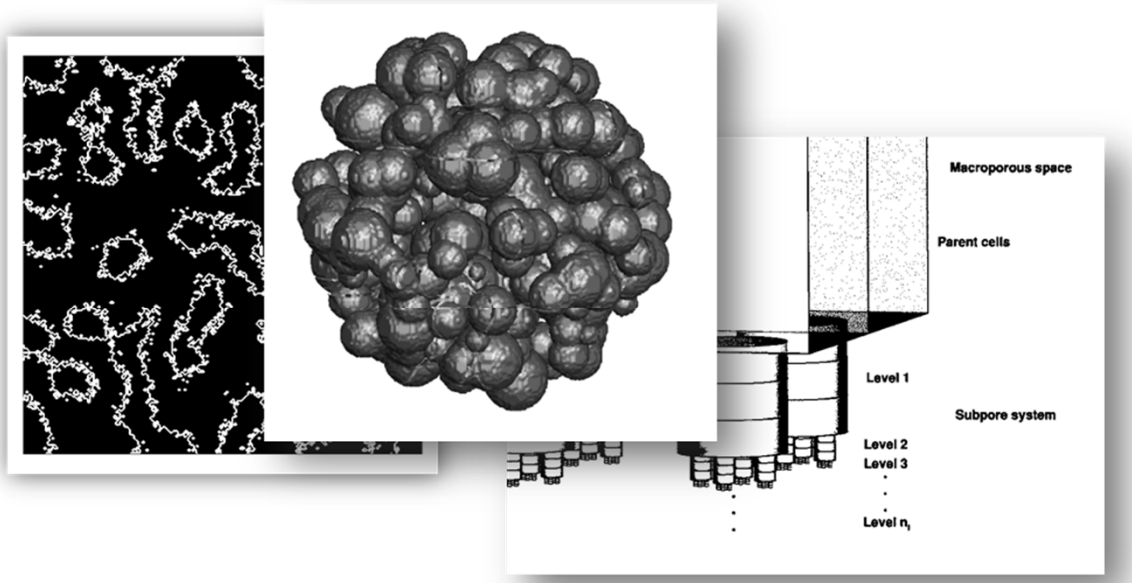
NATIONAL ENERGY TECHNOLOGY LABORATORY




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

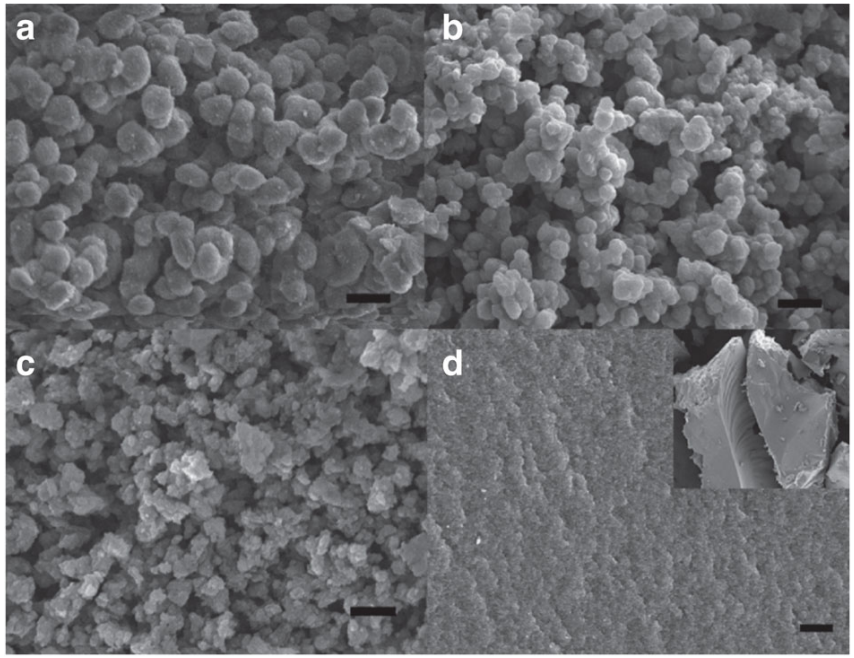
*Support:*
*NETL-ORD's Innovative Process Technologies Field Work Proposal through the RES site support contract at NETL*

Nagendra Krishnamurthy & Danesh Tafti
Mechanical Engineering, Virginia Tech
Blacksburg, VA

U.S. DEPARTMENT OF ENERGY

# 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)



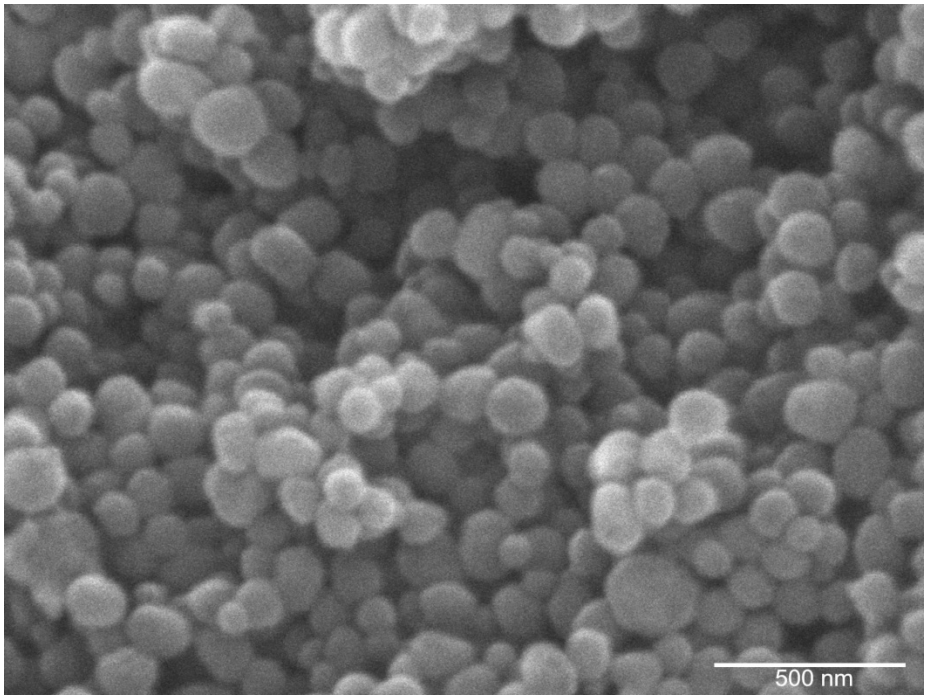

*SEM images of macroporous structures of weakly intergrown spherical particles (source: [1])*

*[1] Mohanty et al (2011)*

# Motivation

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

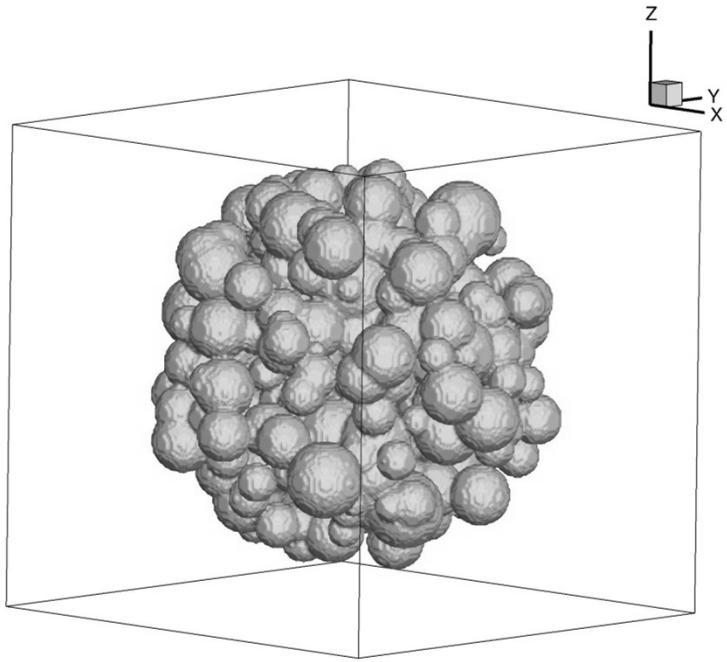
Develop numerical tools to quantify the heat and mass transfer phenomena occurring in porous particles




*SEM image of mesoporous silica (source: Wikipedia)*

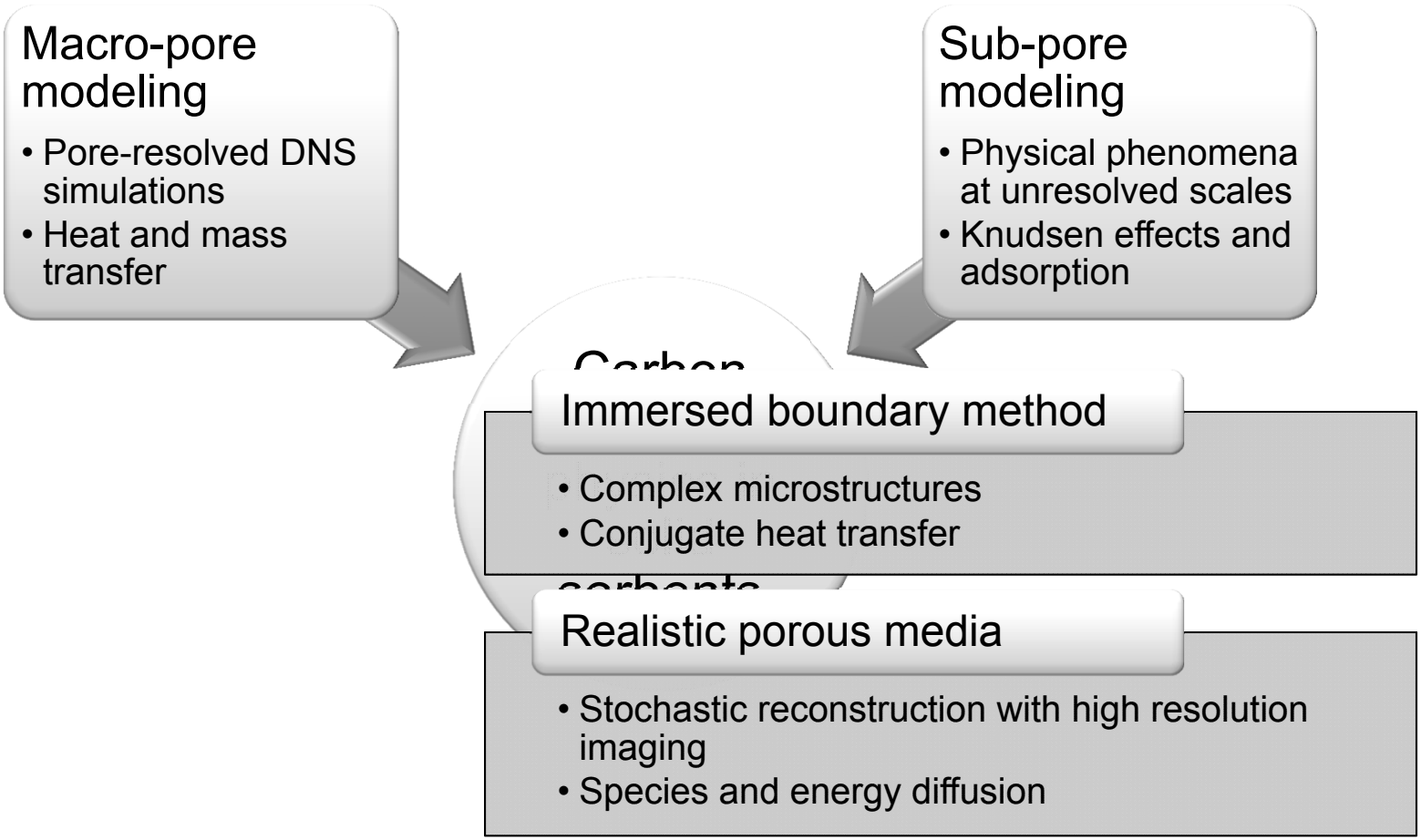
# Challenges

- 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!



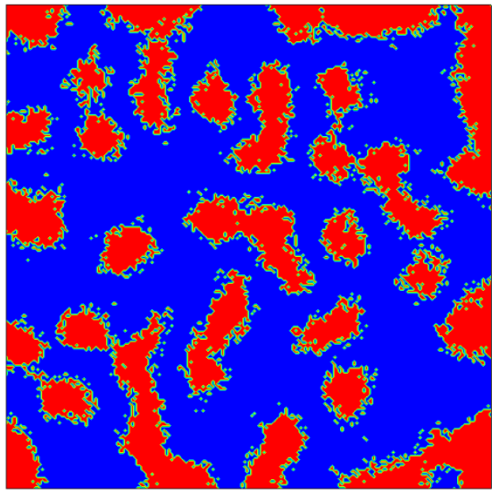

*A porous spherical particle created using stochastic reconstruction with a porosity of 0.40*

# Approach

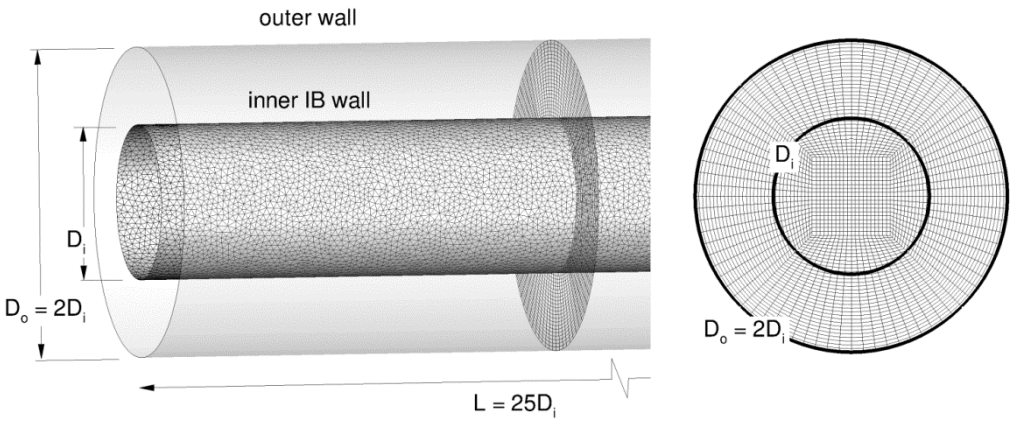

Macro-pore modeling
• Pore-resolved DNS simulations
• Heat and mass transfer
Sub-pore modeling
• Physical phenomena at unresolved scales
• Knudsen effects and adsorption
Immersed boundary method
• Complex microstructures
• Conjugate heat transfer
Realistic porous media
• Stochastic reconstruction with 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

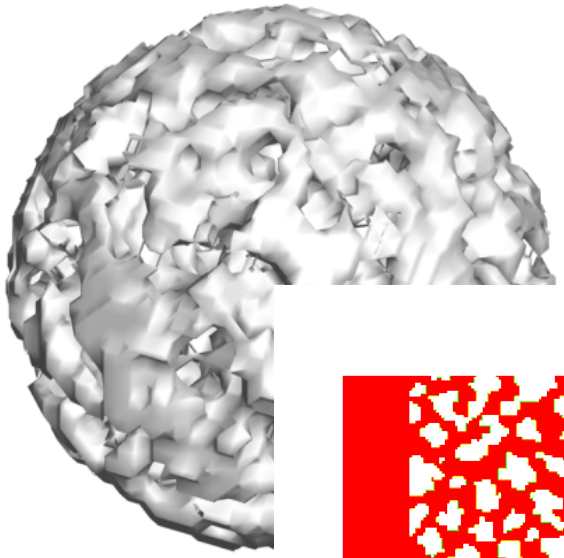


*A 2D porous medium created using stochastic reconstruction with a porosity of 0.70*

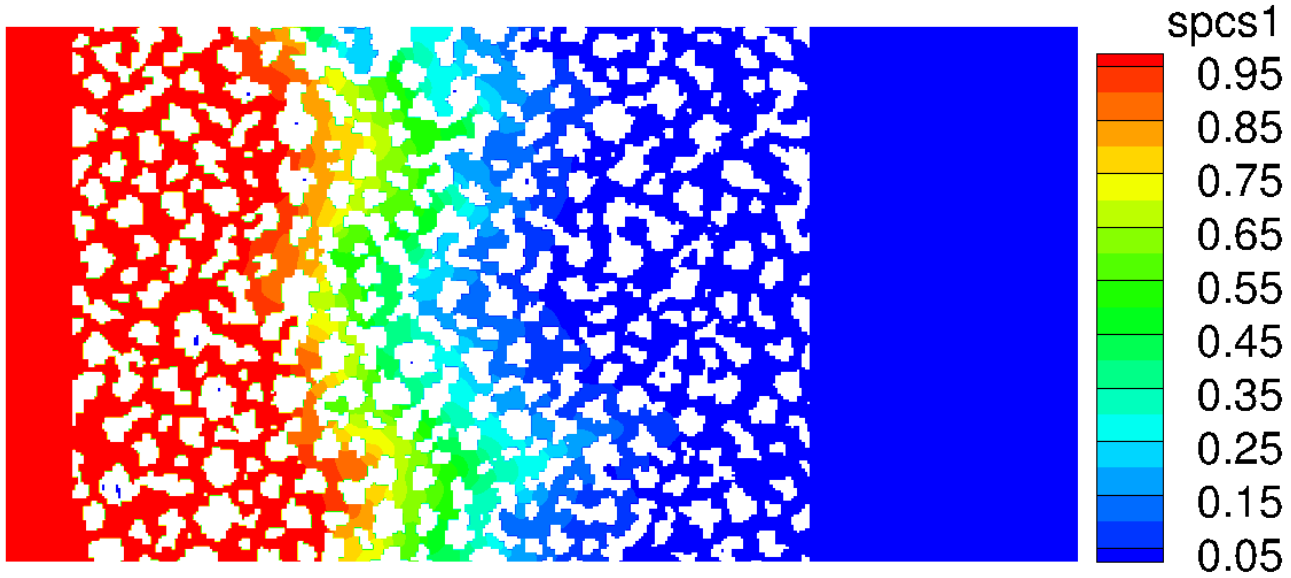



*A thick circular tube simulation with conjugate heat transfer*

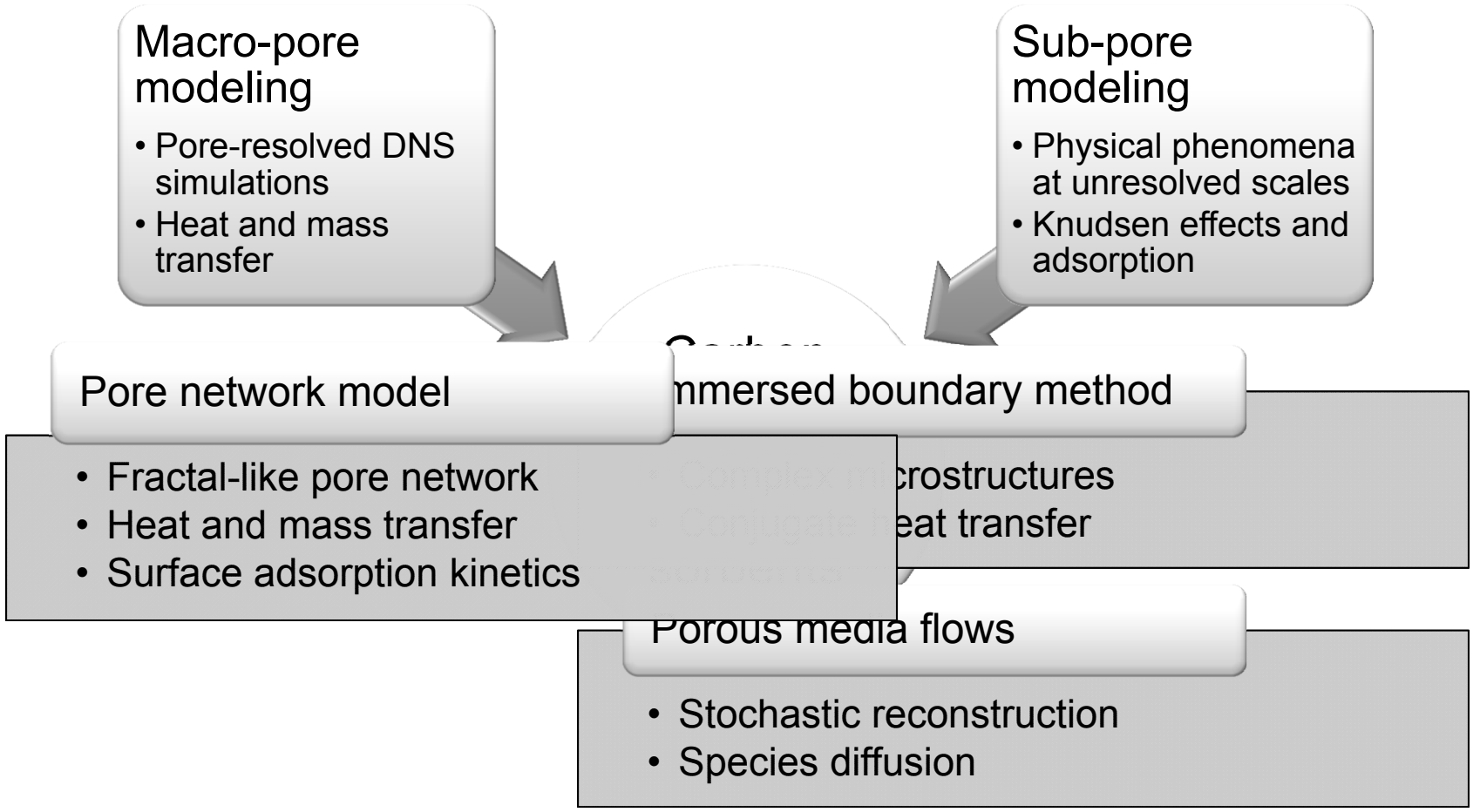
# Immersed Boundary Method (IBM)



*Flows through 2D and 3D reconstructed porous geometries*

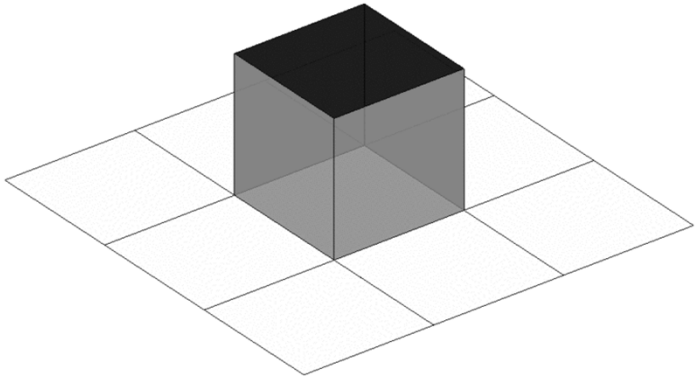


# Approach


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
mmersed boundary method
crostructures
eat 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

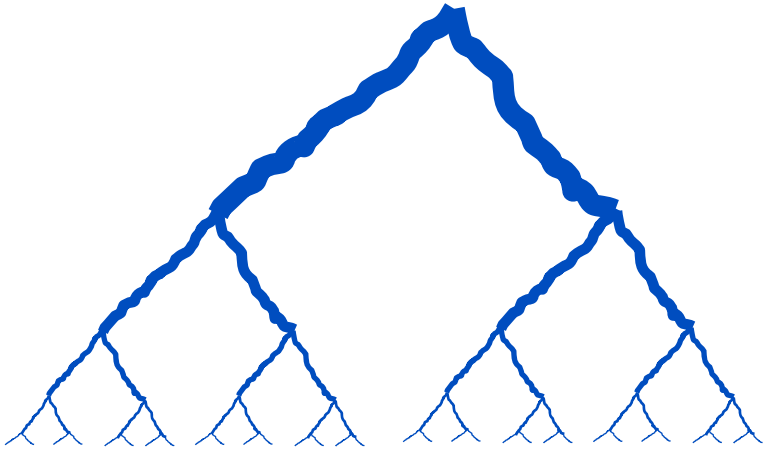


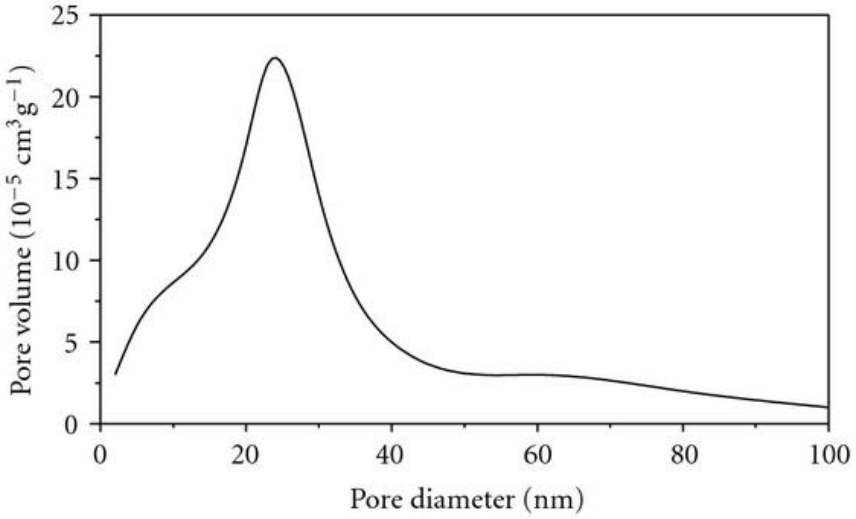
*Example Van Koch surface with cubic structures***

** Source: Wikipedia*

# Pore Network Model

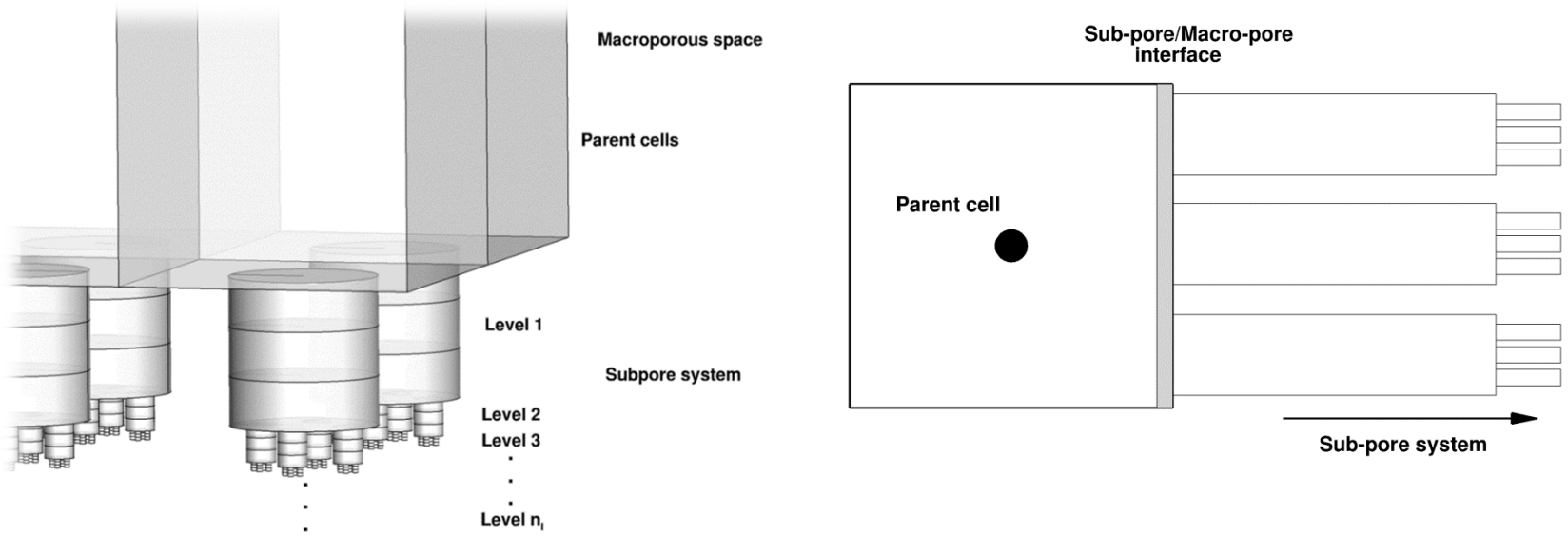
- Geometric parameters
  - Hierarchical levels with larger channels branching into smaller ones
  - Desired pore channel size range and specific area specified based on experimental measurements
  - Number of levels and branches derived to satisfy given pore size distribution (PSD) and porosity






PSD plot from Zhao et al. 2008

# 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

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

- Bosanquet formula

$$\frac{1}{D_{eff}} = \frac{1}{D_{bulk}} + \frac{1}{D_{Kn}} + \cdots$$

- Chapman and Cowling correlation:

$$D_{bulk} = 0.001858\, T^{\frac{3}{2}} \sqrt{\frac{M_1 + M_2}{M_1 M_2}}$$

- 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
  - Sutherlands 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:

$$\frac{\kappa^c_{bulk}}{\kappa^c_0} = \left(\frac{T}{T_0}\right)^{\frac{3}{2}} \cdot \frac{T_0 + S}{T + S}$$

- 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

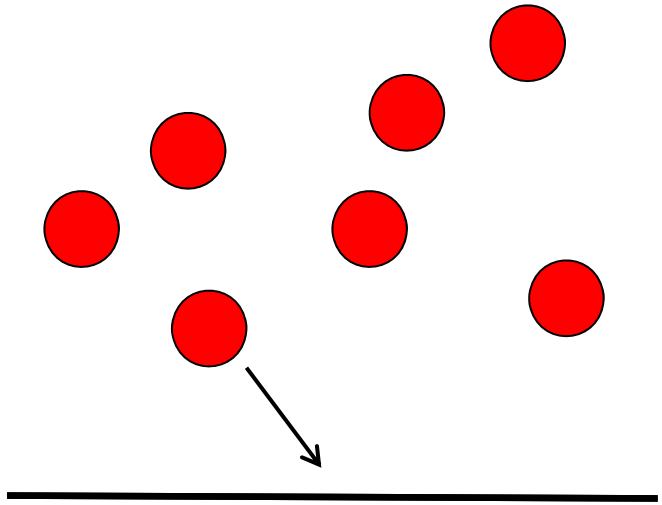
$$S = \mathrm{f}(\theta) \cdot \exp\left(-\frac{E_{ads}}{R_u T}\right)$$

  - Rate of adsorption

$$R_{ads} = S \cdot F$$

  - Rate of desorption

$$R_{des} = g(\theta) \cdot \exp\left(-\frac{E_{des}}{R_u T_s}\right)$$



*Surface with adsorption sites*

  - 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 $\theta$ (form is similar to **[**]Lee et al.**)
- Parameters $N_S, E_{ads}, \Delta S, E_{des}$ will be from **experimental calibration**
- Calibration using equilibrium surface coverage values ($\theta_{eq}$ obtained by using $\frac{d\theta}{dt} = 0$)

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

$$\frac{d\theta}{dt} = K_{ads}(1-2\theta)^2 - K_{des}\theta^2$$

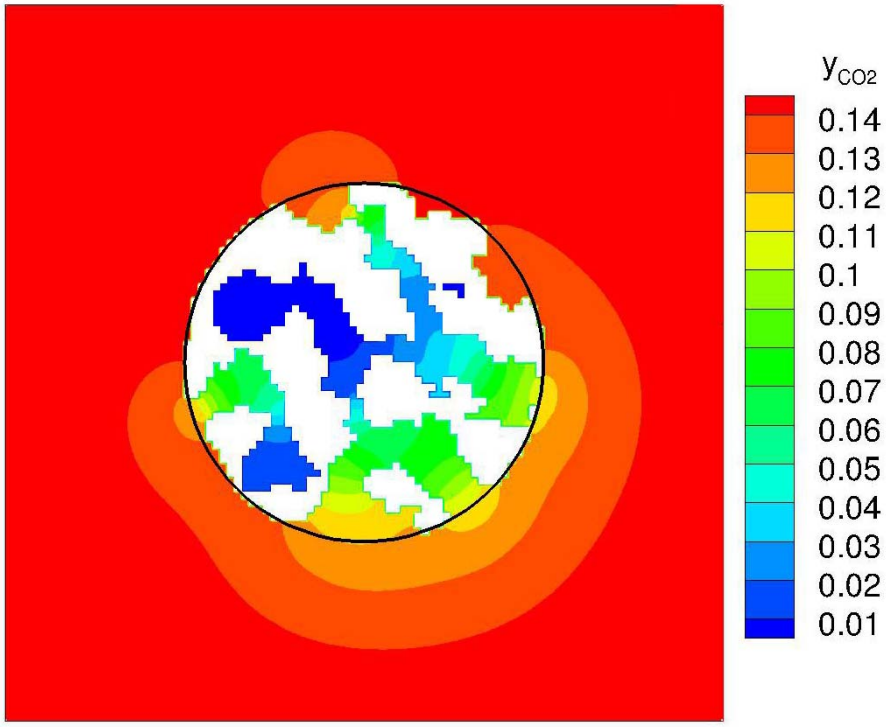
$$K_{ads} = \frac{p}{\sqrt{2\pi m k_B T}} \cdot \frac{1}{N_s} \cdot \exp\left(-\frac{E_{ads}}{R_u T}\right)$$

$$K_{des} = -\frac{e\kappa k_B T}{h} \cdot \exp\left(\frac{\Delta S}{R_u}\right) \cdot \exp\left(-\frac{E_{des}}{R_u T_s}\right)$$

| | |
|---|---|
| $\theta$ | 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) |
| $\Delta S$ | Entropy of adsorption reaction (J/mol/K) |
| $T_s$ | Surface temperature |
| $\kappa$ | pre-exponential correction term |
| $k_B$ | *Boltzmann constant ($1.38\times10^{-23}$ J/K)* |
| $h$ | Plancks' *constant ($6.63\times10^{-34}$ J s)* |

# Problem Description

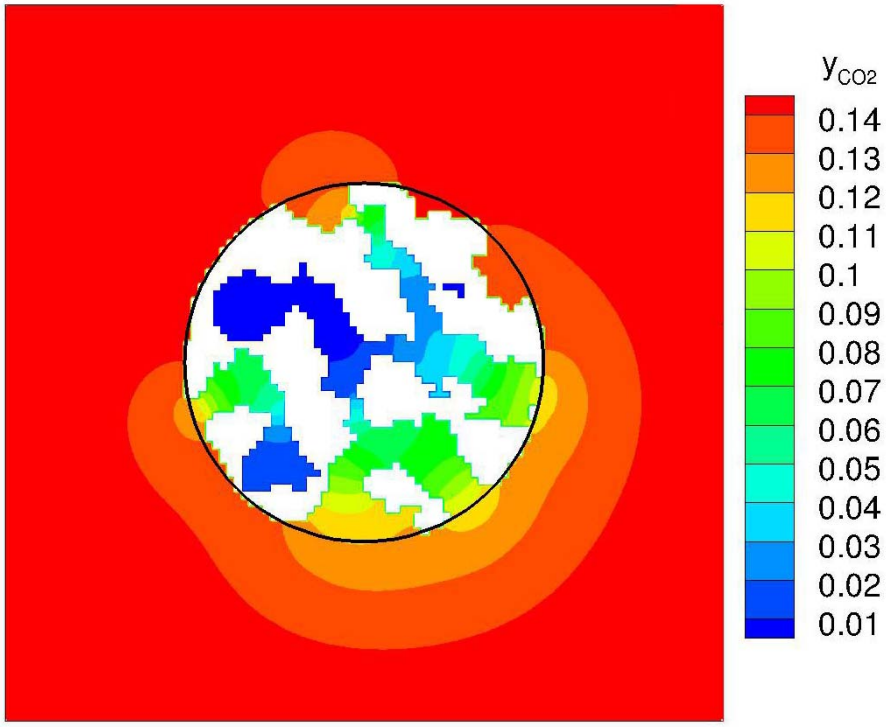
- 2D porous particle of porosity 60%
- Particle pore space initially with 0% CO2
- Ambient conditions
  - 15% CO2 (and 85% N2)
  - Temperature – 300K
- Domain boundaries at ambient condition – acting as infinite sources




*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 $m^2/g$ (increase of 100 times than macro-particle)
  - Four levels with uniform scaling ratio

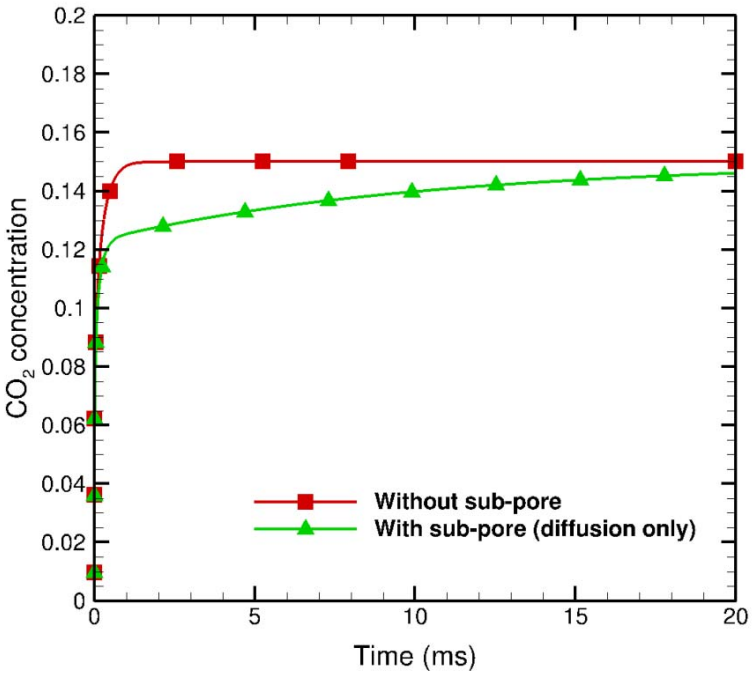



*Sectional view of diffusion of CO2 into a porous particle*

# 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

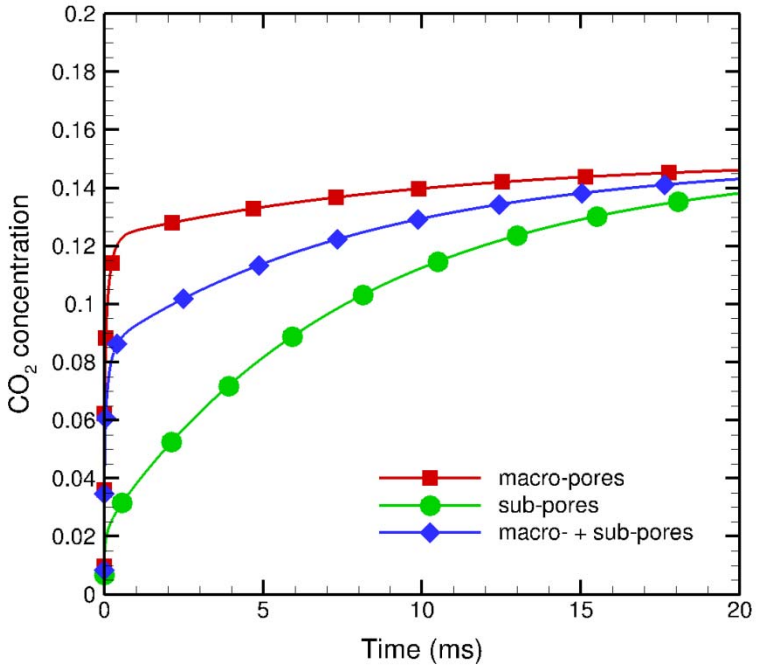
- Macro-pore diffusion expected to be faster
- Sub-pores affect macro-pore saturation!



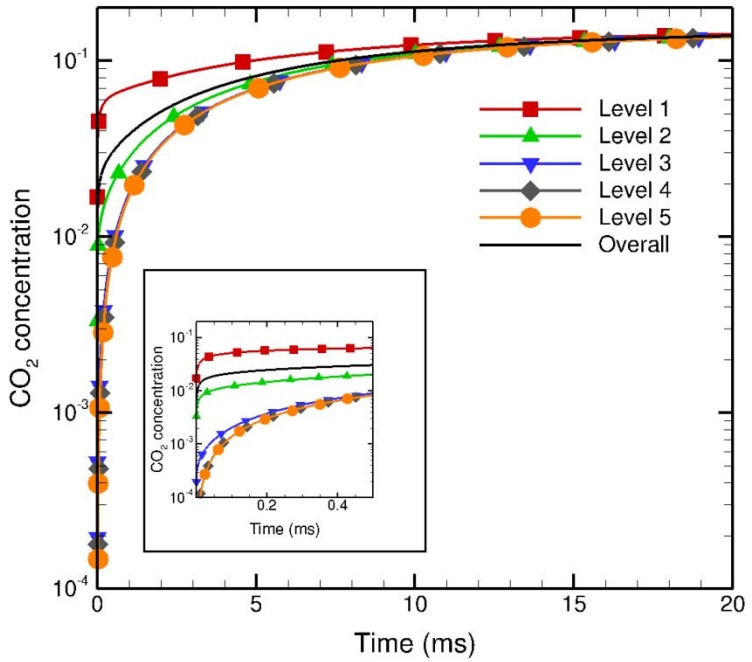

*CO2 concentration level in entire particle macro-pore space*

# Diffusion-only Case

*CO2 concentration averaged over particle pore-space*



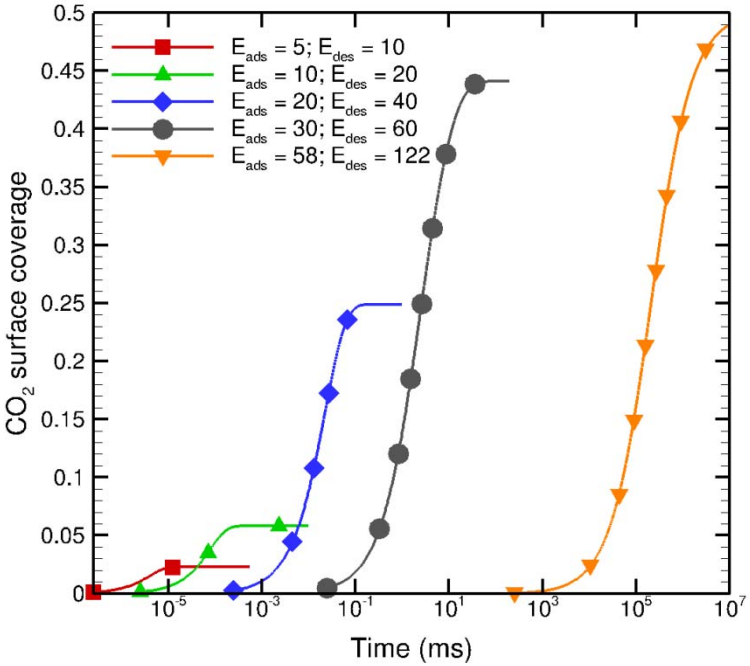

*CO2 concentration averaged on a per-level basis*




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

# Adsorption-only Case

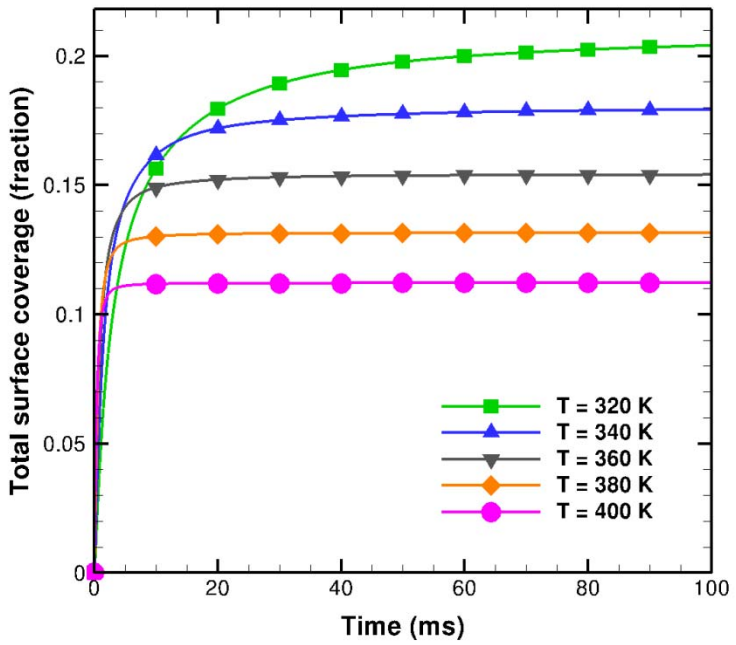
- CO2 concentration within the sub-pore space is 0.15 (constant)
- No dependence on levels because of same pressure/temperature
- Asymptotic value expected to depend on ambient conditions (pressure/temperature) and kinetic parameters
- Expected saturation time depends on the parameters in the surface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

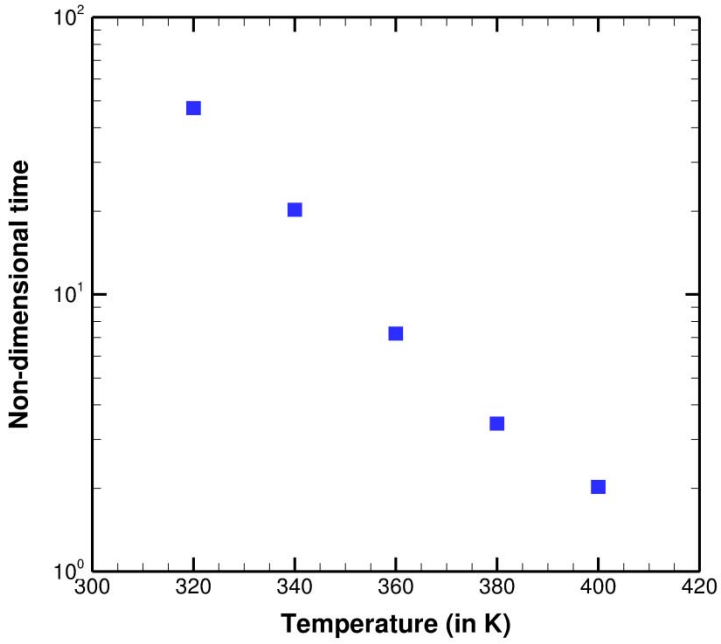



*CO2 surface coverage at different adsorption rates*

# Effect of Temperature – Adsorption only

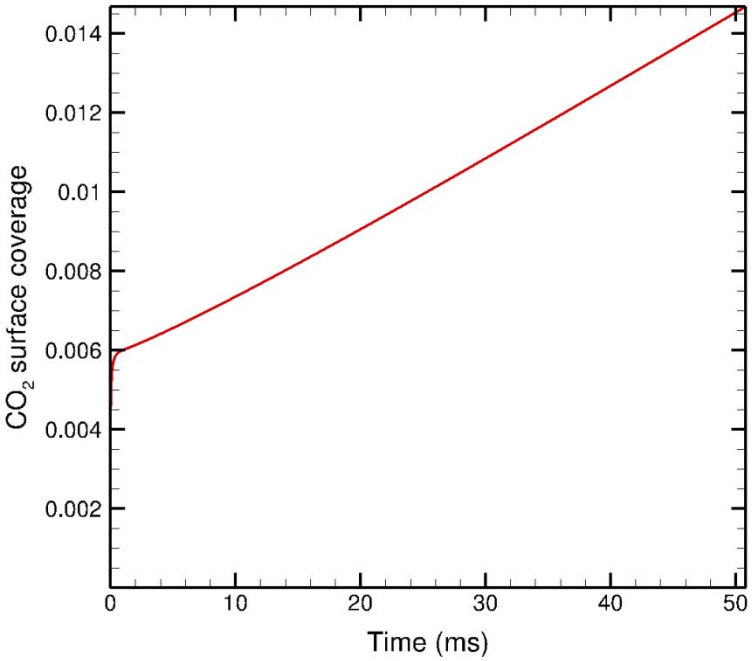
- Adsorption on the particle surface
- Effect of temperature on saturation time



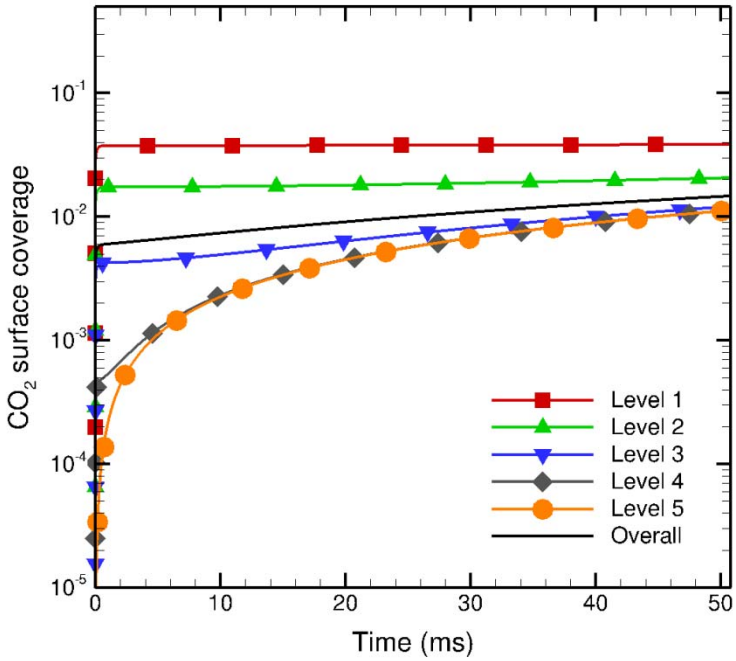



# Diffusion + Adsorption Case

*CO2 surface coverage averaged over all of the sub-pore surface*



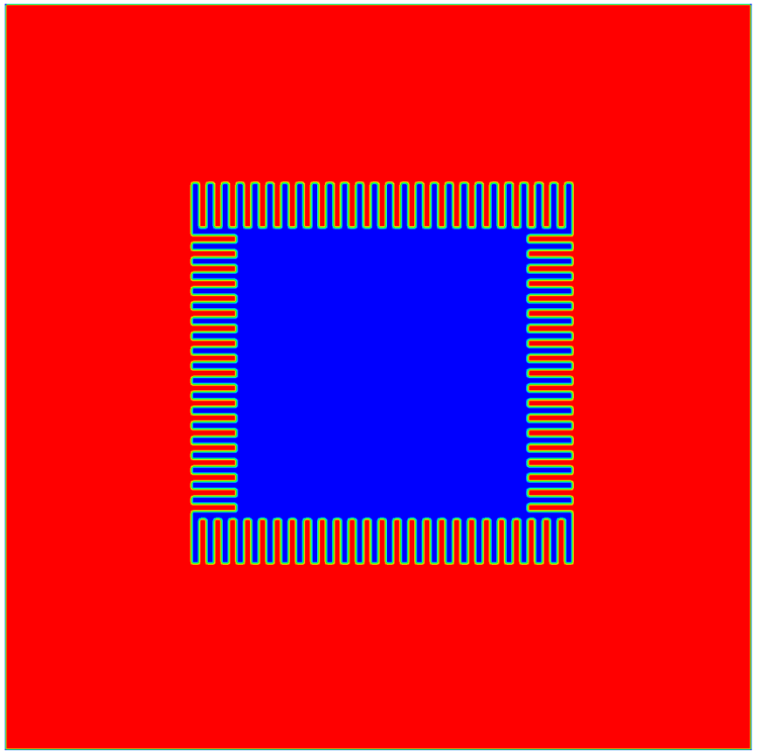

*CO2 surface coverage averaged on a per-level basis within the sub-pore system*




- For $E_{ads}$ = 10 kJ/mol, $E_{des}$ = 20kJ/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

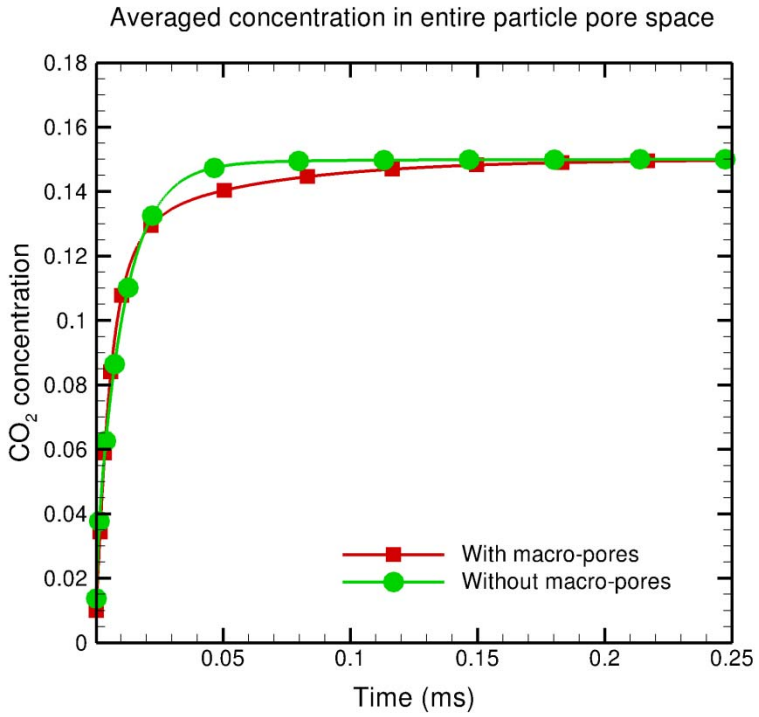
- Square particle with only two channel sizes – 1 and 2 μm
- Case 1 (with macro-pore)
  - Larger channel modeled with IBM, smaller one as a sub-pore
- Case 2 (without macro-pore)
  - Both channels modeled as sub-pores (no IBM)
- Volume contributions of the two channel sizes are maintained to be the same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



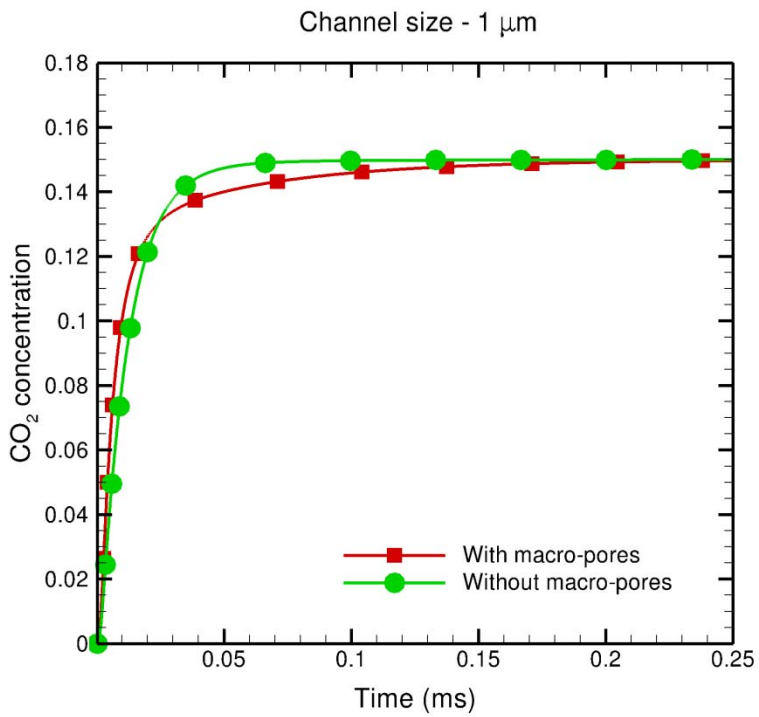
*A square porous particle within a square domain – the larger channels are modeled using IBM as macro-pores (Case 1)*

# 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 m**any reaction-diffusion system** in porous media

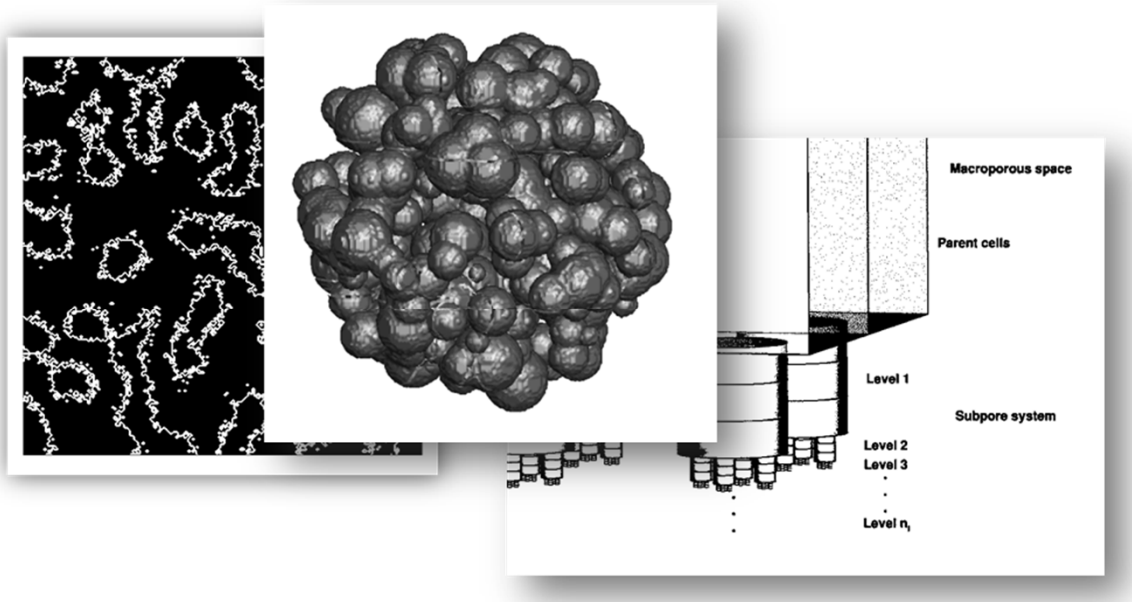
- Sub-pore geometry based on experimental (if available) porosity measurements
- Within sub-pore system, solve for simplified governing equations – **physically accurate, yet tractable** from a practical standpoint
- Applicable to **problems without macro-porosity** – i.e., full particle porosity is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

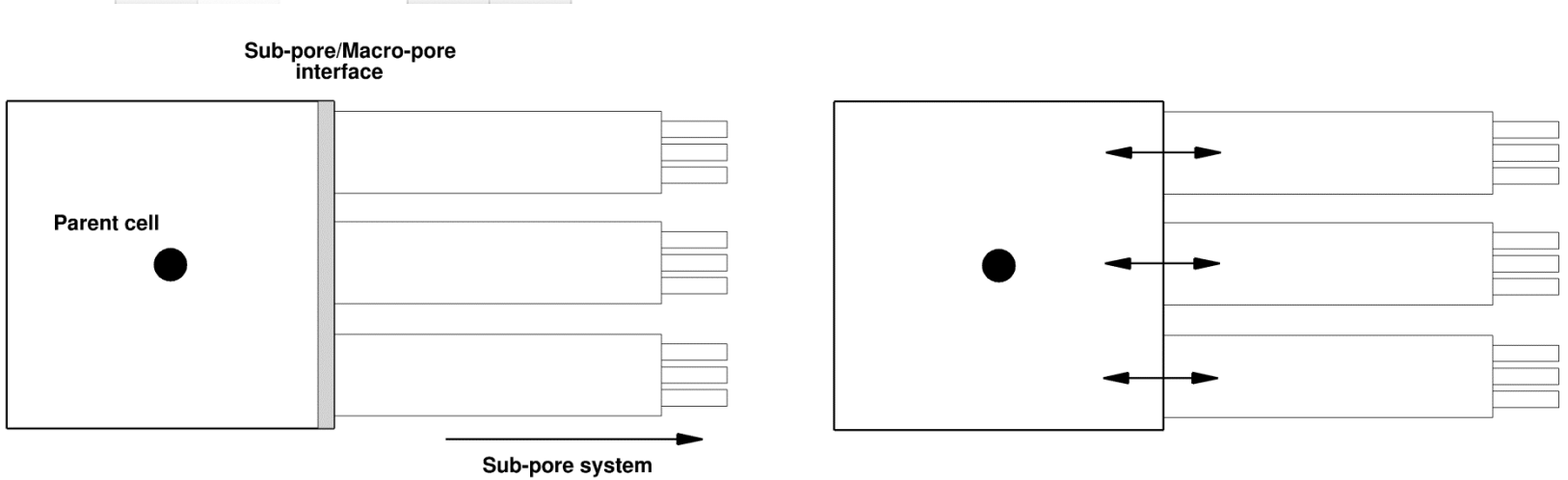
- **Peer-review journals**
  - "Flows Through Reconstructed Porous Media using Immersed Boundary Methods", K. Nagendra and D.K. Tafti, Journal of Fluids Engineering, 2014.
  - "A Novel Approach for Conjugate Heat Transfer Problems in Immersed Boundary Framework", K. Nagendra and D.K. Tafti, Journal of Computational Physics, 2014.
- **Conference proceedings**
  - "Flows Through Reconstructed Porous Media Using Immersed Boundary Methods", K. Nagendra and D.K. Tafti, FEDSM2012-72128, FEDSM 2012, Peurto Rico.
- **Presentations**
  - "Heat and Mass Transfer in Porous CO2 Sorbent Particles", K. Nagendra and D.K. Tafti, NETL Multi-phase Flow Workshop 2011, Pittsburgh PA.
  - "Direct Numerical Simulation of CO2 Diffusion in Reconstructed Solid Sorbent Particles", K. Nagendra and D.K. Tafti, NETL Multi-phase Flow Workshop 2012, Morgantown WV.
  - "A Novel Sub-pore Modeling Methodology for CO2 Capture in Meso-porous Particle Systems", K. Nagendra and D.K. Tafti, NETL Multi-phase Flow Workshop 2013, Morgantown WV.
- **Under preparation**
  - "A subgrid pore network model for reaction-diffusion phenomena in porous media", K. Nagendra and D. K. Tafti
  - "Modeling CO2 diffusion and adsorption in mesoporous silica particles", K. Nagendra and D. K. Tafti




# Thank you!

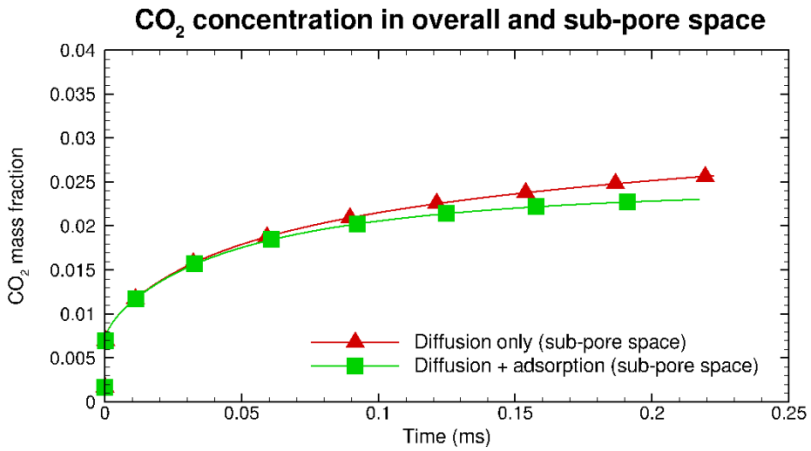
Questions?

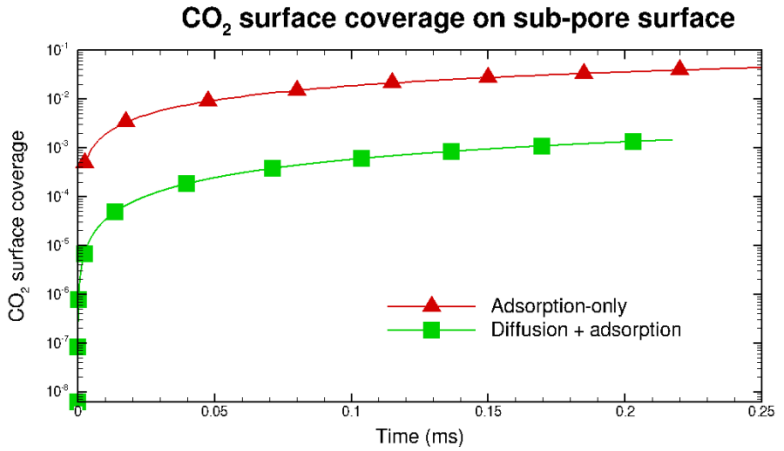
# Sub-pore Model



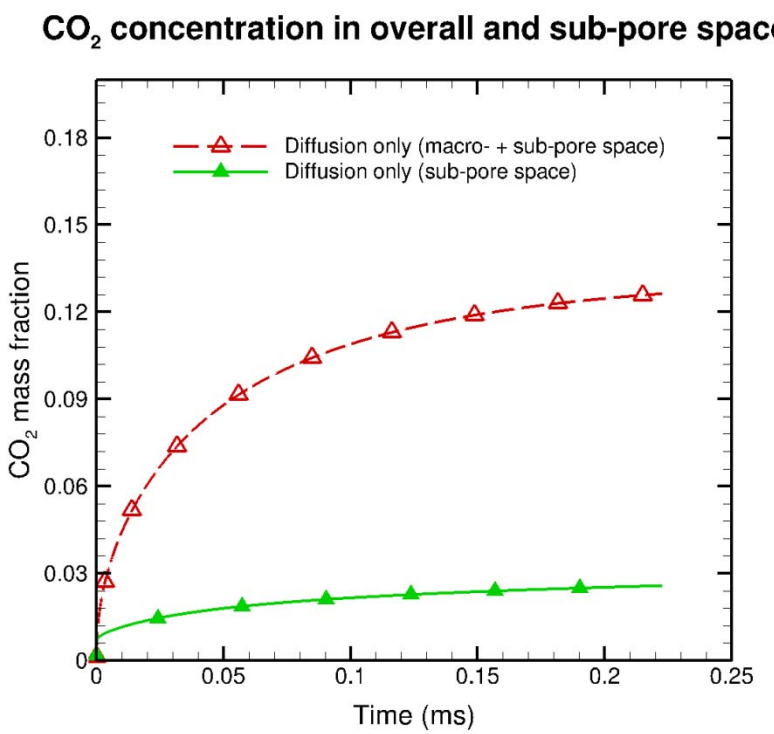
# Multi-scale Challenges

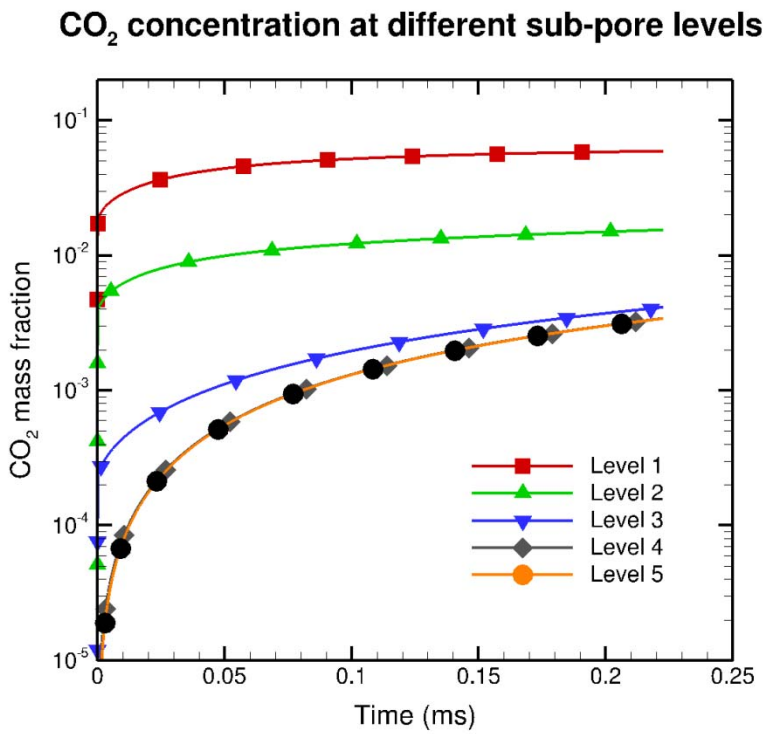
- Widely varying time-scales
  - Diffusion at macro-pore – ~1 ms
  - Diffusion at sub-pore – ~100 ms (expected)
  - Adsorption at surface - ~1-100 s (expected)
- Results in the time-step being extremely small – currently using 1 ns
- Combined behavior is very different than the constituent physical models



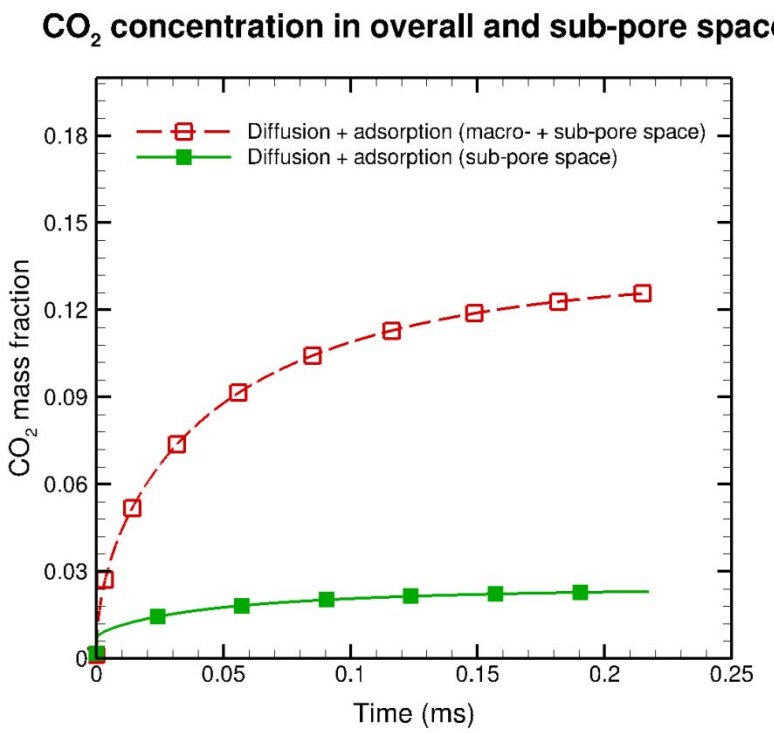
# Diffusion-only Case

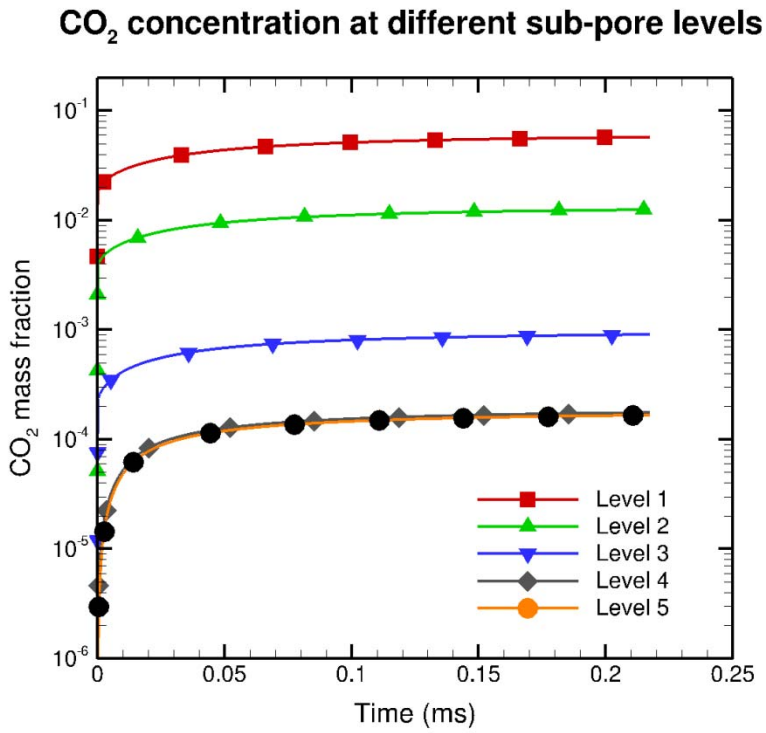



- Sub-pore space saturation takes much longer!
- Smallest channels take longest to saturate…

# Diffusion + Adsorption Case




- 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