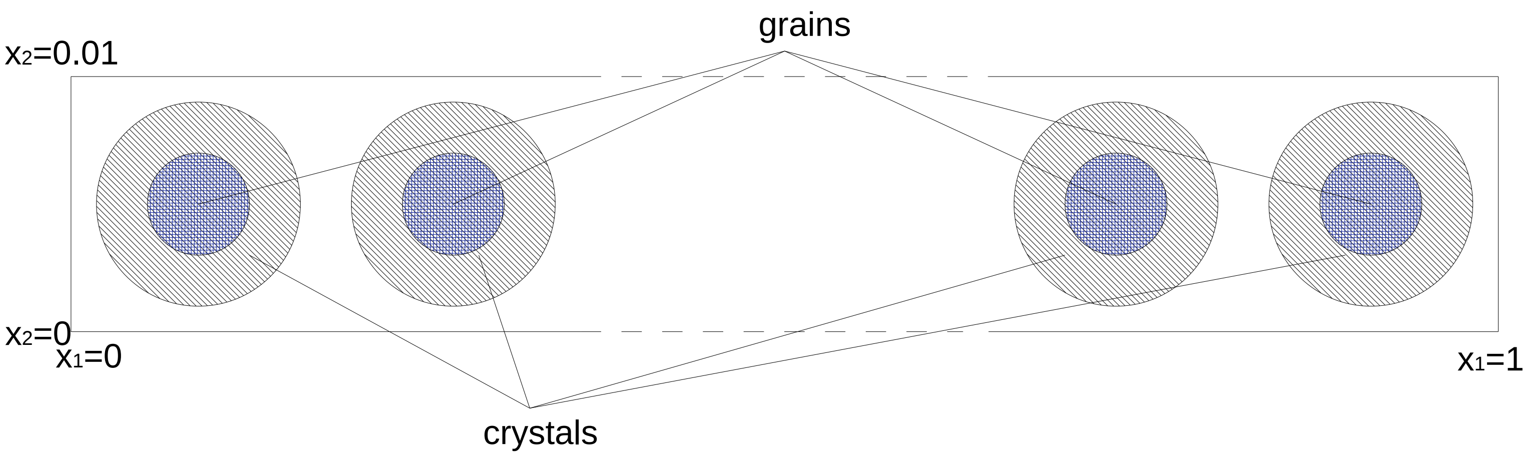
with π_j the corresponding pressure.

Simplification: circular grains

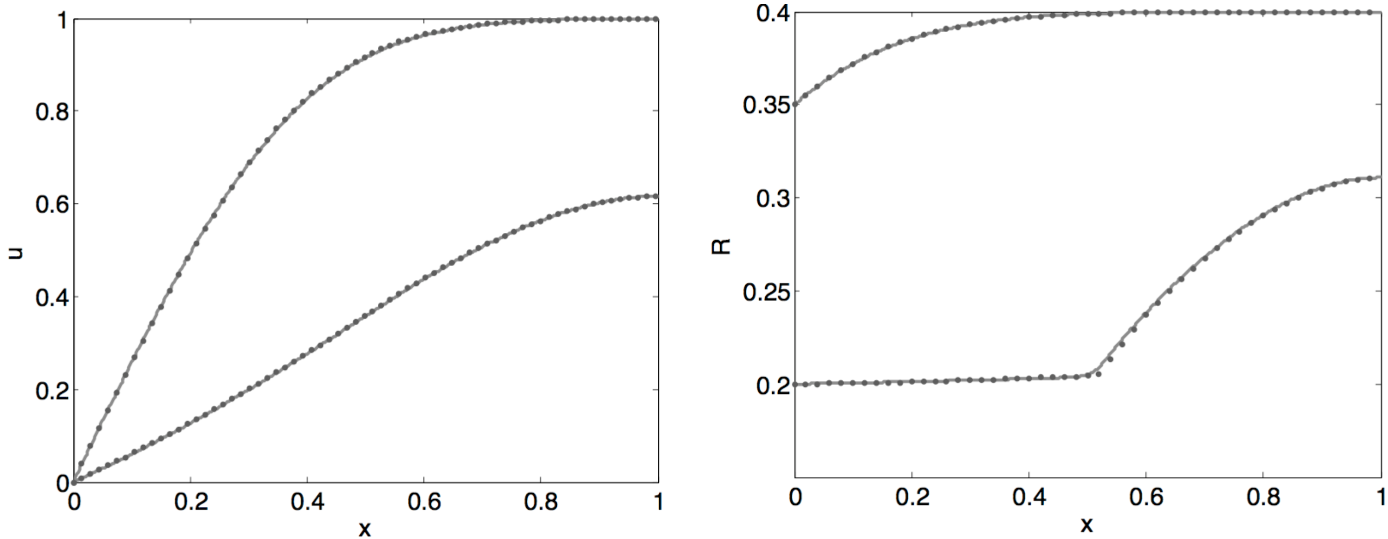
$$\begin{cases} \partial_t R(x,t) = f(u_0, R(x,t)) := k(u_0^2 - H_\delta(R - R_{min})) & x \in \Omega \\ \partial_t((1-\pi R^2)u_0) = \nabla_x \cdot (D\mathcal{A}(R)\nabla_x u_0 - \bar{q}u_0) + 2\pi R f(u_0, R)\rho & x \in \Omega \\ \bar{q} = -\frac{1}{\mu}\mathcal{K}(R)\nabla_x p_0 & x \in \Omega \\ \nabla_x \cdot \bar{q} = 2\pi R K f(u_0) & x \in \Omega \end{cases}$$

Periodicity in x_2 direction

(Similar simplification is possible for ellipses, not for squares!)



Perforated domain
upscaled vs. original equations



Profiles of both 2-D and effective model, for $t = 10$ and $t = 40$.

Dots: 2-D model with $\epsilon = 0.01$

Line: effective model

Open problems / Future directions

* Existence, uniqueness, estimates for microscale free boundary model in 2D/3D?

* Rigorous upscaling (phase-field formulation, with Ch. Eck)

* Blocking of strip ($d = 1/2$)?

* Application to biofilm growth models (with R. Helmig)