Reactive Transport in Porous Media

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Outline

1. Mathematics of Chemical Reactions
2. Uncertainty Quantification & Stochastic PDEs
3. PDF Methods
4. Upscaled effective reaction rate
5. Conclusions

Mathematics of Chemical Reactions

- Any general reversible chemical reaction with n reacting species $A_1, A_2, ...A_n$ can be represented as

$$\alpha_1 A_1 + \alpha_2 A_2 + ... + \alpha_m A_m \rightleftharpoons \alpha_{m+1} A_{m+1} + ... + \alpha_n A_n$$

- The concentration of species A_i is denoted by

$$C_i \equiv [A_i], \qquad i = 1, \ldots, n; \qquad C = \frac{\text{mass of species}}{\text{volume of solution}} = \frac{[M]}{[L^3]}$$

- Each reaction process satisfies a (nonlinear) rate equation

$$\frac{dC_i}{dt} = R(C_1, C_2, ...C_n), \qquad i = 1, \ldots, n$$

Reactive Transport

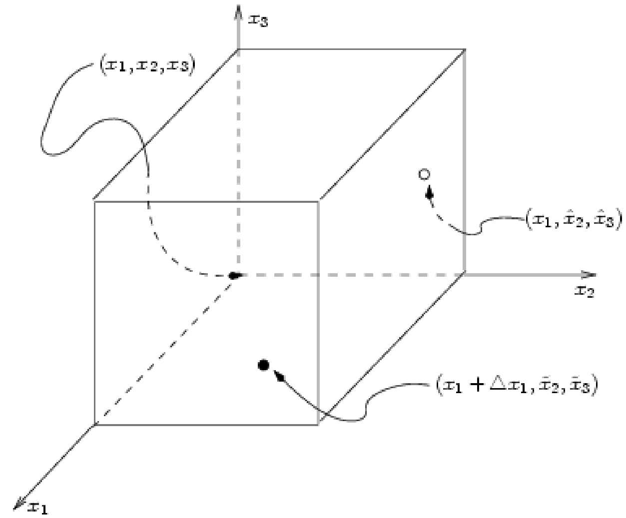
- Transport equations: Mass conservation

Advection

Molecular diffusion

Kinematic dispersion

Chemical reaction



$$\omega \frac{\partial C_i}{\partial t} = \nabla \cdot (\mathbf{D} \nabla C_i) - \nabla \cdot (\mathbf{u} C_i) + R(C_1, \ldots, C_n), \quad i = 1, \ldots, n$$

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Example 1: Adsortption

- The mass concentration of the adsorbed substance:

$$C_2 = \frac{\text{mass of adsorbed solute}}{\text{unit mass of solid}}$$

- The mass of solids in a unit volume of a porous medium:

$$(1-\omega)\rho_s = \frac{\text{unit mass of solids}}{\text{unit volume of porous media}}$$

- The mass of a substance bound to solids in a unit volume:

$$(1-\omega)\rho_s C_2$$

Example 1: Adsorption (cndt.)

- The change in mass per unit volume per unit time:

$$R = -(1-\omega)\rho_s \frac{\partial C_2}{\partial t}, \qquad (R \leq 0)$$

- If adsorption is instantaneous,

$$C_2 \approx K_d C_1, \qquad K_d \equiv \text{the distribution coefficient}$$

- Transport equation (retardation coefficient),

$$\omega R \frac{\partial C_1}{\partial t} = \nabla \cdot (\mathbf{D} \nabla C_1) - \nabla \cdot (\mathbf{u} C_1), \qquad R_c = 1 + \frac{1-\omega}{\omega} \rho_s K_d$$

Example 2: Dissolution

- Dissolution

$$\alpha \mathcal{A} \rightleftharpoons \mathcal{A}_{(s)}, \qquad C \equiv [\mathcal{A}]$$

- Reaction rate equation (effective reaction rate)

$$R \equiv \frac{dC}{dt} = -\alpha k (C^\alpha - C_{\mathrm{eq}}^\alpha)$$

- Transport equation

$$\omega \frac{\partial C}{\partial t} = \nabla \cdot (\mathbf{D} \nabla C) - \nabla \cdot (\mathbf{u} C) - \alpha k (C^\alpha - C_{\mathrm{eq}}^\alpha)$$

Reaction coefficients

- Relation to the structure of a porous medium

$$K_d,\ R_c,\ k = F_1(\text{surface areas}) = F_2(\text{pore structure})$$

- Effective reaction rate

$$k \approx k_0 a, \qquad a \sim \frac{(1-\omega)\lambda}{l}$$

k_0 — laboratory measured rate constant
a — specific surface area
λ — roughness factor
l — characteristic grain size

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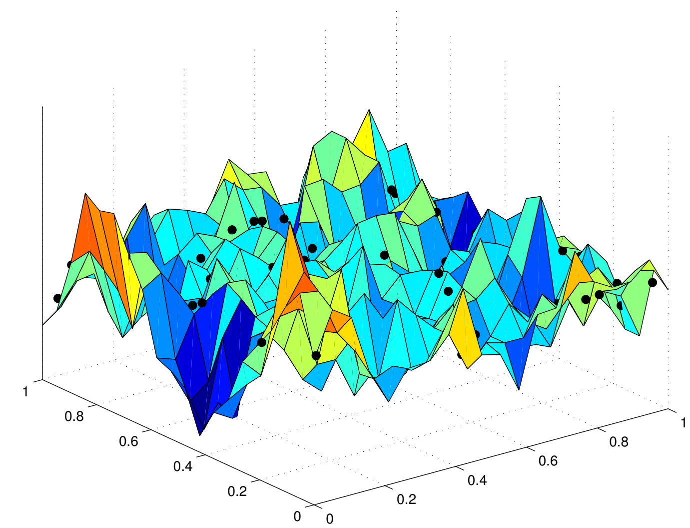
Uncertainty in Environmental Modeling

- Wisdom begins with the acknowledgment of uncertainty—of the *limits* of what we know. David Hume (1748), *An Inquiry Concerning Human Understanding*

- Most physical systems are fundamentally stochastic (Wiener, 1938; Frish, 1968; Papanicolaou, 1973; Van Kampen, 1976):

  - Model & Parameter uncertainty
    - Heterogeneity
    - Lack of sufficient data
    - Measurement noise
      - Experimental errors
      - Interpretive errors



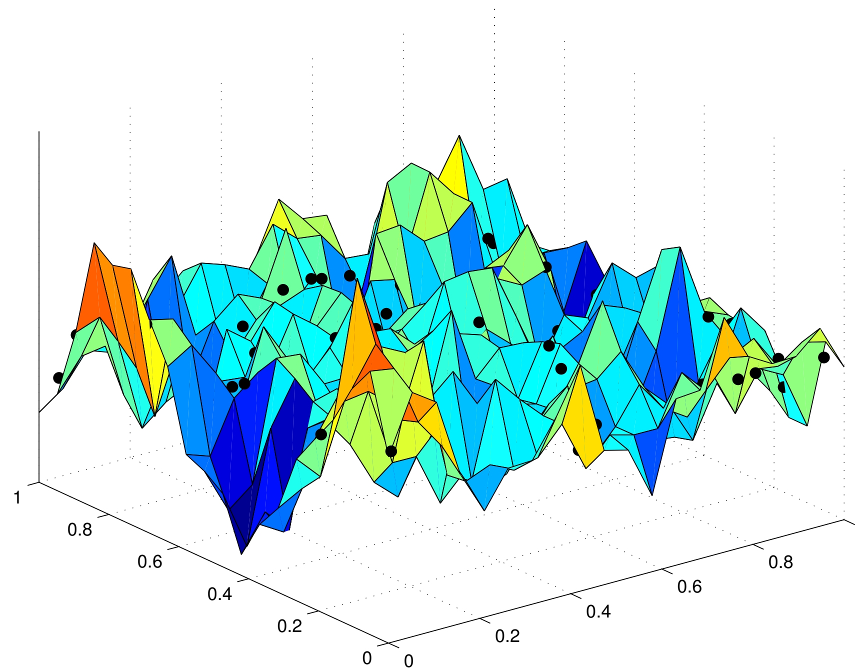
- Randomness as a measure of ignorance

Alternative Frameworks for UQ

- Ignore parameter uncertainty
- Fuzzy logic
- Interval mathematics
- Probabilistic/stochastic approaches
  - Geostatistics
  - Monte Carlo simulations
  - Moment equations
  - PDF methods
  - Etc.
- Upscaling (homogenization)

Stochastic Framework

- Reaction rate $k(\mathbf{x})$
- Random field $k(\mathbf{x}, \omega)$
- Ergodicity
- Transport equations become stochastic
- Solutions are given in terms of PDFs



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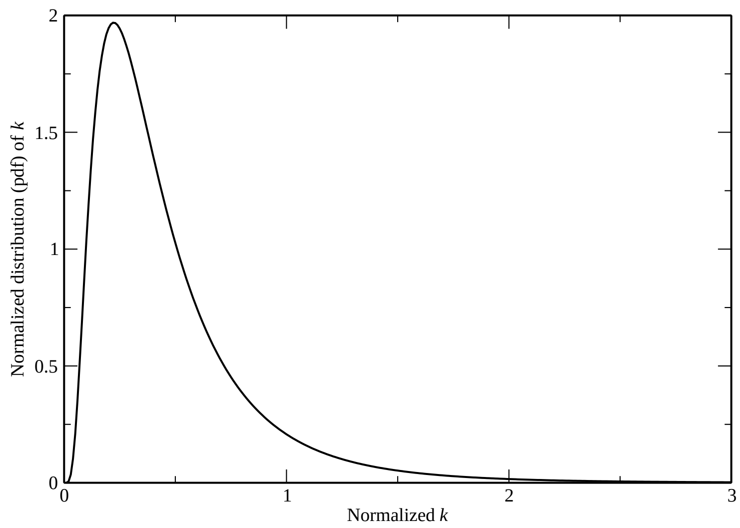
Probabilistic Description of k

Relationship between the distributions of the grain size l and effective rate constant k: $p_k(k)dk \equiv p_l(l)dl$

- Cubic grains

$$p_k(k) = \frac{6\lambda\phi_s k_0}{k^2} p_l\left(\frac{6\lambda\phi_s k_0}{k}\right)$$



- Spherical grains

$$p_l(l) \equiv \frac{1}{l\sigma_l^2\sqrt{2\pi}} \mathrm{e}^{-(\ln l - \mu_l)^2/(2\sigma_l^2)}$$

Stochastic Upscaling

- Meso-scale transport equation:

$$\frac{\partial c}{\partial t} = -\nabla \cdot (\mathbf{v}c) + f_k(c), \qquad f_k = -\alpha k(c^\alpha - C_{\mathrm{eq}}^\alpha)$$

- Uncertain (random) parameters: velocity $\mathbf{v}$ & reaction rates k
- Effective transport equation:

$$\frac{\partial \overline{c}}{\partial t} = -\nabla \cdot (\mathbf{v}_{\mathrm{eff}}\overline{c}) - \alpha k_{\mathrm{eff}}(\overline{c}^\alpha - C_{\mathrm{eq}}^\alpha)$$

- Reynolds decomposition

$$k = \overline{k} + k', \qquad \overline{k} \equiv \int k p_k(k) \mathrm{d}k, \qquad \overline{k'} = 0$$

- Stochastic upscaling vs. deterministic upscaling

Traditional Approaches

- Effective transport equation:

$$\frac{\partial \overline{c}}{\partial t} = -\nabla \cdot (\mathbf{v}_{\mathrm{eff}} \overline{c}) - \alpha k_{\mathrm{eff}} (\overline{c}^{\alpha} - C_{\mathrm{eq}}^{\alpha})$$

- Note that

$$k_{\mathrm{eff}} \neq \overline{k} \qquad \Rightarrow \qquad k_{\mathrm{eff}} = k_{\mathrm{eff}}(\overline{k}, \sigma_k^2, l_k, \ldots)$$

- Standard approaches:
  - $k_{\mathrm{eff}} \approx \overline{k}$
  - Linearization $f_\kappa(c) = f_\kappa(\overline{c}) + \ldots$

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PDF Approach

- Motivation
  - To avoid the linearization
  - To obtain complete statistics
- Raw distribution:

$$\Pi(c, C; \mathbf{x}, t) \equiv \delta(c(\mathbf{x}, t) - C)$$

- Probability density function (PDF):

$$p_c(C; \mathbf{x}, t) = \langle \Pi(c, C; \mathbf{x}, t) \rangle$$

- Concentration moments:

$$\langle c^n(\mathbf{x}, t) \rangle = \int C^n p_c(C; \mathbf{x}, t) dC$$

PDF Equation & Closures

- Stochastic PDE for the raw distribution in $\mathcal{R}^4$: $\tilde{\mathbf{x}} = (x_1, x_2, x_3, C)^T$

$$\frac{\partial \Pi}{\partial t} = -\tilde{\nabla} \cdot (\tilde{\mathbf{v}} \Pi) \qquad \tilde{\mathbf{v}} = (v_1, v_2, v_3, f_\kappa)^T$$

- Deterministic PDE for PDF

$$\frac{\partial p}{\partial t} = -\tilde{\nabla} \cdot (\langle \tilde{\mathbf{v}} \rangle p) - \tilde{\nabla} \cdot \langle \tilde{\mathbf{v}}' \Pi' \rangle$$

- Closure approximations
  - Direct interaction approximation (Kraichnan, 1987)
  - Large-eddy simulations (Koch and Brady, 1987)
  - Weak approximation (Neuman, 1993)
  - Closure by perturbation (Cushman, 1997)

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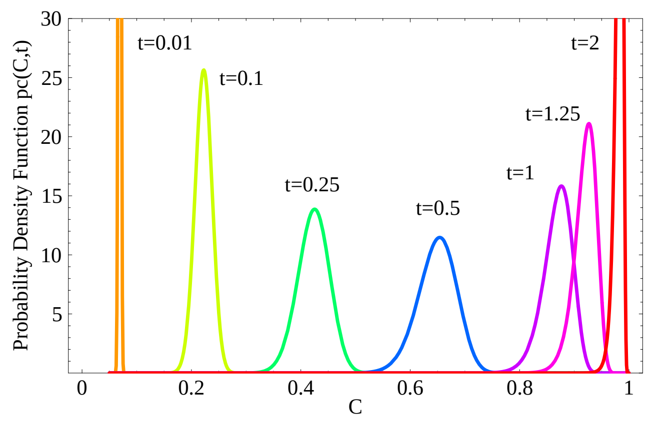
Example: One-Dimensional Batch System

- Mesoscale transport equation

$$\frac{dc}{dt} = -\alpha\kappa(c^\alpha - C_{\text{eq}}^\alpha) \qquad c(0) = C_0$$

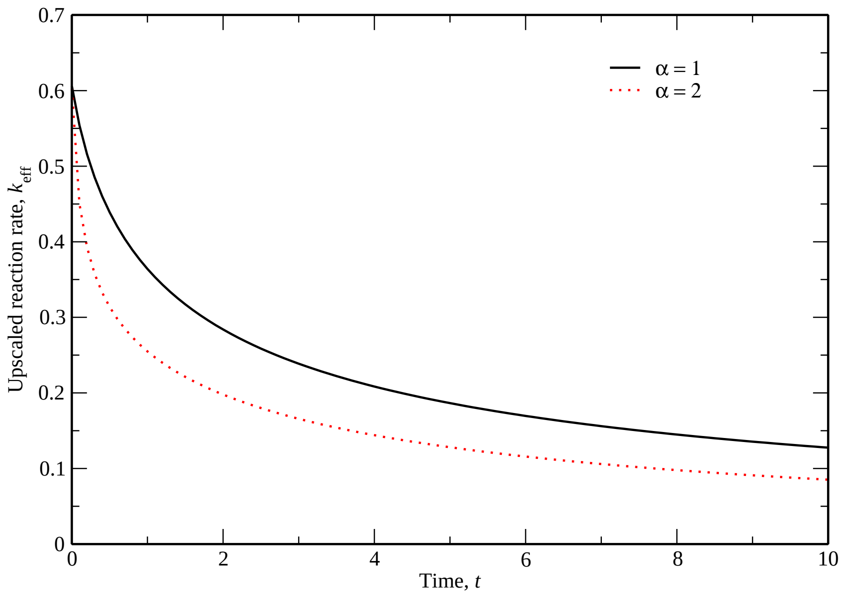
- Exact solution for PDF
  - Find $c[\kappa(Y)]$, where Y is multivariate Gaussian
  - Find $p_c(C) = (dy/dC)p(y)$



Effective (Upscaled) Rate Constant

- Find mean concentration $\overline{c}(t)$
- Define k_{eff} as the coefficient in

$$\frac{d\overline{c}}{dt} = -\alpha k_{\text{eff}} \left(\overline{c}^{\alpha} - C_{\text{eq}}^{\alpha} \right)$$



- $k_{\text{eff}}(0) = \overline{k}$

Perturbation Expansion for PDF

- Gaussian mapping, e.g., $\kappa = f(Y)$ where Y is Gaussian
- Small parameter σ_Y^2
- $p = p^{(0)} + p^{(1)} + \ldots$

$$\frac{\partial p}{\partial t} = -\tilde{\nabla} \cdot (\langle \tilde{\mathbf{v}} \rangle p) - \tilde{\nabla} \cdot \langle \tilde{\mathbf{v}}' \Pi' \rangle \quad \rightarrow \quad \frac{\partial p^{(0)}}{\partial t} = -\tilde{\nabla} \cdot \left[\langle \tilde{\mathbf{v}} \rangle^{(0)} p^{(0)} \right]$$

- Randomness in initial and boundary conditions is easily incorporated
- Solution for the concentration PDF (*à la* Kubo expansion)

$$p(C;t) = \frac{\mathrm{d}Y}{\mathrm{d}C} \sum_{n=0}^{\infty} \frac{\sigma_Y^{2n}}{(2n)!!} \delta^{(2n)}(Y - \langle Y \rangle)$$

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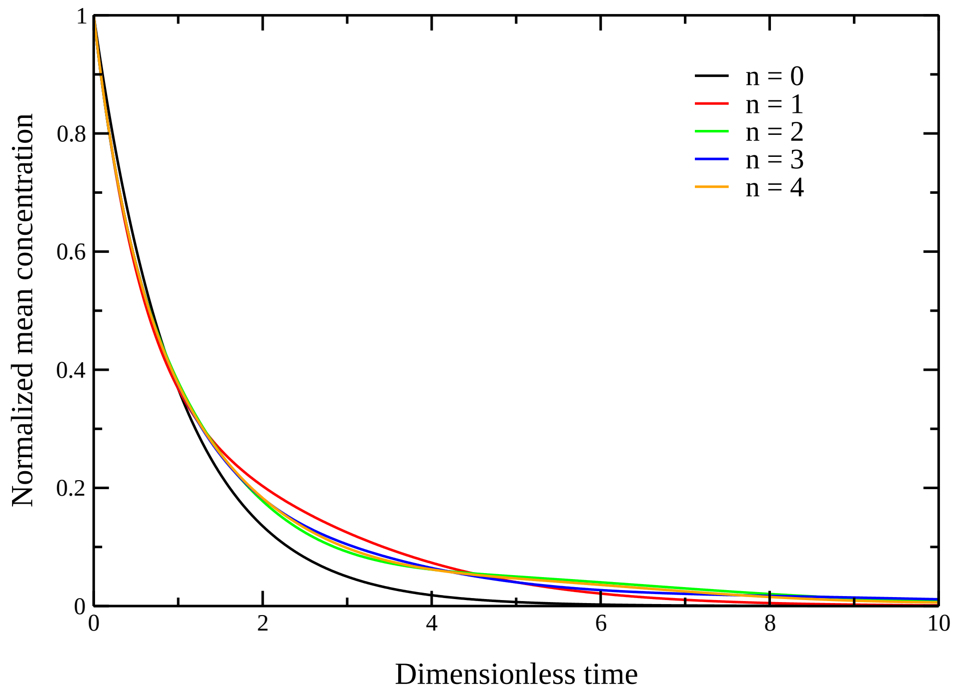
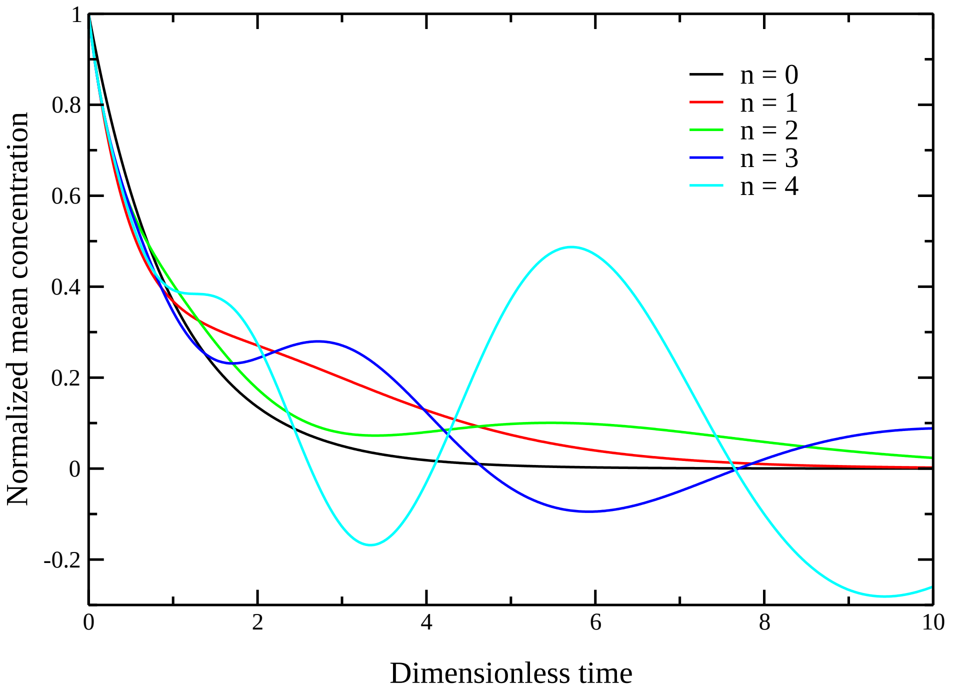
Mean Concentration for Linear Kinetics ($\alpha = 1$)

- Mild heterogeneity ($\sigma_Y^2 = 0.5$)



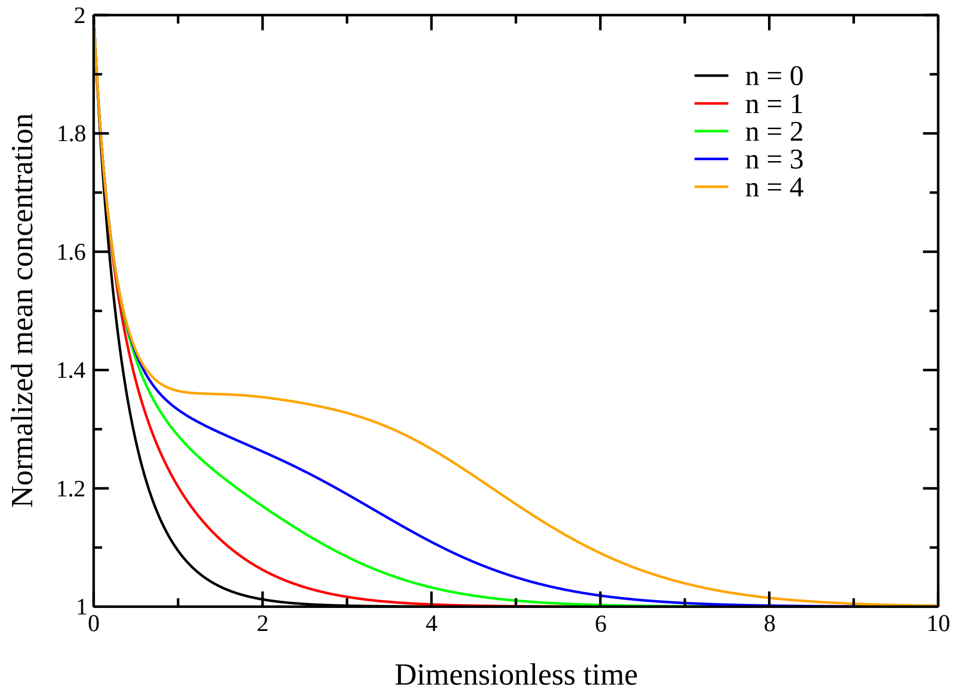
Mean Concentration for Linear Kinetics ($\alpha = 1$)

- Mild-to-moderate heterogeneity ($\sigma_Y^2 = 1.0$)



Mean Concentration for Non-linear Kinetics

- $\alpha = 2$
- Mild heterogeneity ($\sigma_Y^2 = 0.5$)



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Mean Concentration for Non-linear Kinetics

- $\alpha = 2$
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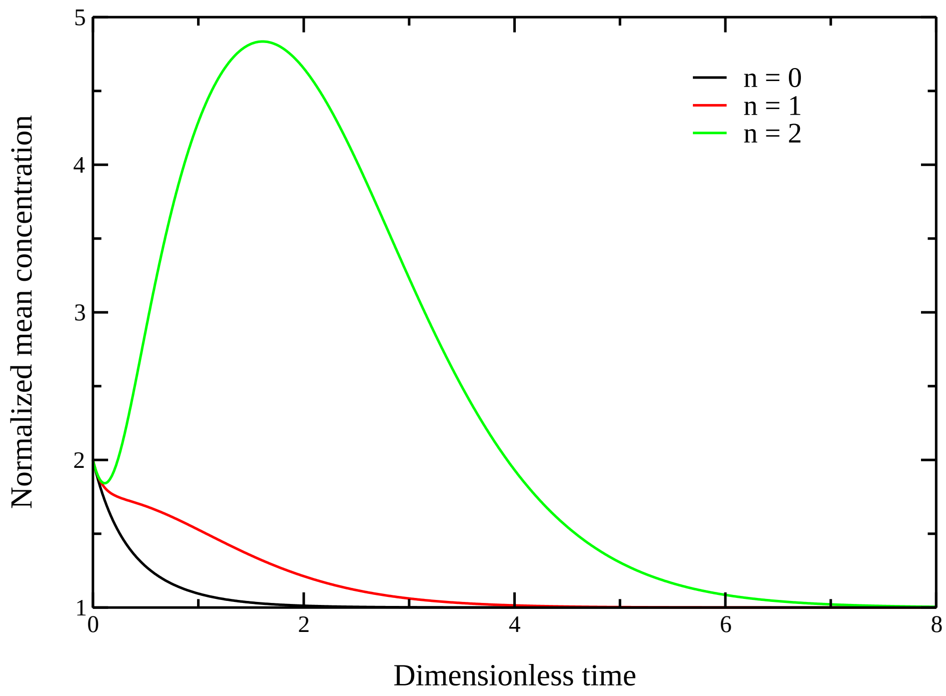


LED Approximation of PDF Equations

- Transport equation

$$\frac{\partial c}{\partial t} = -\nabla \cdot (\mathbf{v}c) + f_\kappa(c) \qquad \text{in} \quad \mathcal{R}^3$$

- Unclosed PDF equation

$$\frac{\partial p}{\partial t} = -\tilde{\nabla} \cdot (\langle \tilde{\mathbf{v}} \rangle p) - \tilde{\nabla} \cdot \langle \tilde{\mathbf{v}}' \Pi' \rangle \qquad \text{in} \quad \mathcal{R}^4$$

- Large Eddy Diffusivity (LED) closure

$$\frac{\partial p}{\partial t} = -\frac{\partial \langle \tilde{u}_i \rangle p}{\partial \tilde{x}_i} + \frac{\partial}{\partial \tilde{x}_j} \left[\tilde{D}_{ij} \frac{\partial p}{\partial \tilde{x}_i} \right]$$

- "Dispersion" coefficient

$$\tilde{D}_{ij}(\tilde{\mathbf{x}}, t) \approx \int_0^t \int_\Omega \langle \tilde{v}_i'(\tilde{\mathbf{x}}) \tilde{v}_j'(\tilde{\mathbf{y}}) \rangle G(\tilde{\mathbf{x}}, \tilde{\mathbf{y}}, t - \tau) d\tilde{\mathbf{y}} d\tau$$

Lagrangian-Eulerian Description

- Governing equations:

$$\frac{\partial c}{\partial t} = -\nabla \cdot (\mathbf{v}c) + f_k(c) \qquad \Rightarrow \qquad \frac{\partial \Pi}{\partial t} = -\tilde{\nabla} \cdot (\tilde{\mathbf{v}}\Pi)$$

- Random Green's function $\mathcal{G}(\tilde{\mathbf{x}}, \tilde{\mathbf{y}}, t-\tau)$

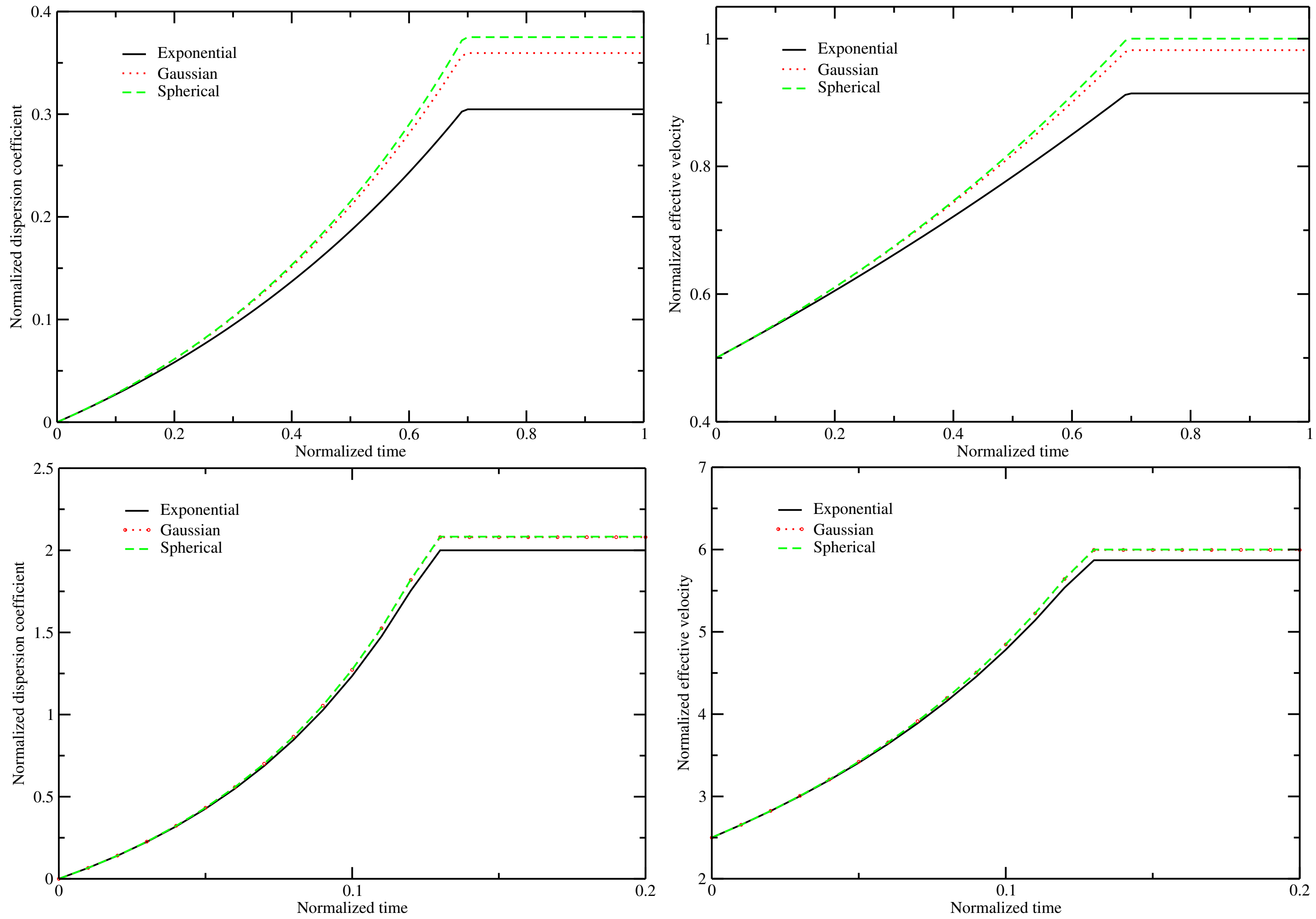
$$\frac{\partial \mathcal{G}}{\partial \tau} + \tilde{\mathbf{v}} \cdot \tilde{\nabla}_{\tilde{\mathbf{y}}} \mathcal{G} = -\delta(\tilde{\mathbf{x}} - \tilde{\mathbf{y}})\delta(t-\tau)$$

- Explicit expression

$$\mathcal{G}(\tilde{\mathbf{x}}, \tilde{\mathbf{y}}, t-\tau) = [1 - \mathcal{H}(\tau - t)]\delta(\tilde{\mathbf{y}} - \tilde{\mathbf{x}}^L), \qquad \tilde{\mathbf{x}}^L = \tilde{\mathbf{x}} + \tilde{\mathbf{v}}(t-\tau)$$

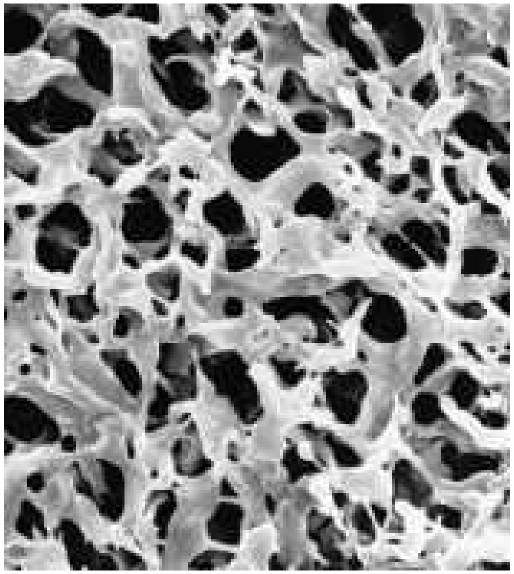
- Mean Green's function: $G(\tilde{\mathbf{x}}, \tilde{\mathbf{y}}, t-\tau) = \langle \mathcal{G}(\tilde{\mathbf{x}}, \tilde{\mathbf{y}}, t-\tau) \rangle$

Effective parameters



Conclusions

- Most physical systems are under-determined due to
  - Heterogeneity
  - Lack of sufficient data
  - Measurement noise



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