Reactive transport in porous media with local mixing limitation: A Lagrangian modeling approach

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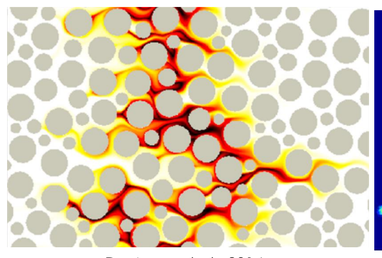
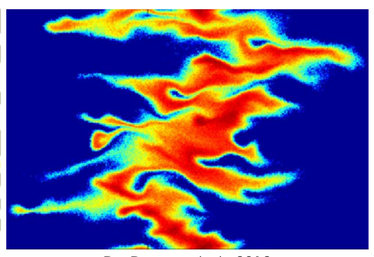
1. INTRODUCTION

- Chemical reactions in porous media are often **limited by mixing**. Local concentration fluctuations occur **at multiple scales** [1,2].



De Anna et al., 2014

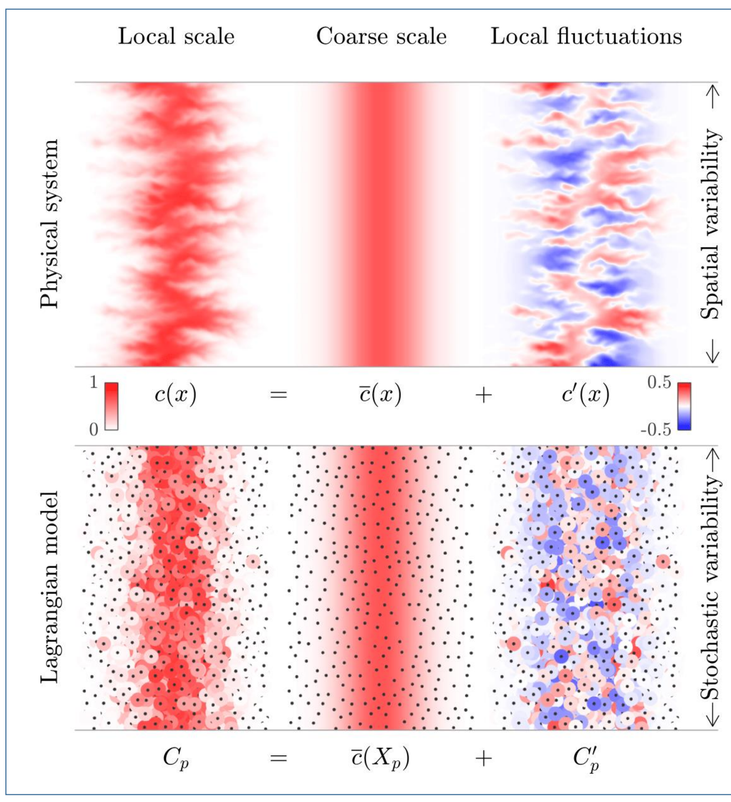


De Dreuzy et al., 2012

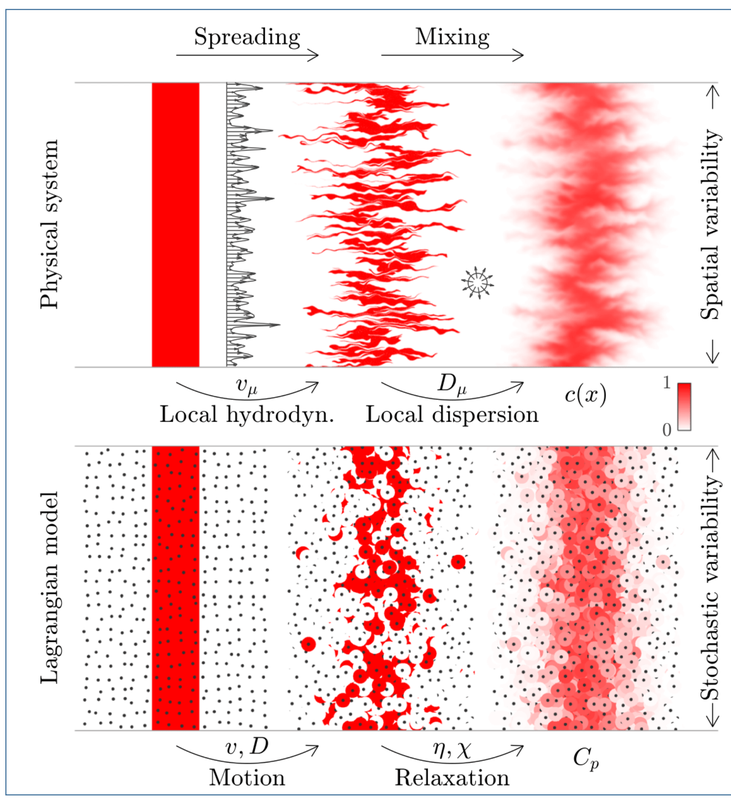
- Consequently, the classical advection-dispersion reaction equation (ADRE) **typically over-predicts mixing and reaction**.
- Thus, a formulation that accounts for the generation, transport and decay of local concentration fluctuations is needed to **correctly model reactions in porous media**.
- We propose a Lagrangian formulation [3] that is able to simultaneously reproduce the coarse-scale transport (e.g., advection-dispersion) of the averaged concentrations (**spreading**) as well as the evolution of the sub-scale fluctuations (**mixing**).

2. CONCEPTUAL MODEL

- Separation of scales



- Spreading & mixing



3. MATHEMATICAL FORMULATION

- The Motion equation governs coarse-scale paths of fluid particles, which drive solute **spreading**. Classical **Brownian motion** [4]:

$$\mathbf{X}_p(t+\Delta t) = \mathbf{X}_p(t) + \mathbf{v}\Delta t + \mathbf{B}\boldsymbol{\xi}\sqrt{2\Delta t}, \quad (1)$$

with $\mathbf{B}\mathbf{B}^{\mathrm{T}} = \mathbf{D}$ and $\boldsymbol{\xi}\sim\mathrm{N}(0,1)$. In this case, in the absence of chemical reactions, **averaged concentrations** $\bar{c}_{\mathrm{A}}$ follow the ADE,

$$\frac{\partial \bar{c}_{\mathrm{A}}}{\partial t} = \mathcal{L}(\bar{c}_{\mathrm{A}}), \qquad \mathcal{L}(u) := \nabla\cdot(-\mathbf{v}u + \mathbf{D}\nabla u). \quad (2)$$

- The choice of Relaxation equation drives the local-scale **mixing** process. We propose the following general **Multi-Rate Interaction by Exchange with the Mean** (MRIEM):

$$C_{\mathrm{A},p}(t) = \sum_i \eta_i\, C_{\mathrm{A},p,i}(t), \quad (3)$$

$$\frac{\mathrm{d}C_{\mathrm{A},p,i}}{\mathrm{d}t} = -\frac{\chi_i}{2}\left[C_{\mathrm{A},p,i}(t) - \bar{c}_{\mathrm{A}}(\mathbf{X}_p(t),t)\right], \quad (4)$$

where through η_i and χ_i one can emulate a mixing process subject to **aging**. A simple parameter choice (DR) is:

$$1-\eta_1 = \eta_2 \equiv \eta, \qquad \chi_1 \to \infty, \qquad \chi_2 \equiv \chi. \quad (5)$$

Then,

$$\frac{\mathrm{d}C_{\mathrm{A},p}}{\mathrm{d}t} = (1-\eta)\frac{\mathrm{d}\bar{c}_{\mathrm{A},p}}{\mathrm{d}t} - \frac{\chi}{2}\left[C_{\mathrm{A},p}(t) - \bar{c}_{\mathrm{A}}\left(\mathbf{X}_p(t),t\right)\right]. \quad (6)$$

4. COVARIANCE AND MIXING STATE

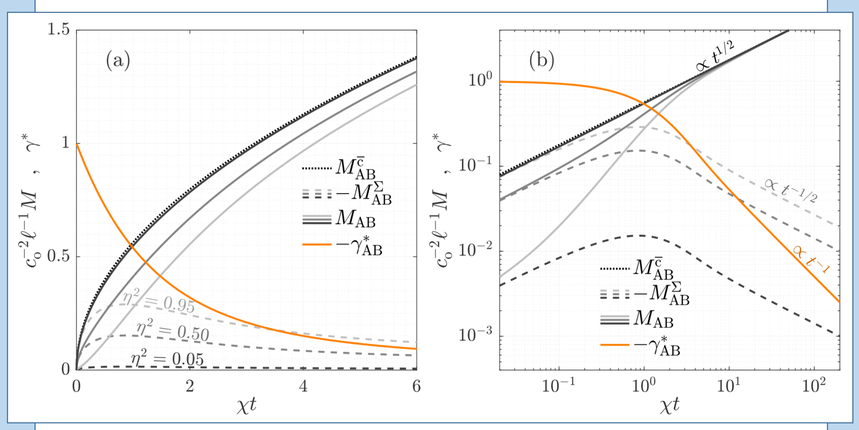
- DR case (5). Let $C'_{\mathrm{A},p}(t) := C_{\mathrm{A},p}(t) - \bar{c}_{\mathrm{A}}\left(\mathbf{X}_p(t),t\right)$. The **concentration covariance** $\Sigma_{\mathrm{AB}} := \langle C'_{\mathrm{A}}C'_{\mathrm{B}}\rangle$ evolves as:

$$\frac{\partial \Sigma_{\mathrm{AB}}}{\partial t} = \underbrace{2\eta^2\nabla\bar{c}_{\mathrm{A}}^{\mathrm{T}}\mathbf{D}\nabla\bar{c}_{\mathrm{B}}}_{\text{Generation}} \underbrace{-\chi\Sigma_{\mathrm{AB}}}_{\text{Decay}} \underbrace{+\mathcal{L}(\Sigma_{\mathrm{AB}})}_{\text{Transport}}. \quad (7)$$

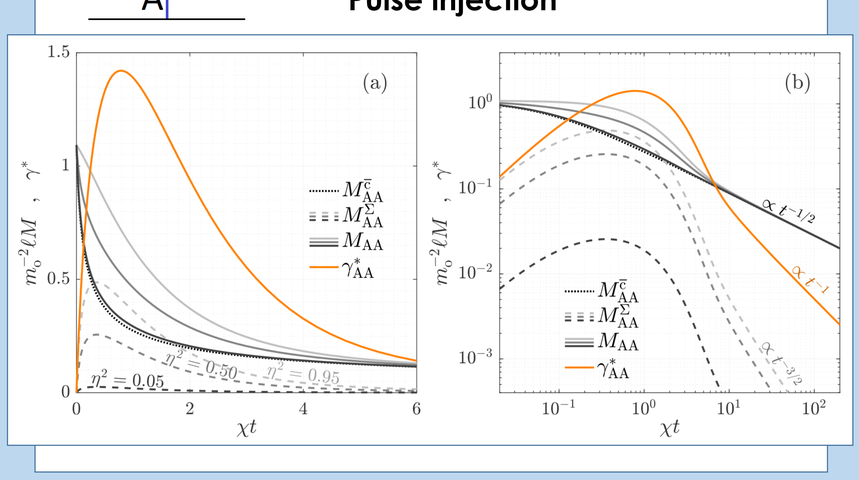
For other parametrizations than (5), decay term becomes more complicated (see [3])

- Analyt. solutions for the **mixing state** ($\int \Sigma_{\mathrm{AB}}\,\mathrm{d}\mathbf{x}$)

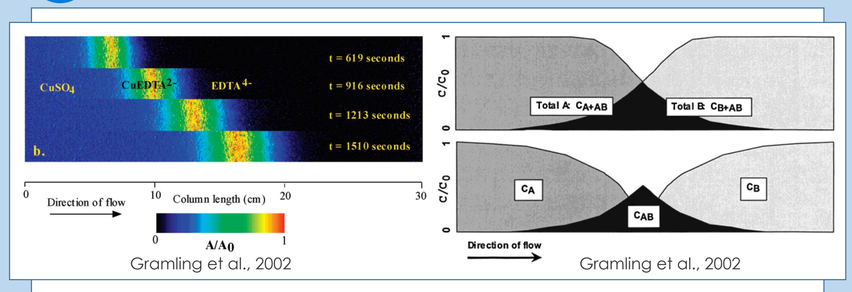
A B **Continuous injection**



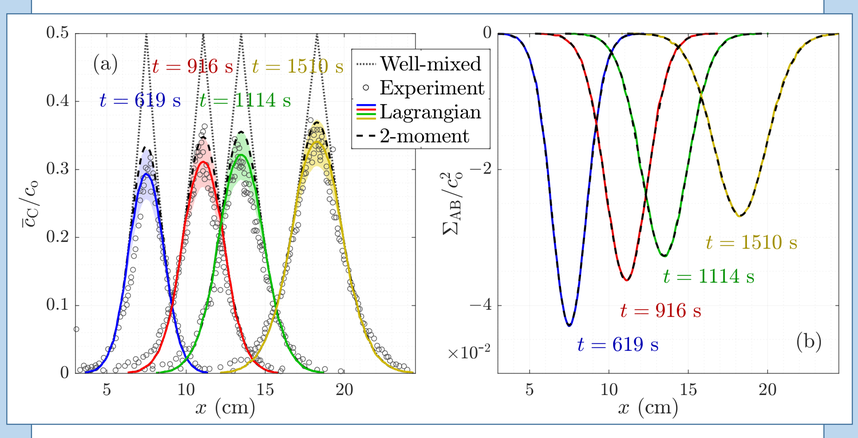
A **Pulse injection**



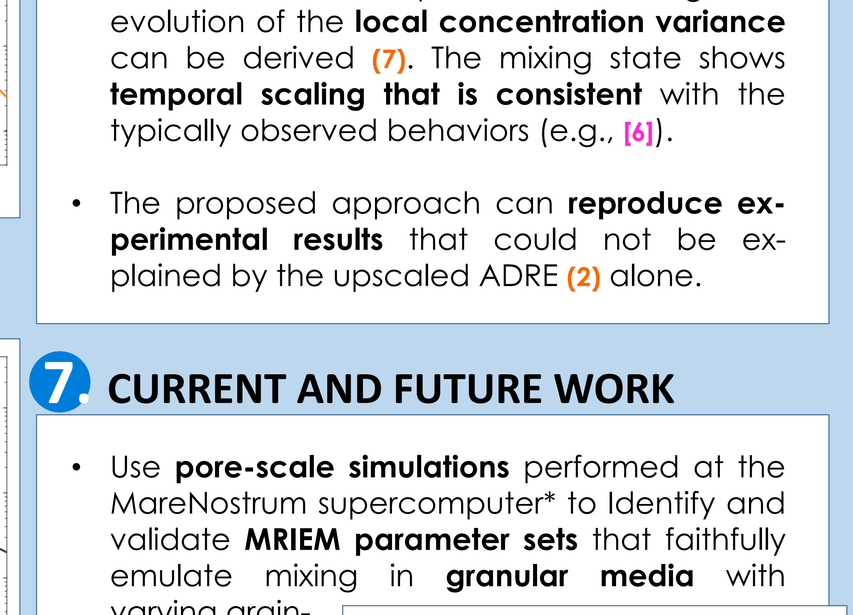
5. REPRODUCING EXPERIMENTAL DATA



- Gramling et al's 2002 experiment [5]: water-saturated sand through which two reactants mix by dispersion and react. Discrepancy btw. ADRE prediction & observations. Results are reproduced with proposed approach:



- $\eta = 0.5$, $\chi = 10^{-3}\ \mathrm{s}^{-1}$. The model's asymptotic transverse mixing length $\ell = \sqrt{4D_\mu/\chi}$ approximately matches the mean pore diameter. Extending values to Raje & Kapoor's experiments (2002) also yields good results:

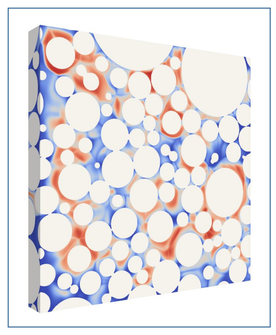


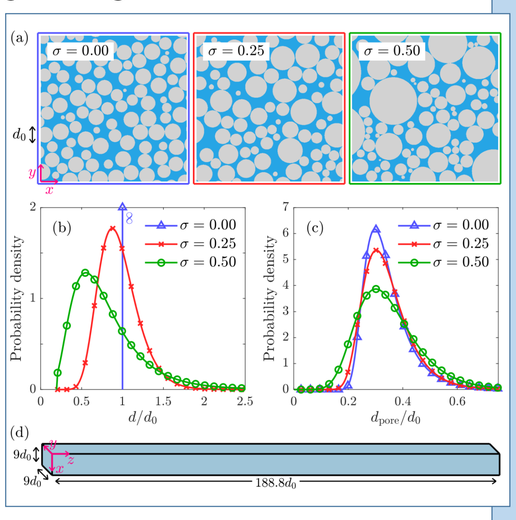
6. SUMMARY AND CONCLUSIONS

- New **Lagrangian** mathematical model where transport of **average concentrations** depends on stochastic fluid-particle motion (1), while **local concentrations** are subject to **MRIEM** (4).
- The differential equation describing the evolution of the **local concentration variance** can be derived (7). The mixing state shows **temporal scaling that is consistent** with the typically observed behaviors (e.g., [6]).
- The proposed approach can **reproduce experimental results** that could not be explained by the upscaled ADRE (2) alone.

7. CURRENT AND FUTURE WORK

- Use **pore-scale simulations** performed at the MareNostrum supercomputer* to Identify and validate **MRIEM parameter sets** that faithfully emulate mixing in **granular media** with varying grain-size heterogeneity & Pe number.





- Future: larger scale, non-Brownian motion, heterog. reactions, complex geochemistry…

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