Mixing and Reaction in Highly Heterogeneous Porous Media

by

Diogo Bolster

Dept. of Civil Engineering and Geological Sciences
University of Notre Dame
Thanks to my collaborators
Heterogeneity => Typically Superdiffusive spreading
Topics I’ll Talk About

• Incomplete Mixing and Slowdown on Chemical Reactions – Fickian and Non-Fickian

• Incomplete Mixing - When Might Tails not be due to fractional type behavior?

• How fractional dispersion can make reactions happen in places where Fickian models say it cannot – And I don’t mean tails.
Topic 1
-
Incomplete Mixing and Slowdown on Chemical Reactions – Fickian and Non-Fickian Transport
What does any of this mean for reactive transport?

Consider the following example:

Instantaneous? Reversible? Equilibrium?
Let’s start easy – forget heterogeneity

• Kinetic, irreversible
  \[ \frac{d[A]}{dt} = k[A][B] \]
  \[ \frac{d[B]}{dt} = k[A][B] \]
  \[ \frac{d[C]}{dt} = -k[A][B] \]

• Analytical Solution if \([A]=[B]\) (assume initially equal \(\rightarrow\) always equal)
  \[ A = A_0/(1+kA_0t) \]
To study this let’s use a numerical model....

• Move Particles with a random walk

• Based on the distance between two particles calculate probability that they will collocate

• Then based on the reaction multiply probability that reaction will occur
Step 1 – Move Particles by Random Motion

Update Particle Positions by $x(t+dt) = x(t) + \xi$

Random Jump Reflecting Dispersion
Step 1 – Move Particles by Brownian Motion

Update Particle Positions by $x(t+dt) = x(t) + \xi$

Random Jump Reflecting Dispersion
Step 1 – Move Particles by Brownian Motion

Update Particle Positions by $x(t+dt) = x(t) + \xi$

Random Jump Reflecting Dispersion
Step 2 – Search for Neighbors of Opposite Particle

Particle 1

Gives distances
s1
s2
s3
Step 3 – Calculate Probability of RXN

Probability of Reaction

\[ \text{Probability of Reaction} = \]  

Probability of Collocation

\[ \text{Probability of Reaction Given Collocation} = \]  

Particles 1-1

Function of distance

Convolution of position densities

Fickian => Gaussian
Fractional => Stable

e.g.

\[ v(s, \Delta t) = \frac{1}{(8\pi D\Delta t)^{d/2}} e^{-\frac{s^2}{8D\Delta t}} \]

Function of reaction

Kinetics

\[ K m_p \, dt \]
Step 4 – Die or Survive

Particle 1 - 1

Generate a random number 0<P<1

If P> Probability of Reaction

Kill both particles

If less move to next blue particle
Step 4 – Die or Survive

Particle 1 - 2

Generate a random number $0 < P < 1$

If $P >$ Probability of Reaction (for this pair)

Kill both particles

If less move to next blue particle
Step 4 – Die or Survive

Particle 1 - 2

Generate a random number $0 < P < 1$

If $P >$ Probability of Reaction (for this pair)

Kill both particles

If less move to next blue particle

And so on Cycling through all blues
Step 4 – Die or Survive

Particle 1 - 2

Generate a random number $0 < P < 1$

If $P >$ Probability of Reaction (for this pair)

Kill both particles

If less move to next blue particle

And so on Cycling through all blues
Repeat for Each red Particle

Particle 2

And so on Cycling through all reds
Then back to Step One (Move Particles)
Non Dimensional Time \( (C_0 K_f t) \)
What do we observe? For 1d Brownian Motion
Other Observations of the Same (different methods of study)

Countless other examples:
- Astrophysics
- Particle Physics
- Biochemical Processes
- Turbulent Environmental Flows
- Population Dynamics
- Warfare Simulation

Benson & Meerschaert 2008, WRR
What’s going on...
Let’s take a look at concentrations in 1d

Early

Intermediate

Late

Benson & Meerschaert 2008, WRR
What’s going on...
Let’s take a look at concentrations in 1d

Early

Intermediate

Late

Isolated Islands of A and B form limiting reaction by how quickly A and B diffuse into one another

Incomplete Mixing

Benson & Meerschaert 2008, WRR

spatial $[A]$, $[B]$

$[A](x)$, $[A]_0$

$[B](x)$, $[B]_0$
But what does this have to with fractional transport?

- Consider the following problem

\[
\frac{\partial C_i}{\partial t} = D \frac{\partial^{\alpha} C_i}{\partial |x|^{\alpha}} - k C_A C_B, \quad i = A, B \quad -\infty < x < \infty
\]

\[
C_i(x, t) = \bar{C}_i(t) + C_i'(x, t)
\]
But what does this have to with fractional transport?

• Consider the following problem

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\]

Average

\[
C_i(x, t) = \overline{C_i}(t) + C'_i(x, t)
\]

Remainder

\[
\frac{\partial \overline{C_i}}{\partial t} = -k\overline{C_A} \overline{C_B} - k\overline{C'_A C'_B}
\]

\[
\frac{\partial C'_i}{\partial t} = D \frac{\partial^{\alpha} C'_i}{\partial |x|^{\alpha}} - k\overline{C_A} C'_B - k\overline{C'_A C'_B} - kC'_A \overline{C_B} + k\overline{C'_A C'_B}
\]
But what does this have to with fractional transport?

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C_i(x, t) = \overline{C}_i(t) + C'_i(x, t)
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\frac{\partial \overline{C}_i}{\partial t} = -k\overline{C}_A \overline{C}_B - kC'_A C'_B
\]

\[
\frac{\partial C'_i}{\partial t} = D \frac{\partial C'_i}{\partial |x|^\alpha} - k\overline{C}_A C'_B - kC'_A \overline{C}_B - kC'_A C'_B + k\overline{C}'_A \overline{C}'_B
\]

\[
f(x, y, t) = \overline{C}'_A(x, t)C'_B(y, t)
\]
But what does this have to with fractional transport?

• Consider the following problem

\[
\frac{\partial C_i}{\partial t} = D \frac{\partial^{\alpha} C_i}{\partial |x|^\alpha} - kC_A C_B, \quad i = A, B, \quad -\infty < x < \infty
\]

\[
C_i(x, t) = \overline{C_i}(t) + C_i'(x, t)
\]

Average

\[
\frac{\partial \overline{C_i}}{\partial t} = -k\overline{C_A} \overline{C_B} - kC_A' C_B'
\]

Remainder

\[
\frac{\partial C_i'}{\partial t} = D \frac{\partial^{\alpha} C_i'}{\partial |x|^\alpha} - kC_A \overline{C_B'} - kC_A' \overline{C_B} - kC_A' C_B' + k\overline{C_A} C_B'
\]

Perturbation closure

\[
f(x, y, t) = \overline{C_A'}(x, t) \overline{C_B'}(y, t)
\]

Closure Problem

\[
f(x, y, t) = \int_{-\infty}^{\infty} R(\xi, y) G(x, \xi, t) d\xi,
\]

\[
\overline{C_A'}(x, 0) \overline{C_B'}(y, 0) = R(x, y)
\]

\[
G(x, \xi, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-2D_t k |x|^{\alpha} t} e^{ik(x-\xi)} dk
\]
So my equation becomes

\[ \frac{\partial C_i}{\partial t} = -kC_i^2 + k \int_{-\infty}^{\infty} R(\xi, x)G(x, \xi, t)d\xi. \]
So

\[ \frac{\partial \overline{C_i}}{\partial t} = -k\overline{C_i}^2 + k \int_{-\infty}^{\infty} R(\xi, x)G(x, \xi, t)d\xi. \]

\[ R(x, y) = \sigma^2 l\delta(x - y) \quad \Rightarrow \quad \frac{\partial \overline{C_i}}{\partial t} = -k\overline{C_i}^2 + k\chi t^{-\frac{1}{\alpha}} \]
So

\[
\frac{\partial \overline{C_i}}{\partial t} = -k \overline{C_i}^2 + k \int_{-\infty}^{\infty} R(\xi, x) G(x, \xi, t) d\xi.
\]

\[R(x, y) = \sigma^2 l \delta(x - y)\]

\[
\frac{\partial \overline{C_i}}{\partial t} = -k \overline{C_i}^2 + k \chi t^{-\frac{1}{\alpha}}
\]

\[
\overline{C_i}(t) = \frac{\sqrt{\chi^*}}{t^{\frac{1}{2\alpha}}} \frac{\left( I_{-\frac{\alpha-1}{2\alpha-1}}(z) - \kappa K_{\frac{\alpha-1}{2\alpha-1}}(z) \right)}{\left( I_{\frac{\alpha}{2\alpha-1}}(z) + \kappa K_{\frac{\alpha}{2\alpha-1}}(z) \right)}
\]

\[
z = \frac{2\alpha \sqrt{\chi^*}}{2\alpha - 1} t^{\frac{2\alpha-1}{2\alpha}}
\]
So

\[
\frac{\partial \bar{C}_i}{\partial t} = -k\bar{C}_i^2 + k \int_{-\infty}^{\infty} R(\xi, x) G(x, \xi, t) d\xi.
\]

\[
R(x, y) = \sigma^2 l \delta(x - y) \quad \Rightarrow \quad \frac{\partial \bar{C}_i}{\partial t} = -k\bar{C}_i^2 + k\chi t^{-\frac{1}{\alpha}}
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\]

\[
z = \frac{2\alpha \sqrt{\chi^*}}{2\alpha - 1} t^{\frac{2\alpha-1}{2\alpha}}
\]

Early Times

\[
\bar{C}_A(t) = \frac{1}{1 + (t - t_0)}
\]
So

\[
\frac{\partial \bar{C}_i}{\partial t} = -k\bar{C}_i^2 + k \int_{-\infty}^{\infty} R(\xi, x)G(x, \xi, t) d\xi.
\]

\[
R(x, y) = \sigma^2 l \delta(x - y)
\]

\[
\frac{\partial \bar{C}_i}{\partial t} = -k\bar{C}_i^2 + k\chi t^{-\frac{1}{\alpha}}
\]

\[
\bar{C}_i(t) = \frac{\sqrt{\chi^*}}{t^{\frac{1}{2\alpha}}} \left( \frac{I_{\frac{\alpha-1}{2\alpha-1}}(z) - \kappa K_{\frac{\alpha-1}{2\alpha-1}}(z)}{I_{\frac{\alpha}{2\alpha-1}}(z) + \kappa K_{\frac{\alpha}{2\alpha-1}}(z)} \right)
\]

\[
\bar{C}_A(t) = \frac{1}{1 + (t - t_0)}
\]

Late Times

\[
\bar{C}_A(t) \sim \sqrt{\chi^*} t^{-1/(2\alpha)}.
\]

\[
z = \frac{2\alpha \sqrt{\chi^*}}{2\alpha - 1} t^{\frac{2\alpha - 1}{2\alpha}}
\]
What does Solution Look like
Validation
Topic 2

- Incomplete Mixing - When Might Tails Exist, but not be due to fractional type behavior?

Or are they and I’m just wrong
Let’s Look at Some Experiments

There are lots of papers trying to model these results.... Using anomalous/fractional transport methods – WE ASK WHY?
Gramling’s Measurements vs Predictions

(a) CuEDTA ($C/C_0$) vs time ($t$) for $t = 619$ seconds

(b) Imaged CuEDTA vs time ($t$) for $Q = 2.7$ ml/min, $t = 1114$ seconds

SPSM prediction vs Imaged CuEDTA

mass of CuEDTA (g) vs time (s)
Gramling’s Measurements vs Predictions

Heavy Tails

Lower Concentrations

Lower Rates of Reaction

ANOMALOUS TRANSPORT??
Anomalous Transport
-
We Don’t Think So

There is no evidence of anomalous transport in non reactive flow experiments through the same column.
Looking closely at Gramling data

Looks a lot like what we called islands from our numerical models.....

Could it be incomplete mixing only?
Our Model

Set up an initial condition with all A on one side and B on the other
Our Model

Move Every Particle – Jump by \textit{dispersion}
Now kill some particles probabilistically for reaction following rules from before
When we use our Methods

Pretty Good Agreement – And we can Explain Why
And the Tails....

We still use conventional transport models – but incorporate incomplete mixing effects!

To quote Dave Benson– in our model particles can ‘advance further into enemy territory before reacting’
SO – Tail does not need to mean anomalous/fractional
Or
Can it be interpreted that way?
Topic 3

If not in the tails, how fractional dispersion can make reactions happen in places where Fickian dispersion cannot
Let’s consider another common, but very distinct chemical reaction
Instantaneous Equilibrium Reactions

\[
\frac{\partial C_i}{\partial t} = D \nabla^2 C_i + r \quad i = 1,2
\]

\[
\frac{\partial C_3}{\partial t} = -r
\]

\[
C_1 C_2 = K
\]
Instantaneous Equilibrium Reaction

\[ \frac{\partial C_i}{\partial t} = D \nabla^2 C_i + r \quad i = 1, 2 \]

\[ \frac{\partial C_3}{\partial t} = -r \]

\[ C_1 C_2 = K \]
\[ \frac{\partial C_i}{\partial t} = D \nabla^2 C_i + r \quad i = 1,2 \]

\[ \frac{\partial C_3}{\partial t} = -r \]

\[ C_1 C_2 = K \]
\[ \frac{\partial C_i}{\partial t} = D \nabla^2 C_i + r \quad i = 1, 2 \]

\[ \frac{\partial C_3}{\partial t} = -r \]

\[ C_1 C_2 = K \]
\[
\frac{\partial C_i}{\partial t} = D \nabla^2 C_i + r \quad \text{for } i = 1, 2
\]

\[
\frac{\partial C_3}{\partial t} = -r
\]

\[
C_1 C_2 = K
\]

Define conservative
\[
U = C_2 - C_1
\]

\[
\frac{\partial U}{\partial t} = D \nabla^2 U
\]

\[
r = (D \nabla U \cdot \nabla U) \left( \frac{d^2 C_1}{dU^2} \right)
\]

4 eqns, 4 unknowns
Local Measure of Mixing – Drives many Reactions

\[ r = \left( D \nabla U \cdot \nabla U \right) \left( \frac{d^2 C_1}{dU^2} \right) \]

- MIXING
- Chemistry
• Local Measure of Mixing – Drives many Reactions

\[ r = (D \nabla U \cdot \nabla U) \]

Interesting, but let’s worry about this later on as heterogeneity plays little role on this

\[ ??? = $$$ \]
How do we Quantify Mixing?

- Local Measure of Mixing – Drives many Reactions

  \[ r = (D \nabla U \cdot \nabla U) \]

- Global Measure of Mixing (integrate r over whole domain)

  \[ M = \int_{\Omega} (D \nabla U \cdot \nabla U) d\Omega = -\frac{1}{2} \frac{d}{dt} \int_{\Omega} U^2 d\Omega \]

Scalar Dissipation Rate
Homogeneous Mixing

A little bit boring, no?
Replace Fickian with Fractional Dispersion

\[
\frac{\partial C}{\partial t} = D \frac{\partial^\alpha C}{\partial |x|^\alpha} + r
\]

\[1 < \alpha \leq 2\]
Take a step back

Recall we can think of this reaction in Terms of a conservative component $u$. Consider a system with $u=\text{constant}$ initially and then we inject a pulse of different $u$ at position $x=0$.

\[
\frac{\partial U}{\partial t} = D \frac{\partial^\alpha U}{\partial |x|^\alpha}
\]

\[U(t = 0) = \delta(x)\]
When $\alpha=2$

Classical Fickian diffusion

\[ r = (D \nabla U \cdot \nabla U) \left( \frac{d^2 C_1}{dU^2} \right) \]
What happens as $\alpha$ changes?
Let’s take a closer look at this
What does this mean for precipitation reactions?

\[ r(x, t) = D_\alpha \sum_{k=1}^{\infty} \binom{\alpha - 1}{k} \frac{\partial^{\alpha-k} u}{\partial |x|^{\alpha-k}} \frac{\partial^k d_c}{\partial x^k} du. \]
What does this mean for precipitation reactions?

Min becomes max $\alpha$ gets smaller
Global Measures – Mixing (Scalar Dissipation)

At early times more anomalous (smaller $\alpha$)=more mixing
At late times – less mixing
Global Measures – Total Reaction Rate

More anomalous – always less reactions (a mixing scale effect???)
Questions