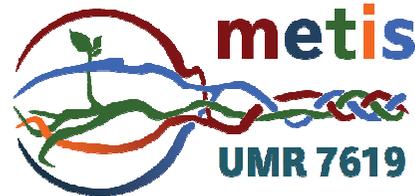


# Coupled charge migration and fluid mixing in reactive fronts



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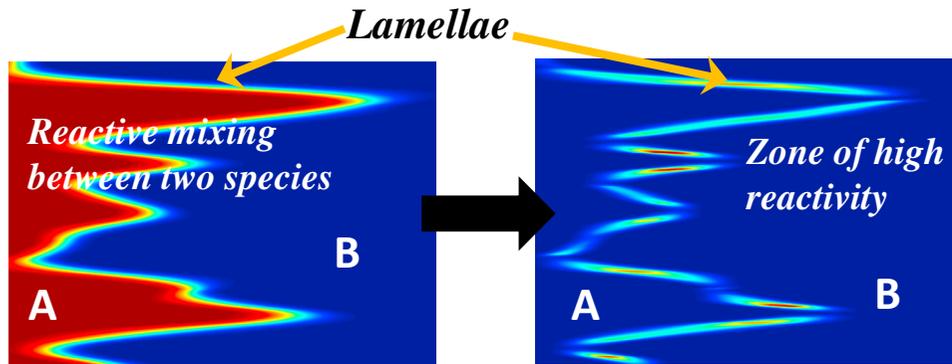
# Overview of the work

# Reactive Mixing in porous media: it's Physics and Importance



## Definition: Reactive Mixing

Chemical Reaction between two species (redox, dissolution, precipitation,...)  
aided/enhanced by fluid flow induced stretching and folding.



## What influences reactive mixing?

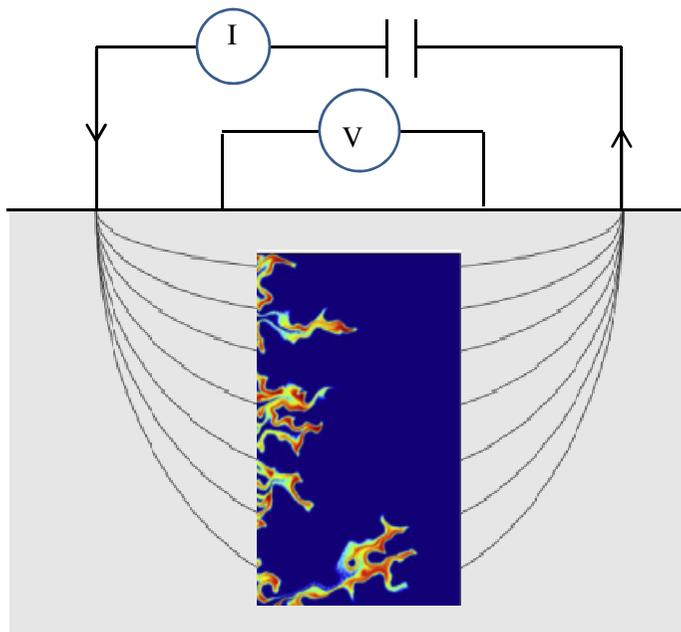
Reaction kinetics;  
Local Stretching Rates;

## Difficulties with in situ measurement

Lack of direct access to the subsurface  
Large uncertainty with reactive tracer test interpretation  
(unknown spatial distribution...)

Can we monitor reactive mixing with geophysical methods ?

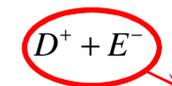
Use **Electrical Conductivity** of the subsurface to measure reaction rate



Schematic representation of conductive tracer movement and electrical measurement

Consider the type of reaction:  $A + B \rightarrow C$

Reacting species:  
weakly conducting

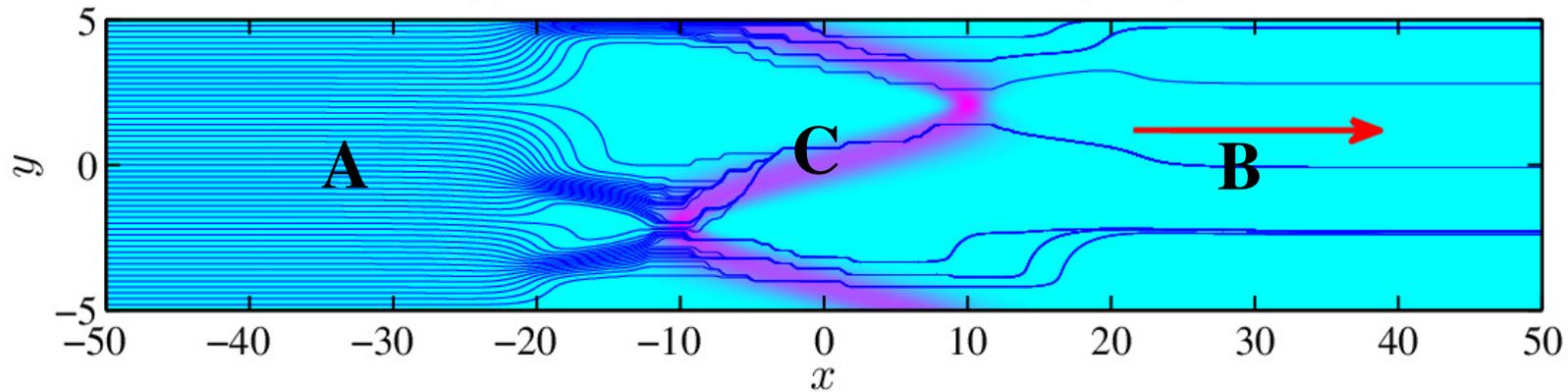


Products: high conductivity

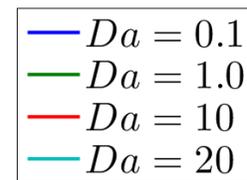
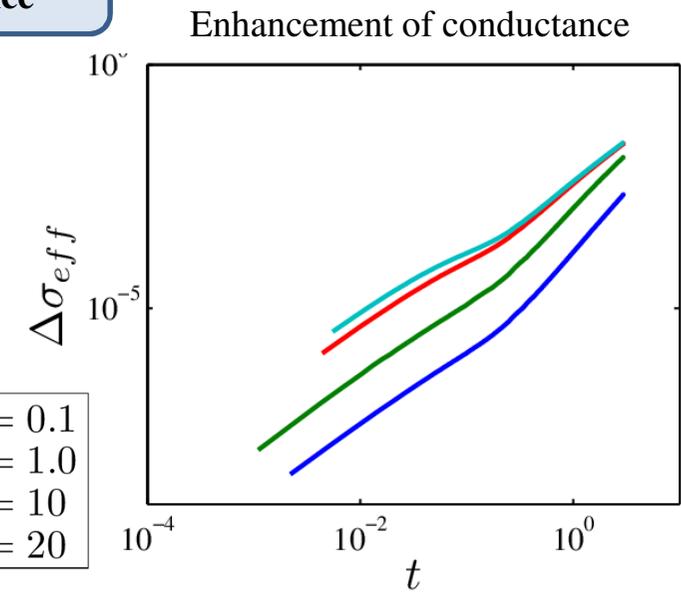
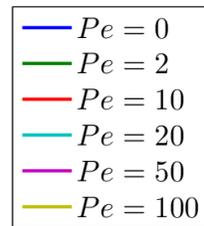
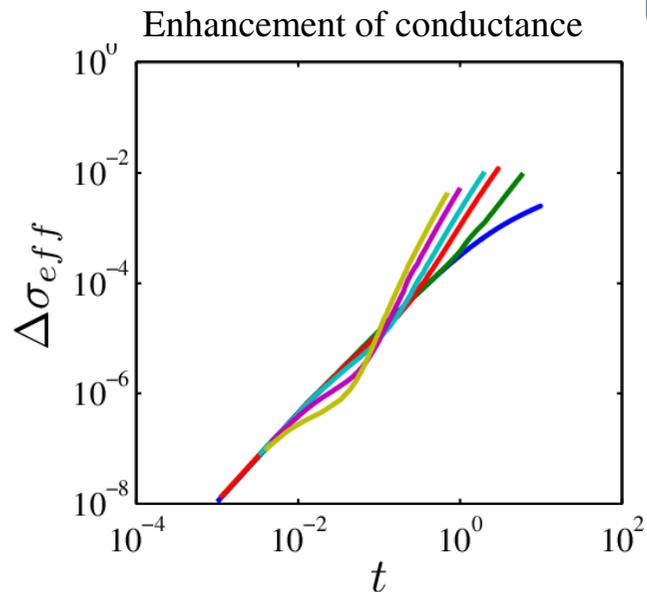
# Geoelectrical signature of reactive mixing



(a) Current Lines + Conductivity Map



Stretching-driven reactive mixing  
impacts Effective Conductance



## Overall Conclusions

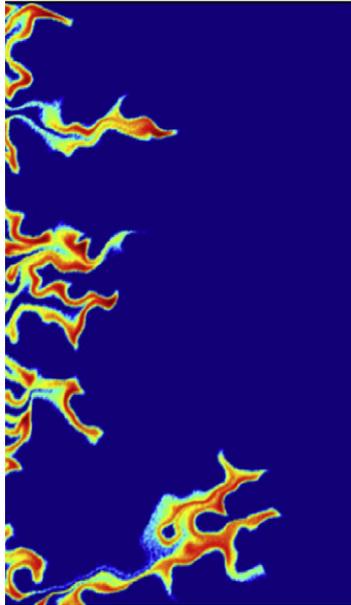
Electrical conductance is highly sensitive to mixing and reaction rates.



A promising method for non-invasive investigation of reactive mixing dynamics in the subsurface

## **Going into Detail**

# What is Reactive Mixing and Why is it important?

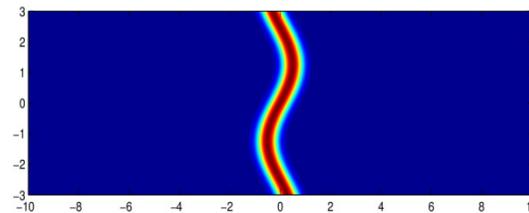


Example of movement of chemical Species in a porous media  
(Dentz et al. J. Cont. Hyd., 2011)

**Definition: Reactive Mixing**  
  
**Chemical Reaction between two species – aided/enhanced by fluid flow induced stretching and folding.**



Reaction Front for a sinusoidally stratified flow: a representative example



**Reaction Front**  
  
**The zone of maximum reactivity between the two species – can have any shape depending on the stretching rate.**

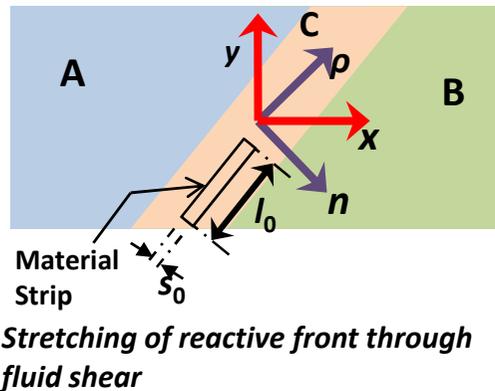
**Why is it important?**

- **Important applications in contaminant transport.**
- **Coupling with microbial activities.**
- **Has important applications in such processes as In Situ Chemical Oxidation (ISCO).**
- **Important consequences in Critical Zone Science.**
- **Other applications like CO<sub>2</sub> storage, oil recovery etc.**

# The Physics of Reactive Mixing

## What influences reactive mixing?

- Reaction kinetics, often expressed in terms of *Damköhler number* ( $Da$ ).
- The rate of fluid flow, which stretches and folds the fluid elements - expressed non-dimensionally in terms of *Péclet number* ( $Pe$ )
- Creation of new *area of contact* between the reactants – formation of more products.
- Amount of stratification in the flow



## Issues with measuring reactive mixing

Main properties to measure: Reaction rate and the mass of the product.

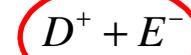
## Difficulties with measurement

- Reactions take place in the subsurface – direct observation is impossible.
- With Boreholes only local measurements are possible.
- Lack of access to the reaction front
- Hence, measurement of front width, mass of product difficult.

# Can effective Measurements be done with Geo-electrics?

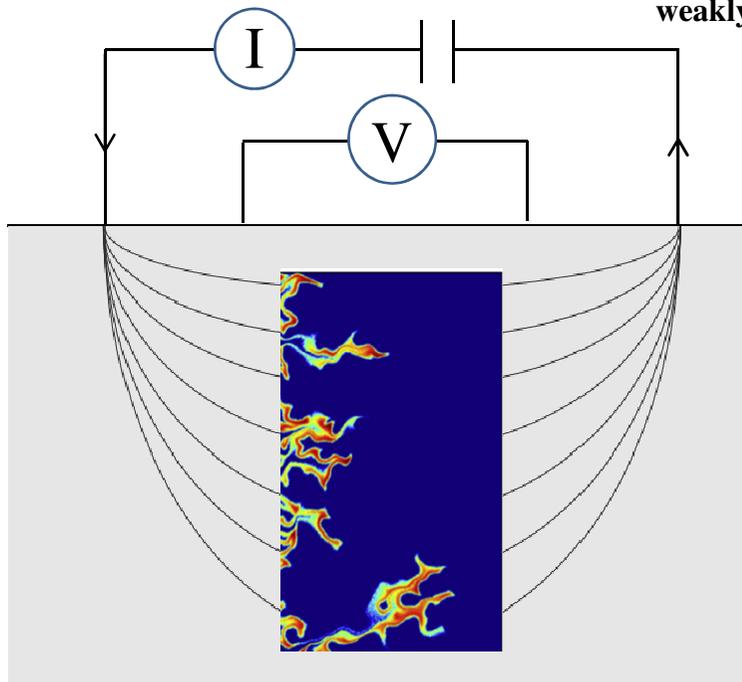
Use Electrical Conductivity of the subsurface to measure reaction rate

Consider the type of reaction:



Reacting species:  
weakly conducting

Products: high  
conductivity



*Schematic representation of conductive tracer movement and electrical measurement*

### The Mechanism of the method

- ❑ Weakly conducting species react – produces ionic species
- ❑ Examples: Some ISCO reactions, for instance using Permanganate as one reactant.
- ❑ Production of ions change the conductivity of the medium.
- ❑ As the reaction progresses, more ions are produced – larger conductivity.
- ❑ Total effective conductivity should be dependent on reaction front, mass of the product.
- ❑ Effective Conductivity also depends on the orientation of the Reaction front.
- ❑ In general: Effective conductivity should strongly depend on  $Da$  and  $Pe$ .

# Aim of this study

**Investigate the effect of stretching-driven reactive mixing on Effective Conductance**

**What kind of Stretching?**

**A Unidirectional stratified flow,  $\mathbf{v} = v(y)\mathbf{e}_x$**

**Special case of interest:**

**Simple Shear flow – uniform stretching**

## Why Shear Flow?

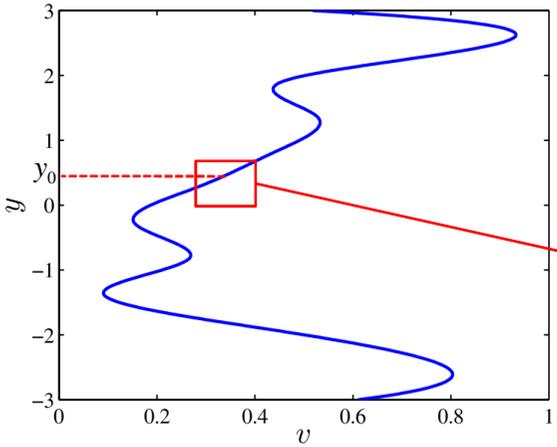
**Any Stratified flow can be decomposed into a combination of shear flows:**

**Velocity can be written as:**

$$\mathbf{v} = \left[ v_0(y_0) + \underbrace{\Gamma(y_0)}_{\text{Local strain rate}} (y - y_0) \right] \mathbf{e}_x$$

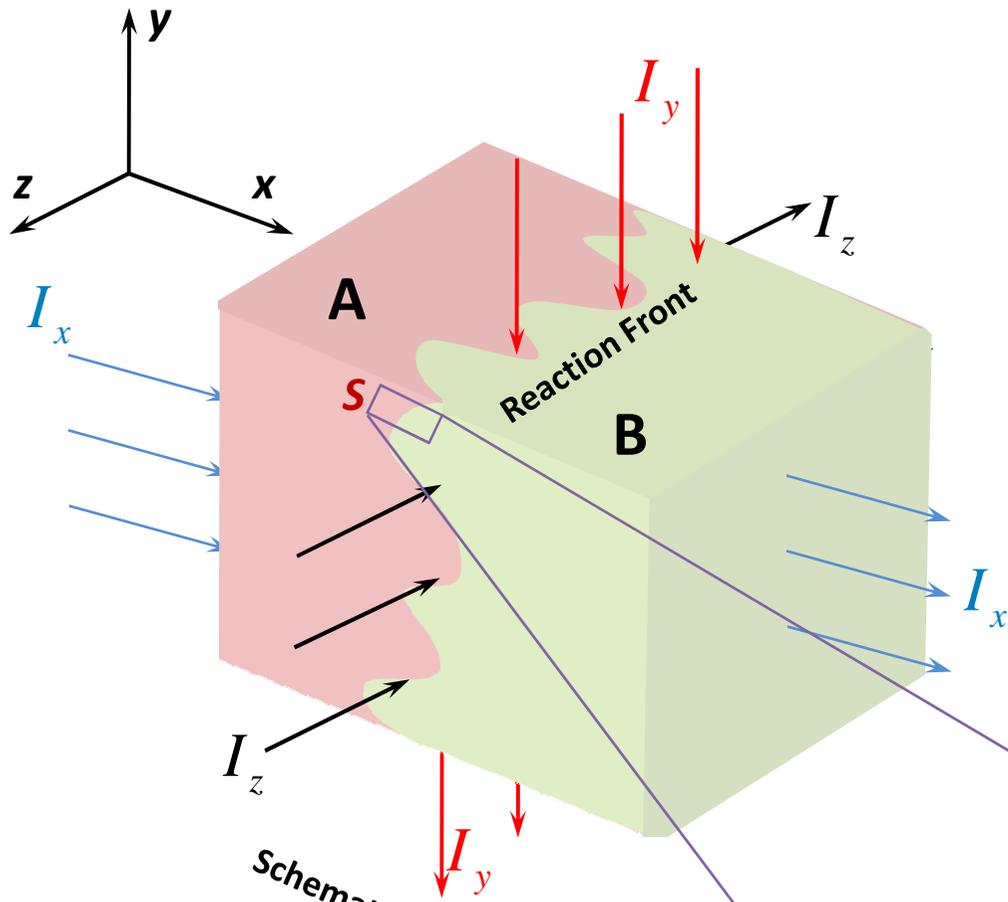
**Local strain rate**

$$\Gamma(y_0) = \left. \frac{dv}{dy} \right|_{y=y_0}$$



*Example of a stratified velocity profile*

# Schematic Description of the Reaction Front



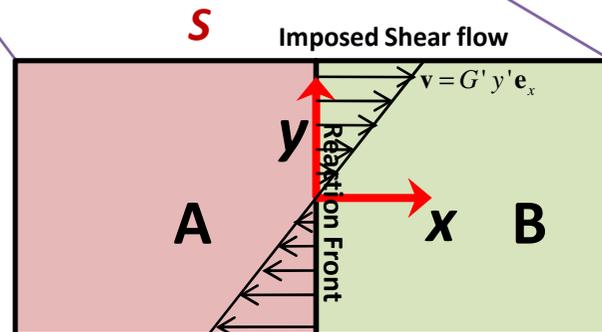
A stratified reaction front

Note:  
We can have three different configuration of electrodes, depending on the primary direction of the current/applied potential difference with respect to the flow direction

Magnified schematic of a part of the front

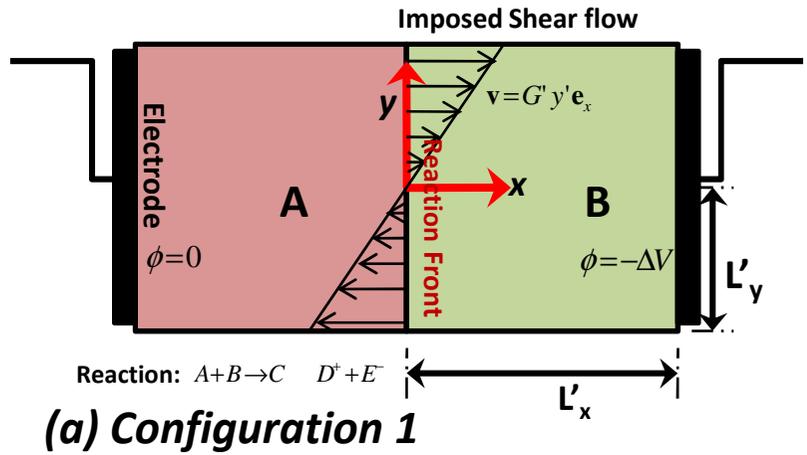
The front in this part is effectively under a shear driven stretching

**S** → Location of interest, which We magnify

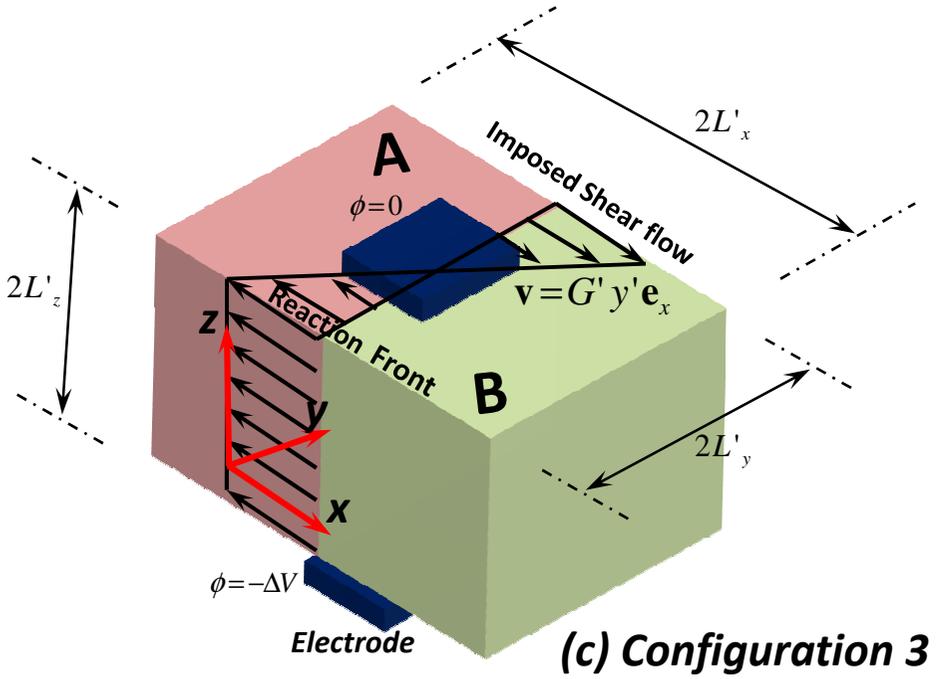
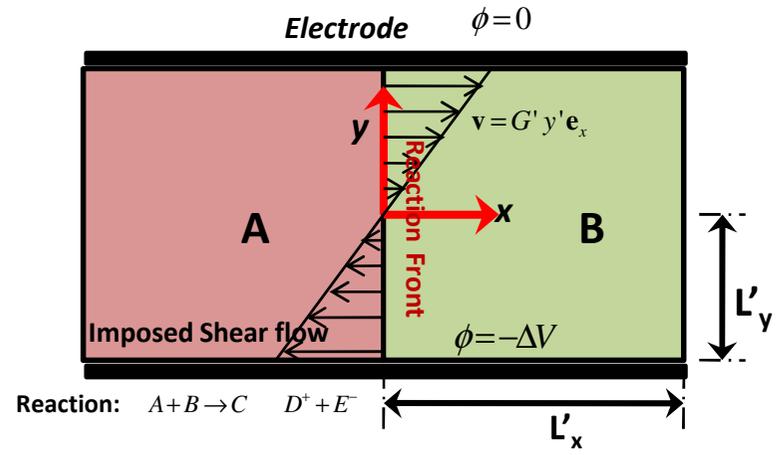


# Schematic Description – The three configurations

**Three Configurations for reactive mixing – Theoretical Analysis**



**(b) Configuration 2**



# Basic Theory: Equations

**Reactive Transport:**

$$\frac{\partial c_a}{\partial t} + \mathbf{v} \cdot \nabla c_a = D \nabla^2 c_a - k c_a c_b$$

$$\frac{\partial c_b}{\partial t} + \mathbf{v} \cdot \nabla c_b = D \nabla^2 c_b - k c_a c_b$$

$$\frac{\partial c_d}{\partial t} + \mathbf{v} \cdot \nabla c_d = D \nabla^2 c_d + k c_a c_b$$

**Local Conductivity:**

$$\sigma = \sigma_r + 2\nu e^2 c_d$$

**Equation for the current:**

$$\nabla \cdot (\sigma \nabla \phi) = 0$$

Species concentration:  $c_a, c_b, c_d$   
 Residual (Background) Conductivity:  $\sigma_r$   
 Ionic Mobility:  $\nu$   
 Potential:  $\phi$   
 Fluid Velocity:  $\mathbf{v}$   
 Reaction constant:  $k$

**Define effective Conductivity:**

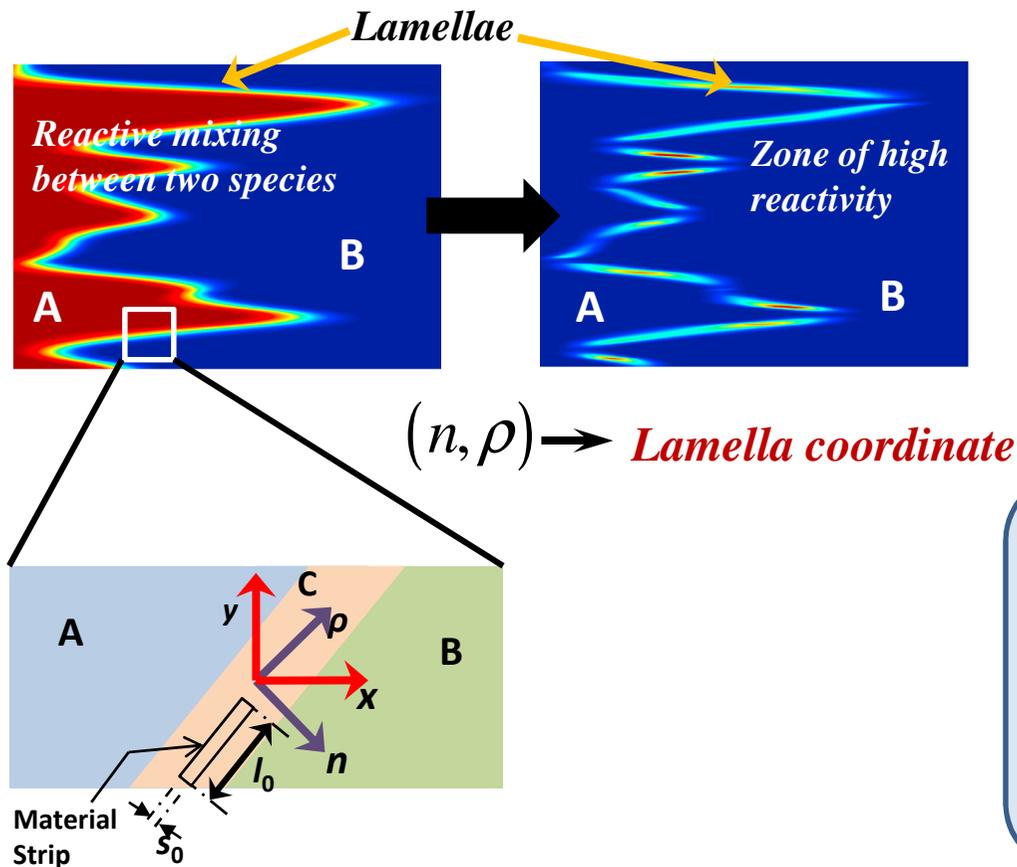
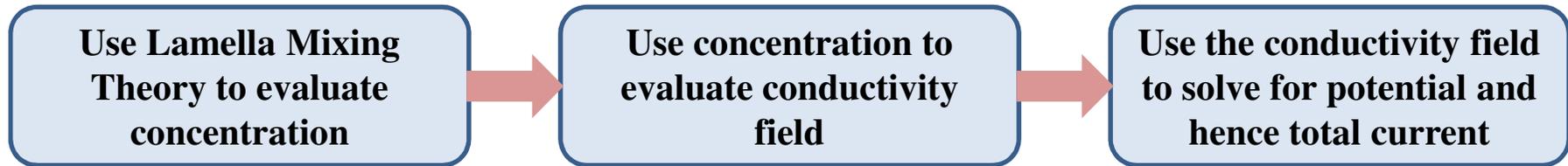
$$\sigma_{eff} = \frac{\text{Current through Electrode}}{\text{Applied Average Electric field} * K_G}$$

Geometrical Factor

**Current through domain cross-section:**

$$I = - \int_{S_{cross}} \sigma \nabla \phi \cdot \mathbf{n} dS$$

# Approach to Solution



## The Lamella Mixing Theory

- **Lamellae:** *Elongated/stretched part of a reactive/mixing front.*
- *Typically lamellae have lengths much larger than their width.*

- *All the transport equations are expressed in Lamellae coordinate.*
- *For lamella length  $\gg$  lamella width, in lamella coordinate, transport equations essentially become a quasi 1-D reaction-diffusion equation in the  $n$  coordinate – transverse to the lamella.*

## Approach to Solution – Continued

**Take Velocity Field:**

$$\mathbf{v} = v(y) \mathbf{e}_x$$

**Strain Rate:**

$$\Gamma(y) = \frac{dv}{dy}$$

**Equations for species A after co-ordinate transformation:**

$$\frac{\partial c_a}{\partial t} - \underbrace{\frac{n}{s} \frac{ds}{dt}}_{\text{Rate of change of thickness of material volume}} \frac{\partial c_a}{\partial n} = \frac{\partial^2 c_a}{\partial n^2} - Da(c_a c_b)$$

Rate of change of  
thickness of material  
volume

**Material Strip  
thickness:**

$$s = \frac{s_0}{\sqrt{1 + Pe^2 \Gamma^2(y) t^2}}$$

**For shear flow:**

$$\Gamma(y) = 1$$

**Characteristic time:**  $t_c = \tau_D = w_0^2 / D$

**Characteristic length:**  $w_0$  - typical mat. width

**Peclet Number:**  $Pe = v_0 w_0 / D$

**Damkohler Number:**  $Da = k w_0^2 c_0 / D$

# Approach to Solution – Continued

## Further simplification

**Wrapped time:**

$$\tau = \int_0^t \frac{du}{s^2(u)}$$

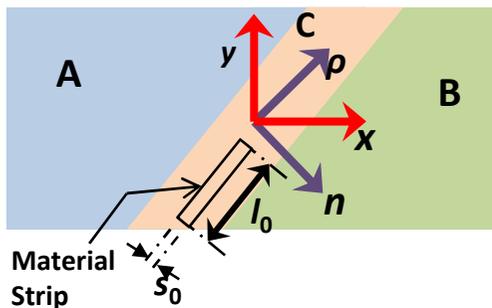
**Normalized space:**

$$z = \frac{n}{s}$$

**Simplified equation:**

$$\frac{\partial c_a}{\partial \tau} = \frac{\partial^2 c_a}{\partial z^2} - Da(s^2 c_a c_b)$$

## Reconstruction of the concentration field for a Shear flow



$$c_d(n, \tau) = c_d(\mathbf{x}, t); \quad \Gamma(y) = 1$$

$$n = \left( \frac{1}{\sqrt{1 + Pe^2 t^2}} \right) x - \left( \frac{Pet}{\sqrt{1 + Pe^2 t^2}} \right) y$$

## Approach to Solution – Continued

- Reaction diffusion equation solved numerically, using finite difference scheme, by marching forward in time.
- The non-linear reaction term was modelled with explicit scheme.
- Small enough time steps were chosen to ensure accuracy of the numerical solutions.
- Species equation solved in the  $z$ - $\tau$  coordinate.
- Reconstruction of concentration in the  $x$ - $y$  field done through interpolation
- The current conservation equation for potential solved numerically, using a fully implicit finite difference scheme.

*Special note:* in configuration 3, the effective conductivity is essentially the average concentration in the domain.

## Results - Overview

### What are we trying to estimate?

- How does the concentration field of the product evolve in time?
- How does the effective conductivity (EC) change with time?
- How does the effective conductivity (or, resistance) evolve for different configurations?
- How does  $Pe$  (the flow rate) influence the effective conductivity (EC)?
- How does  $Da$  (reaction kinetics) influence the EC?
- Which configuration is the most sensitive to the reaction taking place?
- Do all the configurations have similar sensitivity to  $Pe$  and  $Da$ ?

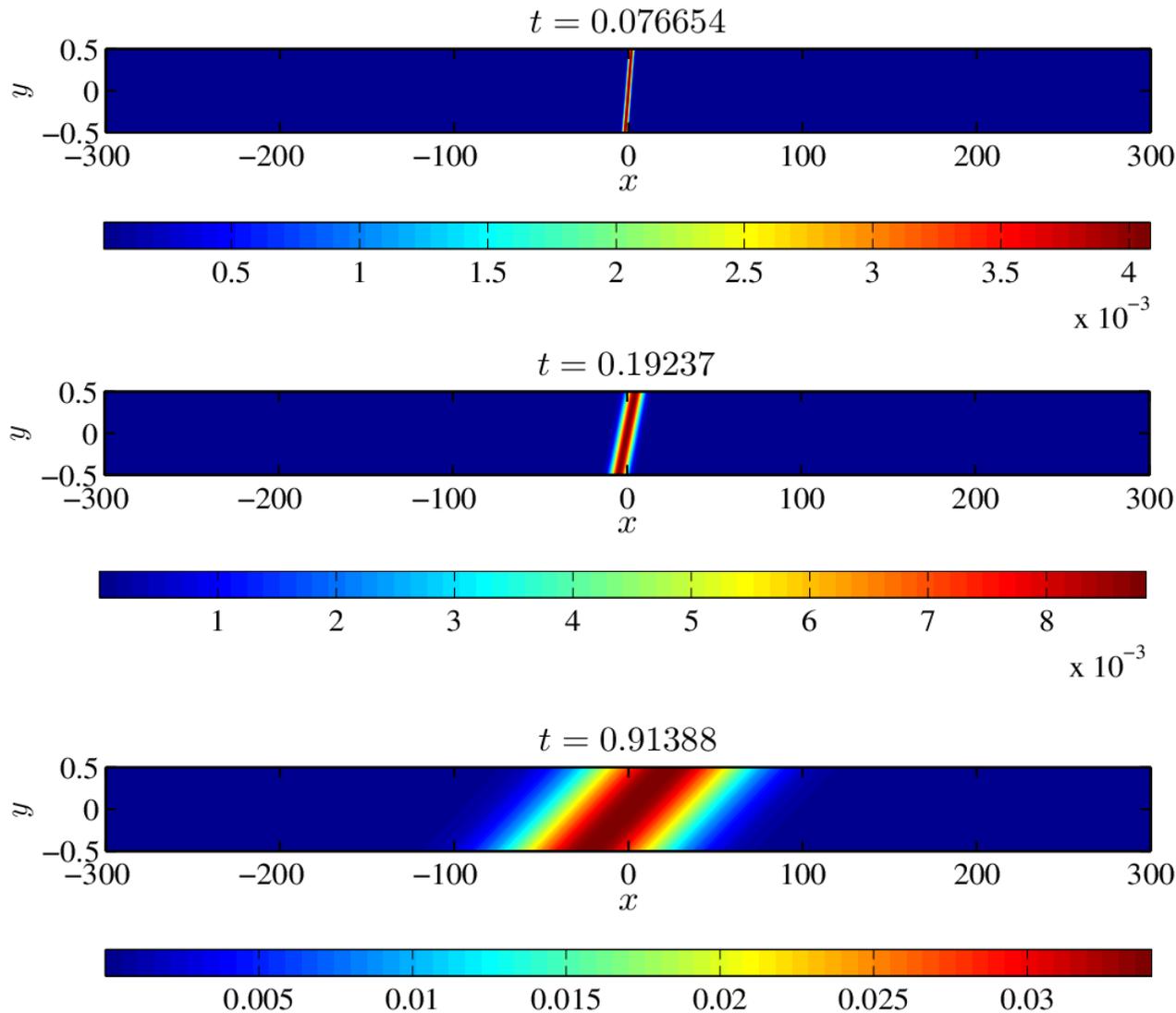
Quantity of interest:

$$\Delta\sigma_{eff} = \sigma_{eff} - \sigma_r$$

Results shown for  
shear flow

$$\Gamma = 1$$

## Results – Concentration field for a Shear flow



### Parameters:

$$Pe = 50; Da = 1; \sigma_r = 10^{-5}$$

- The front is stretched continuously.
- The product is mostly distributed around the reaction front.
- The front-width increases with time.
- The red zone in the middle is the zone of high conductivity.

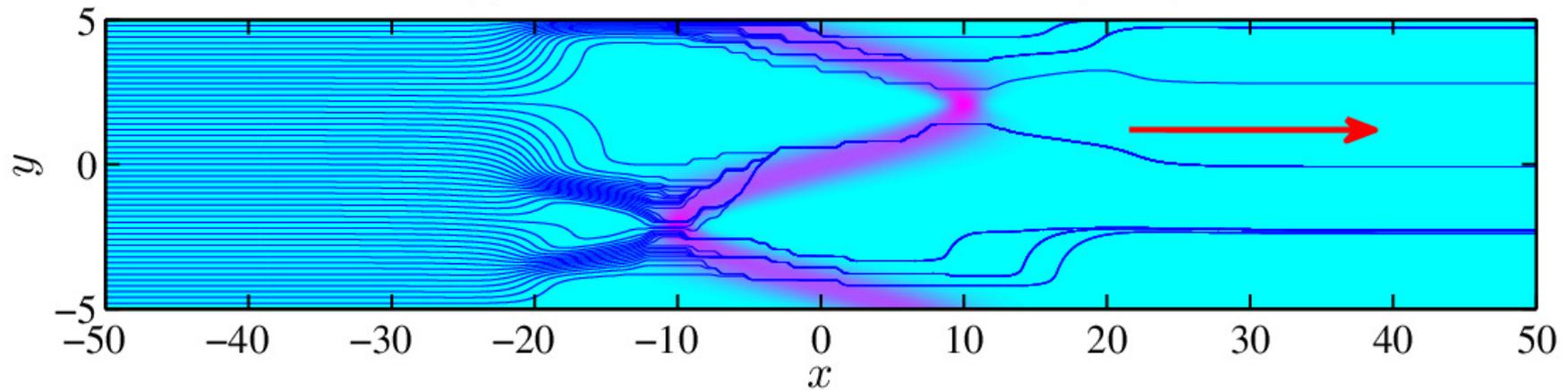
$$t = \frac{t'}{\tau_D}; \tau_D = \frac{w_0^2}{D}$$

**Normalized Concentration distribution of the ion D, one of the products in the XY domain, at three different times – time non-dimensionalized w.r.t diffusion time.**

## Results – Current & Conductivity for Sinusoidally Stratified flow Configuration 1

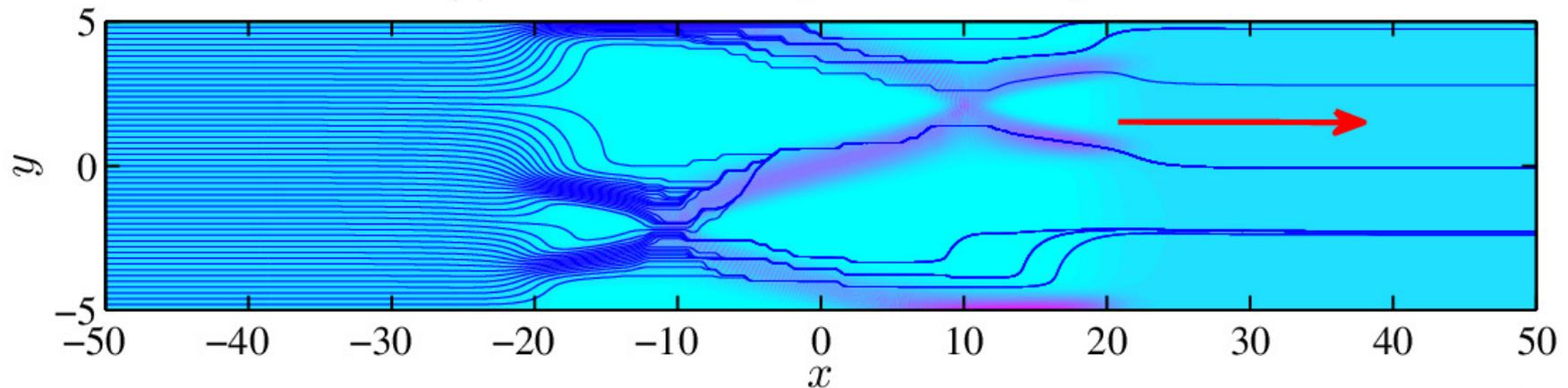


(a) *Current Lines + Conductivity Map*



- Blue – Region of low conductivity (a) & current (b); Pink – Region of high Conductivity (a) & current (b);
- Generally a “circuit” is automatically formed in the domain – the current follows path of the least resistance.

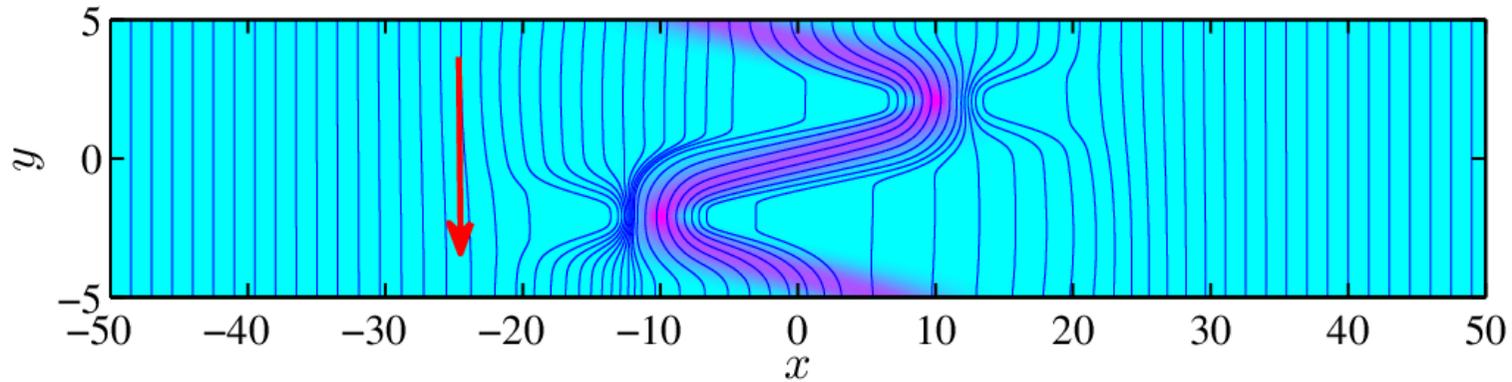
(b) *Current Lines + Current Magnitude*



## Results – Current & Conductivity for Sinusoidally Stratified flow Configuration 2

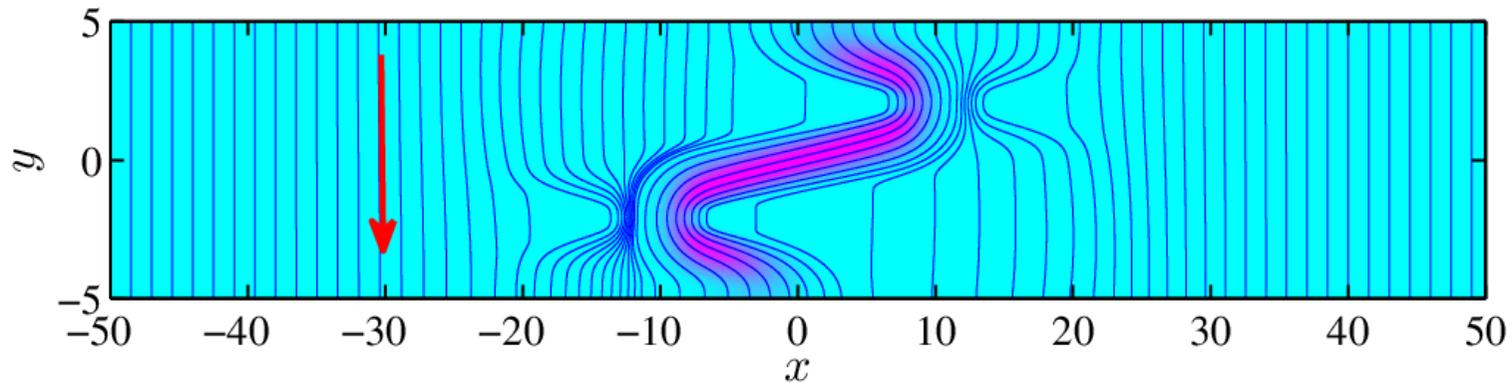


(a) *Current Lines + Conductivity Map*

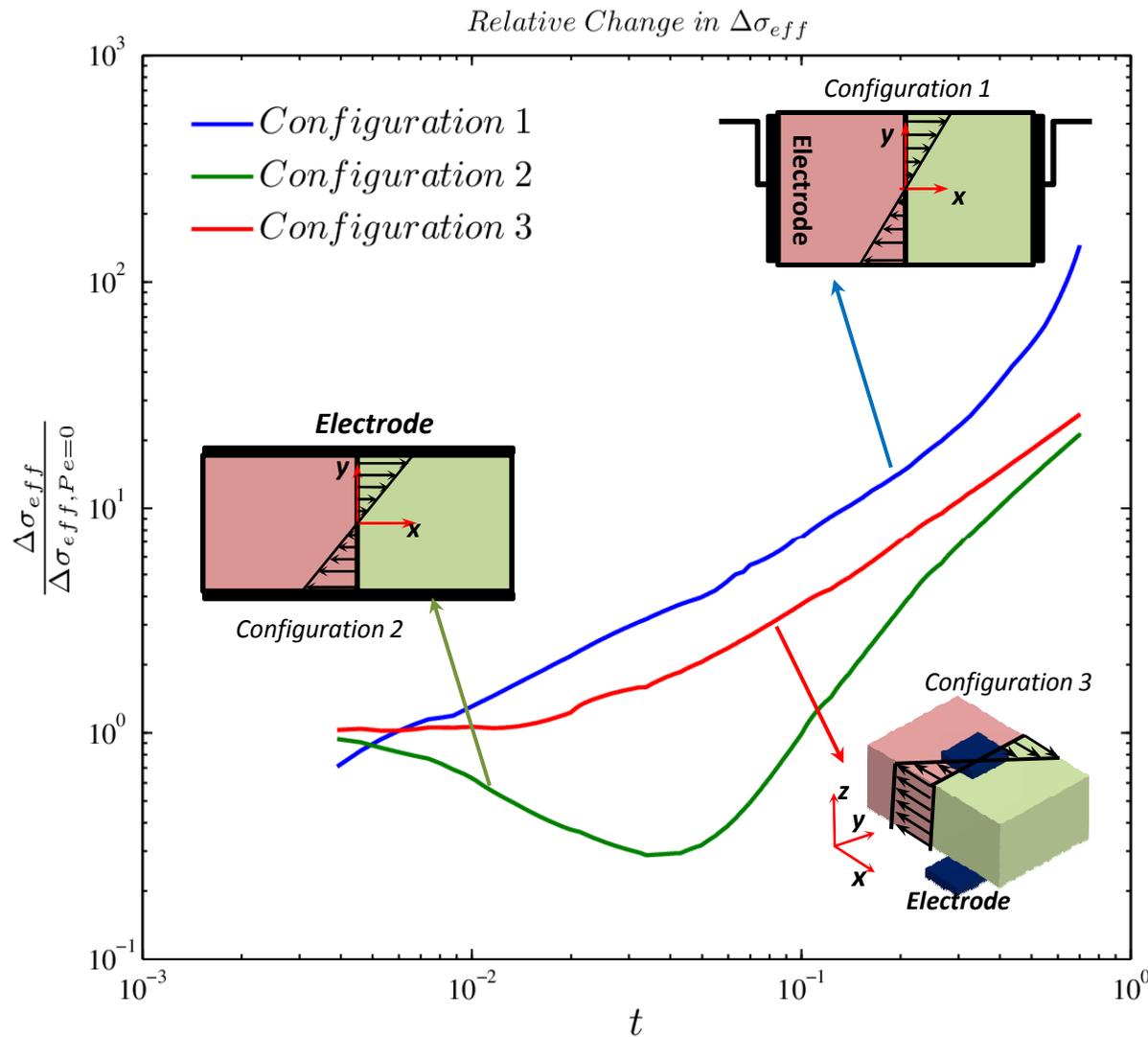


□ The current here strongly follows the reaction front, i.e., the path of least resistance.

(b) *Current Lines + Current Magnitude*



# Results – Effective conductance: Relative Performance



Flow: simple shear

$$\Gamma(y) = 1$$

Relative Increments in the Effective Conductivity with respect to a Reaction-Diffusion front:

$$\Delta\sigma_{rel} = \frac{\Delta\sigma_{eff}}{\Delta\sigma_{eff, Pe=0}}$$

**Question:** Which configuration is most sensitive to flow? (with respect to diffusion)  
**Configuration 1**

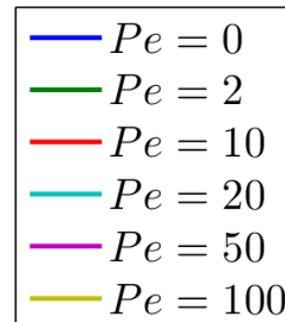
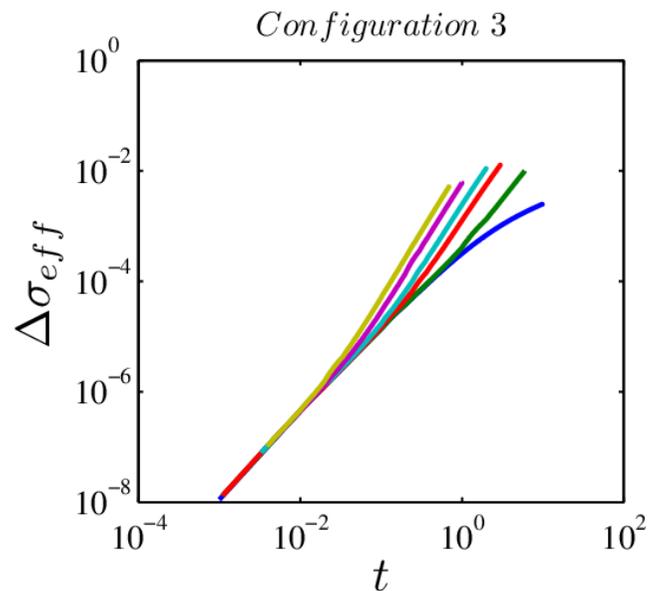
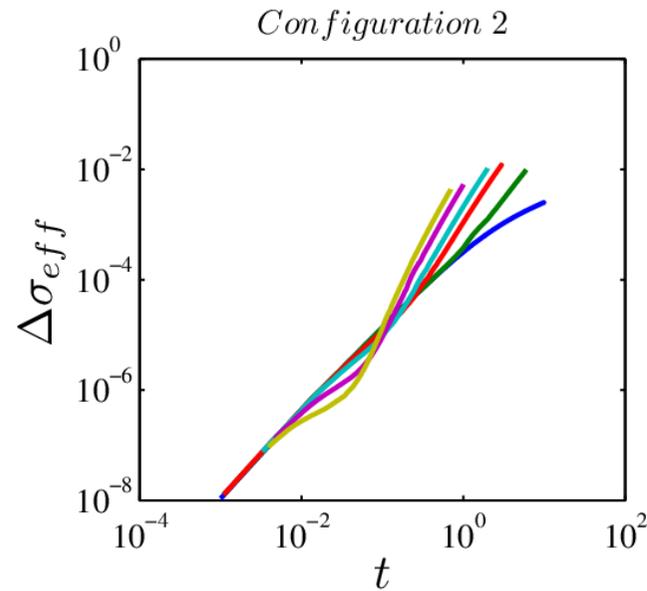
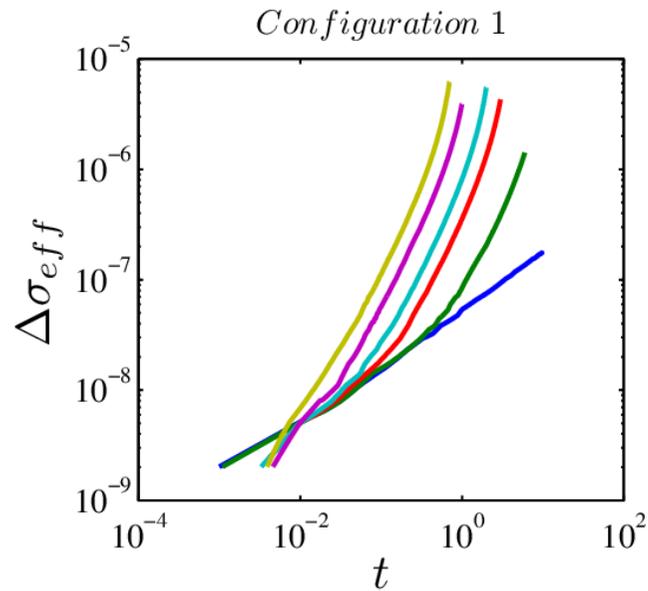
**Point to note:**

☐ In all the configs, conductivity changes significantly.

Time ( $t$ ) has been non-dimensionalized with respect to diffusion time:

$$t = \frac{t'}{\tau_D}; \quad \tau_D = \frac{w_0^2}{D}$$

# Results – Effective conductance: Variation with flow strength

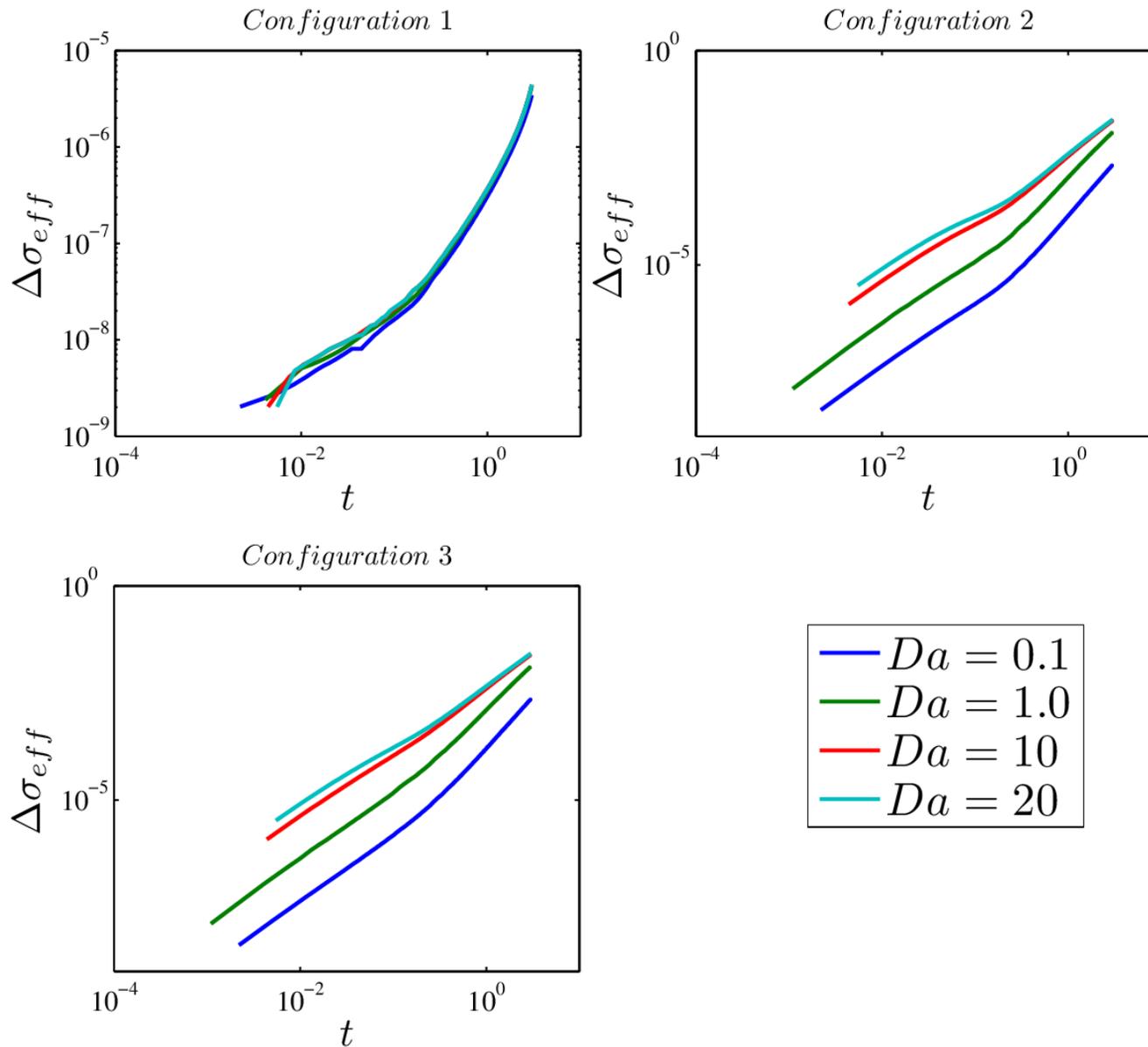


Flow: simple shear

$$\Gamma(y) = 1$$

- Points to note:**
- ❑ The effective conductivity (EC) increases by orders of magnitude with time.
  - ❑ The Effective conductivity is larger for larger values of  $Pe$ .
  - ❑ The EC usually takes off for non-zero  $Pe$ , after a certain time.
  - ❑ The take-off occurs earlier, as  $Pe$  is increased.
  - ❑ The take of is also more prominent for configuration 1.
  - ❑ The net/absolute increase in the EC, is although larger for the other two configs.
  - ❑ Config. 1 – Width of the front. Configs 2, 3 – both mass and width in the front.

# Results – Effective conductance: Variation with reaction kinetics



Flow: simple shear

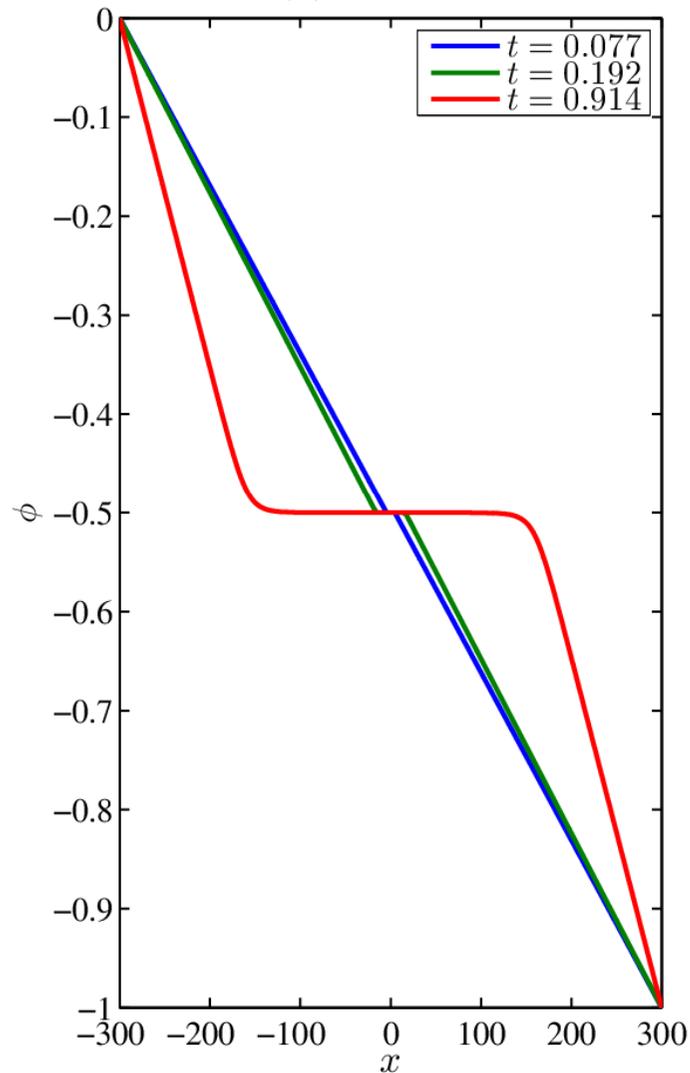
$$\Gamma(y) = 1$$

***Points to note:***

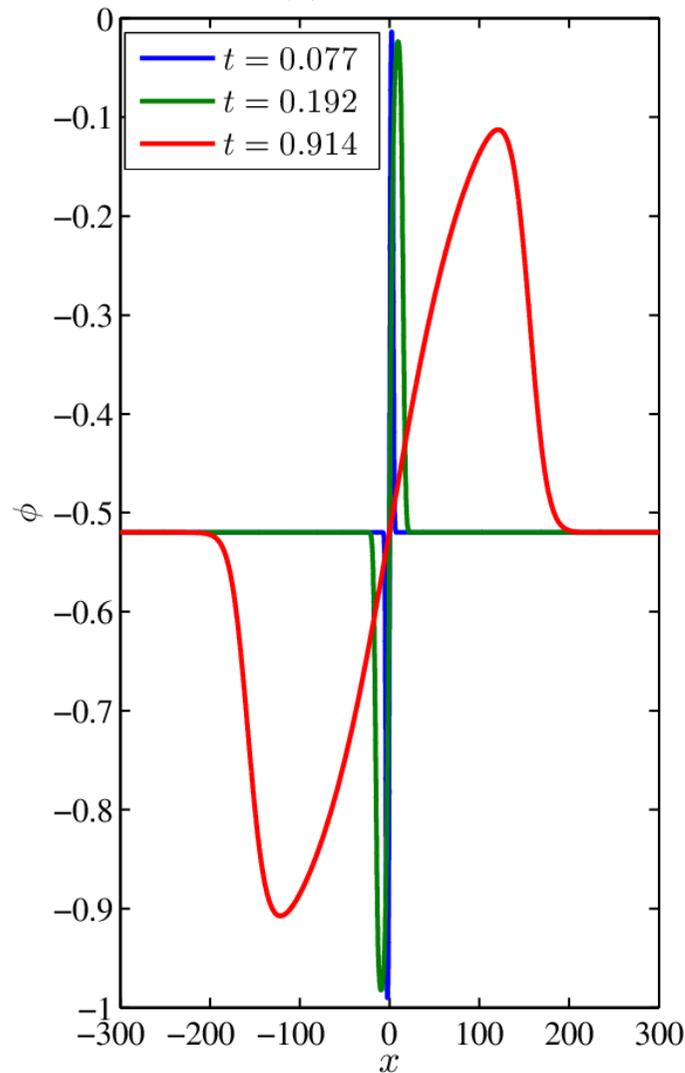
- ❑ The trends are opposite to those of the previous figure.
- ❑ Configs 2 and 3 are more sensitive to reaction kinetics, denoted by  $Da$ .
- ❑ Config. 1 shows almost no sensitivity to the reaction kinetics at all.
- ❑ Reason – config. 1 is not very sensitive to the mass/maximum concentration in the front.
- ❑ Configs. 2 & 3 are stronger functions of the maximum concentration in the front.

## Results – Variations in the potential along the domain centre

(a) *Config. 1*



(b) *Config. 2*



***Points to note:***

- **Config. 1.:** Presence of a zone near the middle, where the potential is nearly constant – the reaction front.
- This zone grows in width with time.
- In rest of the domain – variation of potential almost linear with  $x$ .

***Points to note:***

- **Config. 2.:** Variation is more complex.
- Large changes in the potential where the front is.
- Potential changes sharply at low times; the variation smoothes out as time moves forward.

## Conclusions

- EC changes significantly with time, driven by reaction.
- Net change in the EC is more for configurations 2 and 3.
- Config. 1 is more sensitive to the flow and width/stretching of the front; Shows almost no sensitivity to the reaction kinetics.
- Configs. 2 and 3 – shows sensitivity to flow, but as much as config. 1; Shows good sensitivity to reaction kinetics.
- Overall, the EC strongly depends on the progress of the reaction and front width – can be a potentially promising technique to detect reactive mixing in the subsurface.



**Thank you**