Upscaling Coupled Pore-Scale Reactive Transport Processes to the Continuum Scale

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OUTLINE

• Motivation

• Multi-Scale Continuum Model

• Pore-Scale Models: Lattice Boltzmann & Pore Network Models

• Examples
  – Fracture Media
  – Structured Porous Media

• Conclusion
Reasons for Upscaling Pore-Scale to Continuum Scale

- Validate continuum model
  - Does simple volume averaging work?
  - Obtain continuum constitutive relations from pore-scale model

- Determine form of continuum model (single, dual, …) best suited for given porous medium

- Use pore-scale model to understand effects of multiscale processes at the continuum scale
Multi-Scale Processes
Multi-Scale, Multicomponent Reactive Transport Equations

Primary (bulk) domain:
\[
\frac{\partial}{\partial t} \left( \epsilon_b \varphi_b \Psi_j^b + S_j \right) + \nabla \cdot \epsilon_b \Omega_j^b = \sum_k A_{kb} \Omega_j^{kb} - \sum_s \nu_{js} I_s^b
\]

Secondary (kth matrix) domain:
\[
\frac{\partial}{\partial t} \left( \varphi_k \Psi_j^k + S_j^k \right) + \nabla \cdot \Omega_j^k = -\sum_s \nu_{js} I_s^k
\]

Boundary condition and interfacial flux:
\[
C_j^k (r = r_k, t; r) = C_j^b (r, t), \quad \Omega_j^{kb} = -\varphi_k D_k \left( \frac{\Psi_j^k - \Psi_j^b}{d_{kb}} \right)
\]
Pore-Scale Models

- **Pore-Network Model**
  - Abstraction of pore geometry: pore-scale heterogeneity unconstrained
  - Does not discretize pore space: pore-scale gradients not represented
  - Can handle larger domains compared to LBM
  - Treats minerals reactions through volume averaged rate

- **Lattice Boltzmann Model (LBM)**
  - Resolves individual pore space
  - Compute pore velocity (solves Navier-Stokes equations)
  - Treats mineral reactions as boundary condition at fluid-solid interface
  - Smallest practical resolution ~ 0.1 µm
  - Difficult to impossible to resolve solid phase at very small scales
Evolution equation for particle distribution function

\[ f_\alpha (x + e_\alpha \delta t, t + \delta t) = f_\alpha (x, t) - \frac{f_\alpha (x, t) - f_\alpha^{eq} (\rho, u)}{\tau_f} \]

\[ \rho = \sum_\alpha f_\alpha \quad \rho u = \sum_\alpha e_\alpha f_\alpha \]

D2Q9 lattice

D3Q19 lattice
LBM METHOD OF SOLUTION

• Explicit Finite Difference
  – Streaming \( f_i(x + e_i \delta t, t + \delta t) = f^*_i(x, t) \)

  – Collision \( f^*_i(x, t) = f_i(x, t) - \frac{f_i(x, t) - f^e_i(\rho, u)}{\tau_f} \)

  – Courant-Friedrichs-Lewy Condition \( \text{CFL} = \frac{|e_\alpha|}{\delta x} \frac{\delta t}{\delta x} \leq 1 \)

• Equivalent to Navier-Stokes Equations

• Easily Parallelizable
LATTICE BOLTZMANN METHOD FOR MULTI-COMPONENT REACTIVE TRANSPORT

- **Evolution Equation for Particle Distribution Function**
  \[
g_{a_j}(x + e_\alpha \delta t, t + \delta t) = g_{a_j}(x, t) - \frac{g_{a_j}(x, t) - g_{a_j}^e(C_j, u)}{\tau_{aq}}
  \]

- **Pore Scale Convection-Diffusion-Reaction Equation**
  \[
  \frac{\partial \Psi_j}{\partial t} + (u \cdot \nabla) \Psi_j - \nabla \cdot (D \nabla \Psi_j) = 0 \quad \Psi_j = \sum_{\alpha} g_{a_j}
  \]

- **Surface Reaction Boundary Condition**
  \[
  D \frac{\partial C_j}{\partial n} = \sum_{i=N_c+1}^{N} \nu_{ji} I_i^* + \sum_{m=1}^{N_m} \nu_{jm} I_m^*
  \]
  \[
  D \frac{\partial C_i}{\partial n} = -I_i^*
  \]
  \[
  D \frac{\partial \Psi_j}{\partial n} = \sum_{m=1}^{N_m} \nu_{jm} I_m^*
  \]
  \[
  I_m^* = -k_m \lambda_m (1 - K_m Q_m)
  \]
Moving Boundary Problem: Dissolution and Precipitation in LBM

- Treat solid phase as continuum
  - More than one mineral may coexist at a single node
  - Solid concentration calculated using continuum-based equation:
    \[ \phi_m(r_Q, t + \delta t) = \phi_m(r_Q, t) + \delta t \overline{V_m} a_m I_m^*(r_Q, t) \]
  - Surface area \(a_m\) based on lattice spacing and may include roughness factor

\[ \phi_m(r_Q, t + \Delta t) = 0, \text{ node } Q \text{ removed,} \]
\[ \phi_m(r_Q, t + \Delta t) > 1, \text{ node } R, S \text{ or } T \text{ randomly chosen to become solid node with probability ratio: } P_S = 4P_R = 4P_T. \]
LBM Calculation of Tortuosity

Spatial distribution of concentration at time = 5.21 x 10^5 s

\[ \tau = 1 \]

\[ \tau = 0.76 \]

Control volume (REV)
Fracture-Matrix Interaction
Discrete Fracture Model

Taylor Dispersion 1.5 mm

Continuum Model

- No dispersion
- With dispersion

Fracture (LB simulation)
Matrix (LB simulation)
Example: Structured Porous Medium
# Model Geometry and Continuum Fit Parameters

Table 1: LB geometry and parameters for continuum model. One lattice unit equations $1.25 \times 10^{-4}$ m.

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Units</th>
<th>Bulk</th>
<th>Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Length</td>
<td>$(L_b)$</td>
<td>cm</td>
<td>4</td>
<td>—</td>
</tr>
<tr>
<td>System Width</td>
<td>$(L_w)$</td>
<td>cm</td>
<td>1.2</td>
<td>—</td>
</tr>
<tr>
<td>Matrix Block Size</td>
<td>$(l_m)$</td>
<td>mm</td>
<td>—</td>
<td>3.5</td>
</tr>
<tr>
<td>Channel Width</td>
<td>—</td>
<td>mm</td>
<td>—</td>
<td>0.5</td>
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<tr>
<td>Channel Length</td>
<td>—</td>
<td>mm</td>
<td>—</td>
<td>9.0</td>
</tr>
<tr>
<td>Bulk Volume Fraction</td>
<td>$(\epsilon_b)$</td>
<td>—</td>
<td>0.4896</td>
<td>—</td>
</tr>
<tr>
<td>Porosity</td>
<td>$(\varphi_b, \varphi_k)$</td>
<td>—</td>
<td>1</td>
<td>0.367</td>
</tr>
<tr>
<td>Diffusivity</td>
<td>$(D_b, D_k)$</td>
<td>m$^2$/s$^{-1}$</td>
<td>$10^{-9}$</td>
<td>$8 \times 10^{-10}$</td>
</tr>
<tr>
<td>Specific Surface Area</td>
<td>$(A_b, A_k)$</td>
<td>cm$^{-1}$</td>
<td>5.625</td>
<td>15.10</td>
</tr>
<tr>
<td>Darcy Velocity</td>
<td>$(q_b, q_k)$</td>
<td>m y$^{-1}$</td>
<td>14.4</td>
<td>0</td>
</tr>
</tbody>
</table>
Comparison of Upscaled LB Model to Continuum Model (Tracer)
Linear Kinetics: Stationary State Dissolution

Dual continuum prediction
Equivalence of Dual and Single Continuum Models for a Single Component Stationary-State

- Dual continuum stationary state transport equations:

\[
q \frac{dC_b}{dx} = -k a_b (C_b - C_{eq}) + a_m b \varphi_m D_m \left. \frac{\partial C_m}{\partial y} \right|_{y=0}
\]

\[-\varphi_m D_m \frac{\partial^2 C_m}{\partial y^2} = -k a_m (C_m - C_{eq})\]

\[C_m(y = 0; x) = C_b(x)\]

- Equivalent effective single continuum equation:

\[
q \frac{dC_b}{dx} = -k a_e (C_b - C_{eq})
\]

\[a_e = a_b + a_m b \sqrt{\frac{a_m \varphi_m D_m}{k}} \left( \frac{1 - \exp (-2l_m \sqrt{k a_m \varphi_m D_m})}{1 + \exp (-2l_m \sqrt{k a_m \varphi_m D_m})} \right)\]
Multicomponent System:
100 bars CO$_2$ + Mg + SO$_4$ + Calcite $\rightarrow$ Dolomite + Gypsum

$t = 10^5$ steps

$t = 2 \times 10^5$ steps

$t = 4 \times 10^5$ steps

1 LBM step $= 0.026$ s
Comparison with Single Continuum Model
Continuum and LBM Surface Areas

- **Continuum Model**
  - Different surface areas for precipitation and dissolution
  - Surface evolution empirical:

\[
a_m = a_m^0 \left( \frac{\phi_m}{\phi_m^0} \right)^{2/3}
\]

(Dissolution)

\[
= \text{constant}
\]

(Precipitation)

- **LBM**
  - Surface area is determined by geometry and nucleation kinetics—surface area evolution related to rules for determining geometry evolution
Upscaling LBM Surface Area

![Graph showing the relationship between surface area and distance for different materials.](image)
Conclusions

• Multicomponent Lattice Boltzmann model developed with same chemistry as in continuum models with heterogeneous mineral reactions incorporated as boundary conditions at mineral surface.

• Pore-scale models can provide insight into upscaled continuum model formulations and provide parameter values for permeability, effective diffusivity (tortuosity), micro-scale dispersivity, reactive surface area etc.

• Generally a multi-scale continuum model is needed to fit a pore-scale simulation.
Conclusions [Continued]

• Main difficulty in applying LBM is quantifying pore-scale geometry, mineral distribution and associated surface area at micron (pore) scales.
Future Work

• Validate LBM and apply to realistic pore-scale geometries.

• Investigate upscaling pore-scale sorption processes: can sorption “kinetics” be explained by diffusion processes coupled to fast reaction kinetics in complex pore geometry?
  – Ion exchange
  – Surface complexation and charge balance
    • Nernst-Planck equation

• Evolving multiple continua
  – Weathering: continuous evolution of geometry from fractured (bed rock) to porous medium (saprolite)