MULTIPHASE CHEMICAL KINETICS MODELING FOR AQUEOUS-MINERALS REACTIVE SYSTEMS

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Advances in the **SI**mulation of reactive flow and **TRA**nsport in porous **M**edia

Outline

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Motivation::Modeling Context

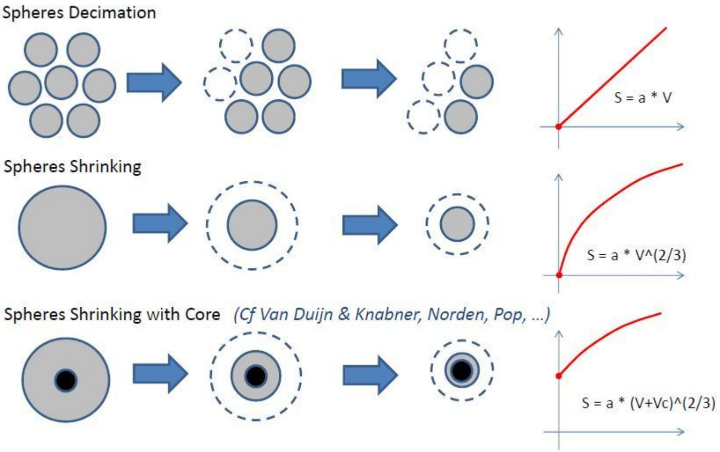
- MultiPhase Chemical System
  - Gas = {H2O(g), CO2 , CH4}
  - Water = {H2O, H+, OH-, HCO3-, CO2(aq), Ca++, CO3– , Na+, Cl-, SiO2(aq)}
  - Calcite = {CaCO3(s)}
  - Quartz = {SiO2(s)}
  - Halite = {NaCl(s)}
- Kinetic Reactions
  - Rkin1: CO2 $\leftrightarrow$ CO2(aq) $[\tau_1]$
  - Rkin2: H2O(g) $\leftrightarrow$ H2O $[\tau_2]$
  - Rkin3: SiO2(aq) $\leftrightarrow$ SiO2(s) $[\tau_3]$
  - Rkin4: Na+ + Cl- $\leftrightarrow$ NaCl(s) $[\tau_4]$

#Phases = 5, #Species = 16, #Reactions = 4

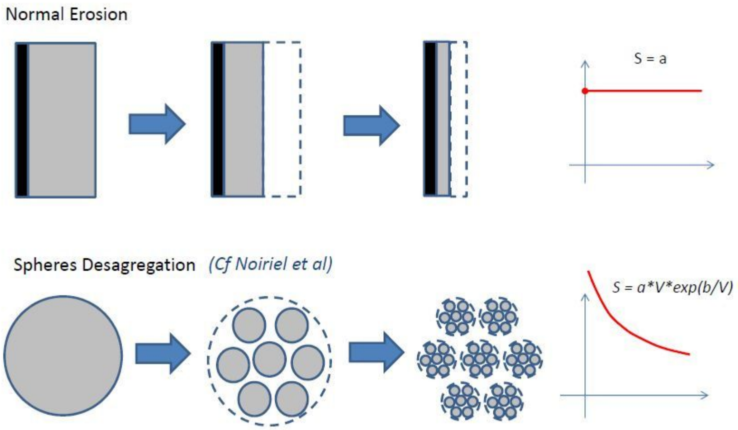
Motivation::Standard Kinetics Model

- Unknowns
  - $n(t) = \{n_i(t)\}_{i \in Species},\; t \in [0, T]$
- Equations
  - $dn_i/dt = \sum_{j \in Reactions} S_{i,j}\tau_j$
  - $n_i(t = 0) = n_i^0$
- Constraints
  - $ni(t) \geq 0$
- Kinetic Law (Law Of Mass Action)
  - $\tau_j = -k_j\, Sr_j \left(\prod_{i, S_{i,j}>0} (a_i/K_i)^{|S_{i,j}|} - \prod_{i, S_{i,j}<0} (a_i/K_i)^{|S_{i,j}|} \right)$
- Activity Model (Ideal Mixing Model)
  - $a_i = x_i$

Motivation::Reactive Surface Models 1/2



Motivation::Reactive Surface Models 2/2

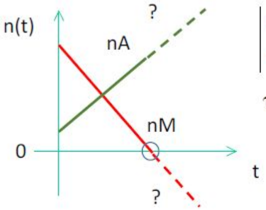


Outline

Limited Kinetics Model::One Mineral With One Reaction Models

- Chemical System:
  - Water = {H2O, A}
  - Mineral = {M}
- Kinetic Reactions:
  - Rkin: A $\leftrightarrow$ M $[\tau]$

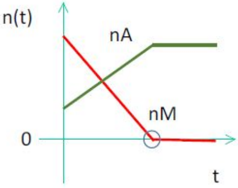
(H) Mineral dissolution domain: $x_A < KA/KM \implies \tau < 0$



Standard Model

$$\begin{cases} dnA/dt = -\tau \\ dnM/dt = \tau \end{cases}$$

$$\tau = -k * (1/KM - xA/KA)$$



Limited Model

$$\begin{cases} dnA/dt = -r \\ dnM/dt = r \end{cases}$$

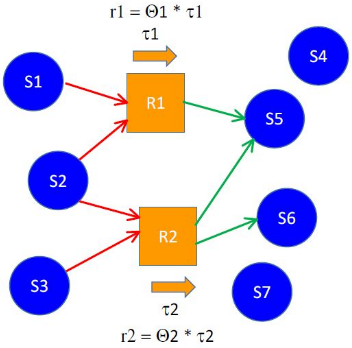
$$r = \tau\hat{}(+) - hM * \tau\hat{}(-)$$
$$= \theta * \tau$$

$$hM = \begin{cases} 0 \text{ if } nM <= 0 \\ 1 \text{ else} \end{cases}$$

$$\Theta = \begin{cases} 0 \text{ if } \tau < 0 \text{ and } nM <= 0 \\ 1 \text{ else} \end{cases}$$

Limited Kinetics Model::Generalized Limited Kinetics Model

- Unknowns:
  - $n(t) = \{n_i(t)\}_{i \in Species},\ t \in [0, T]$
- Equations:
  - $dn_i/dt = \sum_{j \in Reactions} S_{i,j} r_j$, with $r_j = \theta_j \tau_j$
  - $n_i(t = 0) = n_i^0$
- State Variables constraints:
  - $ni(t) \geq 0$
- Control Variables constraints:
  - $\theta_j \in [0, 1]$
  - $\theta_j = 1$ if $\min_{\{i, S_{i,j} < 0\}}(n_i) > 0$

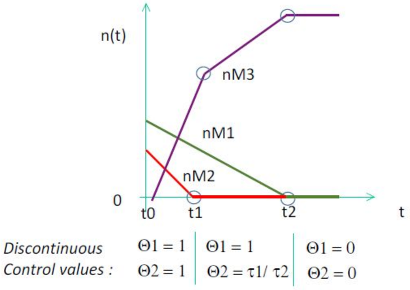


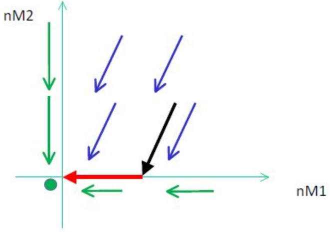
Reactive System Graph and Upwind Limited Kinetics

Limited Kinetics Model::Example

- Chemical System:
  - Min1 $= \{M1\}$
  - Min2 $= \{M2\}$
  - Min3 $= \{M3\}$
- Kinetic Reactions:
  - Rkin1: M1 $\leftrightarrow$ M2 $[\tau_1]$
  - Rkin2: M2 $\leftrightarrow$ M3 $[\tau_2]$
- Equations:

$$\begin{cases} dnM1/dt = -\theta_1\tau_1 \\ dnM2/dt = \theta_1\tau_1 - \theta_2\tau_2 \\ dnM3/dt = \theta_2\tau_2 \end{cases}$$



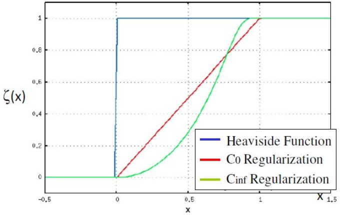


Limited Flow and Trajectory
In the plane (nM1,nM2)

Outline

Limited Model Study[1]::Regularization Approach, Definition

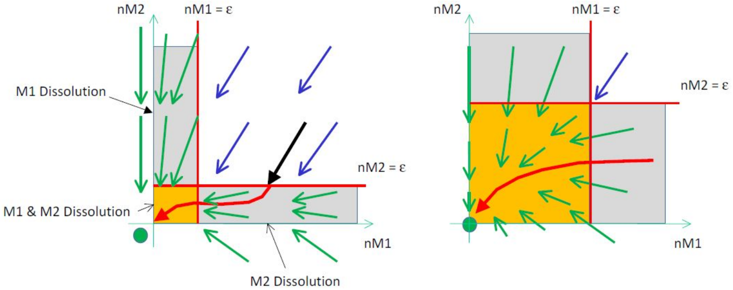
- Regularized Model Equations:
  - $dn_{i,\varepsilon}/dt = \sum_{j \in Reactions} r_{j,\varepsilon}$, with $r_{j,\varepsilon} = \theta_{j,eps}\tau_j$
  - $n_{i,eps}(t=0) = n_i^0$
- Where:
  - $\theta_{j,eps} = f^{Blend}(f_j^{Upwind}(h_\varepsilon))$
  - $h_{i,\varepsilon} = \zeta(n_i/\varepsilon)$: Regularized step limiter
  - f_j^{Upwind}: Filtering of upwind species
  - f^{Blend}: Blending operator ($fMin$, $fProd$,...)
- Regularized step functions:



Heaviside Smoothing Functions

Limited Model Study[1]::Regularization Approach, Example

- Equations: $\begin{cases} dnM1/dt = -\theta_{1,eps}\tau_1 \\ dnM2/dt = \theta_{1,eps}\tau_1 - \theta_{2,eps}\tau_2 \\ dnM3/dt = \theta_{2,eps}\tau_2 \end{cases}$



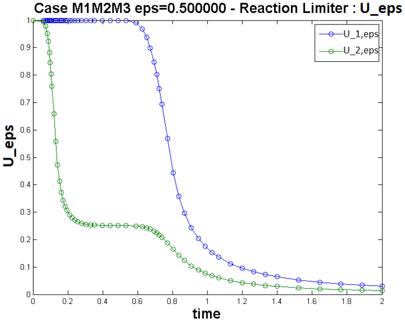
Regularized Flow And Trajectory In the plane (nM1,nM2)

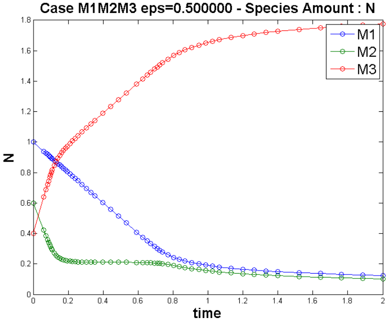
Zoom on the Blending Zone Co-Dissolution of M1 and M2

Limited Model Study[1]::Regularization Approach, Application

- Equations: $\begin{cases} dnM1/dt = -\theta_{1,eps}\tau_1 \\ dnM2/dt = \theta_{1,eps}\tau_1 - \theta_{2,eps}\tau_2 \\ dnM3/dt = \theta_{2,eps}\tau_2 \end{cases}$

(H) Standard rates: $\tau_1 = 1, \tau_2 = 4 \implies \tau_1/\tau_2 = 0.25$





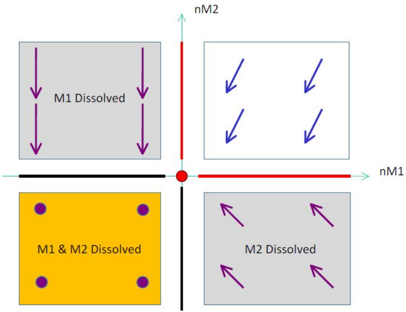
Limited Model Study[2]::Differential Inclusion Approach, Definition

Let B be a sign combinatorics matrix associated to the set of *Species*.
Let $D_k = \{n \in R^{Species}, sign(n_i) = B_i^k\}$

- Piecewise Discontinuous Flow Field :
  - $f_k(n) = \sum_{i \in Species} S_{i,j} r_{j,k}$ if $n \in D_k$, where $r_{j,k} = \theta_{k,j} \tau_j$
- With:
  - $\theta_{j,k} = f^{Prod}(f_j^{Upwind}(\mathcal{H}(n))) = \begin{cases} 1 \text{ if } B_i^k = +1, \forall i \text{ such that } S_{i,j} < 0 \\ 0 \text{ else} \end{cases}$
- Filippov Differential Inclusion Equations:
  - $dn_i/dt = f^{RHS} \in F(n) = Convex(f_k(n)) = \sum_{k \text{s.t.} n \in V(D_k)} \lambda_k f_k(n)$
  - $n_i(t = 0) = n_i^0$

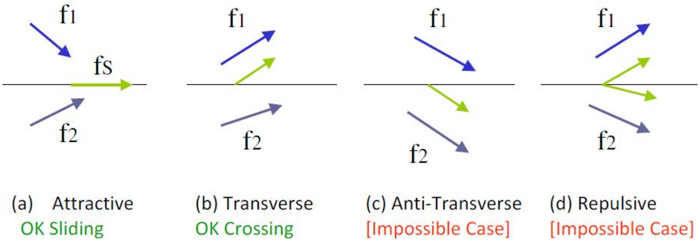
Limited Model Study[2]::Differential Inclusion Approach, Example

- Equations: $$\begin{cases} dnM1/dt = -\theta_{1,k}\tau_1 \\ dnM2/dt = \theta_{1,k}\tau_1 - \theta_{2,k}\tau_2 \\ dnM3/dt = \theta_{2,k}\tau_2 \end{cases}$$



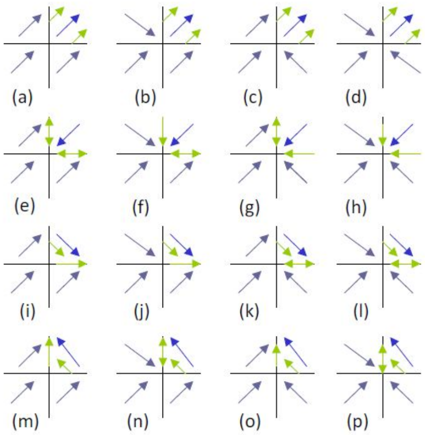
Filippov Piecewise Discontinuous Flow
Sub-Domains and Discontinuity Surfaces

Limited Model Study[2]::Differential Inclusion Approach, Results



Co-dimension 1 cases and Classification

Limited Model Study[2]::Differential Inclusion Approach, Results



(a) OK Transverse
(b) OK Semi-Transverse
(c) Idem (b)
(d) **Not OK : We have to consider the case (0,0) is in convex hull**
(e) OK Attractive Sliding, [Impossible Repulsive] and Sliding Exit idem (f)
(f) OK Attractive Sliding
OK Sliding Exit if (0,0) not in convex hull
(g) Idem (f)
(h) OK Attractive Sliding
(i) OK Outcoming/Transverse (because (0,0) not in convex hull)
(j) Idem (i)
(k) OK Incoming/Transverse
OK Outcoming/Transverse if (0,0) not in convex hull
(l) Idem (k)
(m) Idem (i)
(n) Idem (k)
(o) Idem (i)
(p) Idem (k)

Co-dimension 2 cases and Classification

Limited Model Study[3]::Projected Dynamics Approach

- Projected Dynamics Model Equations:
  - $dn_i/dt = f_i^{Proj}(n)$
  - $n_i(t=0) = n_i^0$

- Where:
  - $f^{Proj}(n)$ is "a projected right hand side" solution of

$$\mathcal{P}(n) : \begin{cases} min \|f - S\tau(n)\|^2 \\ f \in Tc[(R_*^+)^{Species}](n) \\ f_i = \mu_i * S\tau(n) \text{ with } \mu_i \in [0,1] \\ f \in Im(S) \end{cases}$$

Outline

1. Motivation
2. Limited Kinetics Model
3. Limited Model Study
4. Conclusion and Perspectives

Conclusion and Perspectives

- Results
  - A New Generalized Limited Kinetics Model
  - Mathematical study by 3 different Approaches
- Mathematical Issues
  - Additional criteria required to qualify "good solutions" in case of non uniqueness
  - Classification of co-dimension 2 discontinuities to be completed
- Numerical Issues
  - Stiffness of the Regularized Model may avoid large time steps
  - Projected Dynamics algorithm is not fully implicit
- Perspectives
  - Simulation of Multiphase Reactive Transport with Kinetics and Equilibrium
  - Extension to Mixture Phases and Kinetics
  - Study of "Complementarity Type" Global Implicit Formulations

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