Transfers in porous media

Objectives

- To understand the transfer mechanisms in porous media (convection, dispersion, adsorption, transformation) and their mathematical formalism (different forms of the Convection Dispersion Equation - ECD-)
- Interpret results of curves of breakthroughs of pollutants through a layer of soil.

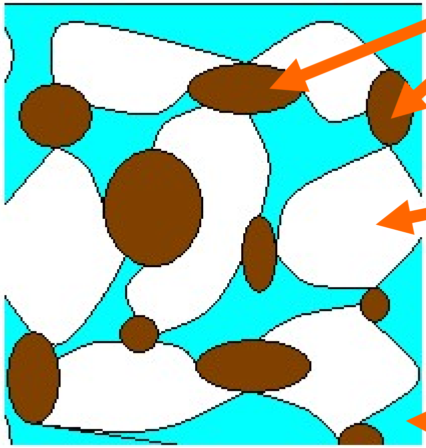
Contents

  – Construction of the Convection Dispersion Equation in its simple form
  – ECD with adsorption, generalized ECD.
  – Breakthrough curves (theoretical, experimental)
  – Practice

Transfers in porous media

Reminders on porous media

Soil, porous medium



Solid phase: grains (silica, limestone, metal oxides ...) + MO? Volume Vs, Mass Ms

Gas phase: air (enriched in gas) Volume Va, Mass Ma << Me and M

Liquid phase : leaching water properties of H2O: good solvent, considered incompressible, Δhvap high, Volume Vw, Mass Mw

Void volume : $\mathbf{V_v = V_w + V_a}$

= blue area + white area

Reminders on porous media

Some facts…

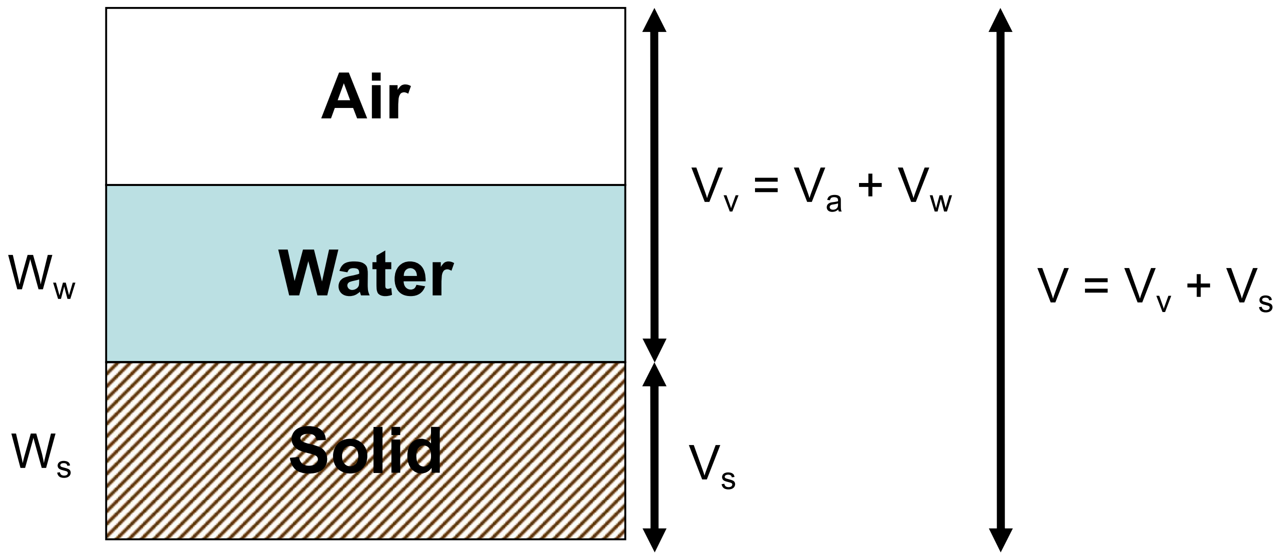
Porosity : $\varepsilon = V_v / Vt$

volumetric water content : $\theta = V_e / V$ $(0 \leq \theta \leq n)$

Saturation (ϵ [0,1]): $s = \theta / \varepsilon$ weighted water content : $W = Ww / Ws$

Solid volumetric mass : $\rho_s = M_s / V_s$ (2700 kg.m^{-3})

Dry volumetric mass : $\rho_d = M_s / Vt$ (1600 kg.m^{-3})



Aims: Data Analysis → Model?

Applications:

Pollutant degradation

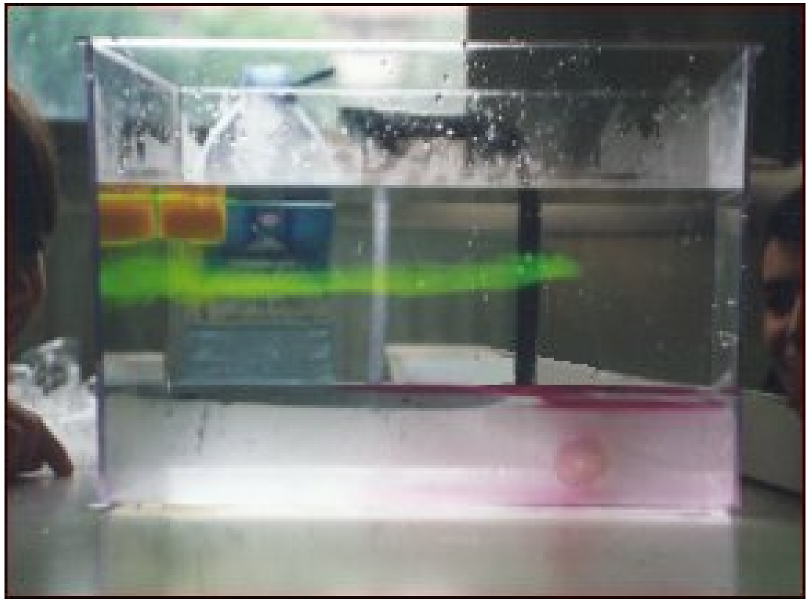
Industrial process

Mass transport

Convection

Deterministic

Molecular diffusion

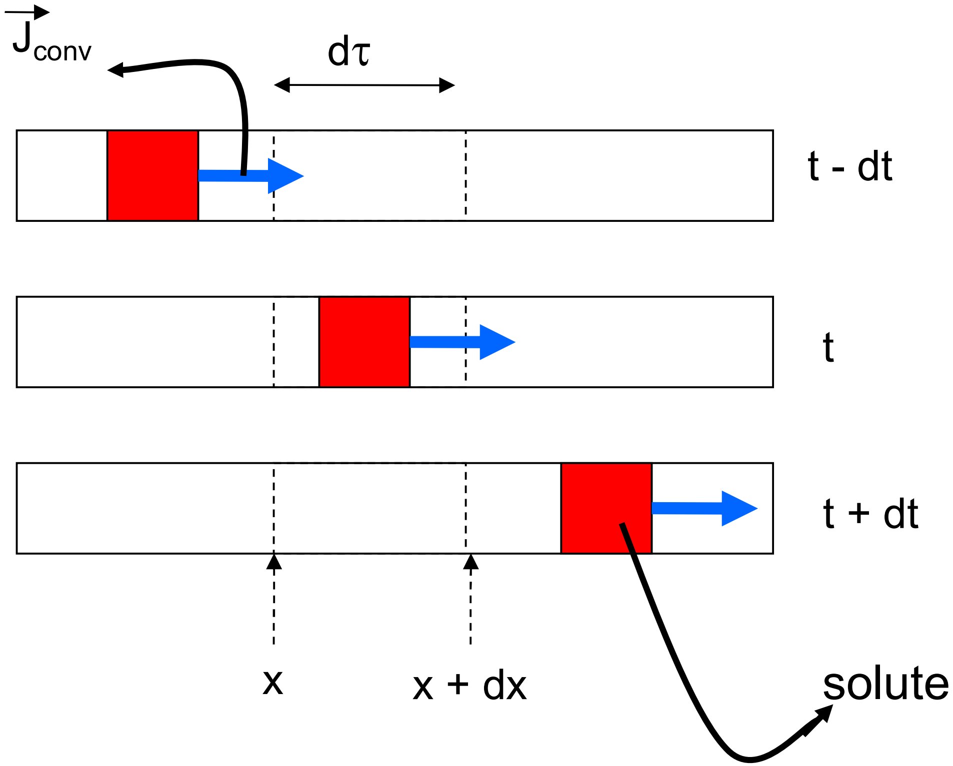


With his fragile hands, diffusion tries to equilibrate the system

Convective transport

Reminder : in Fluid mechanics, continuity $\quad \mathrm{div}(\rho\vec{v}) + \partial\rho/\partial t = 0$

For a solute transported by pure convection (advection) in a fluid velocity $\vec{v}$



The convective flux is :

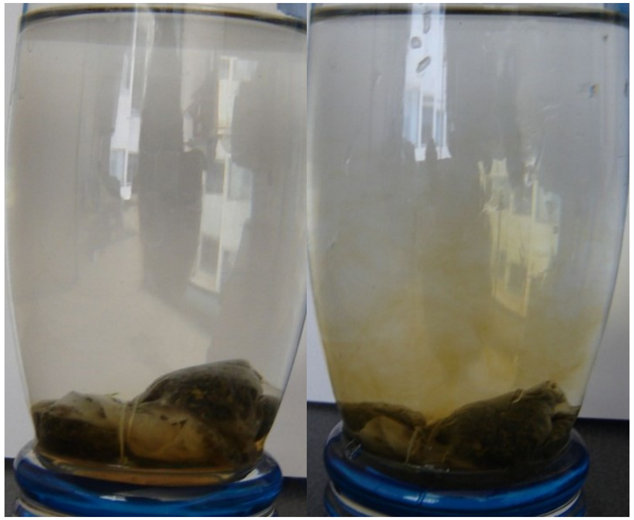
$$\vec{J}_{conv} = \vec{v} * C$$

$$\frac{\partial C}{\partial t} = -\frac{\partial J_{conv}}{\partial x} \quad \text{i.e.}$$

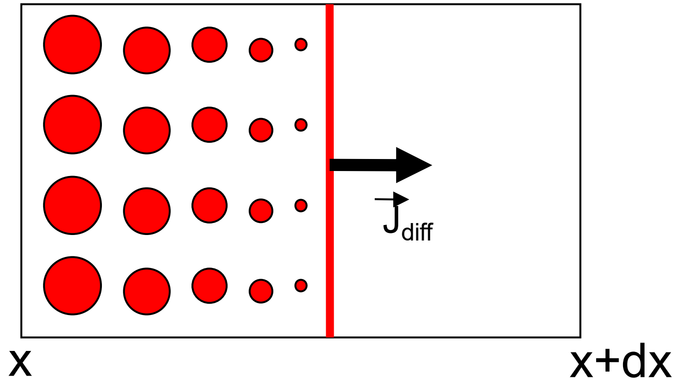
$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial x} = 0$$

diffusion

Diffusion : Fick's law : $\overrightarrow{J_{diff}} = - D_0 * \overrightarrow{grad}\,(C)$



D_0 ($m^2.s^{-1}$) diffusion coeff in water/air
C ($g.m^{-3}$) solute concentration
J_{diff} ($g.m^{-2}.s^{-1}$) diffusive flux of particles



Mass balance :

$$(J(x,t) - J(x+dx,t)).dt = \frac{\partial c}{\partial t}.dx.dt$$

$$-\frac{\partial J}{\partial x}.dx.dt = \frac{\partial c}{\partial t}.dt.dx$$

$$-\frac{\partial J}{\partial x} = \frac{\partial c}{\partial t}$$

diffusion

Diffusion : Fick's law : $\vec{J}_{diff} = - D_0 * \overrightarrow{grad}\,(C)$

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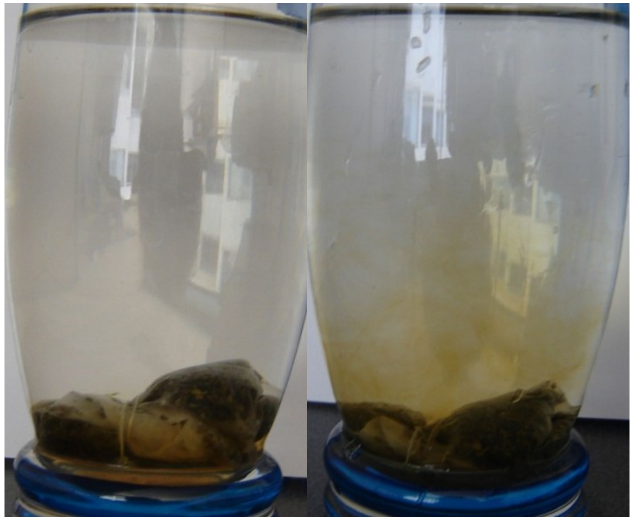
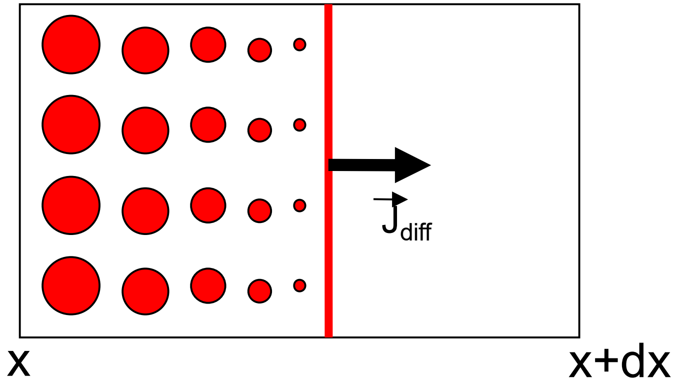




Mass balance :

$$\frac{\partial C}{\partial t} = - \frac{\partial J_{diff}}{\partial x}$$

i.e.

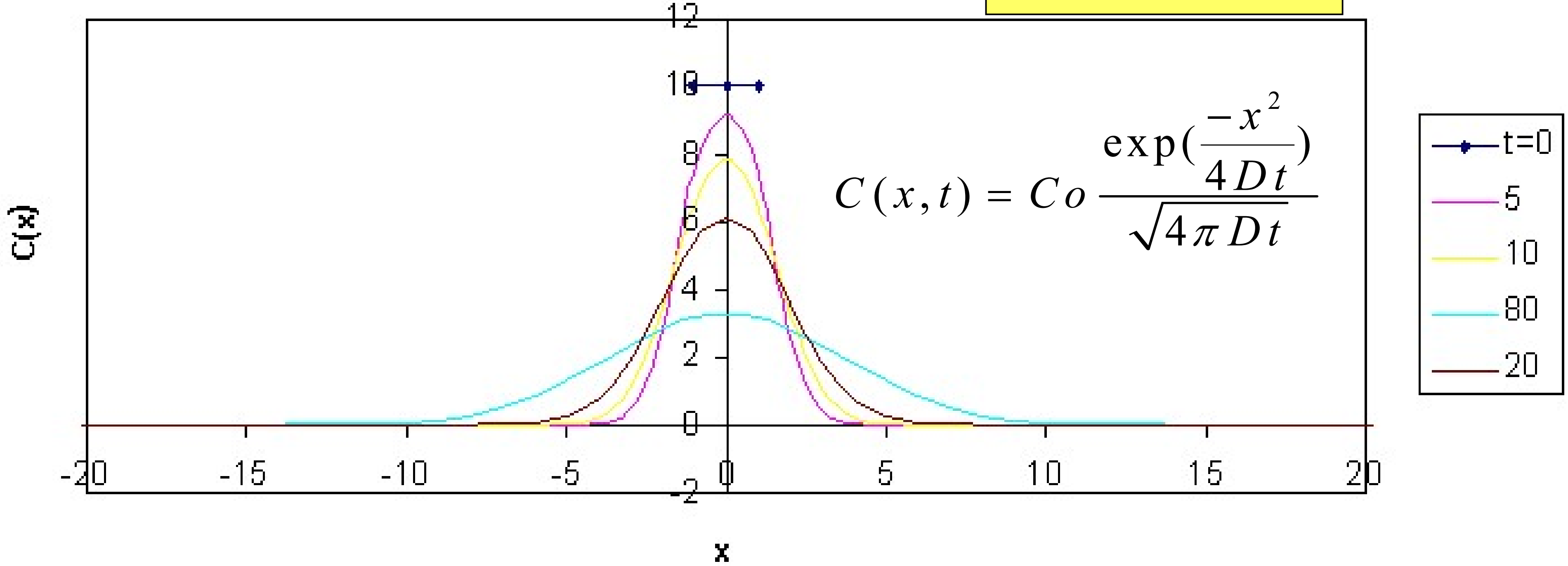
$$\frac{\partial C}{\partial t} = D_0 \frac{\partial^2 C}{\partial x^2}$$

Diffusion equation

From diffusion to dispersion

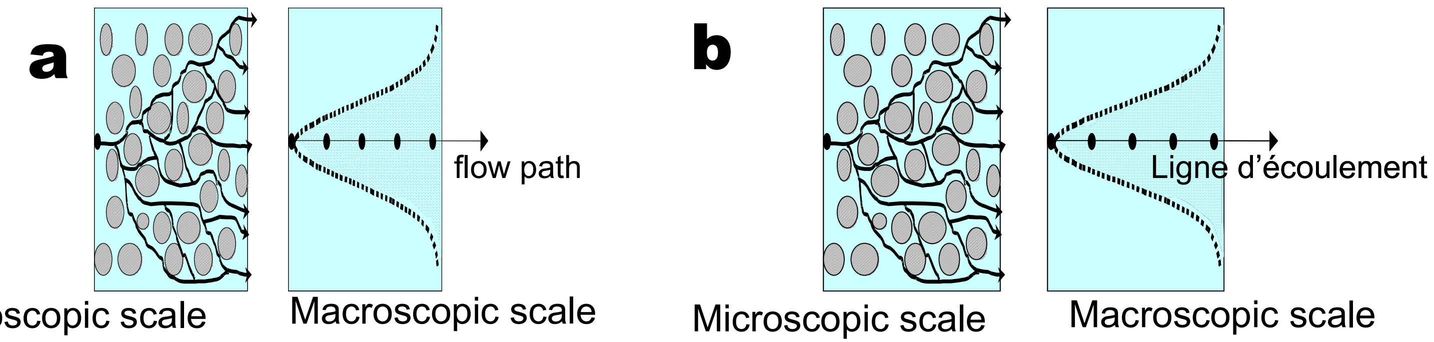
Standard diffusion

$$\frac{\partial C}{\partial t} = D_0 \frac{\partial^2 C}{\partial x^2}$$



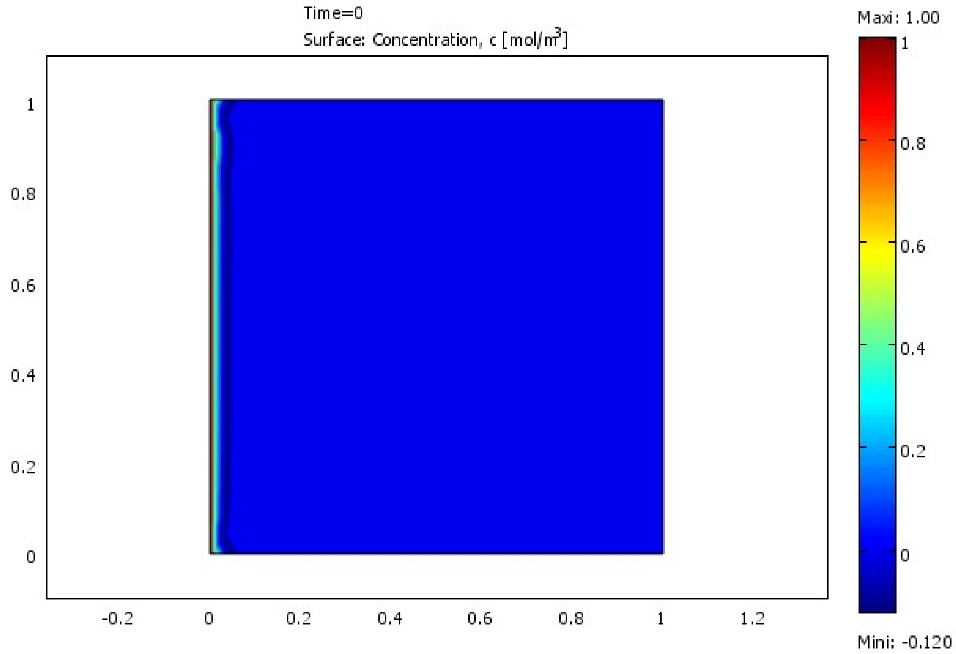
$$C(x,t) = Co \frac{\exp\left(\frac{-x^2}{4Dt}\right)}{\sqrt{4\pi Dt}}$$

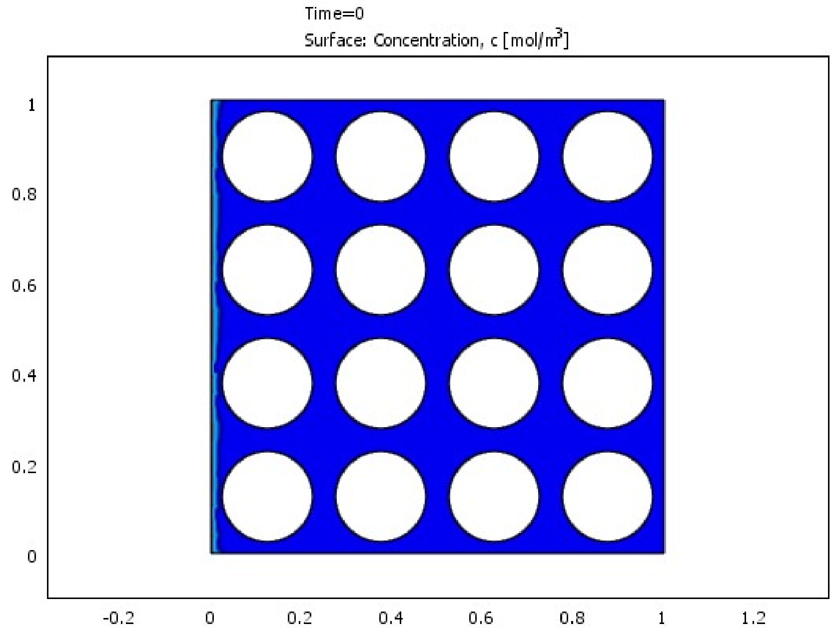
Mechanical dispersion

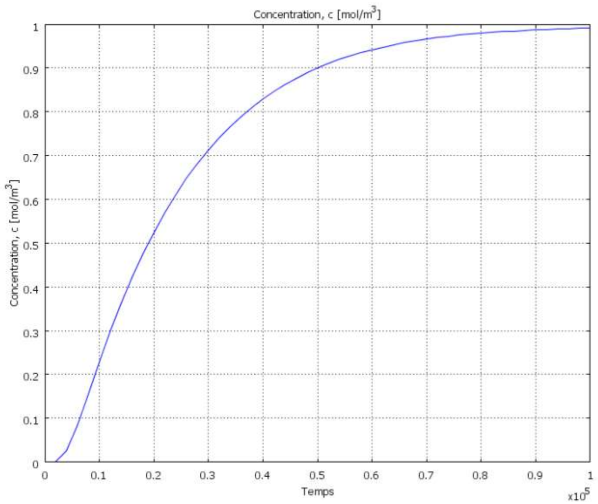


Explanation on the mechanical dispersion

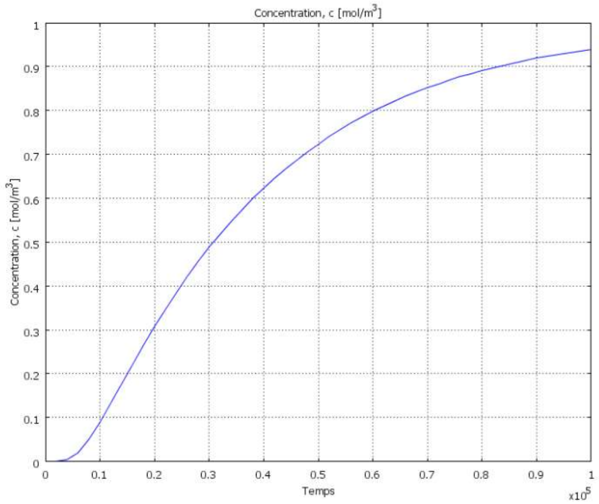
From diffusion to dispersion



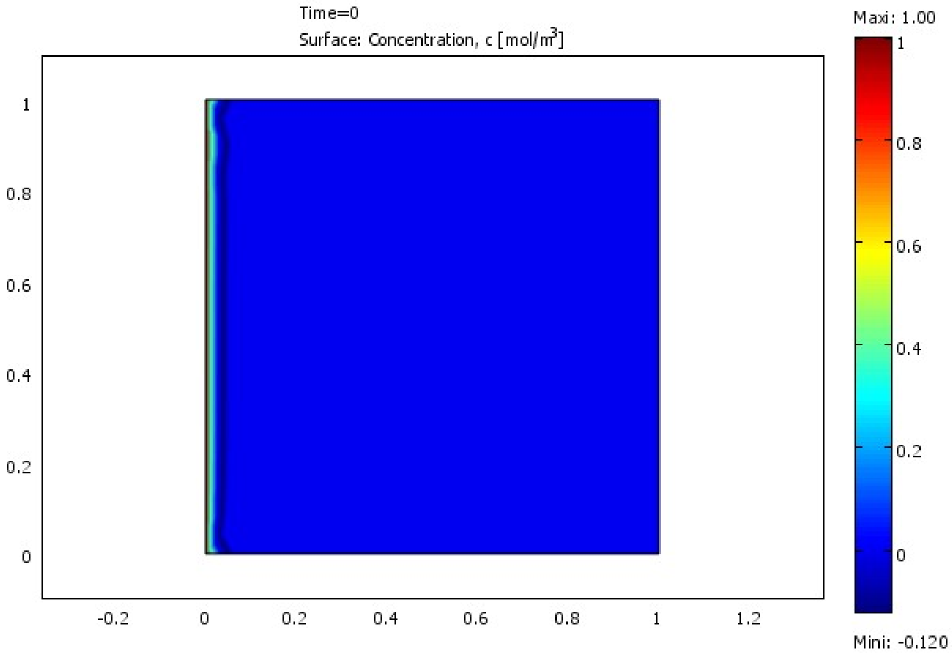


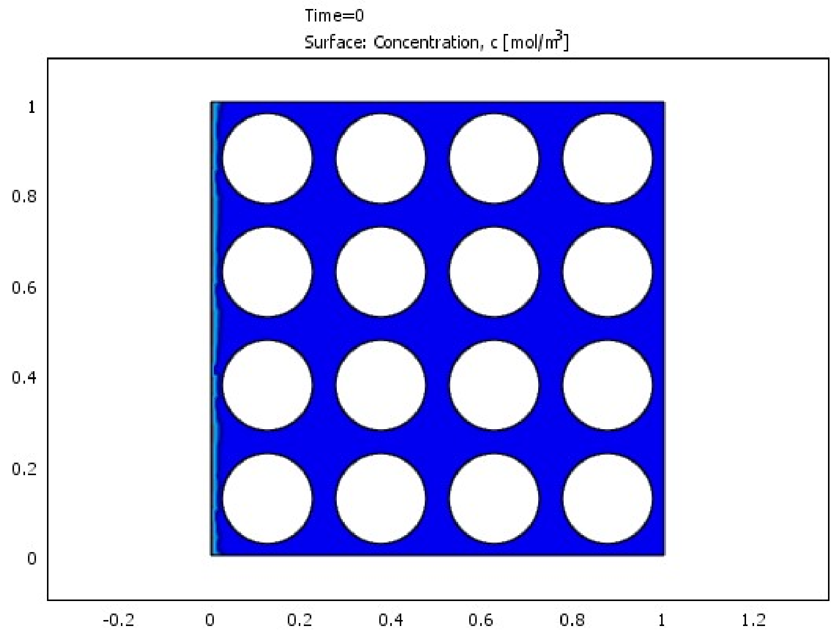


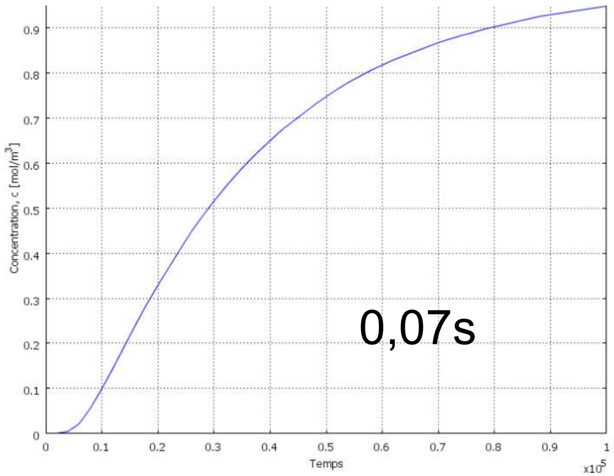
Free diffusion quicker?



Comparison between macro and microscale



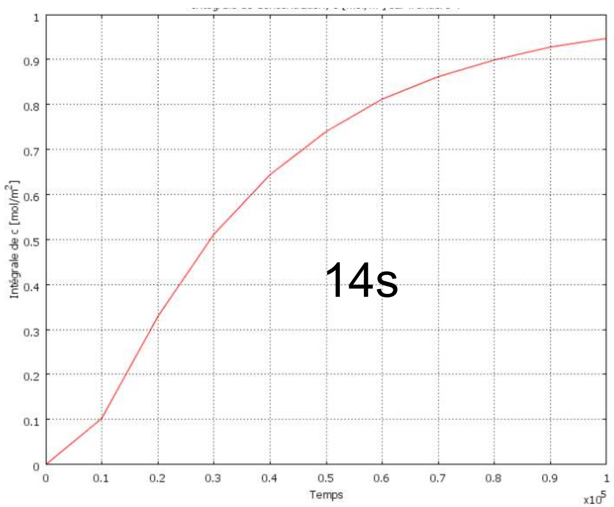




$$\frac{\partial c}{\partial t} = D0\,\frac{\partial^2 c}{\partial x^2}$$

$$0{,}52.\frac{\partial c}{\partial t} = 0{,}52.\frac{D0}{1{,}54}\frac{\partial^2 c}{\partial x^2}$$

0,52? ε
1,54? τ

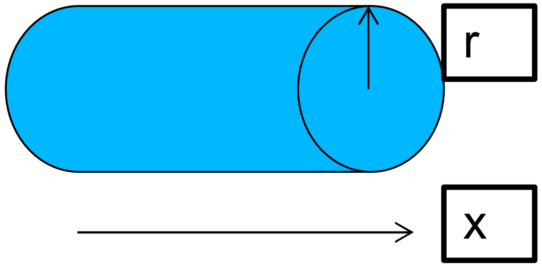


And if we have a flow?

Let's have a look on the taylor dispersion

Flow in a tube

$$\frac{\partial C}{\partial t}+U_0\left(1-\frac{r^2}{a^2}\right)\frac{\partial C}{\partial x}=Dm\left(\frac{\partial^2 C}{\partial r^2}+\frac{1}{r}\frac{\partial C}{\partial r}+\frac{\partial^2 C}{\partial x^2}\right)$$



$$\frac{\partial C}{\partial t}+U_0\left(1-\frac{r^2}{a^2}\right)\frac{\partial C}{\partial x}=Dm\left(\frac{\partial^2 C}{\partial r^2}+\frac{1}{r}\frac{\partial C}{\partial r}\right)$$

if a<<L

$$U_0\left(\frac{1}{2}-\frac{r^2}{a^2}\right)\frac{\partial C}{\partial x_1}=Dm\left(\frac{\partial^2 C}{\partial r^2}+\frac{1}{r}\frac{\partial C}{\partial r}\right)$$

$x_1=x-U_0t/2$

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right)=\frac{U_0}{Dm}\left(\frac{1}{2}-\frac{r^2}{a^2}\right)\frac{\partial C}{\partial x_1}$$

$$\longrightarrow \quad C(x,r)=C(x1,0)+\frac{a^2U_0}{8D_m}\left(\frac{r^2}{a^2}-\frac{r^4}{2a^4}\right)\left(\frac{\partial C}{\partial x_1}\right)$$

Taylor Dispersion (1956)

Flow in a tube

$$C(x,r)=C(x1,0)+\frac{a^2U_0}{8D_m}\left(\frac{r^2}{a^2}-\frac{r^4}{2a^4}\right)\left(\frac{\partial C}{\partial x_1}\right)$$

$$J=\frac{1}{\pi a^2}\int_0^a C(r)U_0\left(\frac{1}{2}-\frac{r^2}{a^2}\right)2\pi r dr$$

Diffusive flux

$$J=\frac{a^2U_0^2}{192D_m}\frac{\partial C}{\partial x_1}$$

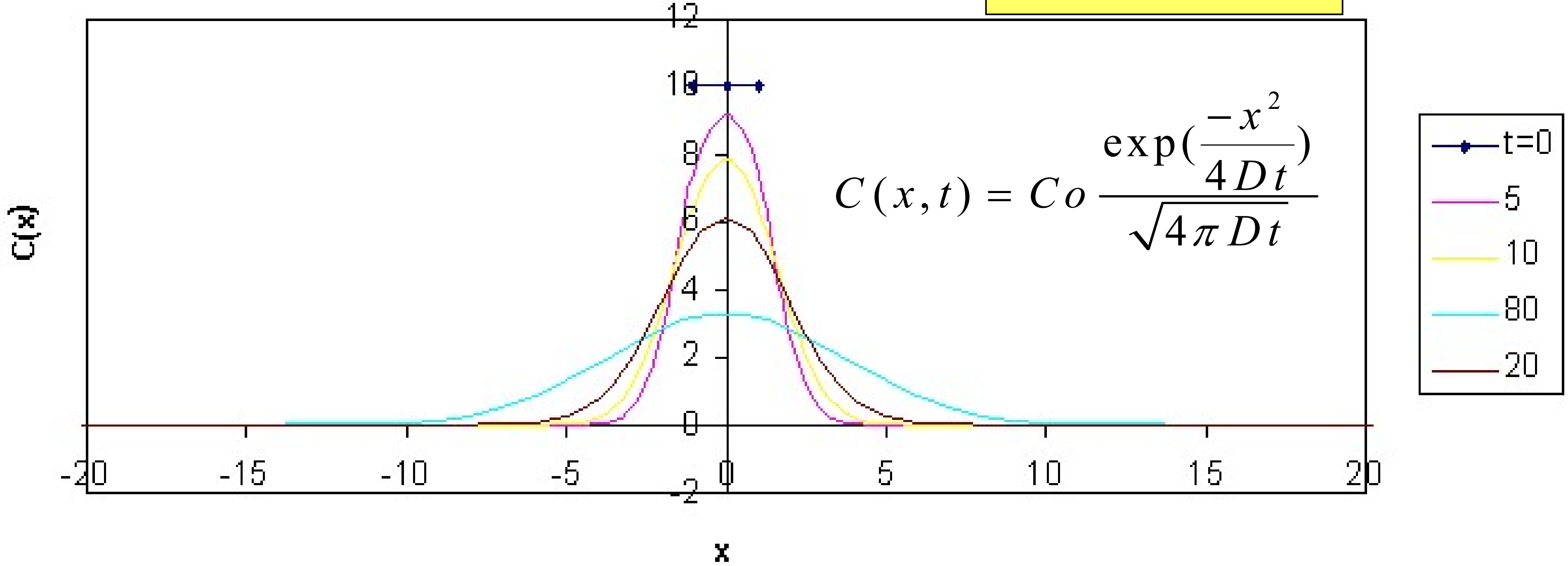
So :

$$Deff=\frac{a^2U_0^2}{192D_m}$$

From diffusion to dispersion

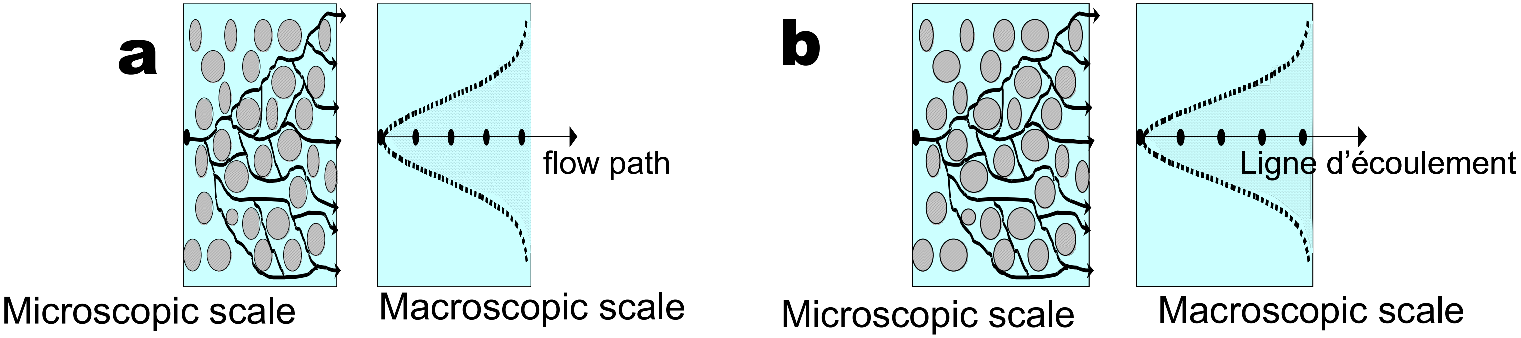
Standard diffusion

$$\frac{\partial C}{\partial t} = D_0 \frac{\partial^2 C}{\partial x^2}$$



$$C(x,t) = Co \frac{\exp\left(\frac{-x^2}{4Dt}\right)}{\sqrt{4\pi D t}}$$

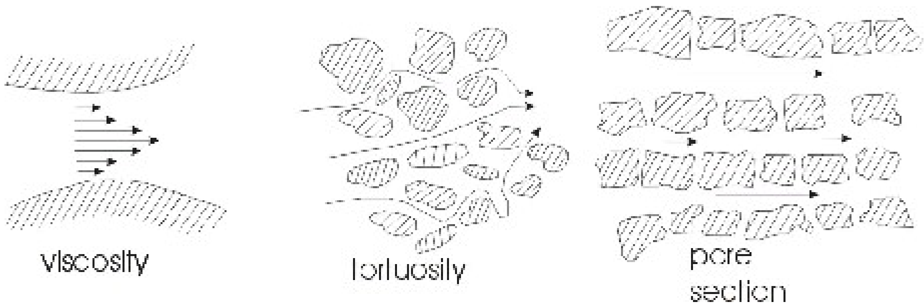
Mechanical dispersion



Explanation on the mechanical dispersion

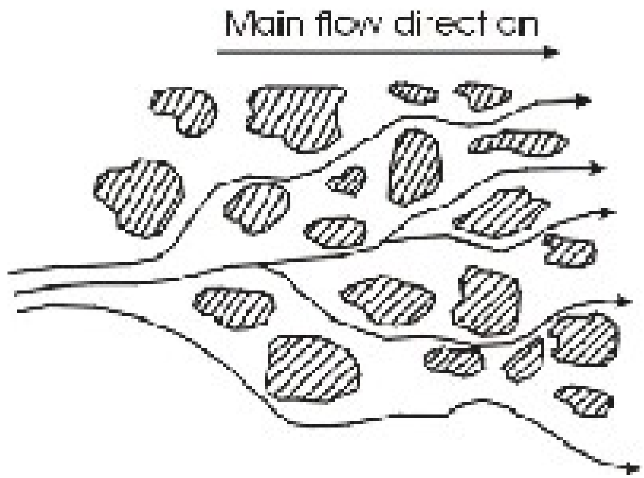
Mechanical dispersion

- Three mechanisms (Bear,1979, Fetter,1991) can be considered when explaining the mechanical dispersion, but all take into account the variation of the pore geometry :
- Due to **viscosity** , velocity presents variations across the pore section; consequently the particles moves faster along the axis than along the pore walls;
- **Differences in the pore cross section** will cause different mean velocity; thus the particles will move faster in some pores than in others.
- The third mechanism is **tortuosity**, which makes that some particles travel along a shorter path than others.



Mechanical dispersion

Tortuosity, as well as pore branching, is also responsible for the lateral spreading which causes the above-mentioned anisotropy. All these microscopic processes have as macroscopic result a continuous mixing of the tracer with the water during the transport. The process of mechanical dispersion along the main flow direction is known as **longitudinal dispersion**, while **transverse dispersion** will develop



Mechanical dispersion

The **dispersion** is governed by the same **Fickean law** as the diffusion. The essential difference is made by the coefficient of proportionality D, known as the mechanical dispersion coefficient, which must express all the experimental observations presented above. As a difference from the diffusion coefficient, the coefficient of dispersion has at least two components to account for the observed anisotropy. Secondly, the dispersion coefficient will be **dependent** on the **velocity** because the dispersion occurs only during the movement of the tracer. Supposing a two dimensional flow model where the flow direction is along the x-axes, the components of the mechanical dispersion coefficient are:

$$D_x = \alpha_L \cdot v_x$$

$$D_y = \alpha_T \cdot v_x$$

Here v_x is the average linear velocity along the x direction, while α_L and α_T are respectively the longitudinal and transverse dispersivities of the medium. Having the dimension of length, the dispersivities are macroscopic parameters, which account for all the spreading phenomena which take place at the microscopic scale. Like the intrinsic permeability, **dispersivity is a material parameter**.

Mechanical dispersion

However, while permeability is related to the average characteristics of the porous medium (mean conductance or tortuosity), dispersivity is related to the variance of these parameters. When the flow direction does not coincide with the coordinate axes, the components of the dispersion coefficients become:

$$D_{xx} = \alpha_L v_x + \left(\alpha_L - \alpha_T\right)\frac{v_x^2}{|v|}$$

$$D_{xy} = D_{yx} = \left(\alpha_L - \alpha_T\right)\frac{v_x v_y}{|v|}$$

$$D_{yy} = \alpha_T v_x + \left(\alpha_L - \alpha_T\right)\frac{v_y^2}{|v|}$$

in which v_x and v_y are the components of the average velocity v. The dispersion coefficient is a second rank symmetric tensor.

Hydrodynamic dispersion

- Because both diffusion and dispersion are generated by the concentration gradient, and taking into account their linearity, the relations are combined and we have:

$$\overline{f}_{Dh} = -n_e \cdot \overline{\overline{D_h}} \cdot \overline{grad\, C}$$

- where **D_h** denotes the coefficient of hydrodynamic dispersion defined as the sum of the mechanical dispersion and effective diffusion coefficients:

where I is the unit matrix.

$$\overline{\overline{D}}_h = \overline{\overline{D}} + D^* \mathrm{I}$$

The mass flux in the relation results from the **superposition** of **dispersion** and **diffusion** fluxes. Actually, the two components of the spreading can not be separated, because pure mechanical dispersion does never exist. Even when the process is predominately dispersive, the diffusion will always act between and along the path lines.

Hydrodynamic dispersion

The weight of the two components was empirically established (Bear, 1979, Domenico & Schwarz, 1991) as a result of a column experiment. For a better presentation two dimensionless numbers will be considered:

1) D_L/D_d, representing the ratio between the longitudinal dispersion and diffusion coefficients

2) Peclet number that express the effectiveness of mass transport by advection to the effectiveness of mass transport by either diffusion or dispersion:

where:

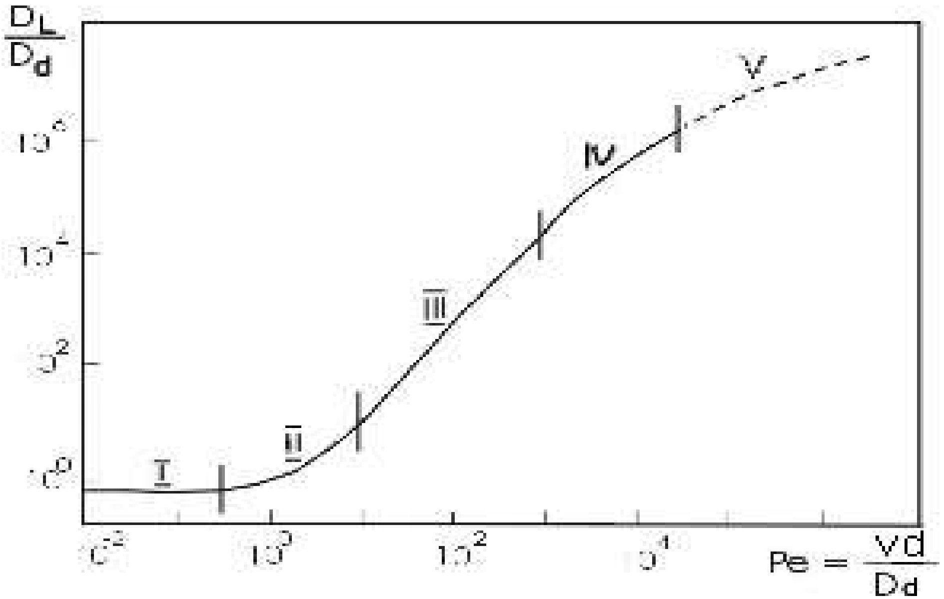
$$P_e = \frac{v \cdot d}{D_d}\ ;\ P_e = \frac{v \cdot L}{D_l}$$

v	linear velocity
d	average grain size
L	traveled distance

Hydrodynamic dispersion

A large value of Pe indicates that the process is dominated by convection, while smaller values denote a diffusive process.

This figure shows, in a simplified form, the results of the column experiment. We have $D_L/D_d = f(Pe)$ graph, five zones can be distinguished:



Zone 1: with Pe < 10-1 where the DL/Dd ratio is constant; because the process is independent of the linear velocity, in this zone the spreading is mainly due to diffusion.

Zone 2: in which 10-1 < Pe ≤ 4. This is a zone in which diffusion and mechanical dispersion have the same magnitude order in the mixing process.

Zone 3: the process is dominated by mechanical dispersion with the empirical relationship

Zone 4: in this zone the diffusion is negligible and a linear relationship between the dispersion and the Peclet number was found. Note that in this zone the Darcy law is still valid

Zone 5: which is also predominately dispersive but out of the range of validity for Darcy's law.

Dispersion

Summary :

- In porous media :

D* is the sum of Dm/τ + a term Pe $^{\alpha}$

-We generally use the classical linear form

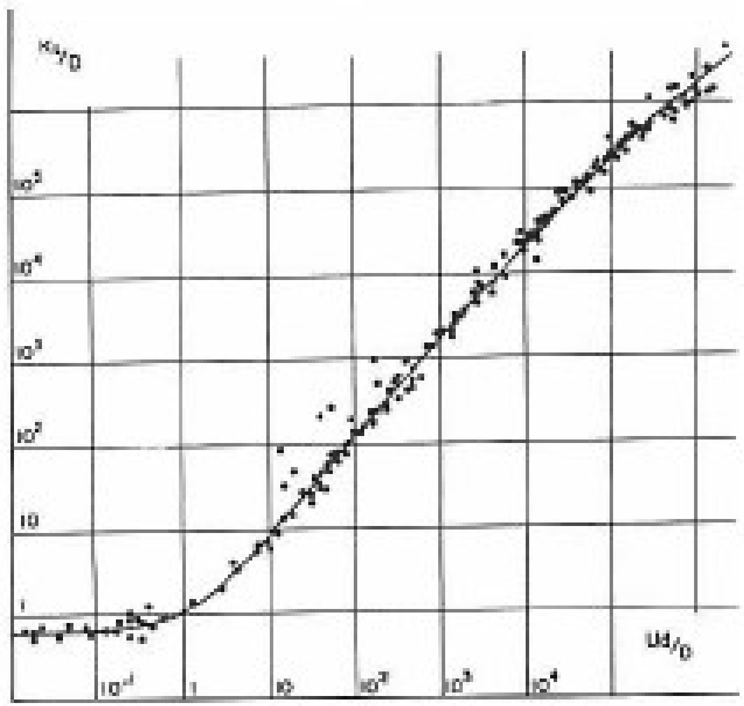


Fig. 23 – Coefficient de diffusion effectif en fonction du nombre de Péclet (d'après Fried & Combarnous, 1971).

$$D^* = \frac{D^m}{\tau}\overline{\overline{I}} + \frac{\alpha_T}{\varepsilon}\left\|\overline{u}\right\|\overline{\overline{I}} + \frac{1}{\varepsilon}(\alpha_L - \alpha_T)\frac{\overline{u}\times\overline{u}}{\left\|\overline{u}\right\|}$$

Upscaling

$$\varepsilon \frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} = \varepsilon D^* \frac{\partial^2 C}{\partial x^2}$$

$$\theta_m \frac{\partial c_m}{\partial t} + v_m \frac{\partial c_m}{\partial x} = D_m \frac{\partial^2 c_m}{\partial x^2} - \alpha\left(c_m - c_{im}\right)$$

Coats et Smith (1964)

$$\theta_{im} \frac{\partial c_{im}}{\partial t} = -\alpha\left(c_{im} - c_m\right)$$

$$\frac{\varepsilon_M \partial C_M}{\partial t} + V \frac{\partial C_M}{\partial x} = \varepsilon_M D^* \frac{\partial^2 C_M}{\partial x^2} - \alpha(C_M - C_{im})$$

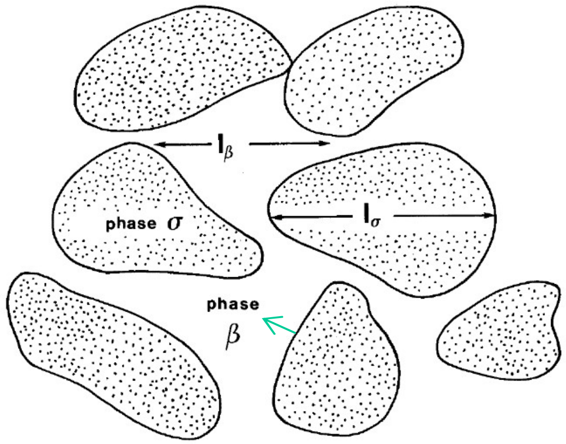
$$\frac{\varepsilon_{im} \partial C_{im}}{\partial t} = \alpha(C_M - C_{im})$$

Practice

Effective diffusion in porous media

Classical Upscaling process

- Mass transfers in porous media ...Several cases, such as passive tracer, reactive, adsorption, ...
- Let's start with the simplest ...



$$\nabla . \mathbf{v}_\beta = 0$$

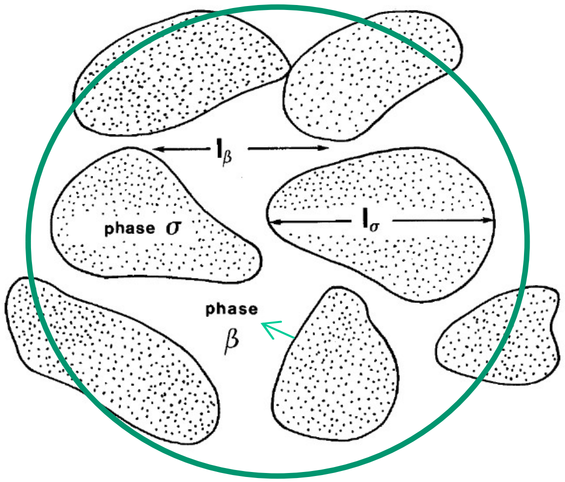
$$\frac{\partial c_\beta}{\partial t} + \nabla . \left(\mathbf{v}_\beta c_\beta \right) = \nabla . \left(D_\beta \nabla c_\beta \right)$$

$$C.L.1 \quad \mathbf{n}_{\beta\sigma} . D_\beta \nabla c_\beta = 0 \quad \text{on } A_{\beta\sigma}$$

upscaling

- Mass transfers in porous media…

$$\frac{\partial \varepsilon_\beta \langle c_\beta \rangle^\beta}{\partial t} + \nabla . \left(\langle \mathbf{v}_\beta \rangle \langle c_\beta \rangle^\beta \right) = \nabla . \left(\varepsilon_\beta \mathbf{D}^*_\beta . \nabla \langle c_\beta \rangle^\beta \right)$$

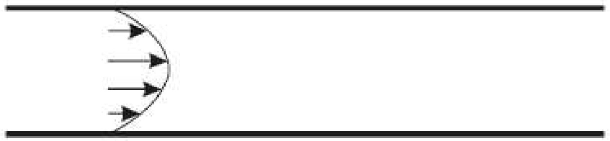


$\mathbf{D}^*_\beta$

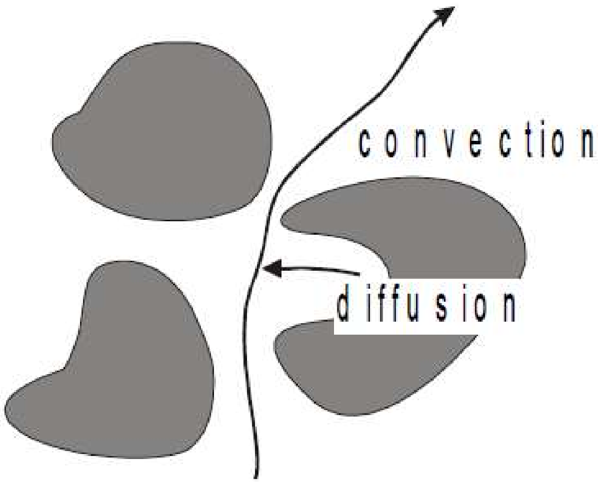
-

-

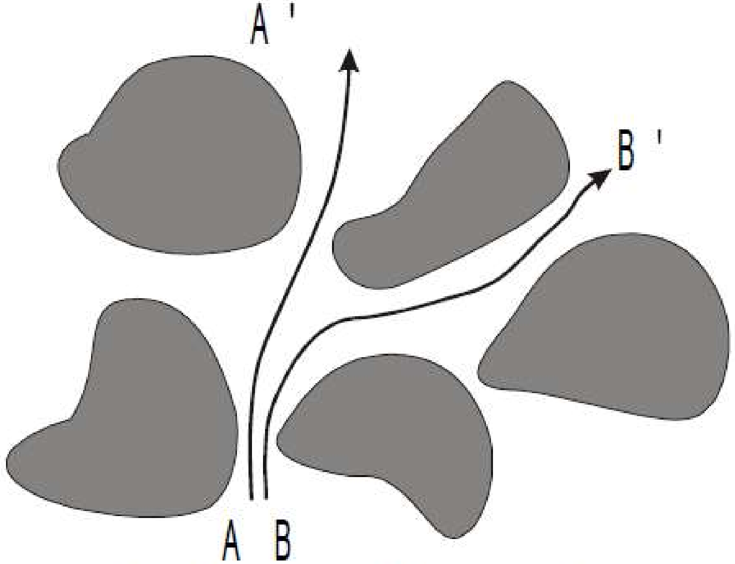
Upscaling



Taylor dispersion



Retardation due to dead-end pores



Mechanical dispersion

Upscaling

- Can we determine this tensor?

Several methods:

- Method of moments (Brenner, Adler)
- Homogenization methods
- Volume averaging methods (Quintard, Whitaker)

Upscaling

- Volume Averaging Technique

$$c_\beta = < c_\beta > + \widetilde{c_\beta}$$

Microscale concentration

$$\left\langle \nabla \psi_\beta \right\rangle = \nabla \left\langle \psi_\beta \right\rangle \quad \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \psi_\beta \, dA$$

$$\left\langle \nabla \cdot \mathbf{A}_\beta \right\rangle = \nabla \cdot \left\langle \mathbf{A}_\beta \right\rangle + \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \mathbf{A}_\beta \, dA$$

$$\left\langle \frac{\partial \psi_\beta}{\partial t} \right\rangle = \frac{\partial \left\langle \psi_\beta \right\rangle}{\partial t} - \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \mathbf{w}_{\beta\sigma} \psi_\beta \, dA$$

Upscaling

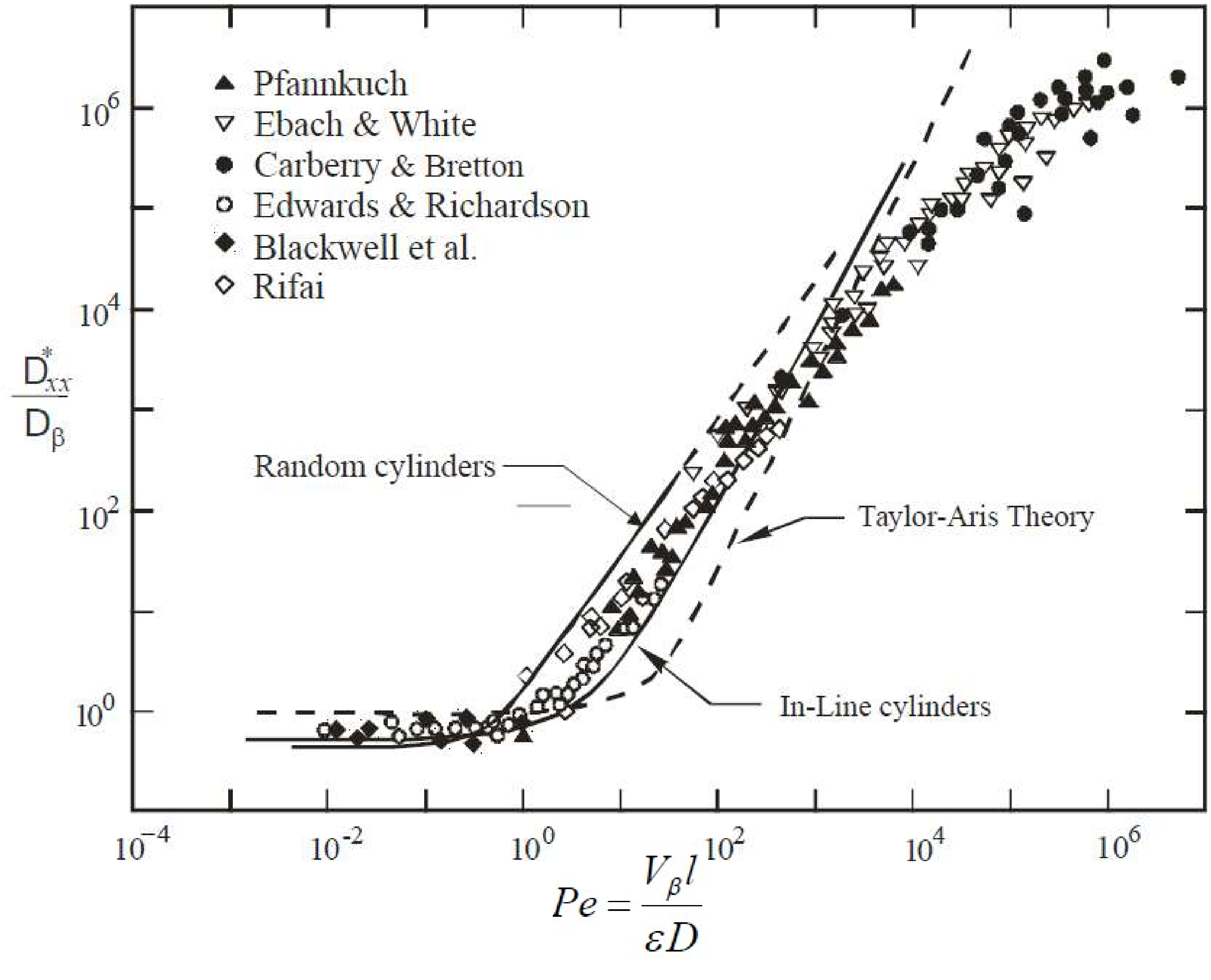
The previous theorems applied to the local diffusion convection equation give:

$$\frac{\partial \varepsilon_\beta \left\langle c_\beta \right\rangle^\beta}{\partial t} + \nabla . \left(\left\langle \mathbf{v}_\beta \right\rangle \left\langle c_\beta \right\rangle^\beta \right) + \nabla . \left(\left\langle \tilde{\mathbf{v}}_\beta \tilde{c}_\beta \right\rangle \right)$$

$$\nabla . \left(\varepsilon_\beta D_\beta \nabla \left\langle c_\beta \right\rangle^\beta + \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_\beta \, dA \right)$$

$$\tilde{c}_\beta = \mathbf{b}_\beta . \nabla \left\langle c_\beta \right\rangle^\beta$$

Upscaling



$$\text{Deff} = Dm.Pe^2 / 48$$

$$\text{P}e = \frac{U_0(a/2)}{D_m}$$

Upscaling

- Dispersion is not a scalar ...
- Effect of the anisotropy generated by the velocity field? $U = U.\overrightarrow{ex}$

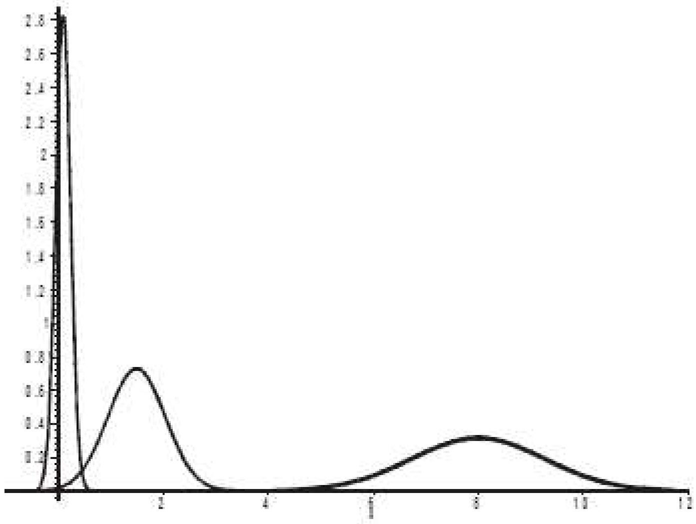
$$\rightarrow D^* = \begin{bmatrix} D_L & - & - \\ - & D_T & - \\ - & - & D_T \end{bmatrix}$$

Example (dispersion linear):

$$\mathbf{D} = \mathbf{D}_0 + \alpha_T \left\| \mathbf{U}_\beta \right\| \mathbf{I} + (\alpha_L - \alpha_T) \frac{\mathbf{U}_\beta \mathbf{U}_\beta}{\left\| \mathbf{U}_\beta \right\|}$$

Upscaling

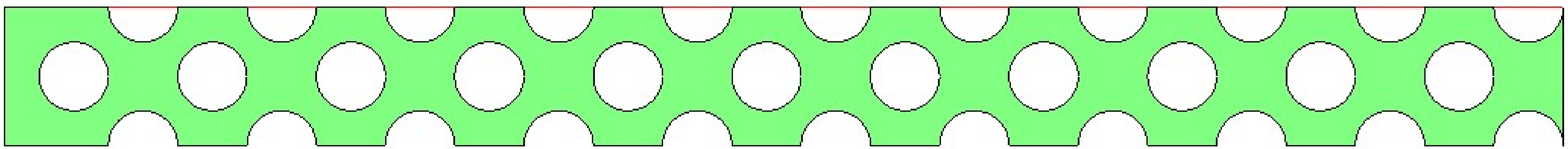
- In some cases we can solve this problem.



$$\frac{c}{c_0} = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{\left(x - Ut\right)^2}{4Dt} \right)$$

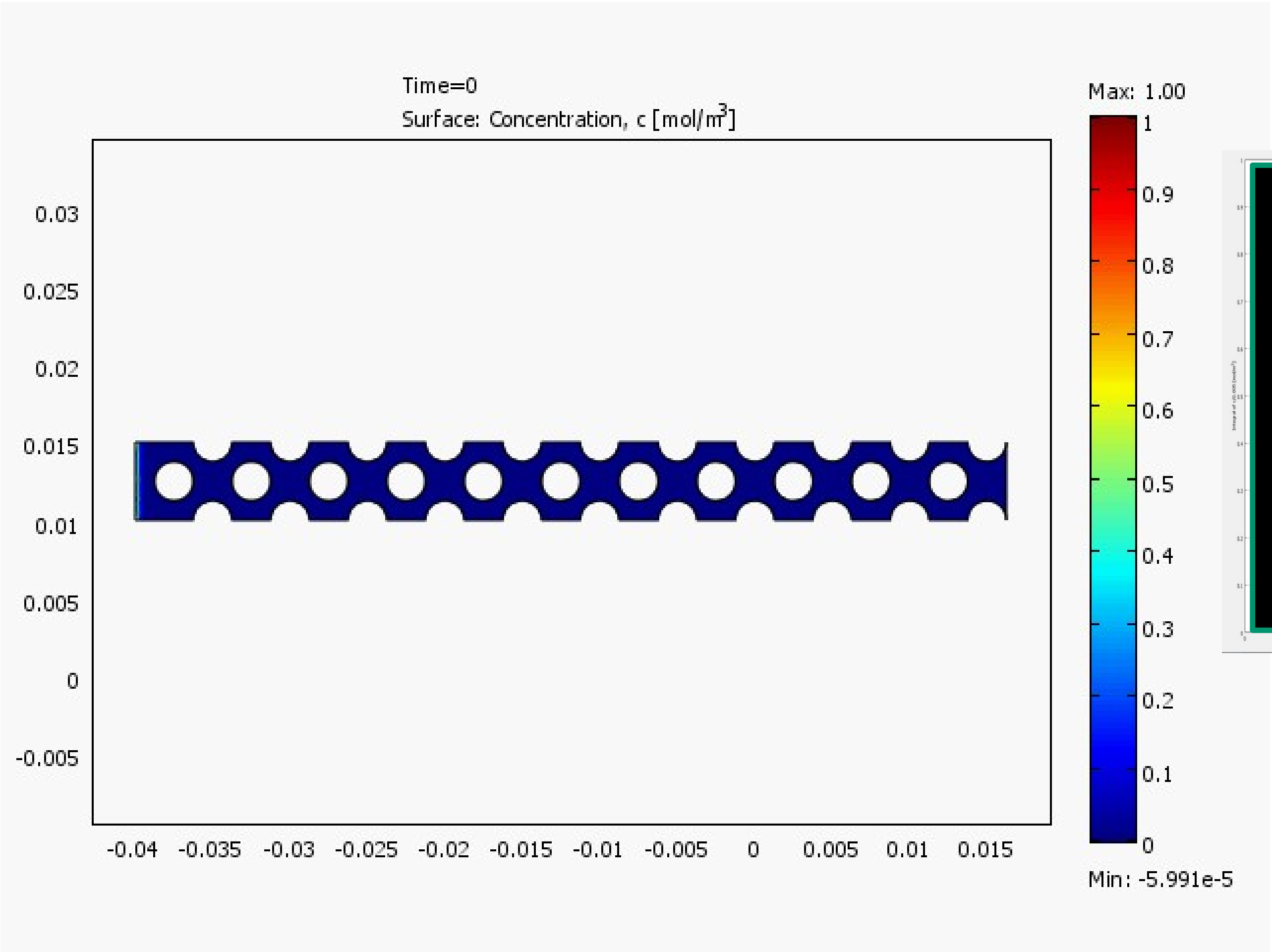
Upscaling

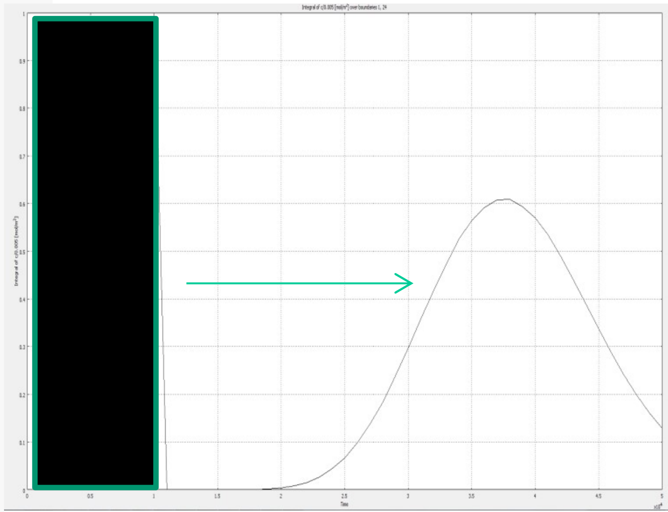
- I take a medium, symmetrical, 2D, mostly 1D flow (Φ = 2.5mm)



Upscaling

- Results Pe~1



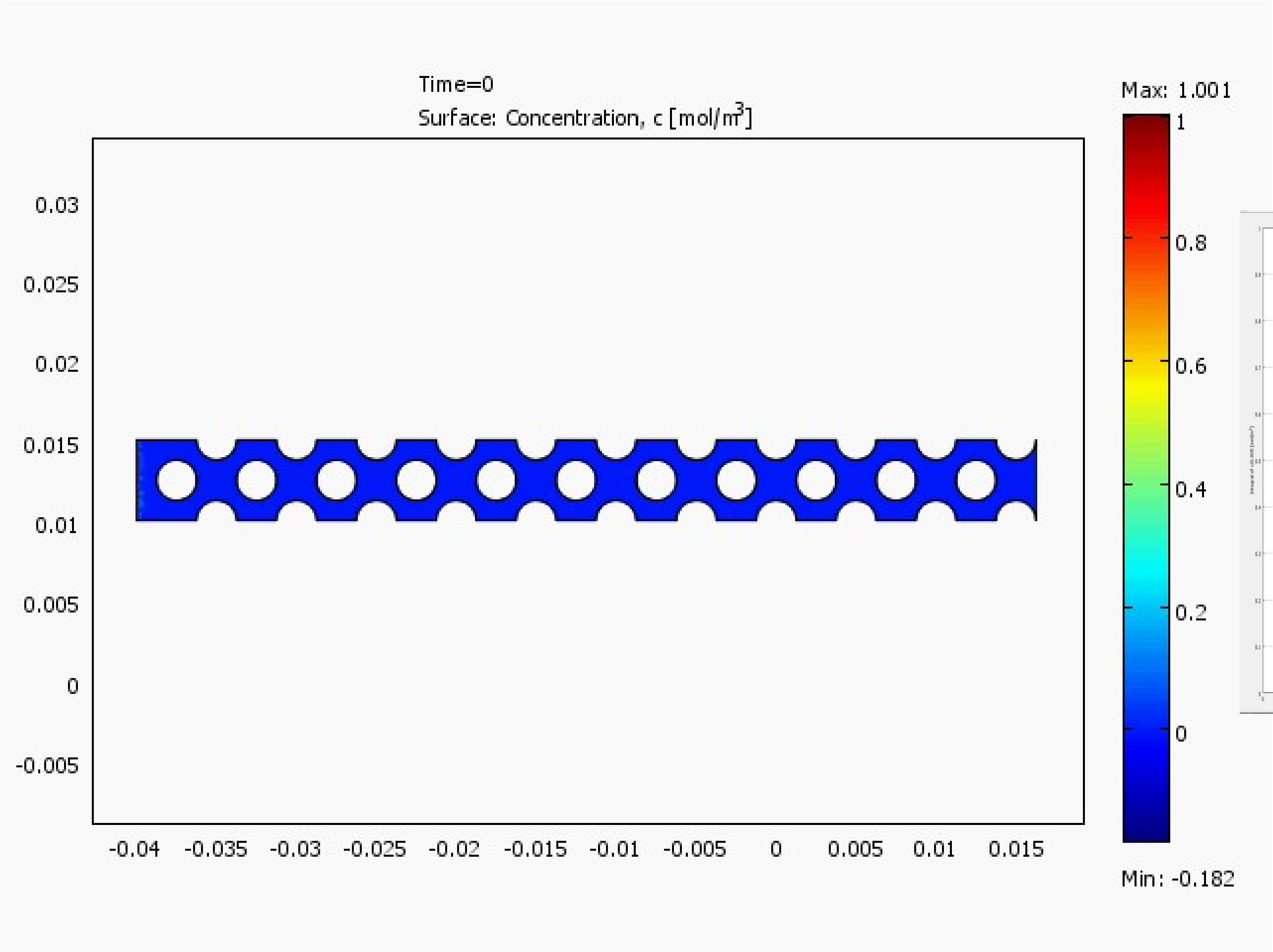


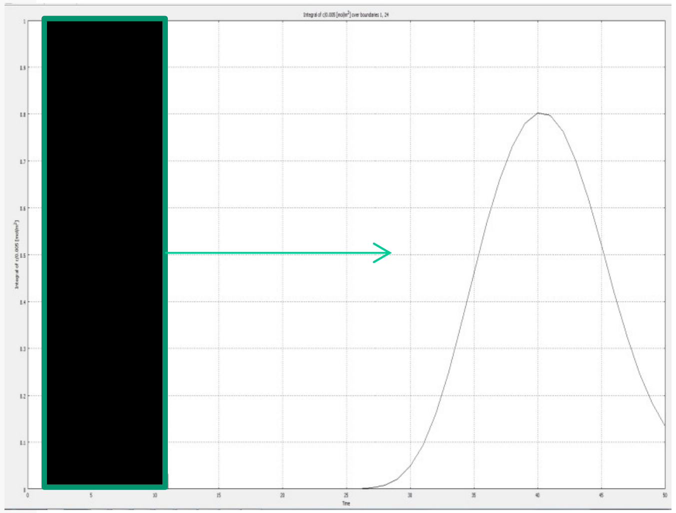
Upscaling

- Observations?

Ecoulements en milieu poreux

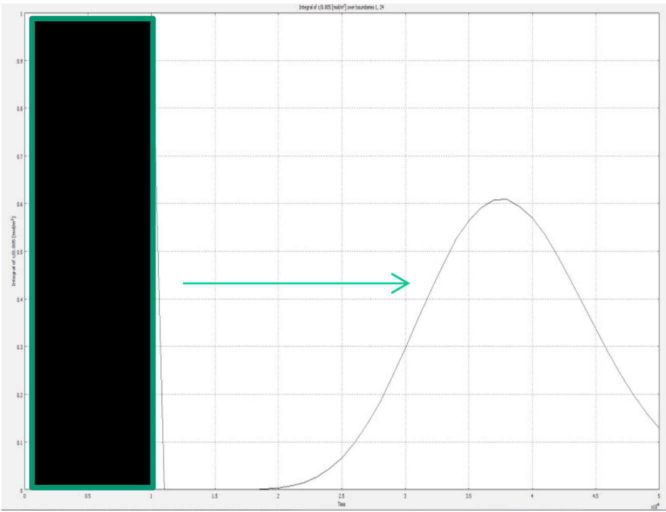
- Same model with Pe>>1

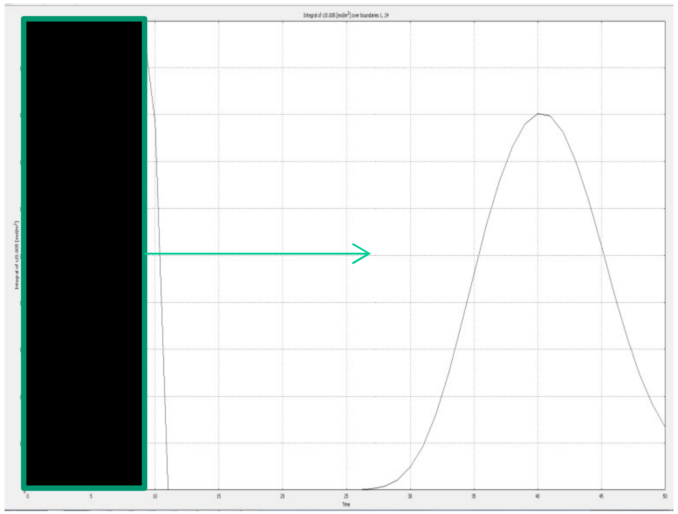




Upscaling

- Flow field effect ?





Upscaling

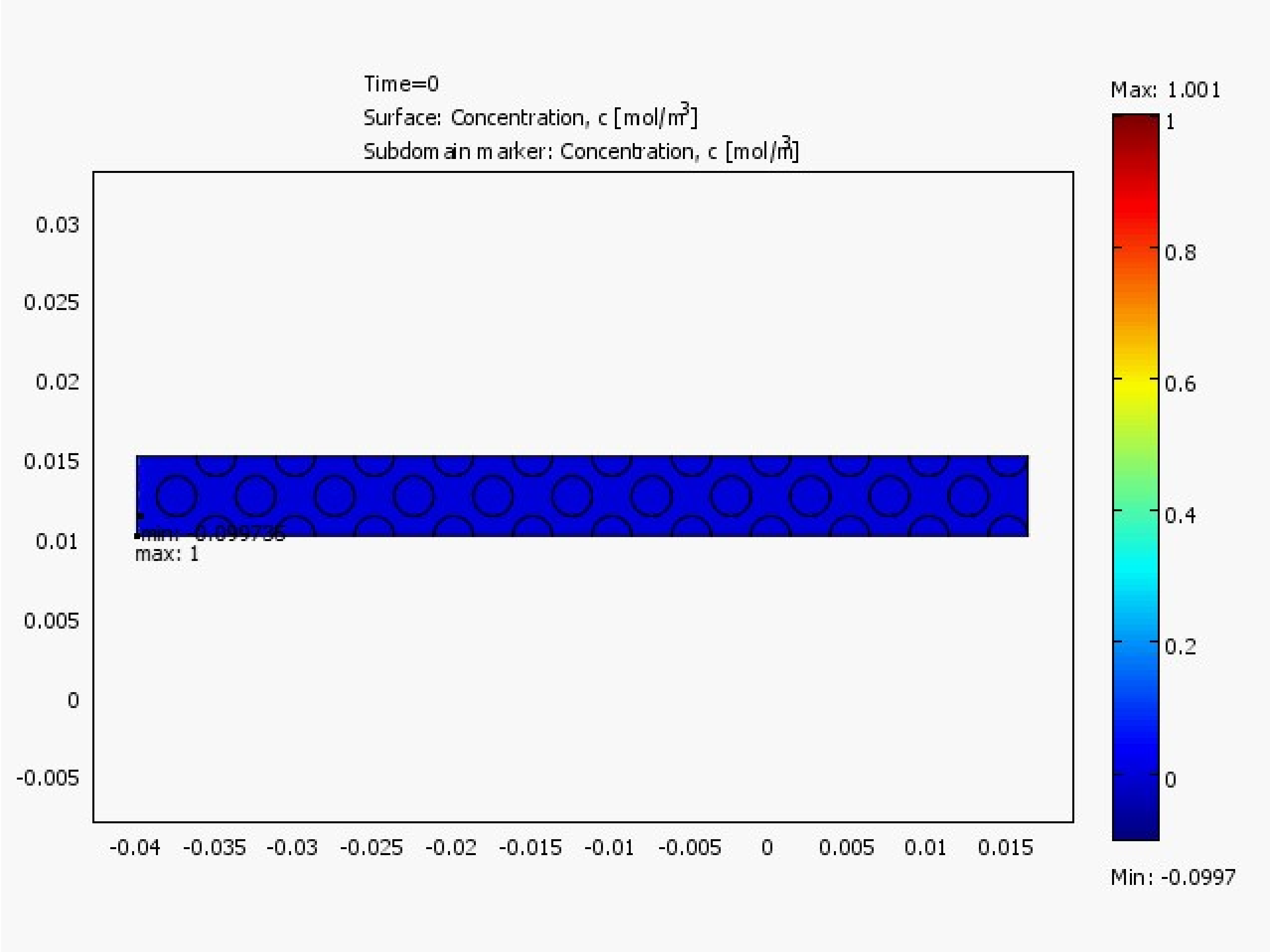
- In case the transport is also in the solid phase

$$\nabla.\mathbf{v}_{\beta} = 0$$

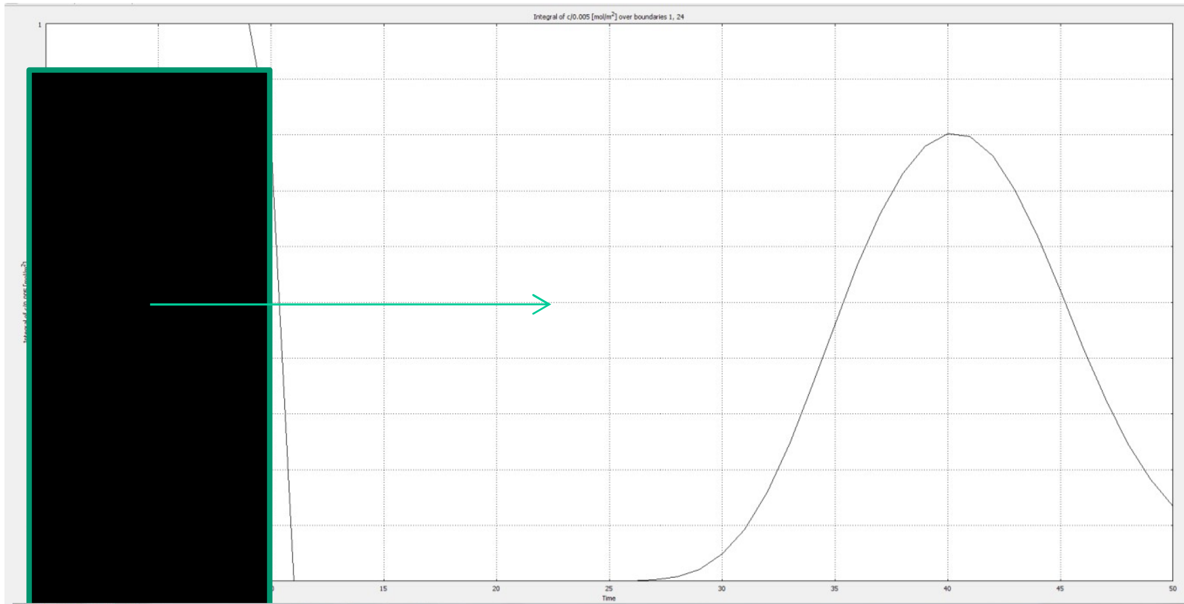
$$\frac{\partial c_{\beta}}{\partial t} + \nabla.\left(\mathbf{v}_{\beta} c_{\beta}\right) = \nabla.\left(D_{\beta} \nabla c_{\beta}\right)$$

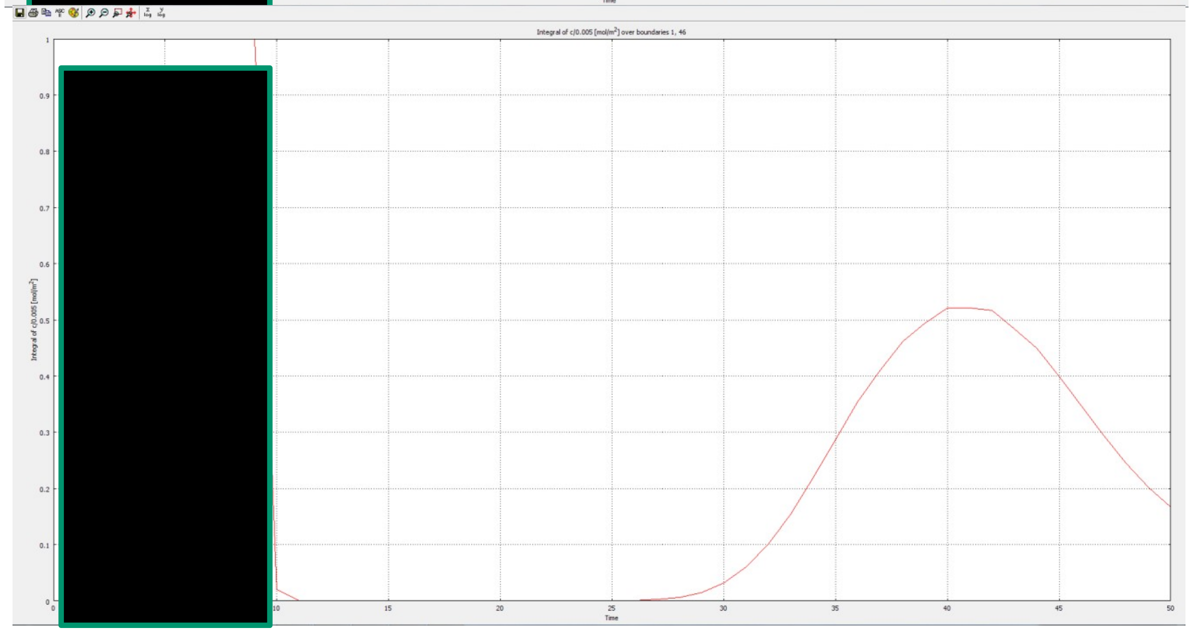
Upscaling

- Adding transport in solid phase : Effects? Elution curves?



Upscaling

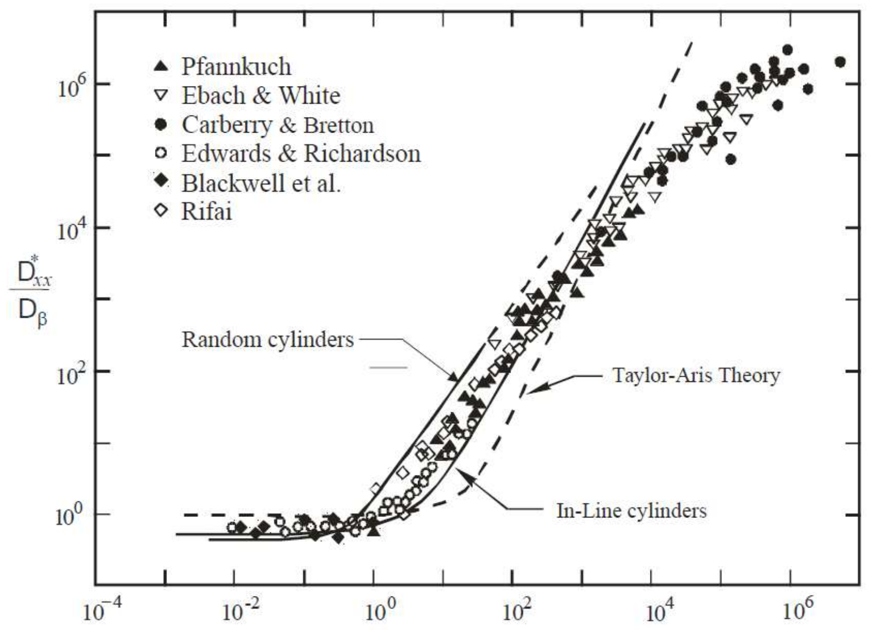

Integral of c/0.005 [mol/m^2] over boundaries 1, 24
Time


Integral of c/0.005 [mol/m^2] over boundaries 1, 46
Integral of c/0.005 [mol/m^2]
Time

Upscaling

What to do and what type of model if we transport a constituent in a porous medium …?

$$\frac{\partial \varepsilon_\beta \left\langle c_\beta \right\rangle^\beta}{\partial t} + \nabla . \left(\left\langle \mathbf{v}_\beta \right\rangle \left\langle c_\beta \right\rangle^\beta \right) = \nabla . \left(\varepsilon_\beta \mathbf{D}^*_\beta . \nabla \left\langle c_\beta \right\rangle^\beta \right)$$



Upscaling

- Take the symmetrical model ...

Determine the coefficients of the macroscopic equation.

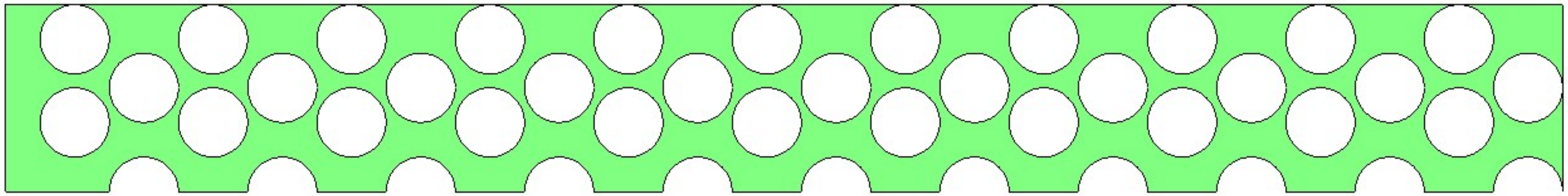
Then compare the response between micro and macro.

That works?

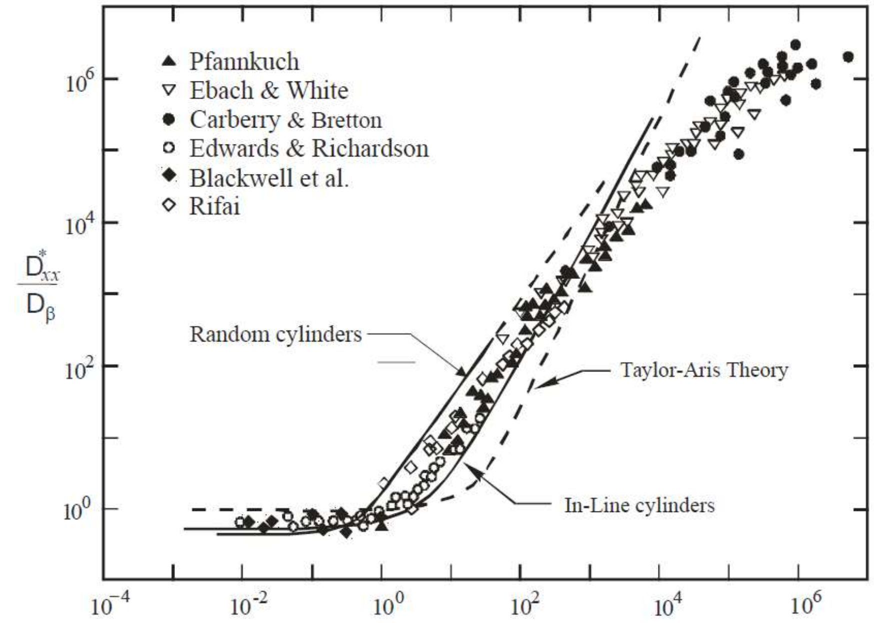
Upscaling

Heterogeneity effects

New medium



Upscaling



$$\frac{\partial \varepsilon_\beta \langle c_\beta \rangle^\beta}{\partial t} + \nabla.\left(\langle \mathbf{v}_\beta \rangle \langle c_\beta \rangle^\beta \right) = \nabla.\left(\varepsilon_\beta \mathbf{D}^*_\beta . \nabla \langle c_\beta \rangle^\beta \right)$$

Upscaling

$$\theta_m \frac{\partial c_m}{\partial t} + v_m \frac{\partial c_m}{\partial x} = D_m \frac{\partial^2 c_m}{\partial x^2} - \alpha\left(c_m - c_{im}\right)$$

Coats et Smith (1964)

$$\theta_{im} \frac{\partial c_{im}}{\partial t} = -\alpha\left(c_{im} - c_m\right)$$

$$\varphi_\omega \varepsilon_\omega \frac{\partial C_\omega}{\partial t} + \mathbf{V}_\omega . \nabla C_\omega = \nabla . \left(\mathbf{D}^*_\omega . \nabla C_\omega \right) - \alpha \left(C_\omega - C_\eta \right)$$

$$\varphi_\eta \varepsilon_\eta \frac{\partial C_\eta}{\partial t} + \mathbf{V}_\eta . \nabla C_\eta = \nabla . \left(\mathbf{D}^*_\eta . \nabla C_\eta \right) - \alpha \left(C_\eta - C_\omega \right)$$

Just….

$$\phi_m c_m \frac{\partial \left\{ P_m \right\}^m}{\partial t} = \nabla . \left(\frac{1}{\mu} \mathbf{K}_m^* . \nabla \left\{ P_m \right\}^m \right) - \frac{\alpha}{\mu} \left(\left\{ P_m \right\}^m - \left\{ P_f \right\}^f \right)$$

$$\phi_f c_f \frac{\partial \left\{ P_f \right\}^f}{\partial t} = \nabla . \left(\frac{1}{\mu} \mathbf{K}_f^* . \nabla \left\{ P_f \right\}^f \right) - \frac{\alpha}{\mu} \left(\left\{ P_f \right\}^f - \left\{ P_m \right\}^m \right)$$