

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

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Outline

❑ Research goals

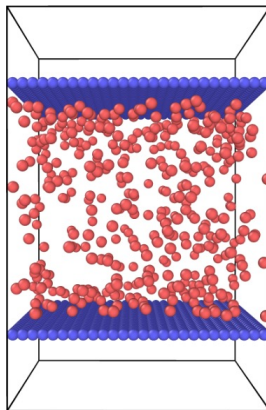
- 1) investigate adsorption behavior
- 2) Scale-translating simulation from micro- to meso-scale

Outline

❑ Research goals

- 1) investigate adsorption behavior
- 2) Scale-translating simulation from micro- to meso-scale

❑ Research method



Molecular simulations
(reveal confined physics at micro-scale)

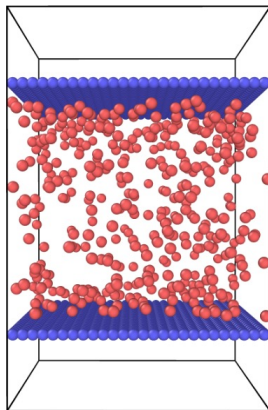
Phase Behavior
(Equation of state)
↙

Outline

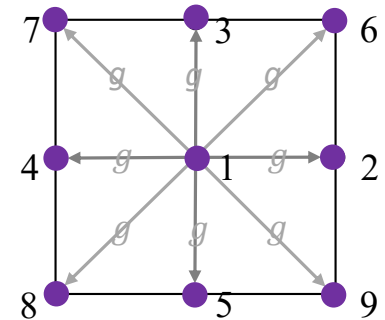
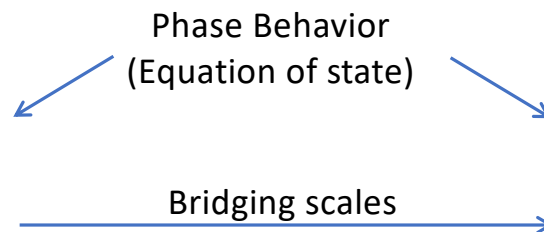
❑ Research goals

- 1) investigate adsorption behavior
- 2) Scale-translating simulation from micro- to meso-scale

❑ Research method



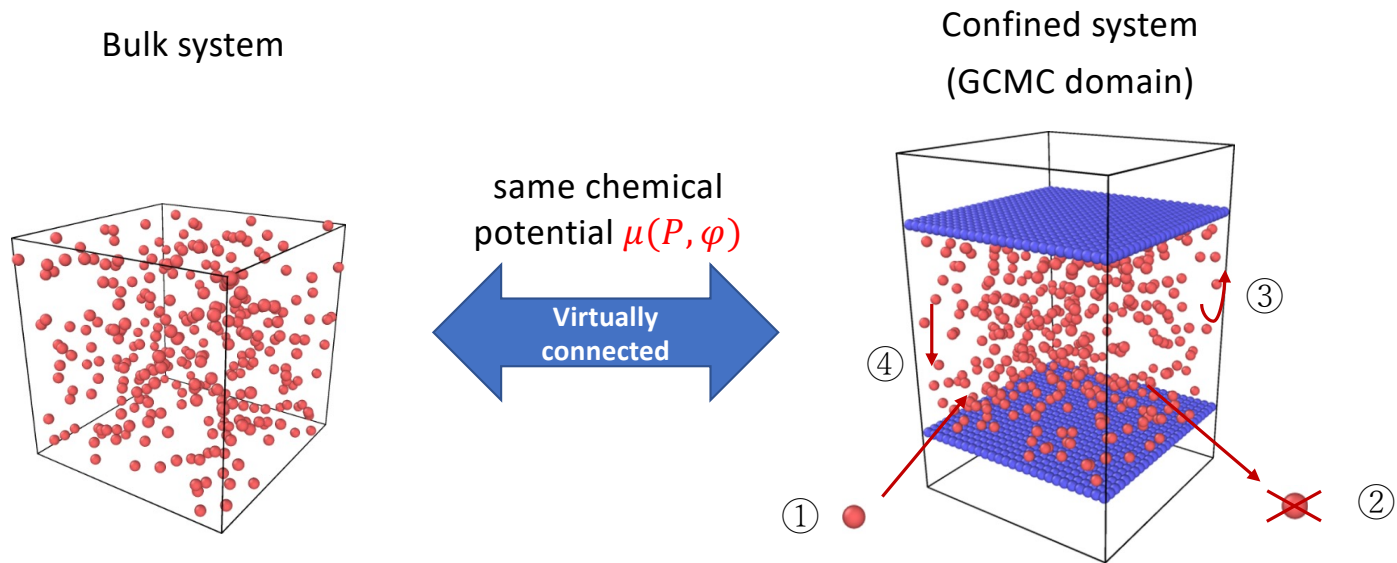
Molecular simulations
(reveal confined physics at micro-scale)



Lattice Boltzmann method
(mimic physics at meso-scale)

GCMC simulations

- Grand Canonical Monte Carlo (GCMC) method

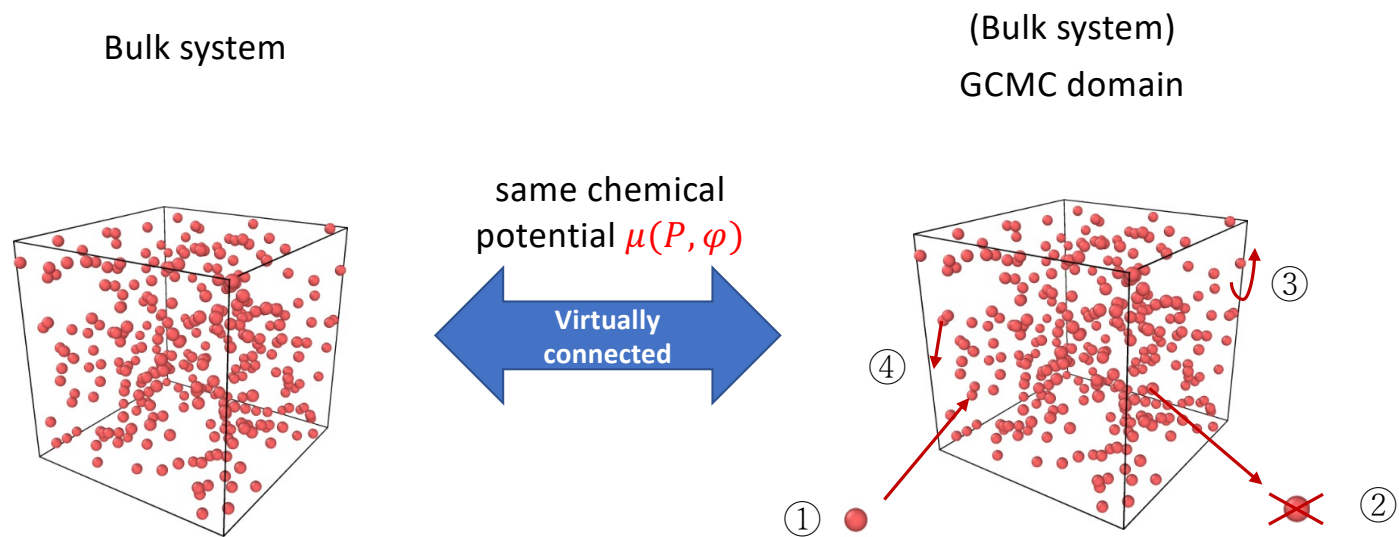


Exchanges of molecules in Mont Carlo simulations

- ① Insertion ② Deletion ③ Rotation 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 ③ Rotation 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 , :

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

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

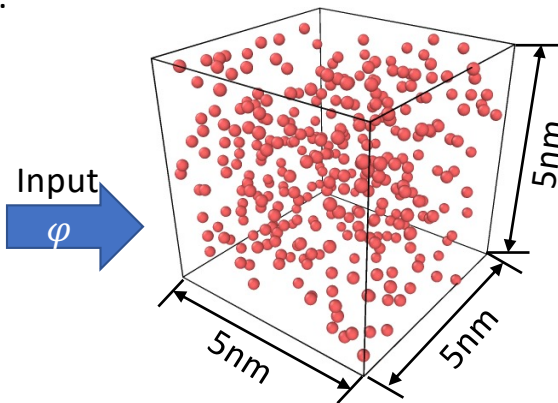
❑ Peng-Robinson (PR)-EOS*

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

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

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

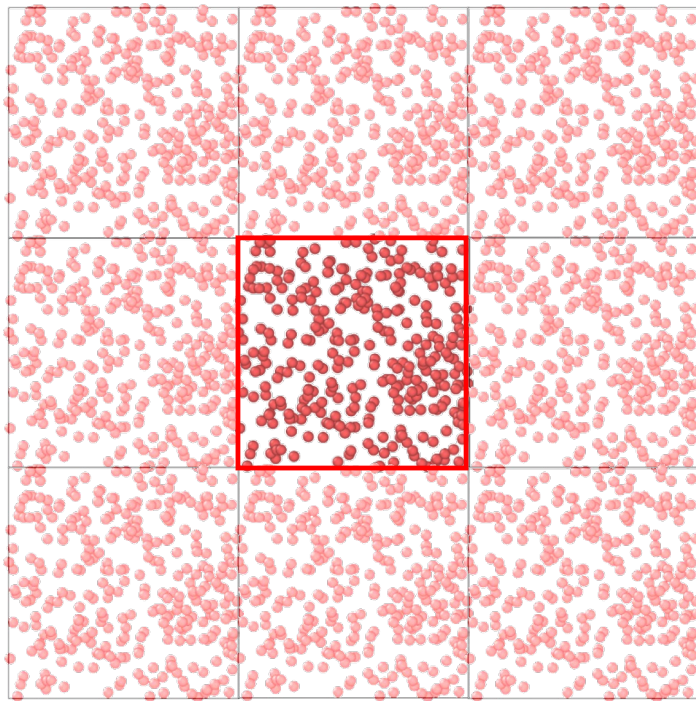
**Peng, D.Y. and Robinson, D.B. *Ind. Eng. Chem. Fundam.* 15: 59-64, 1976.



A pure CH₄ system
of a 5*5*5 nm³ box with
periodic boundary conditions

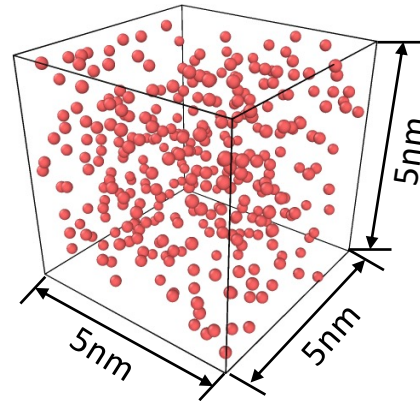
(TraPPE-UA force field)
(nvt ensemble + GCMC)

Validation of GCMC in bulk conditions



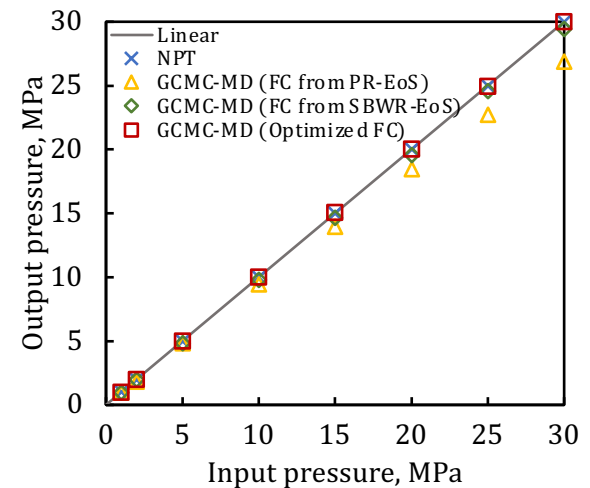
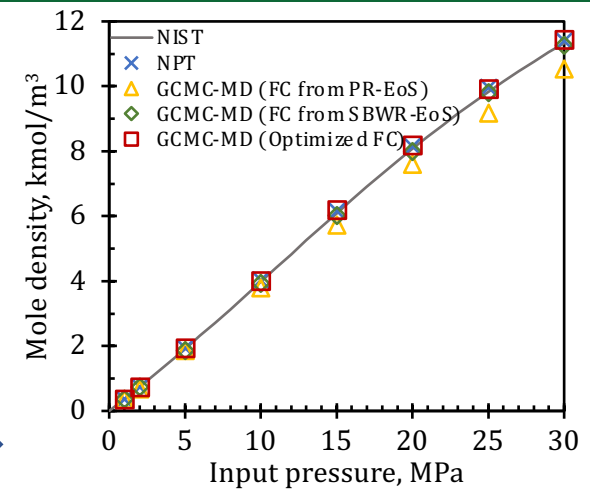
Pure-fluid box with full periodic boundary condition presents bulk fluids

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

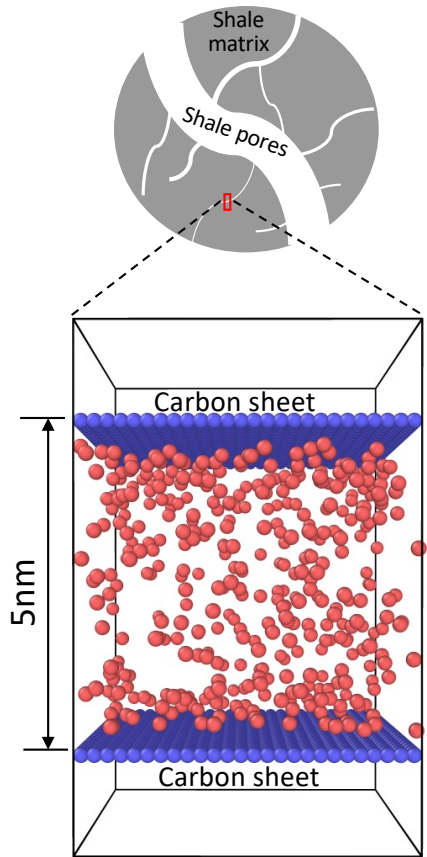


A pure CH₄ system
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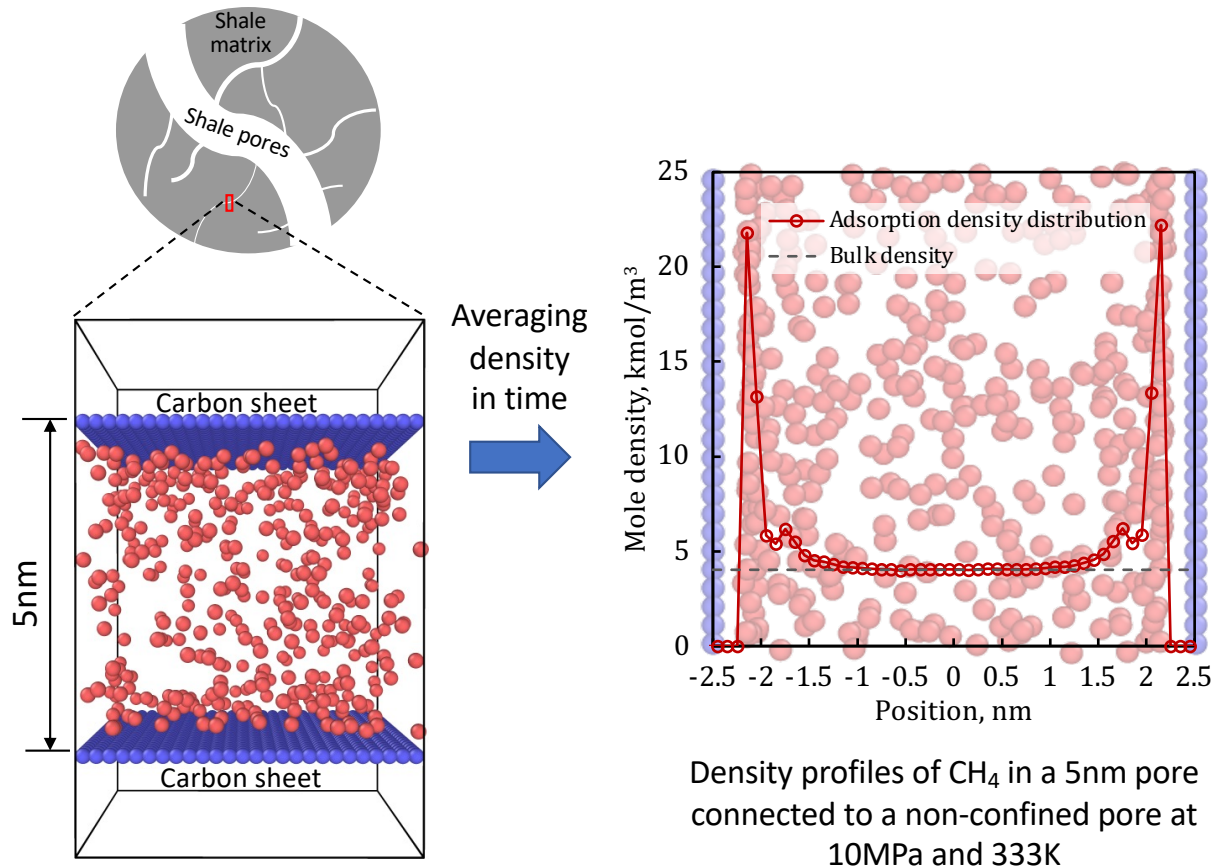


Adsorption density distributions



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

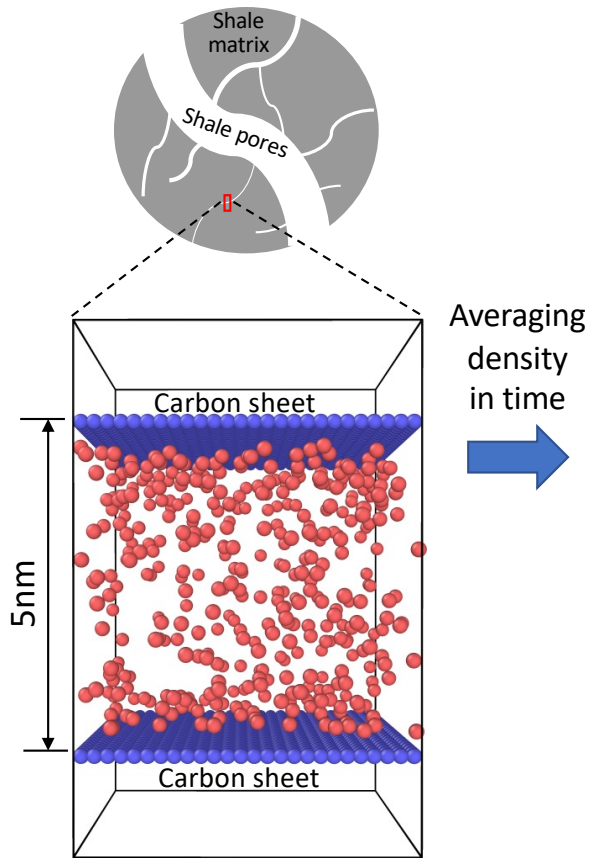
Adsorption density distributions



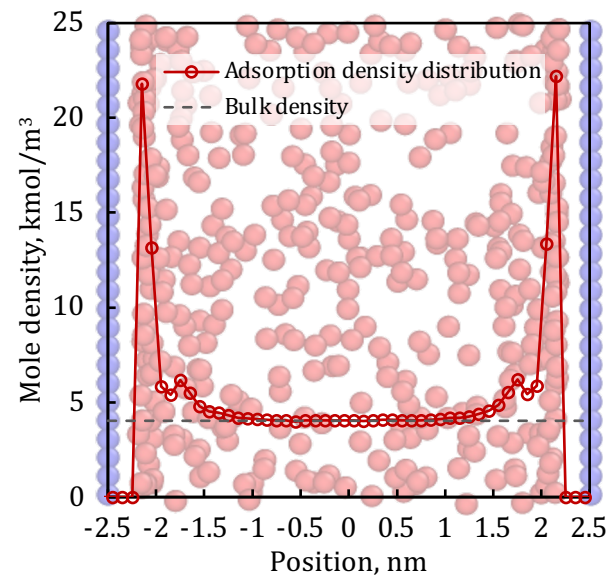
Molecule distributions of CH₄ in a 5nm pore connected to a non-confined pore at 10MPa and 333K

Density profiles of CH₄ in a 5nm pore connected to a non-confined pore at 10MPa and 333K

Adsorption density distributions

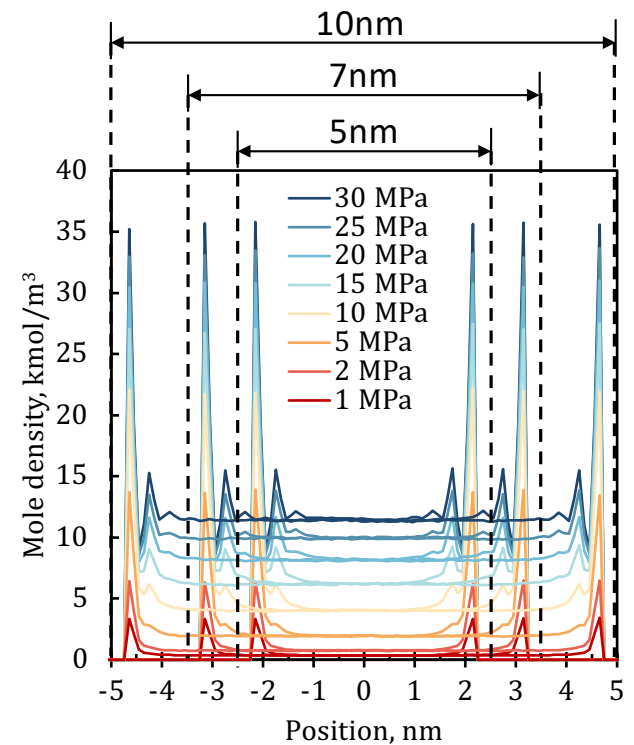


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Density profiles of CH_4 in a 5nm pore connected to a non-confined pore at 10MPa and 333K

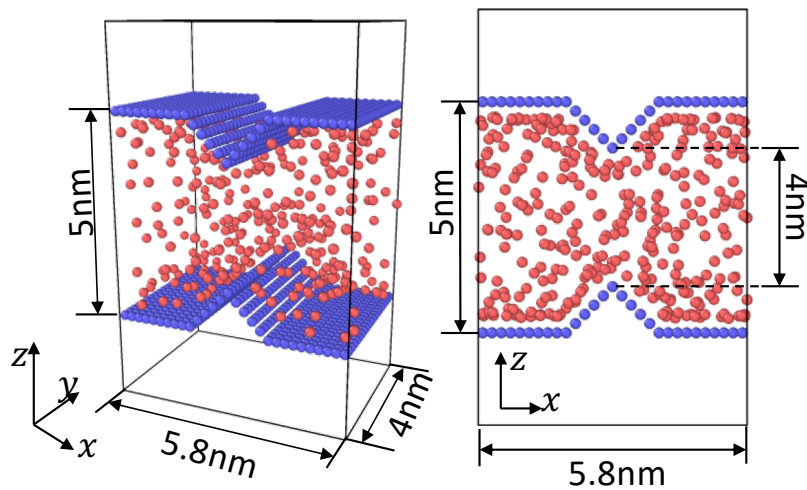
Change pressure
→
Change pore size



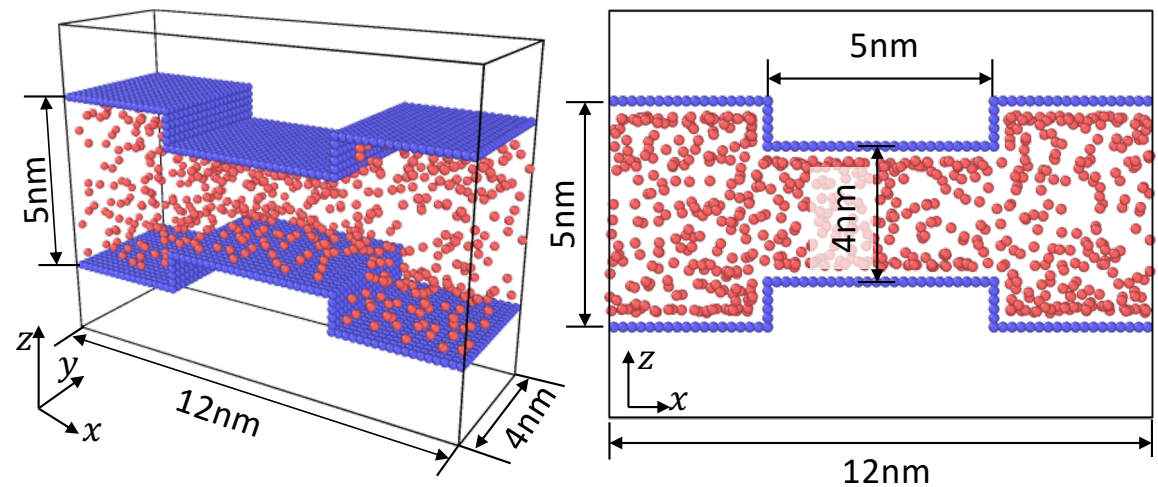
Density profiles vary with pressure and pore size is fixed at 333K

Adsorption in irregular nanopores

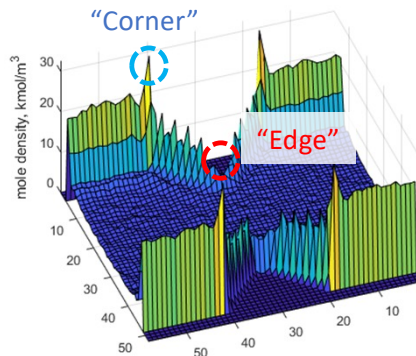
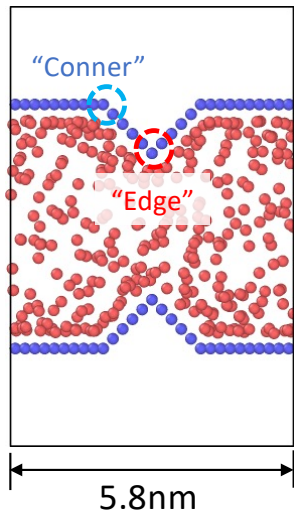
□ Nanopores with triangle structure on surface



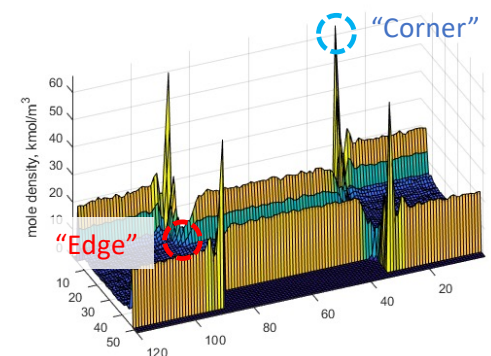
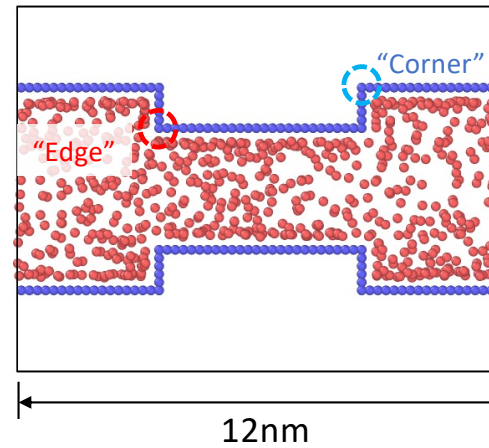
□ Nanopores with rectangle structure on surface



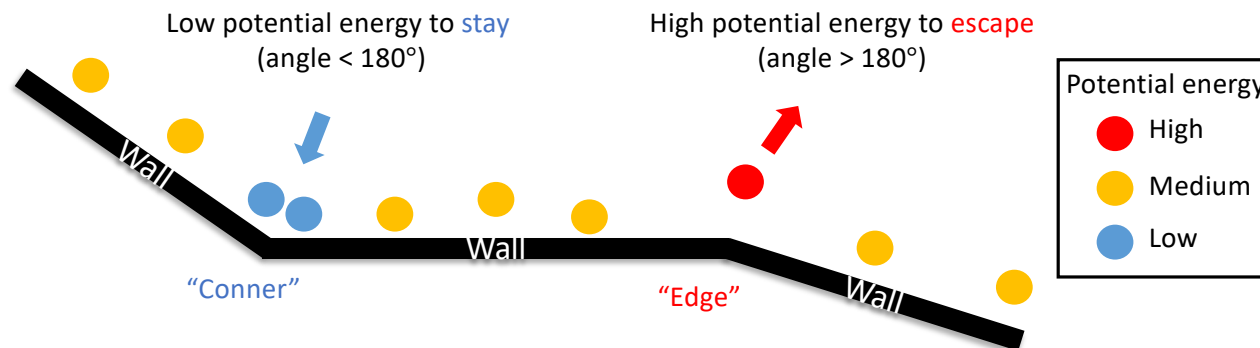
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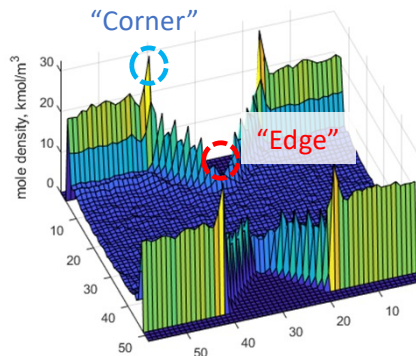
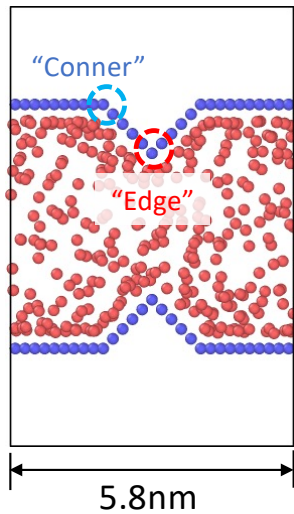
Density profiles from GCMC-MD simulations
(T=333K, P=10MPa)



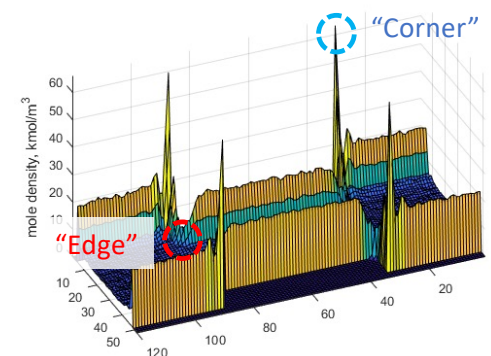
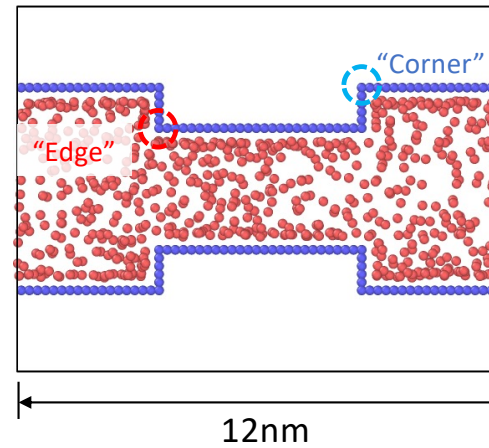
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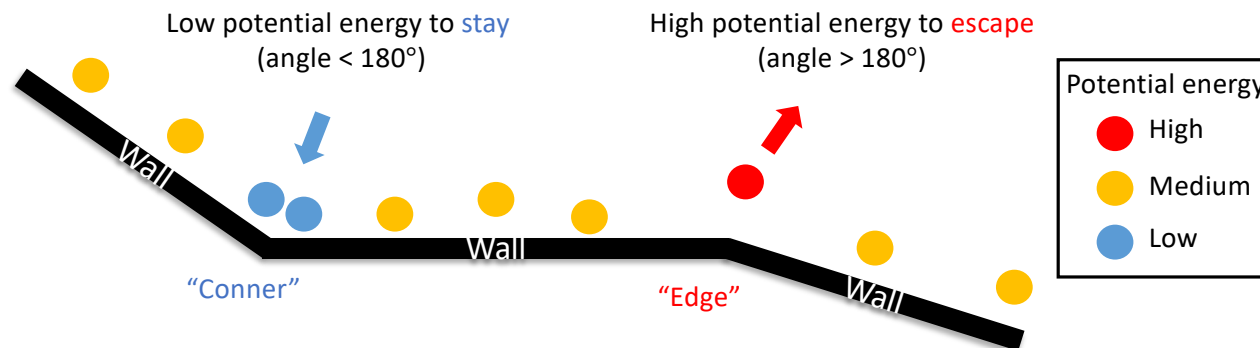
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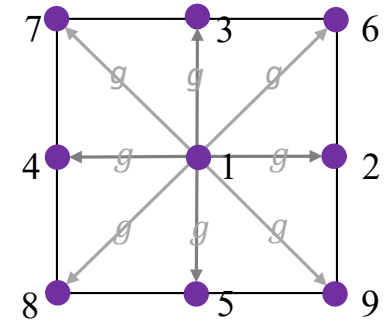
Density profiles from GCMC-MD simulations
(T=333K, P=10MPa)



Lattice Boltzmann method

□ Lattice Boltzmann equation

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



Lattice Boltzmann method

- Lattice Boltzmann equation

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

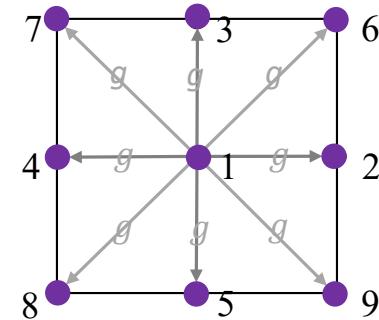
- LB free energy model

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

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.



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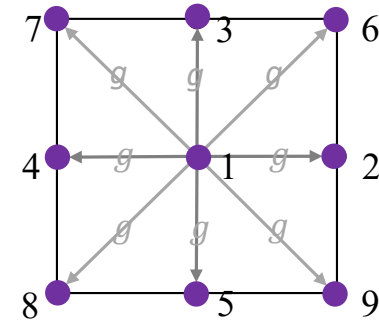
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□ Soave-Benedict-Webb-Rubin (SBWR)-EoS

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

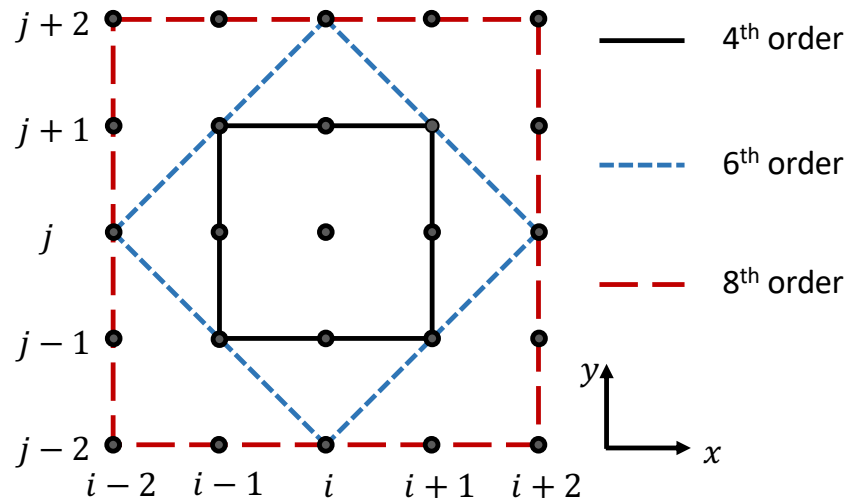
Fugacity, f , :

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



Force schemes in LB

□ Discretization of gradient term

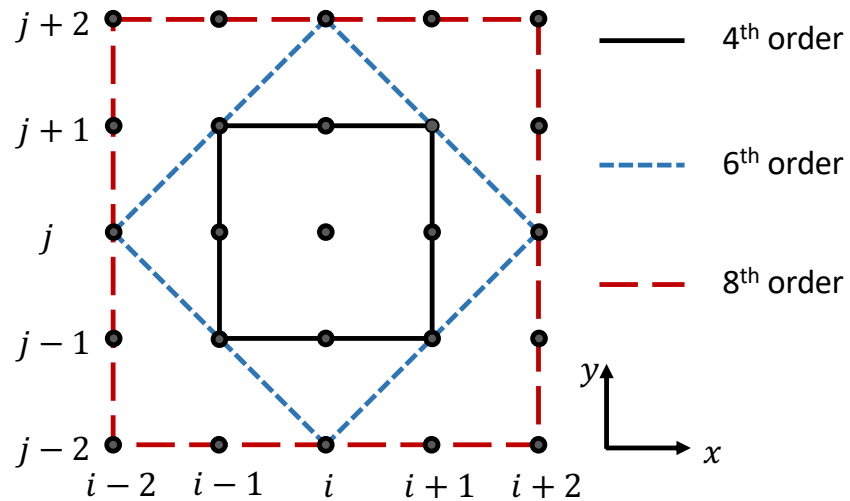


General form of calculating $\nabla\mu$

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

Force schemes in LB

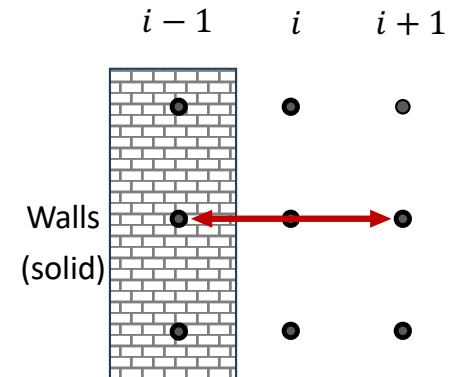
Discretization of gradient term



General form of calculating $\nabla\mu$

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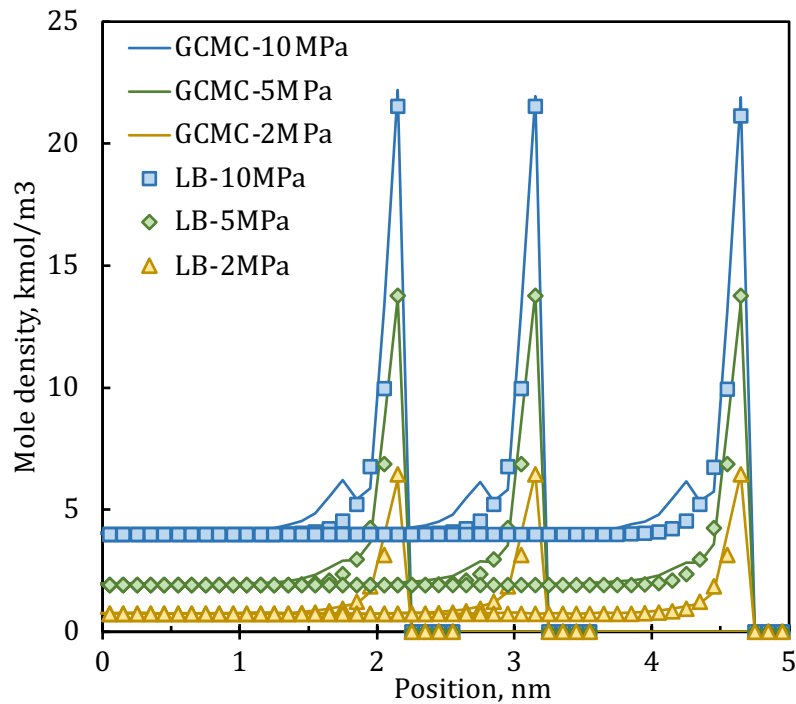
Treatment of fluid-wall interactions



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

($0 < G_{fs} < 1$ 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}

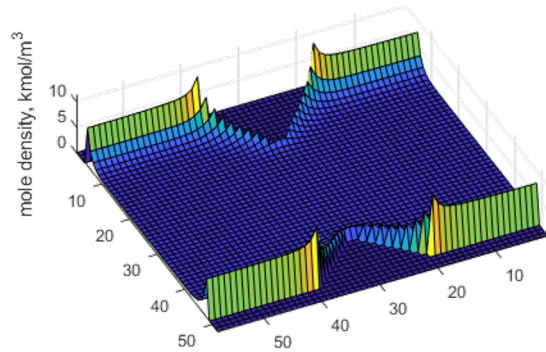
2MPa	5MPa	10MPa
0.809	0.803	0.700



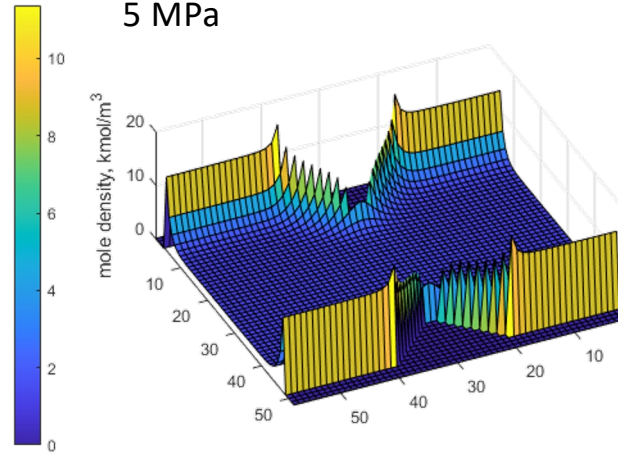
Higher pressure
Larger attractive force
Smaller values of G_{fs}

Adsorption in irregular nanopores

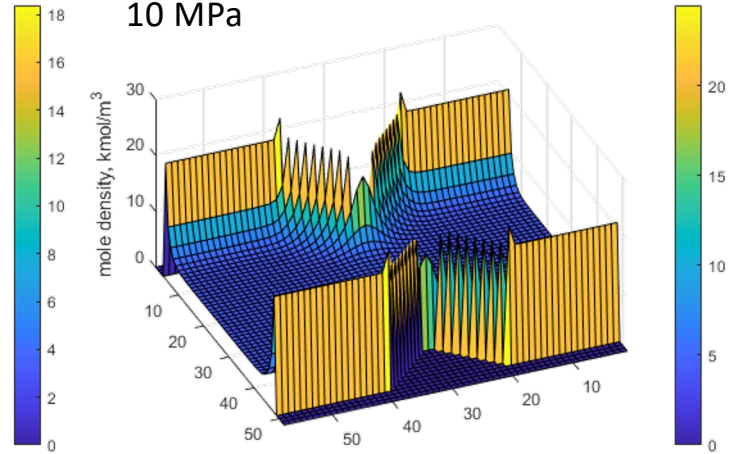
2 MPa



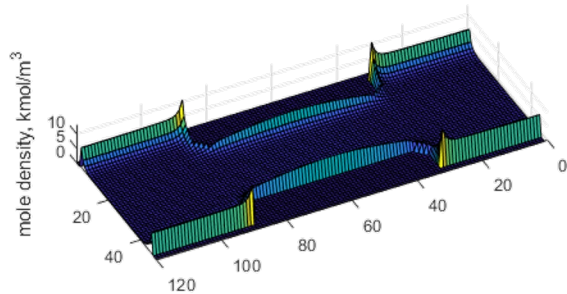
5 MPa



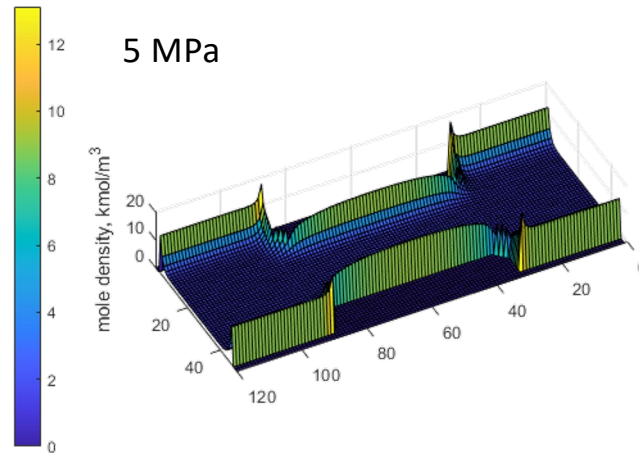
10 MPa



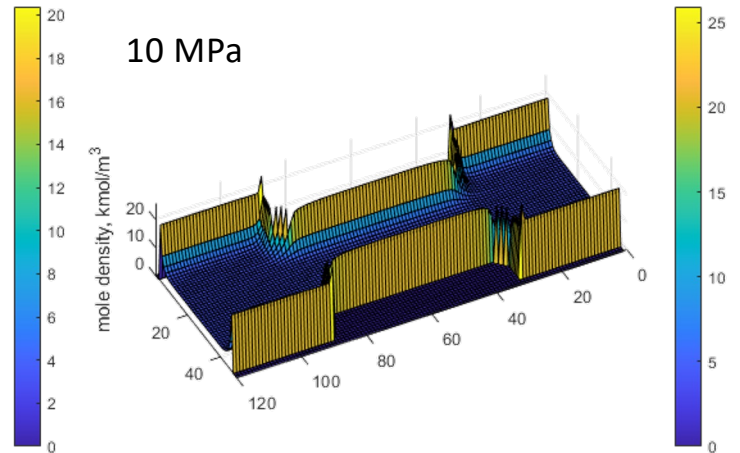
2 MPa



5 MPa

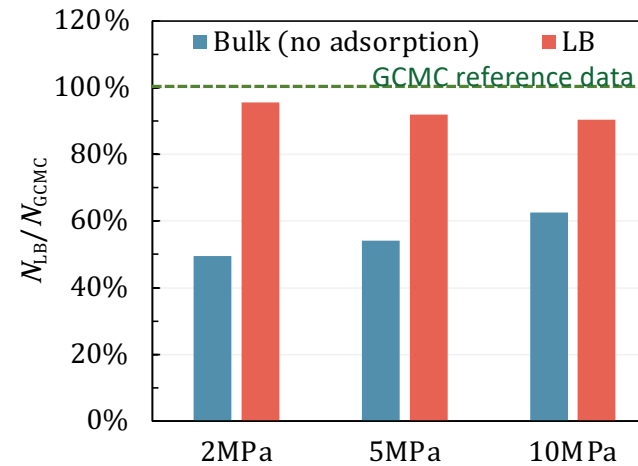
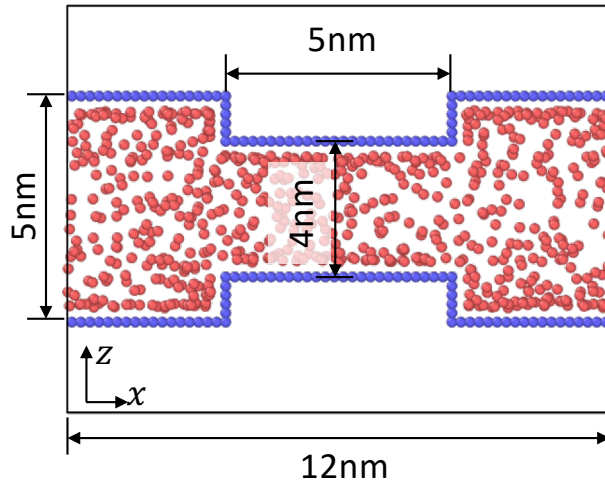
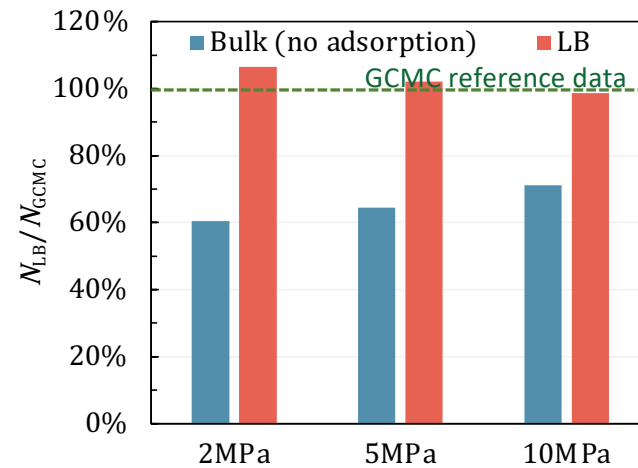
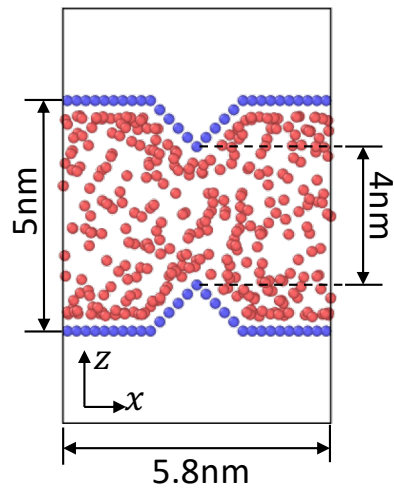


10 MPa

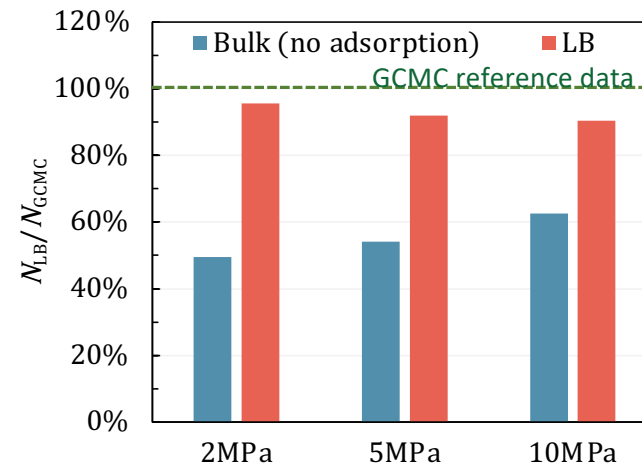
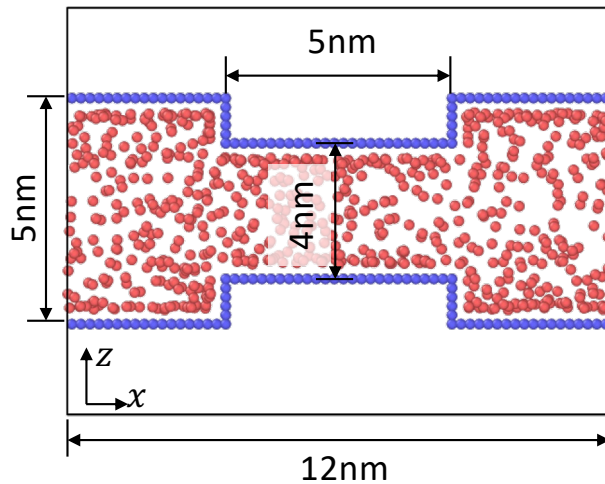
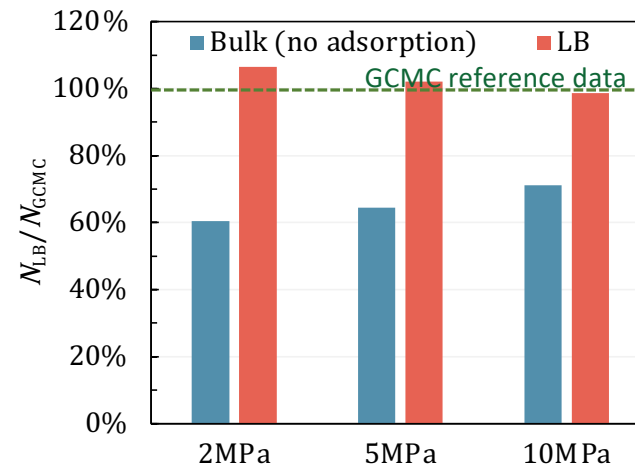
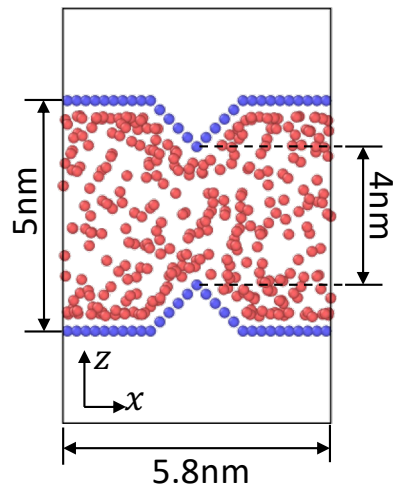


Density profiles from LB simulations (T=333K)

Adsorption in irregular nanopores

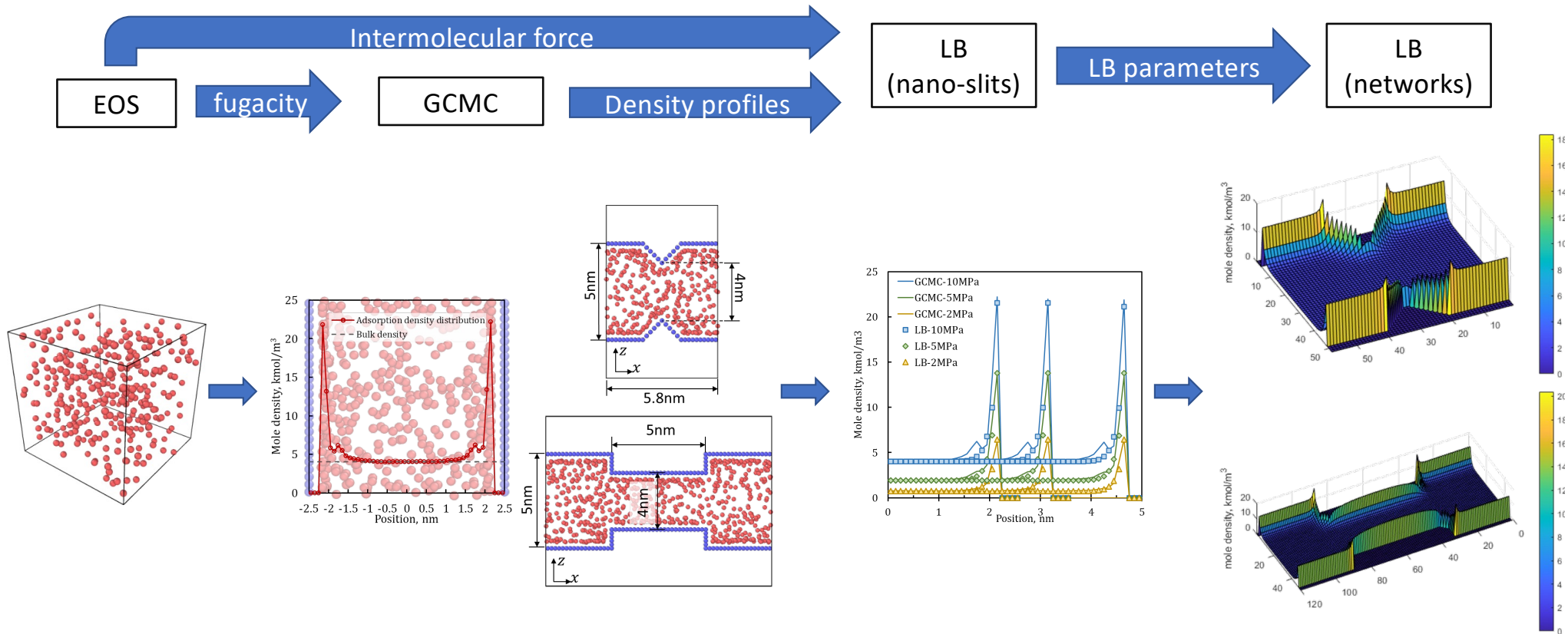


Adsorption in irregular nanopores

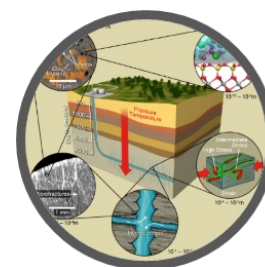


Summary

❑ Bridging adsorption behavior of confined methane across scales



ACKNOWLEDGEMENTS



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OF WATER-HYDROCARBON-ROCK
INTERACTIONS IN UNCONVENTIONAL
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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*.

Thank you!

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