University of Stuttgart
Germany

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MS24 Modeling with Constraints and Phase Transitions
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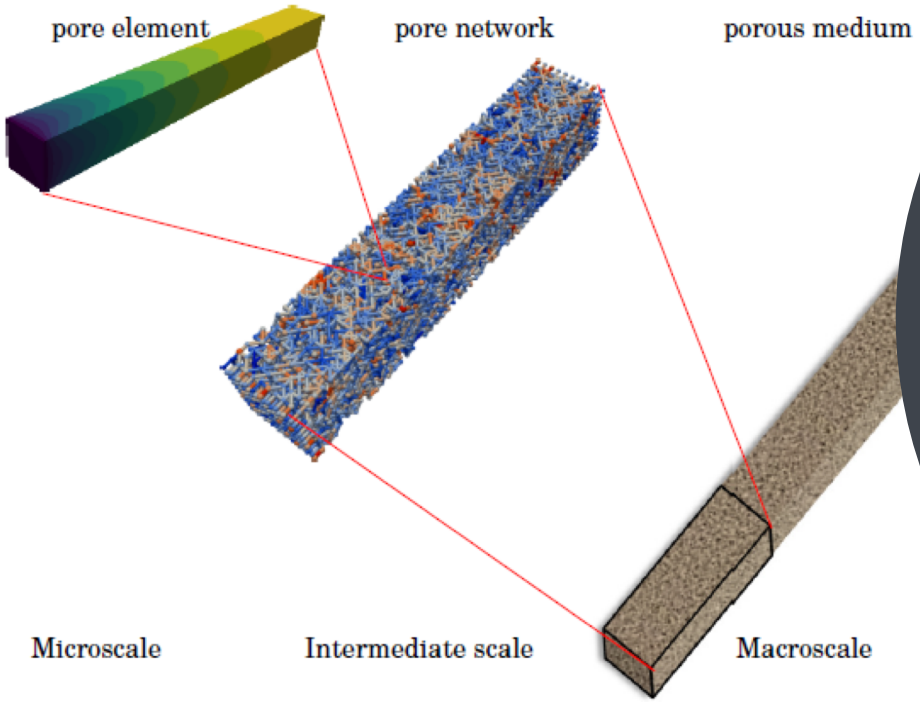

Analysing spatial scaling effects in mineral reaction rates in porous media with a hybrid numerical model

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Motivation

Limits on upscalability from pore to Darcy scale

- The dissolution and precipitation of minerals in porous media are highly localized processes – as opposed to diffusion and advection which involve spatial gradients.

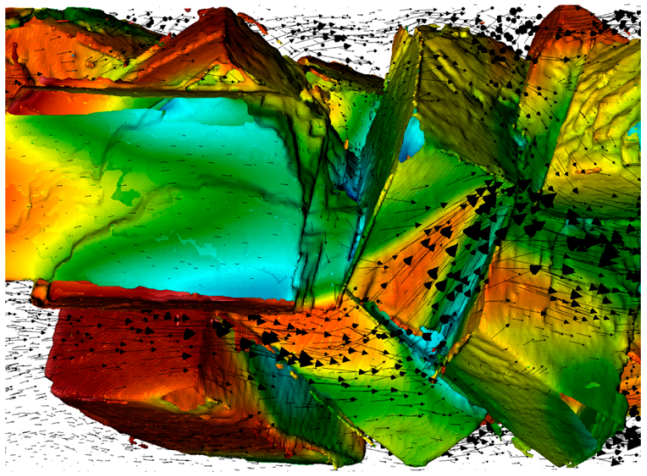
- It has been shown that such local processes can only accurately be upscaled to the Darcy scale if certain criteria are fulfilled:

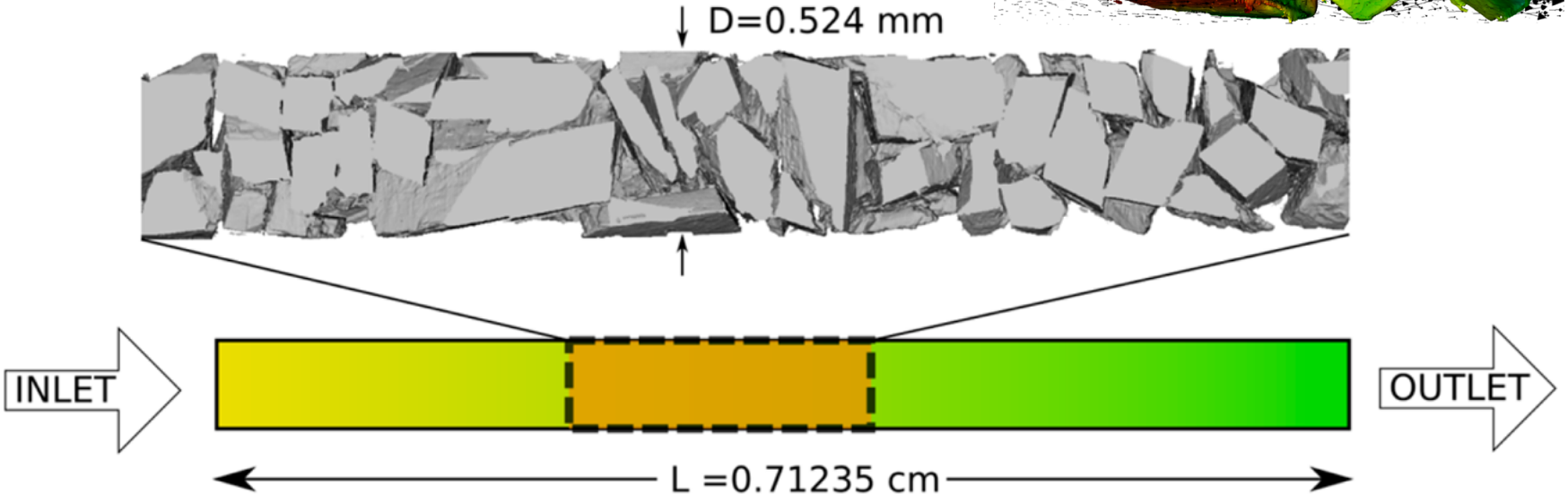
$$Pe < \varepsilon^{-2} \qquad Da < 1 \qquad \frac{Da}{Pe} < \varepsilon$$

Boso, F. and Battiato, I. (2013). Homogenizability conditions for multicomponent reactive transport. *Adv. Wat. Resour.* **62**.

How to overcome these restrictions?

Direct simulations

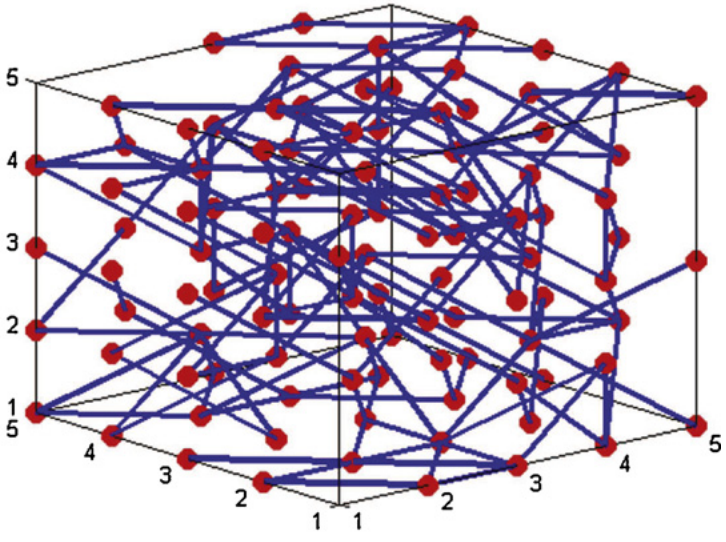


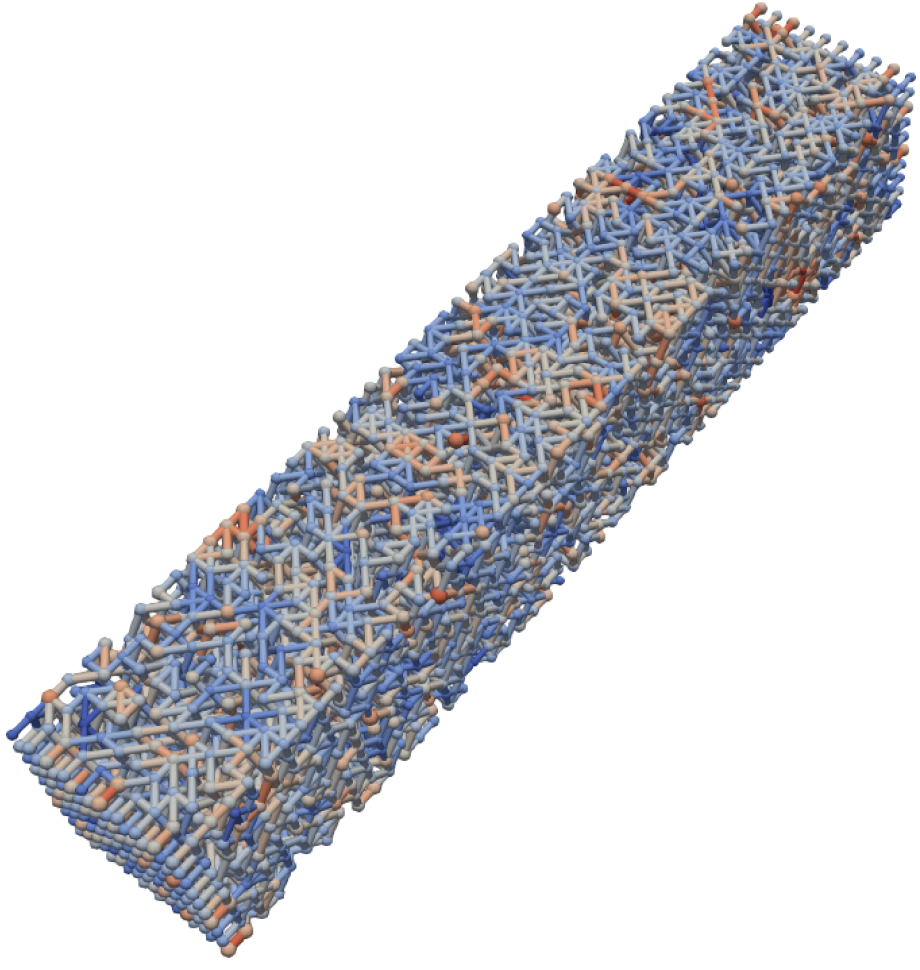


Molins, S. et al (2014). Pore-Scale Controls on Calcite Dissolution Rates from Flow-through Laboratory and Numerical Experiments. *Environ. Sci. Technol.* **48**.

How to overcome these restrictions?

Pore-network models

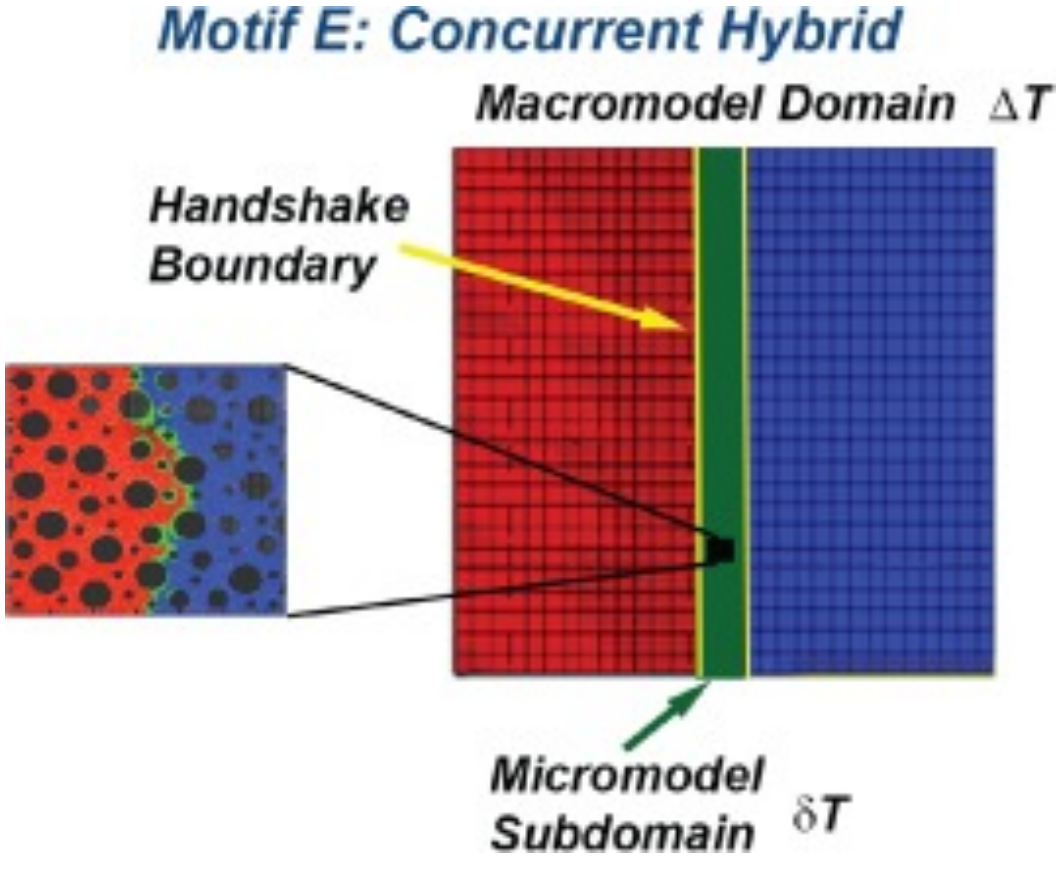




Raoof A. et al (2012). Pore-scale modeling of reactive transport in wellbore cement under CO_2 storage conditions, *Int. J. Greenhouse Gas Control* **11**.

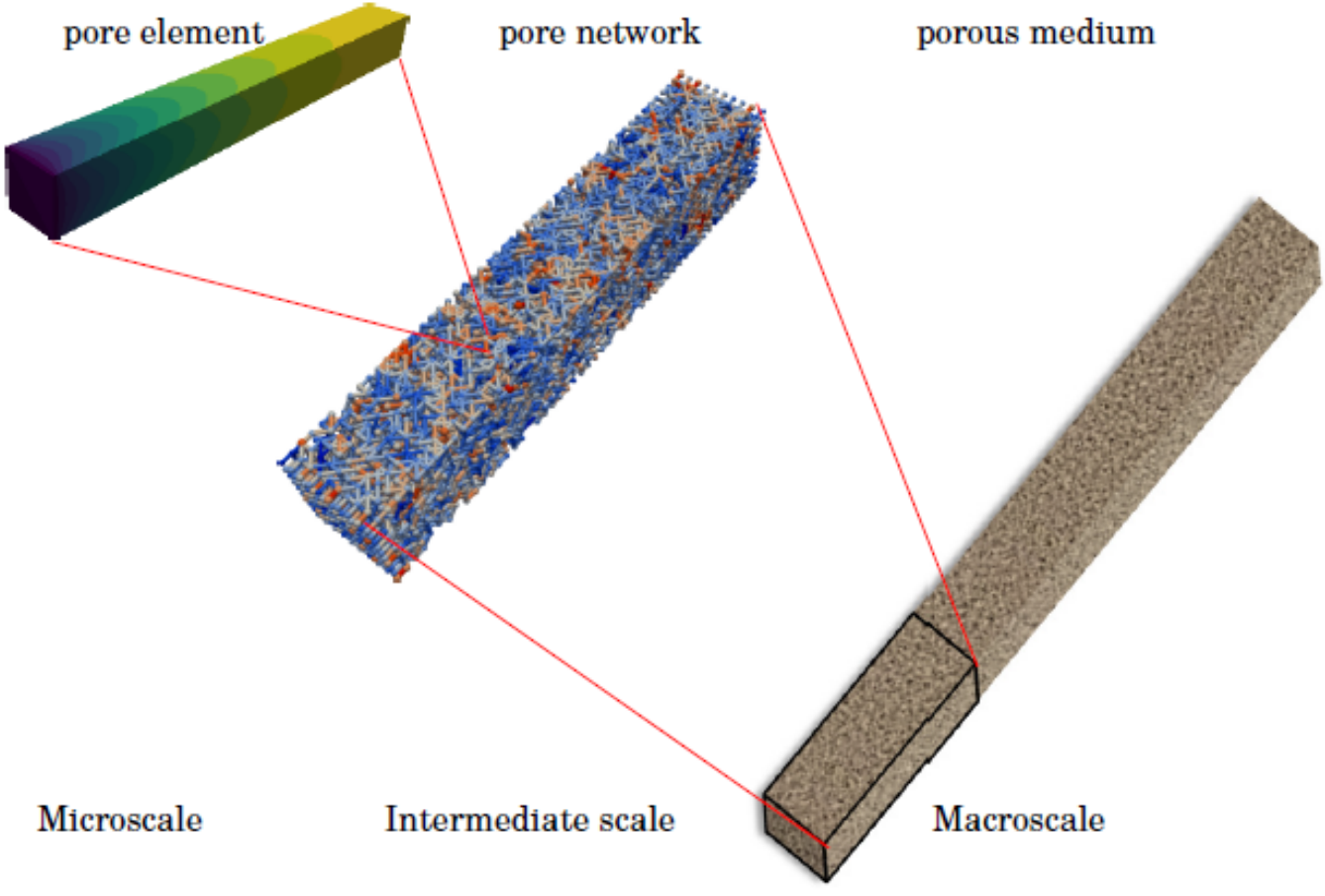
How to overcome these restrictions?

Hybrid Models

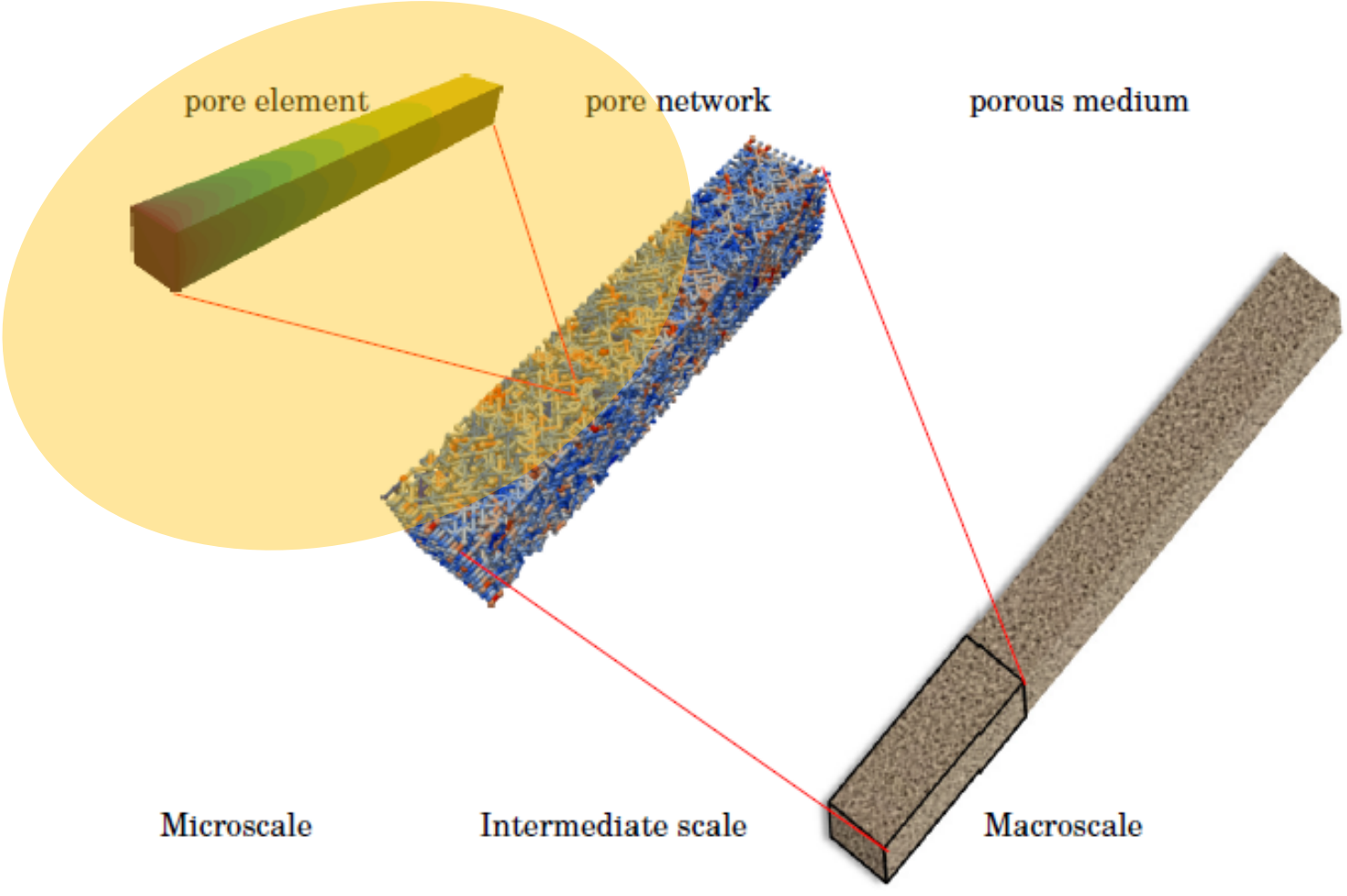


Scheibe, T. D. et al (2015). An Analysis Platform for Multiscale Hydrogeologic Modeling with Emphasis on Hybrid Multiscale Methods, *Groundwater* **53**.

Our hybrid model concept



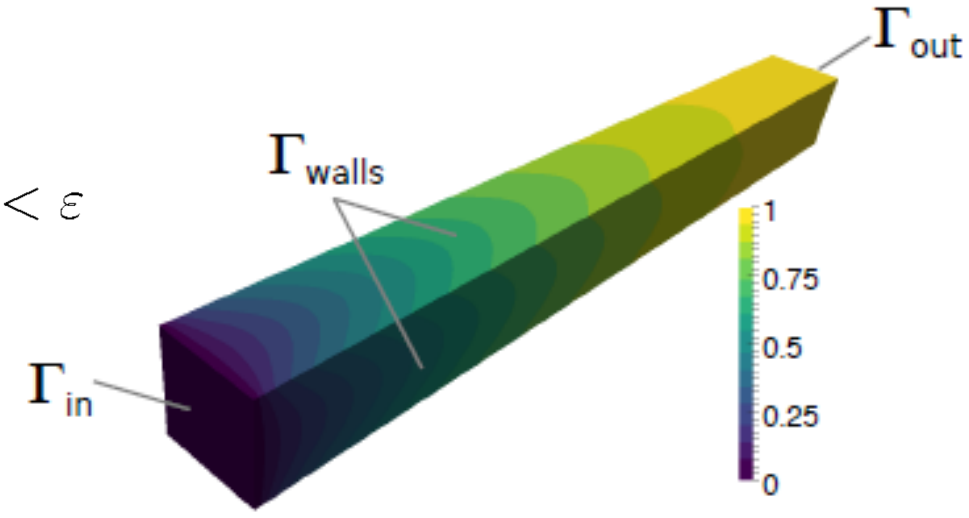
Microscale → Intermediate Scale

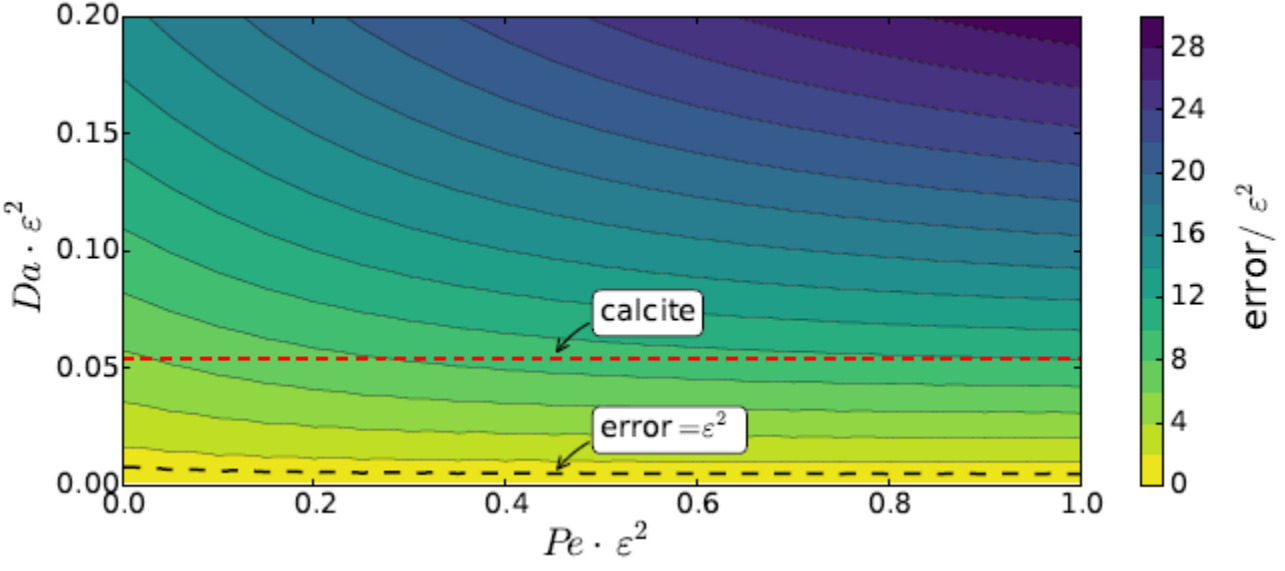


Single elongated pore

$$Pe < \varepsilon^{-2} \qquad Da < 1 \qquad \frac{Da}{Pe} < \varepsilon$$

ε = Ly/Lx = Lz/Lx





Reactive Transport at the micro-scale

Modeling reaction on the surface of calcites

$$\mathrm{CaCO_3} + \mathrm{H^+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Ca^{2+}} + \mathrm{HCO_3^-}$$

$$\mathrm{CaCO_3} + \mathrm{H_2CO_3^*} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Ca^{2+}} + 2\,\mathrm{HCO_3^-}$$

$$\mathrm{CaCO_3} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{Ca^{2+}} + \mathrm{CO_3^{2-}}$$

The total forward (R_f) and backward (R_b) rates can be expressed as:

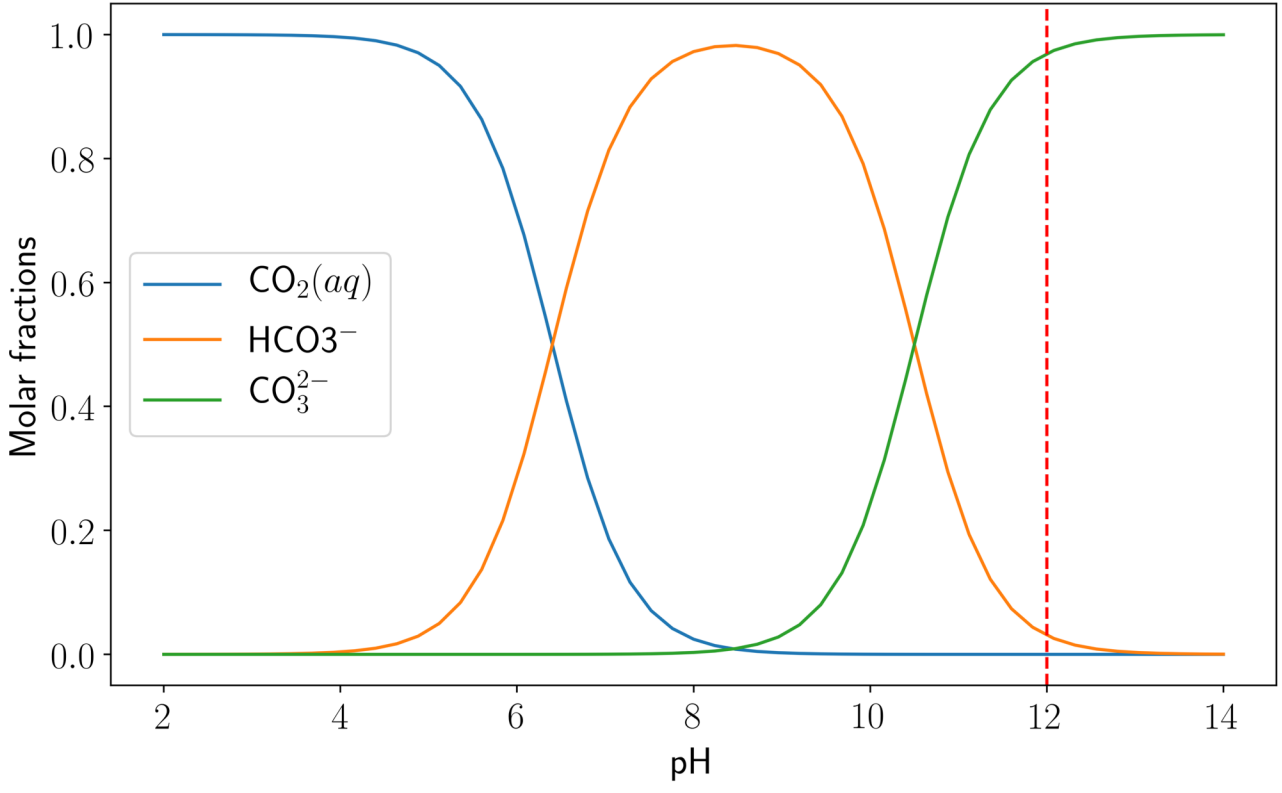
$$R_f = k_1 a_{\mathrm{H^+}} + k_2 a_{\mathrm{H_2CO_3^*}} + k_3,$$

$$R_b = k_{-1} a_{\mathrm{Ca^{2+}}} a_{\mathrm{HCO_3^-}} + k_{-2} a_{\mathrm{Ca^{2+}}} a_{\mathrm{HCO_3^-}}{}^2 + k_{-3} a_{\mathrm{Ca^{2+}}} a_{\mathrm{CO_3^{2-}}},$$

L. Chou et al (1989). Comparative study of the kinetics and mechanisms of dissolution of carbonate minerals. *Chemical Geology* **78**.

Reactive Transport at the micro-scale

Focusing on the simple case where pH>12



W. Dreybrodt (1988). *Processes in Karst Systems: Physics, Chemistry, and Geology*. Springer.

Reactive Transport at the micro-scale

Simplification to one reaction

$$\mathrm{CaCO_3} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{Ca^{2+}} + \mathrm{CO_3^{2-}}$$

The total forward (R_f) and backward (R_b) rates can be expressed as:

$$R_f = k_3,$$

$$R_b = k_{-3} a_{\mathrm{Ca^{2+}}} a_{\mathrm{CO_3^{2-}}},$$

L. Chou et al (1989). Comparative study of the kinetics and mechanisms of dissolution of carbonate minerals. *Chemical Geology* **78**.

Reactive Transport at the micro-scale

Simplification to first-order reaction

- C: Concentration of the calcium ion
- D_c: Diffusion coefficient
- Damköhler number is scaled by the precipitation-rate coefficient

$$D_c \int_\Gamma \hat{\mathbf{n}} \cdot \boldsymbol{\nabla} C d\Gamma = \int_\Gamma (k_3 - k_{-3} C^2) d\Gamma.$$

$$k^*_{-3} = k_{-3}[{\mathrm{CO_3}}^{2-}]$$

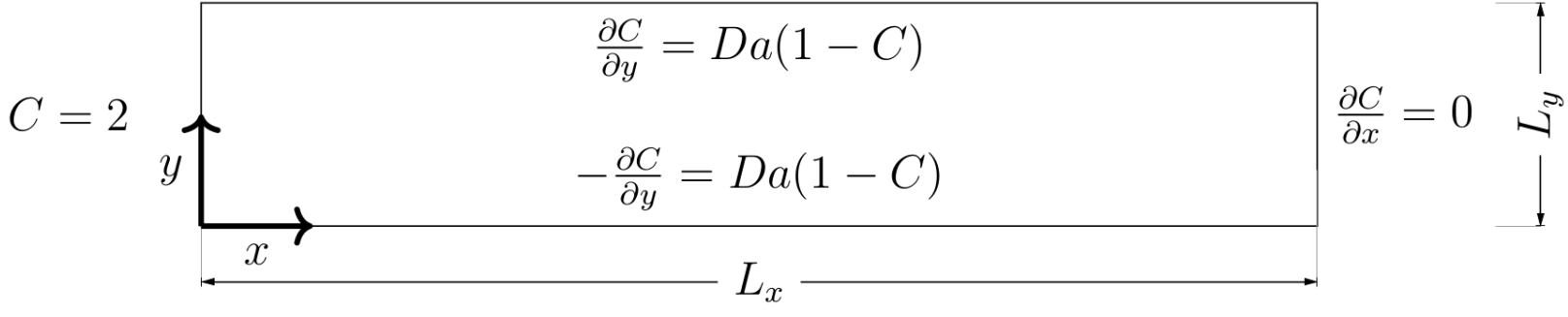
$$Da = \frac{k^*_{-3} L_y}{D_c}.$$

Reactive Transport at the micro-scale

Final mathematical model

Using the lubrication theory approach, ε = Ly/Lx

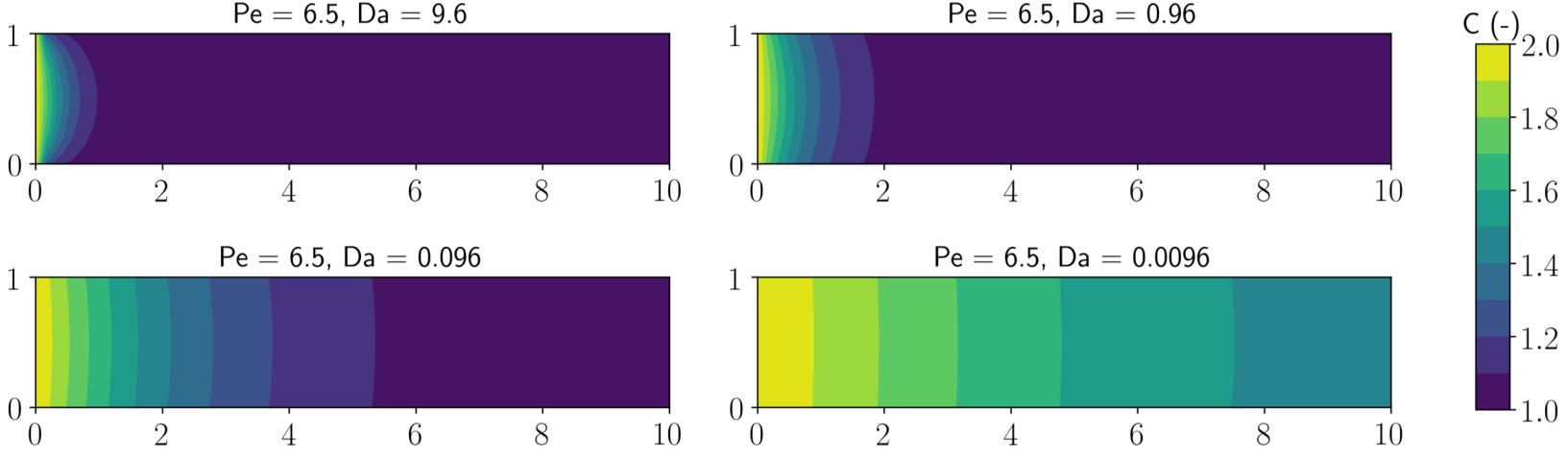
$$Pe\frac{\partial C}{\partial t} + Pe\boldsymbol{u}\cdot\boldsymbol{\nabla}^{*}C - (\frac{\partial^2 C}{\partial x^2} + \frac{1}{\epsilon^2}\frac{\partial^2 C}{\partial y^2}) = 0,$$



Reactive Transport at the micro-scale

Solution snapshots for varying Da

- Solved using FEniCs.
- ε = 0.1



Q. Kang et al. (2014). Pore-scale study of dissolution-induced changes in permeability and porosity of porous media. Journal of Hydrology **517**.

Upscaling to the Pore-Network-scale

Leading-order asymptotic solution

- Diffusion-dominated dissolution problem, Pe << 1.
- Can provide information to pore network models.

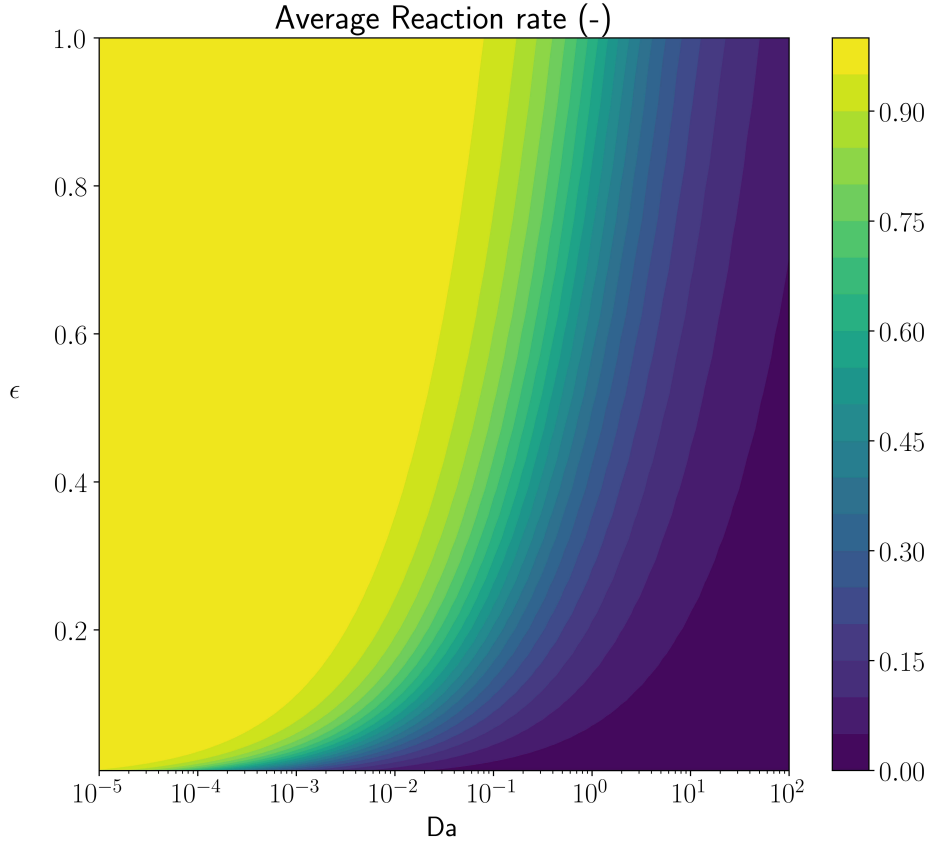
$$C^*(x^*) = \operatorname{sech}\left(\frac{\sqrt{2Da}}{\epsilon}\right)\cosh\left(\frac{\sqrt{2Da}}{\epsilon}(1-x^*)\right)+1$$

The average reaction rate per surface area is

$$\bar{R}_{micro} = k_3\int_0^1 |(1-C^*(x^*))|dx^* = k_3\frac{\tanh\left(\sqrt{2Da}/\epsilon\right)}{\sqrt{2Da}/\epsilon}.$$

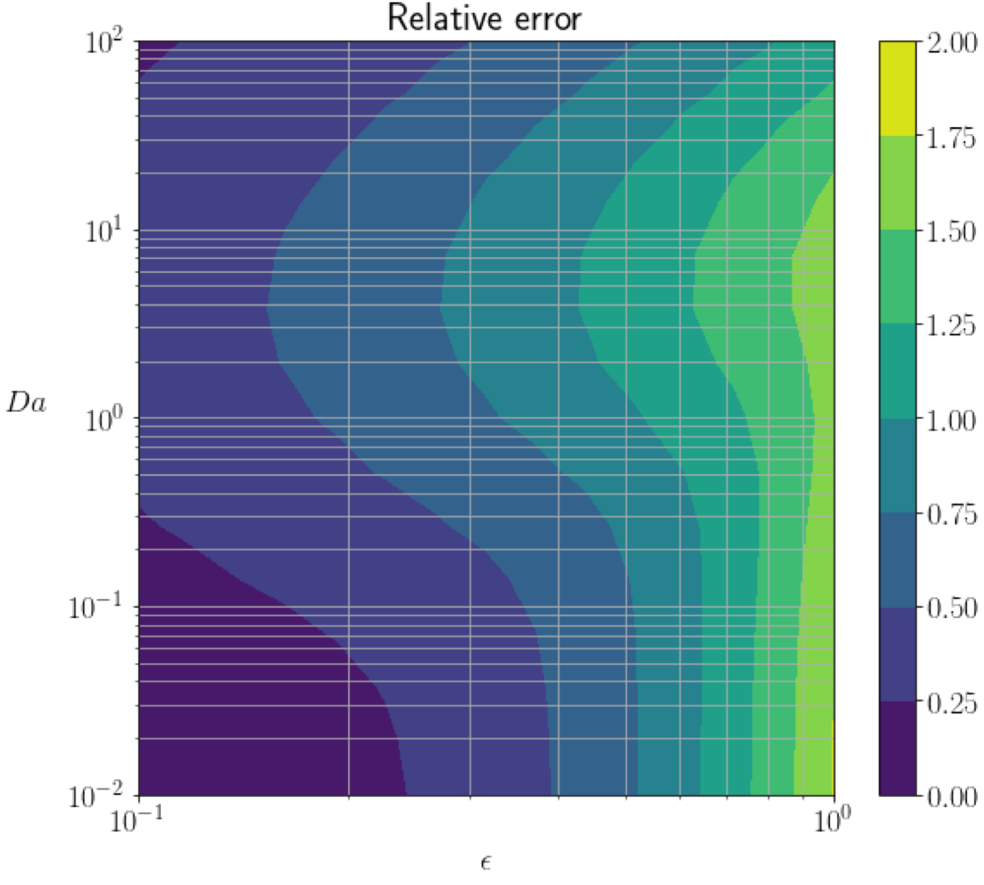
Upscaling to the Pore-Network-scale

Average reaction rates based on leading-order analytical solution

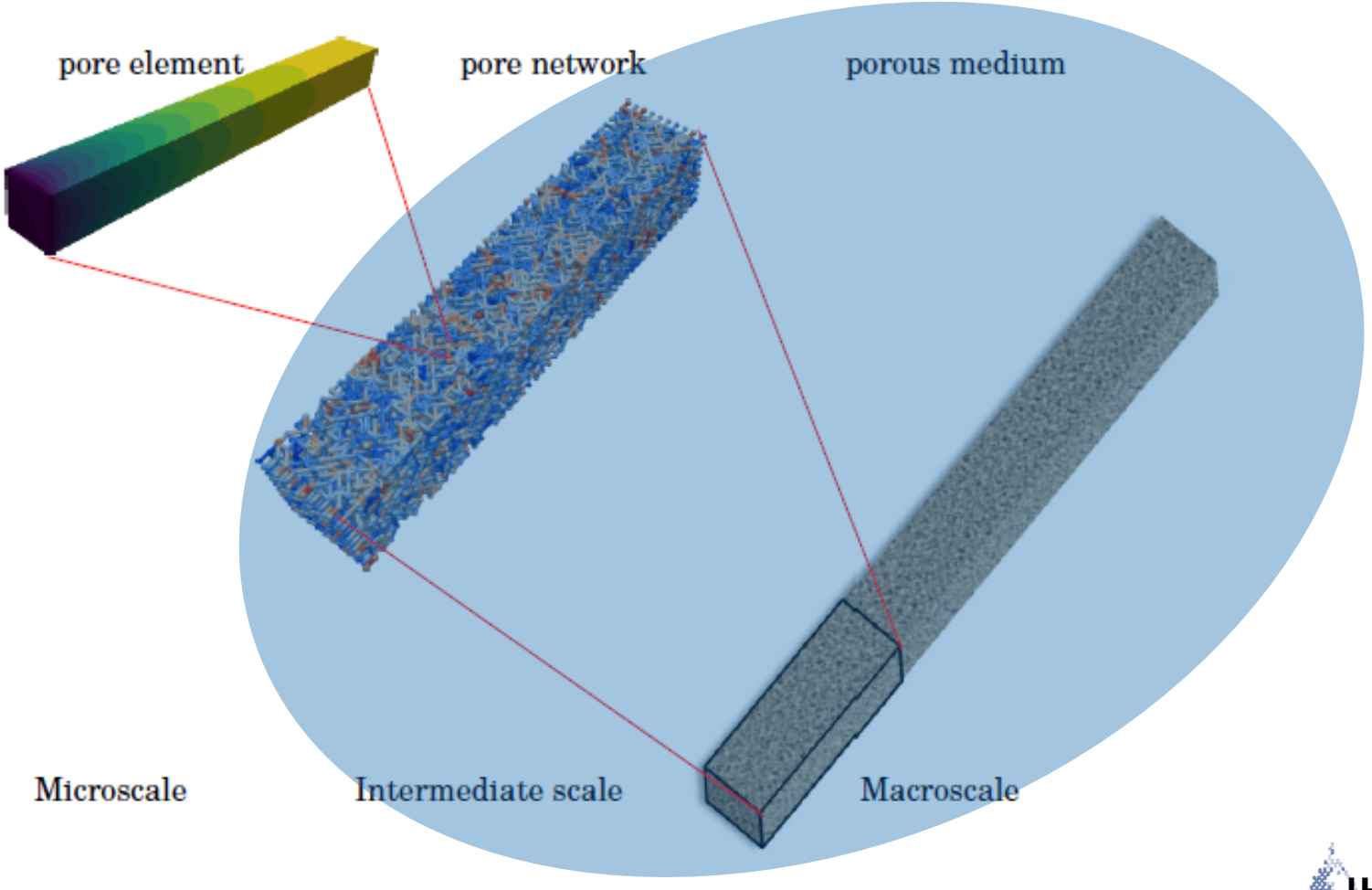


Upscaling to the Pore-Network-scale

Comparison of leading-order analytical with numerical solution



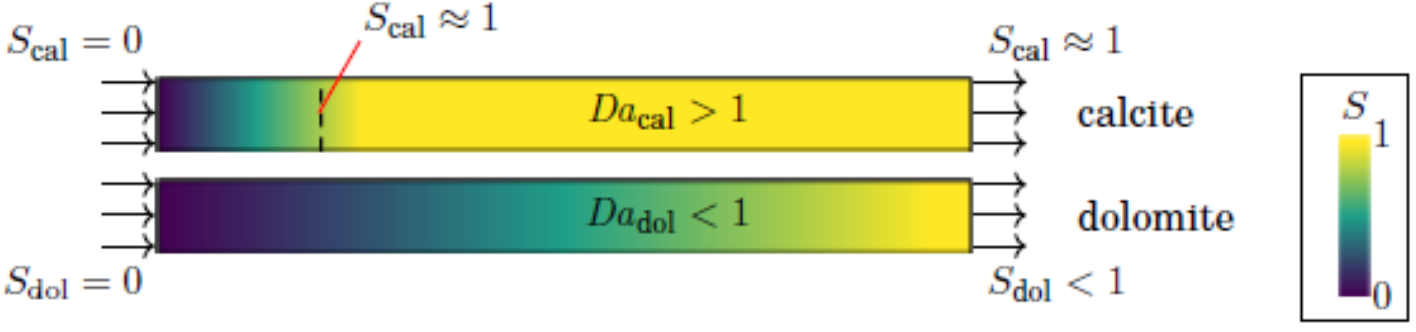
Intermediate Scale ↔ Macroscale



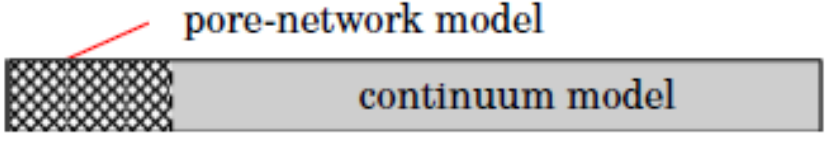
Possible decomposition scenarios

Flow-through setup, small Pe, rapid dissolution only in parts of the domain

a) Flow-through experiment



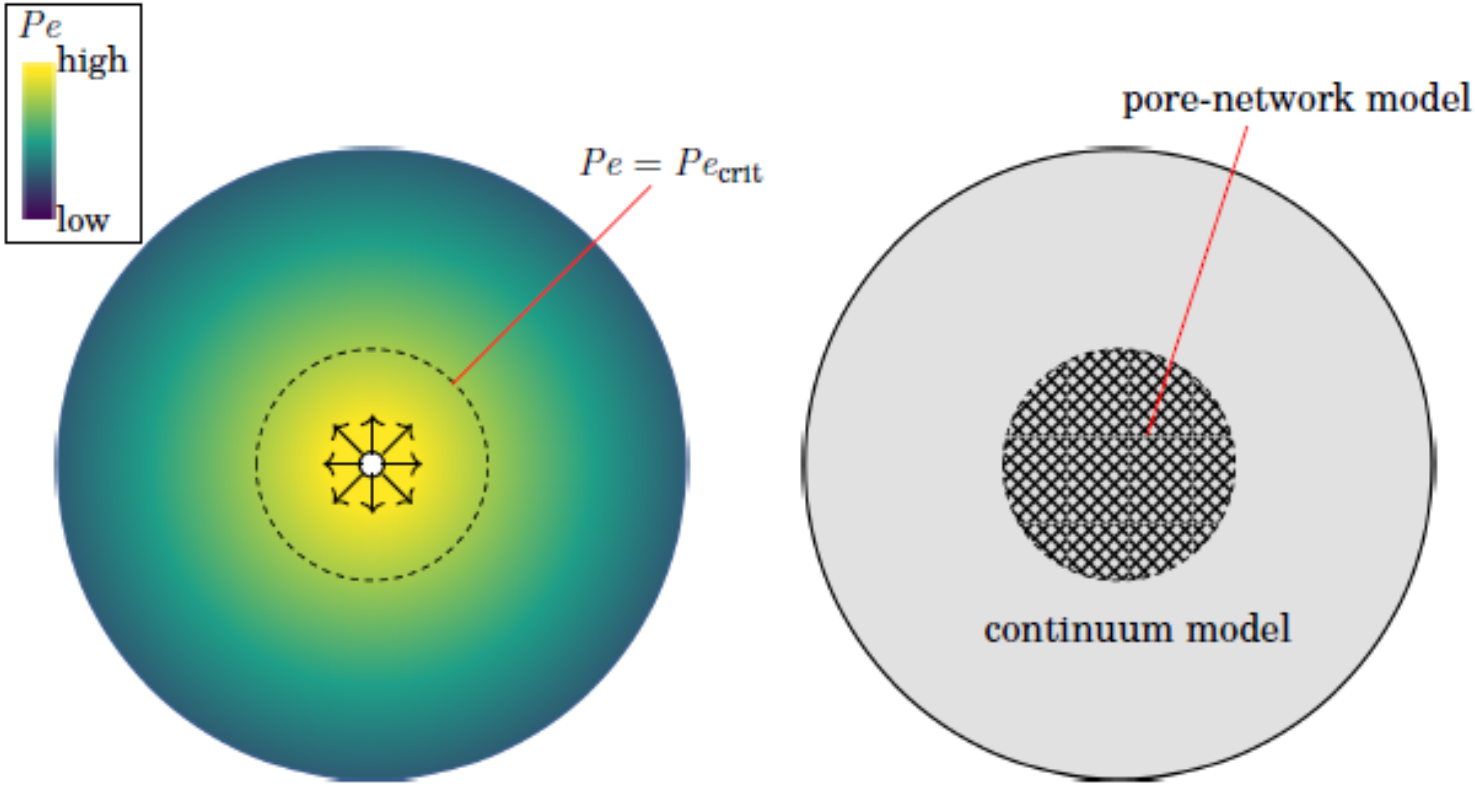
b) Saturation states



c) Model domains

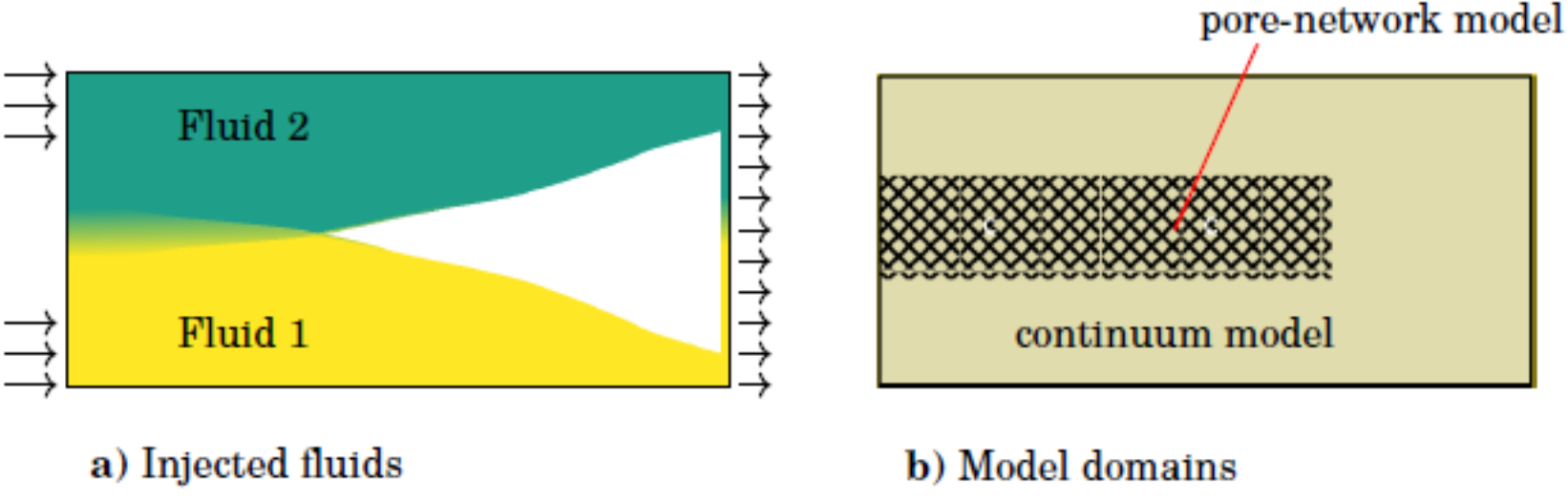
Possible decomposition scenarios

Radial injection, strong variation of Pe



Possible decomposition scenarios

Reacting components injected at different locations, small mixing zone



a) Injected fluids

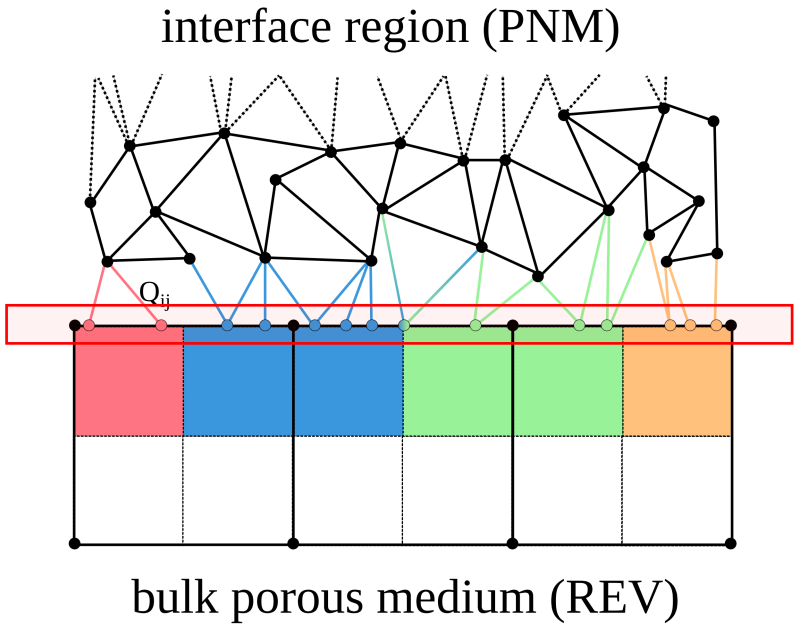
b) Model domains

Darcy – PNM coupling (K. Weishaupt, LH2)

Coupling conditions

$$\int_{\Gamma_{\mathrm{cell}}} [\rho \mathbf{v_f} \cdot \mathbf{n}]^{\mathrm{REV}} \mathrm{d}\Gamma = \sum_{ij, \mathbf{x_i} \in \Gamma_{\mathrm{cell}}} [(\rho Q)_{ij}]^{\mathrm{PNM}}$$

$$[p]^{\mathrm{PNM}} = [p]^{\mathrm{REV}}$$



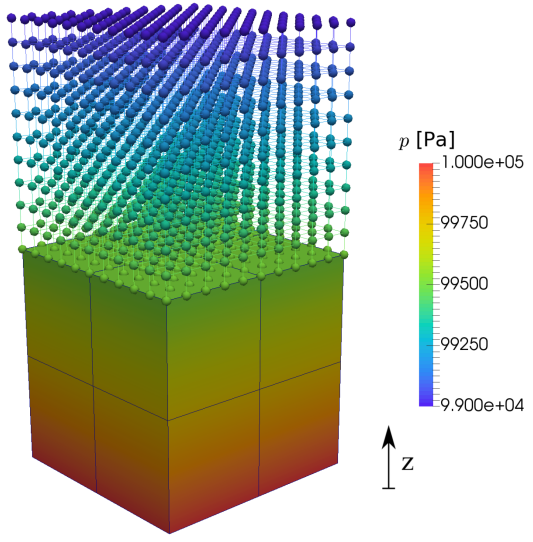
- coupling of **different concepts / scales**

- assumption: pore-scale pressure matches **averaged REV-scale pressure**
  (e.g. Hassanizadeh, & Gray, 1979; Nordbotten et al., 2008)
- assumption: local thermodynamic equilibrium

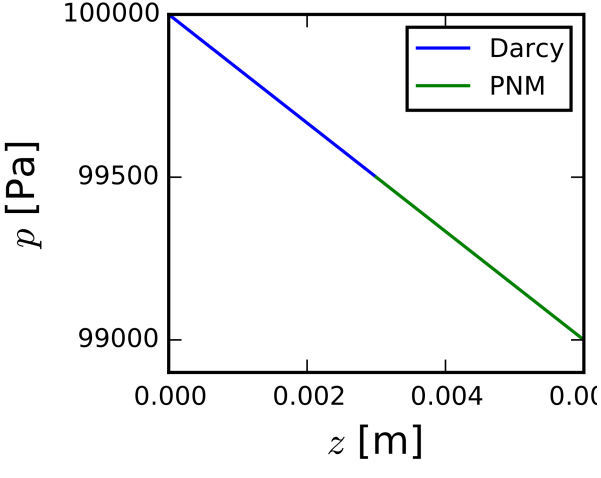
Darcy – PNM coupling (K. Weishaupt, LH2)

Single-phase flow test, w/o transport and reaction

- Dirichlet boundary conditions for p on top and bottom
- Neumann no-flow elsewhere
- upscaled **K** for Darcy domain



- mass conservative
- continuity of pressure
- identical pressure gradients



DuMu^x

LH^2

Summary and future work

- Exploit pore-network models to bridge between pore and Darcy scale.
- Admit fast reactions within the pore elements.
- Use asymptotic analysis and numerical simulations at the pore-element scale to provide information to the pore-network scale.
- Decompose the computational domain into pore-network and Darcy subdomains.

- Consider other pH regimes that involve bicarbonate and carbonic acid.
- Take porosity changes into account.
- Adapt dynamically the decomposition into pore-network and Darcy subdomains.

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Thank you for your attention!

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