A Statistical Mechanics Model for Phase Behavior of Confined Hydrocarbons

MOLECULAR SIMULATION OF PHASE BEHAVIOR

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Agenda

- Introduction
- Purpose
- Starting Point
- Background: Statistical Mechanics
- Methodology
- Future Work

Introduction : Phase Envelope

Under Bulk Condition

- Experimental
  - PVT Cells
- Simulation
  - Equation of State

In Confined Environment

- Experimental
  - PVT Cells are not Useful
  - Not a Certain Methodology Developed Yet
- Simulation
  - Equation of State Modified for Capillary Pressure (Considers Macroscopic Thermodynamic Properties)
  - Statistical Mechanics (Considers Microscopic Interactions i.e. Inter-Particle Interactions)

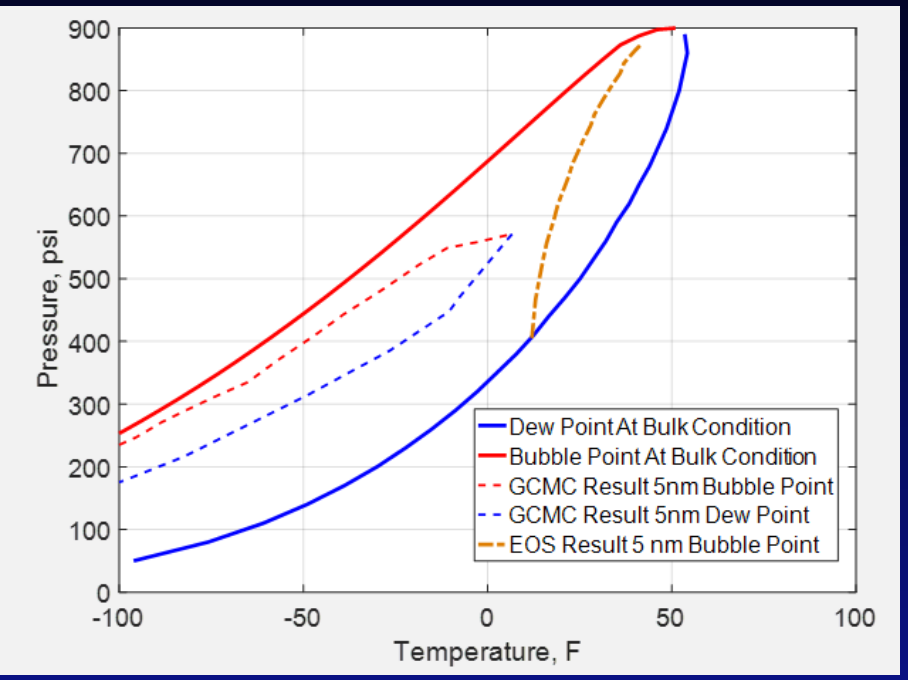
Purpose of The Study

- See the effect of intermolecular forces between the surface and the fluid particles on the phase behavior of hydrocarbons

- Study the phase diagram of a methane ethane mixture
  - using Grand Canonical Monte Carlo (GCMC) Simulation which is based on Statistical Mechanics
  - using EOS-Peng Robinson modified for capillary pressure
  - Incorporate both the capillary forces and the intermolecular forces and plot the phase envelope of the mixture
  - Compare the results of 2nd 3rd and 4th objectives

- Understand change in the critical point of confined fluid

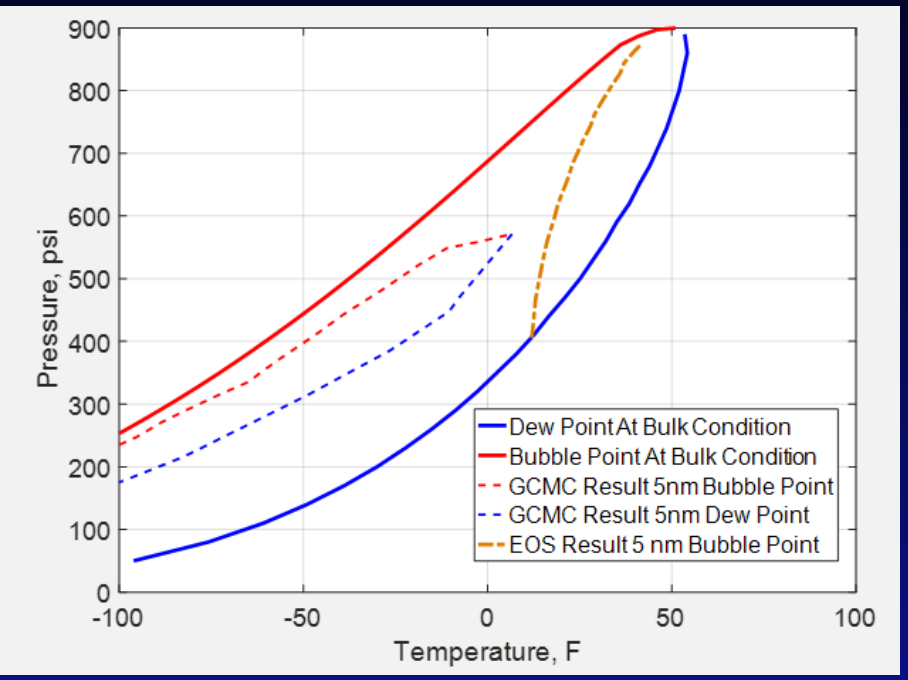
Starting Point



Methane 30% - Ethane 70% Mixture PT Diagram

- We captured the bubble point and dew point lines at bulk condition using EOS
- The yellow line for 5 nm confinement, plotted by Equation of State modified for capillary pressure
  - Modified equation of state did not give a stable result for dew point
- GCMC results 5nm bubble point line is captured from Pitakbunkate & Balbuena.'s (2016) paper using digitizer program

Starting Point



Methane 30% - Ethane 70% Mixture PT Diagram

Observations

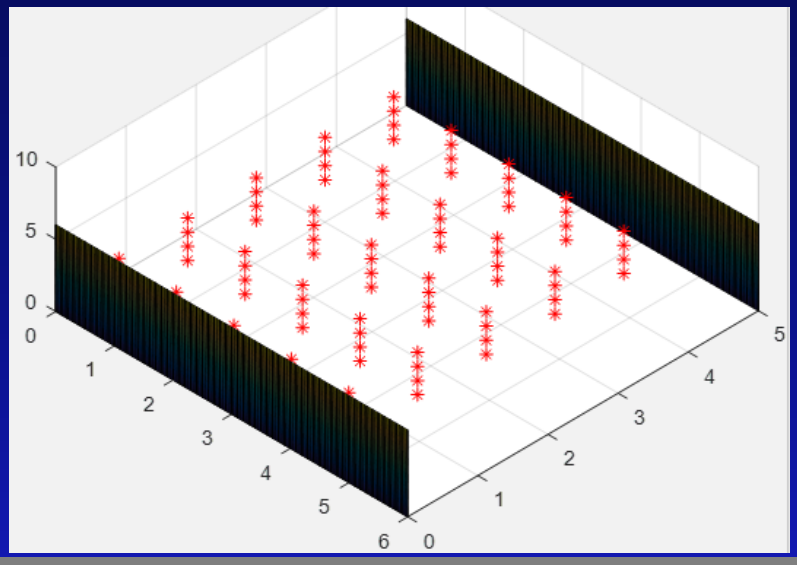
- The GCMC results show a little suppression in bubble point line but a big shift in the critical point
- EOS-PR with capillary pressure shows no shift on critical point; however, we have significant suppression in bubble point
- The reason why we could not get any data for the bubble-point line of EOS-PR-CP below 20 F is that EOS does not have any solution for volume below that point

Background: Statistical Mechanics

Microscopic State → Macroscopic State

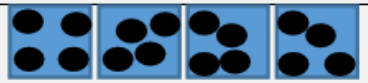
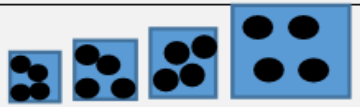
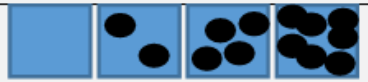
Statistical mechanics is applicable if:

- We don't know the initial conditions with full accuracy,
  - We assume an initial configuration of molecules
- We don't know the laws of motion with infinite precision
  - To deal with it we use Monte Carlo simulation. We choose random motions and calculate the probability of the acceptance of this motion
- The system we are investigating is not a closed system
  - Exchange energy with surroundings



Background: Statistical Mechanics – Ensembles

T ~E, V~P and N~μ are related

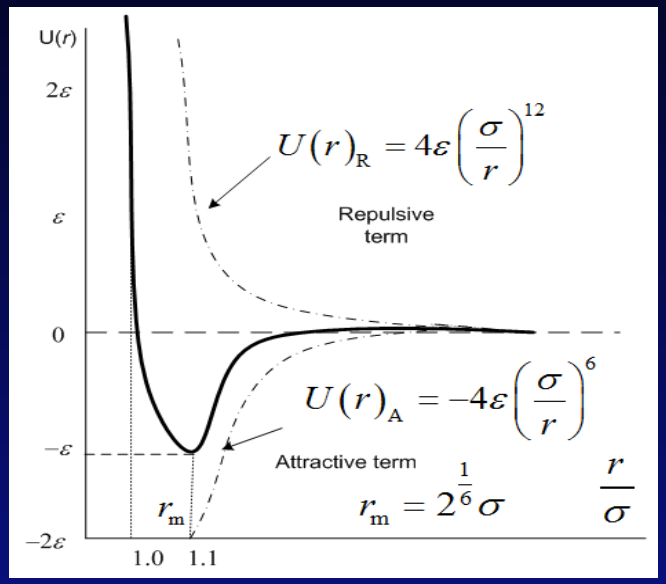
Name of Ensemble	All States of:	Probability Distribution	Schematic
Micro Canonical Ensemble; Constant (EVN)	Given E,V,N	$\pi_i = \frac{1}{\Omega}$	
Canonical Ensemble; Constant (TVN)	All Energies	$\pi(E_i) = \frac{1}{Q} e^{-\beta E_i}$	
Isothermal-Isobaric Ensemble; Constant (TPN)	All Energies and Volumes	$\pi(E_i, V_i) = \frac{1}{\Delta} e^{-\beta(E_i + PV_i)}$	
Grand Canonical Ensemble; Constant (TVμ)	All Energies and Molecule Numbers	$\pi(E_i, N_i) = \frac{1}{\Xi} e^{-\beta(E_i + \mu N_i)}$	

Retrieved from Dr. Amadeu Sum's Lecture Notes (2017)

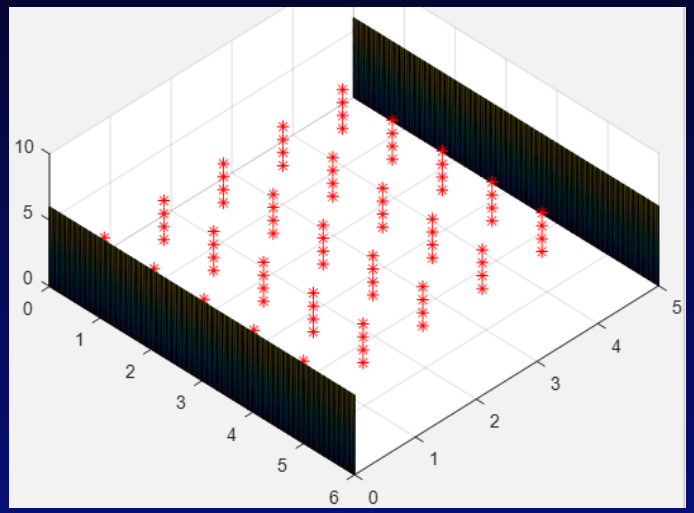
β: Reciprocal Temperature, E: Energy, V: Volume, μ: Chemical Potential, N: of Particles
Ω, Q, Δ and Ξ: Partition Functions

Lennard-Jones Potential

- $U = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$



Retrieved from (Jiang, 2014)



ϵ : depth of the potential well, kJ/mol
σ : finite distance at which the inter particle potential is zero
r : distance between particles, A
r_m : is the distance at which the potential is maximum., A

Background: Monte Carlo Simulation - Algorithm

For each particle in the simulation box

Calculate its Energy $U(r^N)$ by Lennard Jones

Give a random displacement * to the selected particle: new position $(r') = r + \Delta$

Calculate the new energy $U(r'^N)$

Check the acceptance of the displacement from (r^N) to (r'^N)

random number $< \exp(-\beta[U(r'^N) - U(r^N)])$

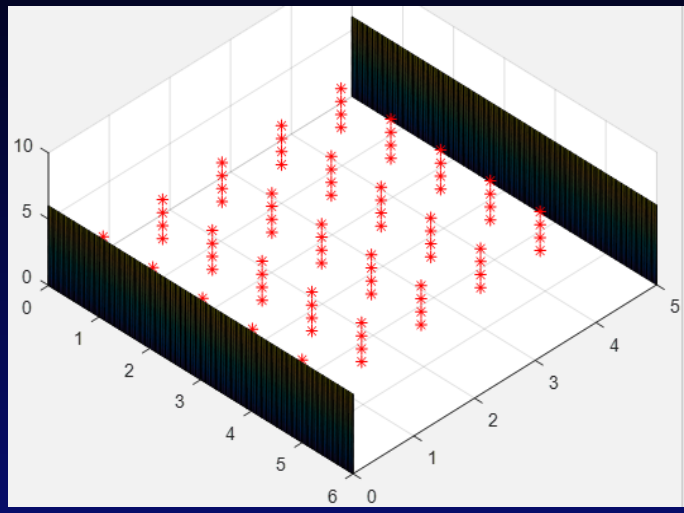
YES

NO

Update the particle position

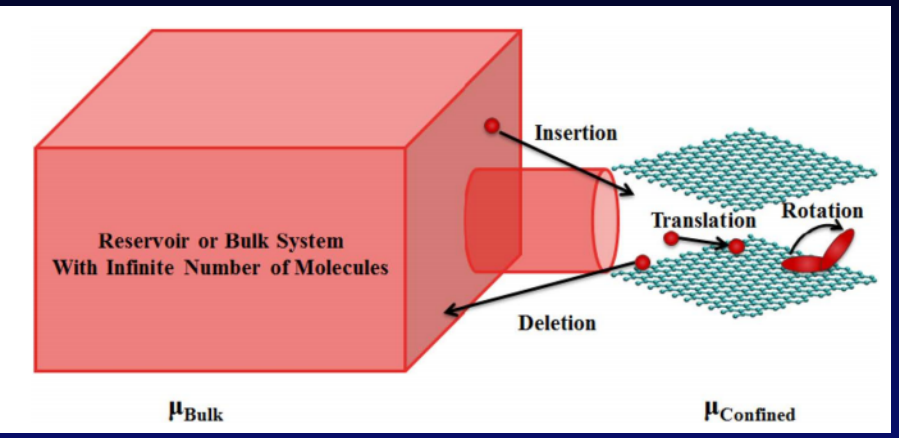
Don't update the position

Run the simulation for next particle



* This algorithm is useful for rotational motion of a particle.

Grand Canonical or μVT Ensemble

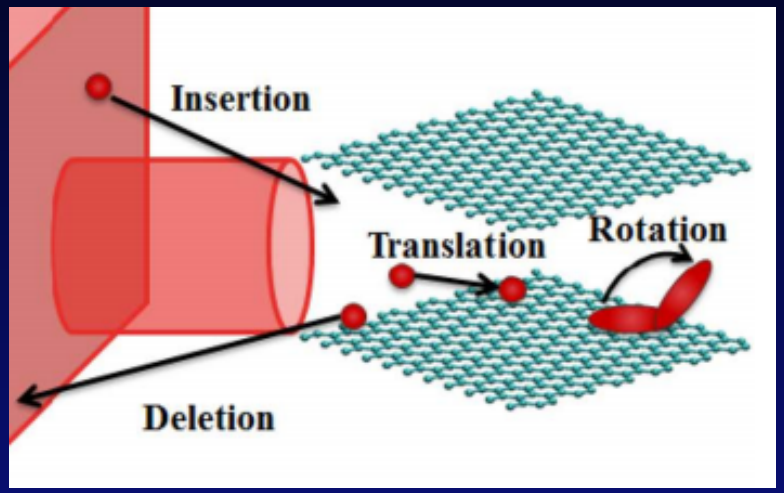


Retrieved from: Pitakbunkate & Balbuena (2016)

The bulk system is connected to the Grand Canonical Ensemble to represent the equilibrium.

$$\mu_{\mathrm{Bulk}}(\mathrm{T},\mathrm{P}) = \mu_{\mathrm{Confined}}$$

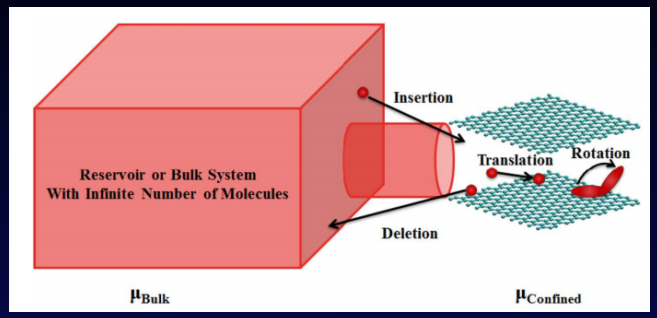
Grand Canonical or μVT Ensemble



Retrieved from: Pitakbunkate & Balbuena (2016)

- Insertion: We create a molecule at a random position
- Translation: A molecule changed its position
- Rotation: Rotation of non-spherical molecule
- Deletion: We remove a molecule from the confined environment to bulk

μVT Algorithm



Determine P, V, T and N. T and V Are Constant, P and N will be Changed for Every Stage

Using EOS, Calculate Fugacity of Components at Given P and T

Calculate Chemical Potential, $\mu = \mu_{id}^{0} + \ln(f)$ where μ_0 is chemical potential under standard conditions, R is the universal gas constant, T is temperature and f is fugacity coefficient

Run Monte Carlo Simulation for transition and rotation for i^{th} particle and calculate the energy U

Calculate $\arg = N\frac{\exp(\beta U)\Lambda^3}{\exp(\beta\mu)V}$

random # < arg

YES

Delete the Particle

NO

Define a random Position for a new particle and insert it. Calculate $\arg = \frac{V\exp(\beta\mu)}{\Lambda^3}\frac{\exp(-\beta U)}{(N+1)}$

random # < arg

NO

Do Nothing

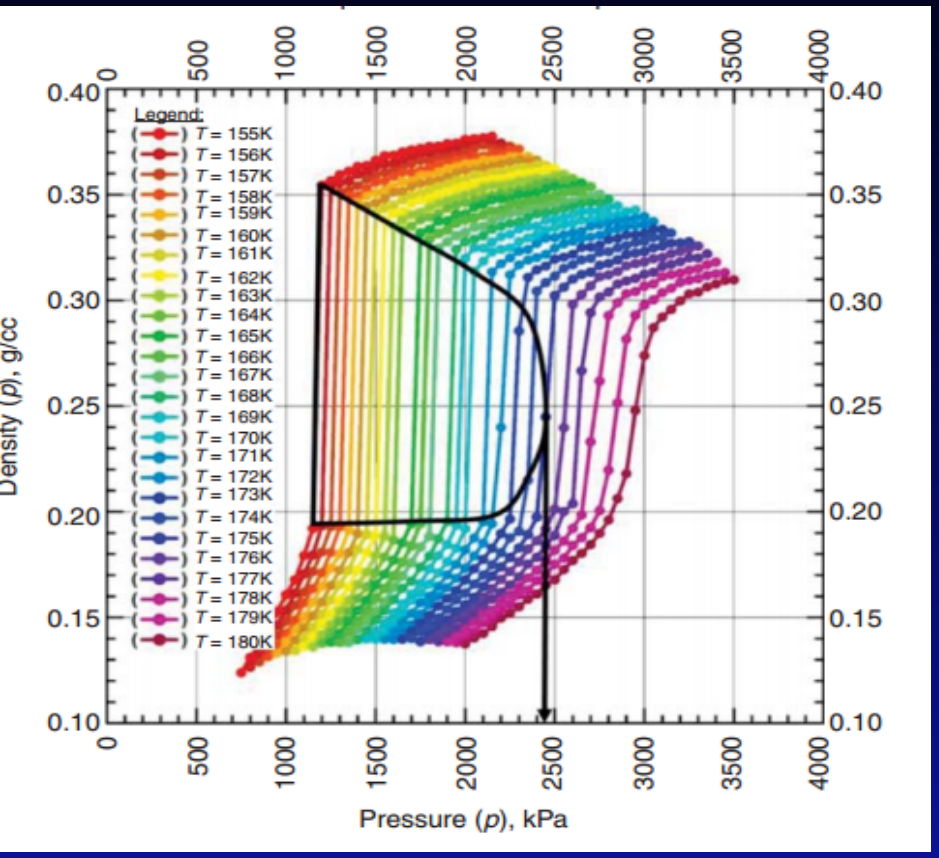
YES

Update N = N + 1

Increase Pressure by 1 psi

Print Density

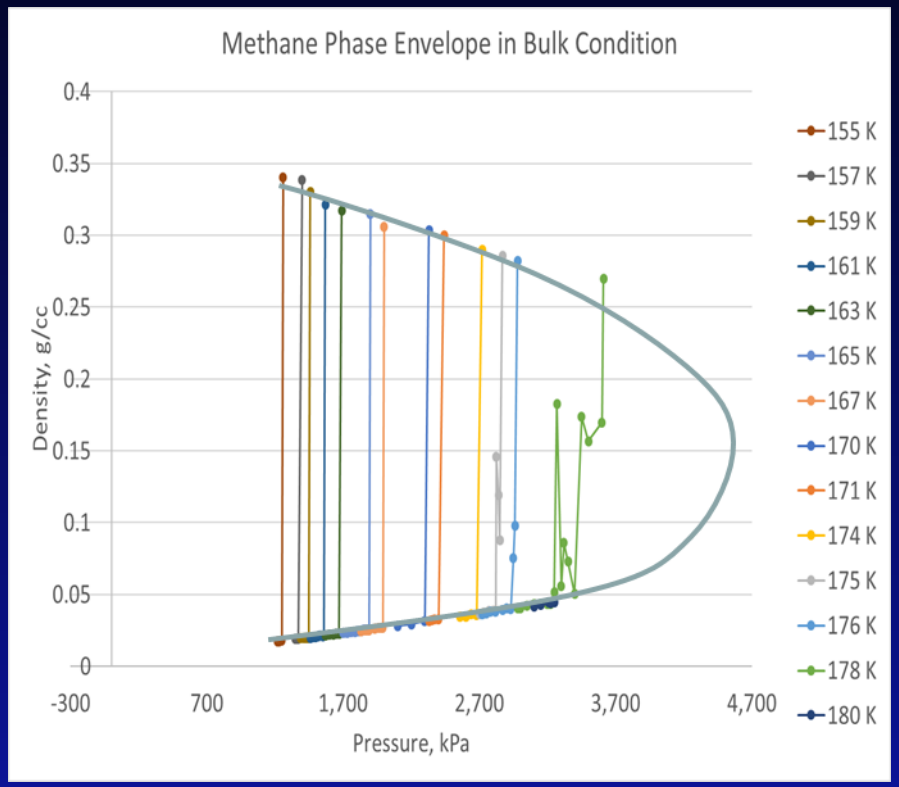
Phase Transition Detection Using GCMC Simulation



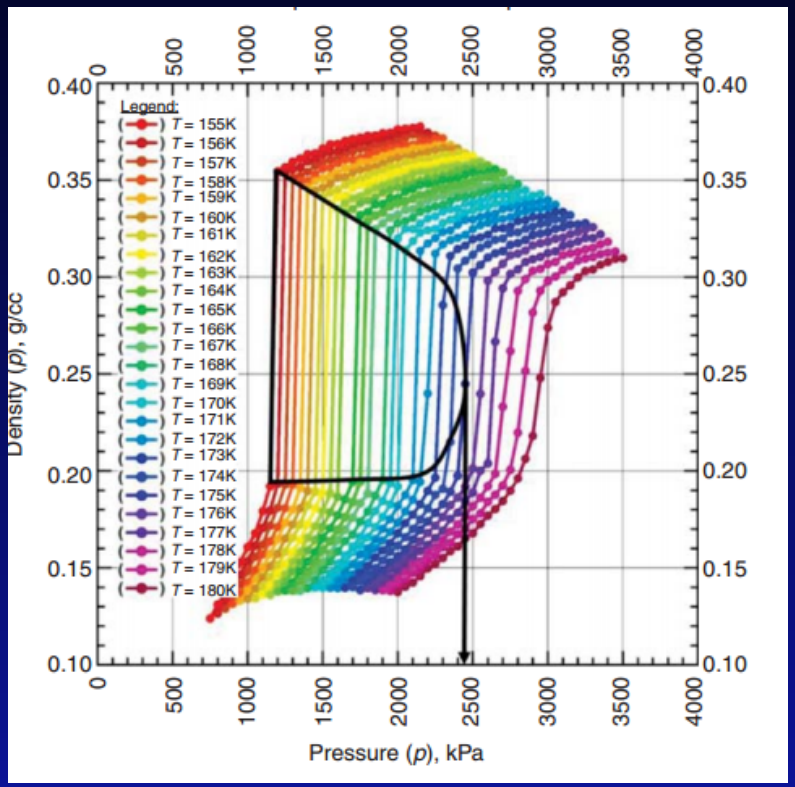
Retrieved from: Pitakbunkate & Balbuena (2016)

- Each colored line represents simulation results for different temperatures from155 K to 180 K
- For constant temperature, the pressure is increased and density data captured
- Densities increase as pressure increases, there is a specific pressure value at which we observe a jump in density
- This point is the phase transition point
- The black line represents the phase envelope in confinement

Methane in Bulk vs 5nm

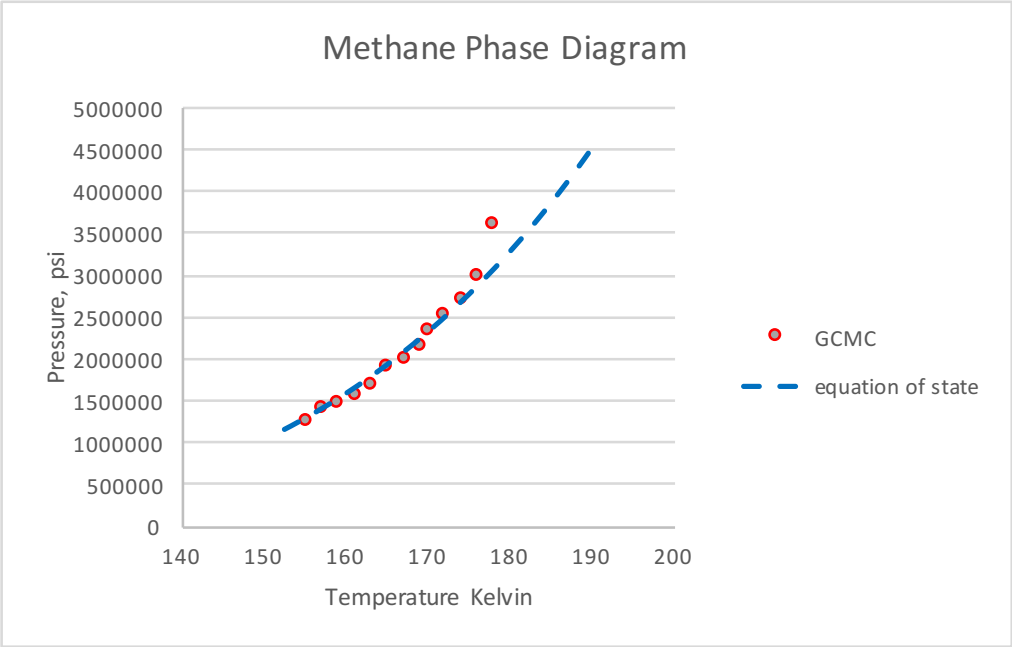


Methane in Bulk
Results Captured from RASPA – Molecular Simulation



Methane in Confinement 5 nm
Retrieved from: Pitakbunkate et. Al. (2016)

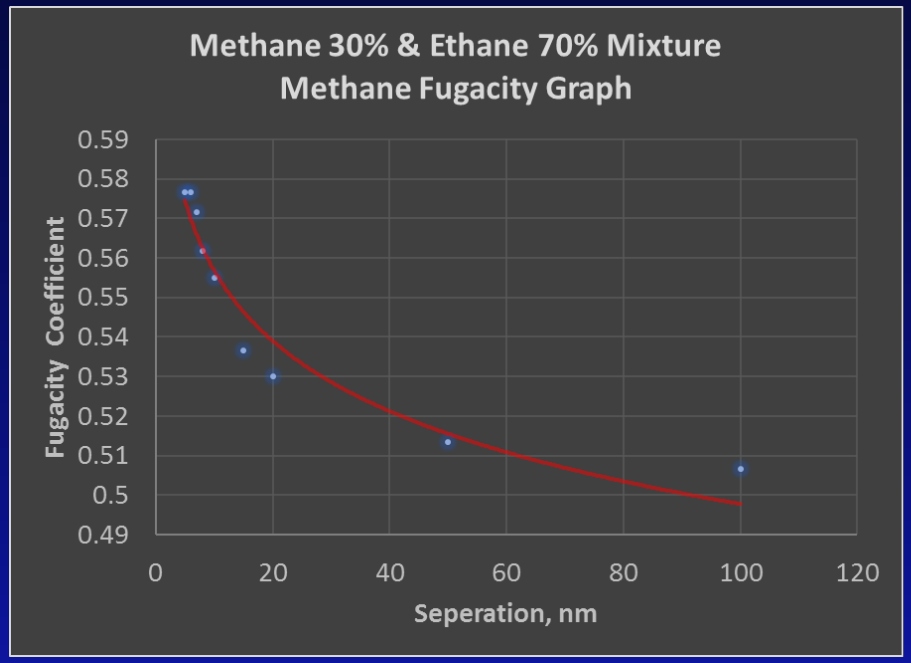
Initial Results

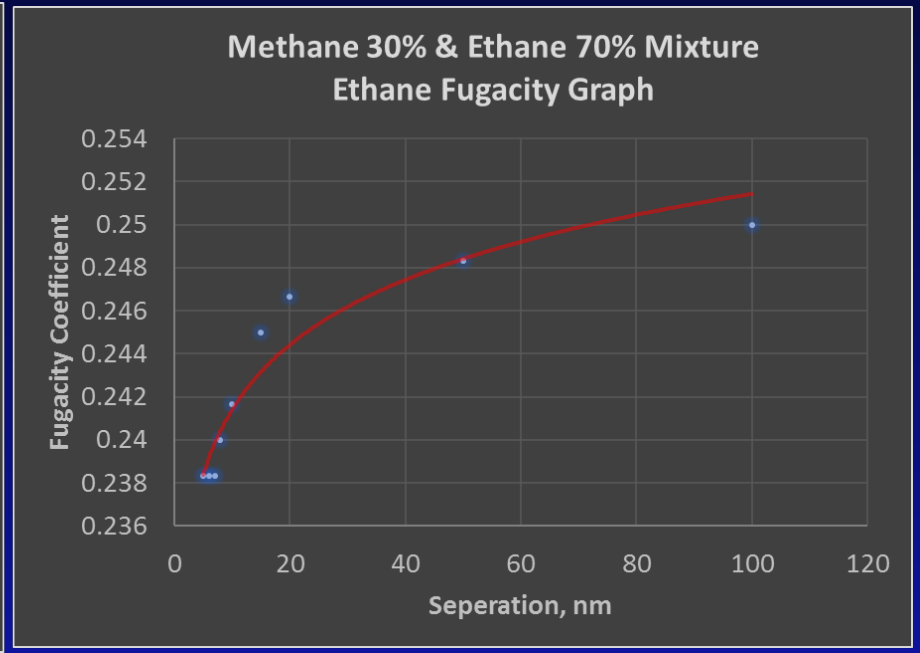


- Both GCMC and Equation of State are in bulk condition
- GCMC gives irregular results at T>=175 Kelvin
  - The reason of this irregularity is not certain
    - Molecular simulation may not work very well near critical point
    - Our simulation inputs may be wrong
- In low temperature zone, we observe a good match

Effect of Confinement on Fugacity

- Fugacity coefficient changes as the pore size changes
- As a result, chemical potential changes

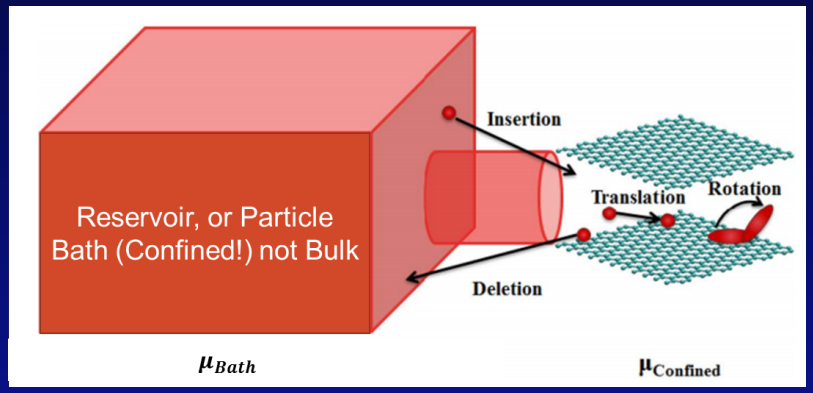




New Approach

Incorporating Capillary and Intermolecular Forces in a Model

Use EOS modified for capillary pressure. The change in fugacity will affect the chemical potential which is an input in GCMC. Hence we will observe change in phase envelope.



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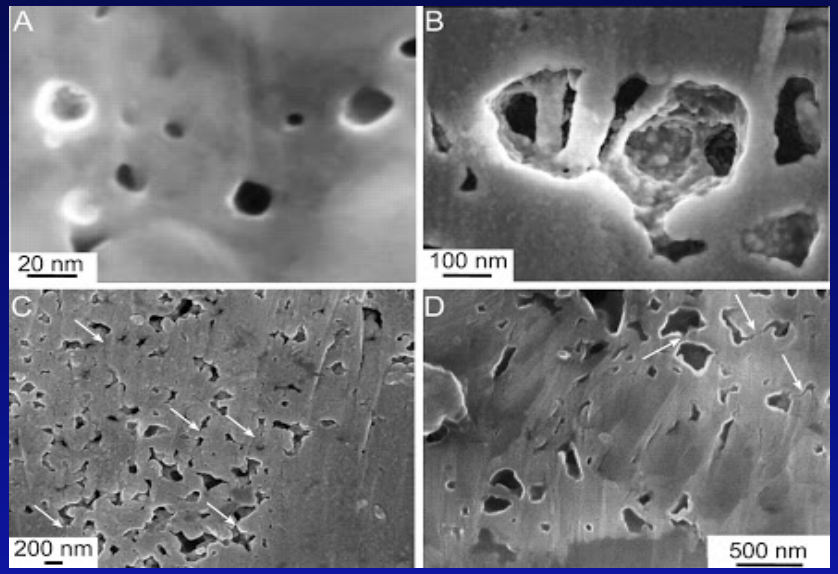

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Wall – Particle Interaction

To consider the interaction between a particle and the surface wall,

we use the following equation for Lennard Jones potential.

$$U = \frac{4\pi\epsilon_s\rho\sigma^3}{3}\left[\frac{\sigma^9}{15r^9} - \frac{\sigma^3}{2r^3}\right]$$

Where,

ϵ_s = depth of the potential well,

σ = finite distance

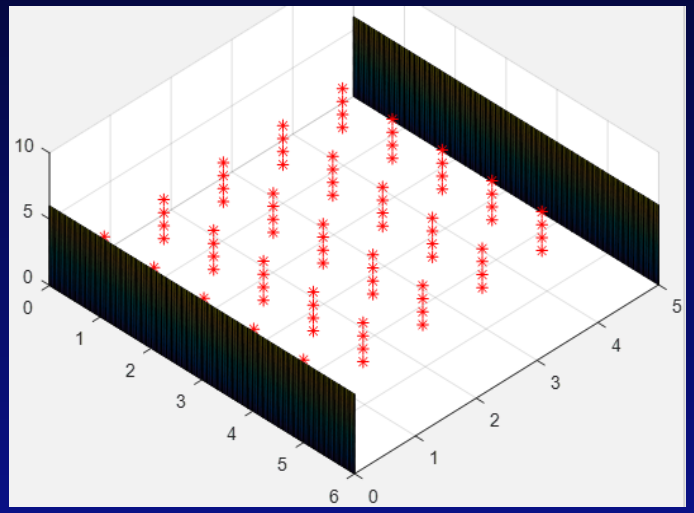
U = 0, A

r = distance between particles, Angstrom

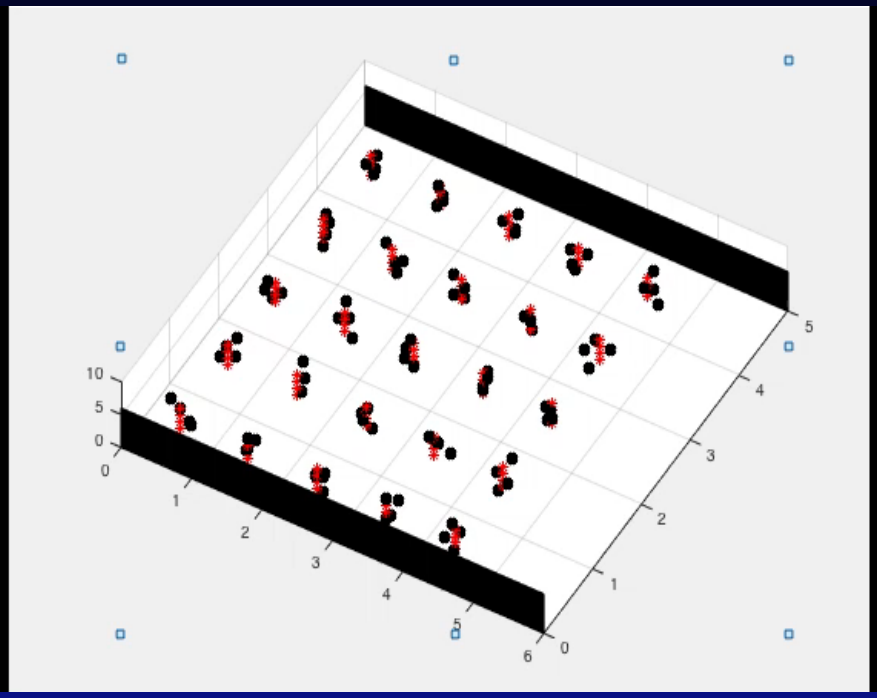
r_m = distance, Angstrom

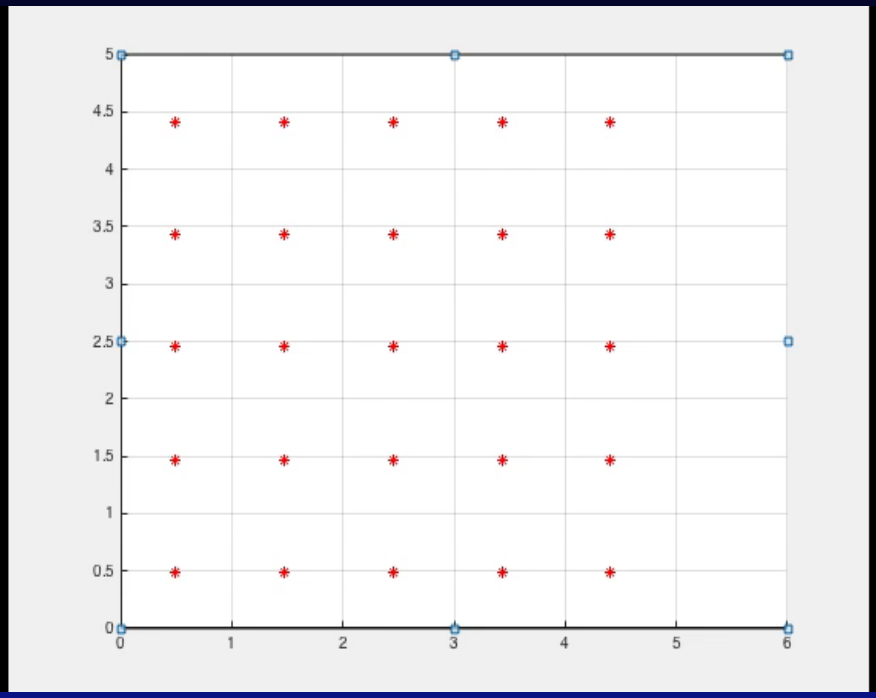
U = maximum energy, kJ/mol

ρ = surface particle density, particle/Angstrom



Behavior of Molecules in Confinement





Future Work

- We get access to high performance computer laboratory in physics department

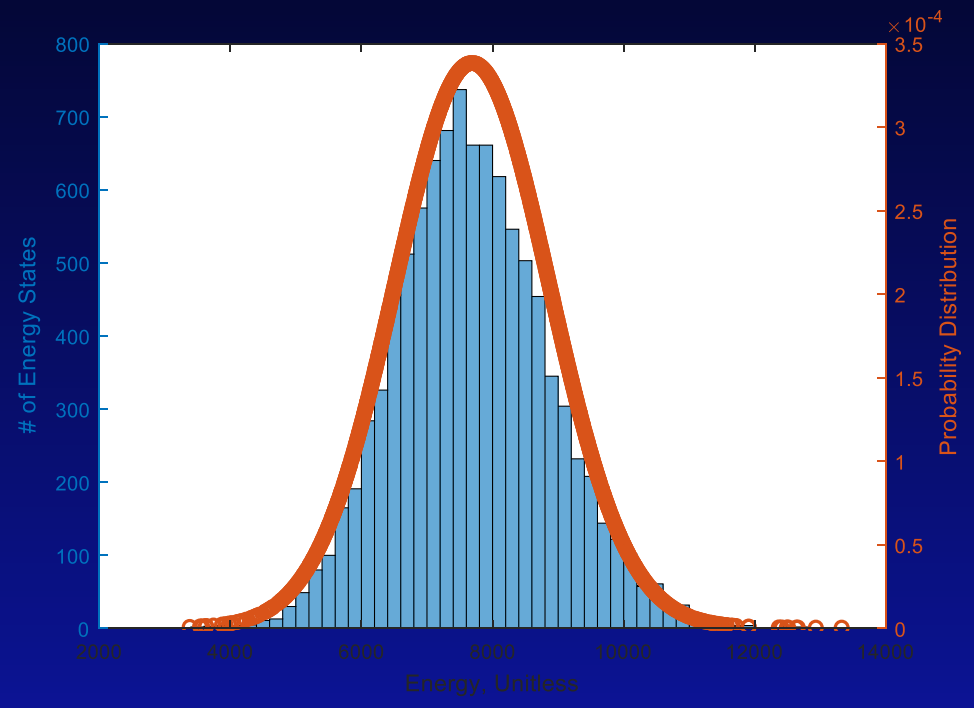
1. Increase the simulation box size, increase the number of Monte Carlo cycles to increase the resolution
2. Run GCMC simulation for methane-ethane mixture in bulk and several confined conditions by RASPA, compare the results with those presented by TAMU
3. Run GCMC simulation for ethane-heptane mixture compare it to experimental results
4. Use fugacity coefficients coming from "Equation of State with capillary effect" and run RASPA

- Compare the results

THANKS

Supporting Slides

Background: Statistical Mechanics – Postulates



- Microstates of equal energy are equally likely
- Even though we have the same energies for different ensembles, their particle configuration may be different
- No matter how different the configurations, we will observe same probability for the ensembles with same energies

Partition Function

- The probability of finding a system in that i^{th} state with energy E_i is proportional to Boltzmann factor $\mathrm{k_B}$.

$$\mathrm{P_i} \propto \mathrm{e}^{\frac{\mathrm{E_i}}{\mathrm{k_B T}}}$$

- Partition function encodes how the probabilities are partitioned among different microstates.

$$\mathrm{P_s} = \frac{1}{\mathrm{Z}} \mathrm{e}^{-\beta \mathrm{E_s}}$$

$$\sum_{\mathrm{s}} \mathrm{P_s} = \frac{1}{\mathrm{Z}} \sum_{\mathrm{s}} \mathrm{e}^{-\beta \mathrm{E_s}} = 1$$

Where

Z : partition function

β : reciprocal temperature $\frac{1}{k_B T}$