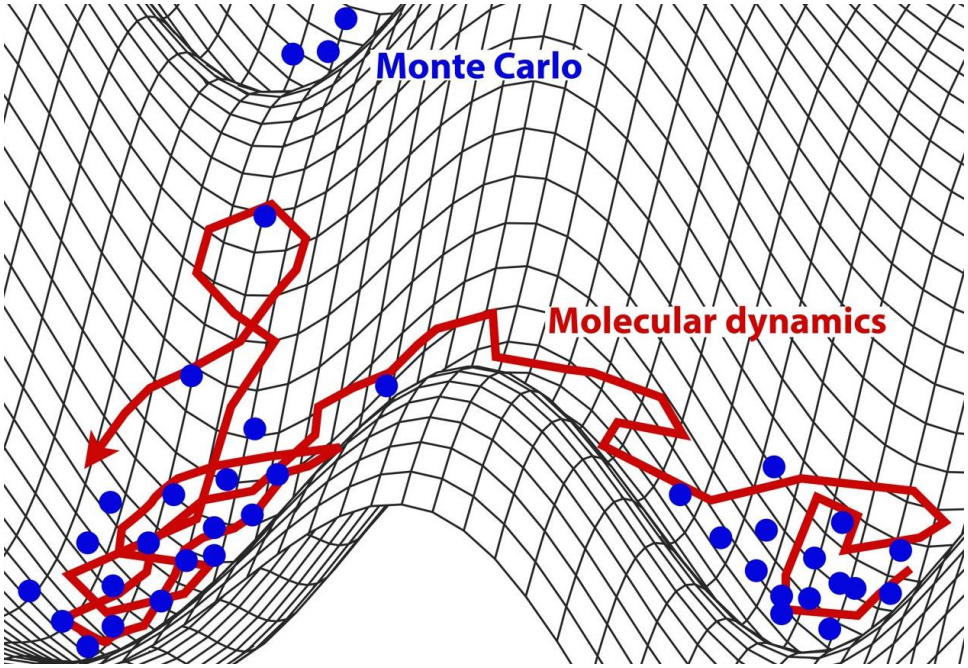
Monte Carlo Basics

Week 2 : How to Sample Ensembles?



2024 Winter Molecular Simulation Seminar

January 26th, 2024

Presenter: Seonghyeon Kang

Advisor: Prof. Chang Yun Son

Week 2 : How to Sample Ensembles?

Three Brief Approaches to Sample Ensemble Average

1. Sampling in Molecular Dynamics Simulation: Thermostat

2. Sampling in Monte Carlo : Monte Carlo Basics

3. Enhanced Methods with Monte Carlo : Enhanced Monte Carlo

Contents

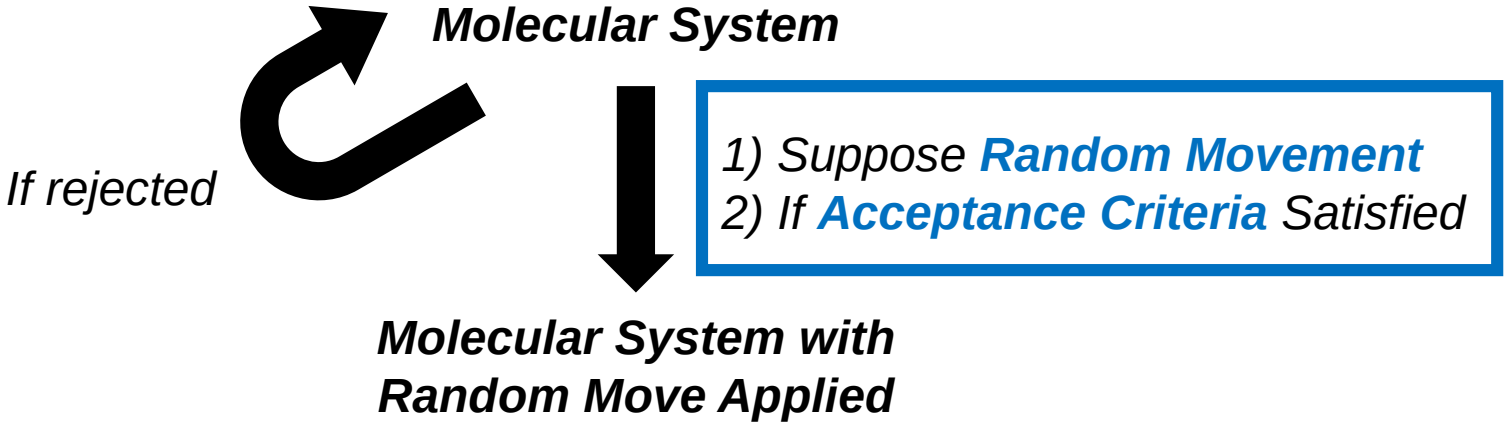
1. What is Monte Carlo Simulation and How does it work?

What is Monte Carlo Simulation?

Monte Carlo (MC) Methods *: Statistical methodologies that* ***derive certain statistical quantities for given system by utilizing random number***

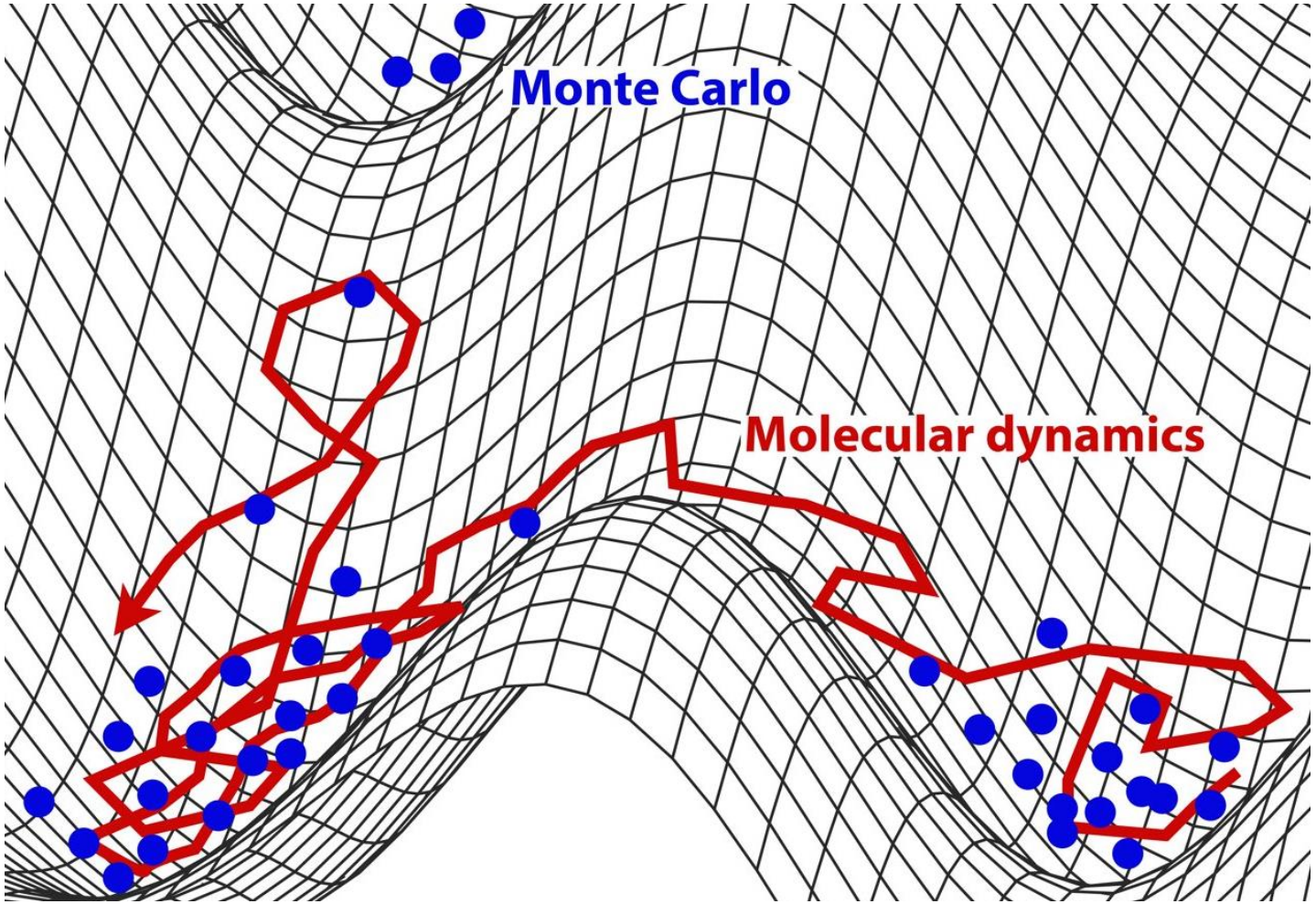
Monte Carlo Simulation *: Molecular Simulation methodologies that use* ***the idea of Monte Carlo Method***

How Monte Carlo Simulation Works? – Metropolis Algorithm



1. What is Monte Carlo Simulation and How does it work?

Monte Carlo Simulation vs Molecular Dynamics Simulations



1. What is Monte Carlo Simulation and How does it work?

Why We Use Monte Carlo Simulation?

Unique Perspective of Monte Carlo Simulation

1. Suggesting Random Movement in Chemical System

- It can also introduce artificial movement that MD cannot

- Particle insertion, Phase Transition, Hole hopping, …

- Mainly treated in this talk

2. Introducing Acceptance Criteria to Derive Specific Statistics

- It can derive the accepted states to certain probability distribution

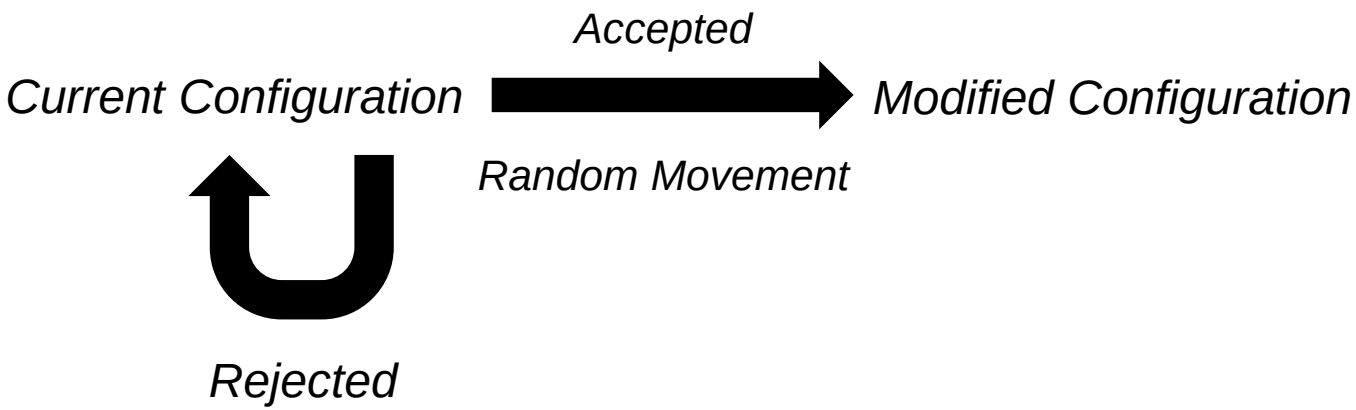
- Ensemble expansion, Enhancing performance of MC or MD, …

- Mainly treated in the next talk(Enhanced Monte Carlo)

2. Monte Carlo Sampling Methods in Various Ensembles

Types of Ensembles : NVE, NVT, NPT, …

NVE Ensemble(Microcanonical Ensemble)



<Acceptance Criteria>
If $\Delta E < 0$: Accept the random movement
If $\Delta E > 0$: Reject the random movement

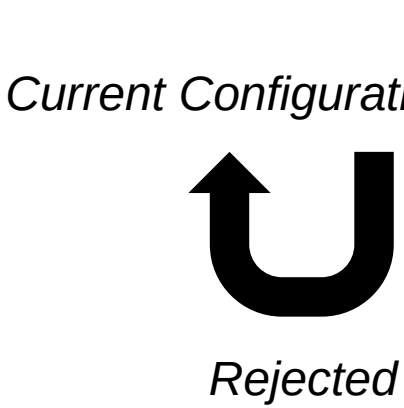
"Exactly the same as energy minimization process!"

Frenkel, D., & Smit, B., Understanding molecular simulation: from algorithms to applications. *Elsevier*. **2023**

2. Monte Carlo Sampling Methods in Various Ensembles

Types of Ensembles : NVE, NVT, NPT, …

NVT Ensemble(Canonical Ensemble)



<Acceptance Criteria>

If $\Delta E < 0$: Accept the random movement

If $\Delta E > 0$: Accept with the probability $e^{-\Delta E/k_b T}$

Else : Reject

$$acc(i \rightarrow j) \Rightarrow min\left(1, exp\left(-\frac{\Delta E}{k_b T}\right)\right)$$

$$\frac{P(state\ 2)}{P(state\ 1)} = \frac{e^{-\Delta E/k_b T}}{1} = \frac{acc(1 \rightarrow 2)}{acc(2 \rightarrow 1)}$$

In Statistical Mechanics (Equilibrium)

In Monte Carlo. (Equilibrium)

$$P(state\ 1)acc(1 \rightarrow 2) = P(state\ 2)acc(2 \rightarrow 1)$$

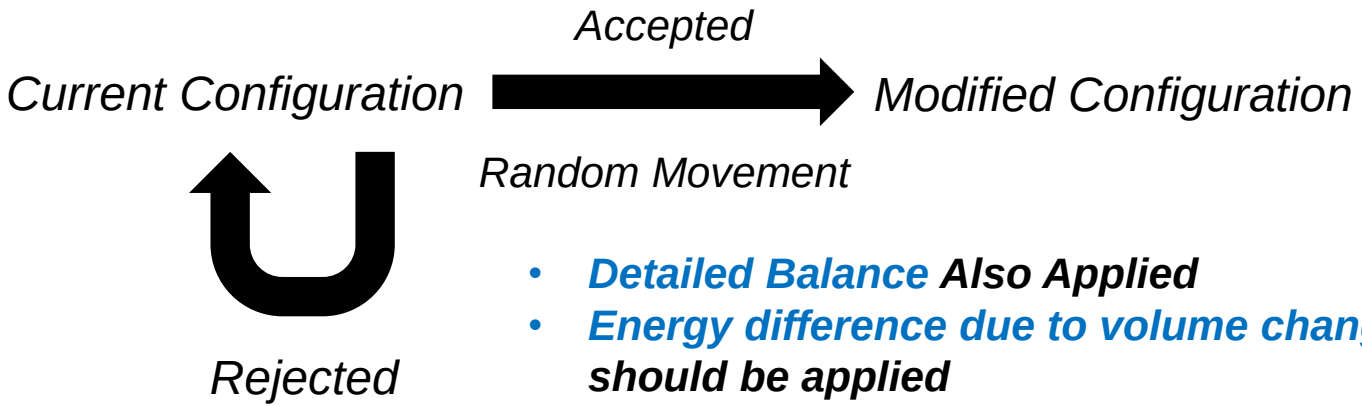
Detailed Balance (Equilibrium Statistics)

Frenkel, D., & Smit, B., Understanding molecular simulation: from algorithms to applications. *Elsevier*. **2023**

2. Monte Carlo Sampling Methods ***in Various Ensembles***

Types of Ensembles : NVE, NVT, NPT, …

NPT Ensemble(Isobaric-Isothermal Ensemble)



- ***Detailed Balance* Also Applied**
- ***Energy difference due to volume change* should be applied**

<Acceptance Criteria>

If $\Delta W = \Delta E + P\Delta V - Nk_B T\Delta(\log(V)) < 0$ ***: Accept the random movement***

If $\Delta W = \Delta E + P\Delta V - Nk_B T\Delta(\log(V)) > 0$ ***: Accept with the probability*** $e^{-\Delta W/k_b T}$

Else : Reject

$$acc(i \rightarrow j) \Rightarrow min\left(1, exp\left(-\frac{\Delta E + P\Delta V - Nk_b T\Delta(\log(V))}{k_b T}\right)\right)$$

Frenkel, D., & Smit, B., Understanding molecular simulation: from algorithms to applications. *Elsevier*. **2023**

2. Monte Carlo Sampling Methods in Various Ensembles

Types of Ensembles : NVE, NVT, NPT, …

NPT Ensemble(Isobaric-Isothermal Ensemble)

Ex) MonteCarloBarostat in OpenMM(2 MD steps + 1 MC Step)

$$r(t+\mathrm{d}t) = r(t) + v(t)\ \delta t + \tfrac{1}{2}a(t)\ \delta t^2,$$
$$v\left(t+\tfrac{1}{2}\delta t\right) = v(t) + \tfrac{1}{2}a(t)\ \delta t,$$
$$ma(t+\delta t) = -\nabla E\left[r(t+\delta t)\right],$$
$$v(t+\delta t) = v\left(t+\tfrac{1}{2}\delta t\right) + a(t+\delta t)\ \delta t,$$

Two MD steps

$$V' = V + R\left[S(\delta V)\right] \qquad r'(t+\delta t) = r(t+\delta t)\left[\frac{V'^{1/3}}{V^{1/3}}\right]$$

One MC step(Trial Move)

$$P(\Delta V) = \begin{cases} \exp\left(-\dfrac{\Delta W}{kT_0}\right), & \Delta W > 0, \\ 1, & \Delta W \le 0. \end{cases}$$

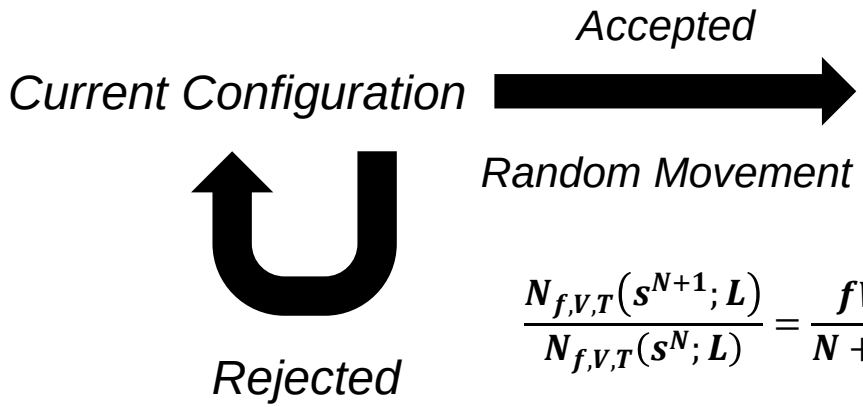
$$\Delta W = (E' - E) + P_0(V' - V) - NkT_0 \ln\frac{V'}{V}$$

One MC step (Acceptance Criteria)

Åqvist, J., Wennerström, P., Nervall, M., Bjelic, S., & Brandsdal, B. O., Molecular dynamics simulations of water and biomolecules with a Monte Carlo constant pressure algorithm. *Chem. Phys. Lett.*, **2004**, *384*(4-6), 288-294.

3. Grand Canonical Monte Carlo : Principles and Applications

Principle : muVT Ensemble(Grand Canonical Ensemble)



$$\frac{N_{f,V,T}(s^{N+1};L)}{N_{f,V,T}(s^{N};L)} = \frac{fV}{N+1} exp\left(-\frac{E(s^{N+1};L)-E(s^{N};L)}{k_bT}\right)$$

<Acceptance Criteria>

1) Displacement of Particles : $acc(i \rightarrow j) \Rightarrow min\left(1, exp\left(-\frac{\Delta E}{k_bT}\right)\right)$

2) Insertion of Particles : $acc(N \rightarrow N+1) \Rightarrow min\left(1, \frac{fV}{N+1} exp\left(-\frac{\Delta E(N+1)-\Delta E(N)}{k_bT}\right)\right)$

3) Removal of Particles : $acc(N \rightarrow N-1) \Rightarrow min\left(1, \frac{N}{fV} exp\left(-\frac{\Delta E(N+1)-\Delta E(N)}{k_bT}\right)\right)$

How to calculate the energy per molecule(Chemical Potential)?

3. Grand Canonical Monte Carlo : Principles and Applications

Principle : muVT Ensemble(Widom's Particle Insertion Method)

$$Q_N = \frac{1}{N!}\int_V \cdots \int_V exp\left(-\frac{E_N}{k_bT}\right) dr_1\, dr_2 \cdots dr_N$$

$$= \int \frac{1}{(N-1)!}\left(\int_V \cdots \int_V exp\left(-\frac{E_{N-1}}{k_bT}\right) dr_1\, dr_2 \cdots dr_{N-1}\right) exp\left(-\frac{\psi}{k_bT}\right) dr_N$$

$$= Q_{N-1}\frac{V}{N}\left\langle exp\left(-\frac{\psi}{k_bT}\right)\right\rangle$$

ψ is the interaction energy of an inserted particle with all other particles in the system

$$\mu_{insert} = \frac{\Delta F}{\Delta N} = \frac{F(N) - F(N-1)}{1} = -k_bTlog\left(\frac{Q_N}{Q_{N-1}}\right) = -k_bTlog\left(\frac{1}{\rho}\left\langle exp\left(-\frac{\psi}{k_bT}\right)\right\rangle\right)$$

Widom's Particle Insertion Method

$$\mu_{insert} = -k_bTlog\left(\frac{1}{\rho}\left\langle exp\left(-\frac{\psi}{k_bT}\right)\right\rangle\right)$$

Widom. B., Some Topics in the Theory of Fluids, *J. Chem. Phys.*, **1963**, 39(11), 2808-2812
Widom. B., Potential-distribution theory and the statistical mechanics of fluids. *J. Phys. Chem.*, **1982**, *86*(6), 869-872.

3. Grand Canonical Monte Carlo : Principles and Applications

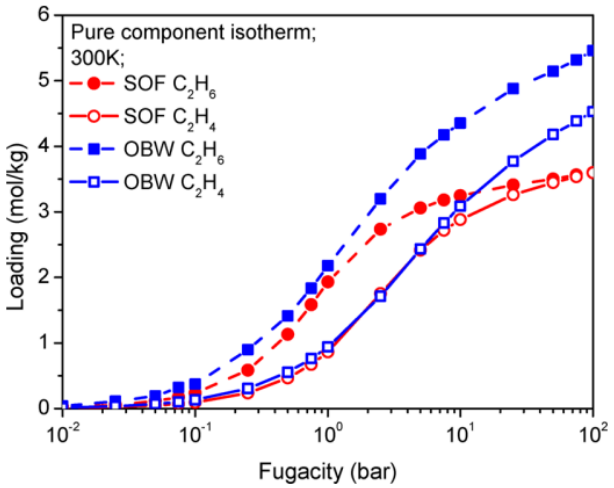
Application: Gas Adsorption

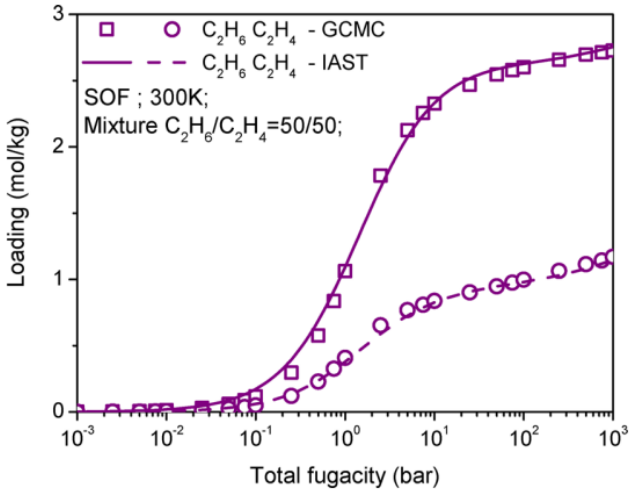
GCMC allowed the molecular simulation with exchange of matter

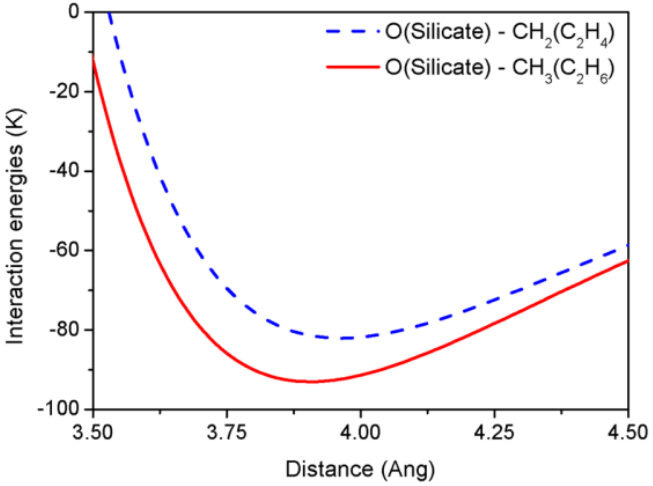
It enabled to applying GCMC to gas adsorption in porous material

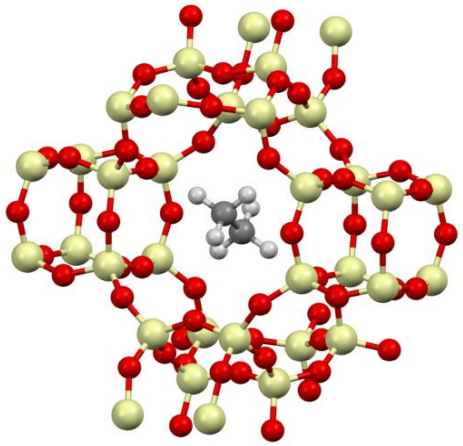
Computed Isotherm + Interaction by using GCMC

Kim, J., Lin, L. C., Martin, R. L., Swisher, J. A., Haranczyk, M., & Smit, B., Large-scale computational screening of zeolites for ethane/ethene separation. *Langmuir,* **2012**, *28(32), 11914-11919.*





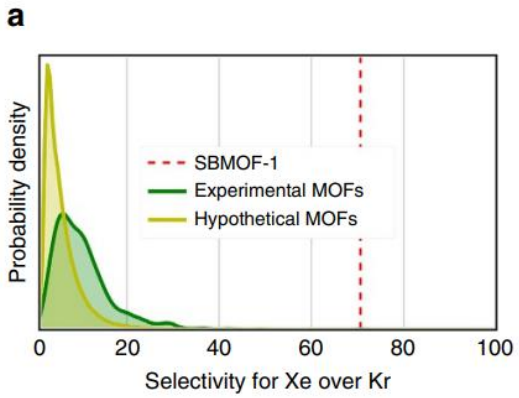


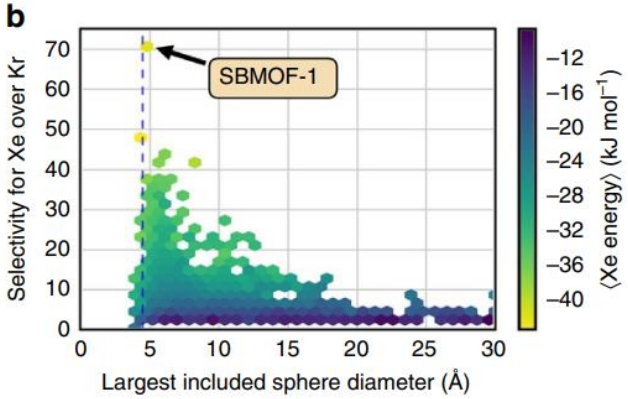


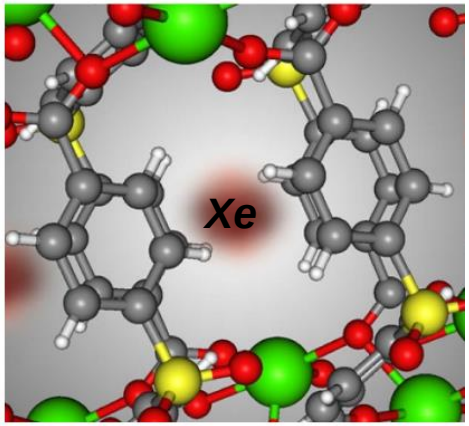
3. Grand Canonical Monte Carlo : Principles and Applications

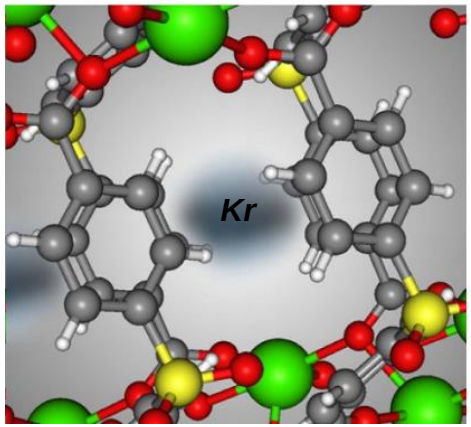
Application: Gas Adsorption

Grand Canonical Monte Carlo + Widom Particle Insertion Method









MOF Screening

$$N_i(p_i) = K_{H,i} p_i (i = Xe, Kr)$$

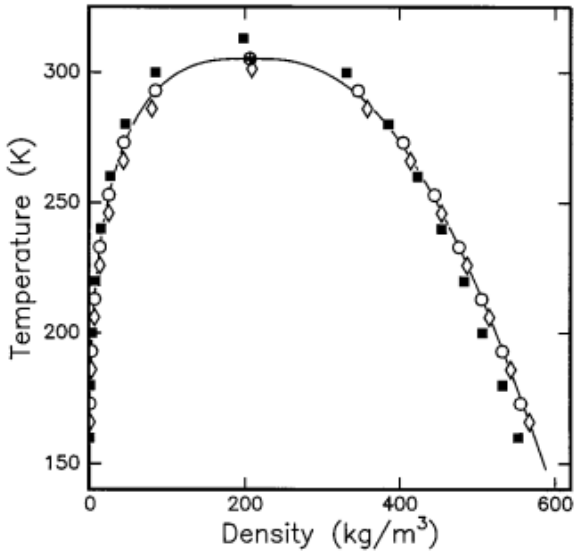
$$K_H = \left\langle e^{-\frac{U}{RT}} \right\rangle / RT$$

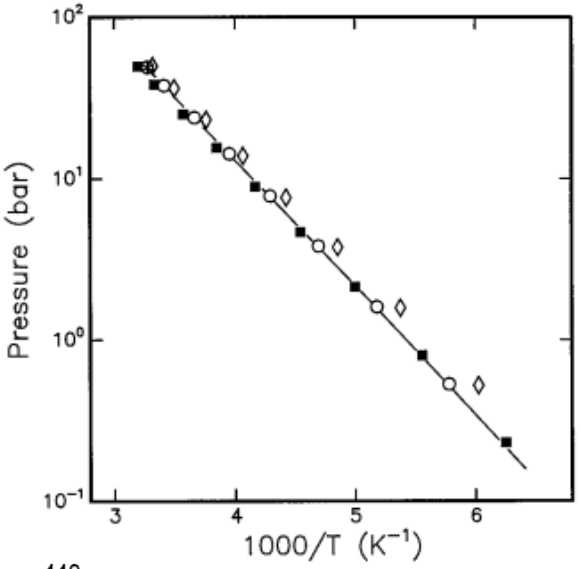
Spatial probability densities sampled from GCMC

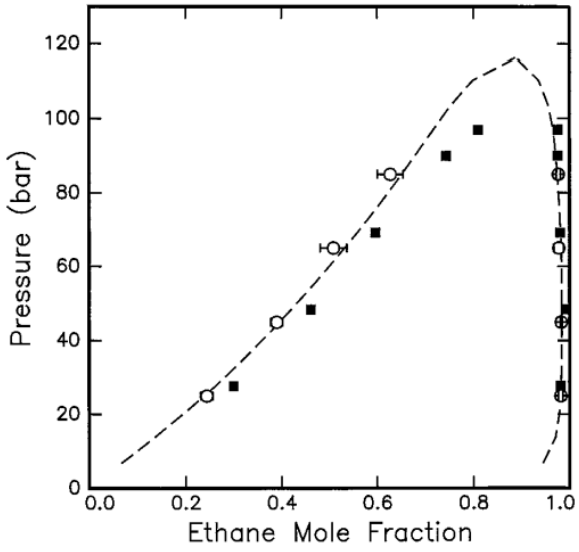
Banerjee, D., Simon, C. M., Plonka, A. M., Motkuri, R. K., Liu, J., Chen, X., ... & Thallapally, P. K., Metal–organic framework with optimally selective xenon adsorption and separation. *Nat. Comm.*, **2016**, *7*(1), ncomms11831.

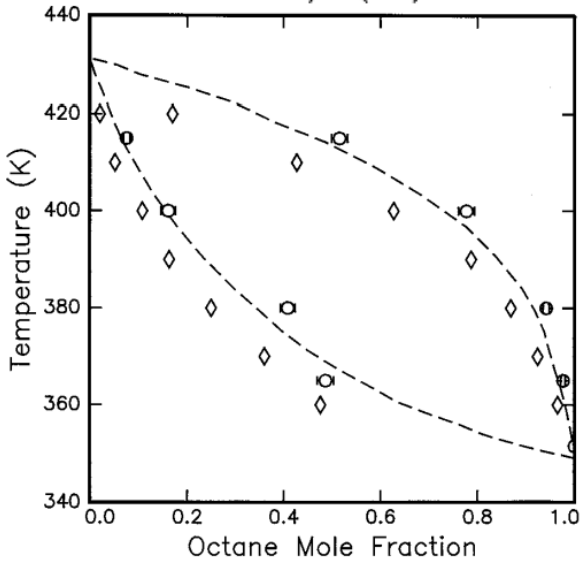
3. Grand Canonical Monte Carlo : Principles and Applications

Application: Vapor-Liquid Equilibrum(Histogram Reweighting)







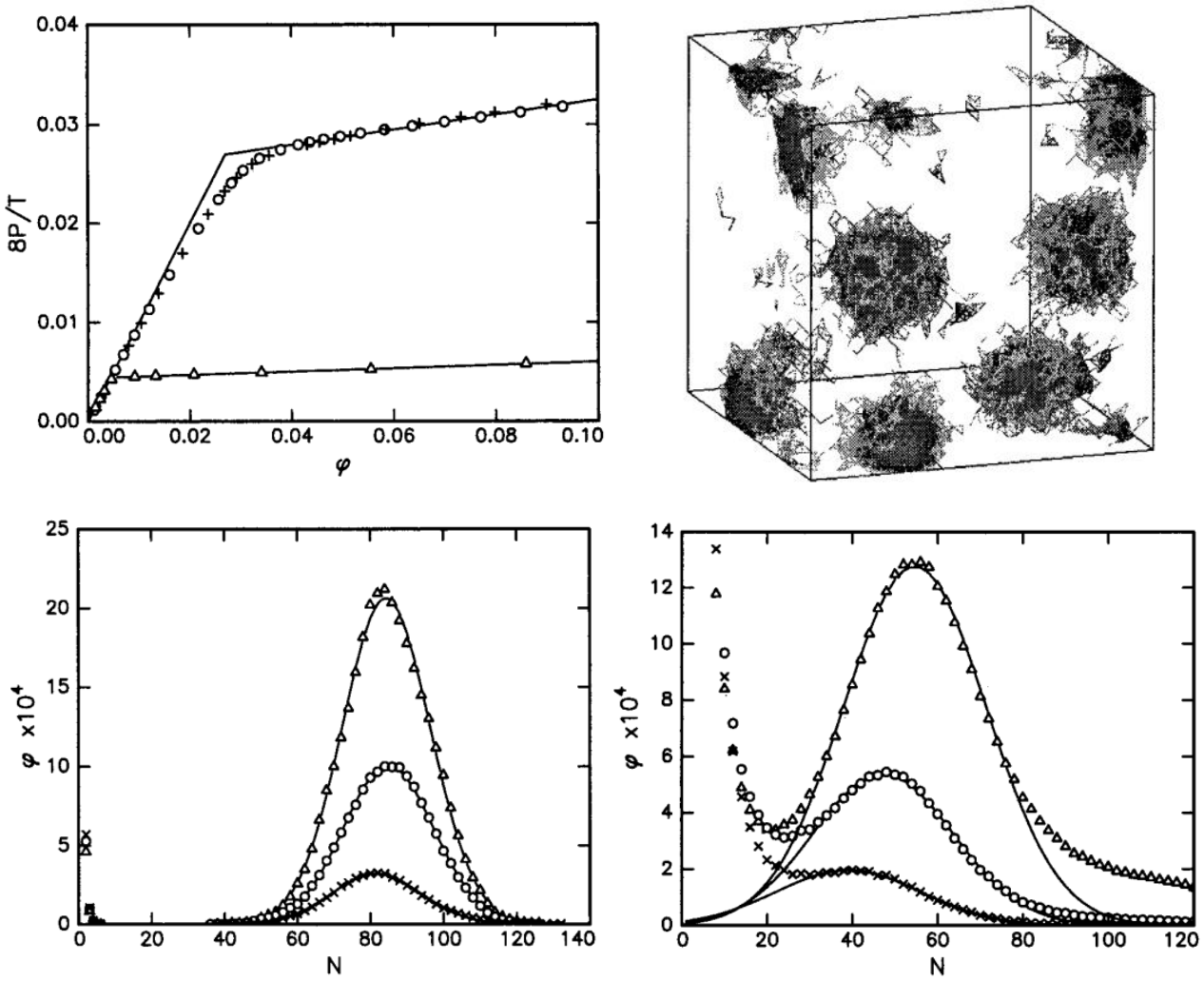


With histogram reweighting method(Next seminar), Vapor-Liquid Equilibrium also can be modelled

Errington, J. R., & Panagiotopoulos, A. Z., A new intermolecular potential model for the n-alkane homologous series. *J. Phys. Chem. B*, **1999**, *103*(30), 6314-6322.

3. Grand Canonical Monte Carlo : Principles and Applications

Application: Critical Micelle Concentration (Histogram Reweighting)



Floriano, M. A., Caponetti, E., & Panagiotopoulos, A. Z. Micellization in model surfactant systems. *Langmuir*, **1999**, *15*(9), 3143-3151.

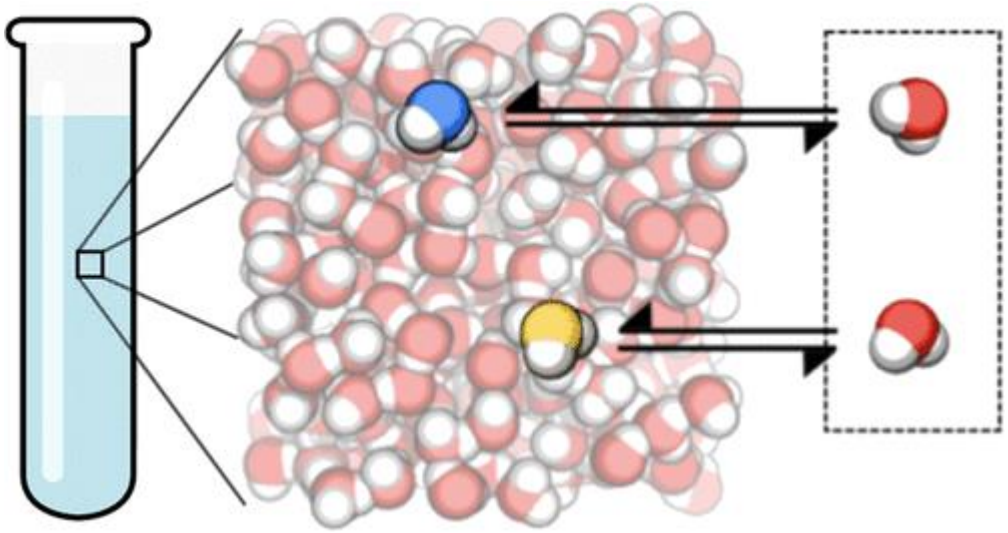
3. Grand Canonical Monte Carlo : Principles and Applications

Technical Issues : Molecule Insertion Problem

In perspective of sampling, acquiring sufficient insertion/deletion move in the phase space is important

However, acceptance ratio for molecule insertion/deletion is significantly low!(Especially high density & low temperature system)

Soroush Barhaghi, M., Torabi, K., Nejahi, Y., Schwiebert, L., & Potoff, J. J. Molecular exchange Monte Carlo: A generalized method for identity exchanges in grand canonical Monte Carlo simulations. *J. Chem. Phys.*, **2018**, *149*(7).



Ross, G. A., Rustenburg, A. S., Grinaway, P. B., Fass, J., & Chodera, J. D., Biomolecular simulations under realistic macroscopic salt conditions. *J. Phys. Chem. B*, **2018**. *122*(21), 5466-5486.

3. Grand Canonical Monte Carlo : Principles and Applications

Solution : Molecular Exchange Monte Carlo

2. Solutions

Configuration-Bias Monte Carlo, Continuous Fractional Component Monte Carlo, Expanded Ensembles, …

- (Controlling acceptance criteria, Next talk : Enhanced Monte Carlo)

Identity exchange move(swapping molecule A and B, Controlling Move)

- Steric issue can be solved. Many simulations (Grand canonical, Semi-grand canonical, Gibbs ensemble, …) use this idea

- However, this method is difficult to generalize in various system

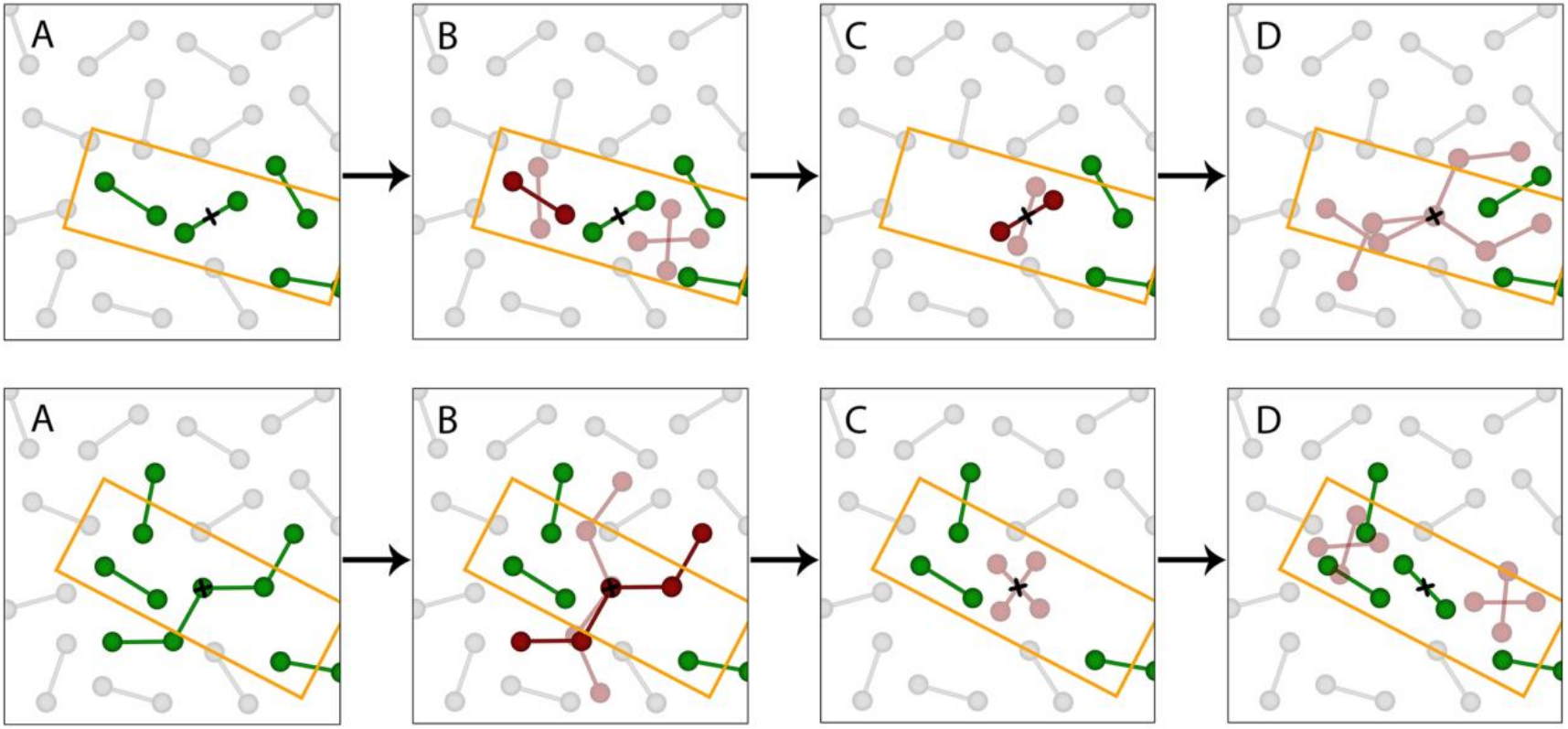
- Solution : Generalized identity exchange move for simulations in the grand canonical ensemble(Molecular Exchange Monte Carlo)

Soroush Barhaghi, M., Torabi, K., Nejahi, Y., Schwiebert, L., & Potoff, J. J. Molecular exchange Monte Carlo: A generalized method for identity exchanges in grand canonical Monte Carlo simulations. *J. Chem. Phys.*, **2018**, *149*(7).

3. Grand Canonical Monte Carlo : Principles and Applications

Solution : Molecular Exchange Monte Carlo

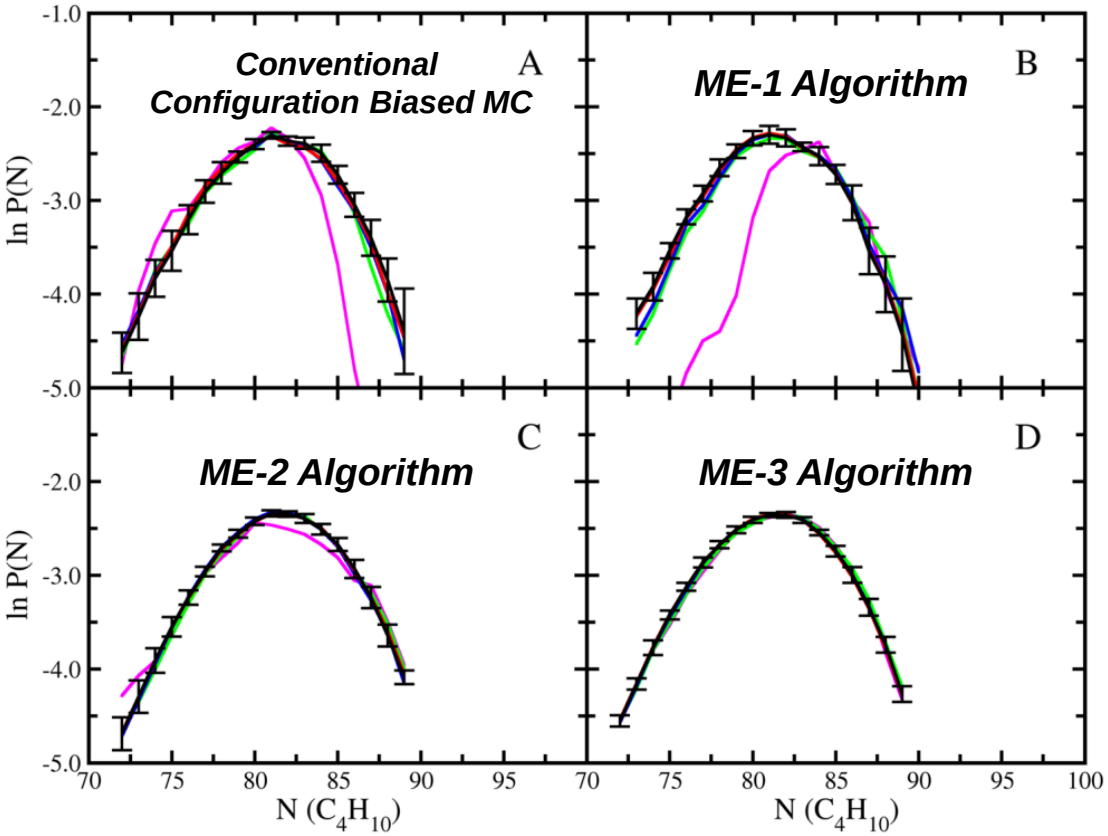
ME-1, ME-2, ME-3 Algorithm

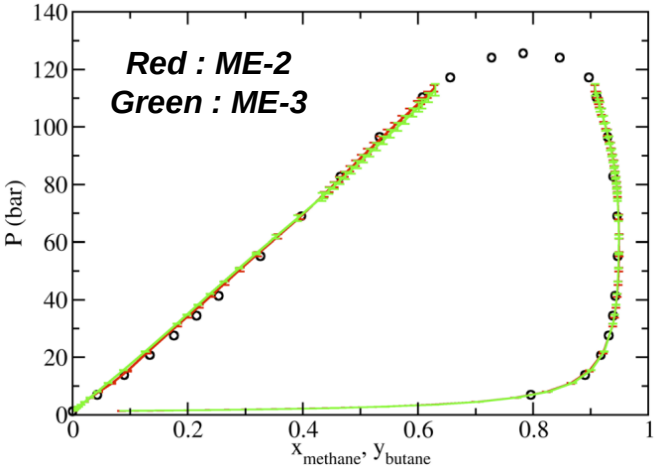


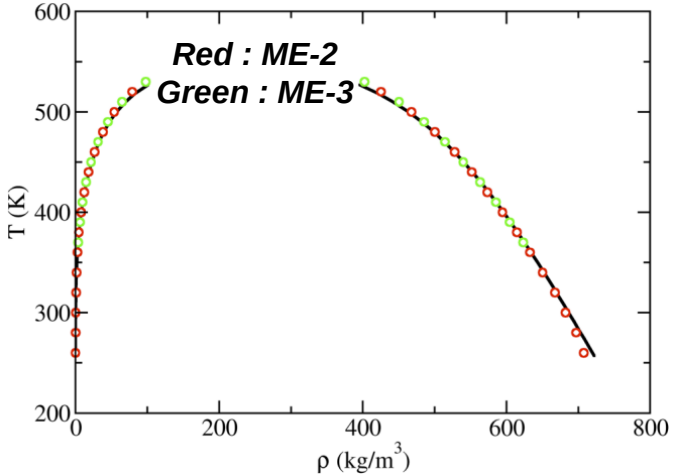
Soroush Barhaghi, M., Torabi, K., Nejahi, Y., Schwiebert, L., & Potoff, J. J. Molecular exchange Monte Carlo: A generalized method for identity exchanges in grand canonical Monte Carlo simulations. *J. Chem. Phys.*, **2018**, *149*(7).

3. Grand Canonical Monte Carlo : Principles and Applications

Solution : Molecular Exchange Monte Carlo





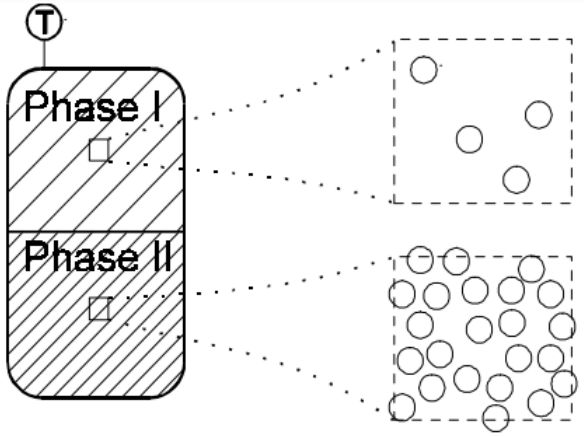


Soroush Barhaghi, M., Torabi, K., Nejahi, Y., Schwiebert, L., & Potoff, J. J. Molecular exchange Monte Carlo: A generalized method for identity exchanges in grand canonical Monte Carlo simulations. *J. Chem. Phys.*, **2018**, *149*(7).

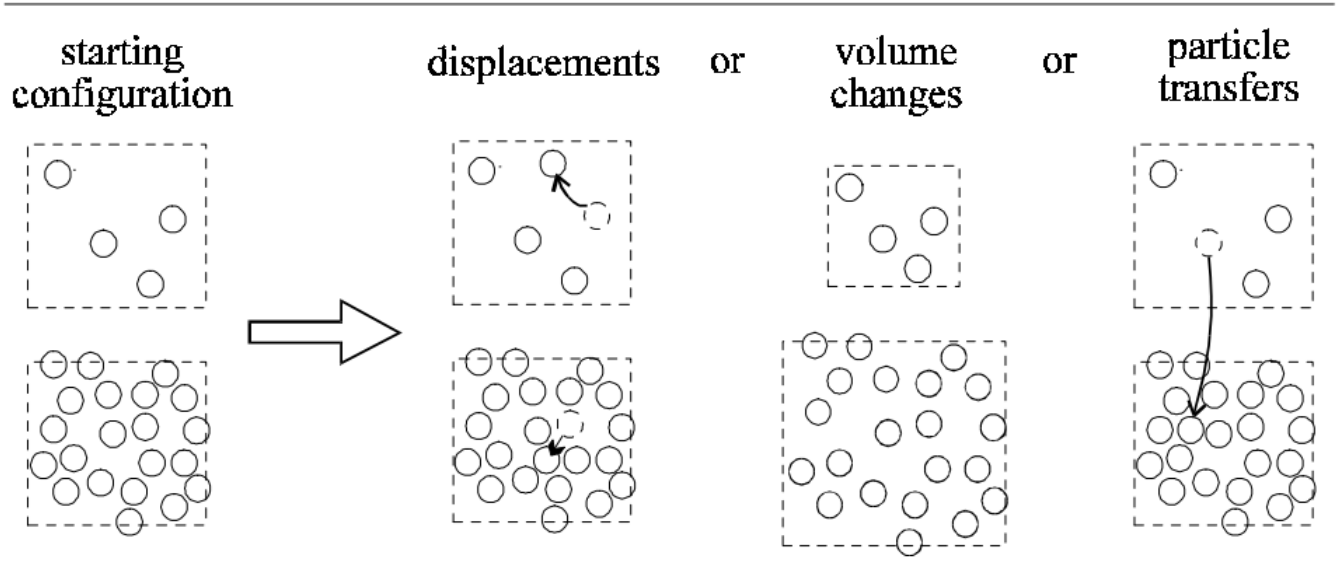
4. Monte Carlo Simulation in Gibbs Ensemble

Principle : Phase Coexistence without Boundary

$$\mu_I = \mu_{II}$$
$$V_I + V_{II} = const.$$
$$T_1 = T_2$$



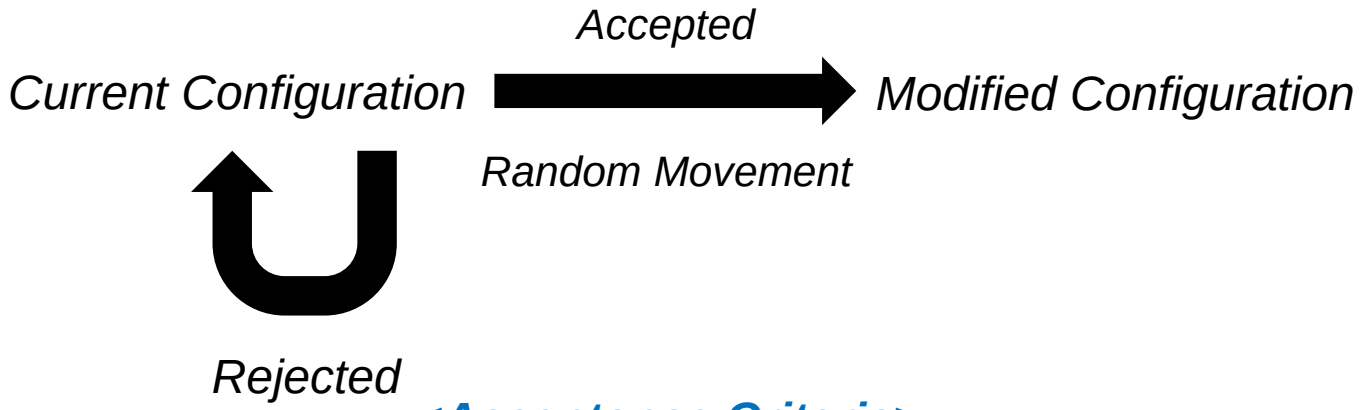
But it is not μPT Ensemble!



Baus, M., Rull, L. F., & Ryckaert, J. P. (Eds.)., Observation, prediction and simulation of phase transitions in complex fluids (Vol. 460)., Springer Science & Business Media, **2012**

4. Monte Carlo Simulation in Gibbs Ensemble

Principle : Acceptance Criteria



<Acceptance Criteria>

1) Displacement : $P_{move} = min\left(1, exp\left(-\frac{\Delta E}{k_b T}\right)\right)$

2) Volume Change :

$$P_{volume} = \min\left[1, \exp\left(-\frac{\Delta U_I + \Delta U_2}{k_b T} + N_I \log\left(\frac{V_I + \Delta V}{V_I}\right) + N_{II}\, log\left(\frac{V_{II} - \Delta V}{V_{II}}\right)\right)\right]$$

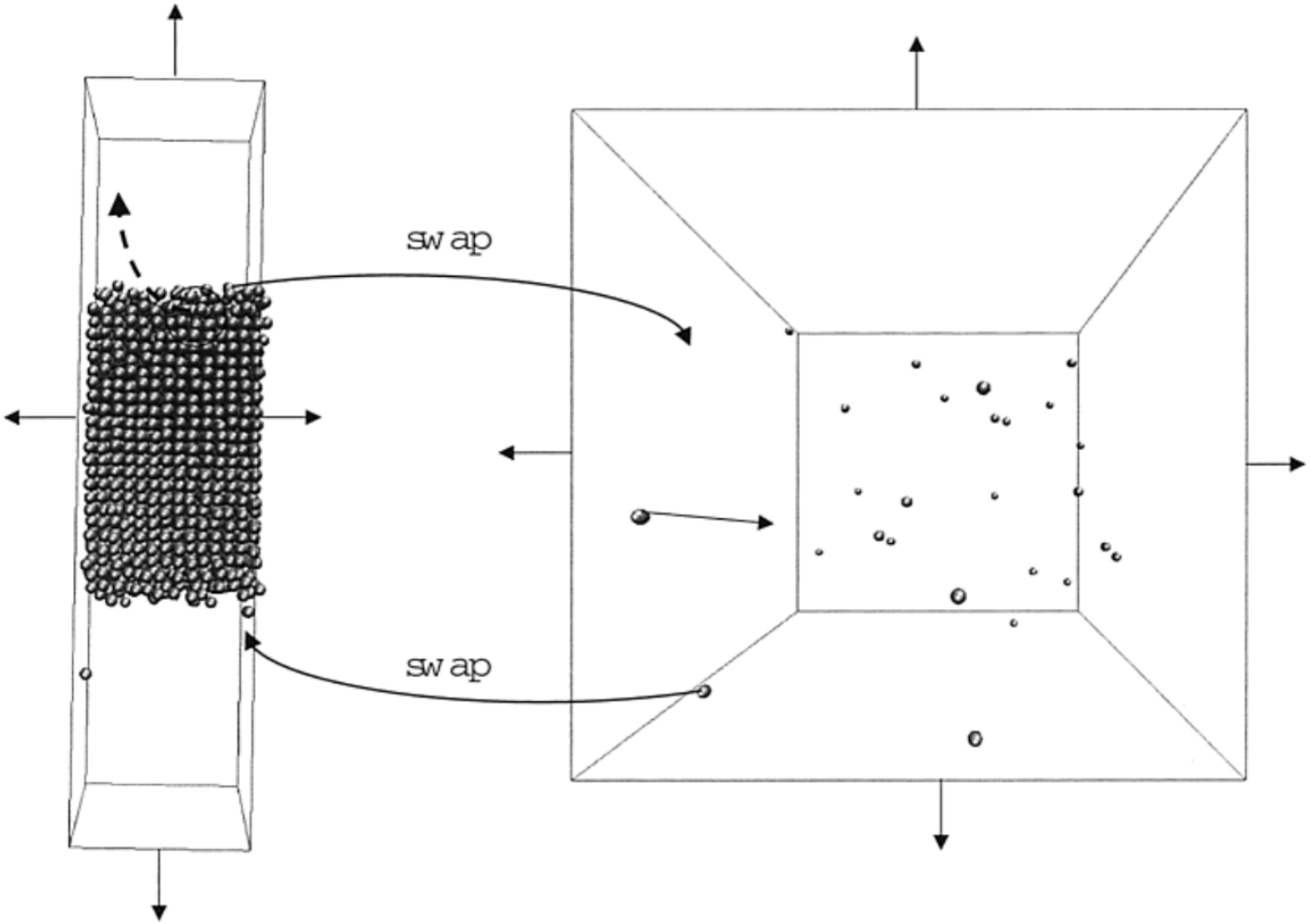
$$\Delta V = \xi \delta v_{max} min(V_I, V_{II}) \;\; (0 < \xi < 1, random, \delta v_{max} : maximum\ volume\ fraction)$$

3) Particle Transfer(I to II): $P_{transfer} = \min\left[1, \frac{N_{II} V_I}{(N_{II}+1) V_I} \exp\left(-\frac{\Delta U_I + \Delta U_2}{k_b T}\right)\right]$

Baus, M., Rull, L. F., & Ryckaert, J. P. (Eds.)., Observation, prediction and simulation of phase transitions in complex fluids (Vol. 460)., *Springer Science & Business Media*, **2012**

4. Monte Carlo Simulation in Gibbs Ensemble

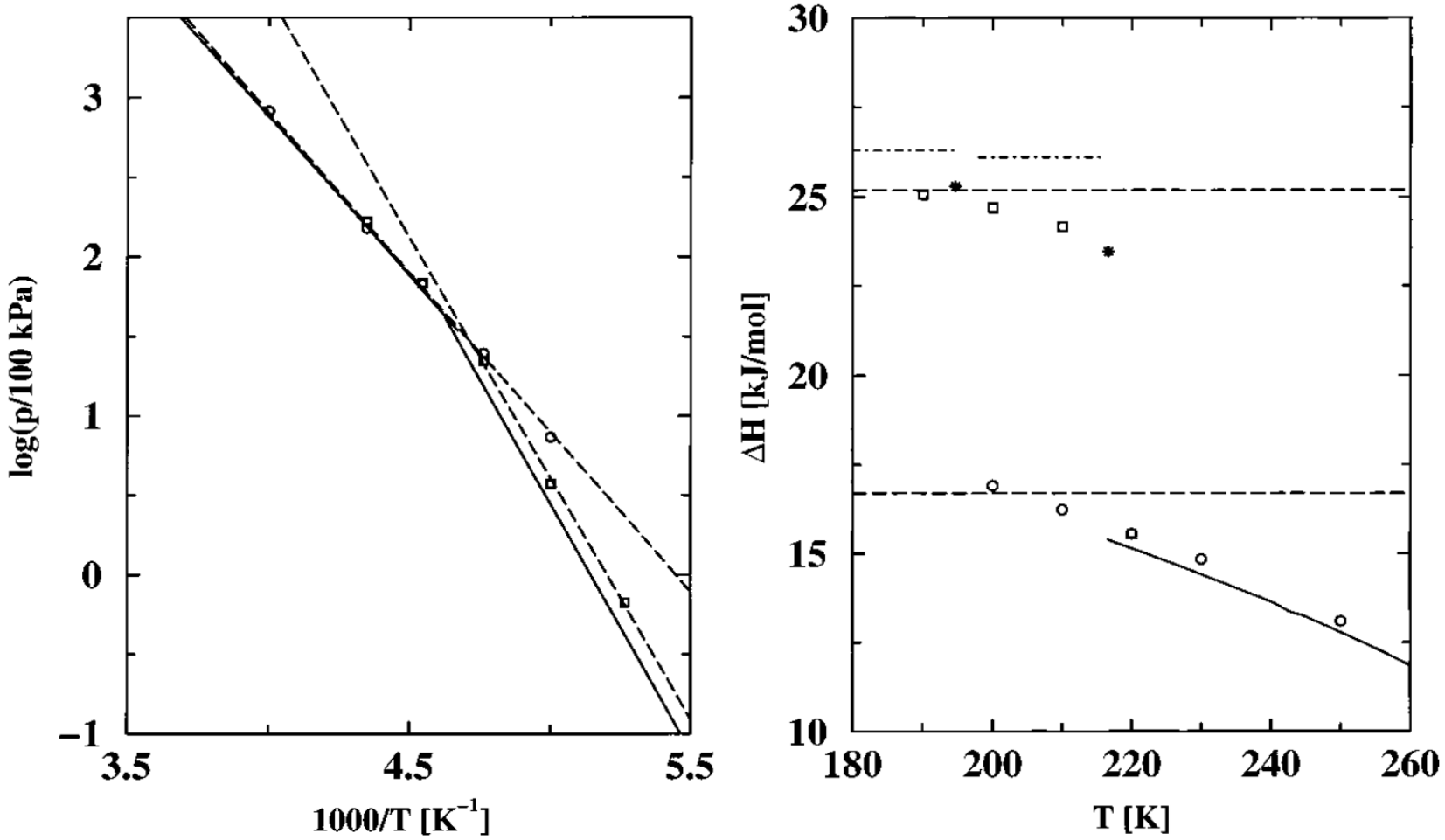
Application : Solid – Vapor Equilibrium



Chen, B., Siepmann, J. I., & Klein, M. L., Direct Gibbs ensemble Monte Carlo simulations for solid− vapor phase equilibria: applications to Lennard− Jonesium and carbon dioxide. *J. Phys. Chem. B*, **2001**, *105*(40), 9840-9848.

4. Monte Carlo Simulation in Gibbs Ensemble

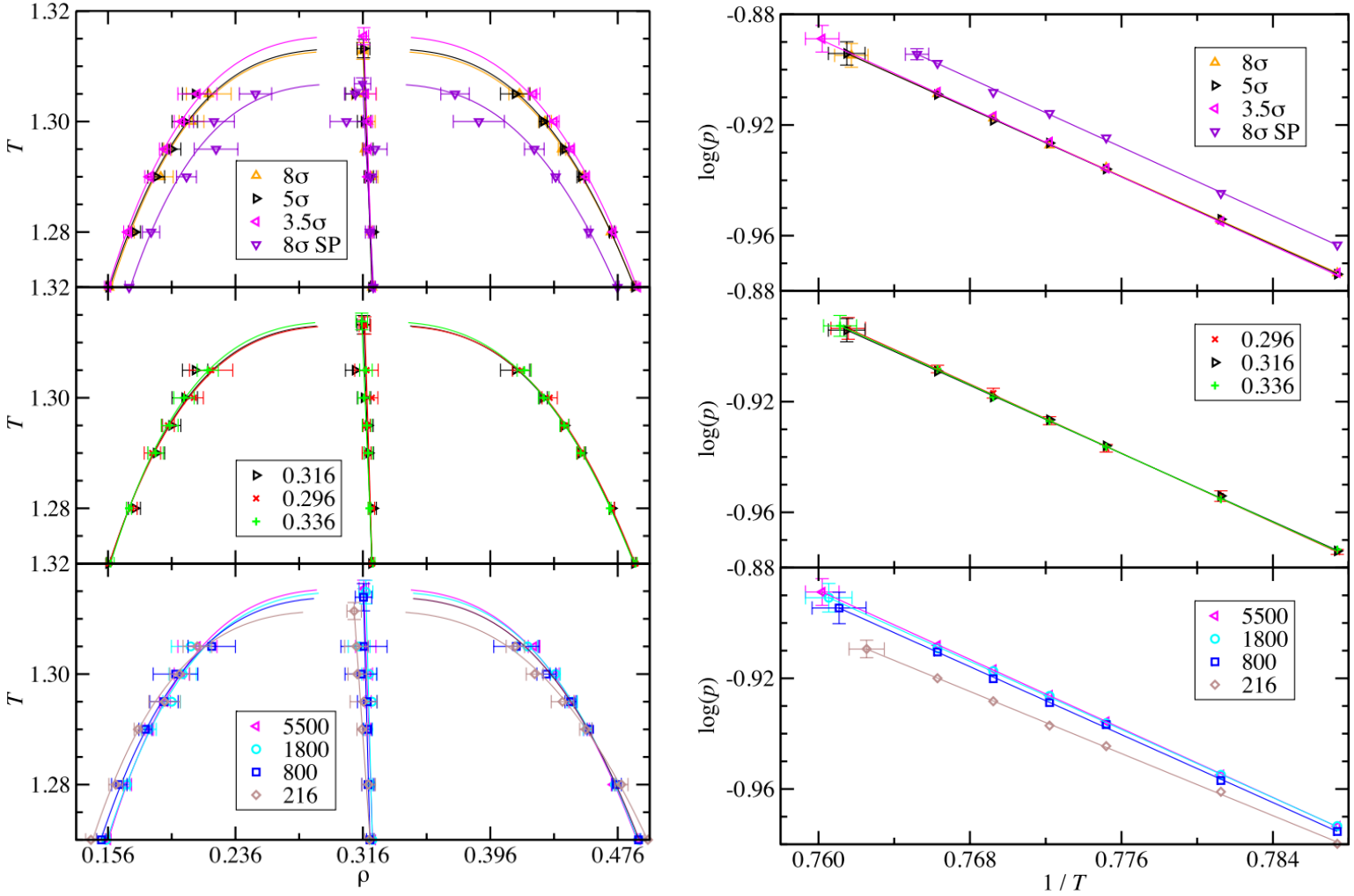
Application : Solid – Vapor Equilibrium



Chen, B., Siepmann, J. I., & Klein, M. L., Direct Gibbs ensemble Monte Carlo simulations for solid− vapor phase equilibria: applications to Lennard− Jonesium and carbon dioxide. *J. Phys. Chem. B*, **2001**, *105*(40), 9840-9848.

4. Monte Carlo Simulation in Gibbs Ensemble

Application : Liquid – Vapor Equilibrium, Critical Point



Dinpajooh, M., Bai, P., Allan, D. A., & Siepmann, J. I., Accurate and precise determination of critical properties from Gibbs ensemble Monte Carlo simulations. *J. Chem. Phys.*, **2015**, *143*(11).

Takeaways

■ *Monte Carlo method is statistical methodology that derive certain statistical quantities for given system by utilizing random number. It contains two main processes : Random Movement and Acceptance Criteria*

■ *By using specific acceptance criteria, we can sample the system with NVE, NVT, and NPT ensemble environment*

■ *Grand Canonical Monte Carlo allowed the molecular simulation with exchange of matter. It contains several principles related to particle insertion and deletion(Acceptance criteria, Widom's particle insertion method, …)*

■ *Gibbs ensemble assume two-phase system as separated systems with particle swapping. It enabled to modelling phase transition phenomena*

Thank you for your kind attention / Q&A