On the solution of the Cattaneo-Maxwell's model for anomalous diffusion inside a catalytic particle

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Contents

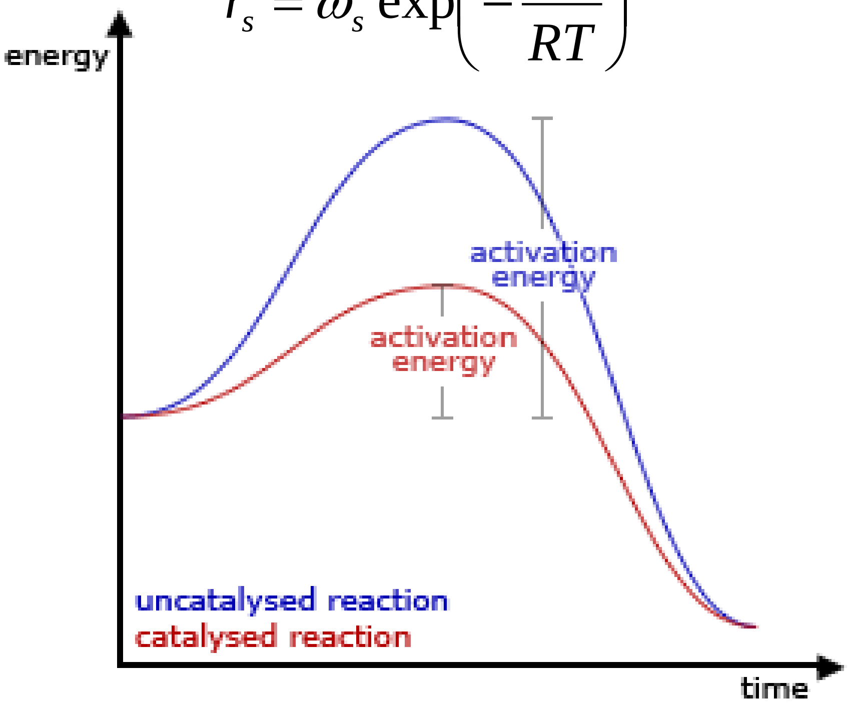
Contents

Motivation

Why do I need a catalyst?

- Catalysts increase the reaction rates by lowering activation energy:

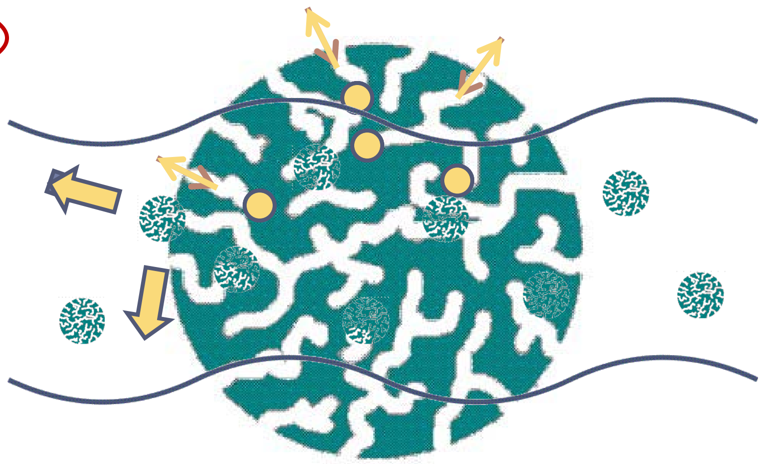
$$r_s = \omega_s \exp\left(-\frac{E_a}{RT}\right)$$



Motivation

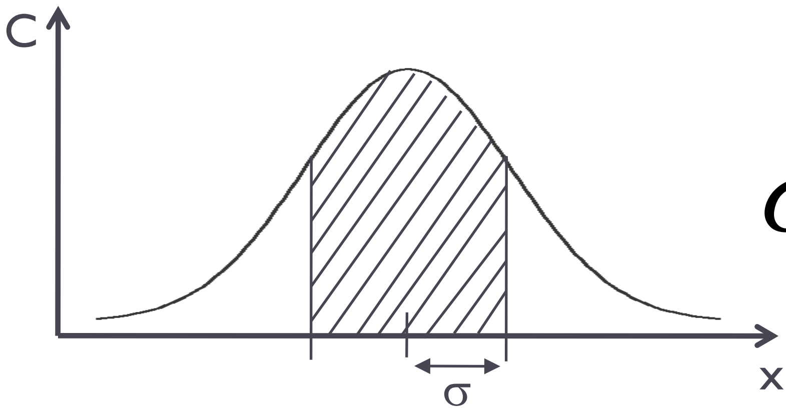
Steps in a reaction with catalytic particles

1. Bulk diffusion of reactants
2. Reactant diffusion to active sites
3. Adsorption onto the active sites
4. Reaction on the active surface
5. Desorption of products
6. Product diffusion to pore mouth
7. Bulk diffusion of products



Motivation

Normal vs. anomalous diffusion



$$\sigma \propto t^{\gamma/2}$$

$$\gamma \begin{cases} <1 & \text{subdiffusion} \\ =1 & \text{normal} \ \blacktriangleright \ \text{(Fick)} \\ >1 & \text{superdiffusion} \end{cases}$$

- M. Küntz, P. Lavallée
  - Water absorption profiles in clay-brick and limestone **(2001)**
    - Propagation of σ faster than $t^{1/2}$ → superdiffusion
  - High concentration diffusion of aqueous $CuSO_4$ **(2004)**
    - Concentration of $CuSO_4$ propagates slower than $t^{1/2}$ → subdiffusion
- K. Ritchie
  - Protein subdiffusion across cell membranes

Motivation

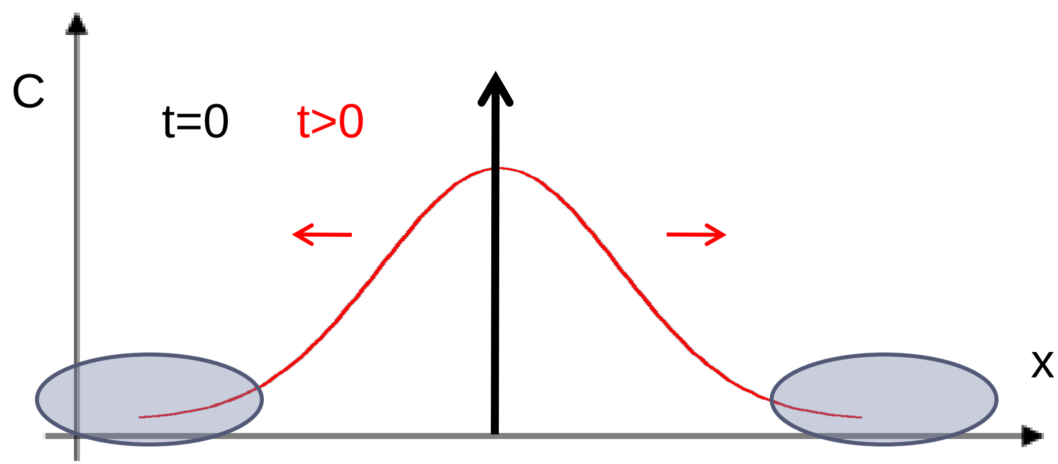
The infinite propagation velocity paradox

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

Fick's law

- A perturbation in any region of the domain is instantly detected everywhere

- This implies infinite propagation velocity!



Motivation

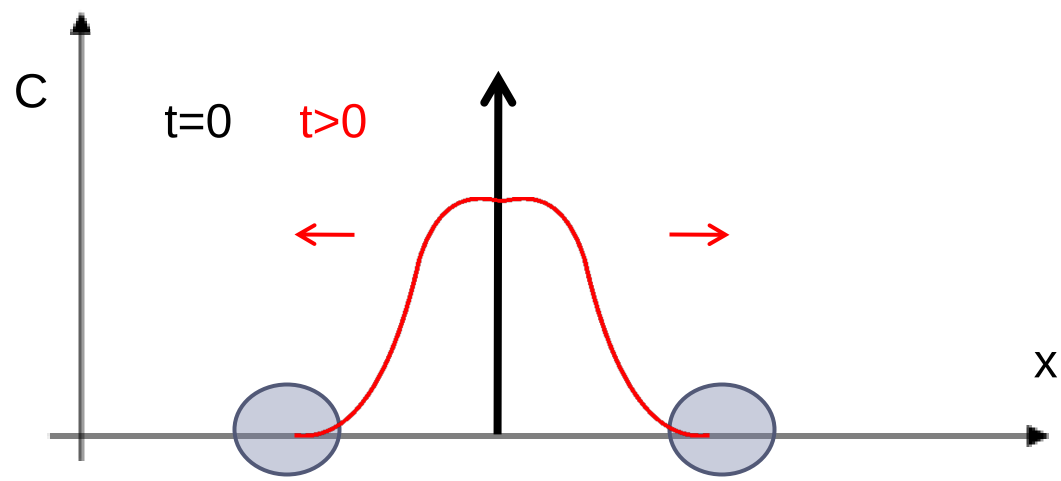
The infinite propagation velocity paradox

$$D\frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} + \tau\frac{\partial^2 C}{\partial t^2}$$

Cattaneo's law

- Finite propagation speed of the information due to the relaxation term

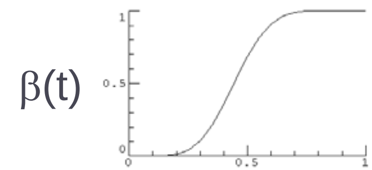
- The affected region extends with time



- Motivation
  - Why do I need a catalyst?
  - Steps in a reaction with catalytic particles
  - Normal versus anomalous diffusion
  - Infinite propagation velocity paradox
- **Numerical model**
  - **1D Transient diffusion in a slab**
  - **Method choice and implementation**
- Results
  - Simulation results and discussion
- Further work
- Summary

Numerical model

1-D transient Cattaneo's diffusion problem



Continuity equation

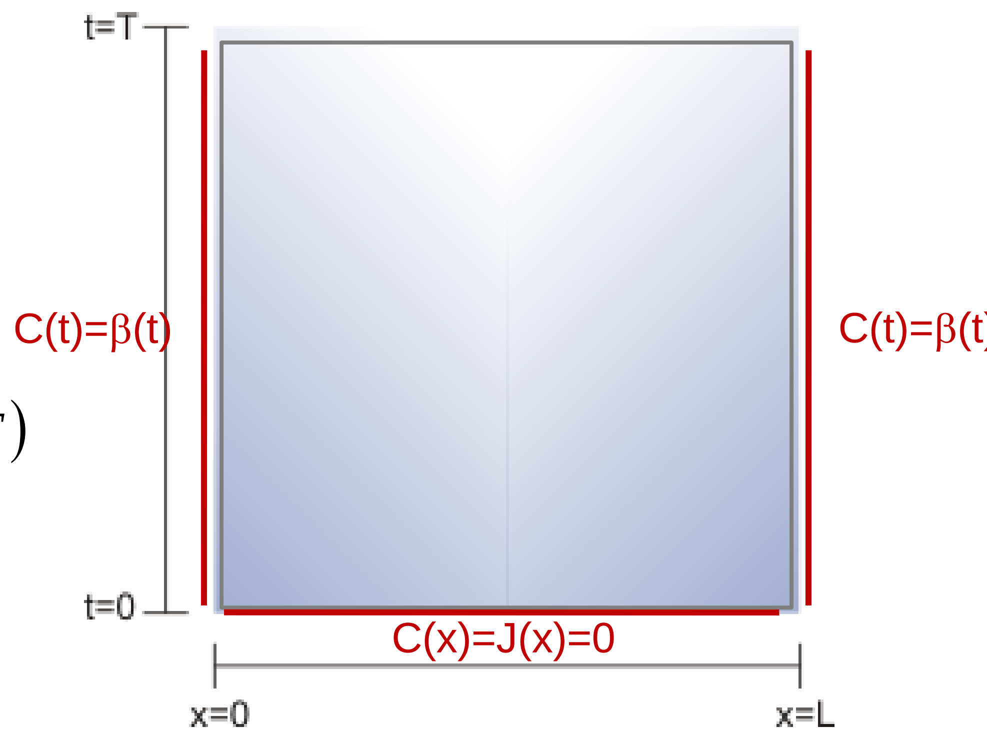
$$\frac{\partial C}{\partial t}+\frac{\partial J}{\partial x}=0 \qquad \text{in } \Omega=(0,L)\times(0,T)$$

Constitutive equation

$$\tau\frac{\partial J}{\partial t}+J=-D\frac{\partial C}{\partial x} \qquad \text{in } \Omega=(0,L)\times(0,T)$$

Initial and Boundary Conditions

$$\begin{cases} C\big|_{t=0}=J\big|_{t=0}=0 \\ C\big|_{x=0}=C\big|_{x=L}=\beta(t) \end{cases}$$



Numerical model

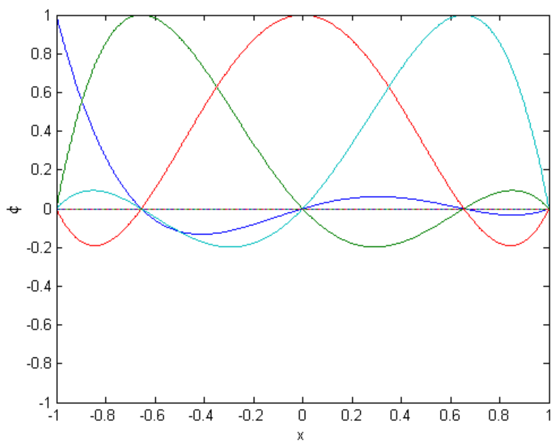
Choice of the numerical method

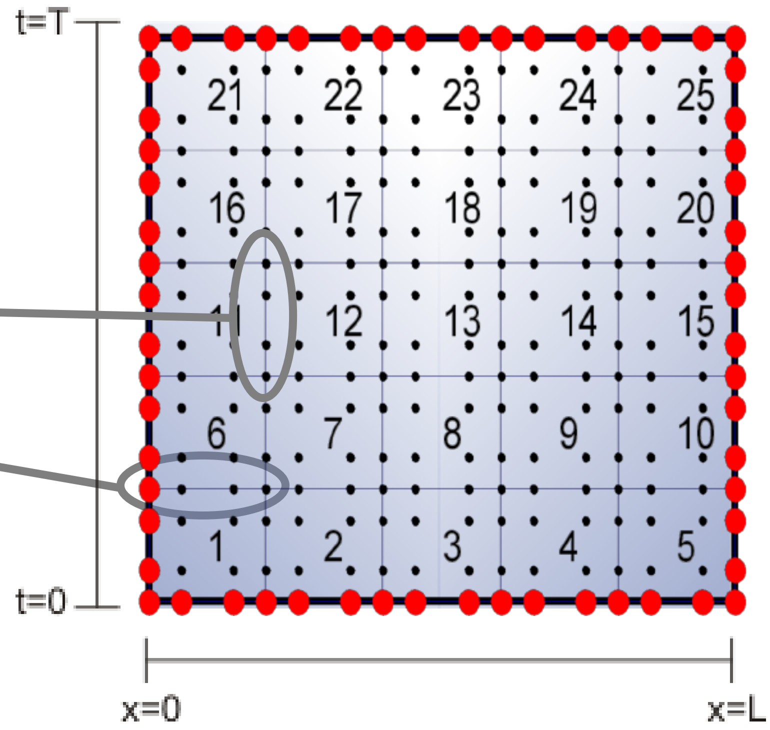
- Modeling → lots of simulations → efficient method is required (acceptable accuracy at low CPU time)
- Traditional approach: FDM and FVM. Very simple, but many discretization points required for desired accuracy
- Galerkin-based FEM: convergence rate like FDM.
- Chosen Method: High Order Least Squares.

Numerical model

Finite element approximation

- N_{ex}, N_{ey} elements
- P_x, P_y order polynomials
- Minimization problem





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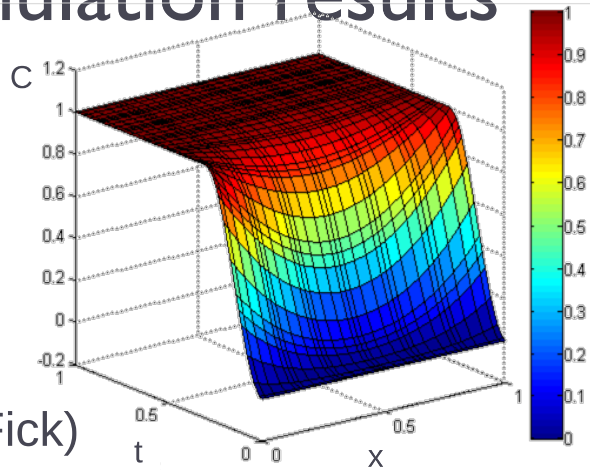
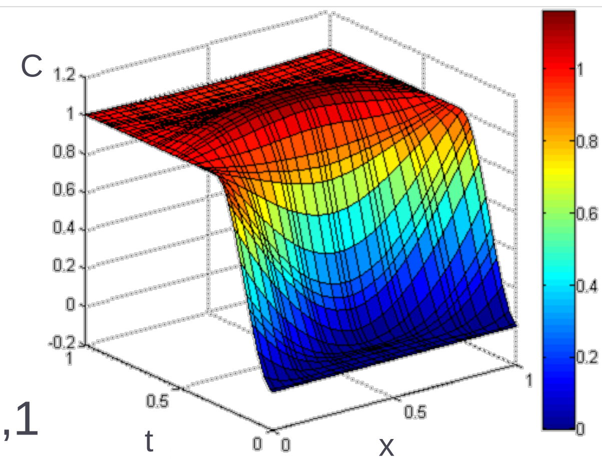
Results

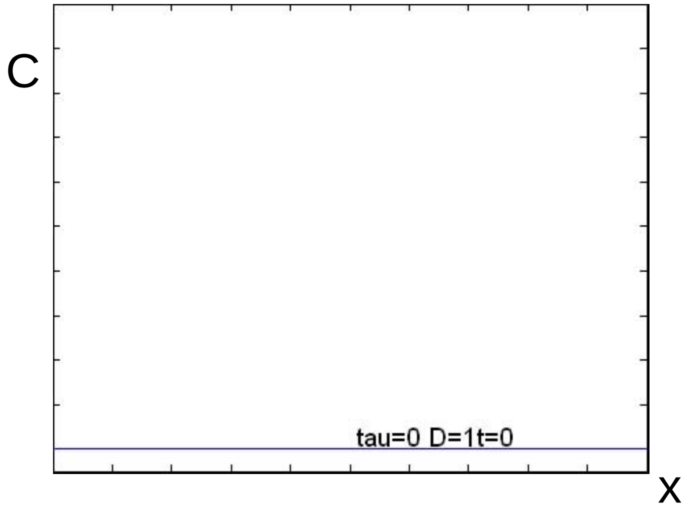
Simulation results

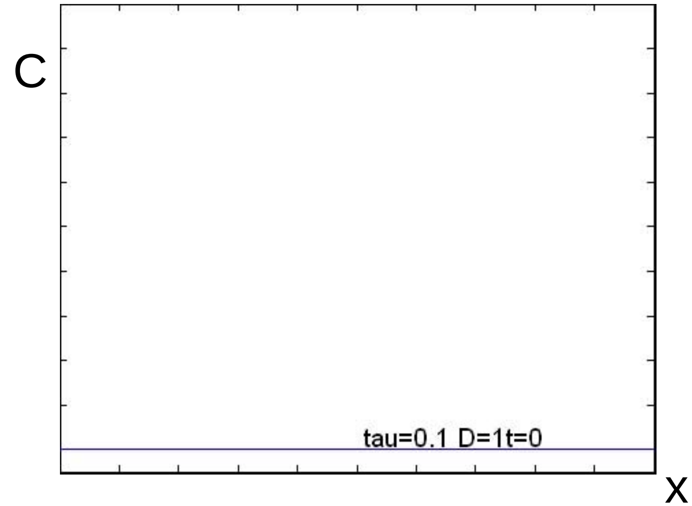


τ=0 (Fick)



τ=0,1

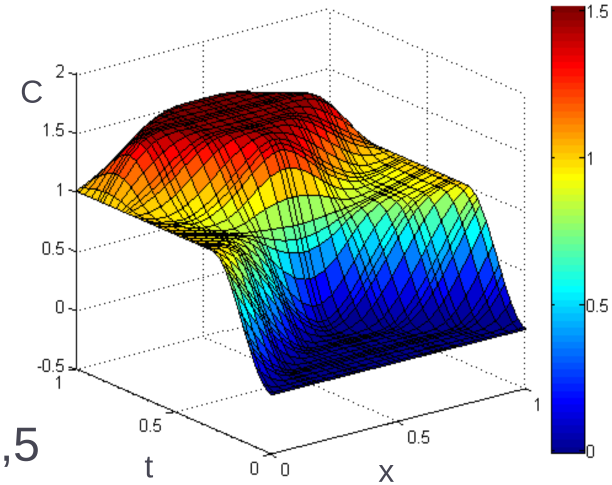




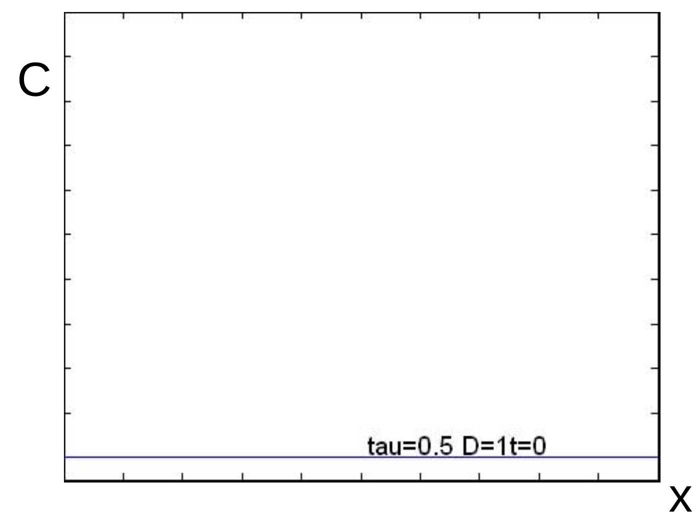
Results

Simulation results

- For increasing values of τ:
  - Finite propagation time proportional to τ
  - Growing oscillation time
  - Growing overshoot in maximum concentration

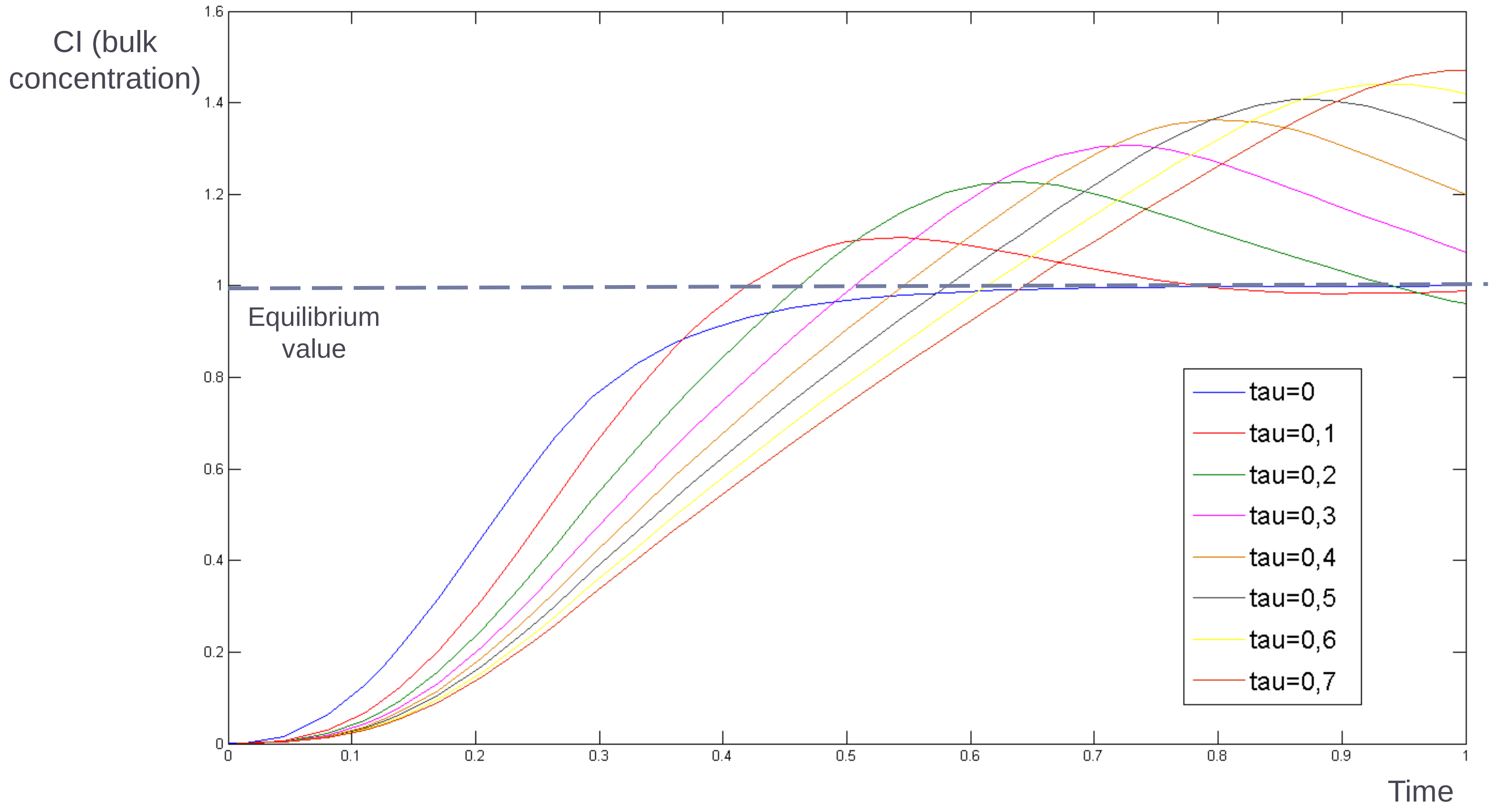


τ=0,5



Results

Evolution of bulk concentration



Further Work

- The presented model can be extended to solve the generalized Cattaneo equation
- This extension would allow to model different degrees of subdiffusive and superdiffusive behaviors
- Work is being done on correlating Cattaneo's equation with microscale models (CTRW)

Summary

- Motivation
  - Fick's law predicts infinite propagation velocity
  - Cattaneo's constitutive law is considered instead
- Numerical model
  - Transient 1-D High Order Least Squares Finite Element Model
  - Solution for the evolution of concentration in a slab
- Results
  - Fick and Cattaneo's models predict the same equilibrium value
  - Cattaneo's model eliminates infinite propagation velocity
  - The model predicts overshoot and oscillations in concentration
- Further work
  - The model can be extended and correlated with microscale models

Thanks! ☺

References

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2. **"Chemical reactor modeling, multiphase reactive flows",** Jakobsen, Hugo A.
3. **"Fluidized bed reactor for polyethylene production. The influence of polyethylene prepolymerization",** Fernandes, F.A.N – Lona L.M.F.
4. **"Fluidization Engineering",** Kunii – Levenspiel
5. **"Chemical Looping Combustion (CLC) A Novel Combustion Technology for CO2 Capture",** Yan R., Wang B., Tee Liang D.
6. **"Elements of Chemical Reaction Engineering",** Scott Fogler H.
7. **"The generalized Cattaneo equation for the description of anomalous transport processes",** Compte A., Metzler R.
8. **"Detection of non-brownian diffusion in the cell membrane in single molecule tracking",** Ritchie K.

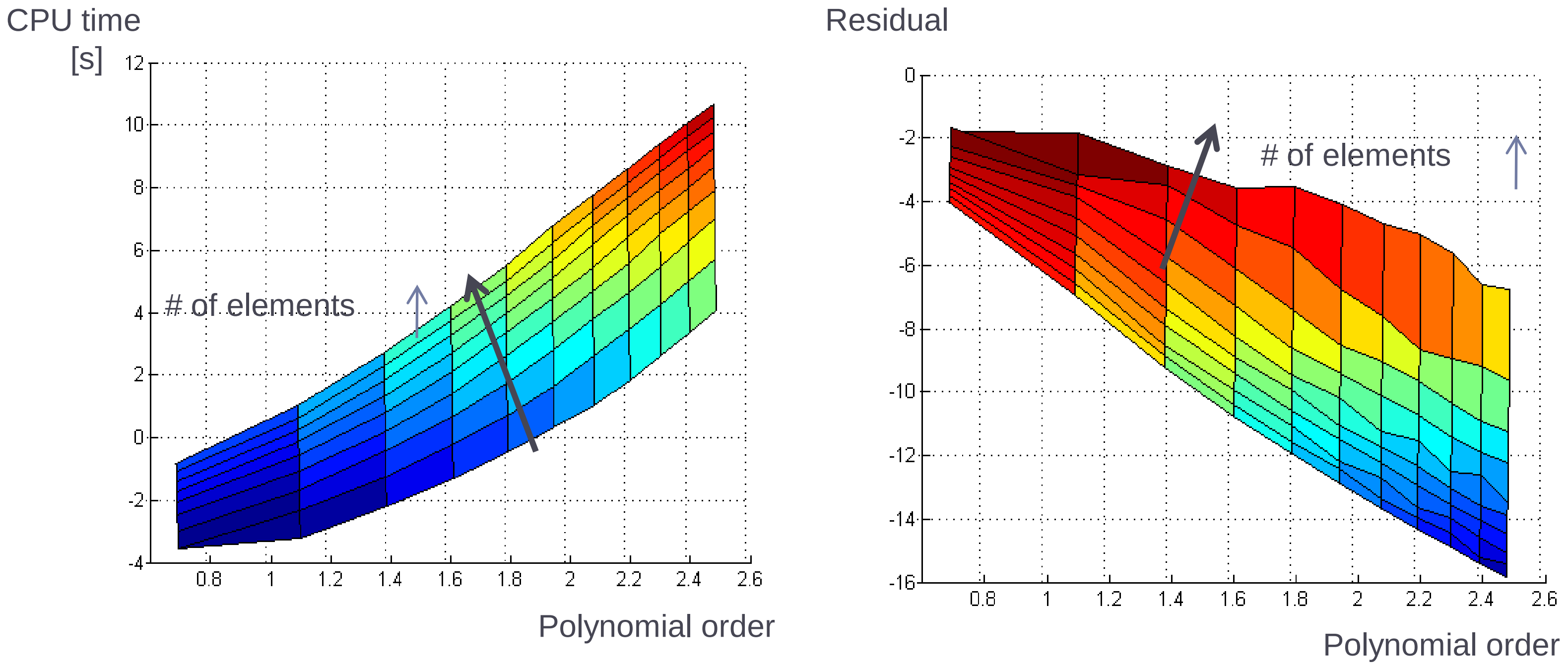
Fractional derivatives

- Definition: $$\left.\frac{d^{\alpha} f(x)}{dx^{\alpha}}\right|_{x=a} = \frac{1}{\Gamma(n-\alpha)} \int_a^x \frac{f^{(n)}(y)}{(x-y)^{\alpha-n+1}} dy$$

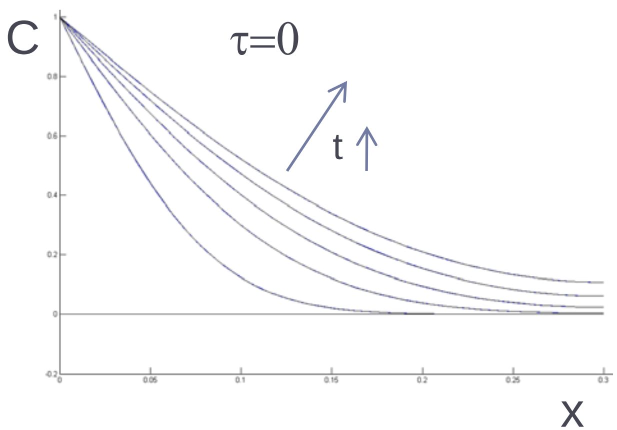
$$\left(\frac{d^{1/\alpha}}{dx^{1/\alpha}}\right)^{\alpha} f(x) = \frac{df(x)}{dx} = f'(x)$$

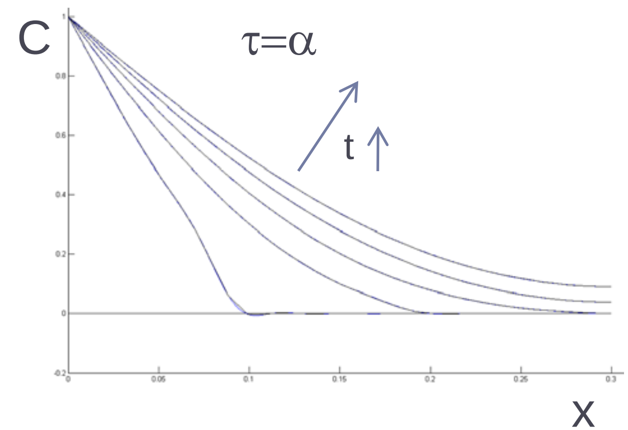
- The integral takes account for the nonlocality

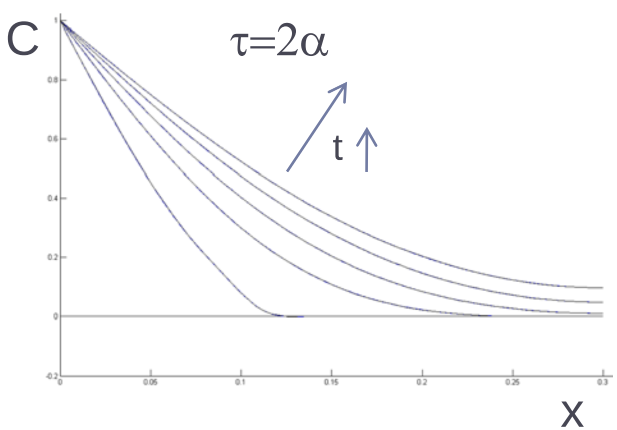
Convergence plots

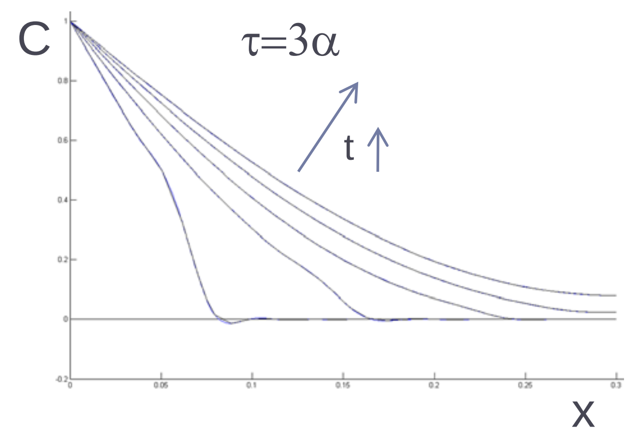


Relaxation time influence in transient









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Experimental work references:

- "Experimental evidence and theoretical analysis of anomalous diffusion during water infiltration in porous building materials" M. Küntz, P. Lavallée
  - Water absorption profiles in clay-brick and limestone
  - Propagation **faster than $t^{1/2}$ → superdiffusion**
- "Anomalous diffusion is the rule in concentration-dependent diffusion processes" M. Küntz, P. Lavallée
  - High concentration diffusion of aqueous $CuSO_4$
  - Concentration of $CuSO_4$ increases **slower than $t^{1/2}$ → subdiffusion**
- "Detection of non-brownian diffusion in the cell membrane in single molecule tracking", K. Ritchie
  - Protein subdiffusion across cell membranes