Chemically Reactive Transport in Heterogeneous Unsaturated Porous Media: Experiments and Simulations

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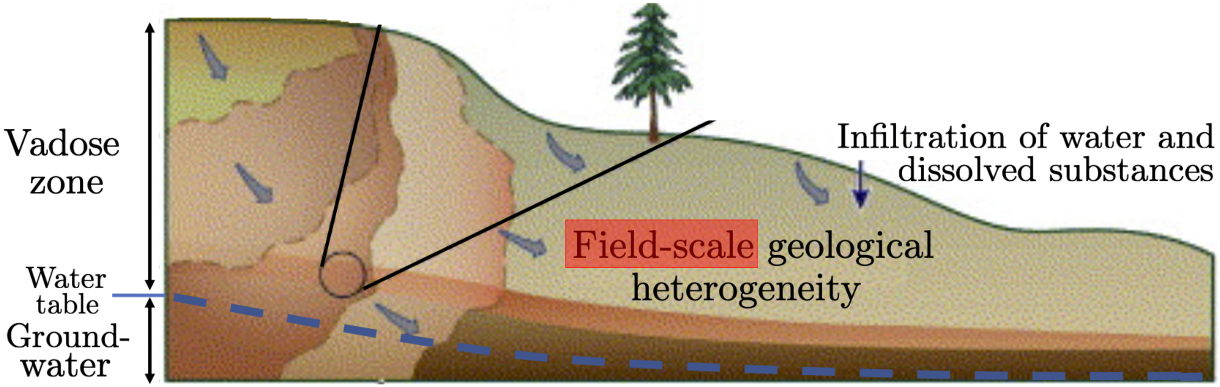
Context: vadose zone

Challenge for:
- groundwater management
- contaminant transport
- agriculture irrigation
- flood control



C. I. Steefel et al. (2005), Earth Planet. Sci. Lett, 240-3-4, 539
A. Velásquez-Parra et al. (2022), Geophys. Res. Lett., 49-3, e2021GL096280

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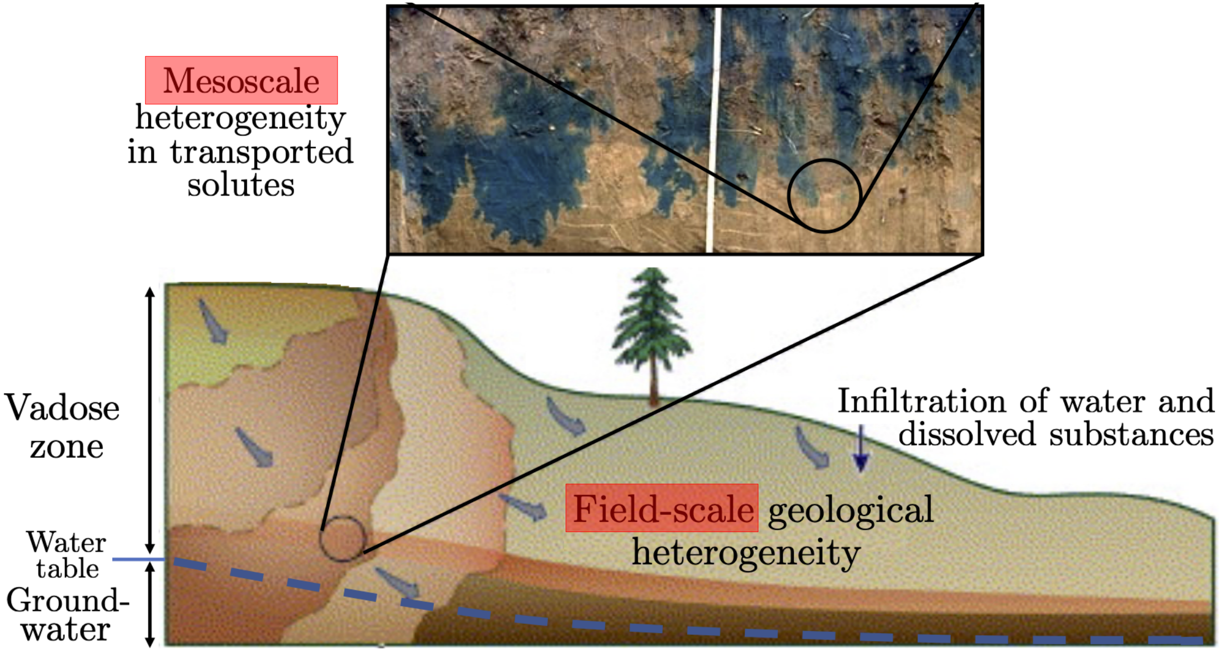

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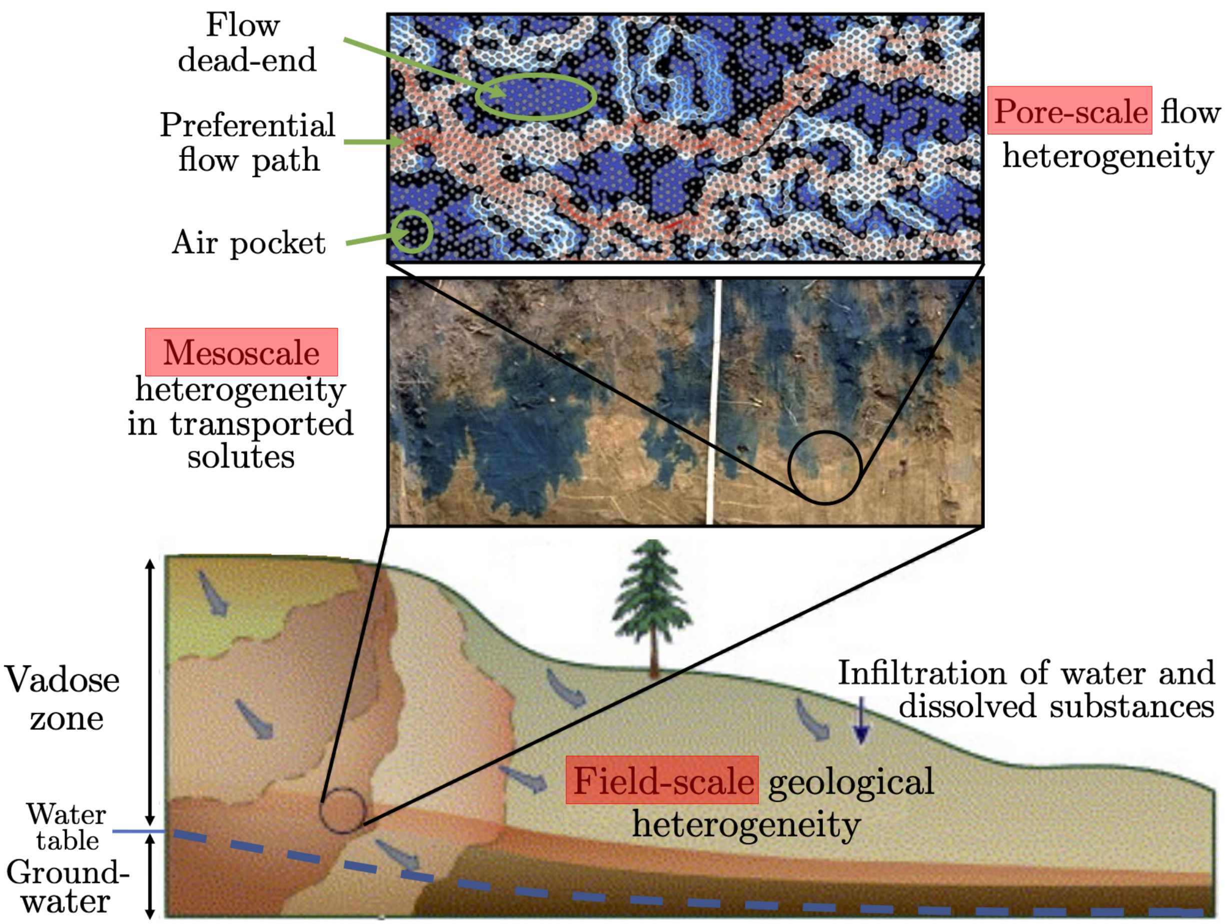

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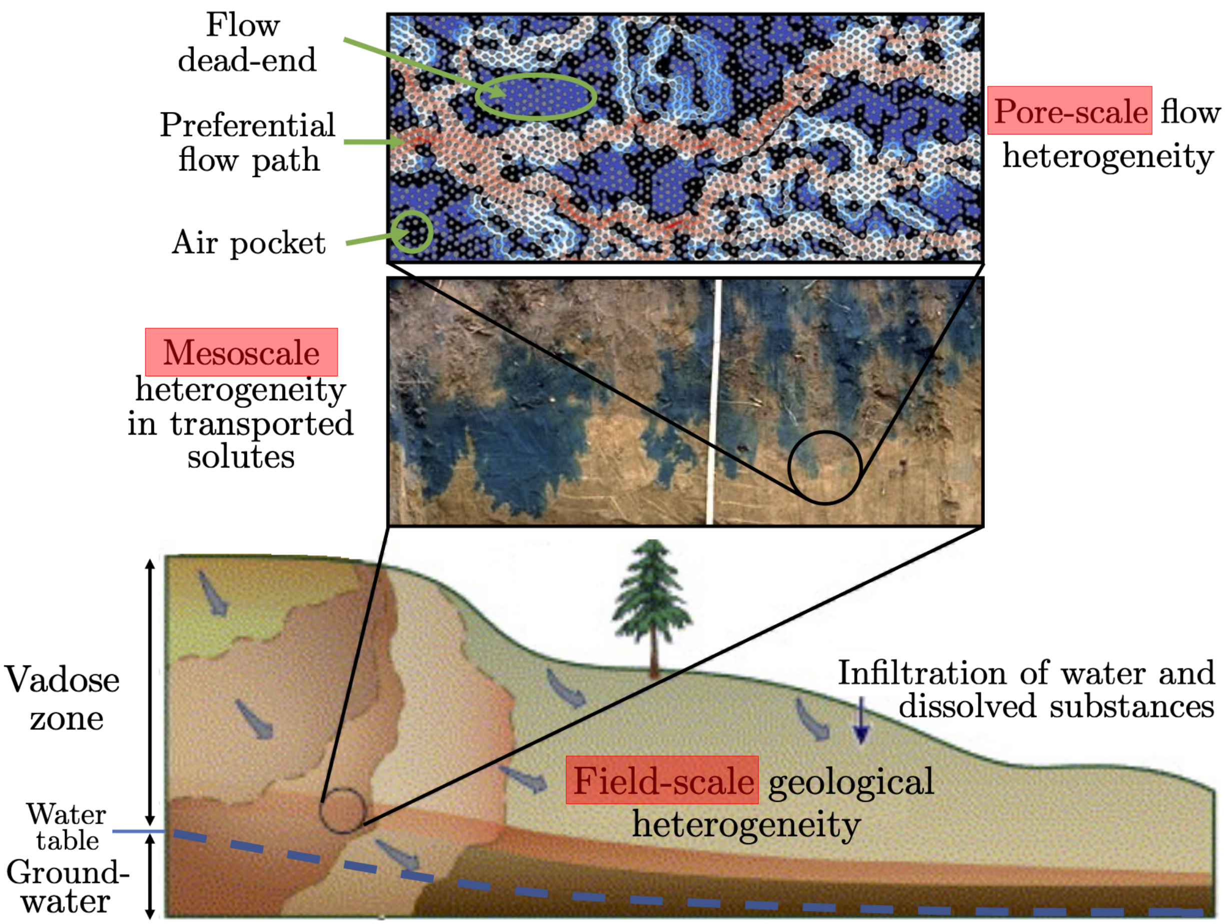

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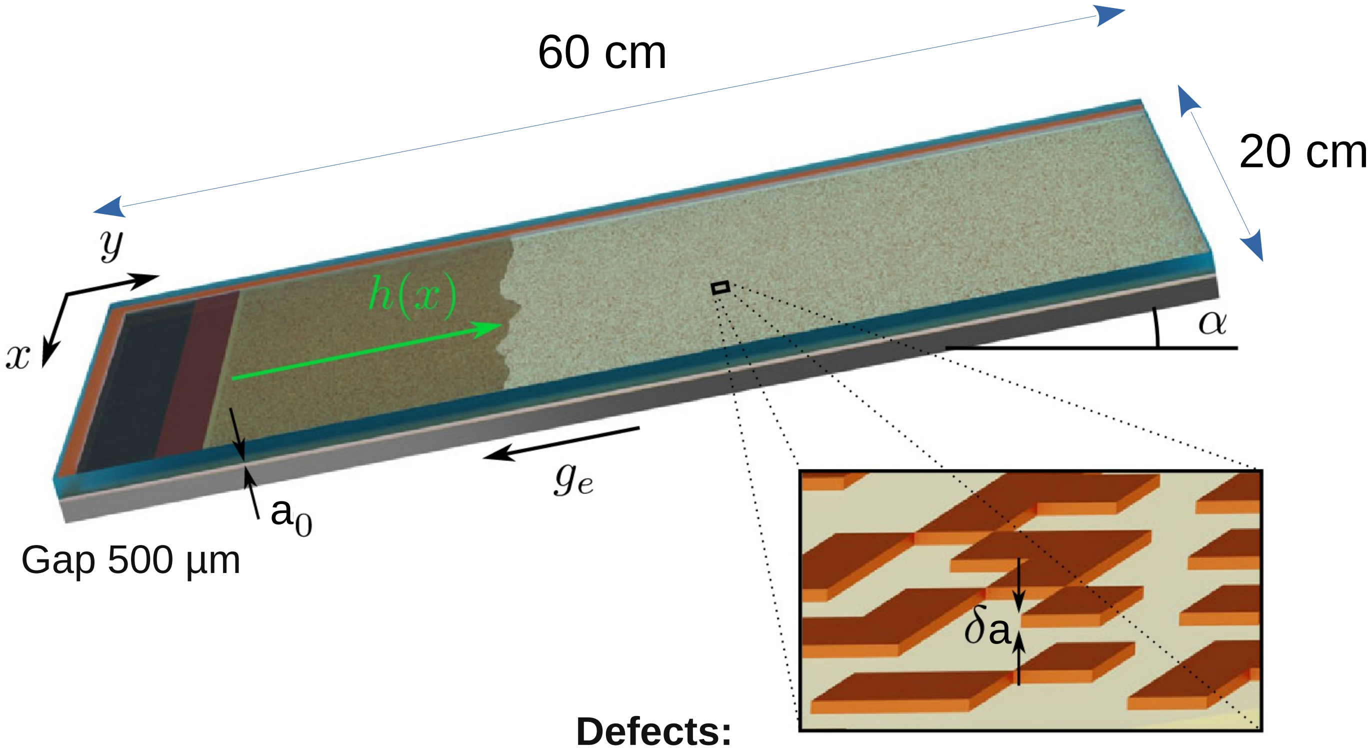
~100 m thick over kms, while flow and transport are driven by pore scale mechanisms
→ **need for upscaling models**

Heteregeneous both in porosity and saturation
→ **anomalous transport**

Non-passive transport in imperfect Hele Shaw



Defects:
400µm squares, amplitude δa = 60 µm

R. Holtzman et al. (2020), Comm. Phys. 3, 222

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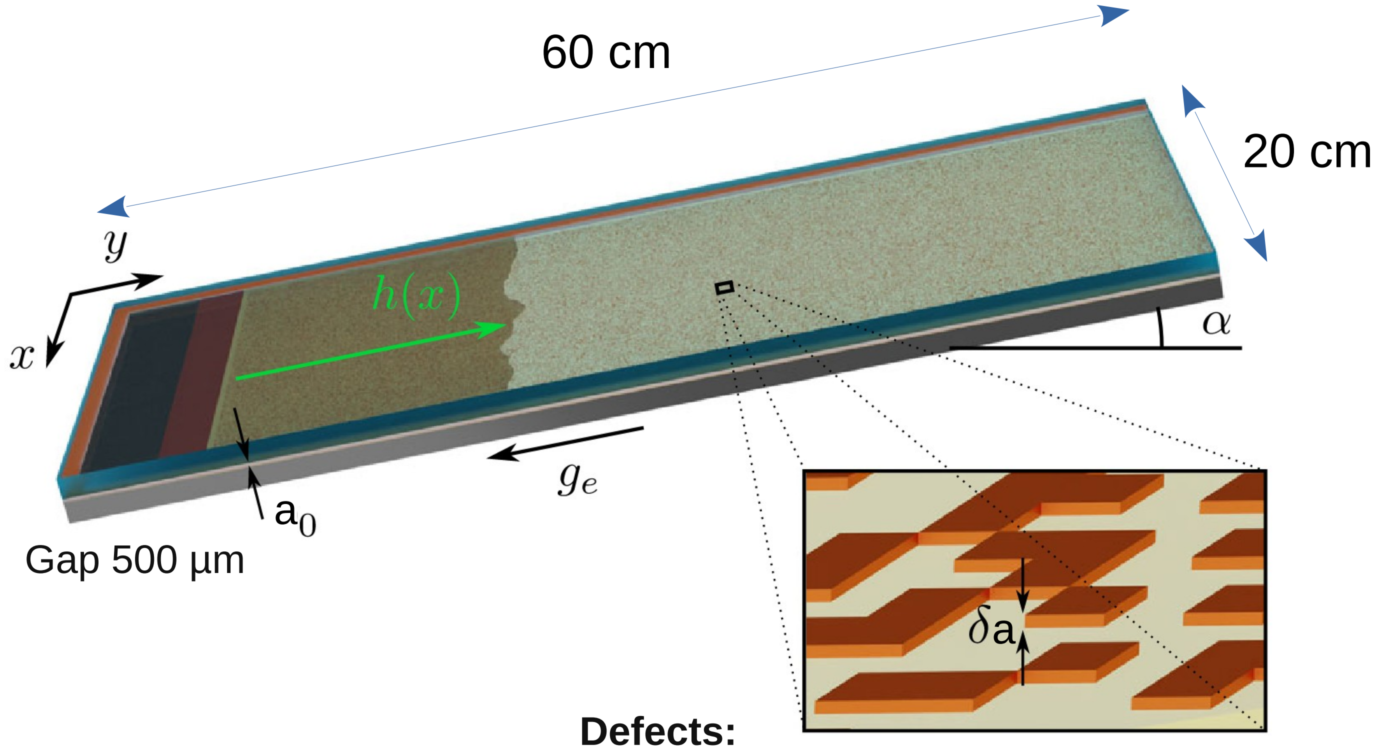


Defects:
400µm squares, amplitude δa = 60 µm

Uncorrelated geometry:
bumps placed at random with fixed height

Small perturbation:
$\delta a/a_0 \sim 10\%$
Flow kept **2D** and barely modified in the bulk
→ Enhanced impact on the **capillary effects**

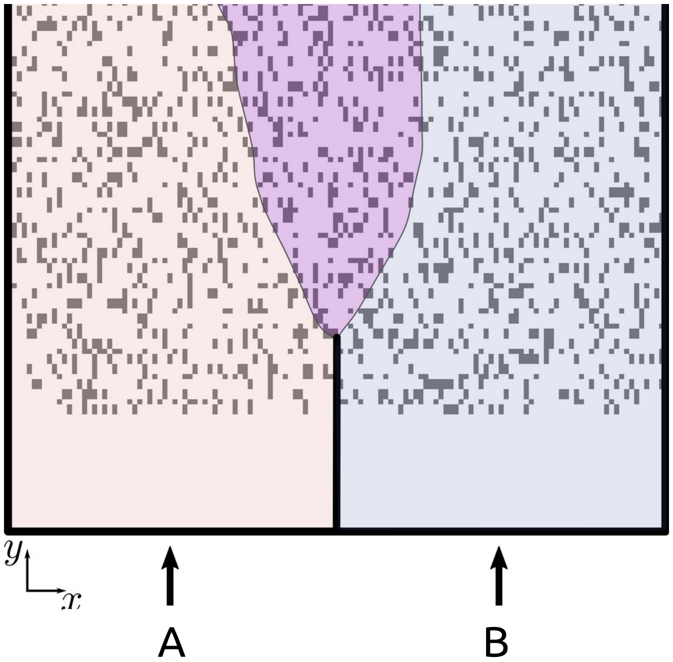
R. Holtzman et al. (2020), Comm. Phys. 3, 222

Chemically reactive transport in imperfect Hele Shaw

<u>Goal of the work</u>

Study chemically reactive transport:

- Role of saturation and topography
- Reaction front parallel to the flow
- Spatio-temporal measurement of reaction rates



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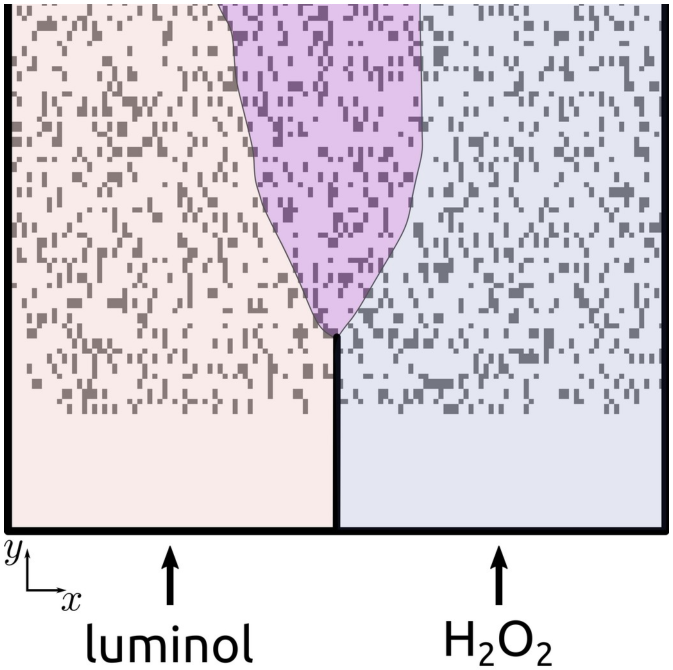
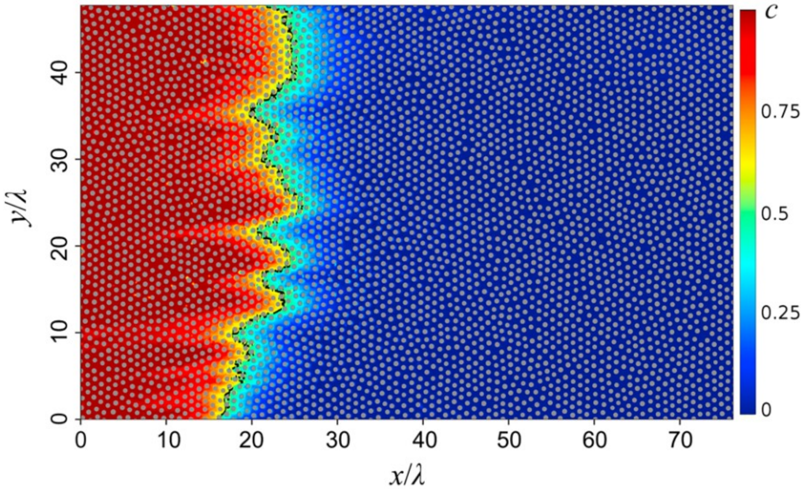


Chemiluminescence: direct measure of the reaction rate

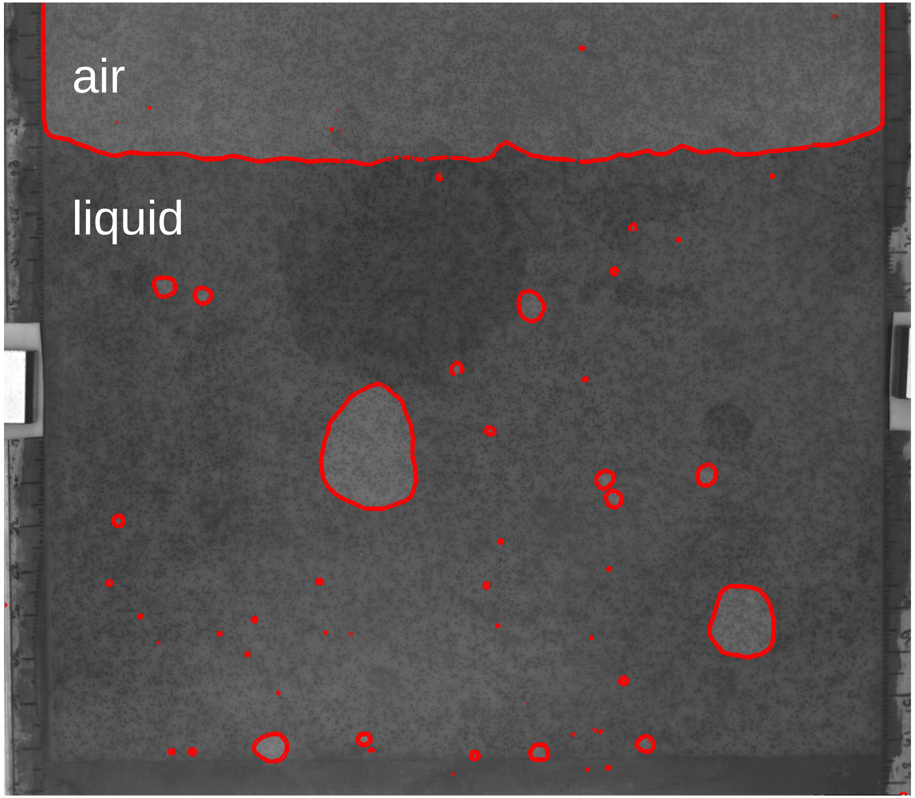


luminol + H_2O_2 + 2OH^-

→ 3-aminophthalatedianion + H_2O + N_2 + photon

Jiménez-Martínez et al (2015), Geophys. Res. Lett., 42, 5316
S. Izumoto et al (2025), J. Fluid Mech. 1013, A4

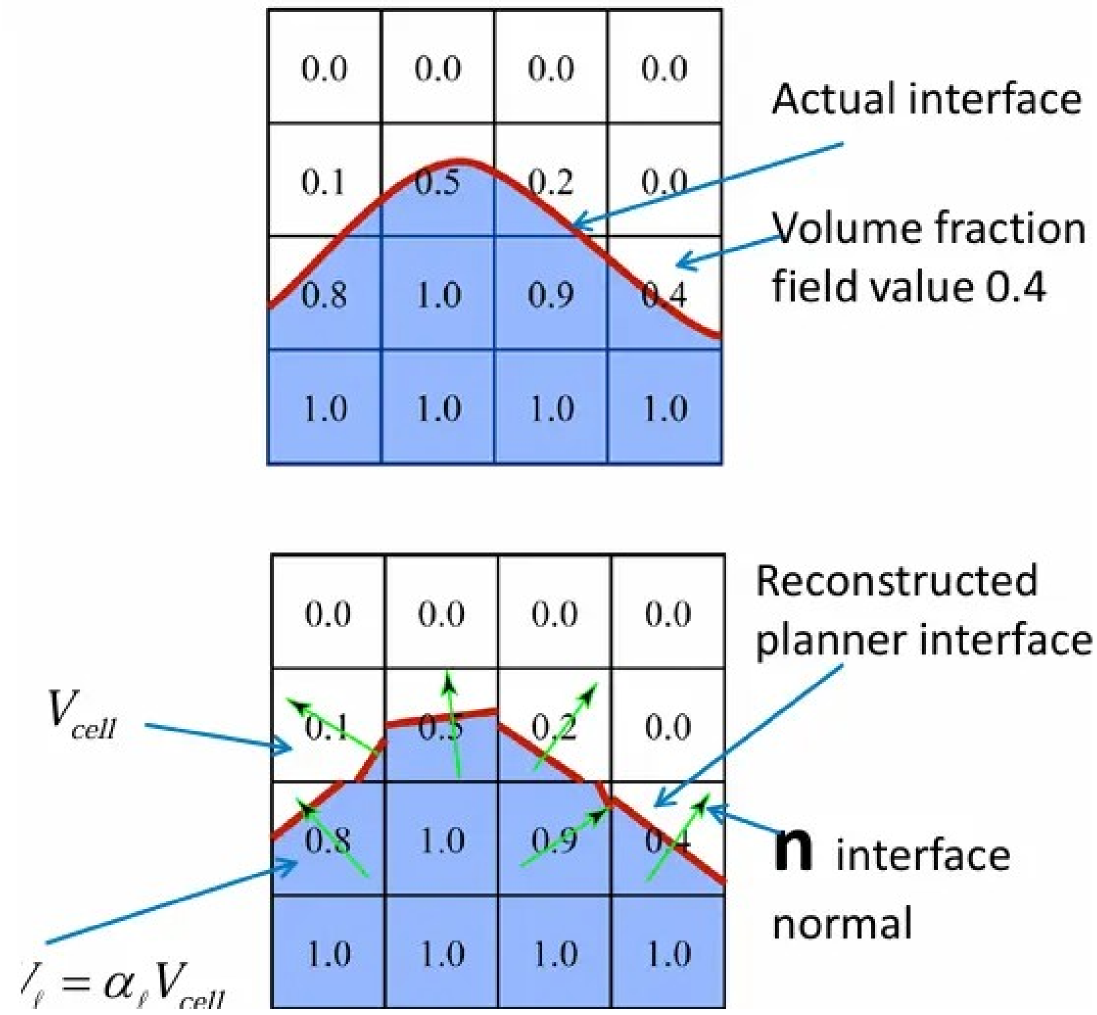
Multiphase flow



Preliminary tests:

- Experimental setup able to produce 2-phase flow using coinjection
- Coexistence of stable bubbles and advected bubbles
- Good tracking of the interface

2-phase simulation: Volume of Fluid (VOF)



Philosophy
Consider only one fluid whose properties depend on a new scalar: the **phase field ɣ**

$$\gamma = \begin{cases} 1 & \text{in fluid 1} \\ 0 & \text{in fluid 2} \\ 0 < \gamma < 1 & \text{at the interface} \end{cases}$$

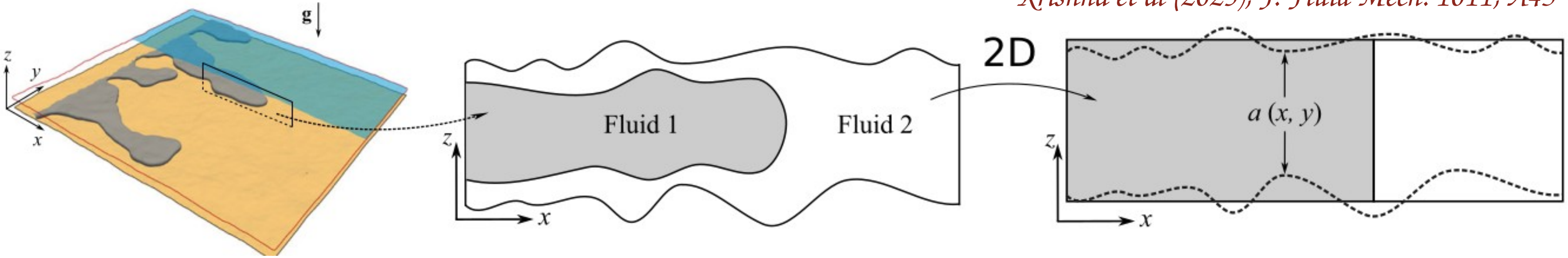
$$\rho(\boldsymbol{x}) = \rho_1 \gamma(\boldsymbol{x}) + \rho_2 (1 - \gamma(\boldsymbol{x}))$$

$$\mu(\boldsymbol{x}) = \mu_1 \gamma(\boldsymbol{x}) + \mu_2 (1 - \gamma(\boldsymbol{x}))$$

$$\boldsymbol{u}(\boldsymbol{x}) = \gamma(\boldsymbol{x}) \boldsymbol{u}_1(\boldsymbol{x}) + (1 - \gamma(\boldsymbol{x})) \boldsymbol{u}_2(\boldsymbol{x})$$

2D simulations: depth averaged flow

Krishna et al (2025), J. Fluid Mech. 1011, A43



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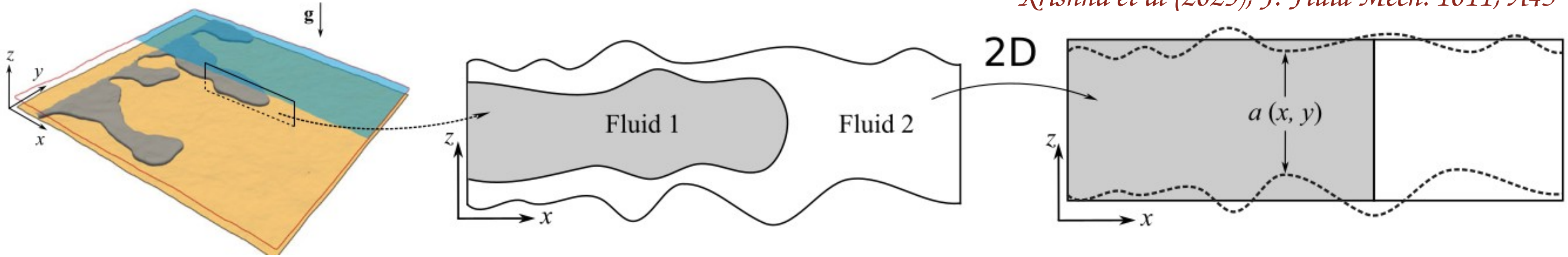

2D simplification:
- Depth-averaged quantities
- Assumes slowly varying aperture field *a*
- No lubrication film
- Consider the flux ***Q* = *aU***

$$\nabla \cdot \boldsymbol{Q} = 0$$

Mass conservation

$$\frac{\partial(\rho \boldsymbol{Q})}{\partial t} = -a\nabla p_d - a\boldsymbol{g}\cdot\boldsymbol{x}\;\nabla\rho$$

Pressure & gravity

$$+\nabla\cdot(\mu\nabla\boldsymbol{Q}) + \nabla\boldsymbol{Q}\cdot\nabla\mu - \frac{12\mu}{a^2}\boldsymbol{Q}$$

Viscosity

$$+a\sigma\left[\frac{\pi}{4}\nabla\cdot\left(\frac{\nabla\gamma}{\|\nabla\gamma\|}\right) + \frac{2}{a}\cos\theta\right]\nabla\gamma$$

Capillarity

Simplified version

$$a\frac{\partial\gamma}{\partial t} + \boldsymbol{Q}\cdot\nabla\gamma + \nabla\cdot\left[\boldsymbol{Q}_r\gamma(1-\gamma)\right] = 0$$

Phase advection

2D simulations: depth averaged flow

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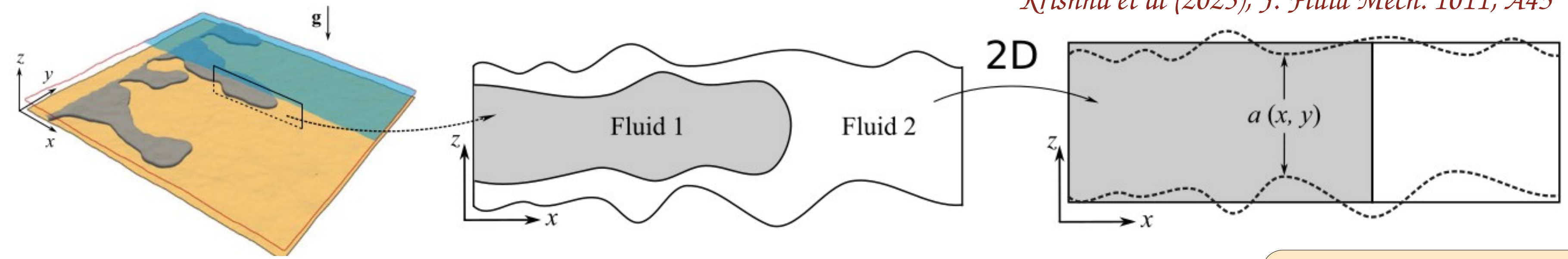

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Capillarity

Correction factor due to the meniscus

I. Lavi et al. (2023) Phys. Rev. Fluids, 8 (12), 124002

Simplified version

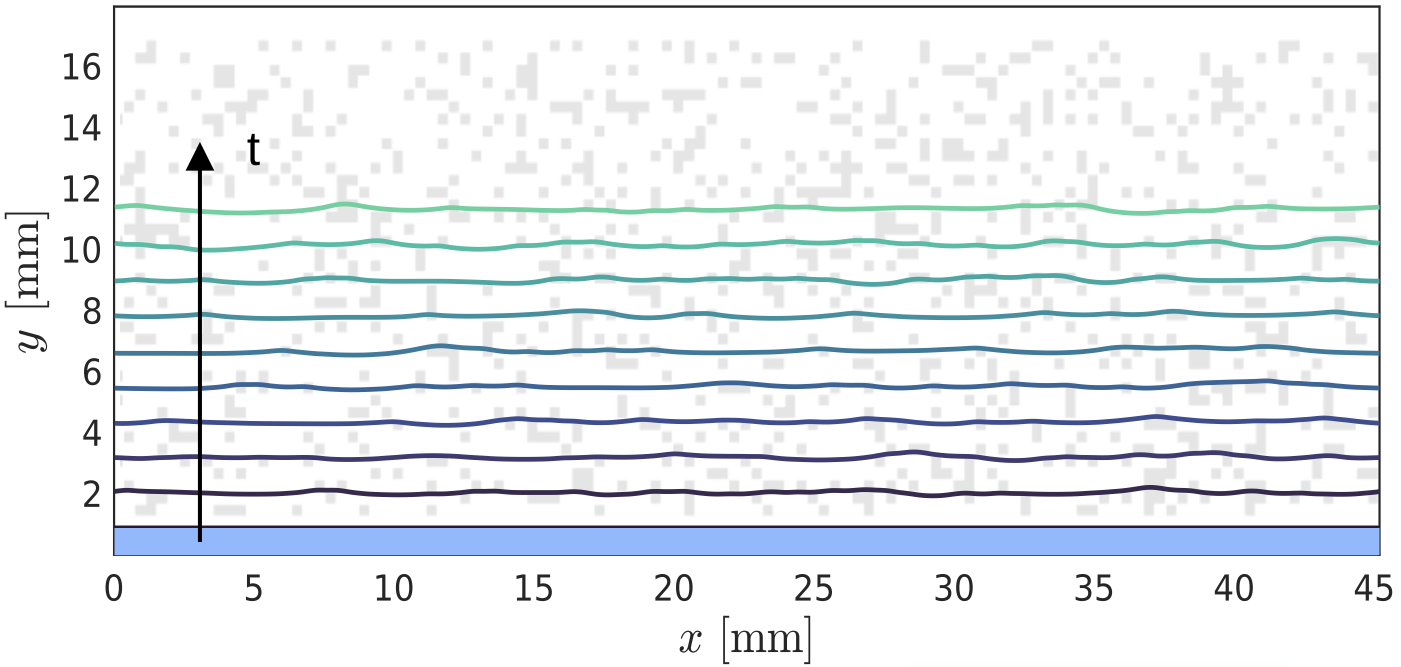
$$a\frac{\partial\gamma}{\partial t} + \boldsymbol{Q}\cdot\nabla\gamma + \nabla\cdot\left[\boldsymbol{Q}_r\gamma(1-\gamma)\right] = 0$$

Phase advection

Imbibition

One defect = 8x8 cells

Numerical challenge:
Defects are very sharp, can match the theory?



Imbibition protocol:
Interface dynamics driven by the capillary number and the permeability

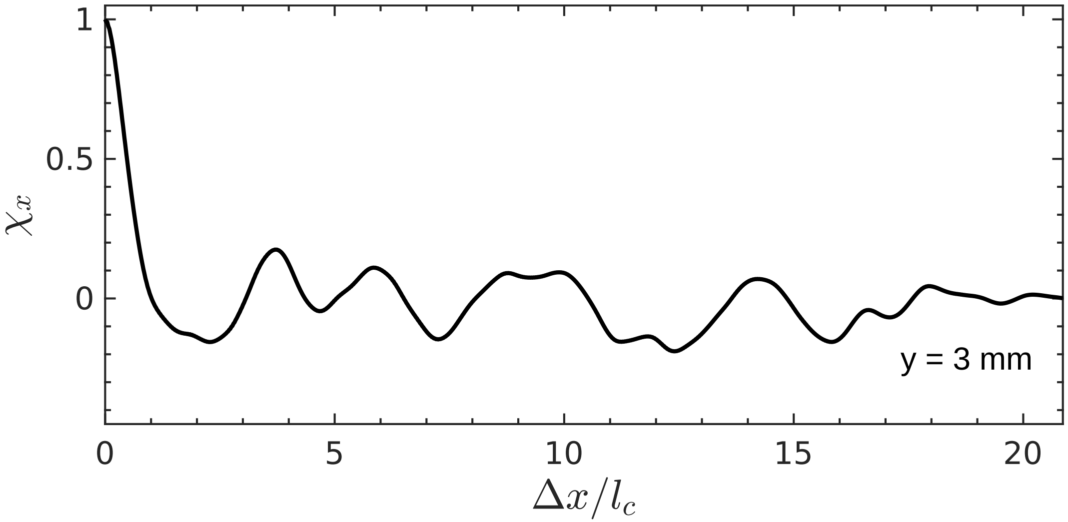
$$Ca = \frac{\mu Q_0}{a_0 \sigma}$$

~ 10^{-3}

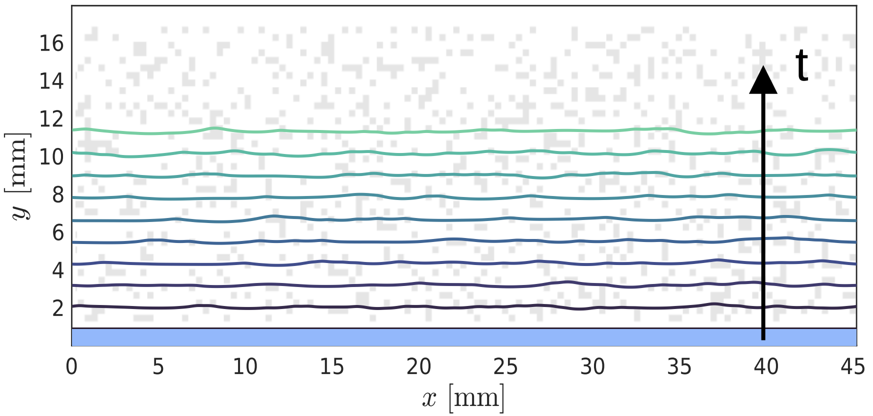
$$l_c = \sqrt{\frac{a_0^2 \pi}{48\ Ca}}$$

~ 2 mm

Imbibition

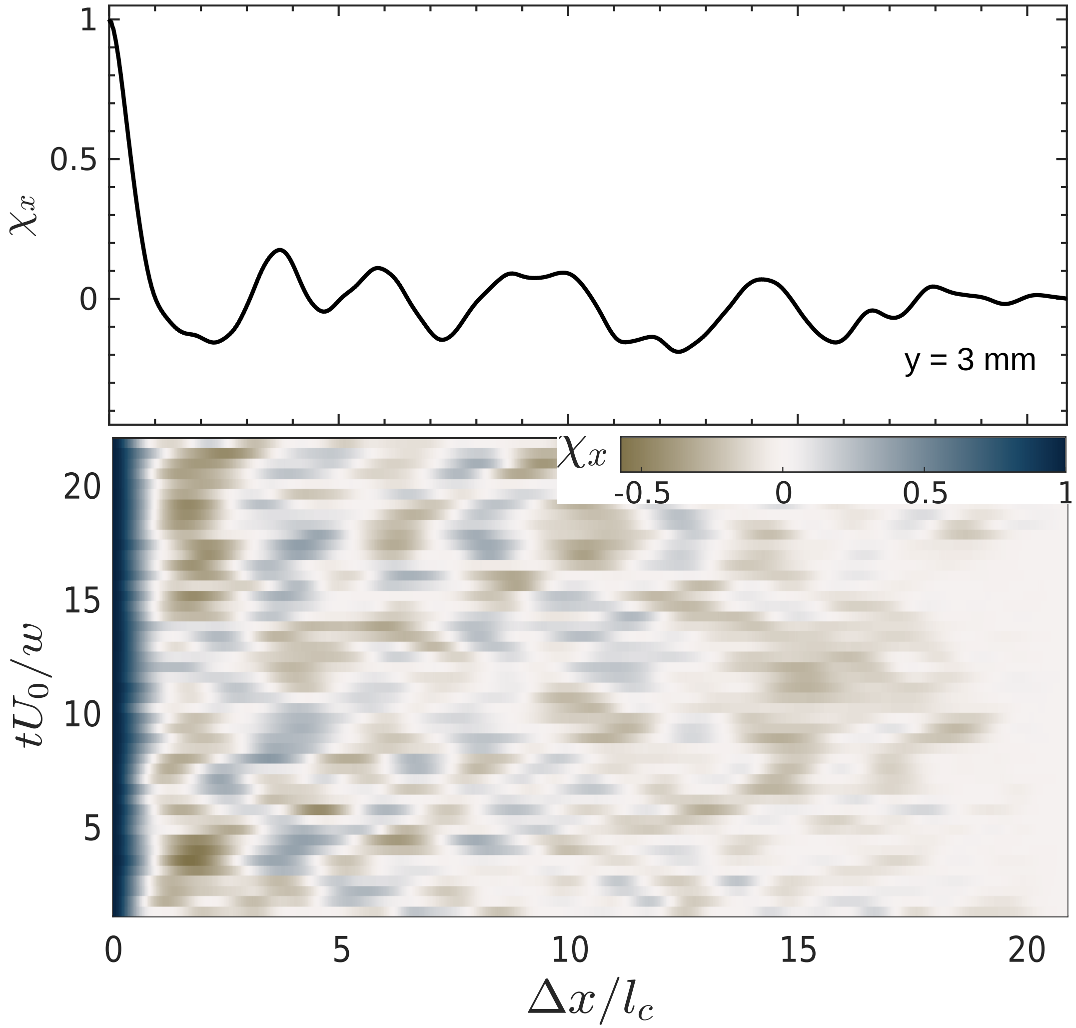


χ_x
$\Delta x / l_c$
y = 3 mm
1
0.5
0
0
5
10
15
20

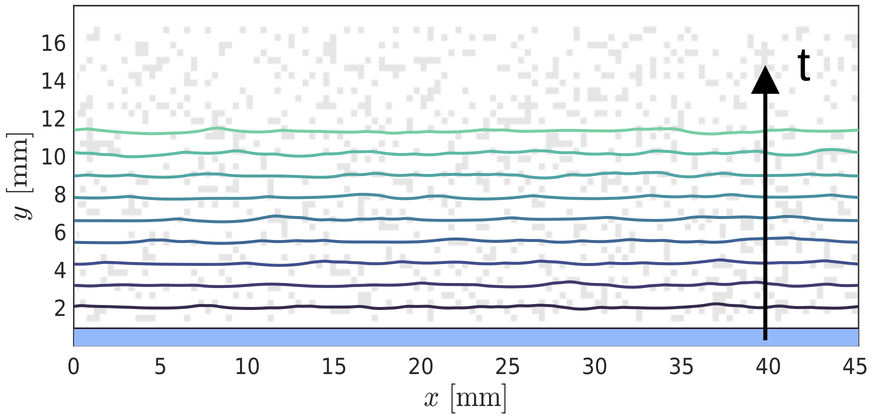


t
y [mm]
x [mm]
16
14
12
10
8
6
4
2
0
5
10
15
20
25
30
35
40
45

Imbibition

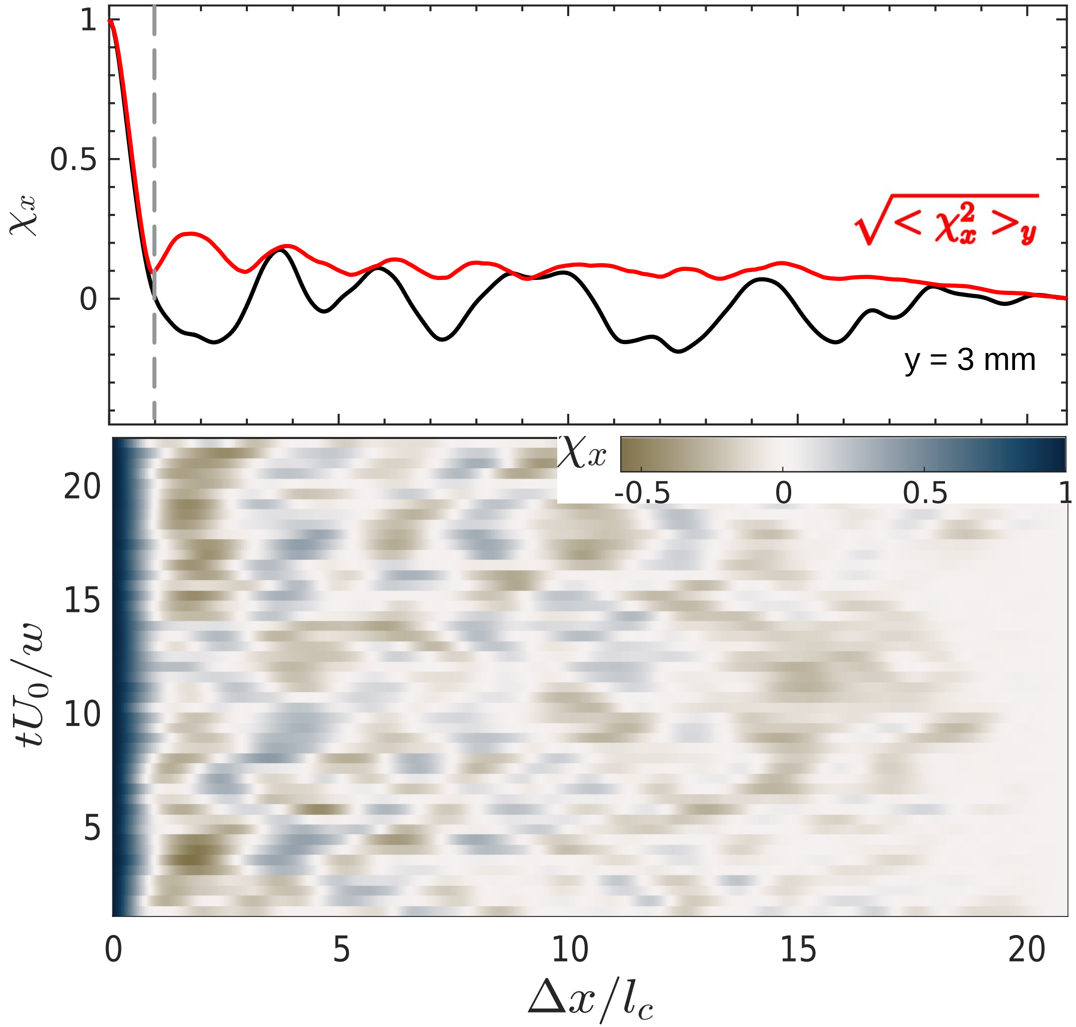


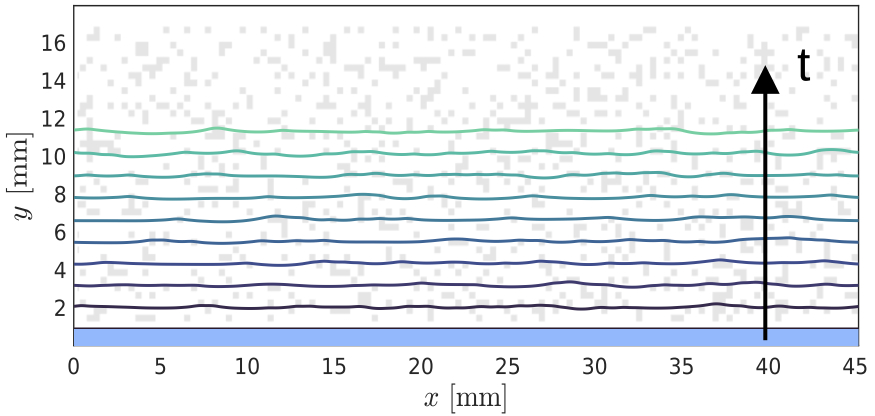
1
0.5
0
χ_x
y = 3 mm
χ_x
-0.5
0
0.5
1
20
15
10
5
tU_0/w
0
5
10
15
20
$\Delta x/l_c$



t
16
14
12
10
8
6
4
2
y [mm]
0
5
10
15
20
25
30
35
40
45
x [mm]

Imbibition





Correlation fully described by l_c

Patterns in the 2D visualization (temporal correlation of the spatial correlation function)

Spurious currents

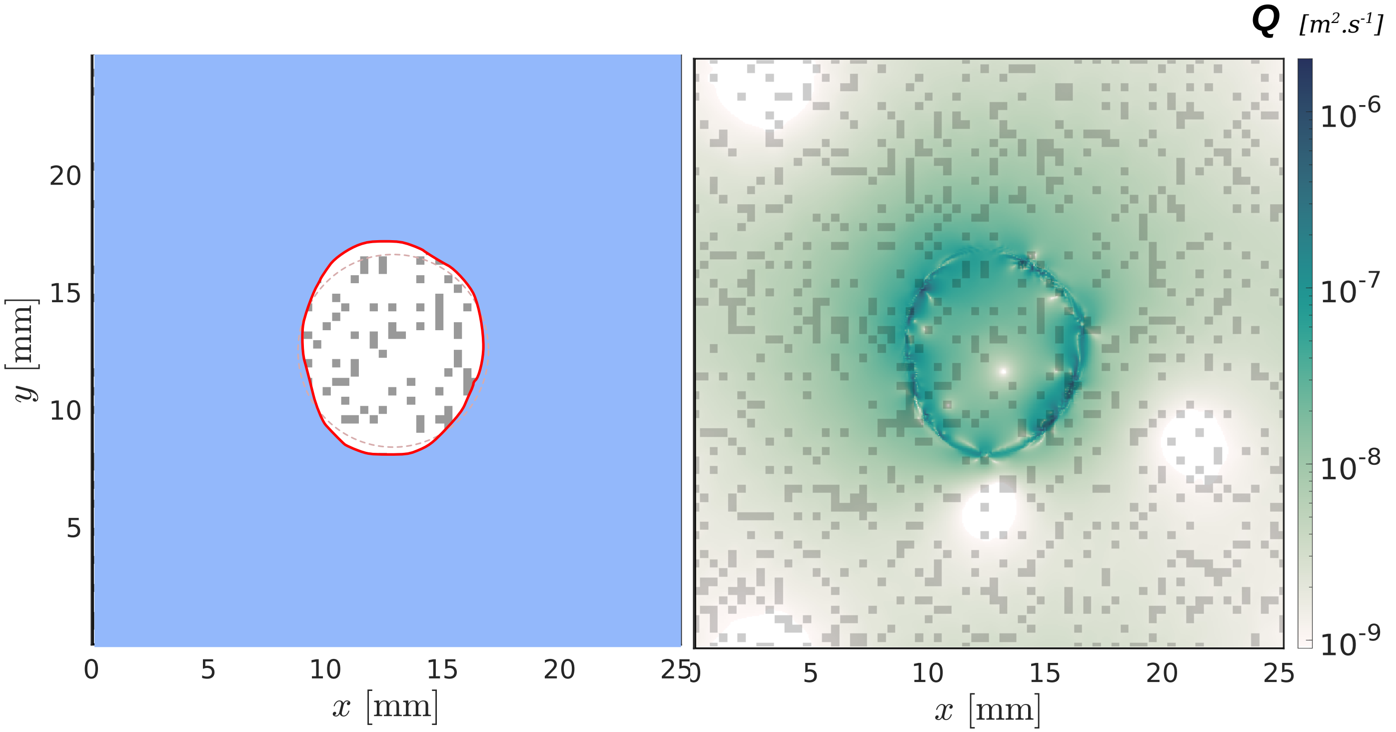
Example of a spherical droplet at rest:

$$\frac{\partial \rho U}{\partial t} = -\nabla p + \sigma \kappa \nabla \gamma = 0$$

$$\kappa = -\nabla \cdot \left(\frac{\nabla \gamma}{||\nabla \gamma||} \right)$$

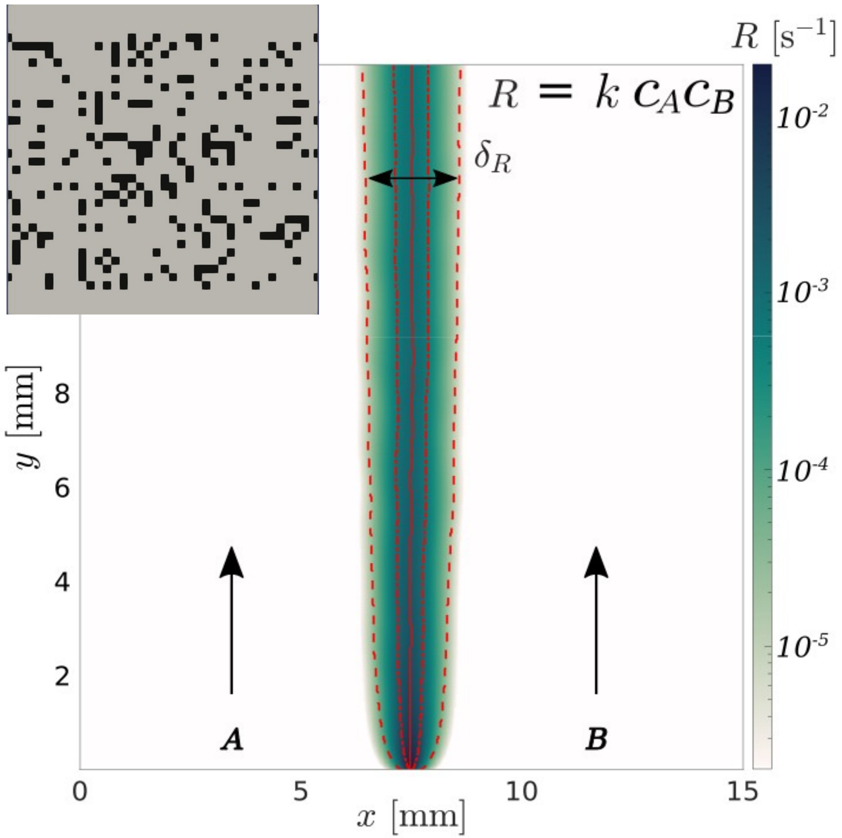
Discrete phase field
→ unbalance of forces

S. Deshpande et al (2013), Comput. Sci .Discov. 5, 014016



Start from a spherical bubble
→ due to the defects the interface deforms to reach a equilibrium state.

Eulerian chemically reactive transport



Random surface, saturated, imposed flux at inlet
Pe ~ 20 Da ~ 5

$$A + B \rightarrow C$$

$$\partial_t(a c_{A/B}) + \nabla(Q c_{A/B}) = P_e^{-1} \nabla(a \nabla c_{A/B}) - D_a a c_A c_B$$

$$\partial_t(a c_C) + \nabla(Q c_C) = P_e^{-1} \nabla(a \nabla c_C) + D_a a c_A c_B$$

Aperture variation modifies the equation

E. Mignot et al (2023), Water Resour. Res., 59, 12

$$P_e = \frac{L Q_0}{D a_0} \qquad D_a = \frac{k C_0 L}{Q_0 / a_0}$$

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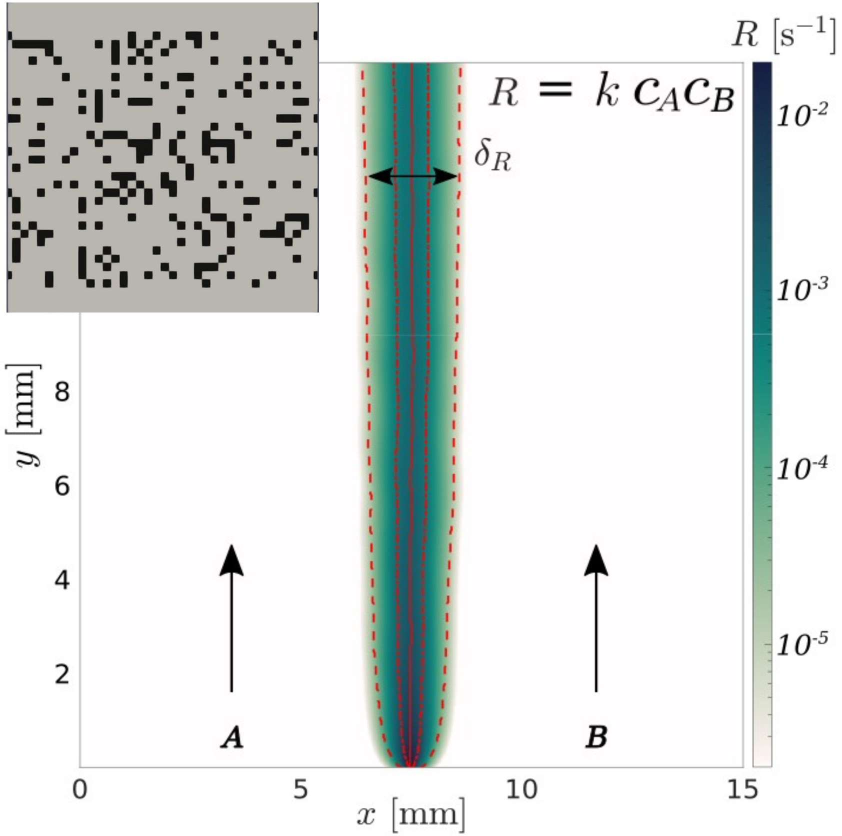

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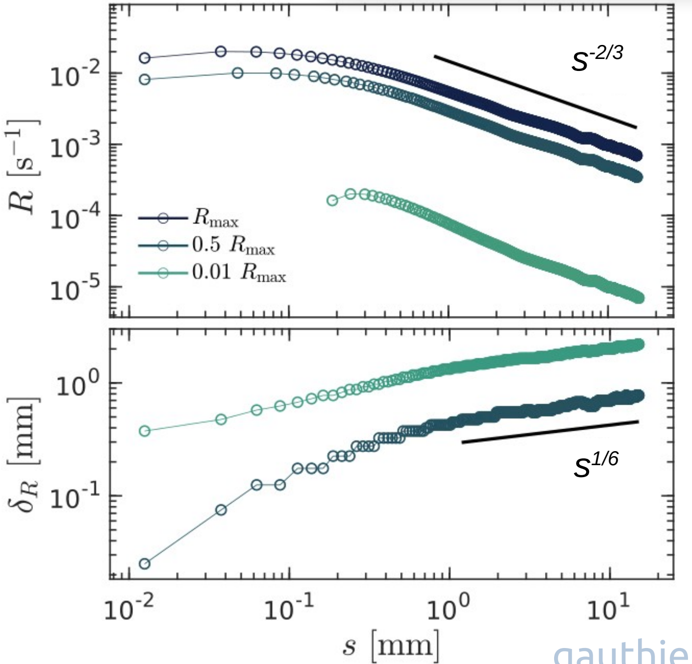

Scaling from theory in saturated media

- *S. Izumoto et al (2025), J. Fluid Mech. 1013, A4*
- *H. Larralde et al (1992), Phys. Rev. A 46(10), R6121*

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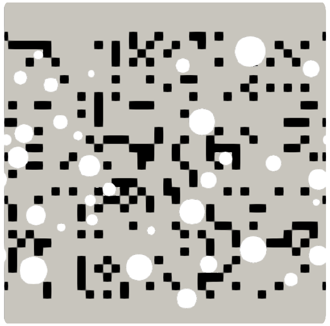
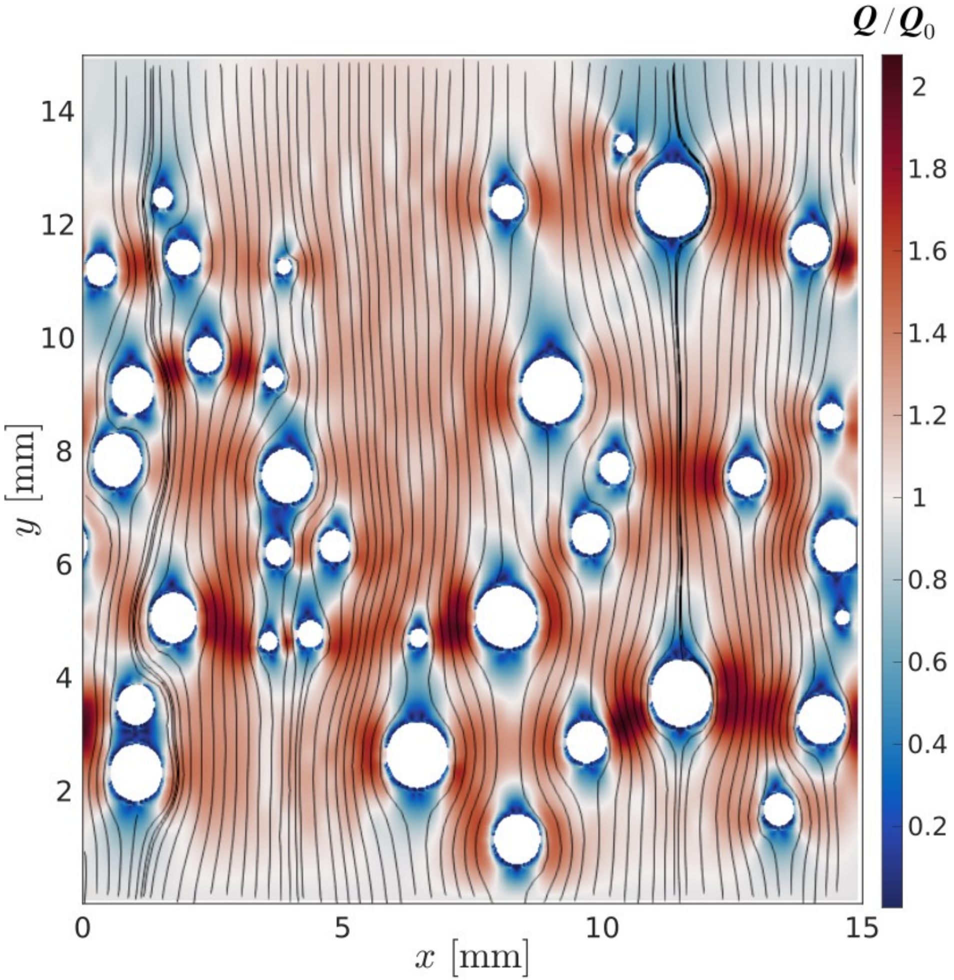
Impact of heterogeneity: flow field

Unsaturated flow:

Initial random bubbles, let evolve with the VoF solver until steady state.
Extrude the bubbles from the mesh, impose slip BC.

Mesh used:
(immobile bubbles)





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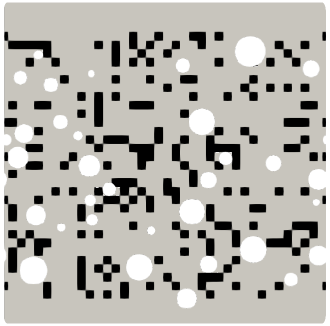
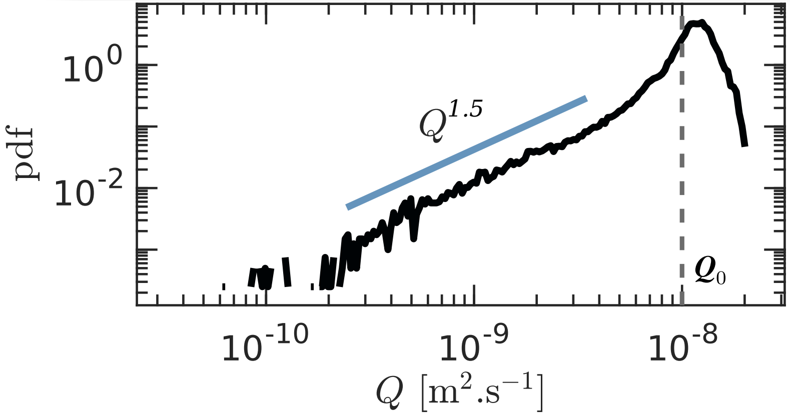
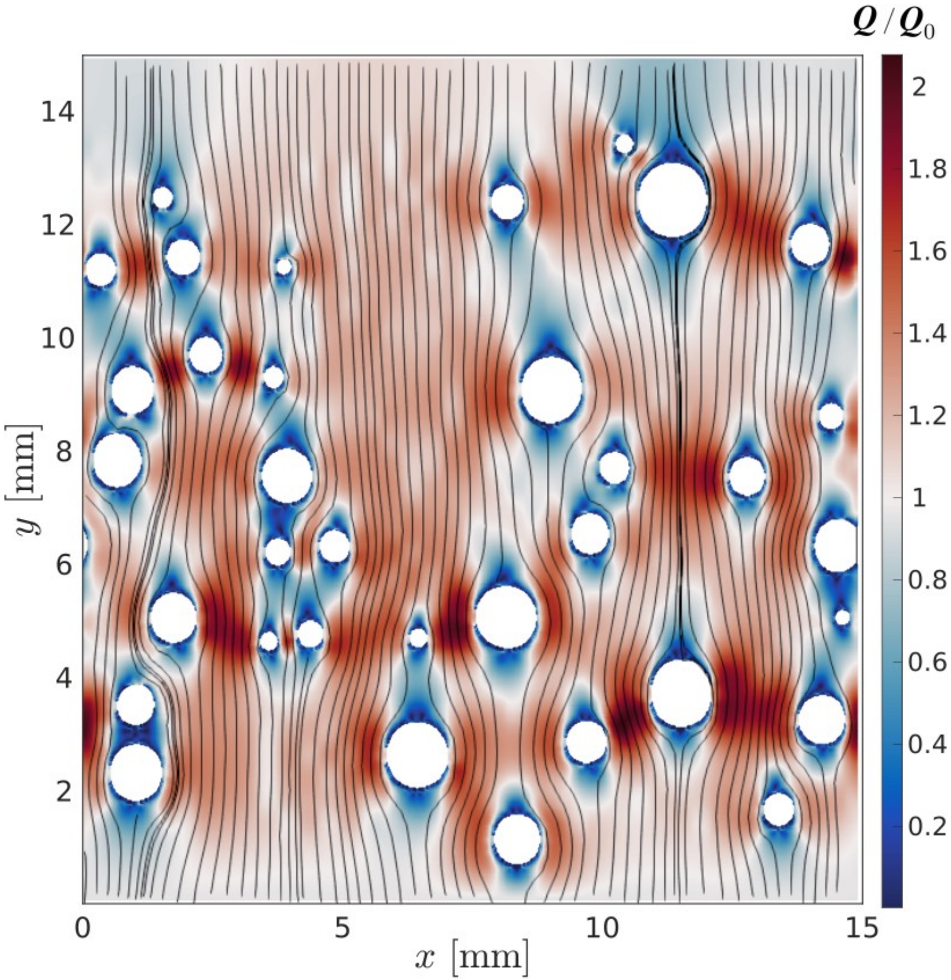
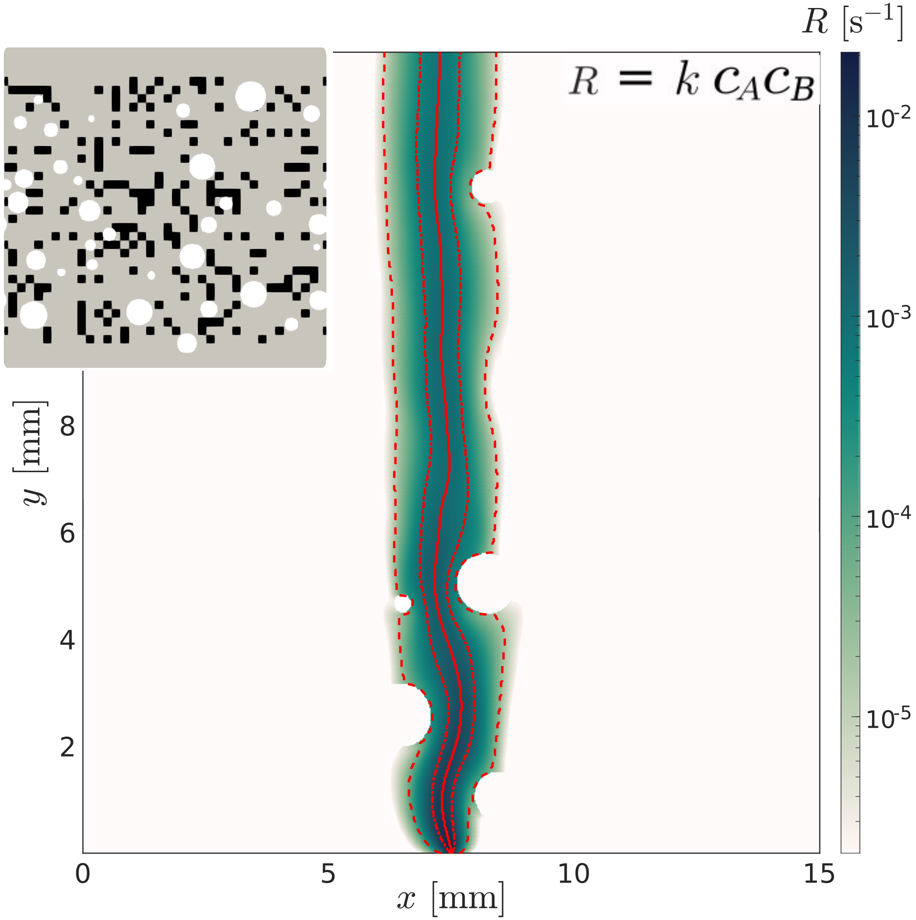




Tailing consistent with unconnected bubbles



Impact of heterogeneity: reactive transport



Random surface, <u>un</u>saturated, imposed flux at inlet
Pe ~ 20 Da ~ 5

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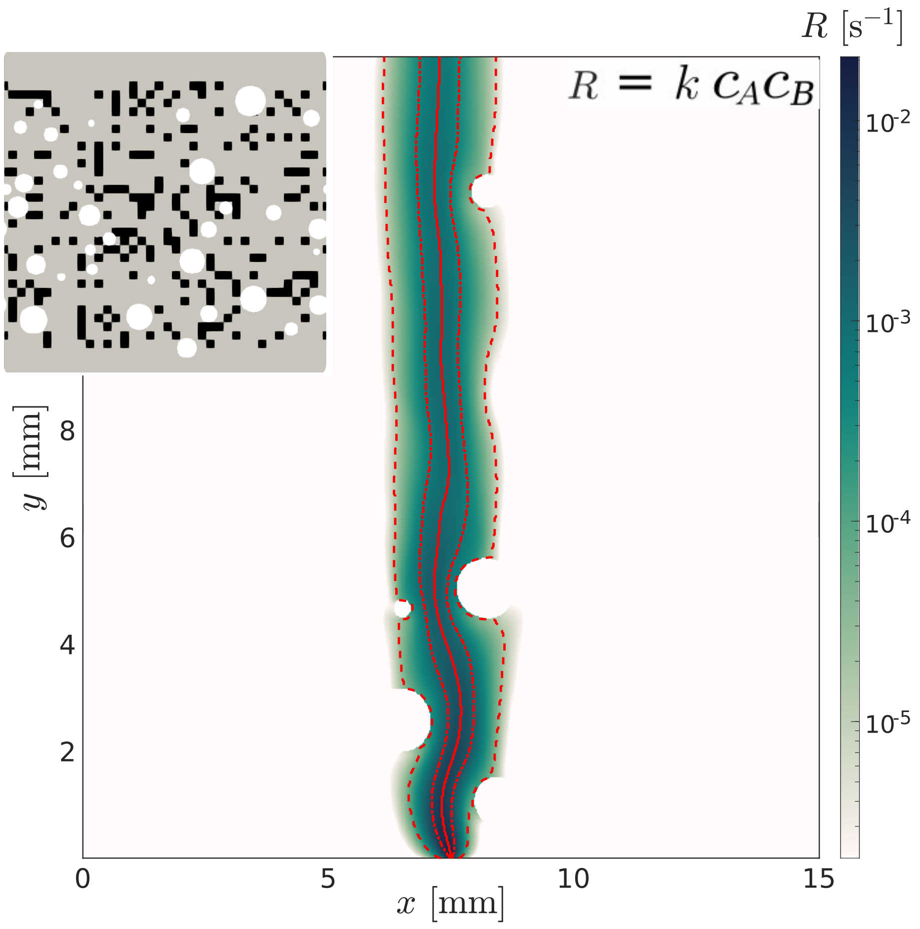

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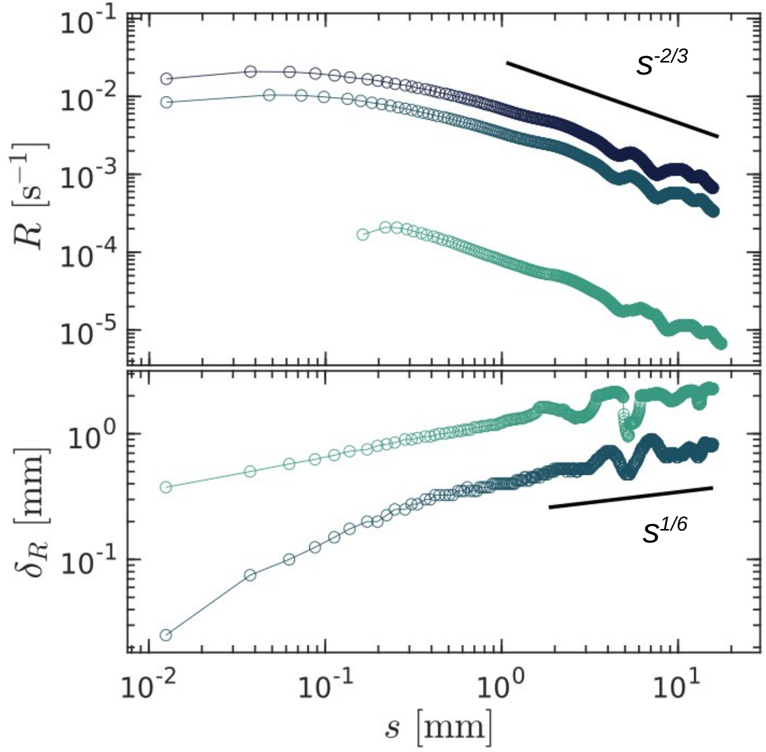
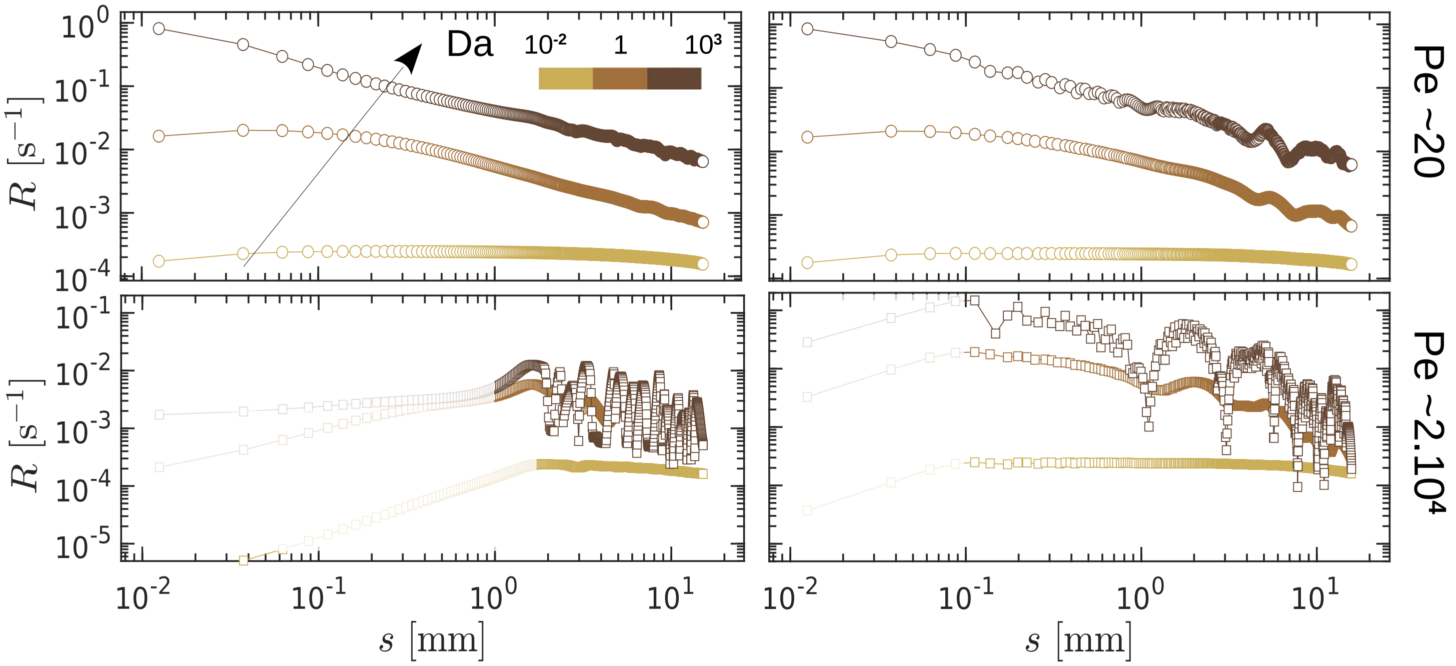
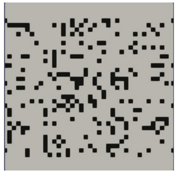


Scalings preserved: mild medium heterogeneity **solely perturb the global behavior**

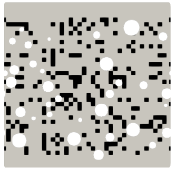
Correlate the fluctuations with the velocity field?

Impact of heterogeneity: reactive transport scalings





Saturated



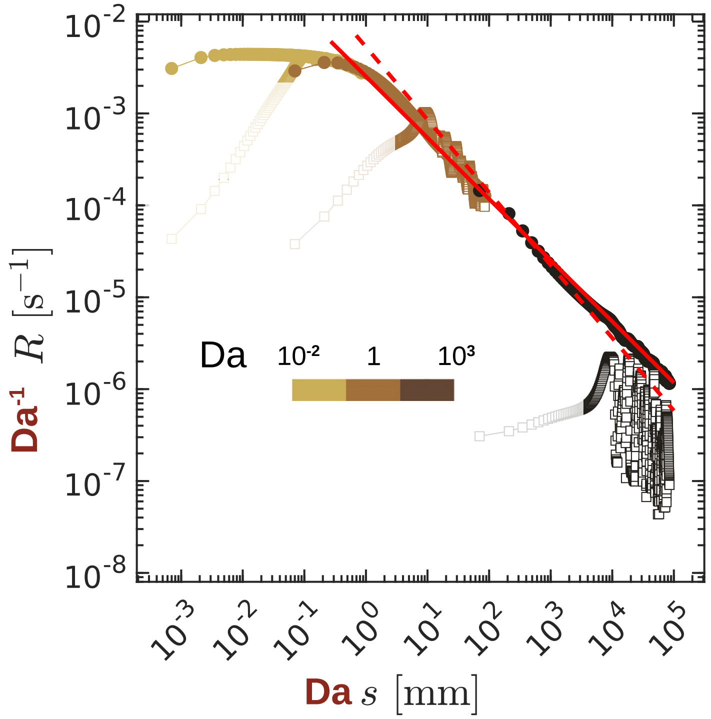
Unsaturated

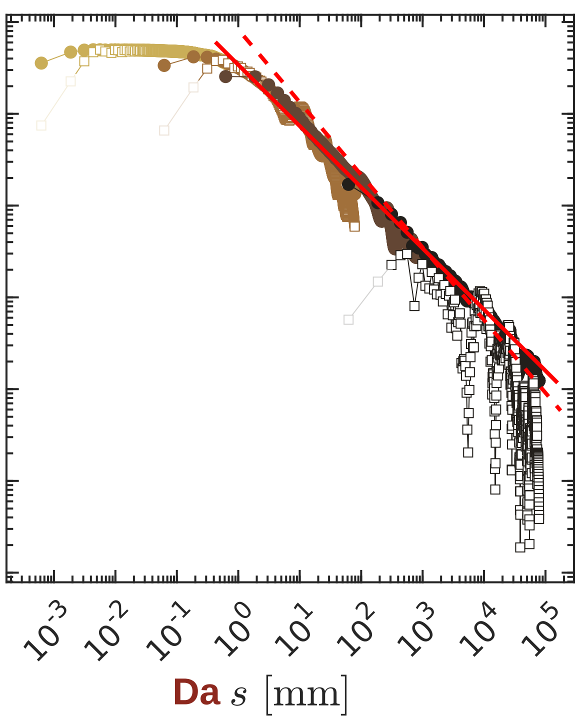
Two regimes

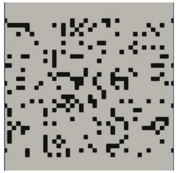
- Kinetic limited: R ~ cst
- Mixing limited: R ~ power law

S. Izumoto et al (2025), J. Fluid Mech. 1013, A4

Impact of heterogeneity: reactive transport scalings







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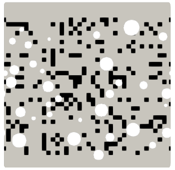


Unsaturated

Rescaling using Da

R / Da (to normalize chemical strength)

Da * s → why ?

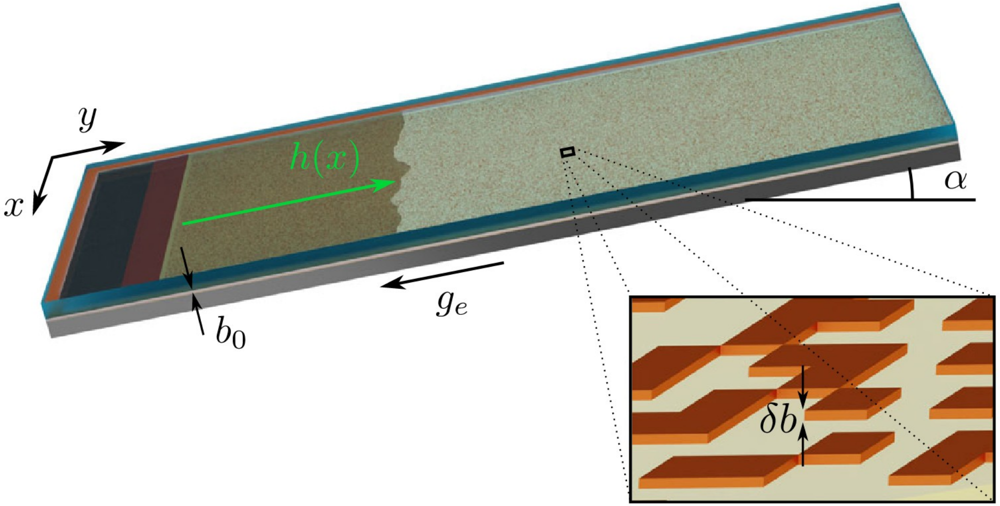
No direct impact on the Pe?

Conclusion

2-phase 2D flow in a varying aperture field
→ minimize the spurious currents

Experimental setup for multiphase flow
→ ready for first experiments

Reactive transport simulations
→ Investigate the scalings



R. Holtzman et al. (2020) Comm. Phys. 3, 222

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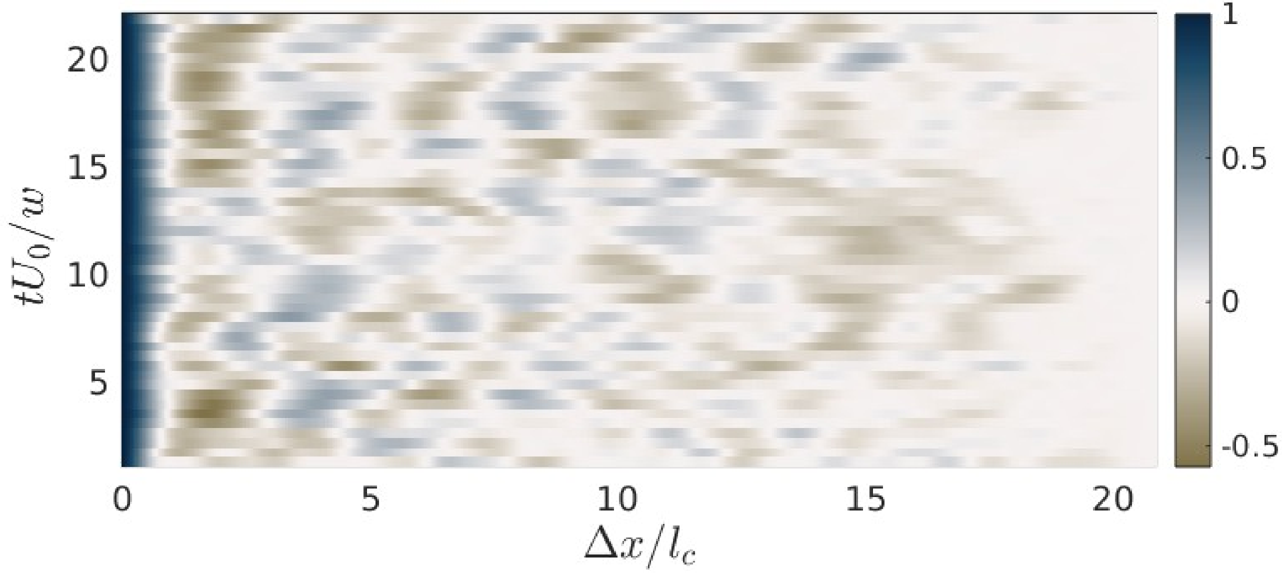
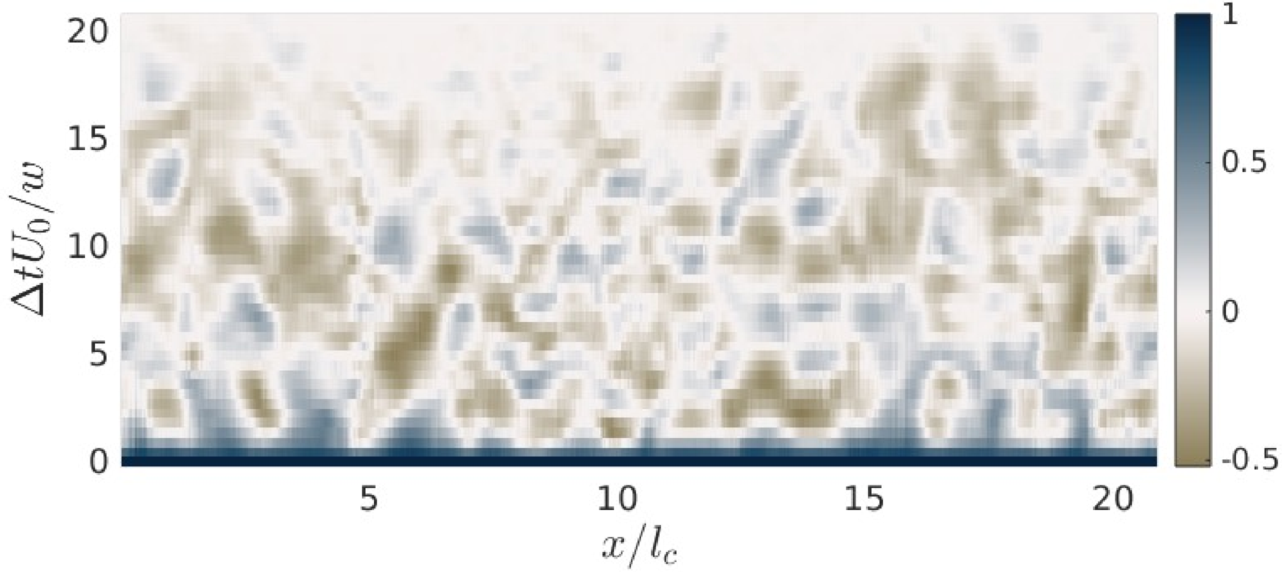
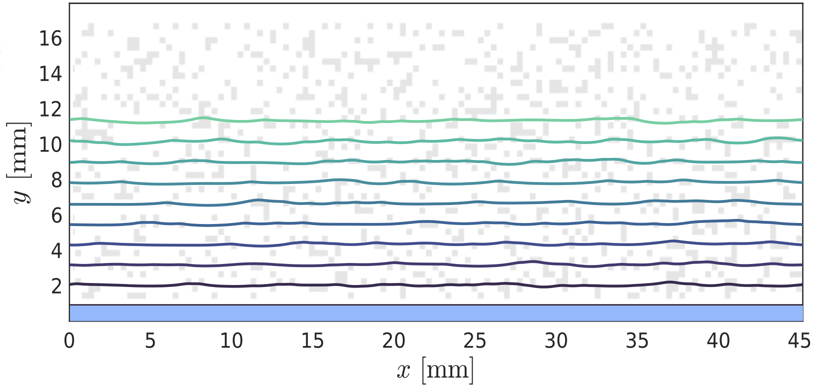

tU_0/w
$\Delta x/l_c$
0
5
10
15
20
1
0.5
0
-0.5


$\Delta tU_0/w$
x/l_c
0
5
10
15
20
1
0.5
0
-0.5


y [mm]
x [mm]
2
4
6
8
10
12
14
16
0
5
10
15
20
25
30
35
40
45

2-phase simulation: Volume of Fluid (VOF)

$$\frac{\partial(\rho \boldsymbol{u})}{\partial t} + [\boldsymbol{u} \cdot (\rho \nabla)]\boldsymbol{u} = -\nabla p + \rho \boldsymbol{g} + \nabla \cdot (2\mu \boldsymbol{E}) + \sigma \kappa \boldsymbol{n} \delta_\Gamma$$

$$\nabla \cdot (2\mu \boldsymbol{E}) = \nabla \cdot (\mu \nabla \boldsymbol{u}) + (\nabla \boldsymbol{u}) \cdot \nabla \mu$$

$$\nabla \cdot \boldsymbol{u} = 0$$

Effectively parameters depends on time and space

$$\rho(\boldsymbol{x}) = \rho_1 \gamma(\boldsymbol{x}) + \rho_2(1 - \gamma(\boldsymbol{x}))$$

$$\mu(\boldsymbol{x}) = \mu_1 \gamma(\boldsymbol{x}) + \mu_2(1 - \gamma(\boldsymbol{x}))$$

$$\boldsymbol{u}(\boldsymbol{x}) = \gamma(\boldsymbol{x})\boldsymbol{u}_1(\boldsymbol{x}) + (1 - \gamma(\boldsymbol{x}))\boldsymbol{u}_2(\boldsymbol{x})$$

Capillary effects and phase field

$$\kappa = \kappa_{xy} + \kappa_z = -\nabla \cdot \boldsymbol{n} = -\nabla \cdot \left(\frac{\nabla \gamma}{\|\nabla \gamma\|} \right)$$

Continuum Surface Force (CSF)

Brackbill, J. U., et al (1992). J. Comp. Phys., 100(2), 335

$$\boldsymbol{f}_\sigma = \sigma \kappa \nabla \gamma$$

Single defect: model

Darcy flow:

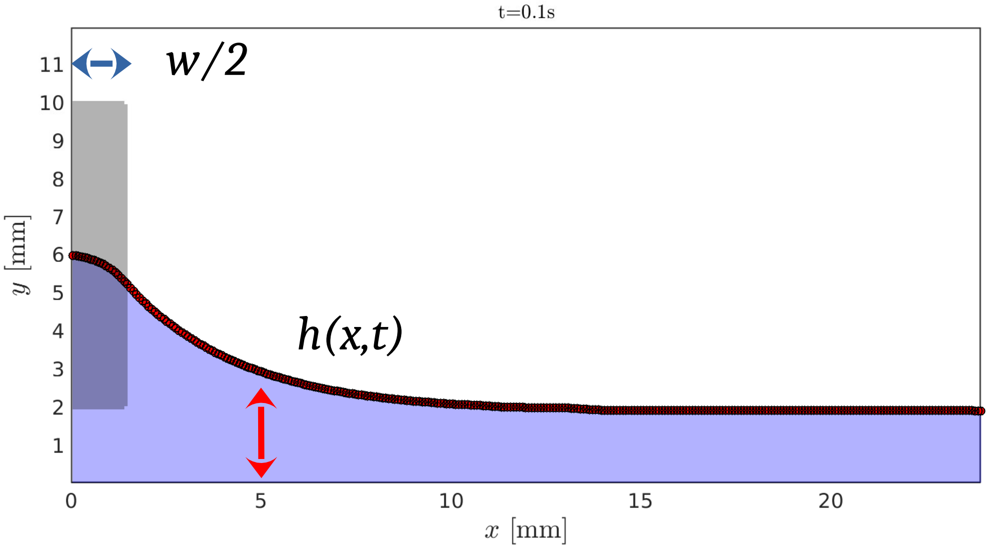
$$Q = -\frac{a^3}{12\mu}\left(\nabla p + \rho g_e\right)$$

$$p_{cap} = \sigma\left(\frac{\pi}{4}\kappa_{xy} - \frac{2\cos\theta}{a(x,y)}\right)$$

$$\kappa_{x,y} = -\frac{h''(x)}{(1+h'(x)^2)^{3/2}}$$

Assumptions: small defect ($\delta a \ll a_0$) and interface deformations (linearized curvature)

$$h(x) = \frac{8}{\pi}\left(\frac{\ell_c}{b_0}\right)^2 \delta b \begin{cases} 1 - e^{-w/2\ell_c}\cosh\left(\frac{x}{\ell_c}\right) & |x| \le \frac{w}{2} \\ \sinh\left(\frac{w}{2\ell_c}\right) e^{-|x|/\ell_c} & |x| > \frac{w}{2} \end{cases}$$



$$l_c = \sqrt{\frac{a_0^2\pi/48}{Ca + Bo}}$$

$$Ca = \frac{\mu Q_0}{a_0\sigma} \qquad Bo = \frac{\rho g_e a_0^2/12}{\sigma}$$

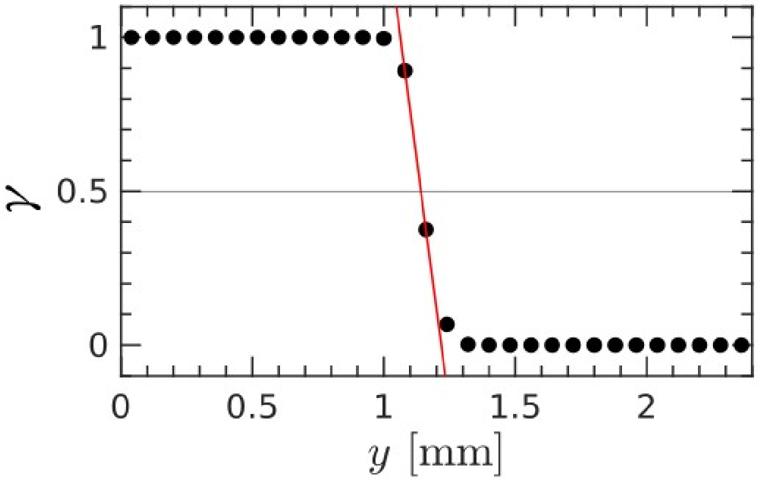
Spurious currents at the air-water interface

$$\boldsymbol{f}_\sigma = \sigma \kappa \nabla \gamma$$

$$\kappa = -\nabla \cdot \left(\frac{\nabla \gamma}{\|\nabla \gamma\|} \right)$$

Phase field ɣ changes very rapidly at the interface. Discretization prohibits accurate computation of the vector $\boldsymbol{f}_\sigma$. Solutions:

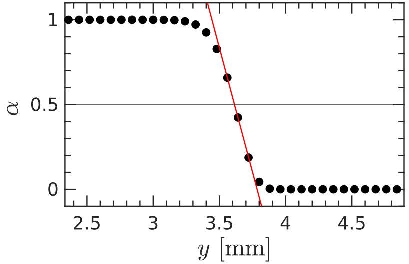
- Refined mesh → not reasonable $\delta t \sim \delta x^2$ (2D sims)
- Smoother interface (lower C_γ) → what thickness seems reasonable?
- Smooth ɣ and ∇ɣ for $\boldsymbol{f}_\sigma$ computation → costly but doable



$$a \frac{\partial \gamma}{\partial t} + \boldsymbol{Q} \cdot \nabla \gamma + \nabla \cdot \left[\boldsymbol{Q}_r \gamma (1 - \gamma) \right] = 0$$

$$\boldsymbol{Q}_r = \min \left[C_\gamma \, \|\boldsymbol{Q}\|, \; \max \left(\|\boldsymbol{Q}\| \right) \right] \boldsymbol{n}$$

Example for C_γ=0



Impact of heterogeneity: reactive transport scalings