Development of Pore-Scale Models for Diffusion-Reaction Systems with Application to CO2 Adsorption

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Motivation

• Porous particles
  – Widely used in chemical processes
  – High surface area and selectivity
  – Categorized based on pore size
    • Microporous (< 2 nm)
    • Mesoporous (2 nm – 50 nm)
    • Macroporous (> 50 nm)

SEM images of macroporous structures of weakly intergrown spherical particles (source: [1])

Motivation

- Mesoporous silica particles, impregnated with polyethyleneimine (PEI) used for carbon capture process
- One of the technologies being pursued for carbon capture and storage (CCS) process

Develop numerical tools to quantify the heat and mass transfer phenomena occurring in porous particles

SEM image of mesoporous silica (source: Wikipedia)
Challenges

- Complex network of porous microstructures
- A multi-physics problem
  - CO2 diffusion
  - Heat Transfer
  - Adsorption-desorption kinetics
- Multi-scale nature
  - Particles are sized ~100 μm while smallest pore channels are ~30 nm!

A porous spherical particle created using stochastic reconstruction with a porosity of 0.40
Approach

Macro-pore modeling
- Pore-resolved DNS simulations
- Heat and mass transfer

Sub-pore modeling
- Physical phenomena at unresolved scales
- Knudsen effects and adsorption

Immersed boundary method
- Complex microstructures
- Conjugate heat transfer

Realistic porous media
- Stochastic reconstruction with high resolution imaging
- Species and energy diffusion
Immersed Boundary Method (IBM)

- Implemented in our in-house code GenIDLEST
- A finite-volume code with non-staggered grid formulation
- Use of curvilinear coordinates
- Capabilities
  - Conjugate heat transfer
  - Species diffusion
  - Wall modeling

A 2D porous medium created using stochastic reconstruction with a porosity of 0.70

A thick circular tube simulation with conjugate heat transfer
Immersed Boundary Method (IBM)

Flows through 2D and 3D reconstructed porous geometries
Approach

Macro-pore modeling
- Pore-resolved DNS simulations
- Heat and mass transfer

Sub-pore modeling
- Physical phenomena at unresolved scales
- Knudsen effects and adsorption

Pore network model
- Fractal-like pore network
- Heat and mass transfer
- Surface adsorption kinetics

Immersed boundary method
- Complex microstructures
- Conjugate heat transfer

Porous media flows
- Stochastic reconstruction
- Species diffusion
Pore Network Model

- A multi-level **hierarchical system** composed of cylindrical pores
- In the pore network model solve equations for
  - Species and heat diffusion
  - Surface adsorption kinetics
- **Coupling** with macro-pore system for mass and energy conservation

*Example Van Koch surface with cubic structures**

Pore Network Model

- Geometric parameters
  - Hierarchical levels with larger channels branching into smaller ones
  - Desired pore channel size range and specific area specified based on experimental measurements
  - Number of levels and branches derived to satisfy given pore size distribution (PSD) and porosity
Pore Network Model

- Diffusion (heat and mass) into sub-pore channels
- Adsorption on the sub-pore channel surface
- Sub-pore/macro-pore interface – coupling with macro-pore system
  - Parent cell included in solution for coupling with macro-system (ensures implicit conservation)
  - Source terms to include the adsorption/desorption effects
Mass and Energy Diffusion Modeling

- 1D unsteady governing equation
- Composition dependent mixture property calculation
- Mass transport
  - Bosanquet formula for effective diffusion coefficient
  - Temperature dependence based on kinetic theory considerations

\[
\frac{\partial (\phi)}{\partial t} = \frac{\partial}{\partial x} \left( \alpha_{\text{eff}} \frac{\partial \phi}{\partial x} \right) + \omega
\]

- Bosanquet formula
\[
\frac{1}{D_{\text{eff}}} = \frac{1}{D_{\text{bulk}}} + \frac{1}{D_{Kn}} + \ldots
\]

- Chapman and Cowling correlation:
\[
D_{\text{bulk}} = 0.001858 T^{3/2} \sqrt{\frac{M_1 + M_2}{M_1 M_2}}
\]

- Knudsen diffusion:
\[
D_{Kn} = \frac{1}{3} d_p \sqrt{\frac{8R_u T}{\pi M}}
\]
Mass and Energy Diffusion Modeling

- 1D unsteady governing equation
- Composition dependent mixture property calculation
- Mass transport
  - Bosanquet formula for effective diffusion coefficient
  - Temperature dependence based on kinetic theory considerations
- Energy transport
  - Sutherland’s law for temperature dependence of thermal conductivity
  - Knudsen number dependence of the bulk conductivity

\[
\frac{\partial (\phi)}{\partial t} = \frac{\partial}{\partial x} \left( \alpha_{eff} \frac{\partial \phi}{\partial x} \right) + \omega
\]

- Sutherland’s law:

\[
\frac{\kappa_{bulk}^c}{\kappa_0^c} = \left( \frac{T}{T_0} \right)^{\frac{3}{2}} \cdot \frac{T_0 + S}{T + S}
\]

- Reduced thermal conductivity

\[
\kappa_{gas} = \frac{\kappa_{bulk}}{1 + Kn \cdot \frac{2 - \alpha_T}{\alpha_T} \cdot \frac{9\gamma - 5}{\gamma + 1}}
\]
Adsorption/Desorption Modeling

- Rate equation derived from first principles
  - Molecular wall impact rate
    \[ F = \frac{p}{\sqrt{2\pi m R_u T}} \]
  - Sticking model
    \[ S = f(\theta) \cdot \exp\left( -\frac{E_{ads}}{R_u T} \right) \]
  - Rate of adsorption
    \[ R_{ads} = S \cdot F \]
  - Rate of desorption
    \[ R_{des} = g(\theta) \cdot \exp\left( -\frac{E_{des}}{R_u T_s} \right) \]
  - Final form for rate equation
    \[ \frac{d\theta}{dt} = R_{ads} + R_{des} \]
Adsorption/Desorption Modeling

- Linear sticking model for CO₂ molecules is used
- Second order rate equation
- Resulting equation is non-linear in θ (form is similar to **Lee et al.**)
- Parameters \( N_s, E_{ads}, ΔS, E_{des} \) will be from experimental calibration
- Calibration using equilibrium surface coverage values (\( \theta_{eq} \) obtained by using \( \frac{dθ}{dt} = 0 \))

\[
\frac{dθ}{dt} = K_{ads}(1 - 2θ)^2 - K_{des}θ^2
\]

\[
K_{ads} = \frac{p}{\sqrt{2πmk_BT}} \cdot \frac{1}{N_s} \cdot \exp\left(-\frac{E_{ads}}{R_uT}\right)
\]

\[
K_{des} = -\frac{eκk_BT}{h} \cdot \exp\left(\frac{ΔS}{R_u}\right) \cdot \exp\left(-\frac{E_{des}}{R_uT_s}\right)
\]

- \( θ \) surface coverage
- \( p \) partial pressure of CO₂
- \( N_s \) no. of ads. sites per unit area
- \( E_{ads} \) Activation energy for adsorption (J/mol)
- \( E_{des} \) Activation energy for desorption (J/mol)
- \( ΔS \) Entropy of adsorption reaction (J/mol/K)
- \( T_s \) Surface temperature
- \( κ \) pre-exponential correction term
- \( k_B \) Boltzmann constant \( (1.38 \times 10^{-23} \text{ J/K}) \)
- \( h \) Planck’s constant \( (6.63 \times 10^{-34} \text{ J s}) \)

** CO₂ adsorption measurements conducted at NETL by Lee et al. (2011 PCC)
Problem Description

- 2D porous particle of porosity 60%
- Particle pore space initially with 0% CO2
- Ambient conditions
  - 15% CO2 (and 85% N2)
  - Temperature – 300K
- Domain boundaries at ambient condition – acting as infinite sources

Sectional view of diffusion of CO2 into a porous particle
Problem Description

• Particle properties
  – Particle diameter - **100 microns**
  – Macro-pore porosity – 50%
  – Sub-pore – 20%
  – Sub-pore channel size range – 1 micron to 30 nm
  – Specific area – 50 m²/g
    (increase of 100 times than macro-particle)
  – Four levels with uniform scaling ratio

Sectional view of diffusion of CO2 into a porous particle
Effect of Sub-pore System

• Four types of simulations
  – No sub-pore system
  – Sub-pore system with mass diffusion only
  – Sub-pore system with adsorption only
  – Sub-pore system with mass diffusion and adsorption

• Macro-pore diffusion expected to be faster
• Sub-pores affect macro-pore saturation!

CO2 concentration level in entire particle macro-pore space
Diffusion-only Case

- Sub-pore space saturation takes much longer!
- Smallest channels take longest to saturate…
Adsorption-only Case

- CO2 concentration within the sub-pore space is 0.15 (constant)
- No dependence on levels because of same pressure/temperature
- Asymptotic value expected to depend on ambient conditions (pressure/temperature) and kinetic parameters
- Expected saturation time depends on the parameters in the surface kinetics
Effect of Temperature – Adsorption only

- Adsorption on the particle surface
- Effect of temperature on saturation time
Diffusion + Adsorption Case

For $E_{\text{ads}} = 10 \text{ kJ/mol, } E_{\text{des}} = 20\text{kJ/mol}$ case
• Similar trend follows at individual levels
• Final **expected value** of saturation is around **0.05** surface coverage
• *A diffusion-limited case* — adsorption behavior is completely different than in adsorption-only case!
Macro-/Sub-pore Interchangeability

- Square particle with only two channel sizes – 1 and 2 μm
- Case 1 (with macro-pore)
  - Larger channel modeled with IBM, smaller one as a sub-pore
- Case 2 (without macro-pore)
  - Both channels modeled as sub-pores (no IBM)
- Volume contributions of the two channel sizes are maintained to be the same between two cases

A square porous particle within a square domain – the larger channels are modeled using IBM as macro-pores (Case 1)
Macro-/Sub-pore Interchangeability

CO₂ concentration levels averaged over entire pore space for the two cases

CO₂ concentration levels averaged over the smaller channel only for the two cases
Conclusions

• A single framework to account for multi-scale, multi-physics problems in porous media
  – Immersed boundary method (IBM) for macro-pore channels
  – Sub-pore modeling methodology for unresolved channels
• A general model that is applicable to many reaction-diffusion system in porous media

• Sub-pore geometry based on experimental (if available) porosity measurements
• Within sub-pore system, solve for simplified governing equations – physically accurate, yet tractable from a practical standpoint
• Applicable to problems without macro-porosity – i.e., full particle porosity is modeled using pore network model
Future Work

• Inclusion of conjugate heat transfer in the simulations
• Run single-particle simulations for different conditions of pressure and temperature to obtain CO2 adsorption isotherms
• Modularize pore network model for use to model full particle in other software frameworks such as MFIX.
Publications

• **Peer-review journals**

• **Conference proceedings**

• **Presentations**

• **Under preparation**
  – “A subgrid pore network model for reaction-diffusion phenomena in porous media”, K. Nagendra and D. K. Tafti
Thank you!

Questions?
Sub-pore Model
Multi-scale Challenges

- Widely varying time-scales
  - Diffusion at macro-pore – ~1 ms
  - Diffusion at sub-pore – ~100 ms (expected)
  - Adsorption at surface - ~1-100 s (expected)
- Results in the time-step being extremely small – currently using 1 ns
- Combined behavior is very different than the constituent physical models
Diffusion-only Case

- Sub-pore space saturation takes much longer!
- Smallest channels take longest to saturate…
Sub-pore space seems to be asymptote at a much lower value of CO2 than ambient.

Similar trend follows (as expected) at different levels.
Effect of Temperature – Diffusion only

- Diffusion (only) into particle pore space
- Effect of temperature on saturation time