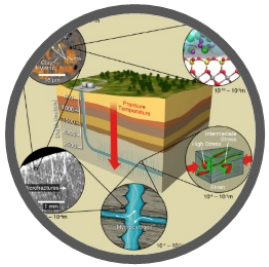
Bridging adsorption behavior of confined methane across scales (H53H-06 2023 AGU Fall Meeting)

Lingfu Liu[1] and Saman Aryana[1]

[1]University of Wyoming

December 21, 2023



CMC - UF

CENTER FOR MECHANISTIC CONTROL OF WATER-HYDROCARBON-ROCK INTERACTIONS IN UNCONVENTIONAL AND TIGHT OIL FORMATIONS

Bridging adsorption behavior of confined methane across scales

Lingfu Liu

Saman Aryana

University of Wyoming

U.S. DEPARTMENT OF ENERGY | Office of Science

Stanford UW USC SLAC ILLINOIS

lliu1@uwyo.edu

Outline

- Research goals

1) investigate adsorption behavior

2) Scale-translating simulation from micro- to meso-scale

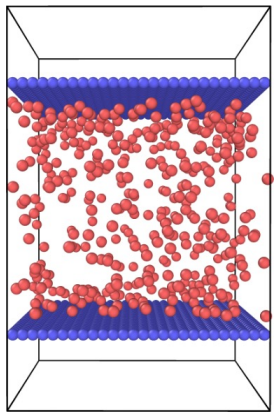
Outline

- Research goals

  1) investigate adsorption behavior

  2) Scale-translating simulation from micro- to meso-scale

- Research method



Phase Behavior
(Equation of state)

Molecular simulations

(reveal confined physics at micro-scale)

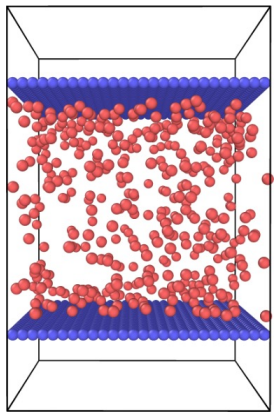
Outline

- Research goals

  1) investigate adsorption behavior

  2) Scale-translating simulation from micro- to meso-scale

- Research method

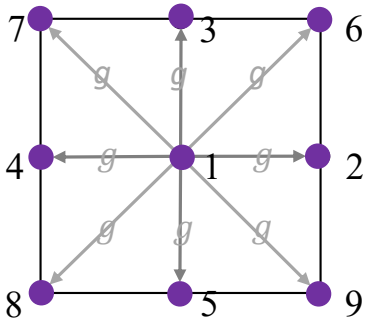


Molecular simulations

(reveal confined physics at micro-scale)

Phase Behavior
(Equation of state)

Bridging scales

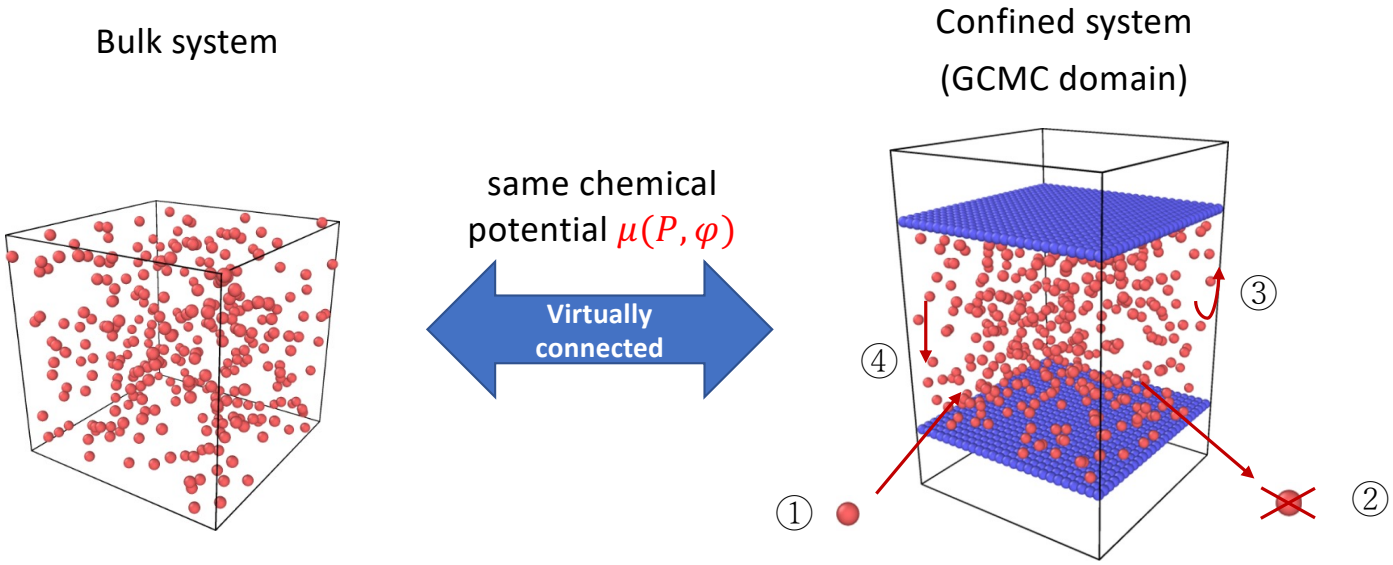


Lattice Boltzmann method

(mimic physics at meso-scale)

GCMC simulations

- Grand Canonical Monte Carlo (GCMC) method

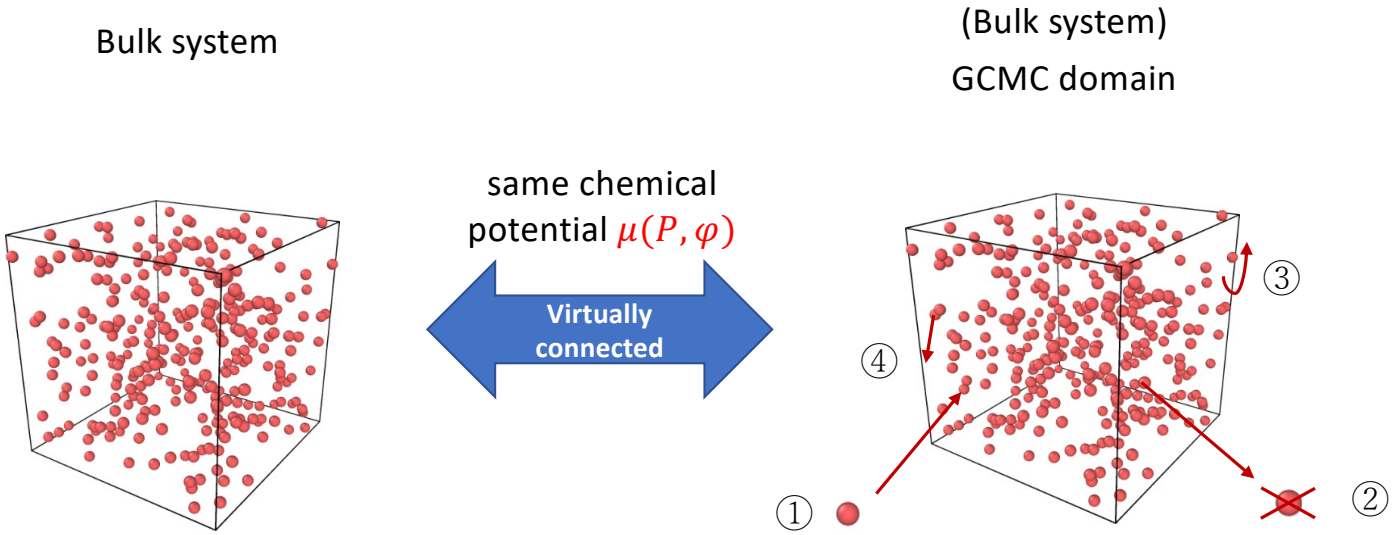


Exchanges of molecules in Mont Carlo simulations

① Insertion ② Deletion ③Rotation ④ Translation

Validation of GCMC in bulk conditions

- Grand Canonical Monte Carlo (GCMC) simulations



Exchanges of molecules in Mont Carlo simulations

① Insertion ② Deletion ③Rotation ④ Translation

Validation of GCMC in bulk conditions

❑ Soave-Benedict-Webb-Rubin (SBWR)-EoS

$$Z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{D}{v^4} + \frac{E}{v^2}\left(1 + \frac{F}{v^2}\right)e^{-\frac{F}{v^2}}$$

$$E_{ij} = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

Fugacity coefficient (FC), φ, and fugacity, f, :

$$\ln\varphi = \ln\frac{f}{P} = (Z-1) - \ln Z + \beta\psi + \frac{1}{4}\delta\psi^4 + \frac{\epsilon}{\Phi}\left[\left(1 + \frac{1}{2}\Phi\psi^2\right)e^{-\Phi\psi^2} - 1\right]$$

*Soave, Giorgio S. *Fluid Ph. Equilib*. 164.2: 157-172, 1999.

❑ Peng-Robinson (PR)-EOS*

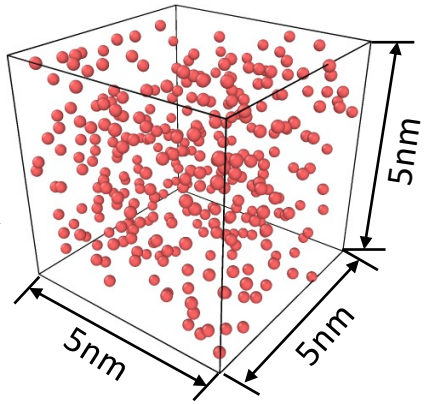
$$P = \frac{RT}{v-b} - \frac{a\alpha}{v^2 + 2bv - b^2}$$

Fugacity coefficient (FC), φ, and fugacity, f, :

$$\ln\varphi = \ln\frac{f}{P} = (Z-1) - \ln\left[\frac{(v-b)P}{RT}\right] + \frac{a\alpha}{\sqrt{8}bRT}\ln\left[\frac{v + (1+\sqrt{2})b}{v + (1-\sqrt{2})b}\right]$$

**Peng, D.Y. and Robinson, D.B. *Ind. Eng. Chem. Fundam.* 15: 59-64, 1976.

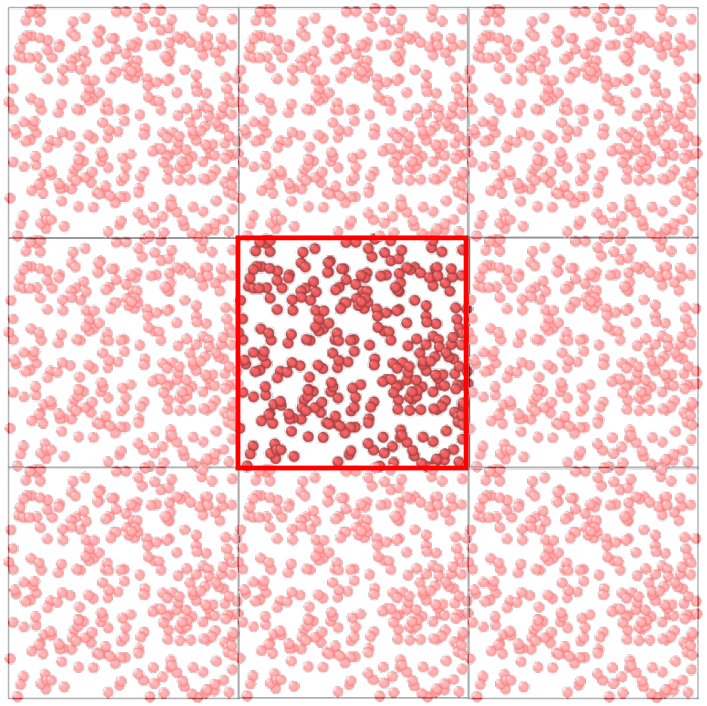
Input φ



A pure CH_4 system
of a 5*5*5 nm^3 box with
periodic boundary conditions

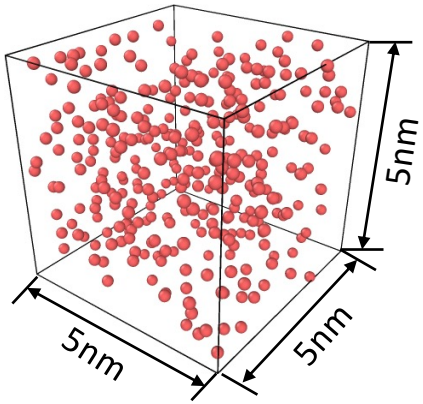
(TraPPE-UA force field)
(nvt ensemble + GCMC)

Validation of GCMC in bulk conditions



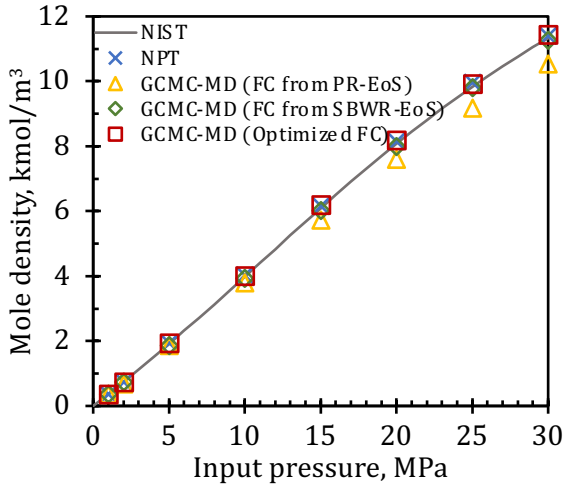
Pure-fluid box with full periodic boundary condition presents bulk fluids

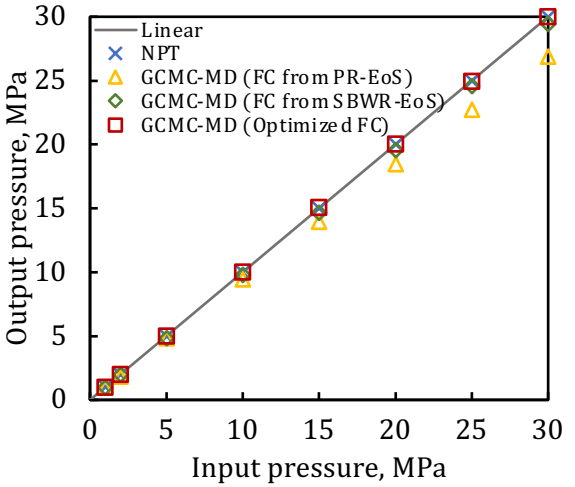
$$E_{ij} = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$



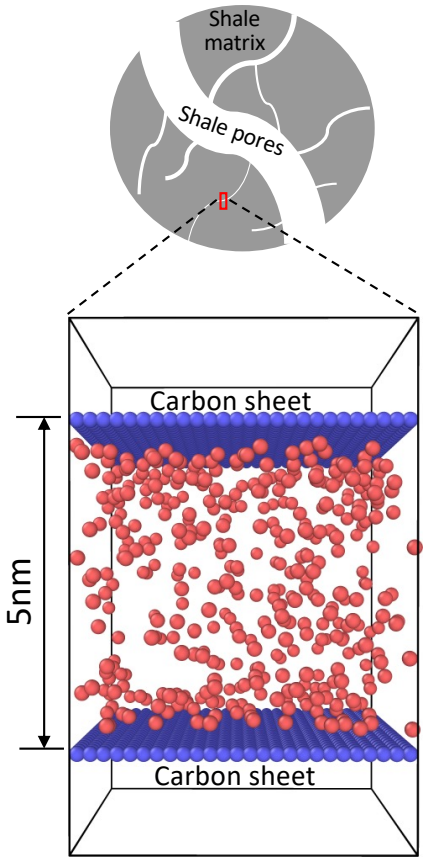
A pure CH_4 system
of a 5*5*5 nm^3 box with
periodic boundary conditions

(TraPPE-UA force field)
(nvt ensemble + GCMC)



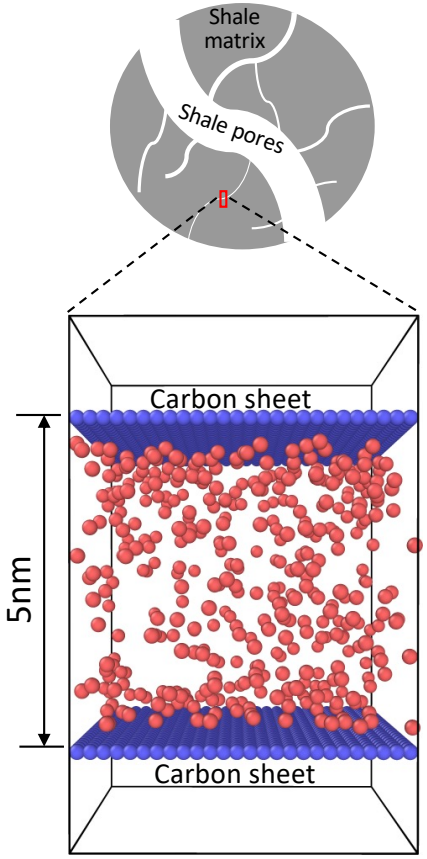


Adsorption density distributions



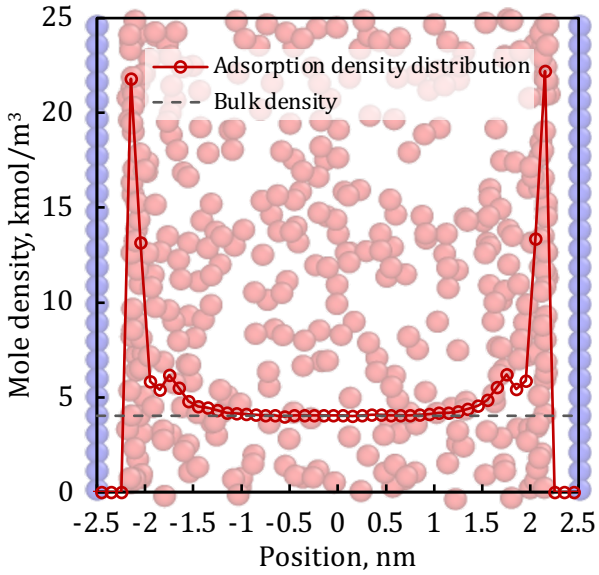
Molecule distributions of CH_4 in a 5nm pore connected to a non-confined pore at 10MPa and 333K

Adsorption density distributions



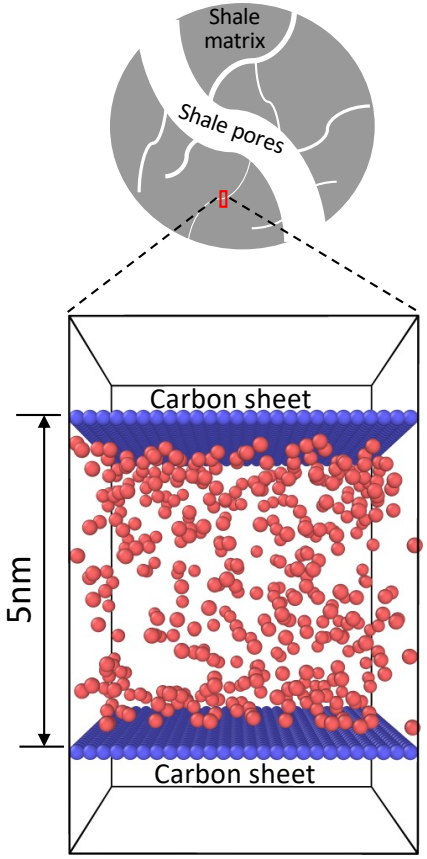
Molecule distributions of CH_4 in a 5nm pore connected to a non-confined pore at 10MPa and 333K

Averaging density in time



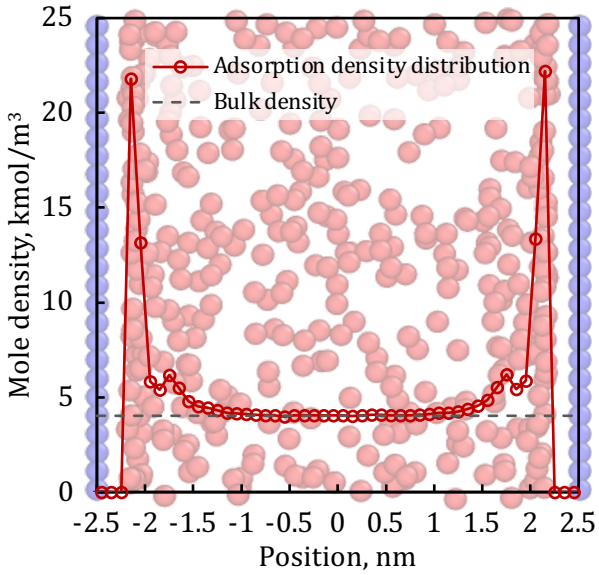
Density profiles of CH_4 in a 5nm pore connected to a non-confined pore at 10MPa and 333K

Adsorption density distributions



Molecule distributions of CH_4 in a 5nm pore connected to a non-confined pore at 10MPa and 333K

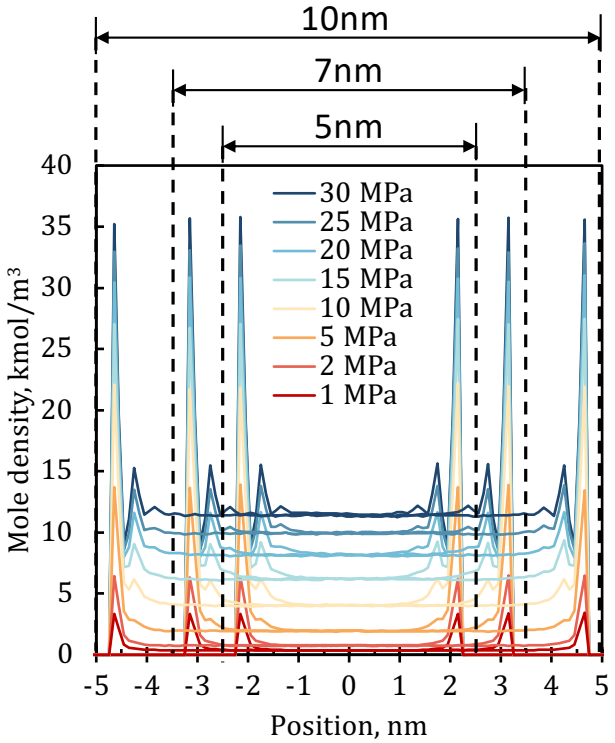
Averaging density in time



Density profiles of CH_4 in a 5nm pore connected to a non-confined pore at 10MPa and 333K

Change pressure

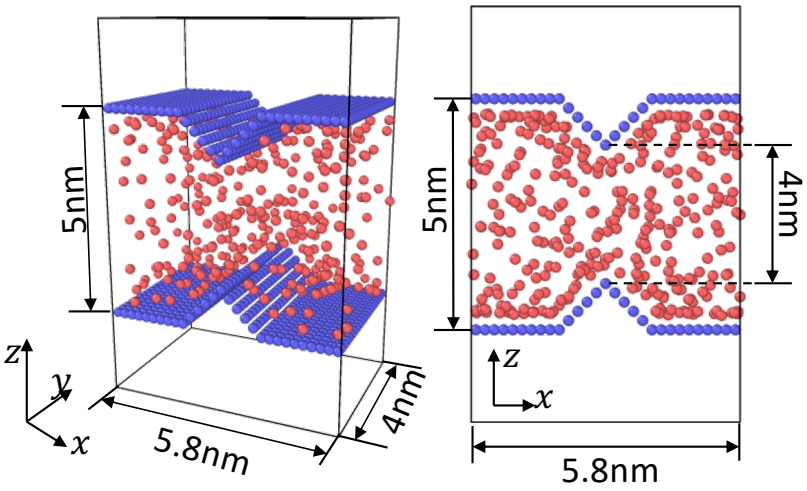
Change pore size



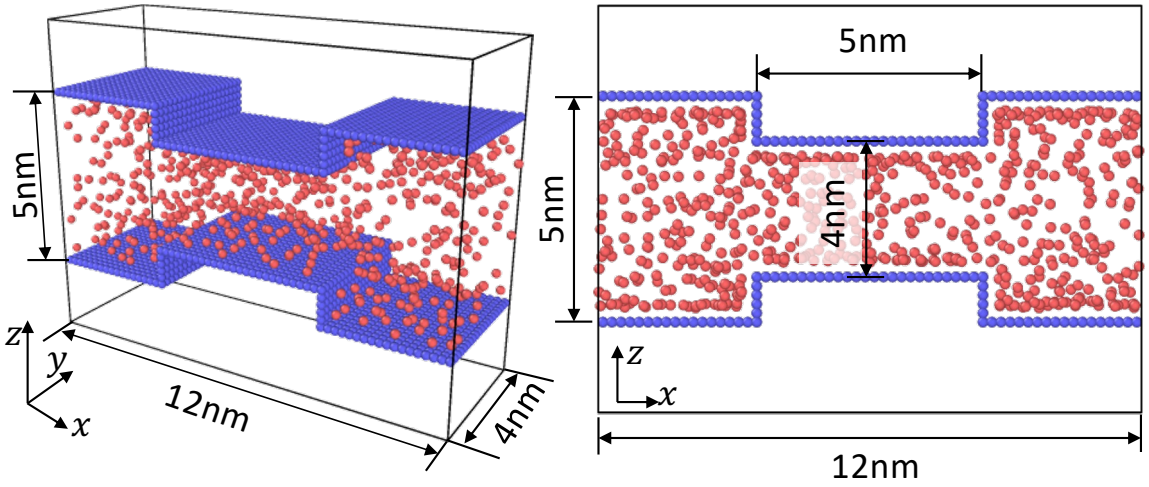
Density profiles vary with pressure and pore size is fixed at 333K

Adsorption in irregular nanopores

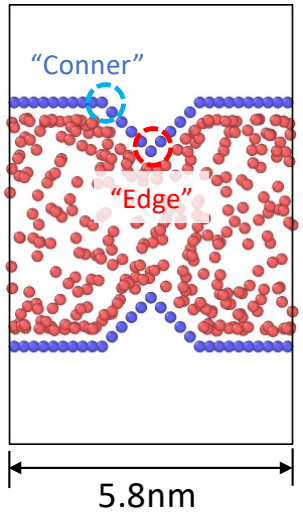
- Nanopores with triangle structure on surface

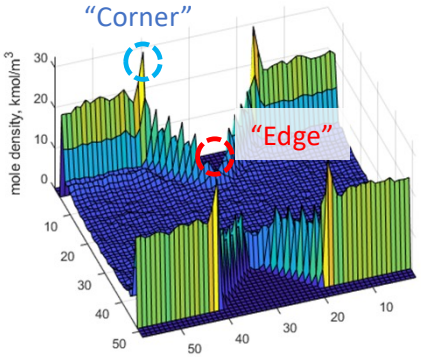


- Nanopores with rectangle structure on surface

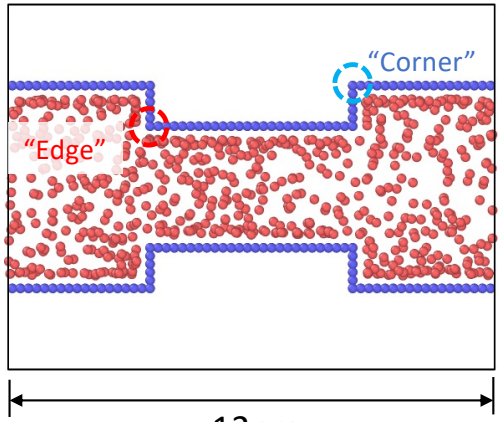


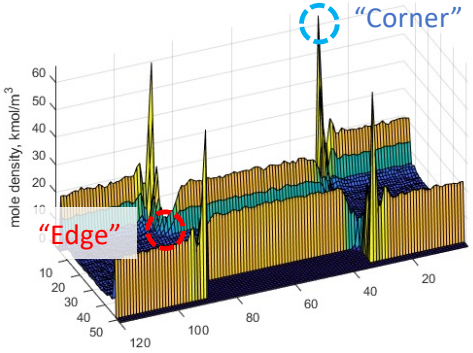
Adsorption in irregular nanopores



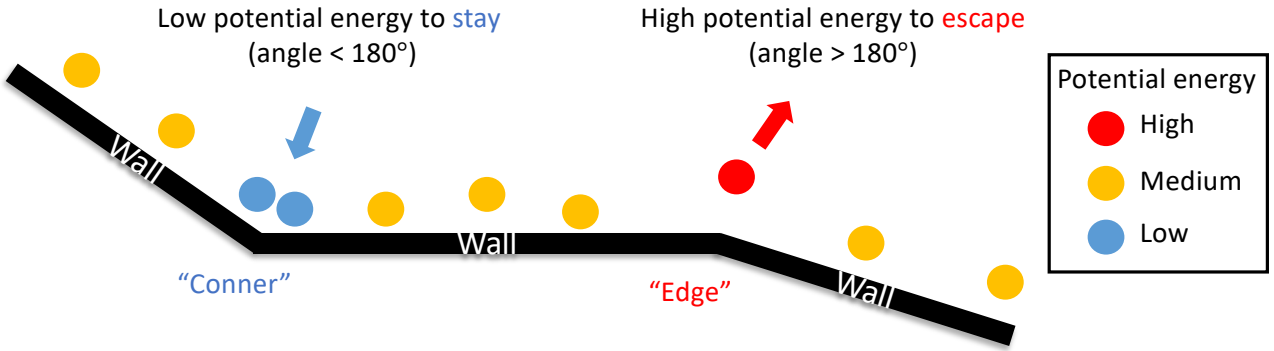


Density profiles from GCMC-MD simulations (T=333K, P=10MPa)

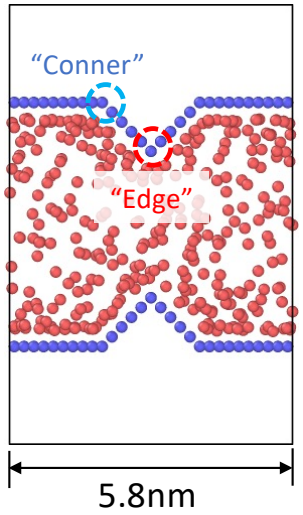


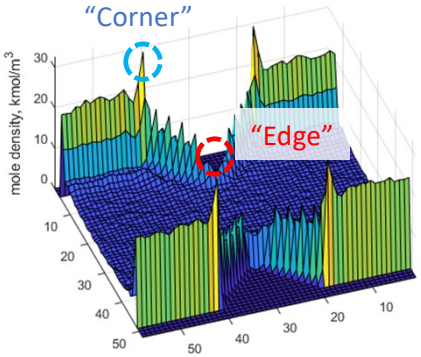


Density profiles from GCMC-MD simulations (T=333K, P=10MPa)

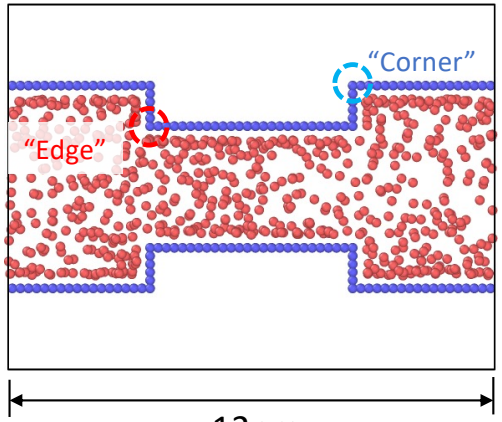


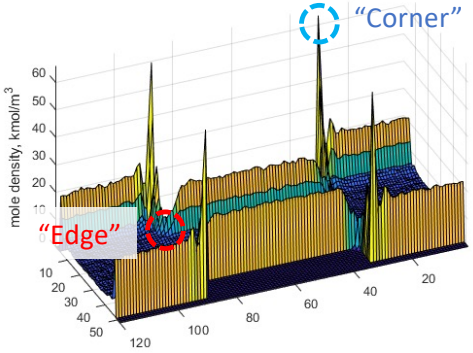
Adsorption in irregular nanopores



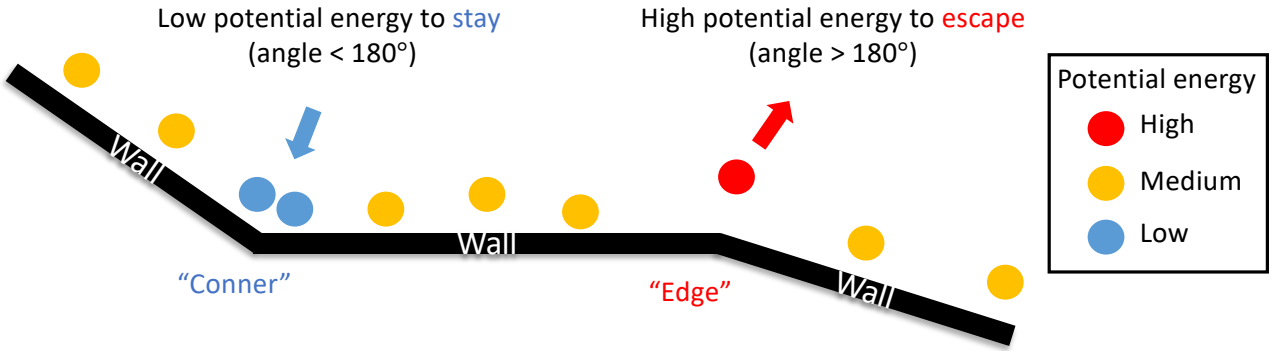


Density profiles from GCMC-MD simulations (T=333K, P=10MPa)





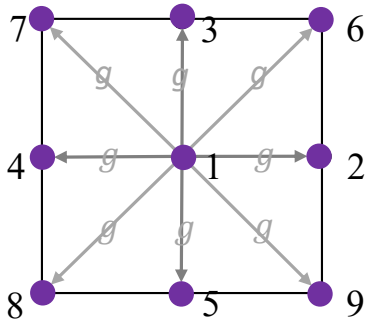
Density profiles from GCMC-MD simulations (T=333K, P=10MPa)



Lattice Boltzmann method

- Lattice Boltzmann equation

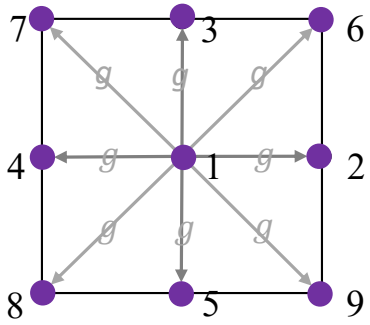
$$g_i(\boldsymbol{x} + \vec{c}_i \delta t, t + \delta t) = g_i(\boldsymbol{x}, t) + \Omega_i^C(g_i(\boldsymbol{x}, t)) + \delta t F_i(\boldsymbol{x}, t)$$



Lattice Boltzmann method

- Lattice Boltzmann equation

$$g_i(\boldsymbol{x} + \vec{c}_i\delta t, t + \delta t) = g_i(\boldsymbol{x}, t) + \Omega_i^C(g_i(\boldsymbol{x}, t)) + \delta t F_i(\boldsymbol{x}, t)$$



- LB free energy model

$$\boldsymbol{F} = -\tilde{\rho}\nabla\mu + c_s^2\nabla\rho$$

μ is chemical potential, $\tilde{\rho}$ is mole density

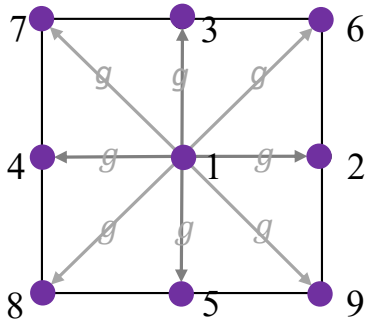
$-\tilde{\rho}\nabla\mu$ is the physical thermodynamic driven force， $\nabla\mu = RT\nabla\ln f$ at constant T (R is 8.314 J /mol/K)

$c_s^2\nabla\rho$ is used to cancel the ideal gas pressure induced by the collision-streaming process of the LBE.

Lattice Boltzmann method

- Lattice Boltzmann equation

$$g_i(\boldsymbol{x} + \vec{c}_i\delta t, t + \delta t) = g_i(\boldsymbol{x}, t) + \Omega_i^C(g_i(\boldsymbol{x}, t)) + \delta t F_i(\boldsymbol{x}, t)$$



- LB free energy model

$$\boldsymbol{F} = -\tilde{\rho}\nabla\mu + c_s^2\nabla\rho$$

μ is chemical potential, $\tilde{\rho}$ is mole density

$-\tilde{\rho}\nabla\mu$ is the physical thermodynamic driven force， $\nabla\mu = RT\nabla\ln f$ at constant T (R is 8.314 J /mol/K)

$c_s^2\nabla\rho$ is used to cancel the ideal gas pressure induced by the collision-streaming process of the LBE.

- Soave-Benedict-Webb-Rubin (SBWR)-EoS

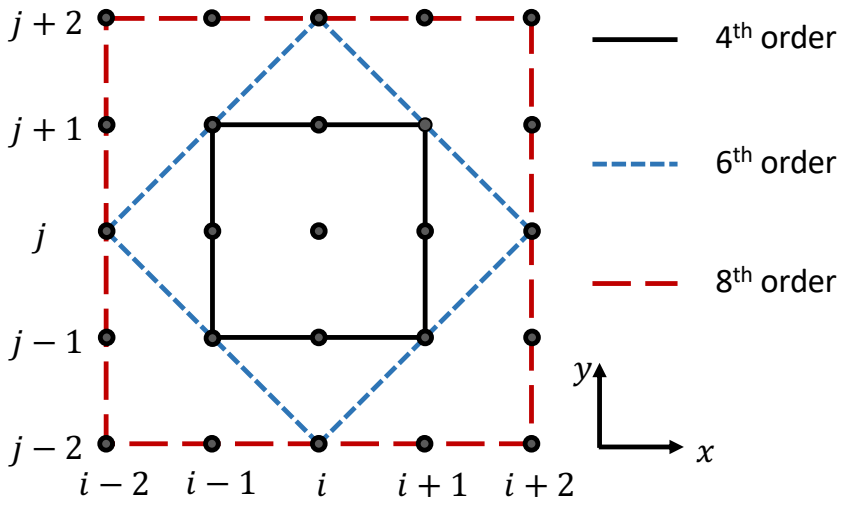
$$Z = \frac{P}{RT\tilde{\rho}} = 1 + B\tilde{\rho} + D\tilde{\rho}^4 + E\tilde{\rho}^2(1 + F\tilde{\rho}^2)e^{-F\tilde{\rho}^2}$$

Fugacity, f, :

$$\ln f = \ln P + (Z - 1) - \ln Z + \beta\psi + \frac{1}{4}\delta\psi^4 + \frac{\epsilon}{\Phi}\left[\left(1 + \frac{1}{2}\Phi\psi^2\right)e^{-\Phi\psi^2} - 1\right]$$

Force schemes in LB

- Discretization of gradient term

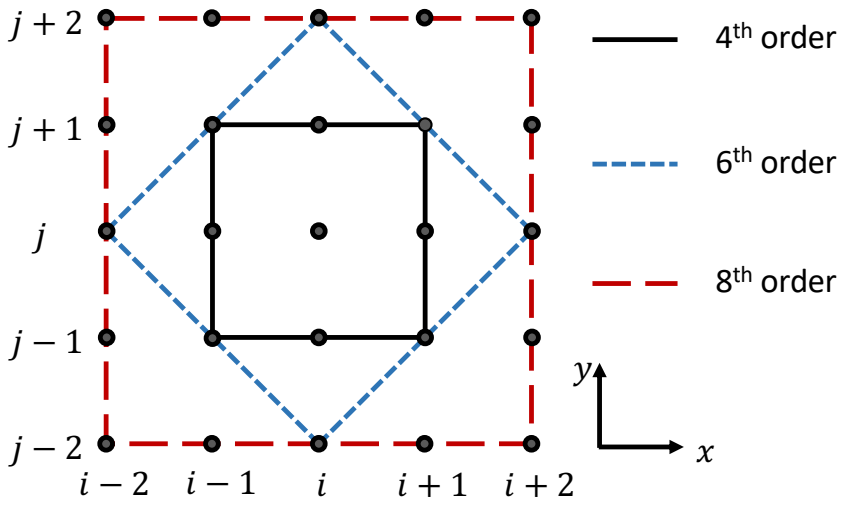


General form of calculating $\nabla\mu$

$$\nabla\mu(\boldsymbol{x}) = \sum_{i}^{N} \omega_{F,i}(\boldsymbol{x} + c\boldsymbol{e}_i\delta t)\mu(\boldsymbol{x} + c\boldsymbol{e}_i\delta t)\,\boldsymbol{e}_i$$

Force schemes in LB

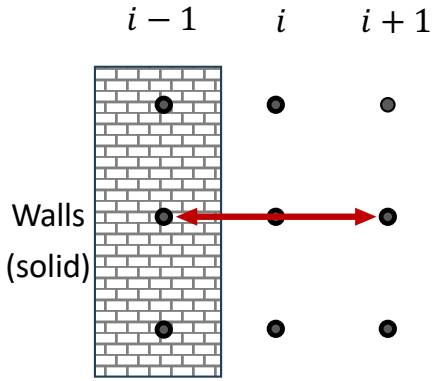
- Discretization of gradient term



General form of calculating $\nabla\mu$

$$\nabla\mu(\boldsymbol{x}) = \sum_{i}^{N} \omega_{F,i}(\boldsymbol{x} + c\boldsymbol{e}_i\delta t)\mu(\boldsymbol{x} + c\boldsymbol{e}_i\delta t)\,\boldsymbol{e}_i$$

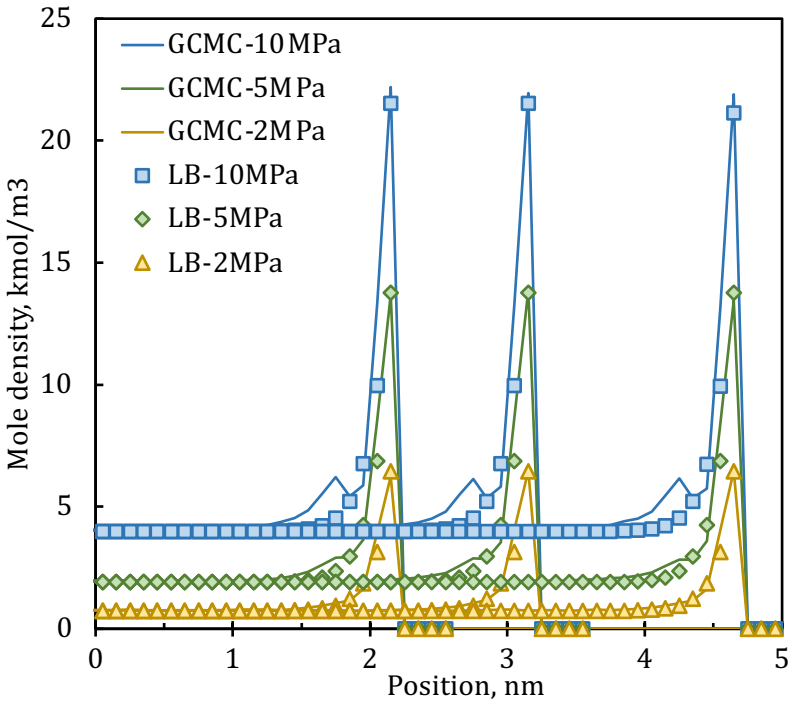
- Treatment of fluid-wall interactions



$$\mu(i-1) = G_{\mathrm{fs}} * \mu(i),$$

$(0 < G_{\mathrm{fs}} < 1$ represent attractive force$)$

Density profiles comparison in nano-slits



Density comparison between GCMC-MD reference data and LB simulation results with various pore size and pressure conditions.

Obtained values of G_{fs}

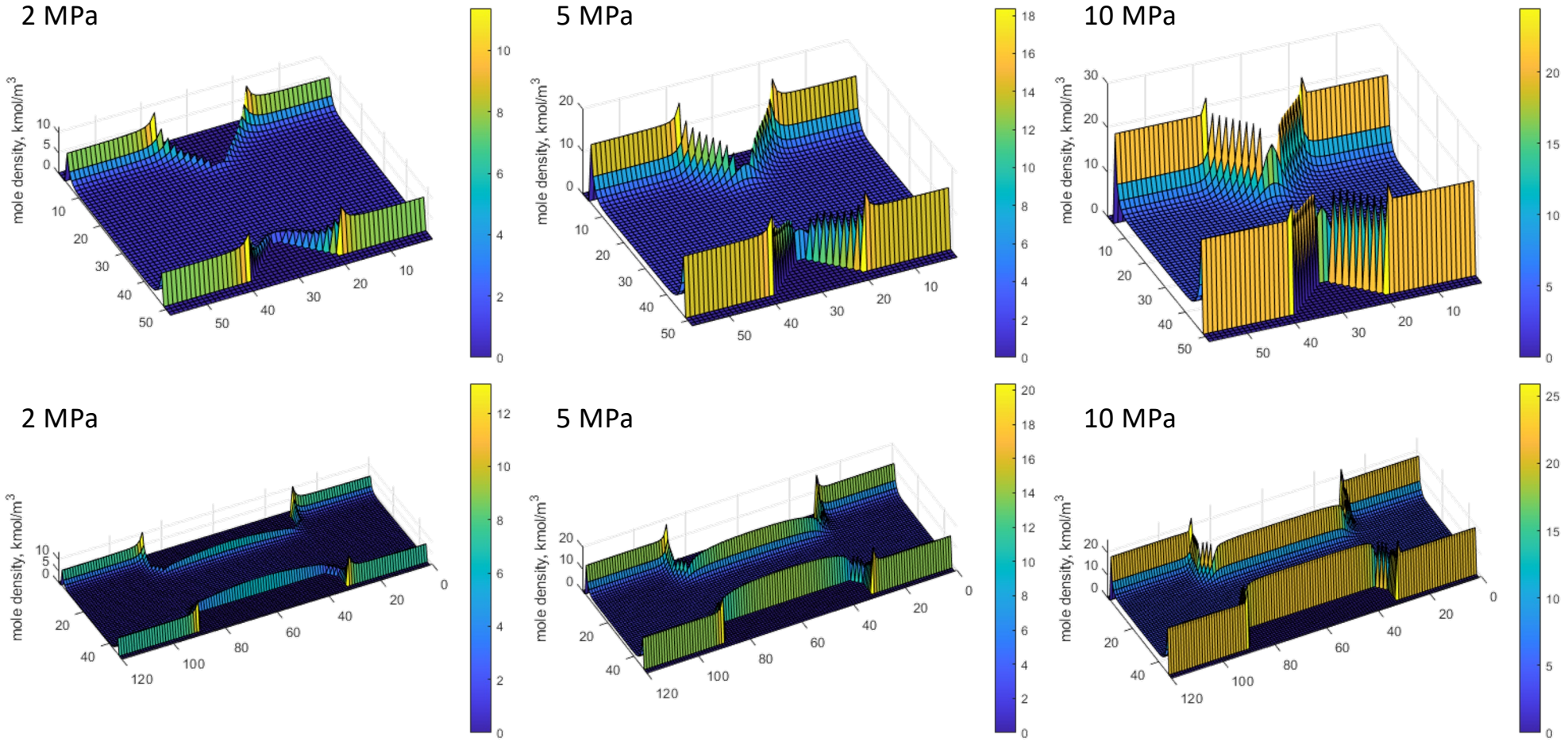
2MPa	5MPa	10MPa
0.809	0.803	0.700

Higher pressure

Larger attractive force

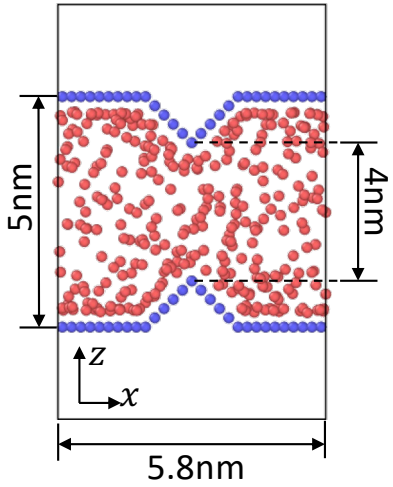
Smaller values of G_{fs}

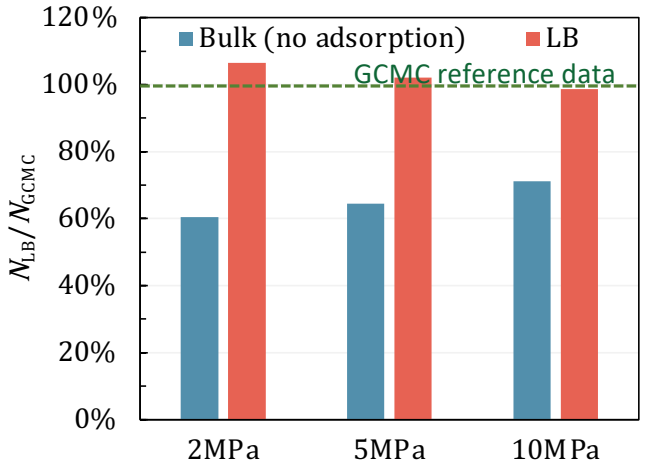
Adsorption in irregular nanopores

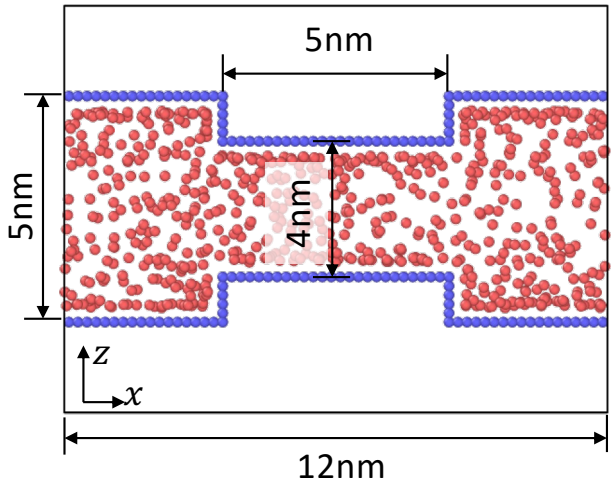


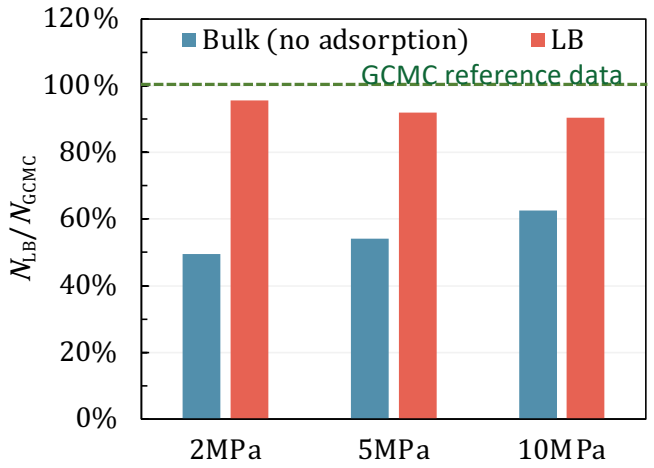
Density profiles from LB simulations (T=333K)

Adsorption in irregular nanopores

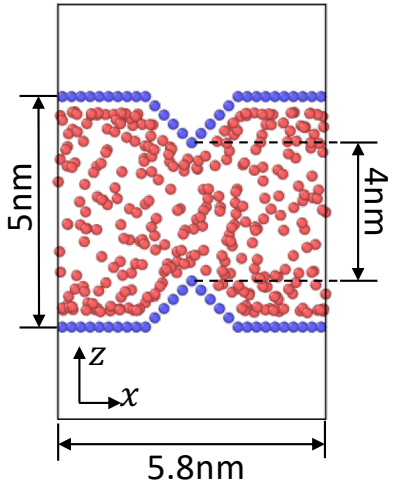


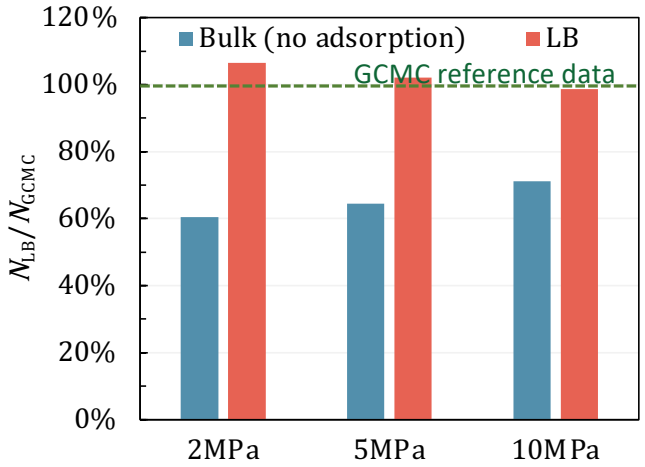


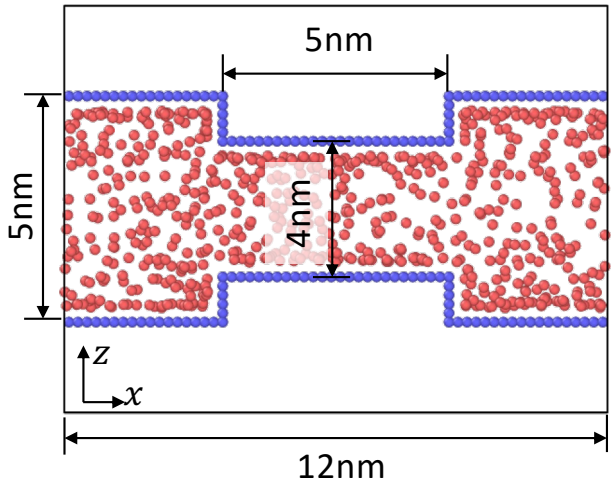


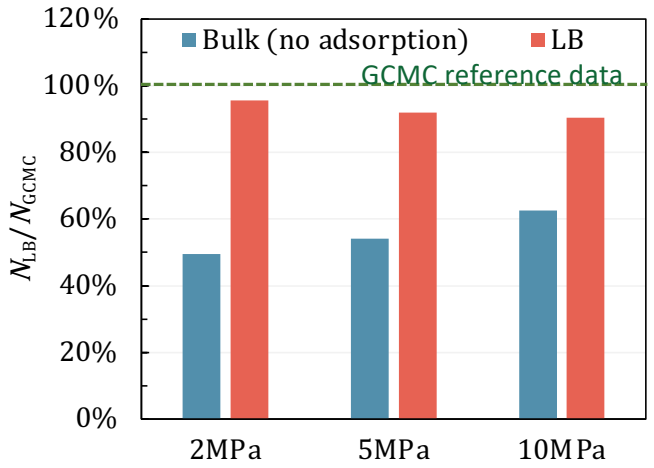


Adsorption in irregular nanopores



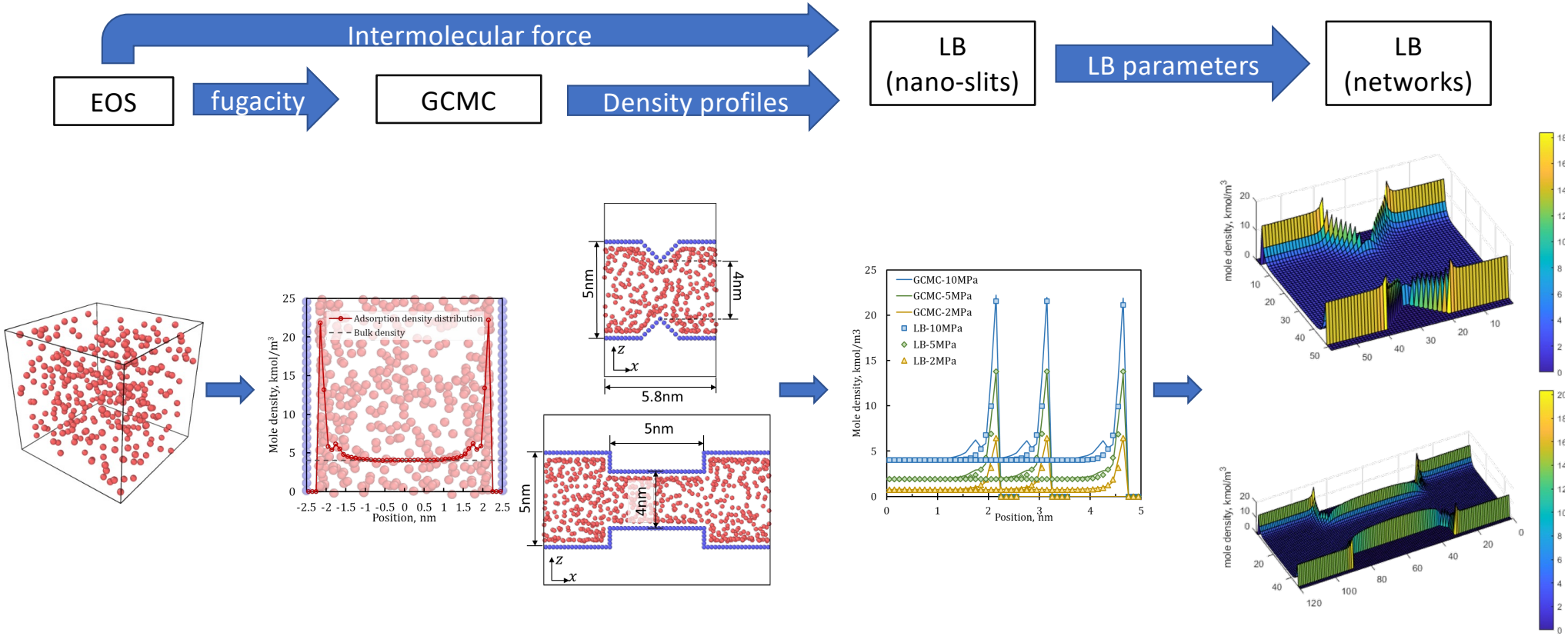




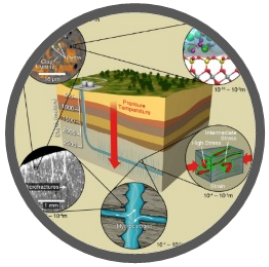


Summary

- Bridging adsorption behavior of confined methane across scales



ACKNOWLEDGEMENTS



CMC - UF

CENTER FOR MECHANISTIC CONTROL OF WATER-HYDROCARBON-ROCK INTERACTIONS IN UNCONVENTIONAL AND TIGHT OIL FORMATIONS

This work was supported as part of the Center for Mechanistic Control of Unconventional Formations (CMC-UF), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science under *DOE (BES) Award DE-SC0019165.*

U.S. DEPARTMENT OF ENERGY | Office of Science

Stanford UW USC SLAC ILLINOIS

Thank you!

lliu1@uwyo.edu