Reactive Transport

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Objective

- Motivate the need for Reactive transport
- Present a methodology to do it

CONTENTS

- Background
  - Framing reactive transport
  - Types of problems: is it needed?
  - A bit of chemistry
- General approach
- Examples
- What about heterogeneity?
Porous media

• Fluid flow
  - Momentum conservation
  - Fluid mass conservation

• Transport
  - Solute mass conservation
  - Advection
  - Diffusion/Dispersion

• Reactive Transport
  - Chemical reactions

• Mechanical deformation
  - Equilibrium
  - Constitutive law (rheology)
  - Compatibility
  - Eff stress law

K, T, S, recharge, B.C’s, geometry

\[
S_s \frac{\partial h}{\partial t} = \nabla (K \nabla h) + w
\]

Dispersivity, porosity

\[
\phi \frac{\partial c}{\partial t} = \nabla (D \nabla c) - q \nabla c = \mathcal{L}(c)
\]

Equilibrium constants and Kinetic rates

\[
\phi \frac{\partial c}{\partial t} = M \mathcal{L}(c) + R
\]

Visco-Elast, failure, ... param

\[
\nabla(\sigma) - b = 0
\]

Increasing math complexity

Increasing practical difficulty

... and we are just starting...
Reactive transport requires **two ingredients**

1) **Transport** (advection, dispersion, mixing, and all that)

2) **Reactions**: many types, complex (**you need to work with someone who knows** the types of reactions we are going to work with), but conceptually easy

3) We need **appropriate nomenclature** to work with these things (**a table** is a flat surface on which you can eat... or work... with 3 or four legs that separate it from the soil...)
But, aren’t there many reactions?

Indeed!

The technology of geochemistry is complex
but not conceptually difficult
Ingredient 1: solute transport

- Advection: $v = q/\phi$ (q proportional to $K$)
- Dispersion: Proportional to: $\alpha q$
- Reactions
- Mass Conservation

\[ \phi \frac{\partial c}{\partial t} = \nabla (D \nabla c) - q \nabla c + f - r \]

Written compactly

\[ L_t (c) = -q \cdot \nabla c + \nabla \cdot (D \nabla c) \]
To simplify chemistry, let us introduce matrix notation ... even better, vector space notation

- **Traditional notation**
  - $\text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^{2-}$
  - $\text{H}_2\text{CO}_3 \rightarrow 2\text{H}^+ + \text{CO}_3^{2-}$

- **Matrix notation**

  $S_e \log a = \log K$

  $ \begin{pmatrix} 1 & 1 & -1 & 0 \\ 2 & 1 & 0 & -1 \end{pmatrix} \begin{pmatrix} \log a_{\text{H}^+} \\ \log a_{\text{CO}_3^{2-}} \\ \log a_{\text{HCO}_3^-} \\ \log a_{\text{H}_2\text{CO}_3} \end{pmatrix} = \begin{pmatrix} \log K_1 \\ \log K_2 \end{pmatrix}$

- $K_1 = \frac{a_{\text{H}^+}a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}}$
- $K_2 = \frac{a_{\text{H}^+}^2 a_{\text{CO}_3^{2-}}}{a_{\text{H}_2\text{CO}_3}}$
Ingredient 2: Chemical reactions: Stoichiometric matrix

- **Assume a chemical system**

  \[
  \begin{align*}
  CO_3^{2-} &= HCO_3^- - H^+ \\
  CO_2 &= HCO_3^- + H^+ - H_2O \\
  Ca^{2+} &= CaCO_3s + H^+ - HCO_3^- 
  \end{align*}
  \]

  Let \( r_i \) be the number of moles of reactants that evolve into products for the \( i \)-th reaction

- **Stoichiometric Matrix** (rows: reactions; columns: species)

  \[
  S = \begin{pmatrix}
    H^+ & HCO_3^- & CO_3^{2-} & CO_2 & Ca^{2+} & CaCO_3s & H_2O \\
    -1 & 1 & -1 & 0 & 0 & 0 & 0 \\
    1 & 1 & 0 & -1 & 0 & 0 & -1 \\
    1 & -1 & 0 & 0 & -1 & 1 & 0
  \end{pmatrix}
  \]

  The columns of \( S \) can be viewed as the contribution of reactions to each species

- **Reaction rate: Mass balance**

  \[
  R = S^t r
  \]

  Contribution of reactions to the mass balance of each species
Reactive transport

- **Reactions**
  
  $r_1 \quad \text{CO}_3^{2-} = \text{HCO}_3^- + \text{H}^+$
  
  $r_2 \quad \text{CO}_2 = \text{HCO}_3^- + \text{H}^+ - \text{H}_2\text{O}$
  
  $r_3 \quad \text{Ca}^{2+} = \text{CaCO}_3 + \text{H}^+ - \text{HCO}_3^-$

  Let $r_i$ be the number of moles of reactants that evolve into products for the $i$-th reaction.

- **Transport of all species**
  
  $\phi \frac{\partial \text{H}^+}{\partial t} = L(\text{H}^+) - r_1 + r_2 + r_3$

  $\phi \frac{\partial \text{HCO}_3^-}{\partial t} = L(\text{HCO}_3^-) + r_1 + r_2 - r_3$

  $\phi \frac{\partial \text{CO}_3^{2-}}{\partial t} = L(\text{CO}_3^{2-}) - r_1$

  $\phi \frac{\partial \text{CO}_2}{\partial t} = L(\text{CO}_2) - r_2$

  $\phi \frac{\partial \text{Ca}^{2+}}{\partial t} = L(\text{Ca}^{2+}) - r_3$

- **Recall $S$**

  $S = \begin{pmatrix}
  H^+ & \text{HCO}_3^- & \text{CO}_3^{2-} & \text{CO}_2 & \text{Ca}^{2+} & \text{CaCO}_3^{\alpha} & \text{H}_2\text{O} \\
  -1 & 1 & -1 & 0 & 0 & 0 & 0 \\
  1 & 1 & 0 & -1 & 0 & 0 & -1 \\
  1 & -1 & 0 & 0 & -1 & 1 & 0
  \end{pmatrix}$

  Primary \quad Secondary \quad Constant Ac.
Formulation of Reactive transport problems

\[ \frac{\partial c}{\partial t} = M \Lambda(c) + S_e^t r_e + S_k^t r_k(c) \quad n_s \text{ transport equations} \]

\[ S_{ea} \log c_a = \log K \quad n_r \text{ algebraic equations} \]

\[ r_k = r_k(c) \]

Looks awful! \((n_r + n_s \text{ unknowns at every point})\)

Seek tricks and/or simplifications

And, thus, insight
So... objectives of this presentation

- Is reactive transport needed?
  - Wouldn't it be sufficient to find the residence time distribution to find out the total amount of reactions?
- Can be understood?
- Can be solved efficiently?
  
  ... and the answer is YES

- Do we really know how to do it?
  
  ... not quite... but getting there
  
  ... hopefully
Why worry about reactive transport? 

Ex: Karst development in coastal areas

Waters 1 and 2 are in equilibrium. Yet, the mixture is undersaturated.
Calcite dissolution in coastal aqf.

Mixture of two calcite saturated waters may be under or oversaturated with respect to calcite.

To simulate this effect, consider 1D diffusion experiment.
Saturation Index

\[ SI = \log \left( \frac{[CO_3^{2-}][Ca^{2+}]}{K_s} \right) \]

- SI > 0  Oversaturated \Rightarrow Precipitation
- SI = 0   Equilibrium
- SI < 0  Undersaturated \Rightarrow Dissolution

![Graph](image_url)
Simple mixing (no transport)

Saturation Index (SI)

Mixing leads to maximum undersaturation for 20% fresh water and max. dissolution for 50% mixing

Dissolution rate (controlled by diffusion)

Reaction Rate

Dissolution rate proportional to Diff coeff. and maximum at the fresh water end
Speciation

Dissolution causes diffusion of CO$_2$ (acidity) at the freshwater end, which drives further dissolution.
Sensitivity to $CO_2$

Reducing concentration of $CO_2$ at the freshwater end, causes an increase in subsaturation. Therefore, one would expect an increase in dissolution rate.

However, dissolution rate is dramatically reduced.
First conclusion

The interplay between transport and reactions is non-trivial. Saturation index calculations are needed but they fail to indicate
1) how much calcite is dissolved, which is controlled by mixing rate,
2) nor where (or under which conditions) dissolution rate is maximum.

Simulating reactive transport is needed to understand the fate of reacting solutes!

(Rezaei et al, 2005)
Still, isn’t it too difficult?

• Yes, if using brute force
• However, a number of “tricks” are possible, depending on the type of chemical system
  - If all reactions in equilibrium (Desimoni et al, 2005)
  - If also kinetic reactions (Molins et al, 2007)
  - In general (Saaltink et al, 1998)
The basic trick: components

\[
\frac{\partial \mathbf{c}}{\partial t} = M \mathbf{L}(c) + S_e^t \mathbf{r}_e + S_k^t \mathbf{r}_k(c)
\]

Choose component matrix \( U \), such that

\[
US_e^t = 0 \implies US_e^t \mathbf{r}_e = 0
\]

Then,

\[
U \frac{\partial \mathbf{c}}{\partial t} = UML(c) + US_k^t \mathbf{r}_k(c)
\]

\( n_s - n_r \) transport equations.

(A good choice of \( U \) allows to decouple (some of) these equations!)

Components: \( u = U \mathbf{c} \)

Linear combinations of species that remain unaltered by equilibrium reactions.
Example

- **Chemical system**
  \[ CO_3^{2-} = HCO_3^- - H^+ \]
  \[ CO_2 = HCO_3^- + H^+ - H_2O \]
  \[ Ca^{2+} = CaCO_3 + H^+ - HCO_3^- \]

- **Stoichiometric Matrix**
  \[ S_e = (S_1 ; -I) \]
  \[
  S_e = \begin{pmatrix}
  H^+ & HCO_3^- & CO_3^{2-} & CO_2 & Ca^{2+} \\
  -1 & 1 & -1 & 0 & 0 \\
  1 & 1 & 0 & -1 & 0 \\
  1 & -1 & 0 & 0 & -1
  \end{pmatrix}
  \]

- **Components matrix**
  \[ U = (I ; S_1^+) \]
  \[
  U = \begin{pmatrix}
  H^+ & HCO_3^- & CO_3^{2-} & CO_2 & Ca^{2+} \\
  1 & 0 & -1 & 1 & 1 \\
  0 & 1 & 1 & 1 & -1
  \end{pmatrix}
  \]

- **Components**
  \[ u_1 = H^+ - CO_3^{2-} + CO_2 + Ca^{2+} \] (acidity)
  \[ u_2 = HCO_3^- + CO_3^{2-} + CO_2 - Ca^{2+} \] (Total Inorganic Carbon)
Role of components

\[
\phi \frac{\partial H^+}{\partial t} = L(H^+) - r_1 + r_2 + r_3 \\
\phi \frac{\partial HCO_3^-}{\partial t} = L(HCO_3^-) + r_1 + r_2 - r_3 \\
\phi \frac{\partial CO_3^{2-}}{\partial t} = L(CO_3^{2-}) - r_1 \\
\phi \frac{\partial CO_2}{\partial t} = L(CO_2) - r_2 \\
\phi \frac{\partial Ca^{2+}}{\partial t} = L(Ca^{2+}) - r_3 \\
\]

\[
\begin{pmatrix}
H^+ & HCO_3^- & CO_3^{2-} & CO_2 & Ca^{2+} \\
1 & 0 & -1 & 1 & 1 \\
0 & 1 & 1 & 1 & -1
\end{pmatrix}
\]

Components are linear combinations of species such that equilibrium r’s cancel out, so that \( \phi \frac{\partial u_1}{\partial t} = L(u_1) \)
# Procedure

1. Define **chemical system** and components

2. Solve transport equations for **components** (and/or primary species)

3. **Speciation**: Compute species concentrations from components (and/or primary species)

4. Substitute species back into transport equations to obtain **reaction rates**
Analytical solution for 2 species

Assume 2 species (e.g. SO$_4^{2-}$ and Ca$^{2+}$) in eq. with gypsum

**Step 1: Chemical system**

Reaction $\text{Ca}^{2+} + \text{SO}_4^{2-} \overset{\text{CaSO}_4}{\rightarrow} [\text{Ca}^{2+}] \cdot [\text{SO}_4^{2-}] = K$

Stoichiometric matrix $S_e = (-1 \quad -1 \quad 1)$

Components: $U = (1 \quad -1) \Rightarrow u = [\text{Ca}^{2+}] - [\text{SO}_4^{2-}]$ is conservative!

**Step 2: Solve transport of $u$**

Transport equations

where $L_4(c) = -q \cdot \nabla c + \nabla \cdot (D \nabla c)$

$\frac{\partial (\phi C_1)}{\partial t} - L_4(C_1) = -r \quad (1)$

$\frac{\partial (\phi C_2)}{\partial t} - L_4(C_2) = -r \quad (2)$

$(1)-(2)$ yields: $\frac{\partial (\phi u)}{\partial t} = L_4(u)$
Step 3: Speciation

Solve

\[ u = C_1 - C_2 \]

Together with \[ C_1 \cdot C_2 = K \]

\[ C_1 = \frac{u + \sqrt{u^2 + 4K}}{2} \]

\[ C_2 = \frac{-u + \sqrt{u^2 + 4K}}{2} = C_2(u) \]

Step 4: Compute \( r \)

Plugging \( C_2 \) into

\[ \frac{\partial (\phi C_2)}{\partial t} - L_4(C_2) = -r \]

\[ L_4(c) = -q \cdot \nabla c + \nabla \cdot (D \nabla c) \]

We obtain

\[ r = \frac{\partial^2 C_2}{\partial u^2} [\nabla u^T \cdot D \cdot \nabla u] \]

\[ \frac{\partial^2 C_2}{\partial u^2} = \frac{2K}{(u^2 + 4K)^{3/2}} \]

Chemistry

Transport
Mixing of several waters

Step 3: Speciation

Can be very complex, but \( C_2 = C_2(\alpha) \)

Where \( \alpha \) is the mixing ratio (possibly a vector)

Step 4: Compute \( r \)

Plugging \( C_2 \) into \( \frac{\partial (\phi C_2)}{\partial t} - L_4 (C_2) = \]

We obtain \( r = \frac{\partial^2 C_2}{\partial \alpha^2} \left[ \nabla \alpha^T \cdot D \cdot \nabla \alpha \right] \)

That is,

1) Transport \( \alpha \)
2) Use any code (e.g., PHREEQE, RETRASO,...) to compute speciation
Mixing rate controls (fast) reactions

- Mixing controls fast chemical reactions
  (de Simoni et al, 2005, 2007; Valocchi & Cirpka, 2007)

- In fact, reaction rate of equilibrium reactions
  \[ r = \mathbf{H} \mathbf{c}^T \mathbf{D} \mathbf{c} = f_Q \cdot f_m \]

- Natural choice for (local) mixing rate
  \[ f_m = \nabla^T c \mathbf{D} \nabla c \]
  (de Simoni et al, 2005, 2007; Kitanidis, 1994)
In the case of aqueous and dissolution-precipitation reactions in equilibrium:

1. Reactive Transport is indeed easy!
2. Only need to solve for independent components. In the calcite example: 2 components are needed (+salinity)...
   Actually, it suffices to work with mixing ratios... (Desimoni et al., 2007). And, now, not even that (just mixing rates!)

3. Mixing drives fast reactions
Does it work?

- Slower than predicted reaction rates

Far slower than predicted reaction rates

(White & Peterson, 1990)
But do we know how to represent mixing? Does dispersion represent mixing?

Dispersion = the rate of growth of plumes

Therefore Dispersion = spreading rate

Mixing reflects local gradients (internal disorder within a plume)

\[ D = \frac{1}{2} \frac{\partial \sigma_{ii}^2}{\partial t} \]
Non-local (in t) formulations for RT

Willmann et al (WRR, 2010) simulated RT through heterogeneous medium

Conservative Component

reaction rates

\[ r(x, z, t) = H \cdot \nabla^T c \cdot D \cdot \nabla c \]
Non-local (in t) formulations for RT

Willmann et al (WRR, 2010) predicted quite accurately the overall (integrated in $t$ and $z$) reaction rate, and thus mixing using a MRMT formulation. Non-local formulations reproduce mixing, but Willman required a tracer test to characterize memory function, can it be defined from site characterization?
Conclusion 2

- Non-local formulations reproduce
  - Scale dependence of dispersion (spreading)
  - Scale dependence of apparent porosity
  - Tailing
  - Not too bad for reaction rates (mixing)
  - and easy to implement in existing codes!

- Mixing is the critical issue, but:
  - Can mixing be defined from geological characterization?
  - Is it true that mixing well represented by MRMT?
OBJECTIVE

• Test validity of MRMT
  - First, separate mixing from spreading
  - Second, select right memory function
Numerical simulations of mixing in heterogeneous porous media

- Multi-lognormal permeability fields
- Log permeability field variance $s^2_{\ln K}$
- Gaussian correlation function
- Correlation length $\lambda = 10$
- Permeator boundary conditions
- Steady flow

- Initial line injection
- Domain size 512x8192
- Local advection-diffusion
- Peclet number:

$$Pe = \frac{\lambda v \nabla h}{D} = 10^2 - 10^3$$
Differentiating mixing and dispersion

Pure dispersion

Spreading, but no dilution

2\sigma_X

Pure mixing

Dilution, but no spreading

\sigma_C
Global mixing and spreading

Spreading (characterized by $\sigma_x$)

Mixing characterized by global mixing rate

$\chi(t) = \int_\Omega D \left| \nabla c(x, y, t) \right|^2 \, dx \, dy$

$= \frac{d}{dt} \int_\Omega c^2 \, dx \, dy$

incomplete mixing
Use dissipation rate to compute overall mixing

Overall mixing rate

\[ \chi(t) = \int_{\Omega} \nabla c(x,y,t) \cdot D \nabla c(x,y,t) dV = \frac{1}{2} \frac{d}{dt} \left( \int_{\Omega} c^2(x,y,t) dV \right) = \frac{1}{2} \frac{d}{dt} M_2 \]

Mixing state

Separate mixing rate (and state) into macrodispersion driven (reference) and internal disorder driven
Separating mixing and spreading?

1. Decompose $c$:

$$ C = \bar{c} + c' $$

2. Vertical averaging

$$ \bar{c}(x,t) = \frac{1}{L_y} \int_{0}^{L_y} c(x,y,t) dy $$

3. Compute variance of averaged concentration (reference mixing state, controlled by macrodispersion)

$$ M_1(t) = \int_{0}^{L_x} \bar{c}^2 dx \quad M_G = \frac{m_0^2}{2L_x \sqrt{\pi} \sigma_L} $$

4. Compute "internal mixing" (caused by internal disorder):

$$ M_2(t) = \int_{\Omega} (c')^2 dV $$
Separating mixing and spreading?

\[ M_1(t) = \int_0^{L_x} \bar{c}^2 \, dx \quad M_G = \frac{m_0^2}{2L^2 \sqrt{\pi} \sigma_L} \quad M_2(t) = \int_\Omega (c')^2 \, dV \]

1. Clearly:

\[ M(t) = \int_\Omega c^2 \, dx \quad M_G + M_2 \]

2. Therefore, it is natural to measure "internal disorder" by:

\[ \gamma(t) = \frac{M_2(t)}{M_G(t)} = \frac{M(t) - M_G(t)}{M_G(t)} \]
Characterizing the $\gamma$ function

Mixing and spreading identical at late times (even though not fully mixed)
$\sigma^2 = 1$

$\sigma^2 = 9$
understanding the $\gamma$ function

$\sigma^2 = 1$

$\sigma^2 = 9$
understanding the $\gamma$ function

$t=3.3$

$\sigma^2=1$

$\sigma^2=9$
understanding the $\gamma$ function
understanding the $\gamma$ function
Variance of $c'$

[Kapoor and Gelhar, 1994; Kapoor and Kitanidis, 1998]

Smoothing (variance reduction by diffusion)

\[
M'_2(t) + \frac{2d}{(a \varepsilon(t))^2} M_2(t) = -M'_G(t)
\]

Mixing scale (Le Borgne et al, 2011)

Velocity shear creates disorder

It works!

(De Dreuzy et al., WRR, 2012)
Characterizing $\gamma_{\text{max}}$ and $t_{\text{max}}$

$t_{\text{max}}$ Drops down with $Y$ variance

$\gamma_{\text{max}} \big/ \sqrt{\text{Pe}}$ Grows linearly with $Y$ variance
MRMT formulations do reproduce the shape of gamma
But not the actual values!
Summary and conclusions

- Spreading can be described by the pdf and transition pdf of veloc, which leads to CTRW, MRMT, fADE, ...

- These formulations overcome the ADE problems, but rely heavily on a proper characterization of mixing.

- We developed methodology for effective mixing that relies on the evolution of the variance of c'.

- Non local equations parameters (memory function) look valid, but not quite.

- Any idea?
REFERENCES
REFERENCES (2)


Redox reactions involve exchange of electrons (e\textsuperscript{-}). The species giving electrons away is called "electron donor", the one receiving is the "electron acceptor", eg.

\[
\begin{align*}
\text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + e^- \\
\text{O}_2 + 4\text{H}^+ + 4e^- & \rightarrow 2\text{H}_2\text{O}
\end{align*}
\]

\[
4 \text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O}
\]

Iron is donor (is oxidized). Oxygen is acceptor (is reduced).

These reactions are exothermic. Life on Earth is sustained on the energy freed by these reactions.
Biochemical reactions: the natural redox cycle

- Redox reactions catalyzed by microorganisms
- Special case: organic matter degradation, the electron donor is organic matter (generically, CH$_2$O). The natural sequence is:
  - $\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ \hspace{1cm} $\Delta G=120$ kcal/mol C
  - $\text{CH}_2\text{O} + 0.8\text{NO}_3^- + 0.8\text{H}^+ \rightarrow \text{CO}_2 + 0.4\text{N}_2 + 1.4\text{H}_2\text{O}$ \hspace{1cm} $\Delta G=114$
  - $\text{CH}_2\text{O} + 2\text{MnO}_2 + 4\text{H}^+ \rightarrow \text{CO}_2 + 2\text{Mn}^{2+} + 3\text{H}_2\text{O}$ \hspace{1cm} $\Delta G=81$
  - $\text{CH}_2\text{O} + 4\text{Fe(OH)}_3 + 8\text{H}^+ \rightarrow \text{CO}_2 + 4\text{Fe}^{2+} + 11\text{H}_2\text{O}$ \hspace{1cm} $\Delta G=28$
  - $\text{CH}_2\text{O} + 0.5\text{SO}_4^{2-} + \text{H}^+ \rightarrow \text{CO}_2 + 0.5\text{H}_2\text{S} + \text{H}_2\text{O}$ \hspace{1cm} $\Delta G=25$
  - $\text{CH}_2\text{O} (0.5 \text{CH}_2\text{O} + 0.5 \text{CH}_2\text{O}) \rightarrow 0.5\text{CO}_2 + 0.5\text{CH}_4$ \hspace{1cm} $\Delta G=22$

The most efficient organisms dominate each stage, inhibiting the development of the ones below. Yet, their success is their nemesis, as they exhaust their electron acceptor. This opens the path for the next organism down the ladder, which dominates the next stage. Overall, this leads to a natural zonation.
Why biological degradation

- Control metal mobility
  - Many immobile when sulphide present
  - Some immobile in aerobic conditions
- Control degradation of organic matter
- Highly reducing conditions allow eliminating “recalcitrant” compounds
  - That are not eliminated in “normal” treatment
  - That are often endocrine inhibitors
Redox zones at the Vejen (Denmark) landfill

Organic compounds and, specifically, the most recalcitrant ones have disappeared.

Water contains Fe$^{2+}$, Mn$^{2+}$, etc.

With SO$_4^-$, some NO$_3^-$

With SO$_4^-$, but not CH$_4$, etc

Water contains Fe$^{2+}$, Mn$^{2+}$, H$_2$S, CH$_4$, etc
Conclusions

• Is Reactive transport needed?
  – Reaction (rate, where, when, under which conditions) are controlled by transport.

• Can be understood?
  – All it takes is to understand components
  – The difficult part is to choose the relevant species and reactions.

• Can be solved efficiently?
  – Similar effort as conservative transport
Reactions are driven by disequilibrium

Disequilibrium is driven by actual mixing

We need to know how to evaluate actual mixing!

Current stochastic transport theories fail to do so!