Mixing and Reaction in Highly Heterogeneous Porous Media

by

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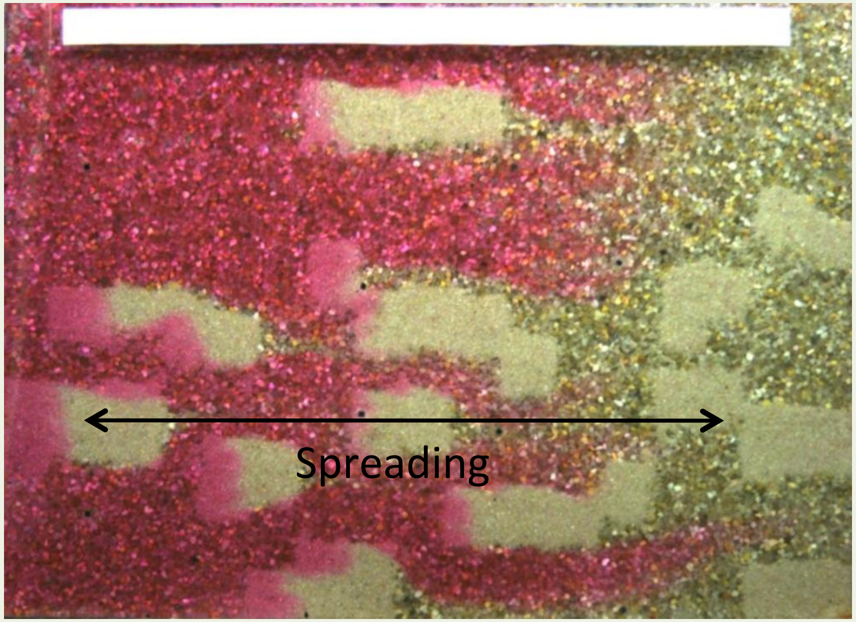
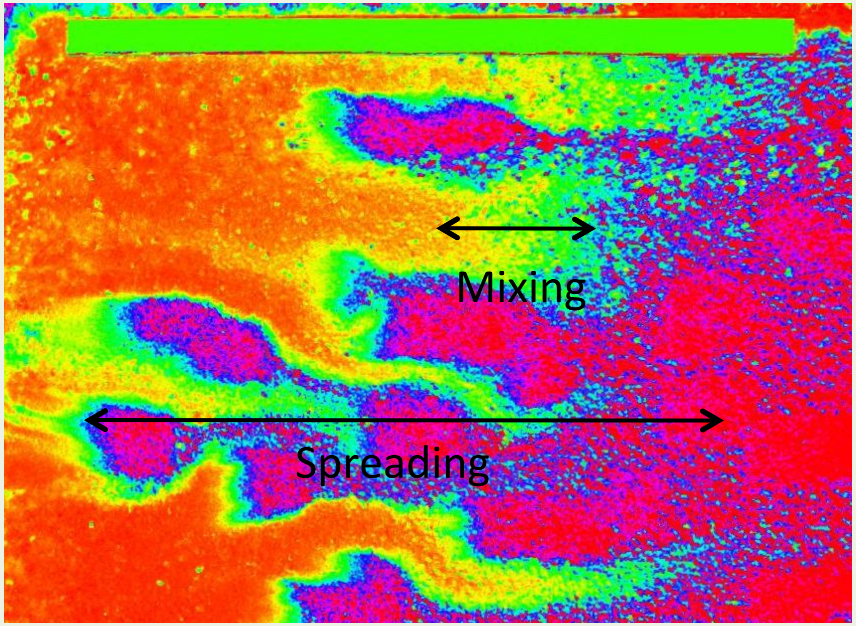
Thanks to my collaborators


TAMRON


B
A

Heterogeneity
Spreading vs Mixing





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

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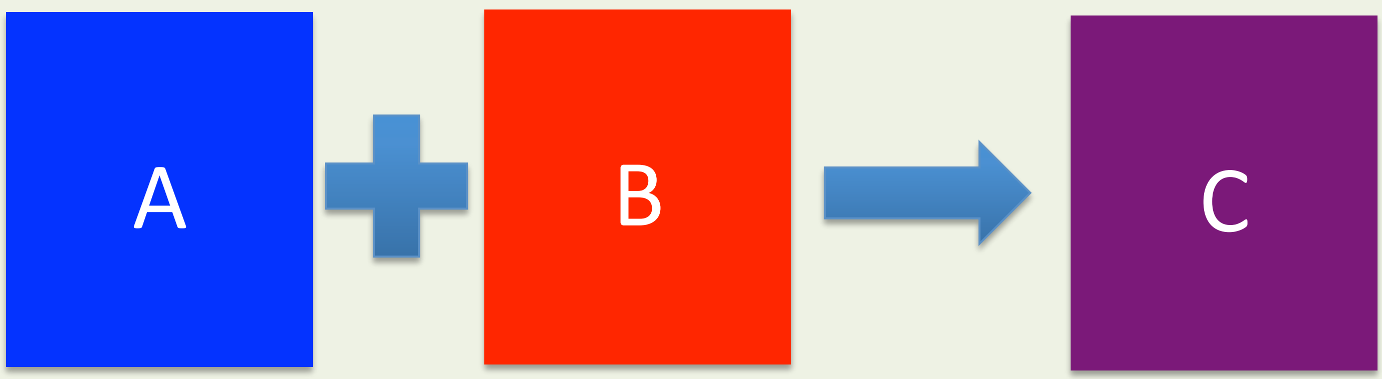
Incomplete Mixing and Slowdown on Chemical Reactions – Fickian and Non-Fickian Transport

What does any of this mean for reactive transport?

Consider the following example:



Instantaneous? Reversible? Equilibrium?

Let’s start easy – forget heterogeneity

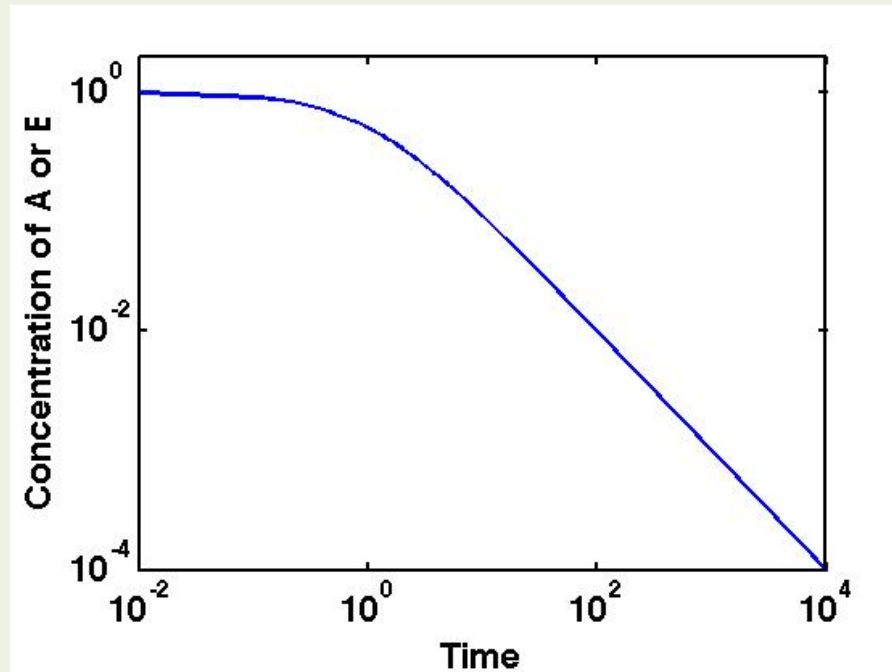
- Kinetic, irreversible

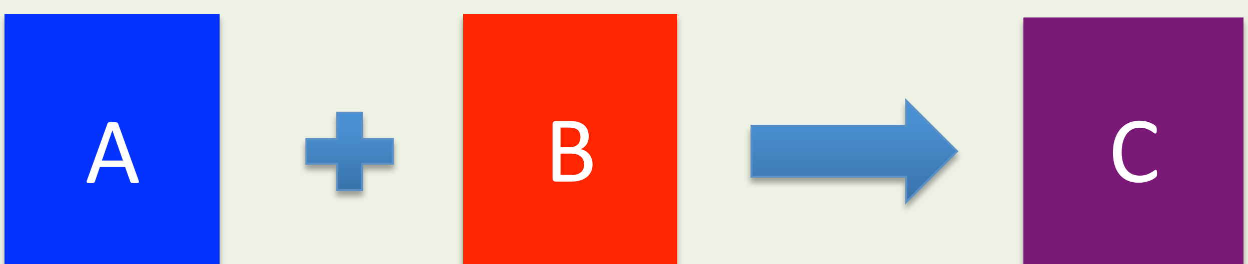
  d[A]/dt=k[A][B]

  d[B]/dt=k[A][B]

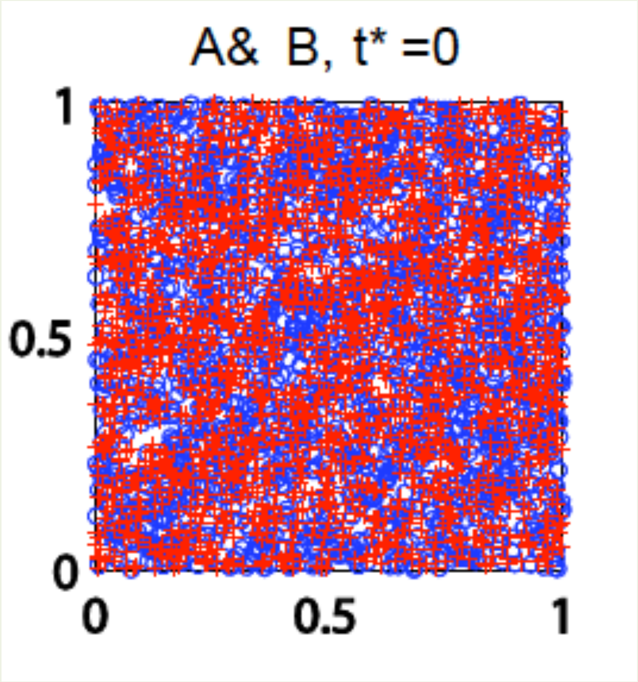
  d[C]/dt=-k[A][B]

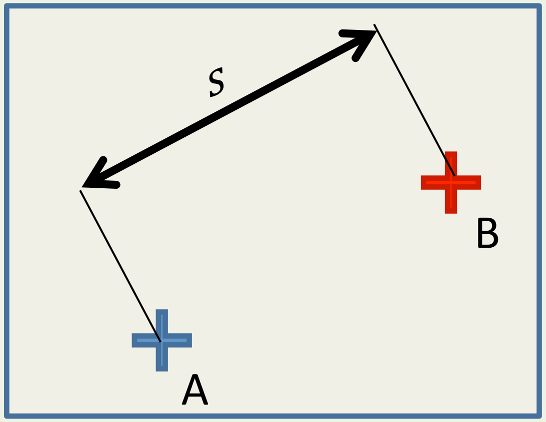
- Analytical Solution if [A]=[B] (assume initially equal –> always equal)
- $A=A_0/(1+kA_0t)$





To study this let's use a numerical model….



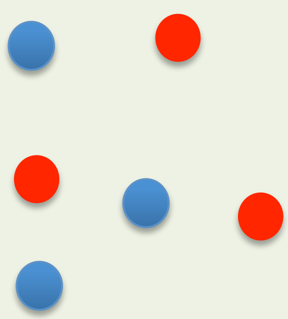


- Move Particles with a random walk
- Based on the distance between two particles calculate probability that they will collocate
- Then based on the reaction multiply probability that reaction will occur

Step 1 – Move Particles by Random Motion

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

Random Jump Reflecting Dispersion



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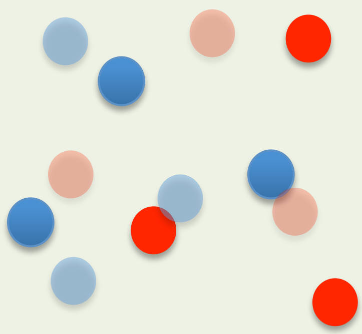
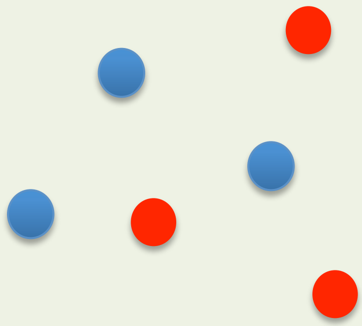
Random Jump Reflecting Dispersion



Step 1 – Move Particles by Brownian Motion

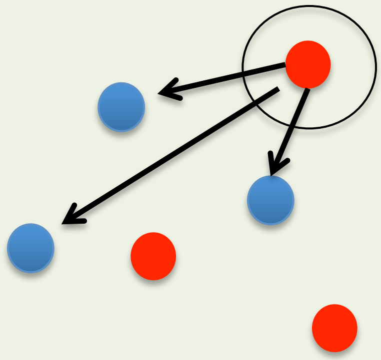
Update Particle Positions by **x**(t+dt)=**x**(t)+ξ

Random Jump Reflecting Dispersion



Step 2 – Search for Neighbors of Opposite Particle

Particle 1



Gives distances

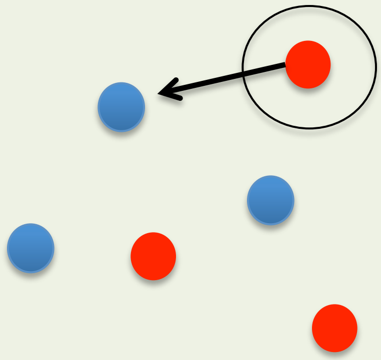
s1

s2

s3

Step 3 – Calculate Probability of RXN

Particle 1-1



Probability of Reaction

=

Probability of Collocation

function of distance

-

Convolution of position densities

-

Fickian=> Gaussian

Fractional=>Stable

e.g.

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

X

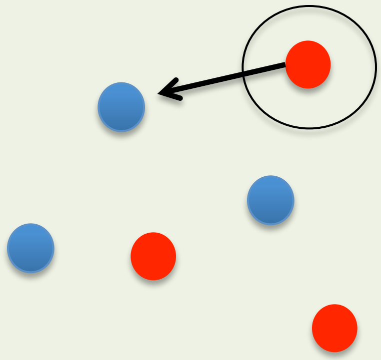
Probability of Reaction Given Collocation

function of reaction Kinetics

$K\, m_p\, dt$

Step 4 – Die or Survive

Particle 1 - 1



Generate a random number 0<P<1

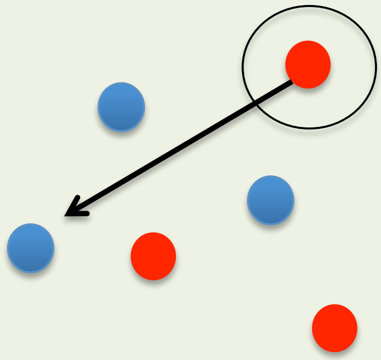
If P> Probability of Reaction

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

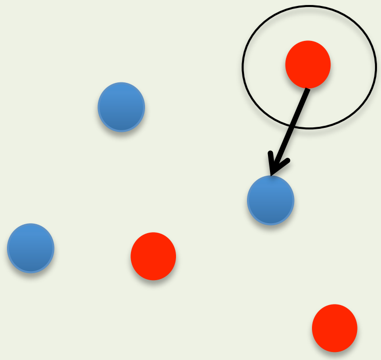
If P> Probability of Reaction (for this pair)

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)

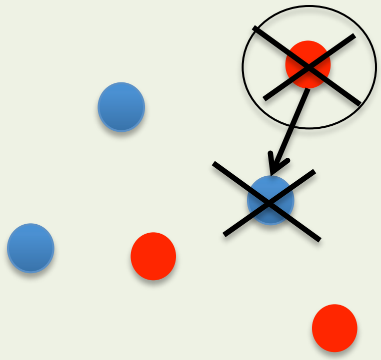
Kill both particles

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)

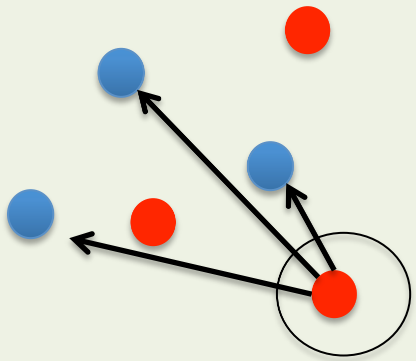
Kill both particles

If less move to next blue particle

And so on Cycling through all blues

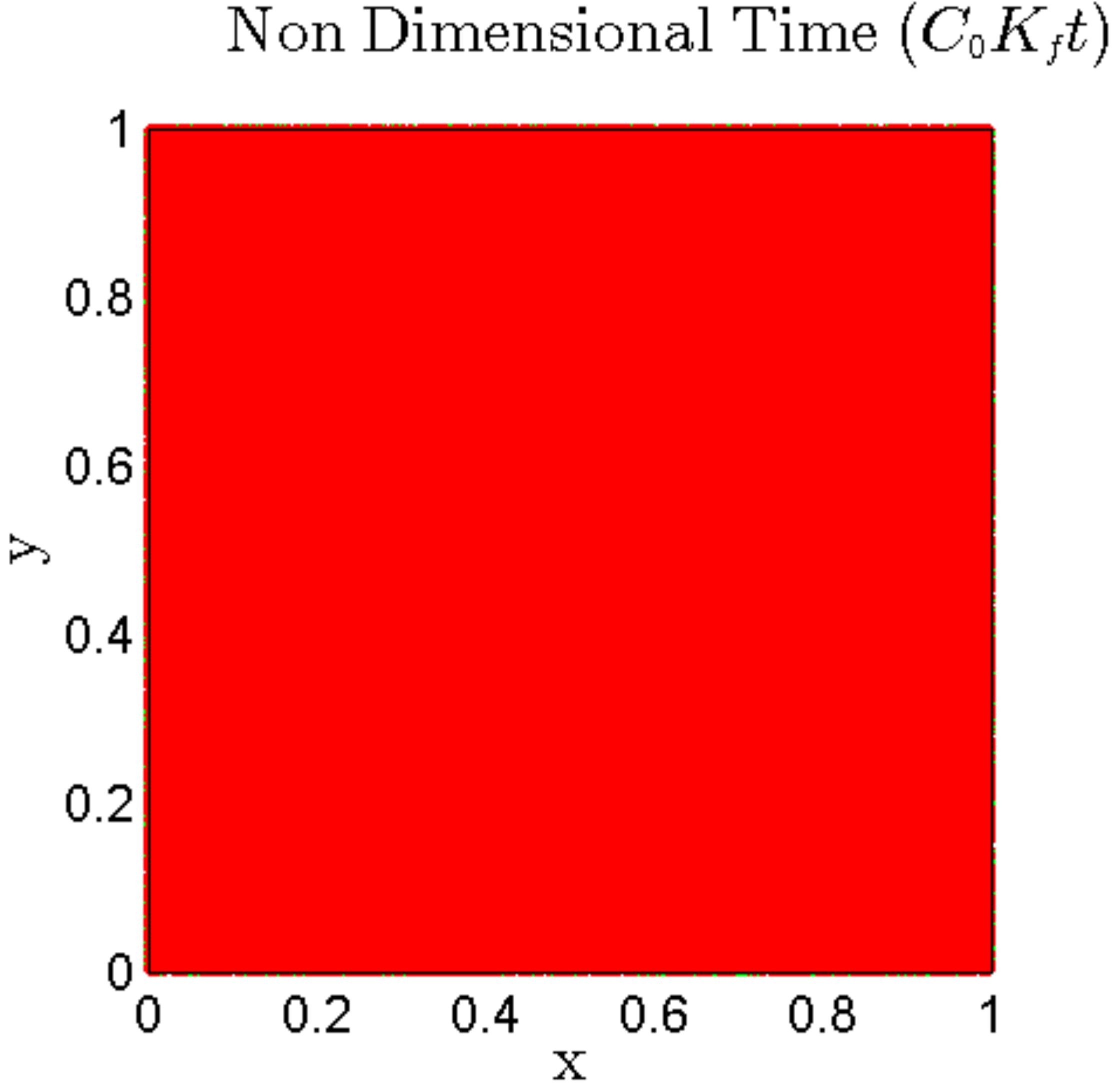
Repeat for Each red Particle

Particle 2

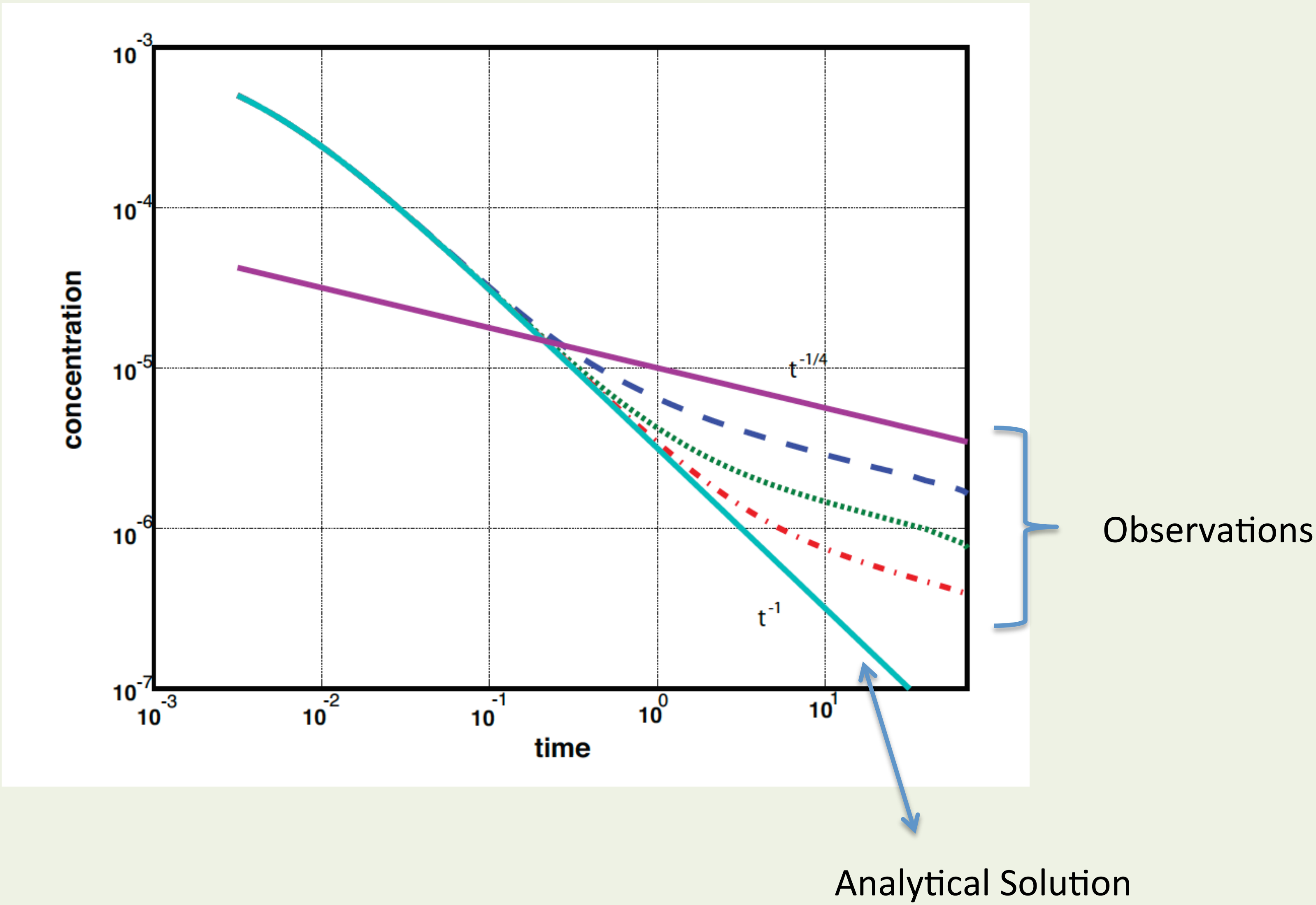


And so on Cycling through all reds

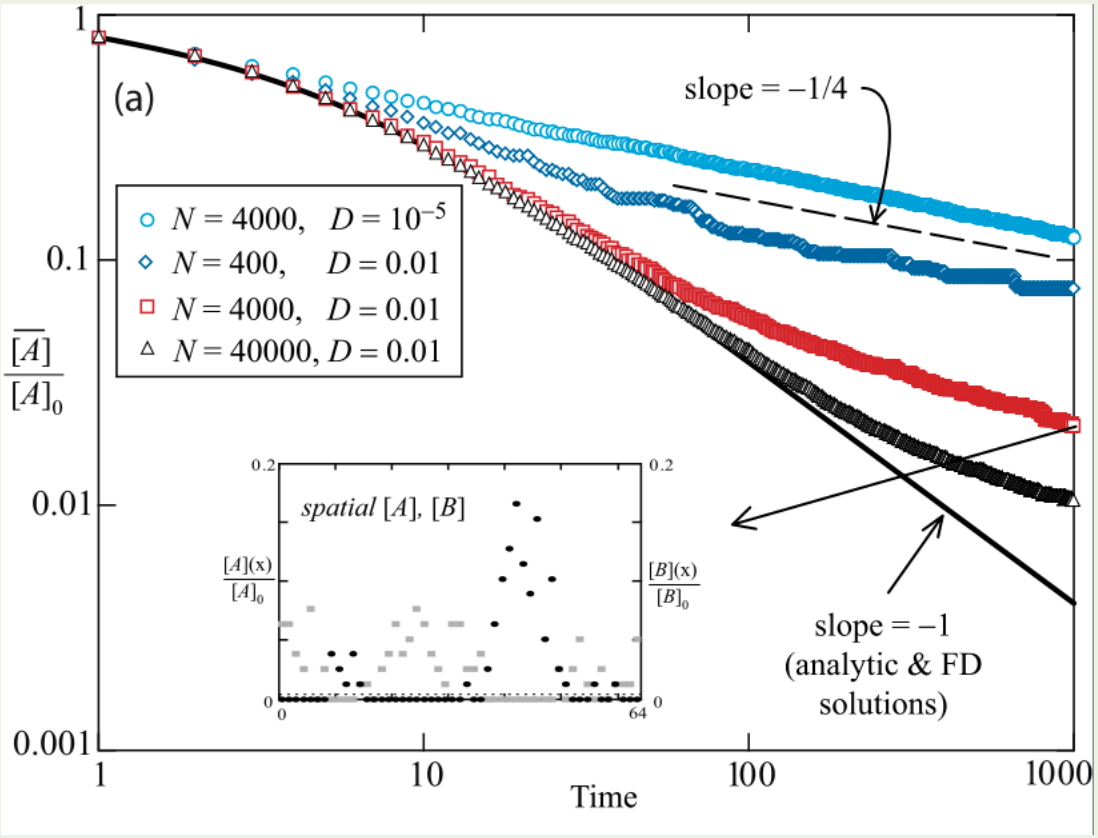
Then back to Step One (Move Particles)


Non Dimensional Time $(C_0 K_f t)$
y
x
0
0.2
0.4
0.6
0.8
1

What do we observe? For 1d Brownian Motion



Other Observations of the Same (different methods of study)



Benson & Meerschaert 2008, WRR

Countless other examples:

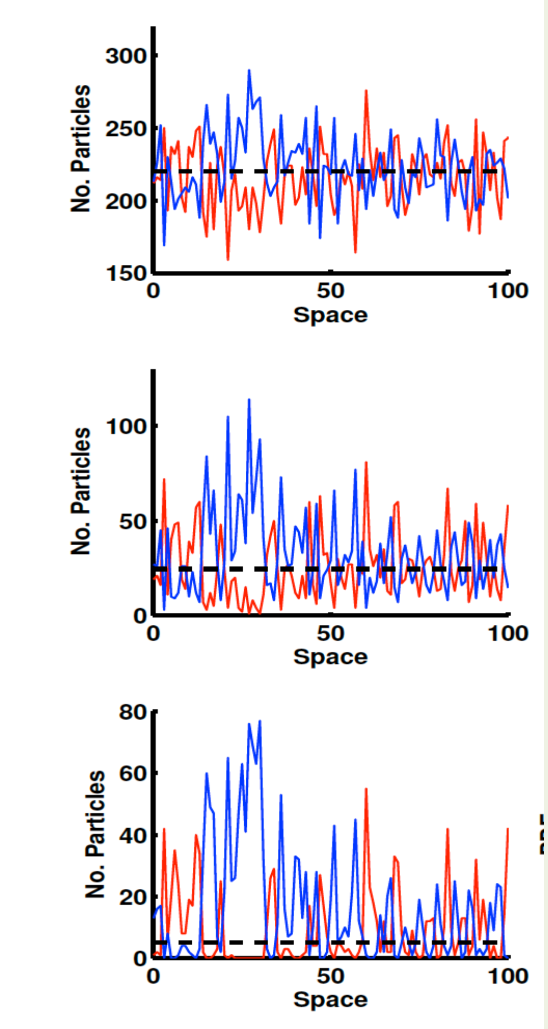
Astrophysics
Particle Physics
Biochemical Processes
Turbulent Environmental Flows
Population Dynamics
Warfare Simulation

What's going on…
Let's take a look at concentrations in 1d

Early

Intermediate

Late



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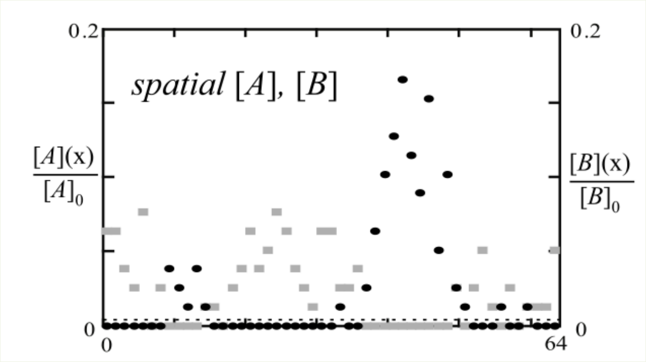

What's going on…
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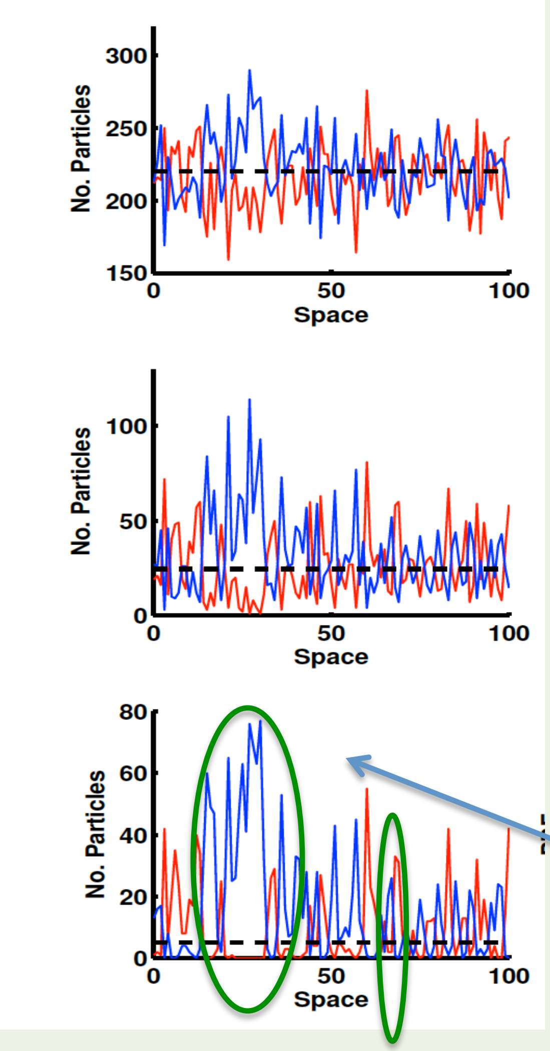

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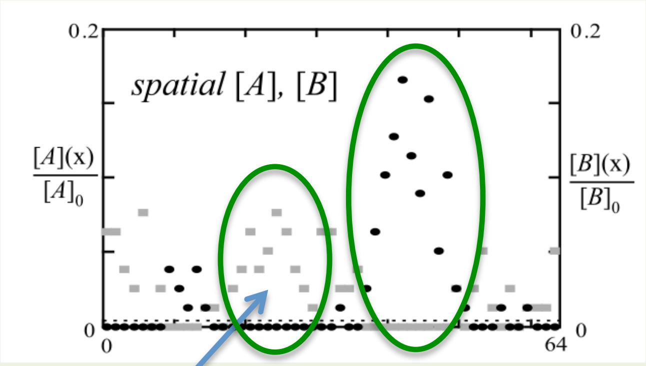
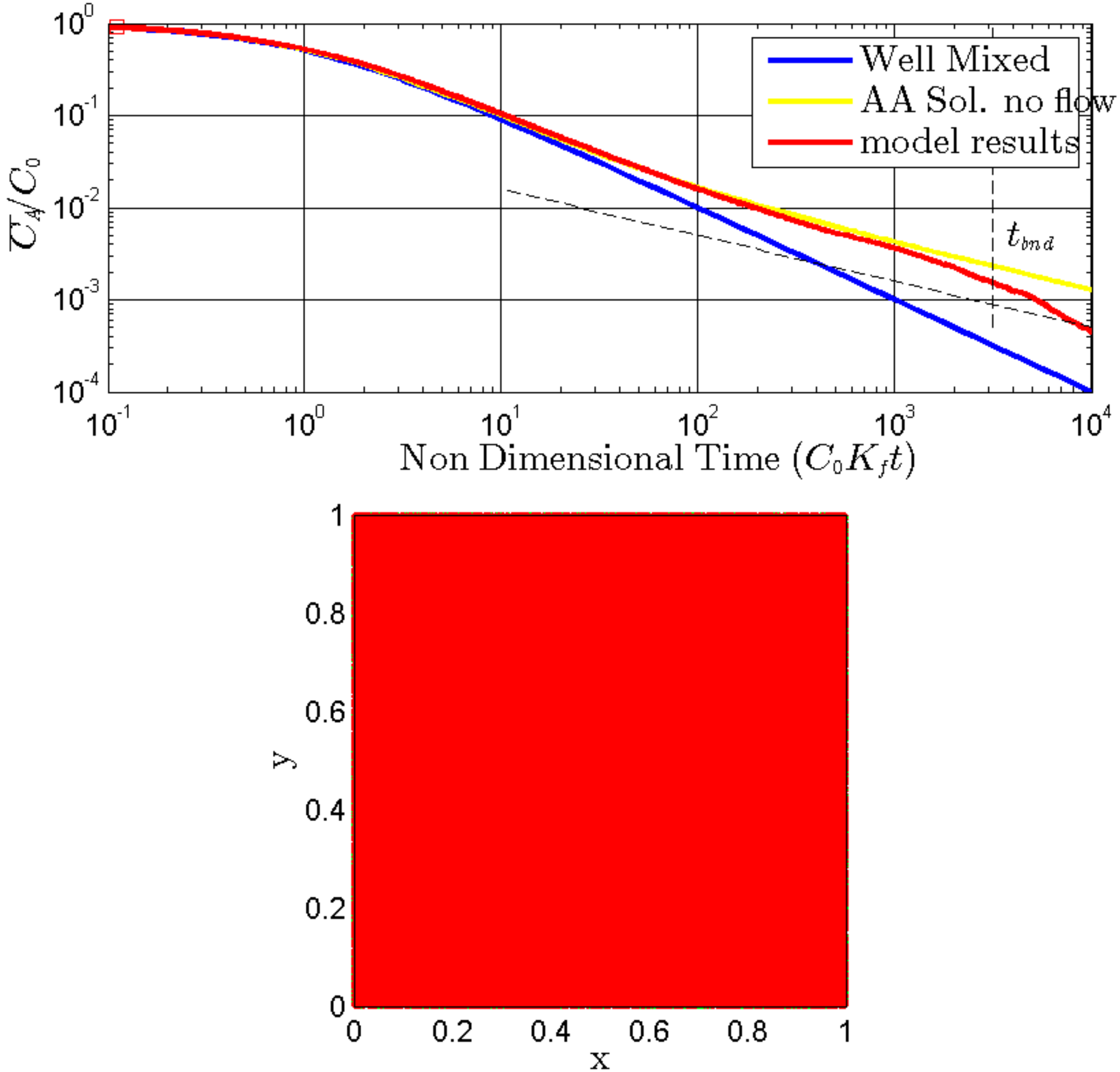


Isolated Islands of A and B form limiting reaction by how quickly A and B diffuse into one another

Incomplete Mixing



Well Mixed
AA Sol. no flow
model results
t_{bnd}
$\overline{C_A}/C_0$
Non Dimensional Time (C_0K_ft)
y
x

But what does this have to with fractional transport?

- Consider the following problem

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

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

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Average

Remainder

$$\frac{\partial \overline{C_i}}{\partial t} = -k\overline{C_A}\ \overline{C_B} - k\overline{C_A' C_B'}$$

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

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Perturbation closure

Closure Problem

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

But what does this have to with fractional transport?

- Consider the following problem

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Average

Remainder

$$\frac{\partial \overline{C_i}}{\partial t} = -k\overline{C_A}\;\overline{C_B} - k\overline{C_A' C_B'}$$

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Perturbation closure

Closure Problem

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

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

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

$$G(x,\xi,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-2D_\dagger |k|^\alpha t} e^{ik(x-\xi)}dk$$

So my equation becomes

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

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

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

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

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

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

So

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

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Early Times

$$\overline{C_A}(t) = \frac{1}{1+(t-t_0)}$$

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

So

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

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

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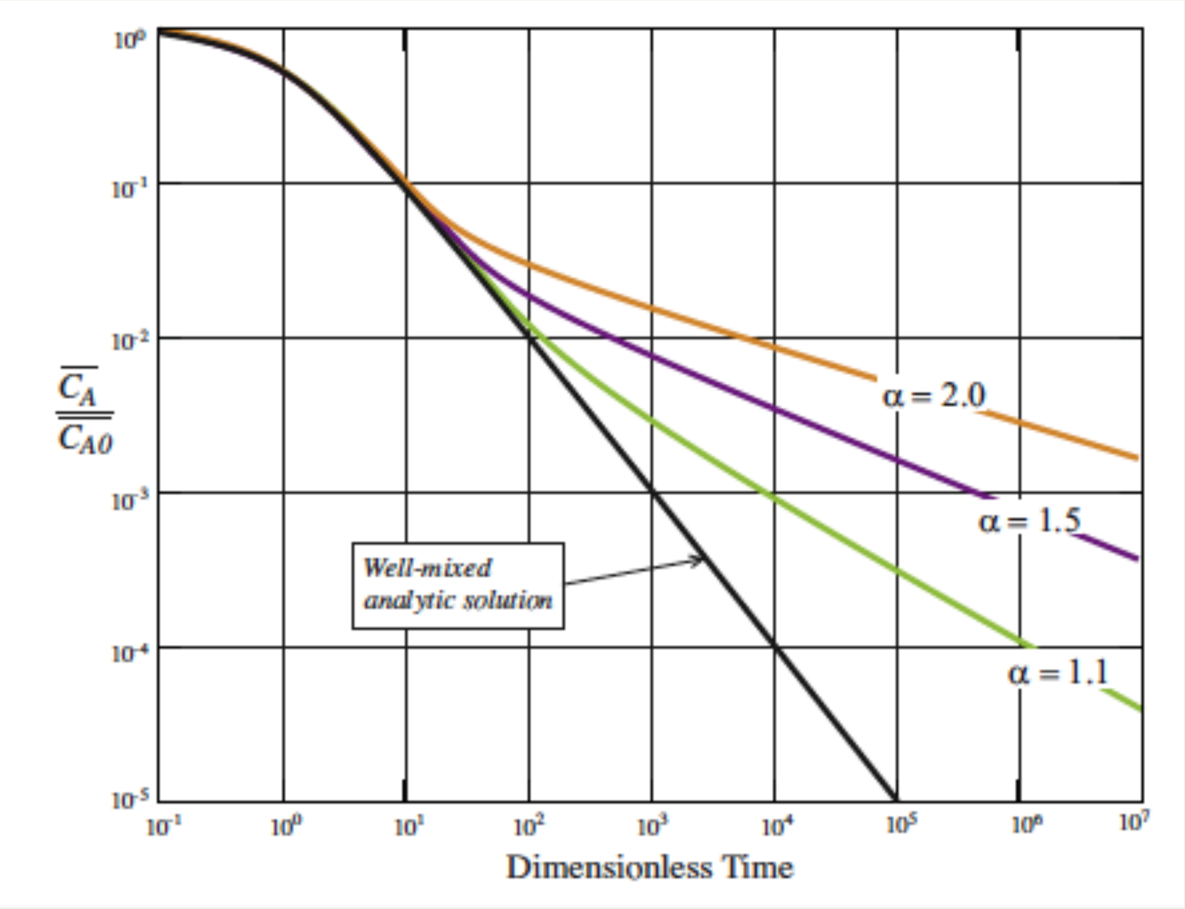
$$z = \frac{2\alpha\sqrt{\chi^*}}{2\alpha - 1} t^{\frac{2\alpha-1}{2\alpha}}$$

$$\overline{C_A}(t) = \frac{1}{1 + (t - t_0)}$$

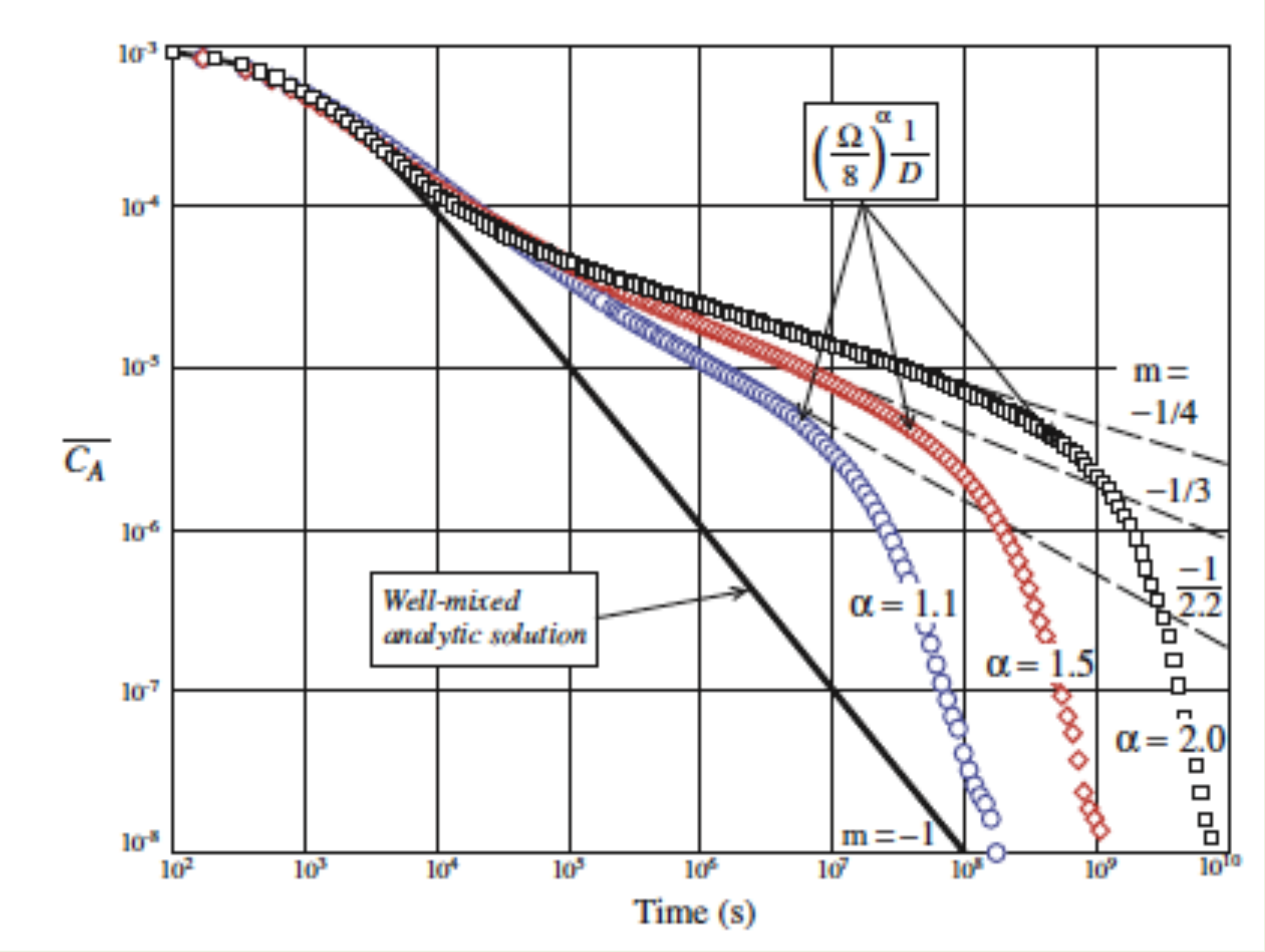
Late Times

$$\overline{C_A}(t) \sim \boxed{\sqrt{\chi^*} t^{-1/(2\alpha)}}.$$

What does Solution Look like



Validation



$\overline{C_A}$
Time (s)
$\left(\frac{\Omega}{8}\right)^{\alpha}\frac{1}{D}$
Well-mixed analytic solution
m = −1/4
−1/3
$\frac{-1}{2.2}$
m = −1
α = 1.1
α = 1.5
α = 2.0

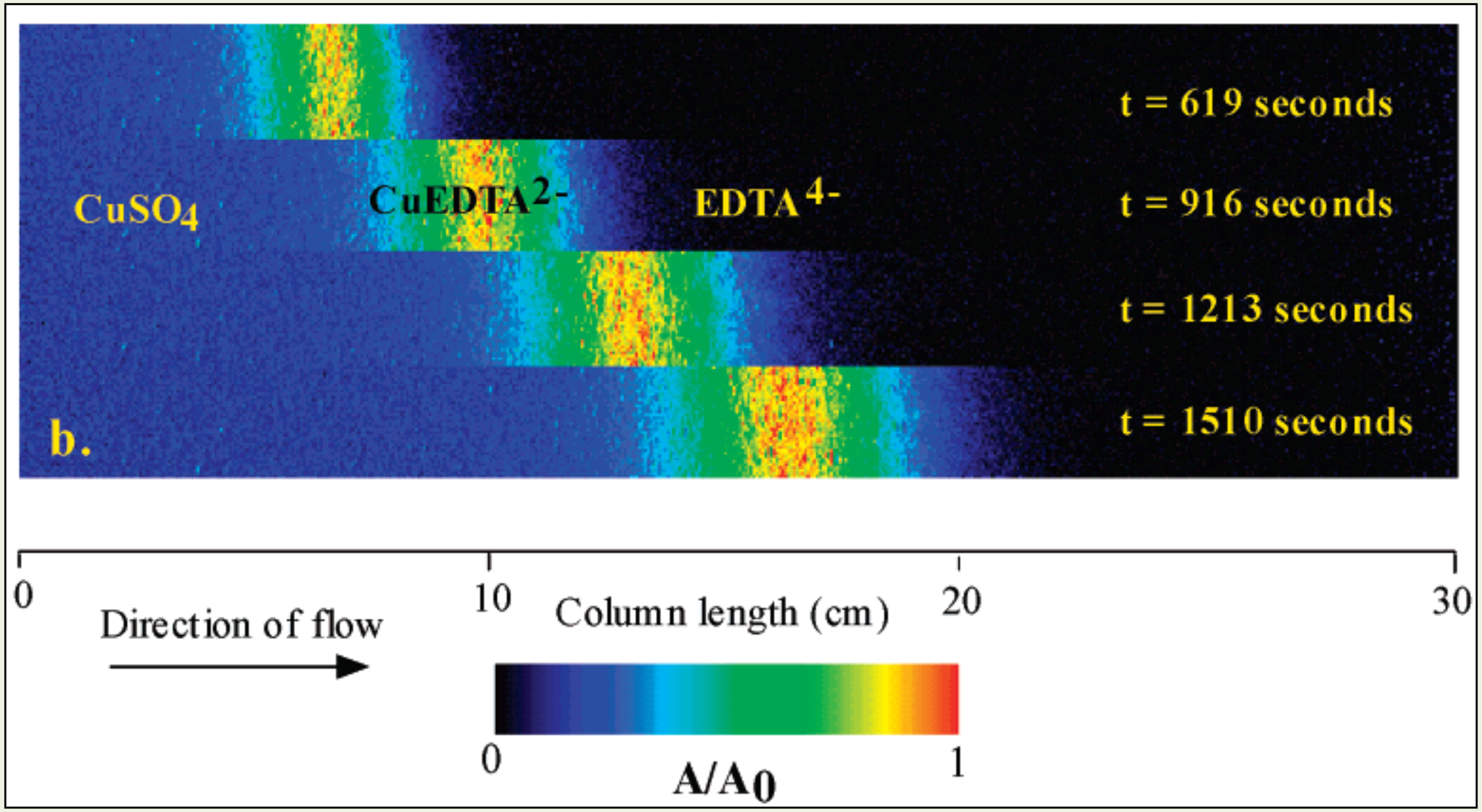
Topic 2

-

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

Or are they and I’m just wrong

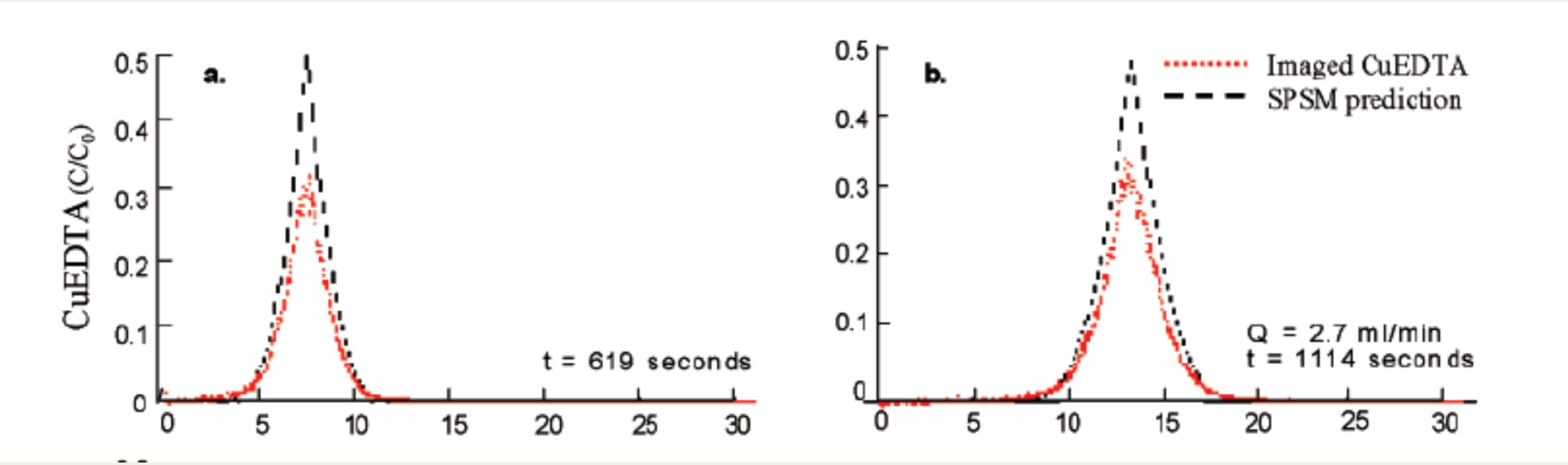
Let’s Look at Some Experiments

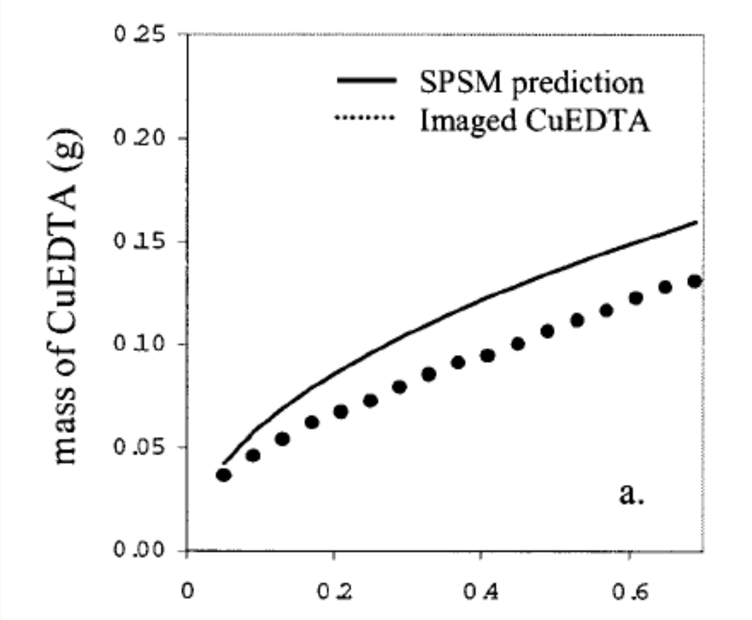


Famous Experiment by Gramling et al

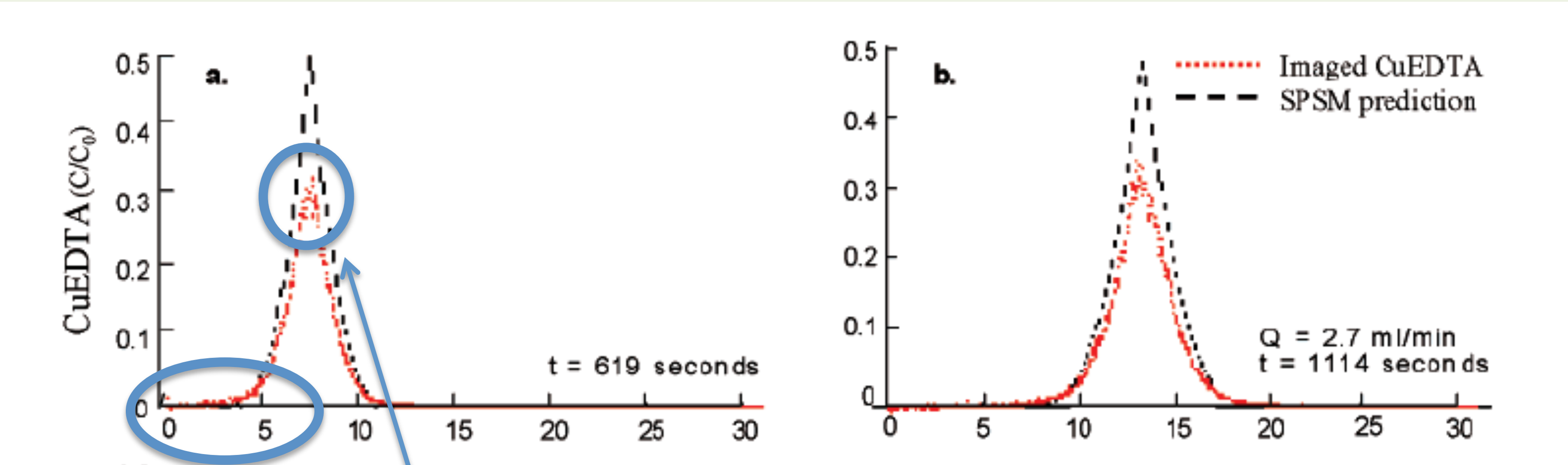
there are lots of papers trying to model these results…. Using anomalous/fractional transport methods – WE ASK WHY?

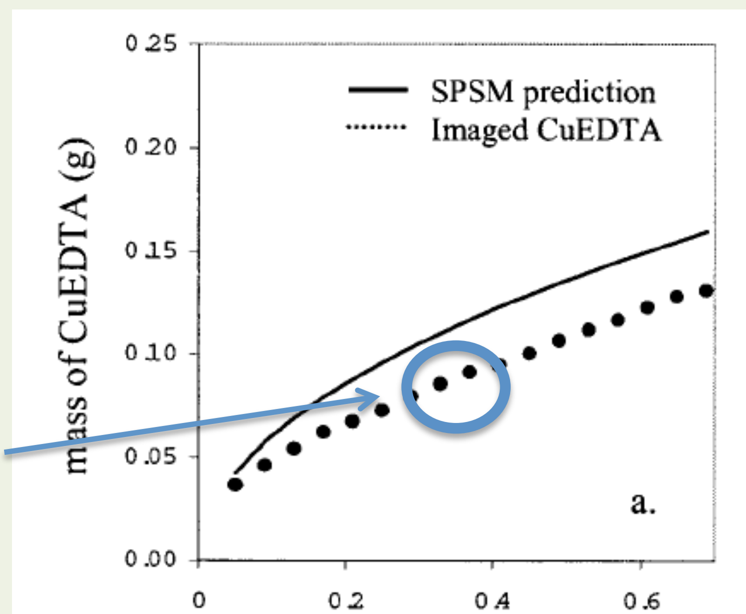
Gramling's Measurements vs Predictions





Gramling's Measurements vs Predictions





Heavy Tails

Lower Concentrations

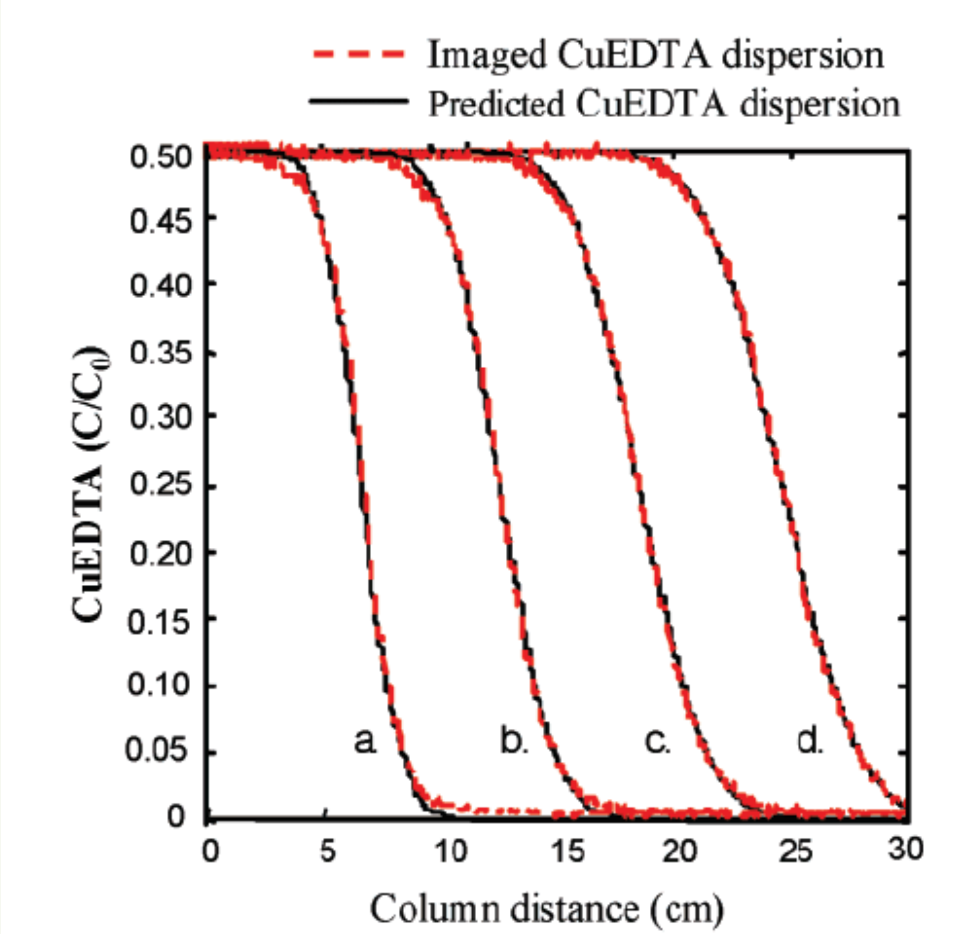
Lower Rates of Reaction

ANOMALOUS TRANSPORT??

Anomalous Transport

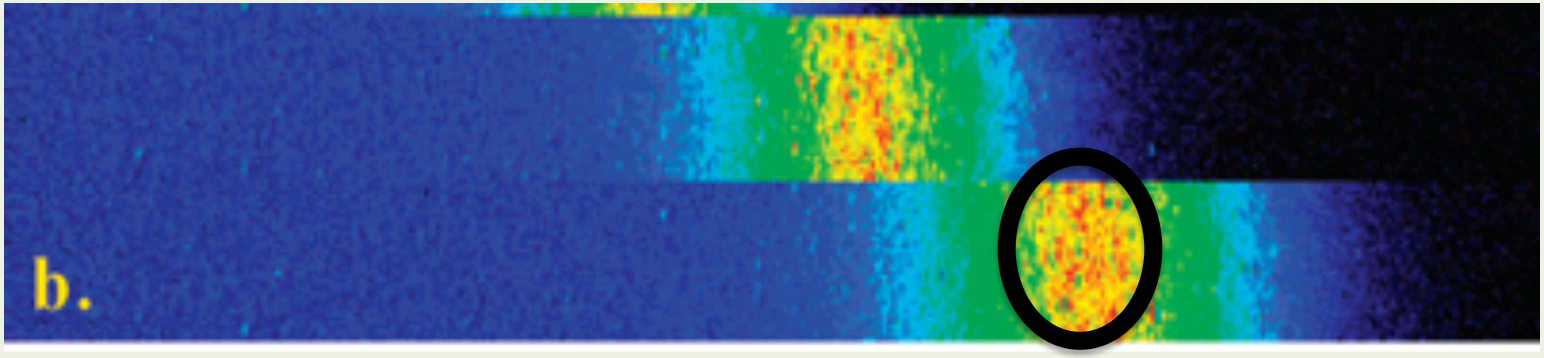
-

We Don't Think So



There is no evidence of anomalous transport in non reactive flow experiments through the same column

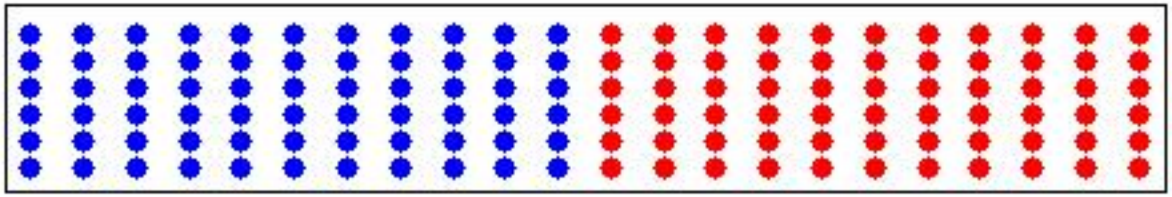
Looking closely at Gramling data



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

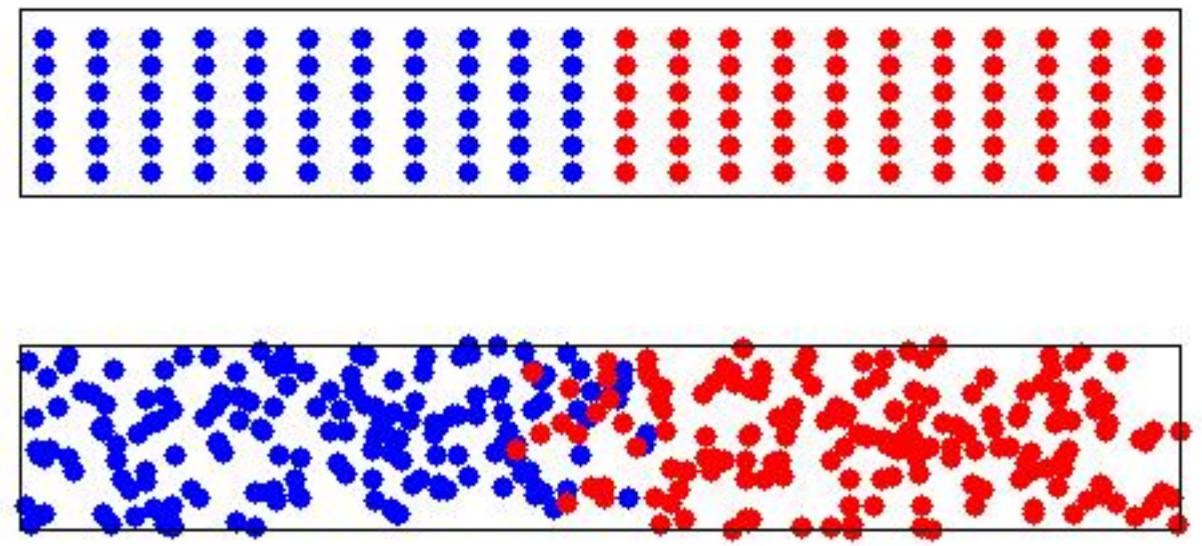
Could it be incomplete mixing only?

Our Model



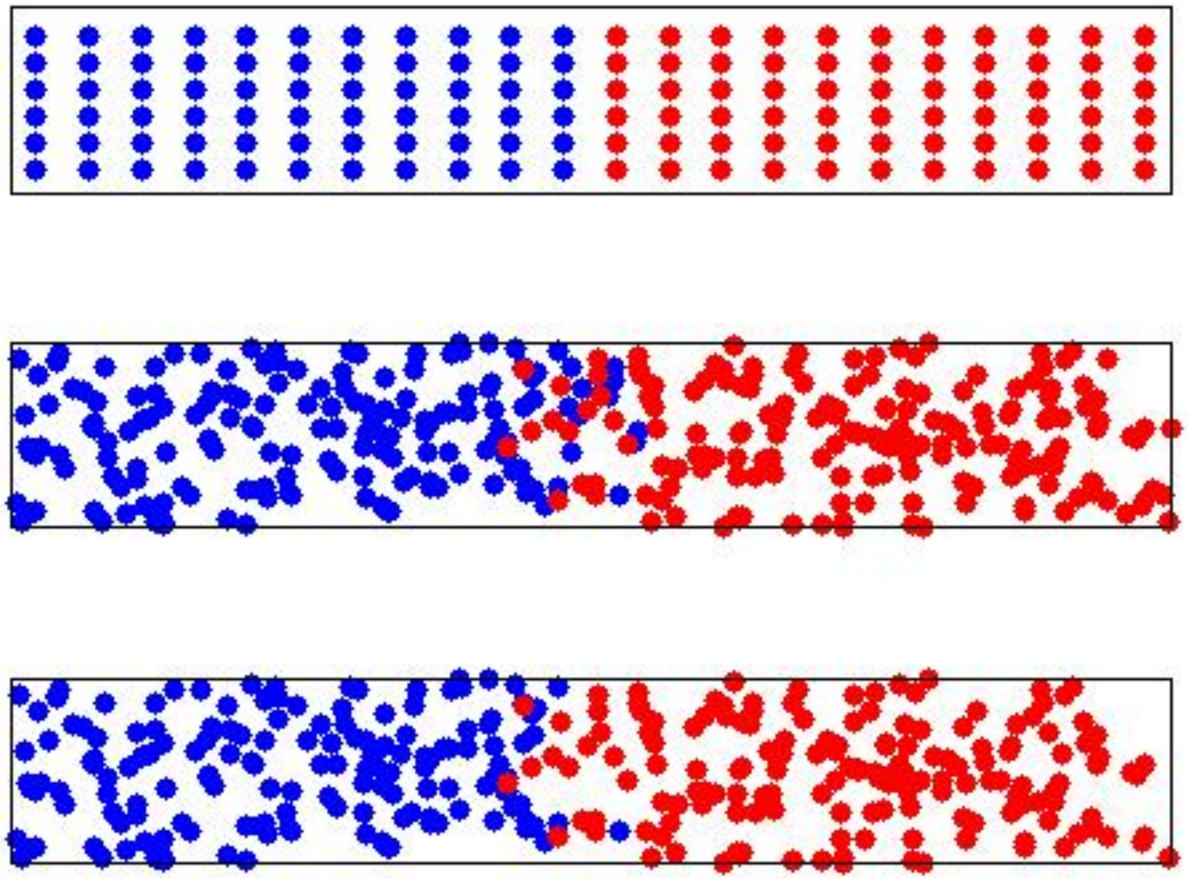
Set up an initial condition with all A on one side and B on the other

Our Model



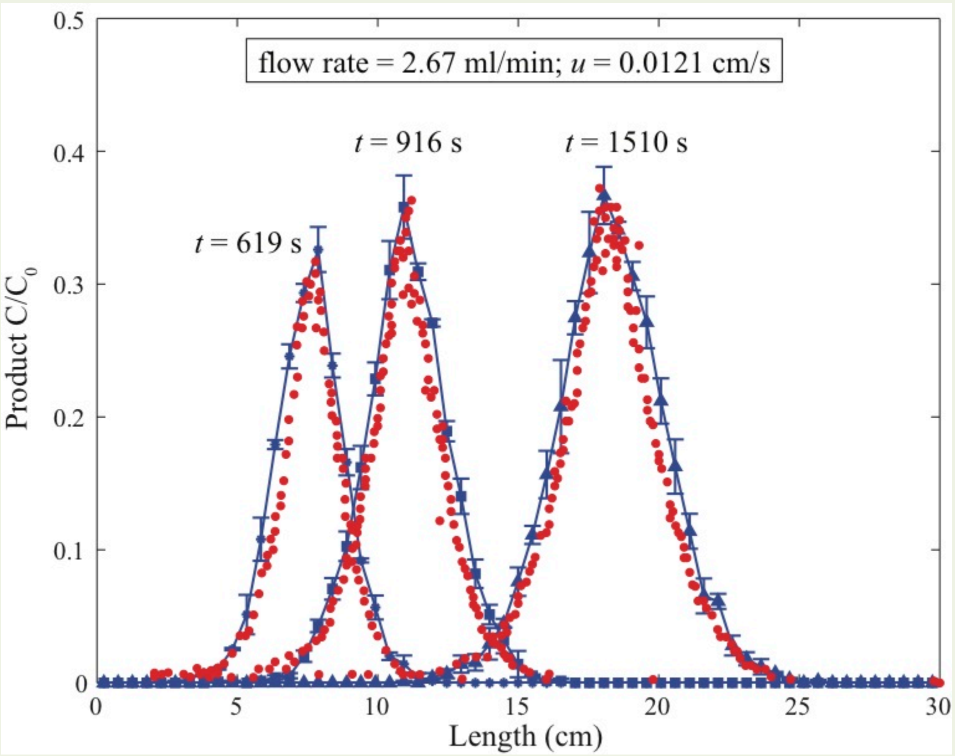
Move Every Particle – Jump by ***dispersion***

Our Model

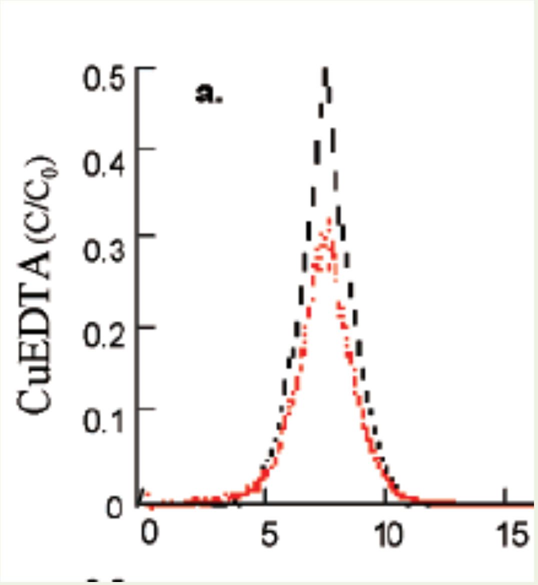


Now kill some particles probabilistically for reaction following rules from before

When we use our Methods

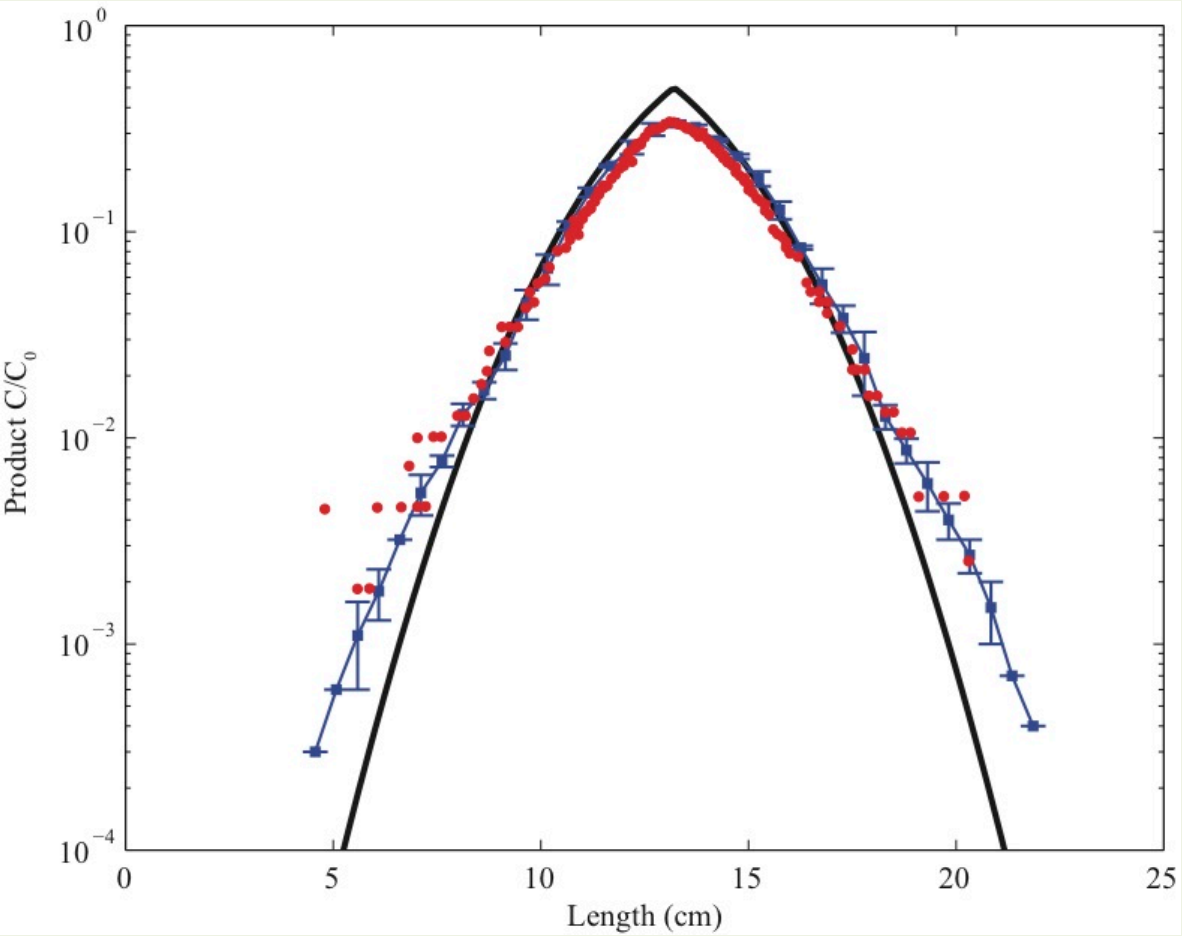


VS



Pretty Good Agreement – And we can Explain Why

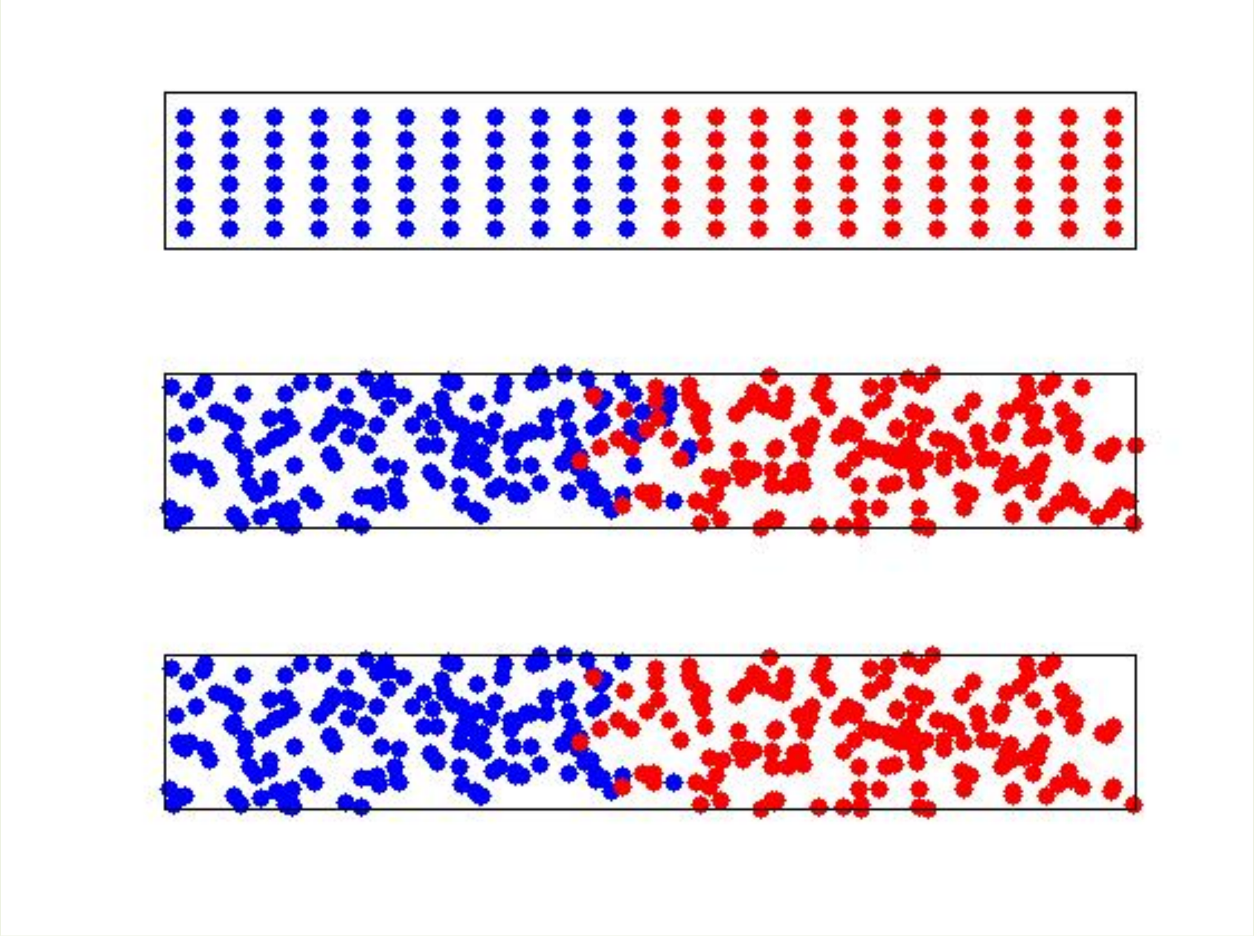
And the Tails....



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’

Our Model



SO – Tail does not need to mean anomalous/fractional

Or

Can it be interpreted that way?

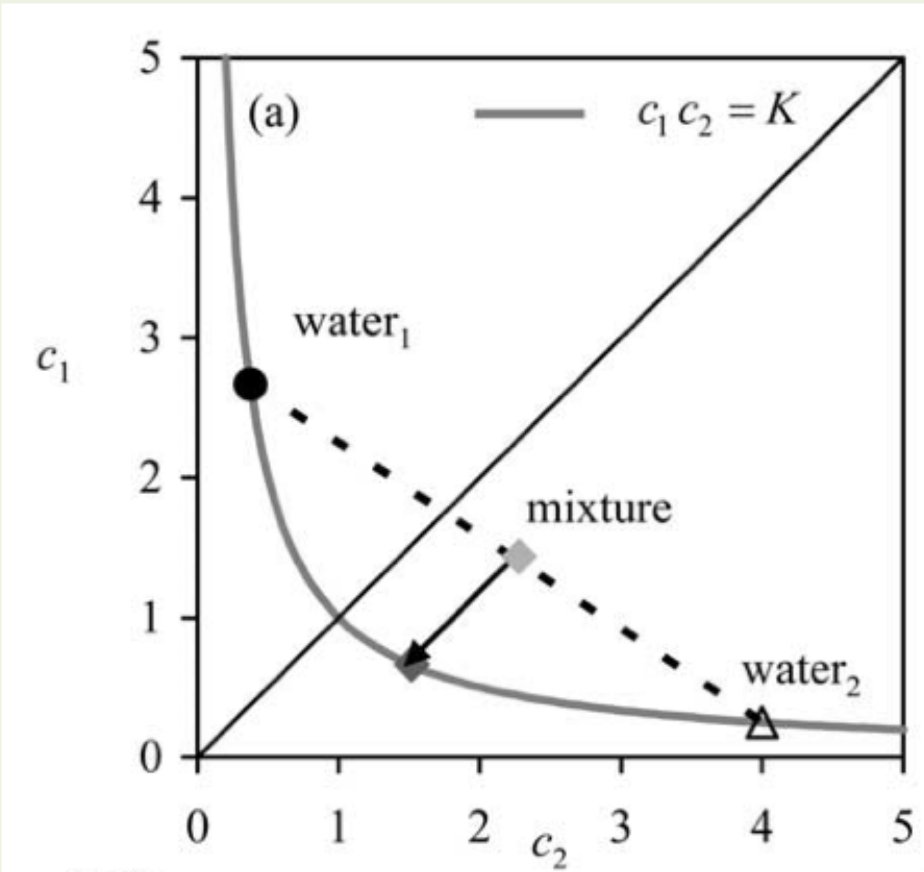
Topic 3

-

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



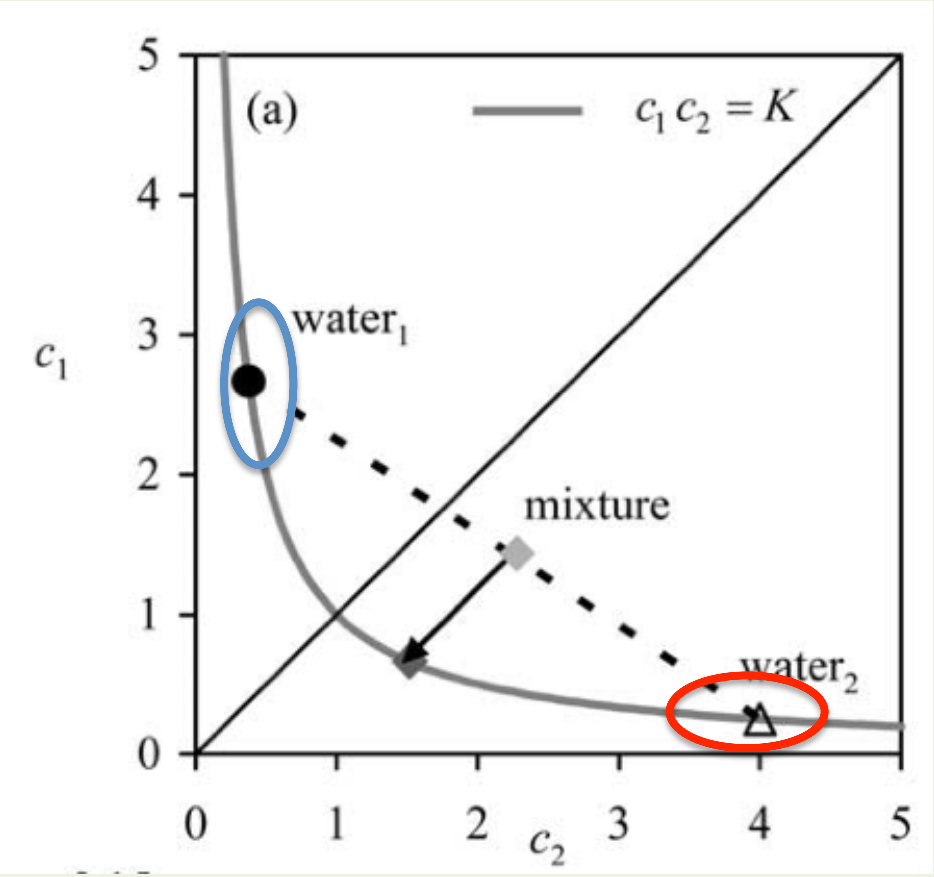
$$\frac{\partial C_i}{\partial t} = D\nabla^2 C_i + r \quad i = 1,2$$

$$\frac{\partial C_3}{\partial t} = -r$$

$$C_1 C_2 = K$$

Equilibrium

Instantaneous Equilibrium Reaction



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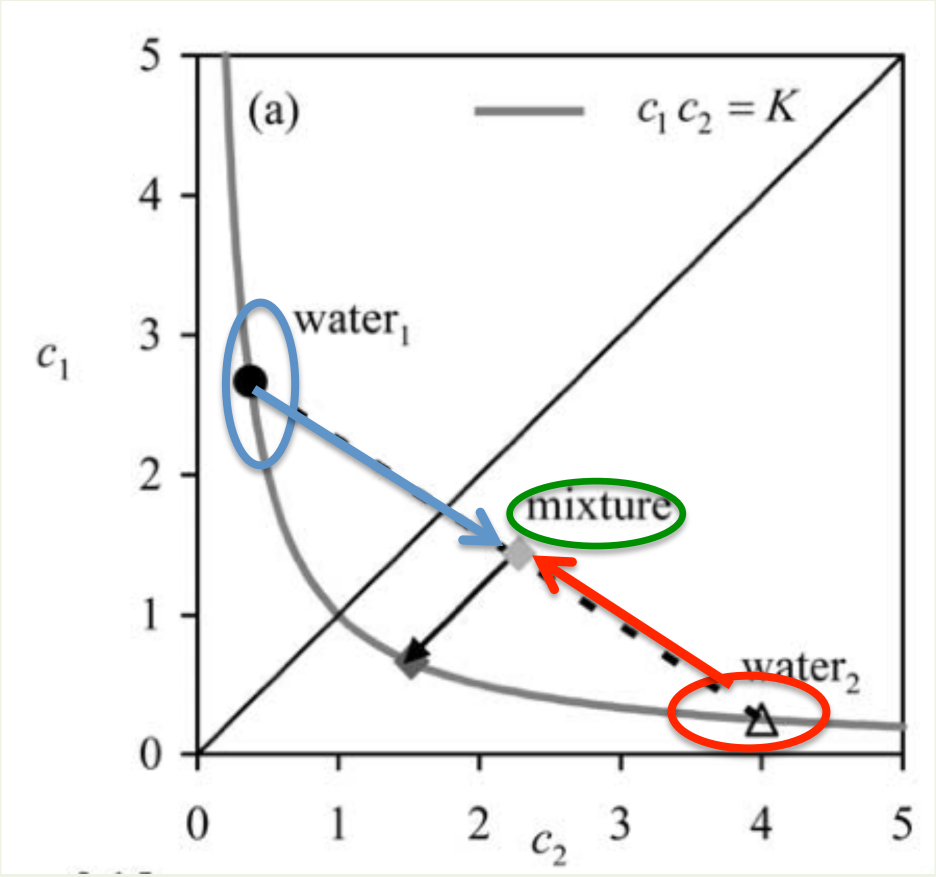

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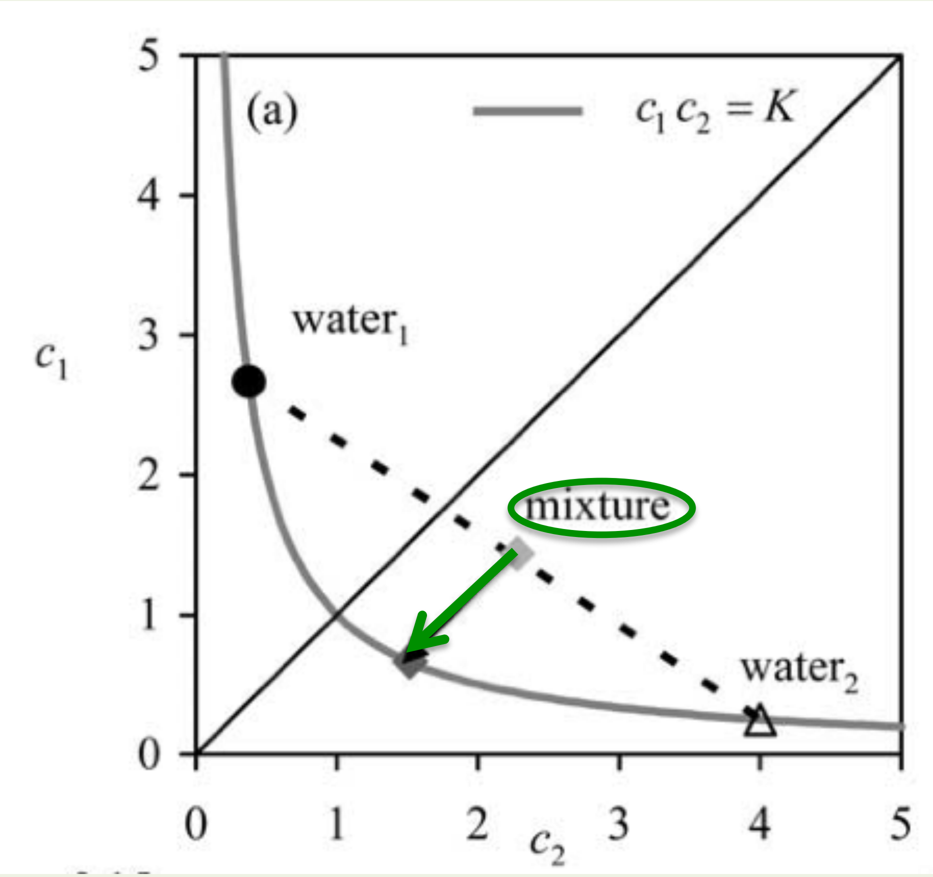

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4 eqns, 4 unknowns

Define conservative

$$U = C_2 - C_1$$

⇩

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

$$r = (D\nabla U . \nabla U)\left(\frac{d^2 C_1}{dU^2}\right)$$

- Local Measure of Mixing – Drives many Reactions

$$r = \underbrace{\left(D\nabla U.\nabla U\right)}_{\text{MIXING}} \quad \underbrace{\left(\frac{d^2 C_1}{dU^2}\right)}_{\text{Chemistry}}$$

- Local Measure of Mixing – Drives many Reactions

$$r = \underbrace{\left(D\nabla U . \nabla U\right)}_{\text{MIXING}} \underbrace{\left(\frac{d^2 C_1}{dU^2}\right)}_{\text{Chemistry}}$$

MIXING

Chemistry

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

???=$$$

How do we Quanitify Mixing?

- Local Measure of Mixing – Drives many Reactions

$$r = \left(D\nabla U . \nabla U\right) \quad \left(\frac{d^2 C_1}{dU^2}\right)$$

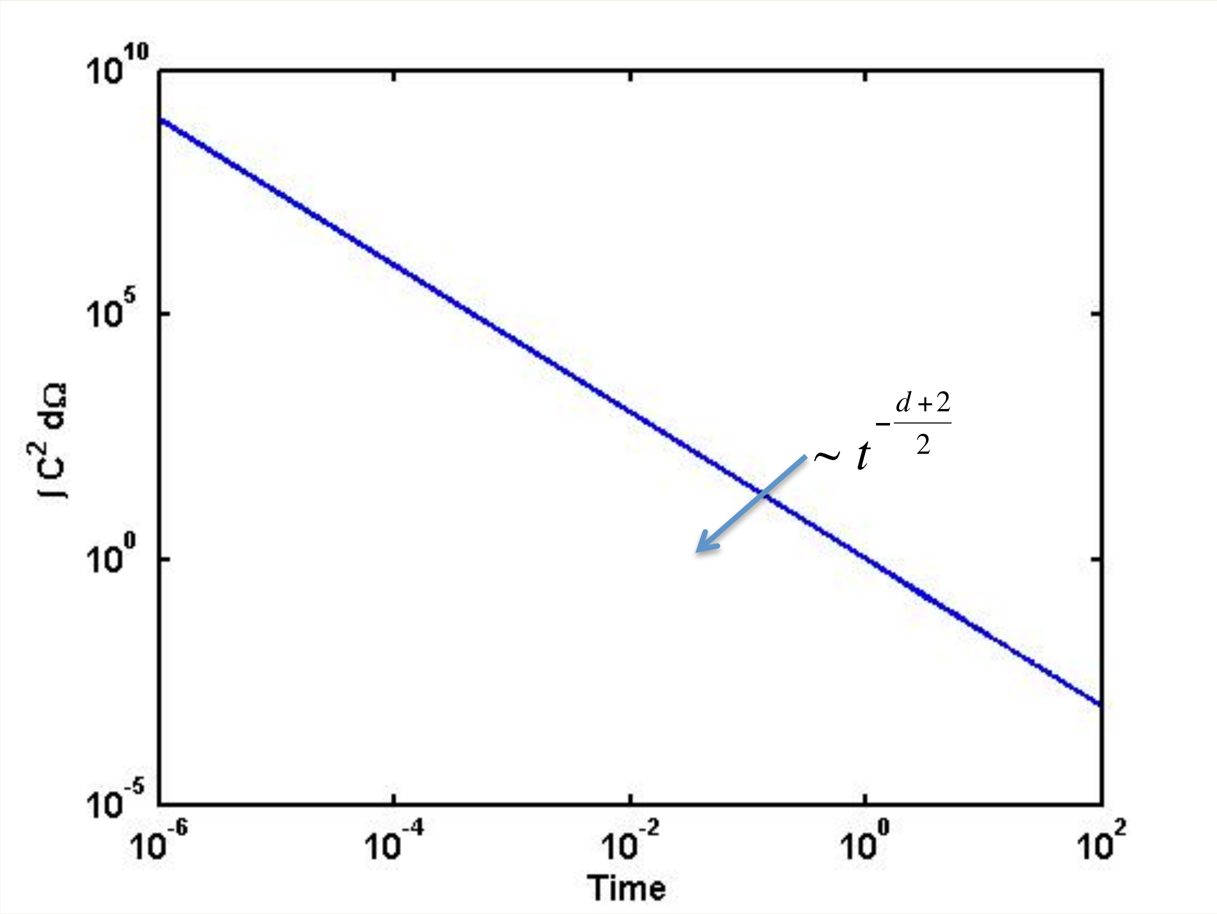
MIXING

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

$$M = \int_{\Omega} \left(D\nabla U . \nabla U\right) d\Omega = -\frac{1}{2}\frac{d}{dt}\int_{\Omega} U^2 d\Omega$$

Scalar Dissipation Rate

Homogeneous Mixing



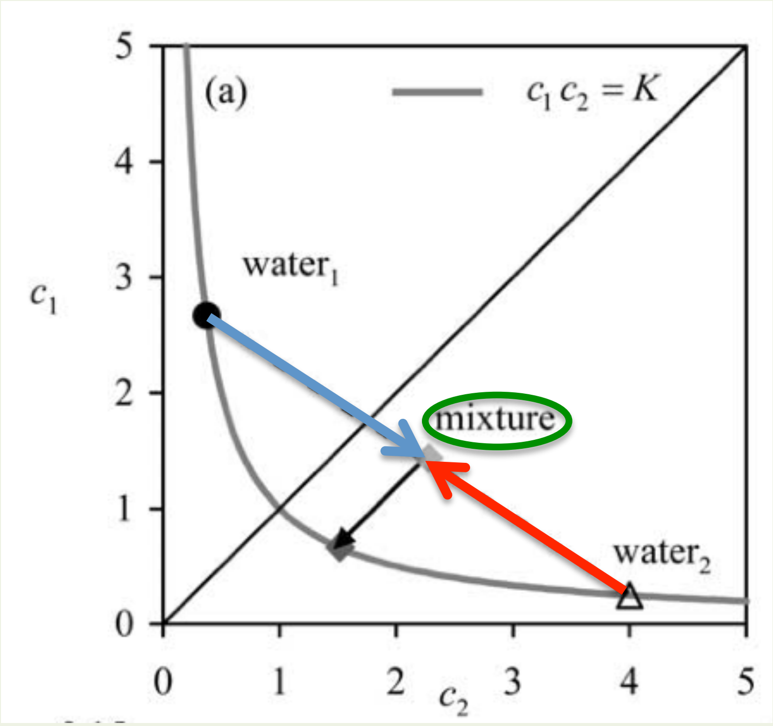
A little bit boring, no?

Replace Fickian with Fractional Dispersion

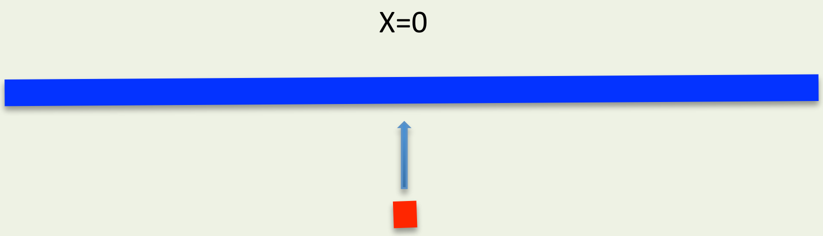
$$\frac{\partial C}{\partial t} = D \frac{\partial^{\alpha} C}{\partial |x|^{\alpha}} + r$$

$$1 < \alpha \leq 2$$

Take a step back



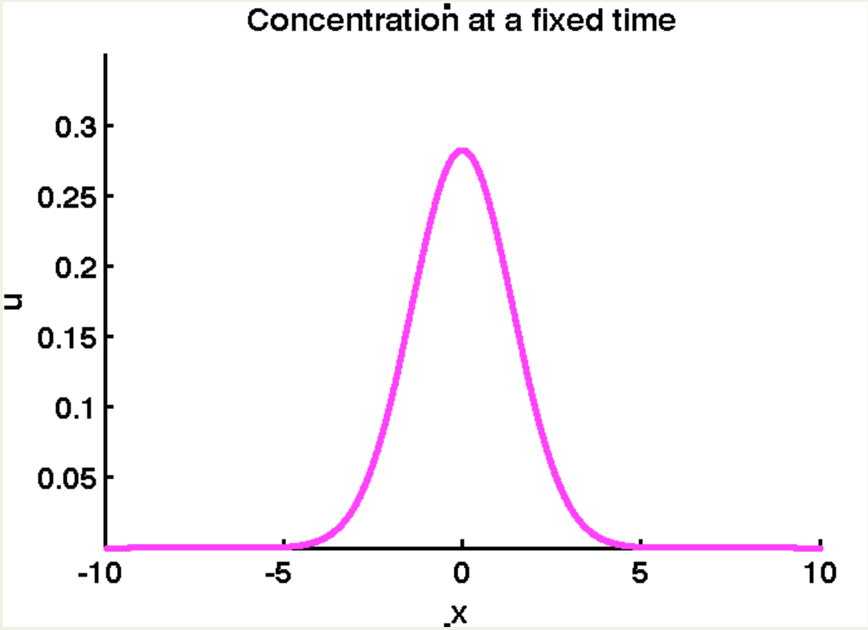
Recall we can think of this reaction in Terms of a conservative component u. Consider a system with u=constant initially and then we inject a pulse of different u at position x=0.

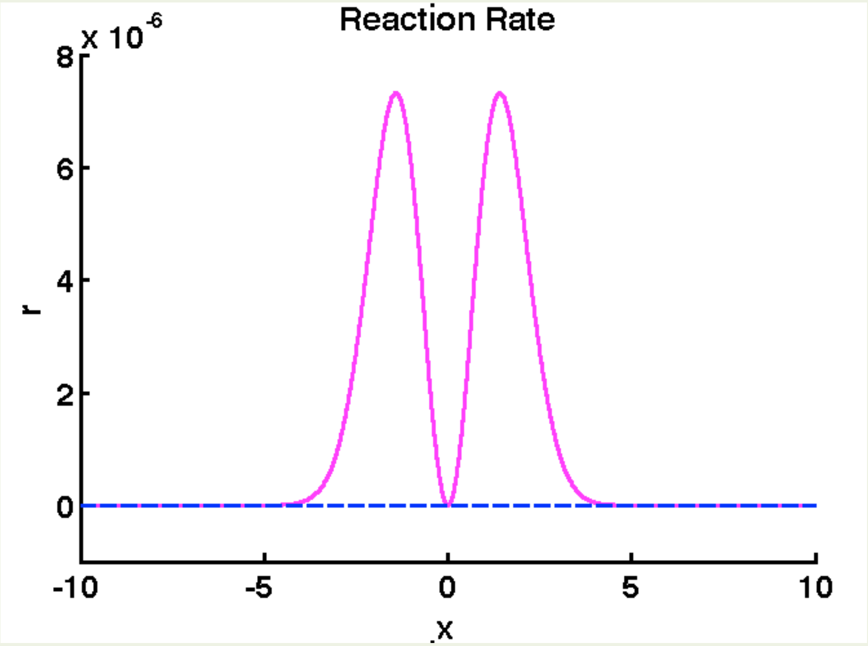


$$\frac{\partial U}{\partial t} = D\frac{\partial^{\alpha} U}{\partial |x|^{\alpha}}$$

$$U(t=0) = \delta(x)$$

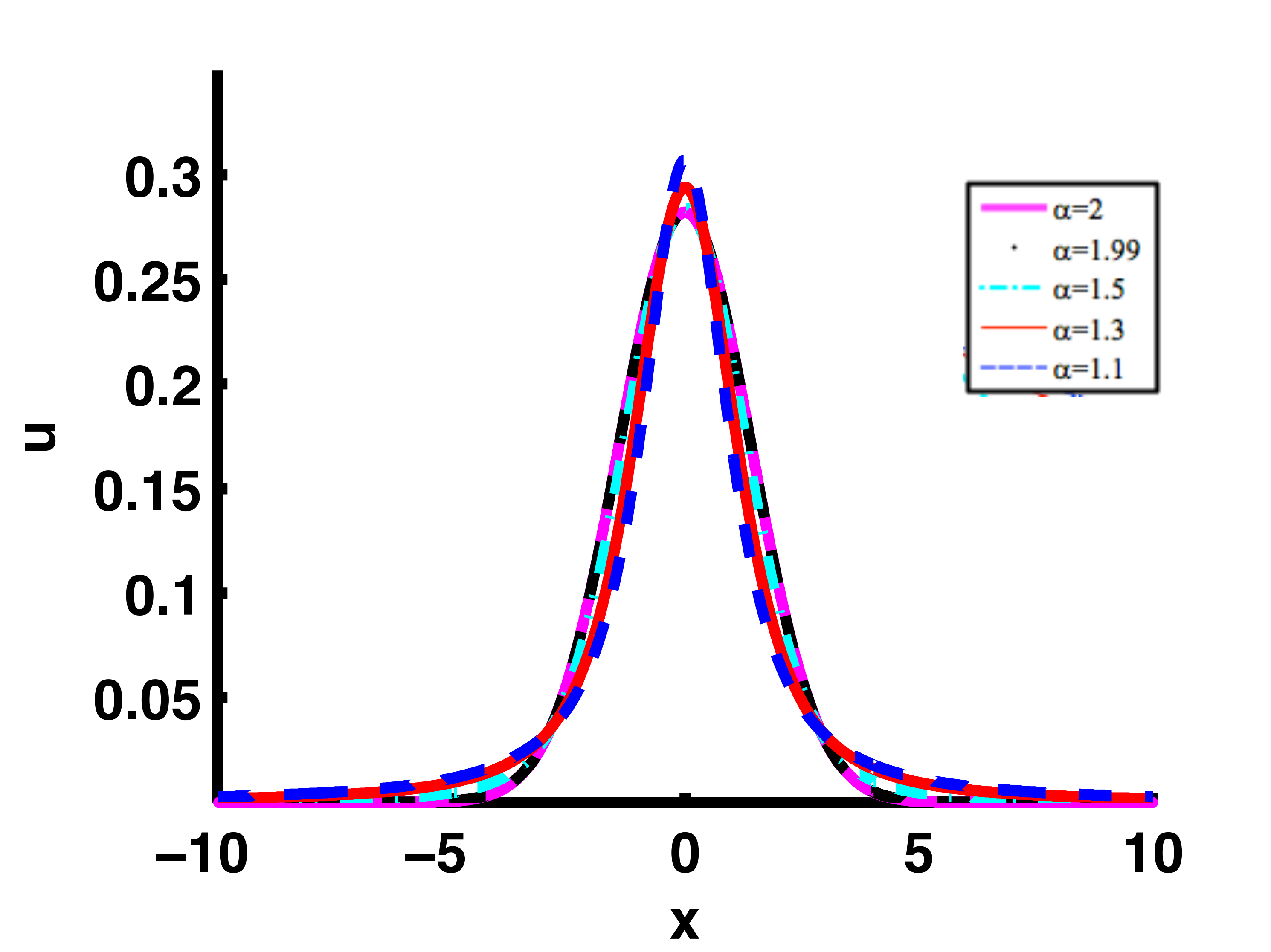
When α=2
Classical Fickian diffusion



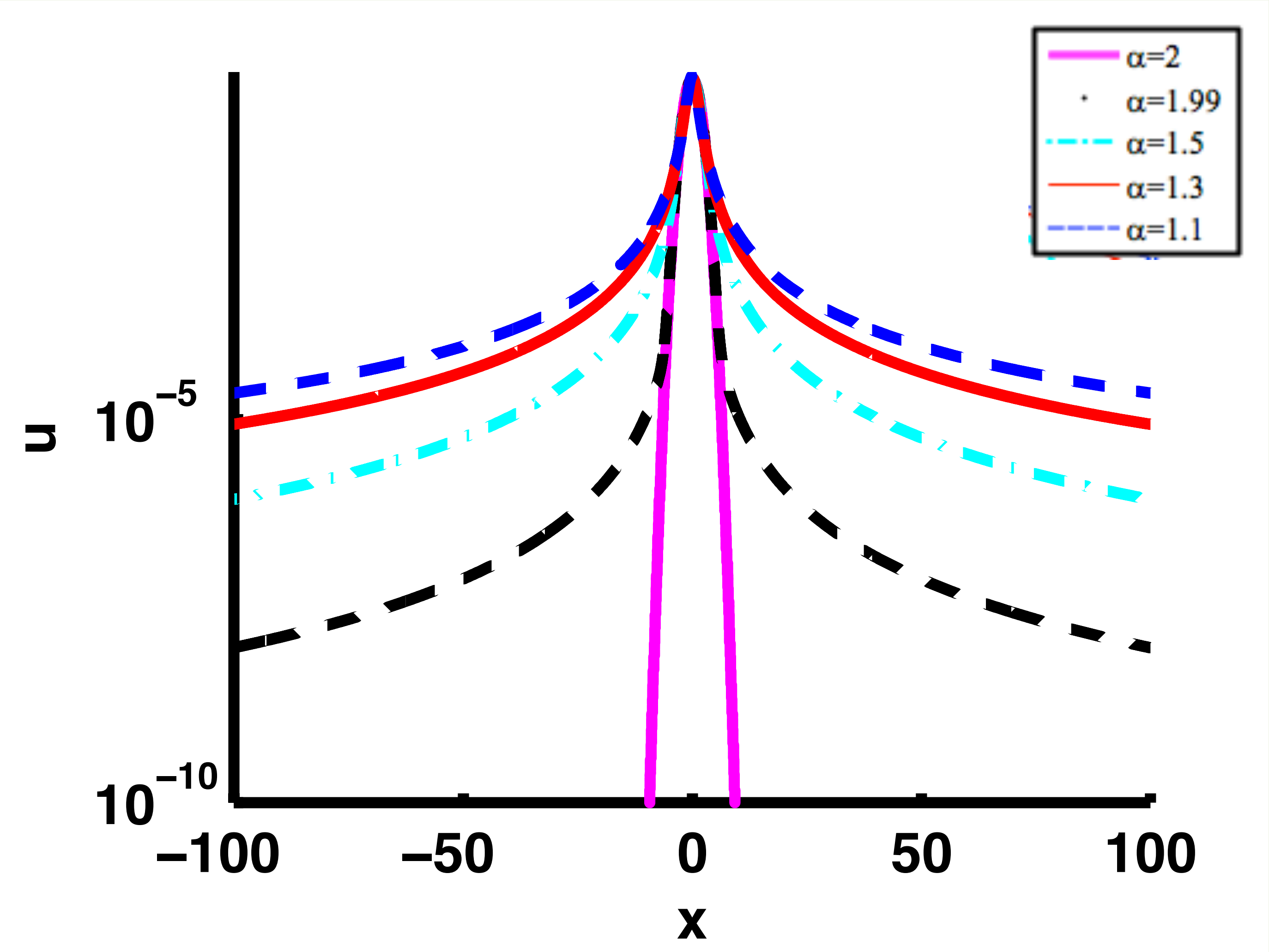


$$r = \left(D\nabla U . \nabla U\right)\left(\frac{d^2 C_1}{dU^2}\right)$$

What happens as α changes?

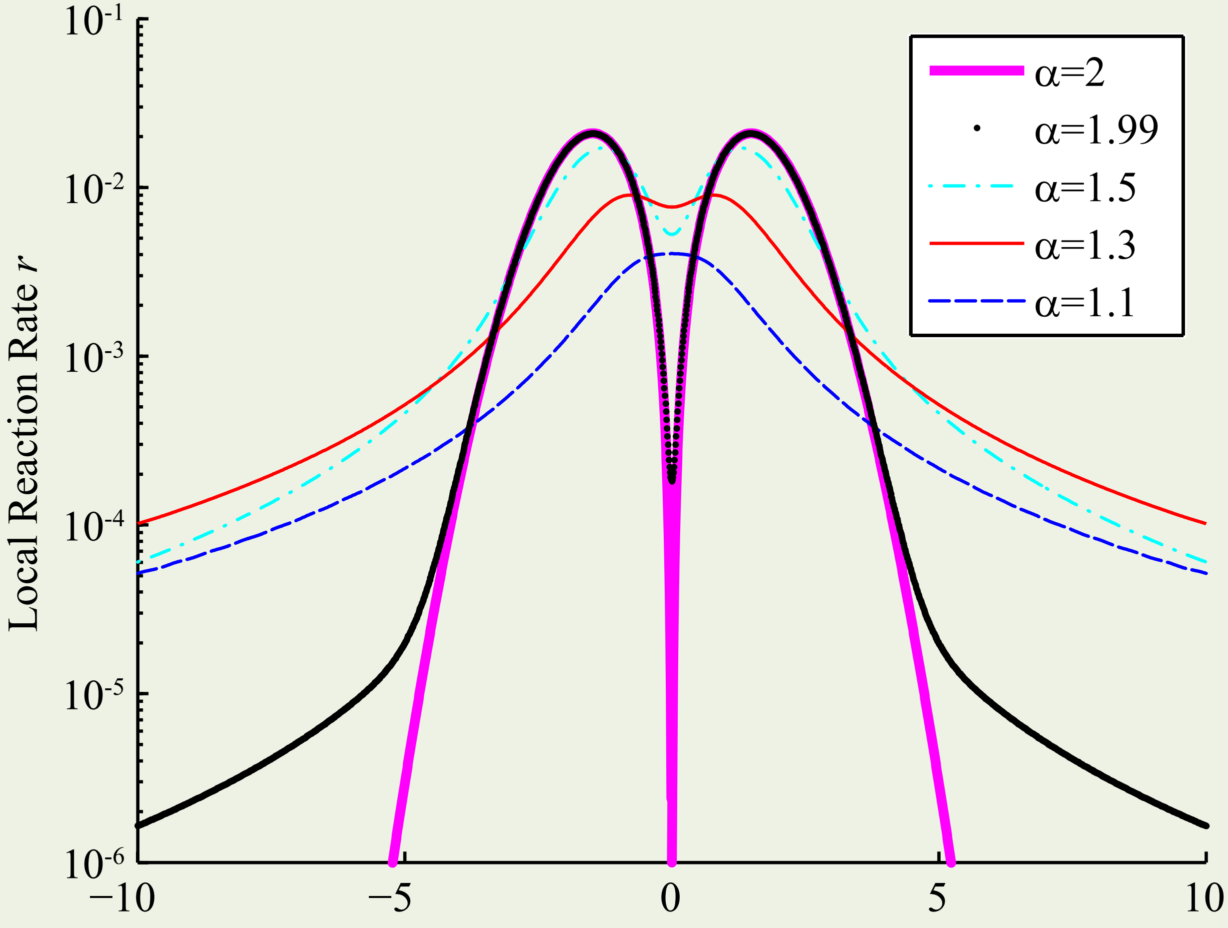


Let's take a closer look at this



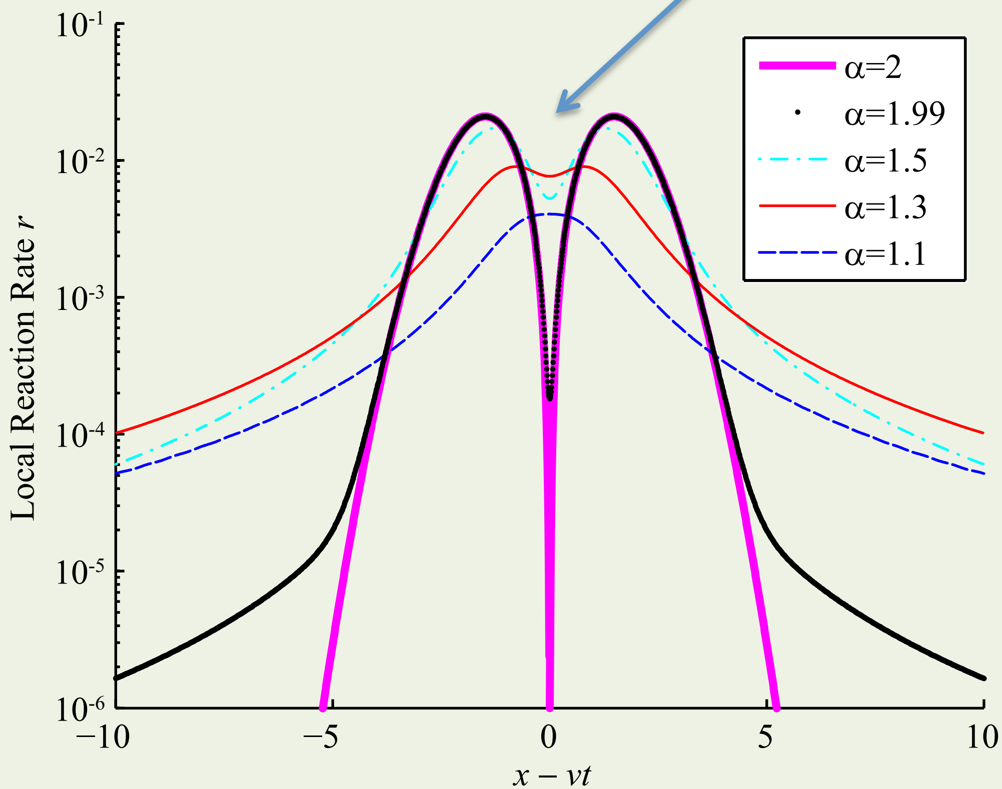
What does this mean for precipitation reactions?

$$r(x,t) = D_\alpha \sum_{k=1}^{\infty} \binom{\alpha - 1}{k} \frac{\partial^{\alpha-k} u}{\partial |x|^{\alpha-k}} \frac{\partial^k}{\partial x^k} \frac{dc}{du}.$$

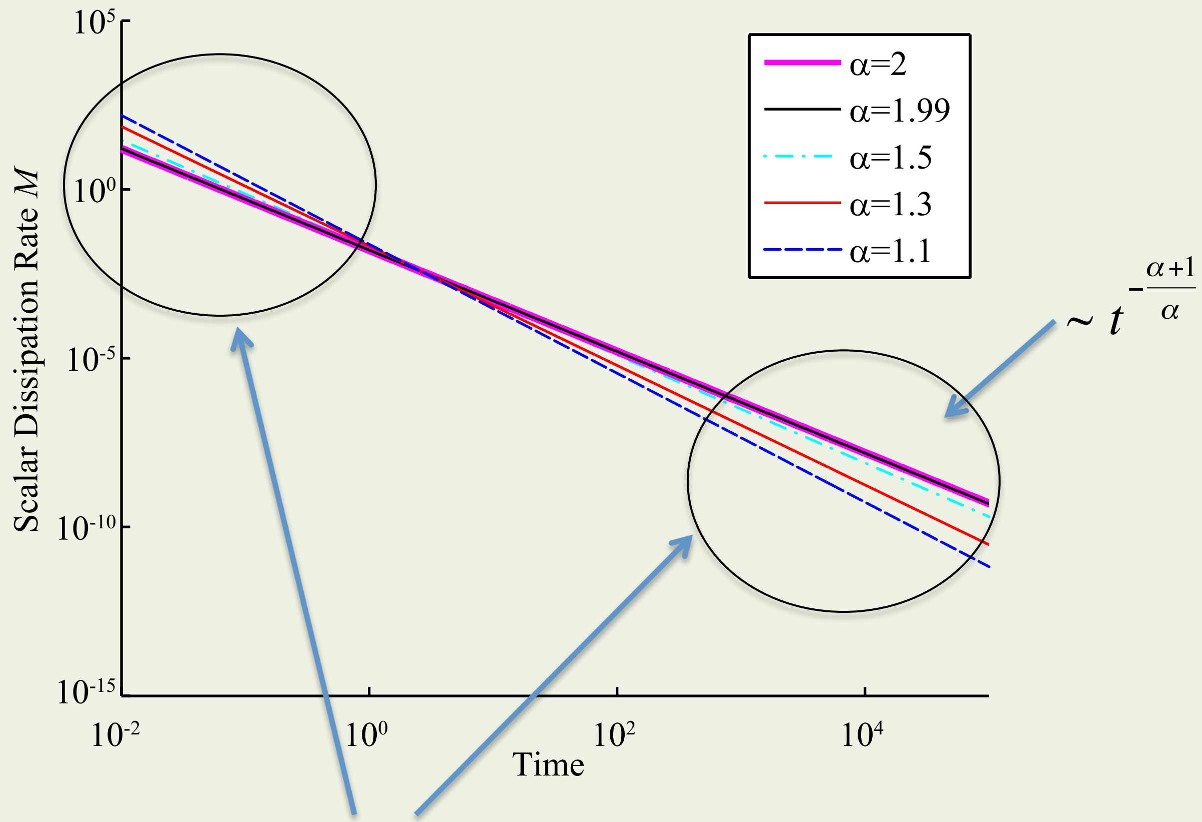


What does this mean for precipitation reactions?

Min becomes max α gets smaller

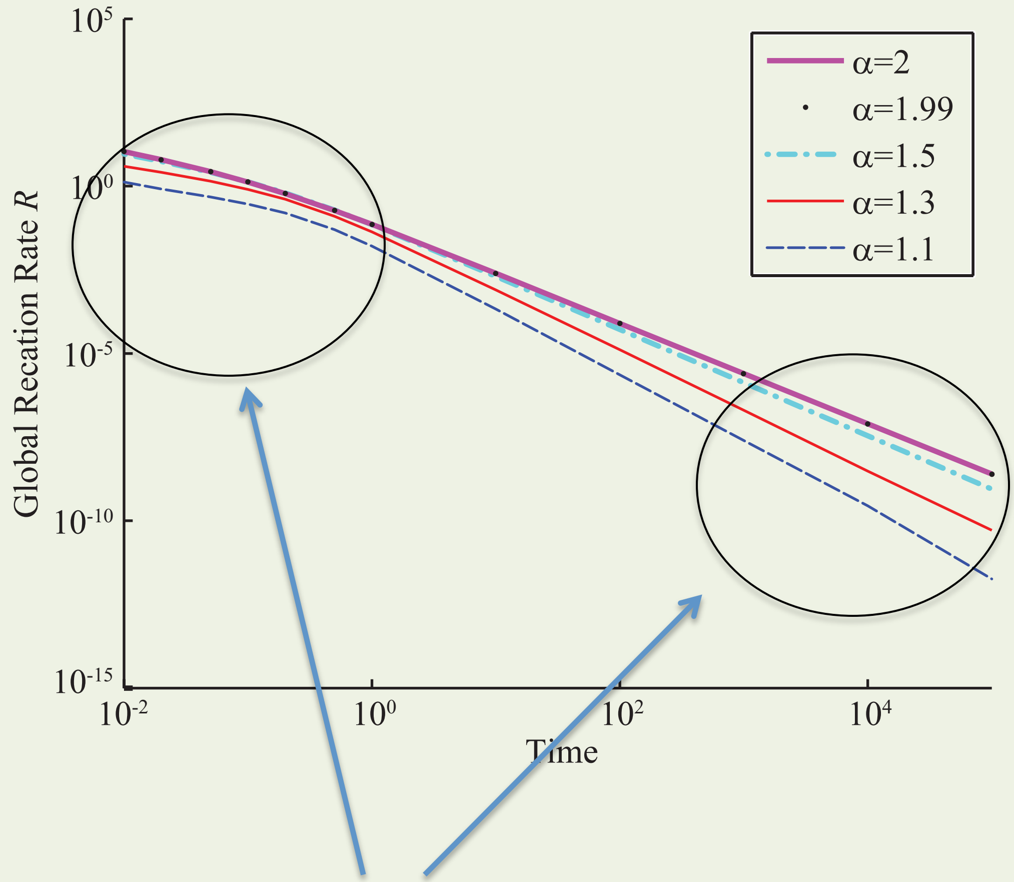


Global Measures – Mixing (Scalar Dissipation)



At early times more anomalous (smaller α)=more mixing
At late times – less mixing

Global Measures – Total Reaction Rate



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

Questions