A simulation study of reactive flow in 2-D involving dissolution and precipitation in sedimentary rocks

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Applications of reaction kinetics in transport phenomena:

- Stimulation of petroleum reservoirs
- Environmental contaminant transport
- Mineral mining
- Geological sequestration CO_2
- Chemical weathering
- Concrete degradation
- Hydrothermal processes
- Bioremediation

Complex problem!!

Accounting for both physical and chemical heterogeneity of rocks at different length scales is a challenge.

Chemical heterogeneity present at the level of grain scale ⟹ responsible for different reaction rates ⟹ dynamic evolution of pore space ⟹ Affects transport property at larger scale.

Plan of Talk

- Simulate 2-D porous rock structure

- Solve the Stokes' equation using FDM to study the velocity distribution of fluid flowing through the rock structure under a constant pressure gradient.

- Simulate reactive flow using Random walk methods with dissolution and precipitation following Gillespie stochastic algorithm

- Study temporal changes in porosity and permeability as a function of Peclet number, concentration of reactive solute and ratio of Damkholer number.

Modeling the porous rock

Motivation is

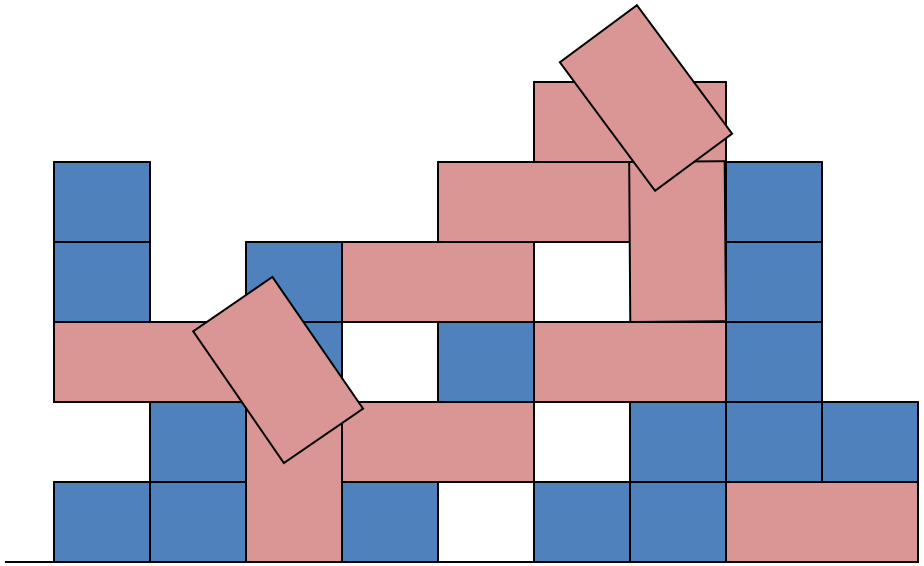
- To create a porous structure (e.g. sedimentary rock) by a realistic deposition process –

With following characteristics:

- Connected pore phase
- Tunable porosity in range 0.2-0.6

Bidisperse Ballistic Deposition (BBDM)

(Dutta et.al.,JGR,2003)



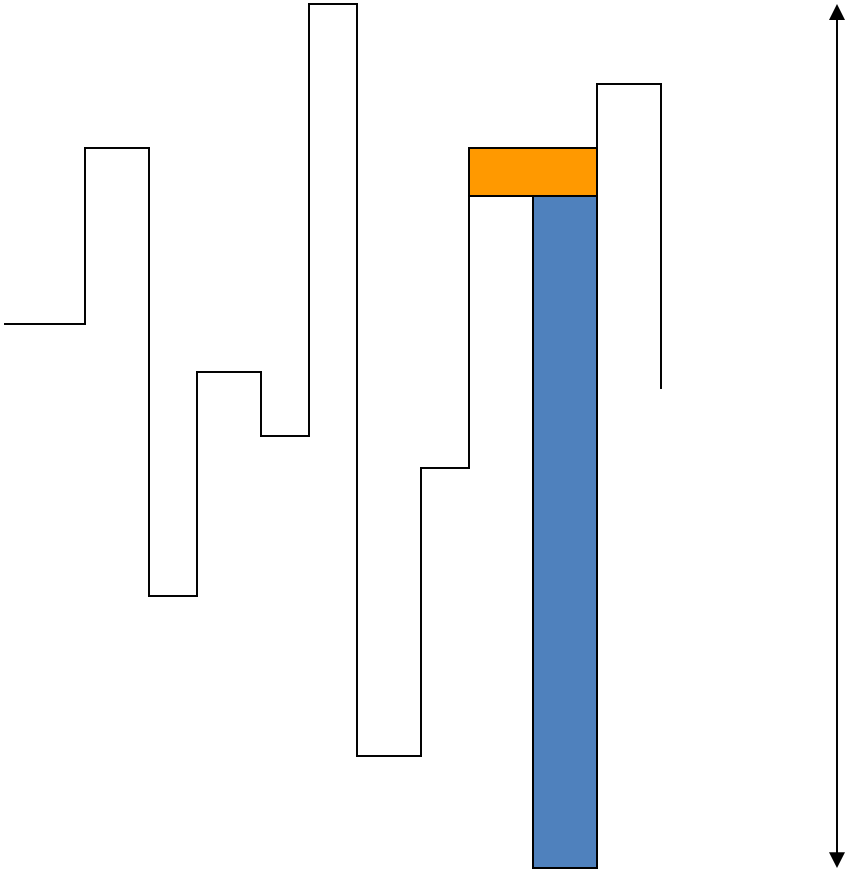
p ≡ fraction of small particles (1x1x1)

(1-p) ≡ fraction of large particles (2x1x1)

- Tunable porosity

Hoshen-Kopelmann algorithm used to detect connected pore space.

Effect of the interface



Large grain

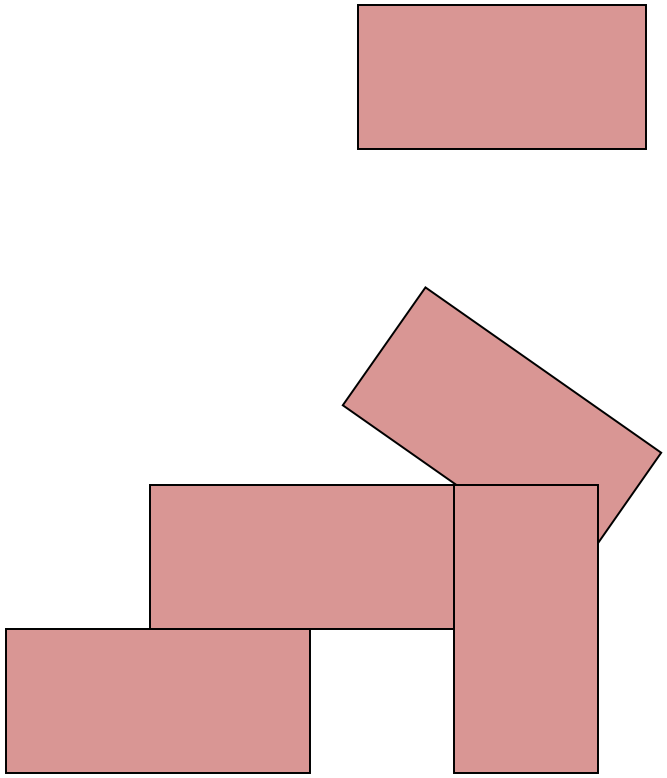
Introduces correlation between adjacent columns

Sufficient time must be allowed so that Interface saturates and bulk has a definite average porosity

Relaxed Ballistic Deposition Model

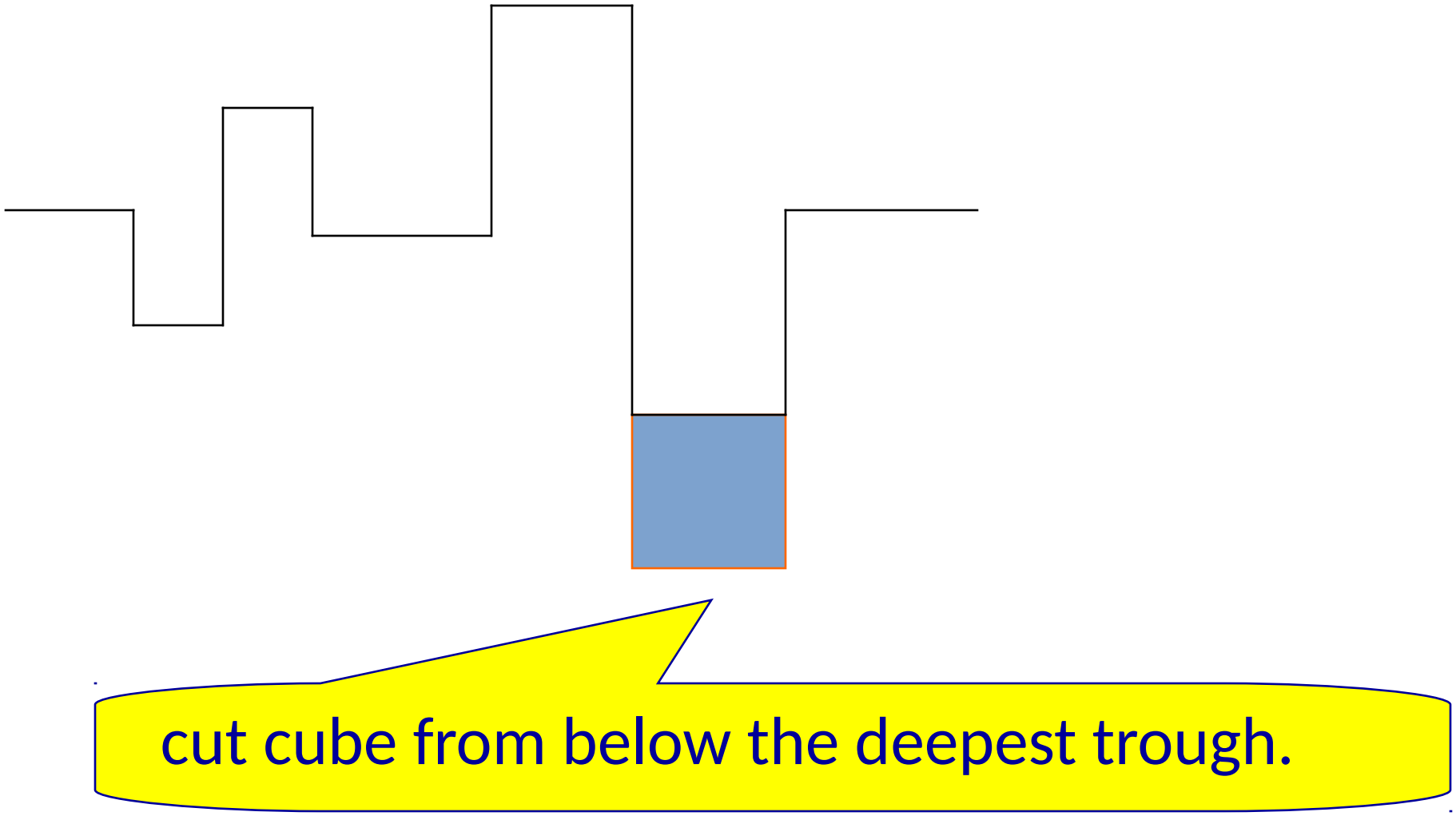
R BBDM

Grain size
1x1x2



Topples to a more stable position

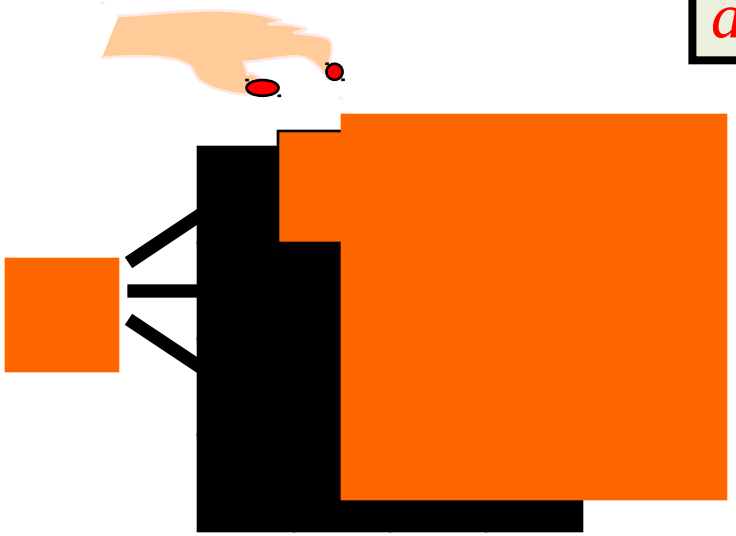
Selecting the cubic sample



cut cube from below the deepest trough.

Algorithm

- Generate 3d structure of size 128^3.
- Cut out a 2-d vertical slice.
- Scoop out a 32^2 from a 128^2
- Magnify 32^2 to 128^2.



•Each cube is observed at an increased magnification

• Realistic velocity profile with no-slip can be implemented at the walls.

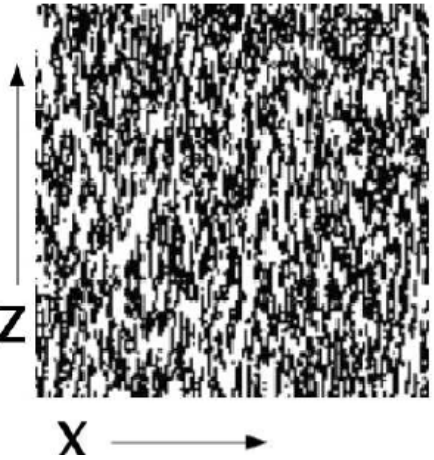
Structure

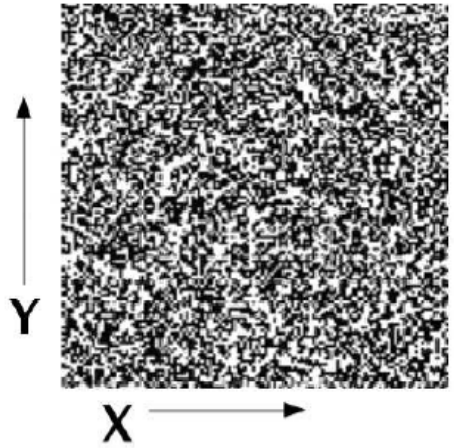
High porosity sample
ϕ=0.45(p=0.5)

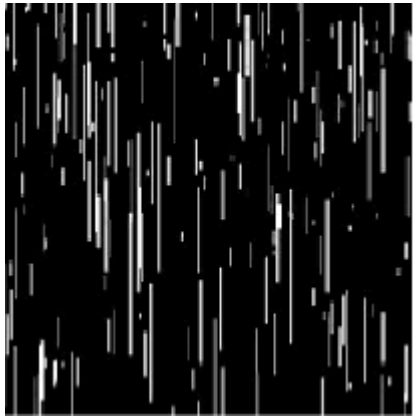
Pore

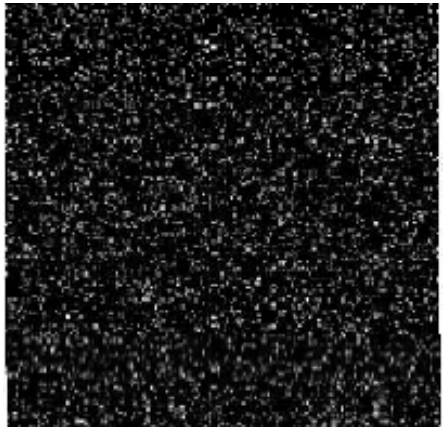
Grain

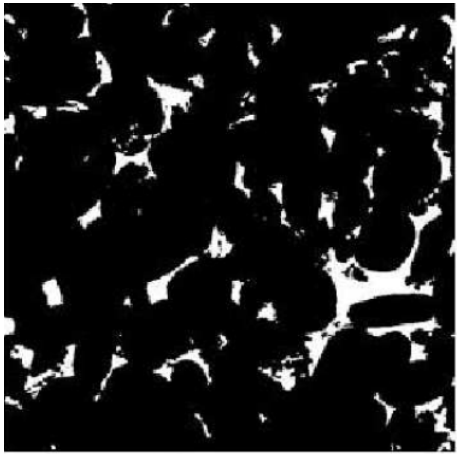
Low porosity sample
ϕ=0.27(p=0.95)

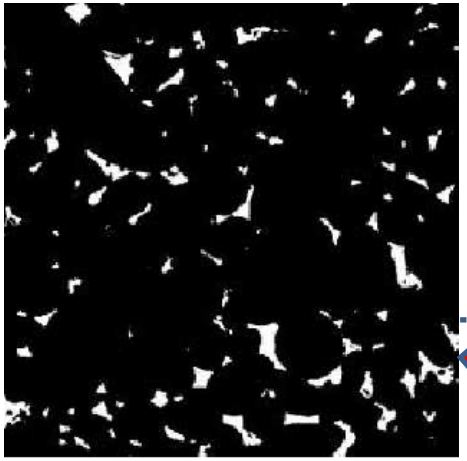






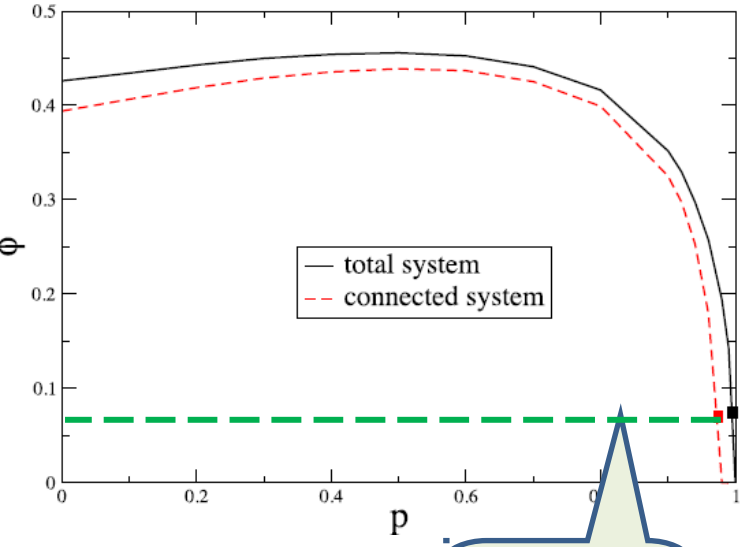






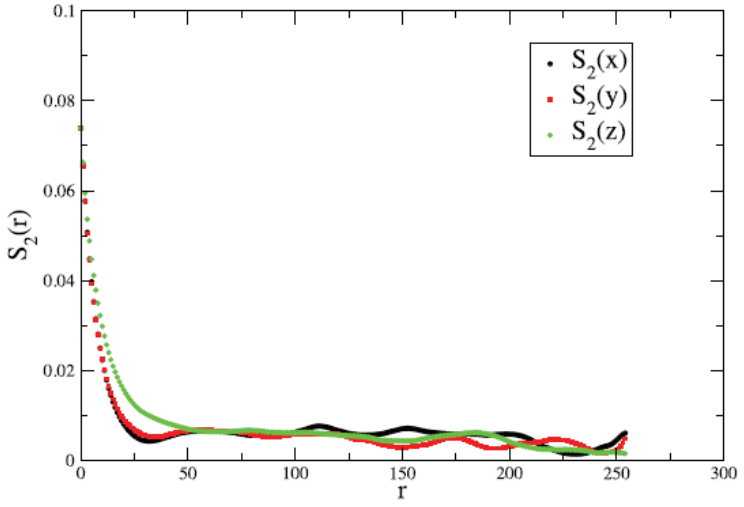
Sections of oolitic limestone(pure calcite) from the Mondeville formation of Middle Jurassic age (Paris Basin, France).

Microstructure of pore structure

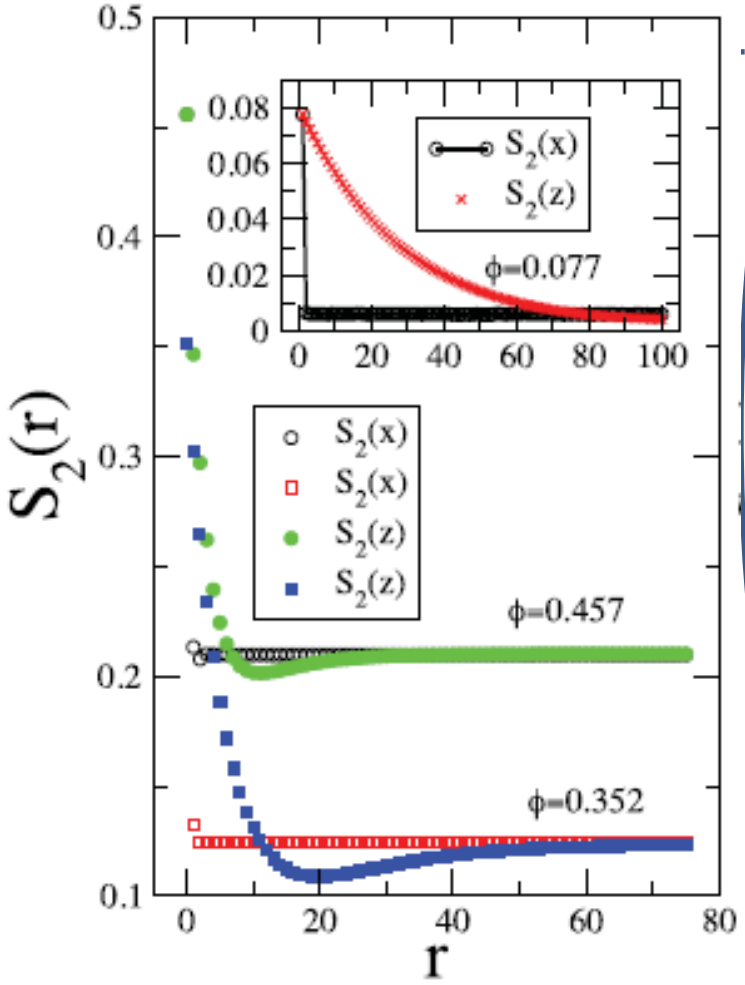


Real rock

Porosity



REAL



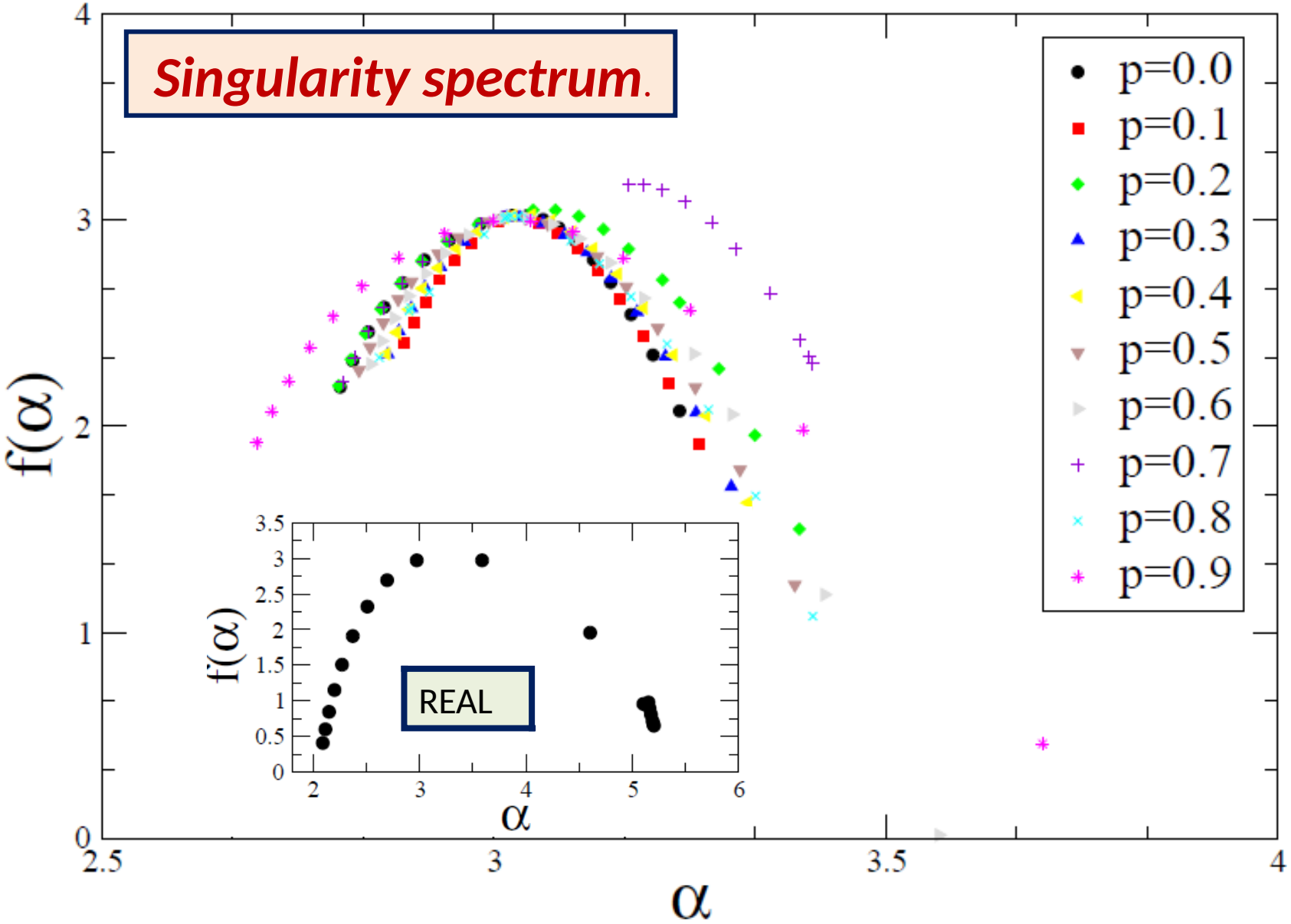
SIMULATED

2-pt density correlation

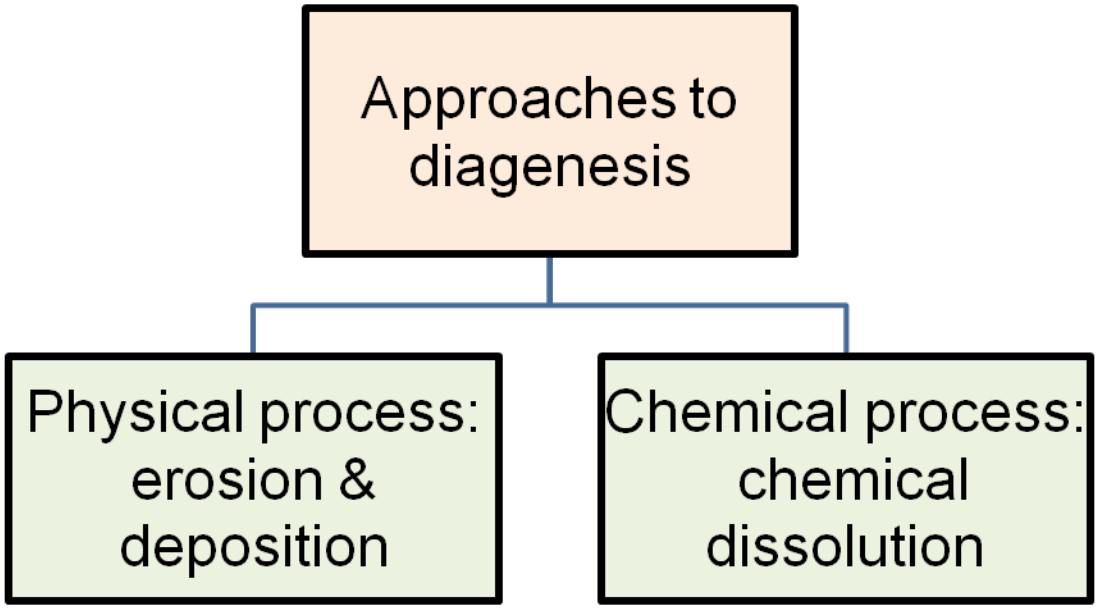
$$S_2 = < \rho(\mathbf{r}')\rho(\mathbf{r}'+\mathbf{r}) >$$

The ***Lipschitz–Hölder exponent***

$$\alpha(q) = -\frac{d\tau(q)}{dq}$$



Restructuring of the pore space



Mathematical model

Navier Stoke's equation:

$$\rho\left[\frac{\partial V}{\partial t}+(V.\nabla)V\right]+\nabla P-\mu\nabla^2 V=f_e$$

$\nabla \Rightarrow$ divergen erator

∇ or

V

$P \Rightarrow$ pressure

$\rho \Rightarrow$ de of fluid

$\mu =$

$f_e \Rightarrow$

Negligible for slow viscous flow

Absent when no external forces act on the fluid

Mathematical model

Stoke's equation:

$$\frac{\partial V}{\partial t} = -\frac{1}{\rho}\nabla P + \eta \nabla^2 V \qquad \text{.....(1)}$$

Equation of continuity:

$$\nabla . V = \frac{\partial \rho}{\partial t} = 0. \qquad \text{.....(2)}$$

Vanishes for incompressible fluid

$\eta \Rightarrow$ kinematic viscosity

Numerical model

Final equations to be iterated till steady state

$$\nabla^2 P^{n+1} = \frac{\rho}{\Delta t}(\nabla . \vec{V}^{n}) \qquad \text{.....(6)}$$

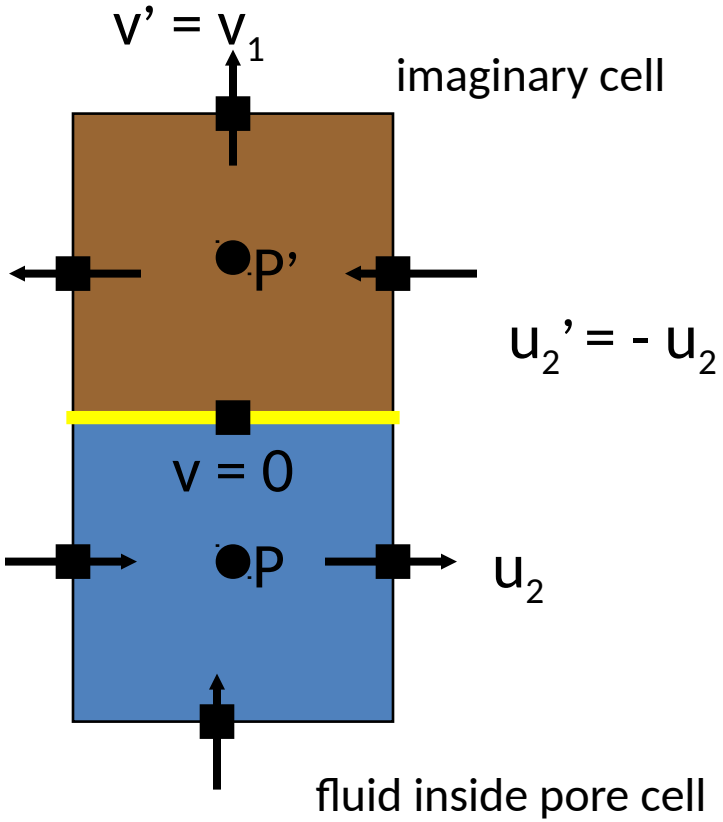
$$\frac{\vec{V}^{n+1} - \vec{V}^{n}}{\Delta t} = -\frac{1}{\rho}\nabla P^{n+1} + \eta \nabla^2 \vec{V}^{n+1} \qquad \text{.....(7)}$$

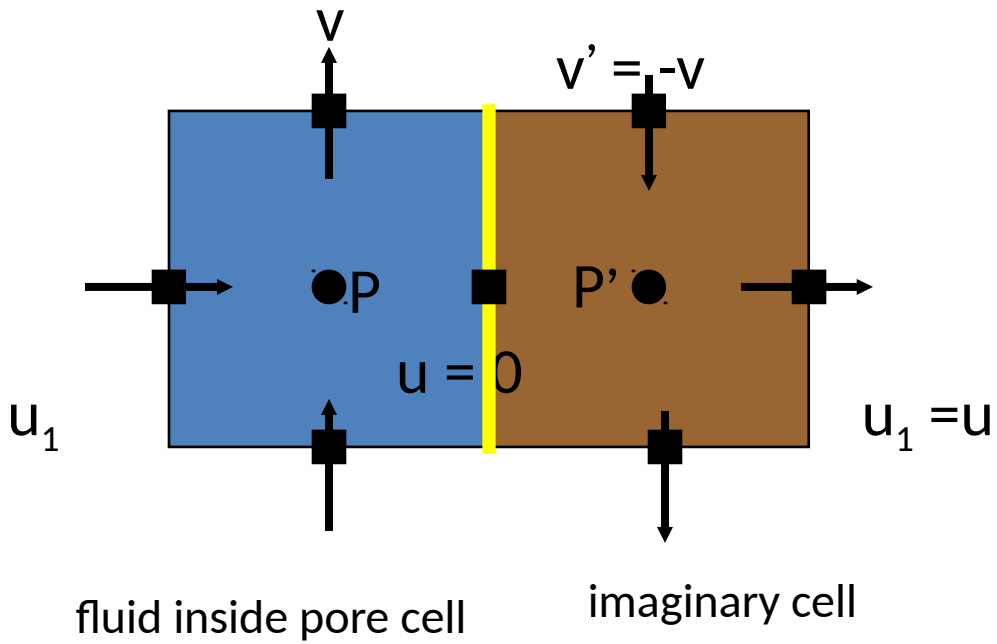
At $n = 0$, $\vec{V}^{0} = 0$

$\left| \vec{V}^{n+1} - \vec{V}^{n} \right|_{\infty} < \varepsilon$

Rewrite equation (3)

Pore-rock interface





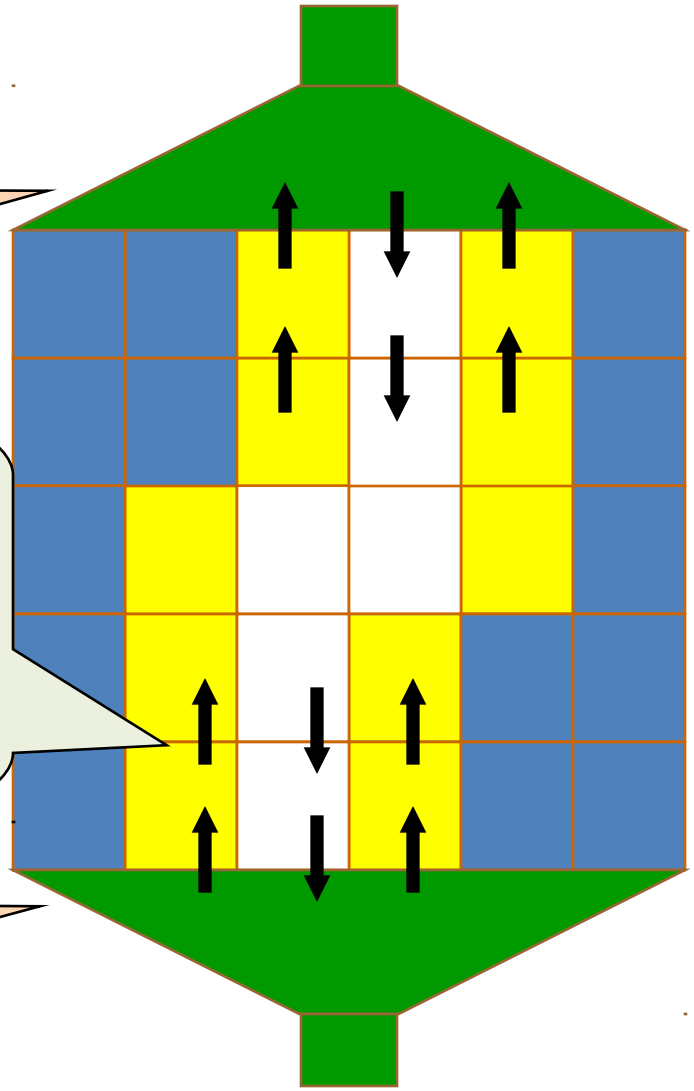
Need for imaginary grids- to take care of terms appearing outside the flow region in the P, u & v equations

More B.C.

Inlet pressure specified

Fluid enters and exits normally at entry and exit

Outlet pressure specified



Rock cell

Imagin-ary cell

Fluid cell

Darcy's Equation:

$$\mathbf{Q} = (\kappa / \mu)\nabla P$$

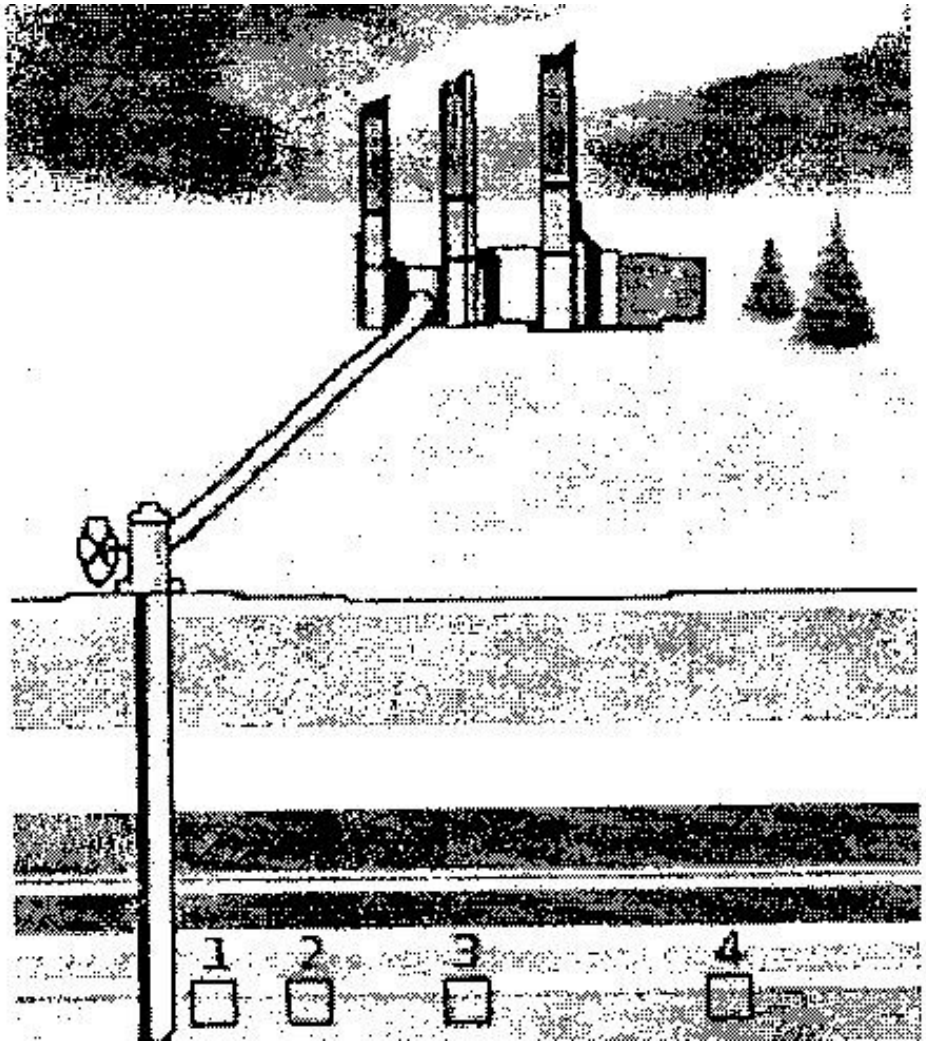
where $\mathbf{Q} \equiv$ flux

$\kappa \equiv$ permeability

$\mu \equiv$ kinematic viscosity

$\nabla P \equiv$ pressure gradient

Application: CO_2 sequestration



- CO_2 mixed with H_2O under high pressure forced underground.
- Mass transfer reactions between the reactive fluid and the mineral occur

- Reaction characteristics change as distance from inlet increases

Dissolution and Precipitation

Dissolution in the simplest form:

$A + M_1 \longrightarrow B$

A → reactive solute carried by fluid

M_1 → mineral that can be dissolved

B → product of dissolution, carried

The forward dissolution rate:

$dc_A/dt = - R_d\, c_{A,}$ c_A → concentration

R_d → dissolution r

Precipitation in the simplest form:

B → M_2 , where B reacts with anions released from dissolution to precipitate M_2

$CO_2 + H_2O \leftrightarrow H^+ + HCO^{-3}$

$A \equiv H^+$; $M_1 \equiv Mg_2SiO_4$

$Mg_2SiO_4 + 2H^+ \rightarrow Mg^{++} + H_2SiO^-_4$

$B \equiv Mg^{++}$

$Mg^{++} + HCO_3^- \leftrightarrow MgCO_3 + H^+$

$M_2 \equiv MgCO_3$

Precipitation may be described by

$$dc_B/dt = -R_P c_B \ ,$$

c_B → concentration of cations B at any t;

R_p → precipitation reaction constant.

Using Gillespie's stochastic algorithm which describes the survival time for a particular particle,

Dissolution probability $P_d = 1 - e^{-R_d t_{res}}$

and

Precipitation probability $P_p = 1 - e^{-R_p t_{res}}$

The reaction rates for dissolution and precipitation: $R_d = k_1 \sigma \Omega_A$ and $P_p = k_2 \sigma \Omega_B$ respectively.

k_1, k_2 are kinetic coeffs. for dissolution and precipitation; σ specific surface area, and $\Omega_B(\Omega_A)$ is a function of the concentration of the species.

Two important flow parameters:
Peclet number: UL/D
Damkholer number: kL^2/D

Simulation of reactive flow:

- Pressure and velocity at every pore calculated .

- Initial porosity and permeability calculated using Darcy's law.

- Random walkers mimic reactive species

- A walker is capable of either advection or diffusion, which it decides stochastically.

- The velocity component having higher magnitude at every cell, determines the direction of advection in that cell.

- Diffusion however can occur in all directions with equal probability.

- The probability of advection and diffusion is given by

$$P_{diff} = 1/\{4(Pe + 1)\}$$

$$P_{adv} = 1 - P_{diff}$$

where Pe = UL/D ≡ Peclet Number

U ≡ local velocity,

L ≡ grid length

D ≡ diffusivity.

Algorithm contd……

- Fixed number of walkers, mimicking the partial pressure of CO_2 dissolved in H_2O released at t=0.

- Walker moves one step with appropriate velocity.

- movement occurs in `constant distance' jumps

- time of travel τ of each walker is different and appropriate to local velocity, i.e. $\tau \alpha 1/v_{lc}$

- $t_{res} = \tau/2$

• c_A at any instant is calculated as the number of active walkers w_A per unit volume of the fluid.

Dissolution is a stochastic process. A walker w_A dissolves a site of M_1 creating a new pore while releasing a cation w_B in the fluid.

•The walker w_A `dies' after it completes dissolution.

•Walker w_B, being carried by the fluid, moves following the same rules as the walkers w_A.

•A single w_B can cause precipitation at a single pore mesh cell

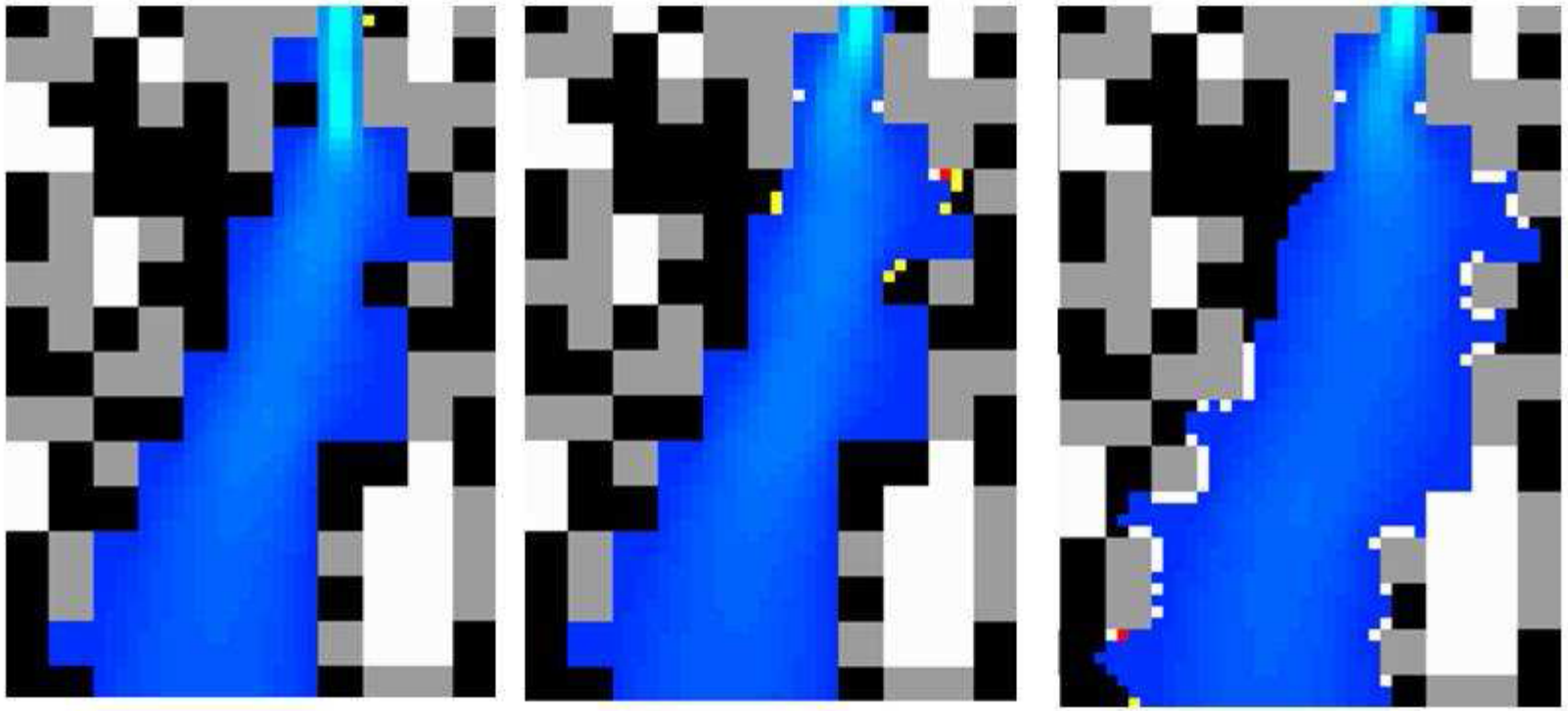
- Dissolution and precipitation is done in parallel.

- The concentration of the reactive species A in the fluid, decreases with distance from the inlet, as we have assumed the reaction is irreversible and there is no further replenishment of the active species A

- The time development of the changes that the fluid causes as it flows through the sample is tracked.

- Flow modulated properties of the sample such as porosity, permeability, specific surface area are tracked over 150 time-steps.

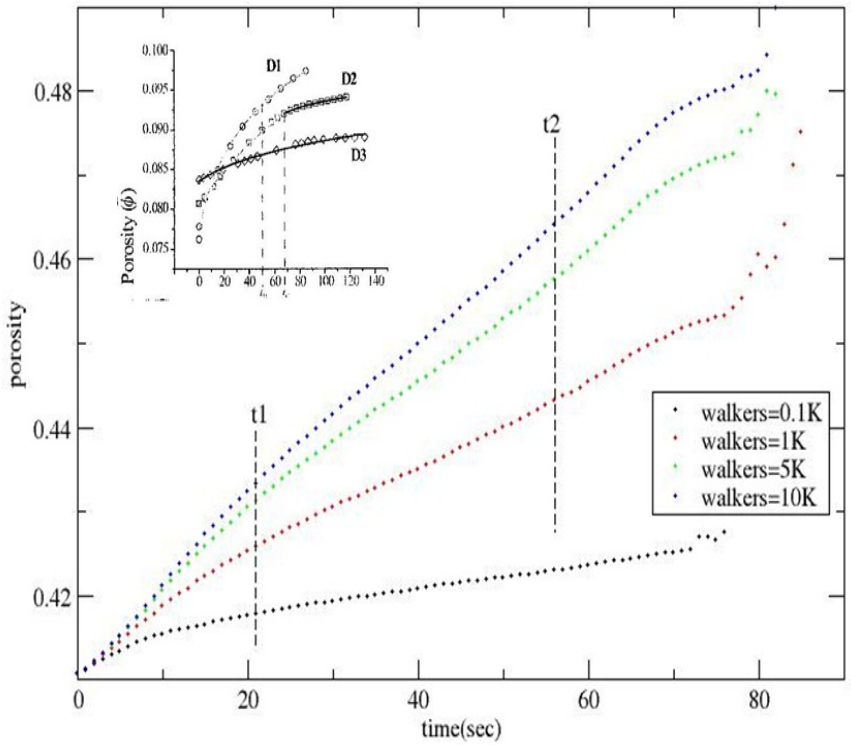
t=0 t=24 t=100



(a) (b) (c)

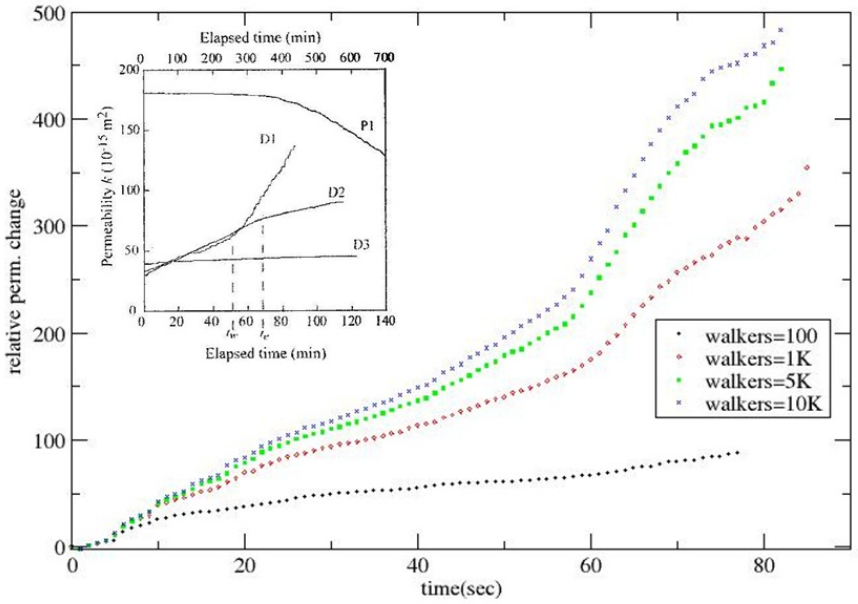
Panels show the time development in a channel for P = 1K, w_A = 10K and Da_d/Da_p= 10.

Only Dissolution

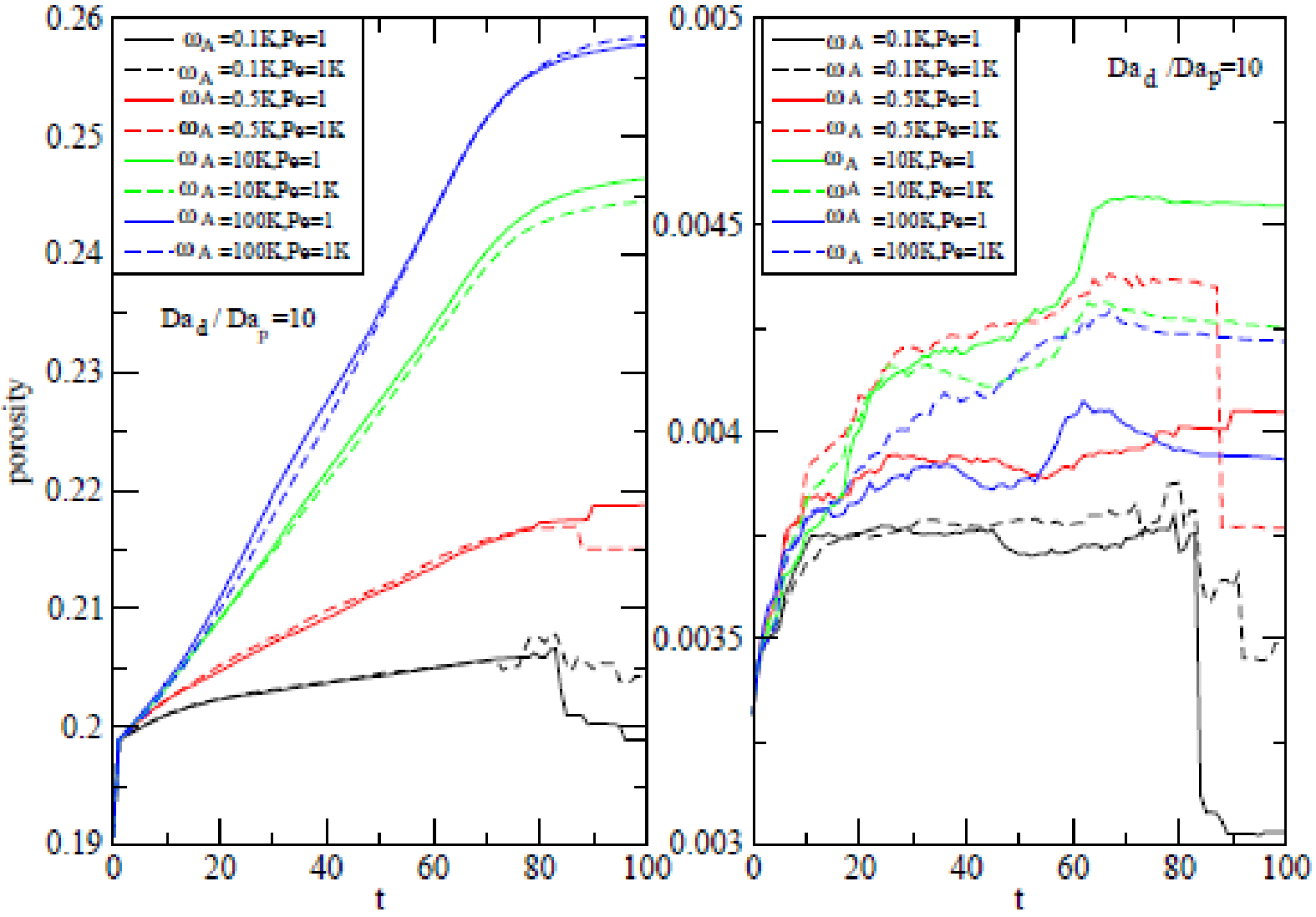


Porosity

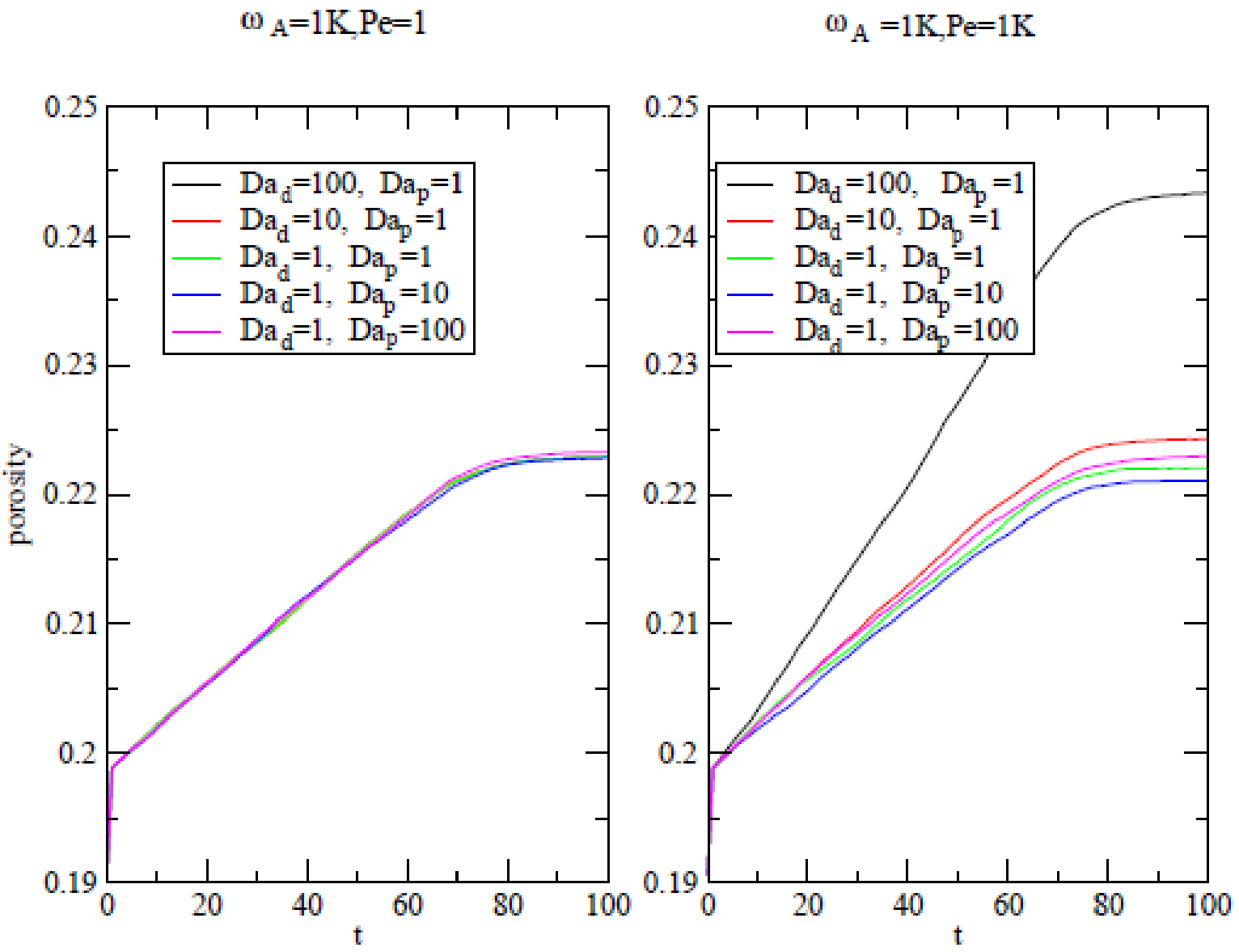
Relative Permeability



Sadhukhan et al. J Hydrology, 2012

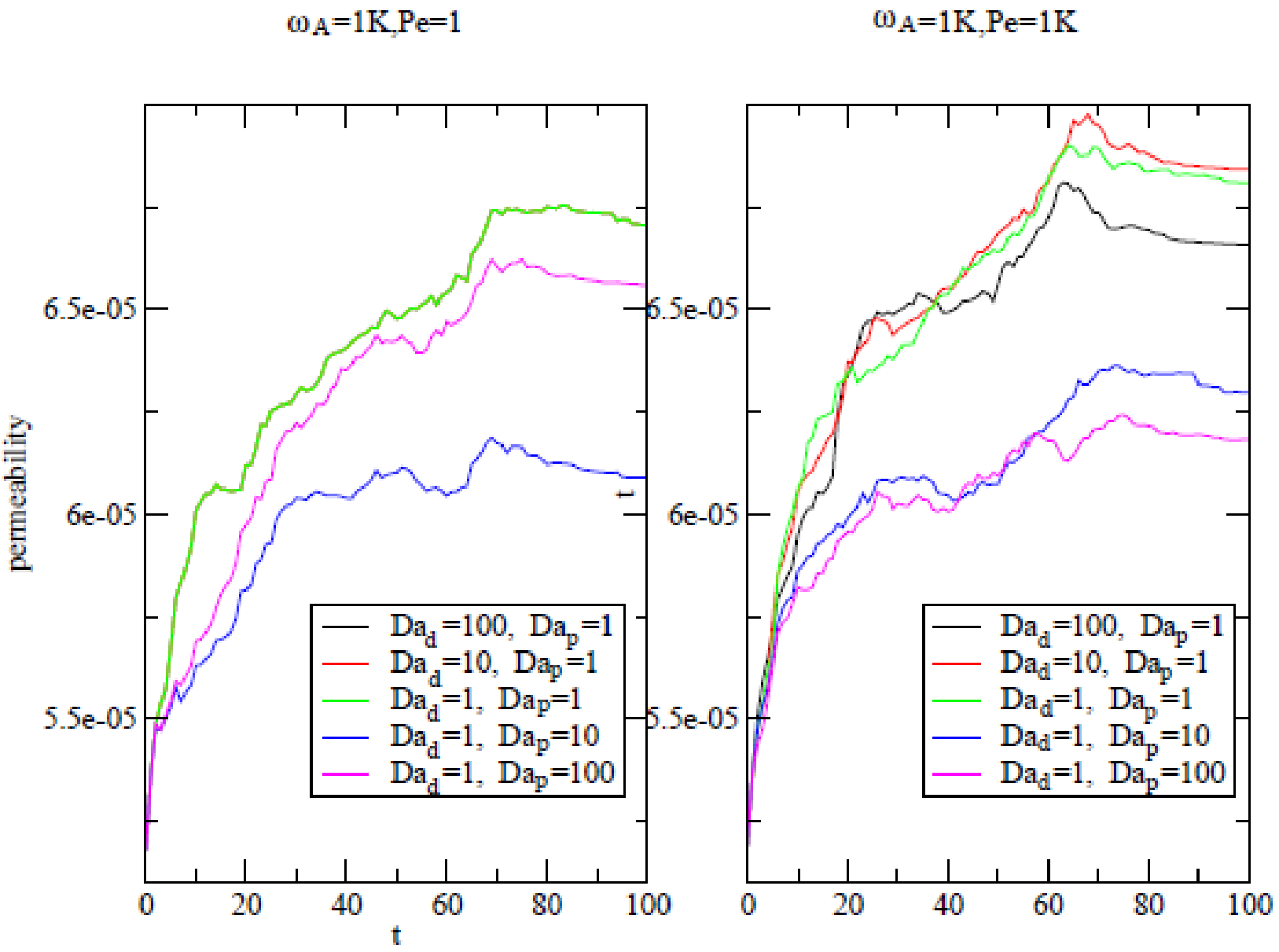


Variation of porosity and permeability for constant Da_d/Da_p, variable conc., variable *Pe*



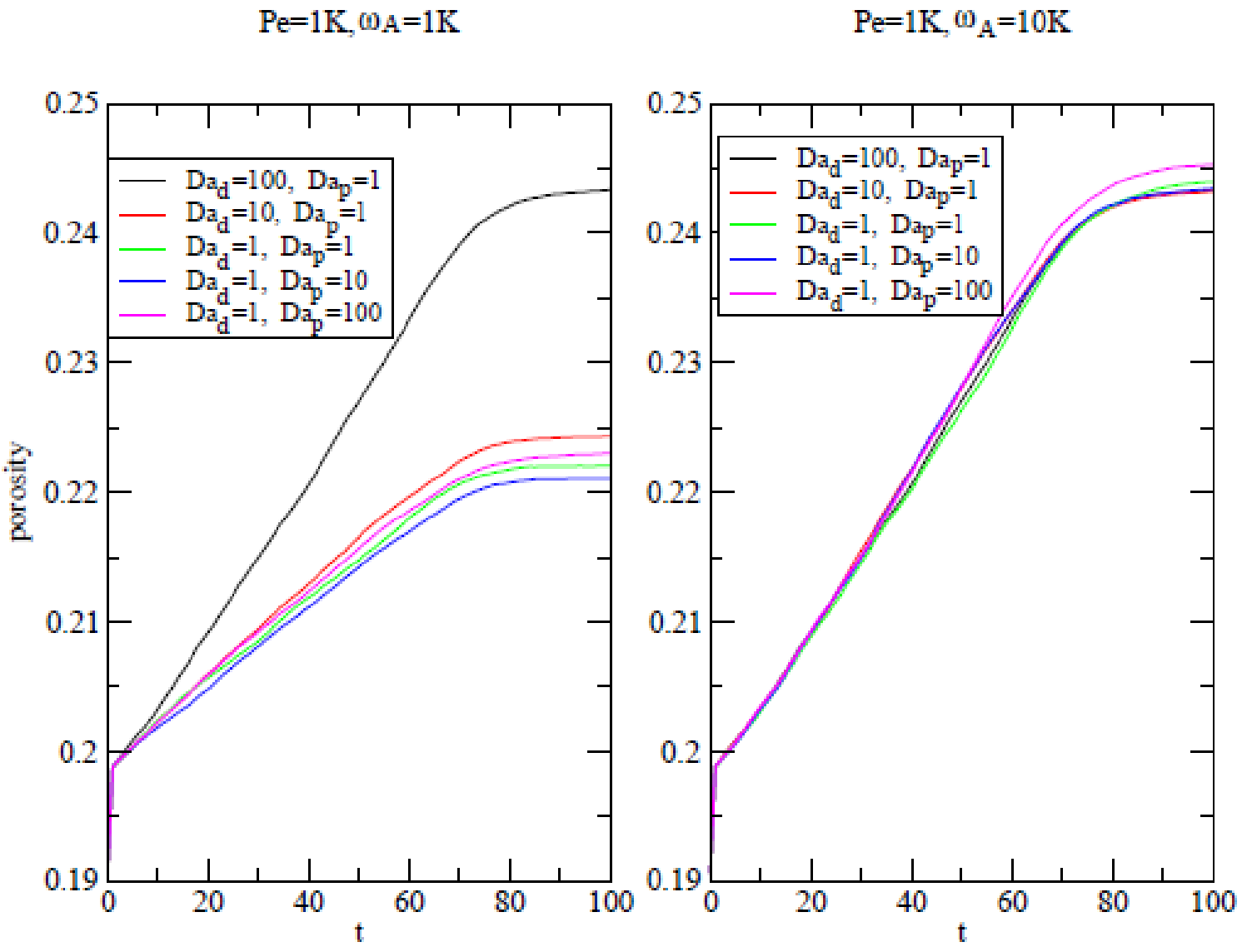
Porosity changes: Fixed Conc. of w_A, variable Da_d/Da_p

Left panel: low *Pe*; Right panel : High *Pe*

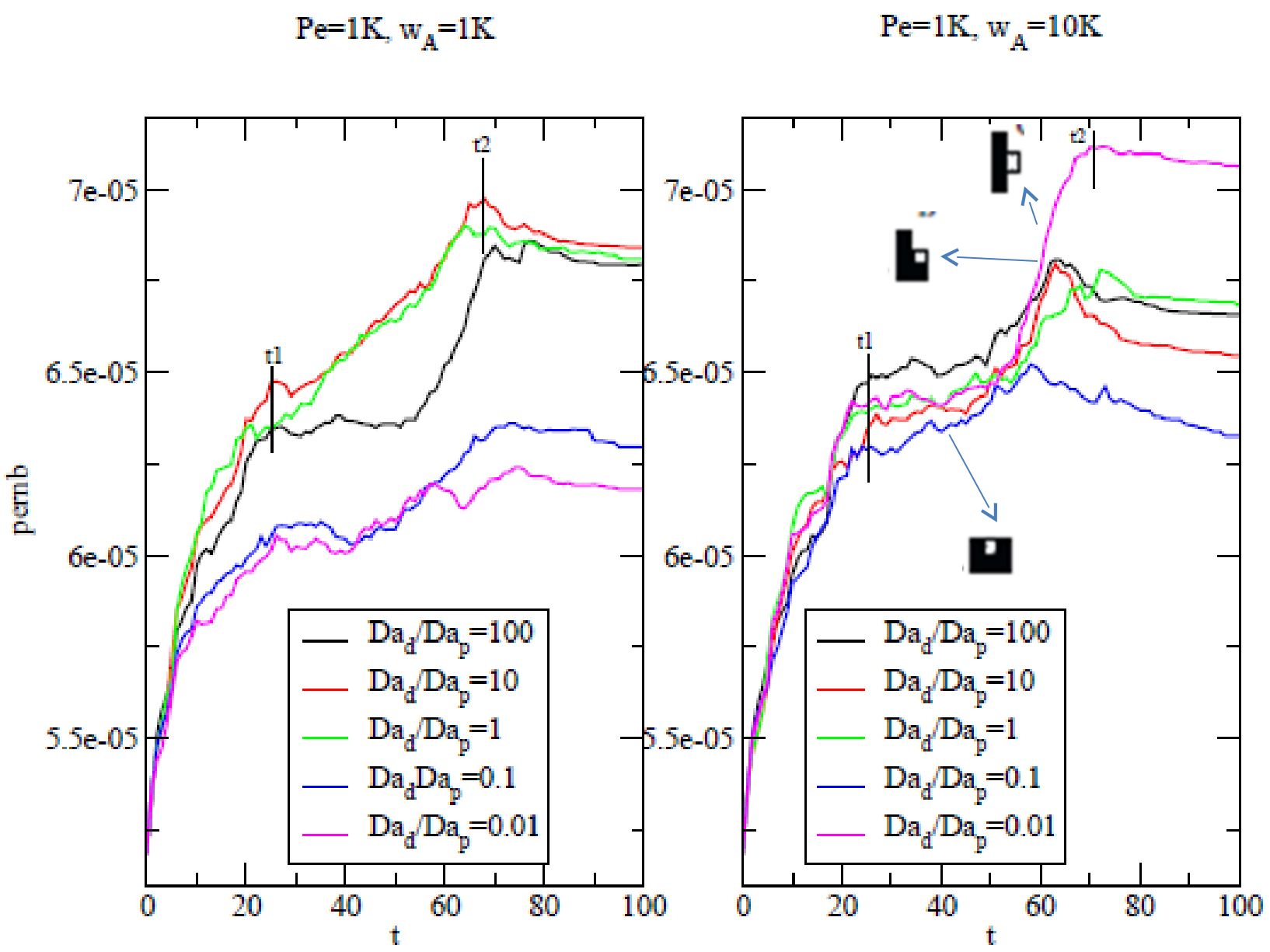


Permeability changes: Fixed Conc. of w_A, variable Da_d/Da_p

Left panel: low *Pe*; Right panel : High *Pe*



Fixed *Pe* and variable Da_d/Da_p. Porosity change for low and high concentration.



Permeability changes: Fixed *Pe*, variable Da_d/Da_p

Left panel: low conc.of w_A; Right panel : High conc.of w_A

Conclusions:

- Apart from the complex geometry of the pore space, dissolution and precipitation reactions are determined by the combination of several parameters including the Pe that control the flow rate, the concentration of the reactants and the kinetic reaction coefficients.

- Results indicate that the reaction rates of dissolution have a greater affect than the corresponding rates governing precipitation but the impact is greater for higher Pe and lower concentration of reactive solute w_A

- Porosity and permeability can attain their desired value only through an optimum combination of these parameters.

Moreover as in our system dissolution and precipitation can occur simultaneously, a direct comparison with available experimental

The Team

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Some references:

1.Dutta, Tapati., Tarafdar, S., 2003. J. Geophys. Res. 108 (B2), 20–62.

2. Sadhukhan .et.al., Physica A 387 (2008) 4541-4546

3.Dutta et.al., 9th WMSCI, Orlando, Florida, 2005

4.Sadhukhanet.al.,Model.Simul.Mater.Sci.Eng.,15(2007)773

5.Dutta et.al., J.Geophys. J.Int.,169 (2007) 1366

6. Sarkar et.al., MIT Earth Resources Lab. Indus. Consortium Meeting,2004

7. A.Giri et al. Geophys. J. Int.,(2012),**192**, 1059-1069

8. Luquot et al., Chem. Geology, 265 (2009) 148-159

9. Sadhukhan et al.; J. Hydrol. (2012), **450,** 134

THANK YOU