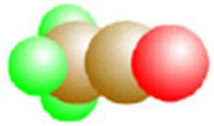
Applied Statistical Mechanics
Lecture Note - 12

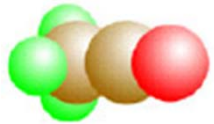


고려대학교

Advanced Topics in Molecular Monte Carlo Method

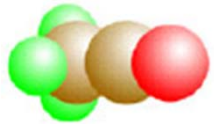
고려대학교
화공생명공학과
강정원

Contents



고려대학교

Introduction



고려대학교

- Previous simulation methods : Properties of a single isolated phase
- Molecular Simulation Techniques can be extended to multiple phases
  - Thermodynamic Phase Coexistence : Two or more phases are equally stable
  - Condition of Phase Coexistence

$$T^{\alpha} = T^{\beta}$$

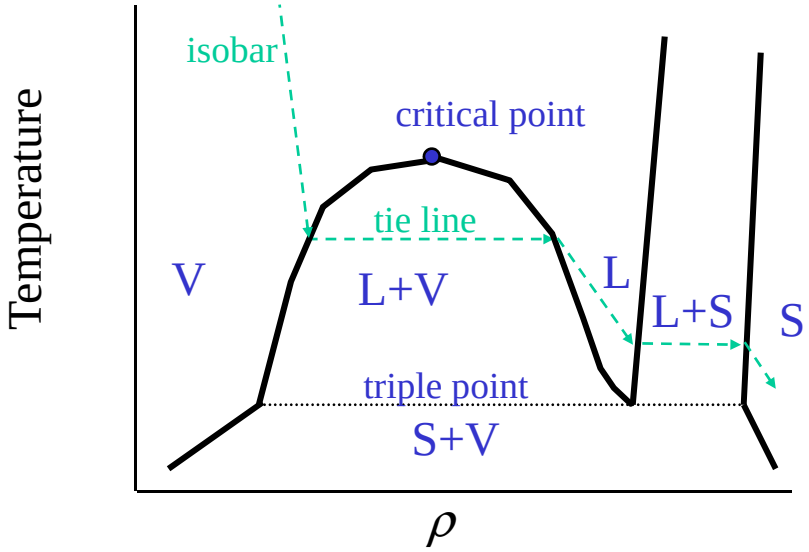
$$p^{\alpha} = p^{\beta}$$

$$\mu_i^{\alpha} = \mu_i^{\beta} \qquad i = 1,..,C$$

Phase Diagrams

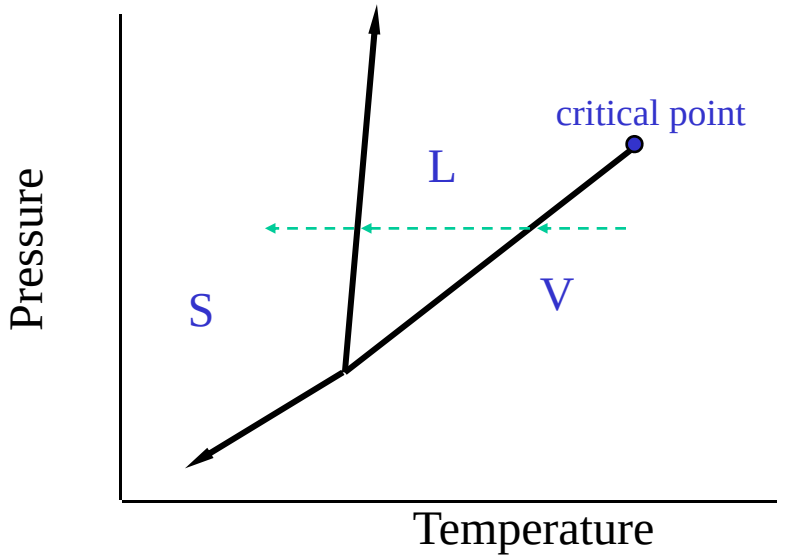
고려대학교

two-phase regions



ρ-T diagram

two-phase lines



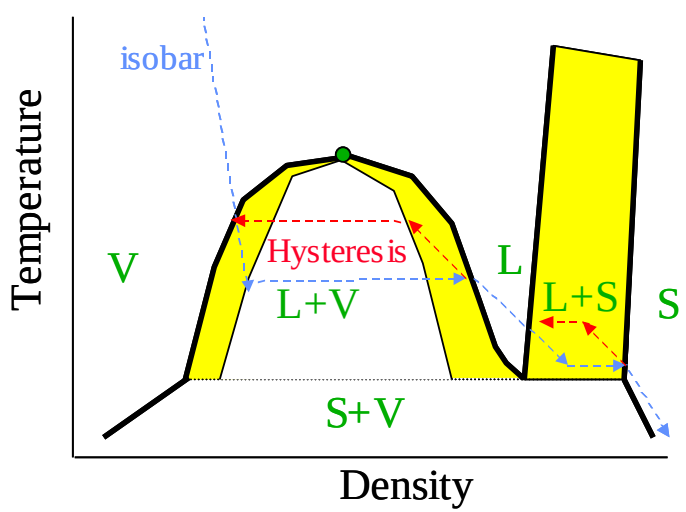
TP diagram

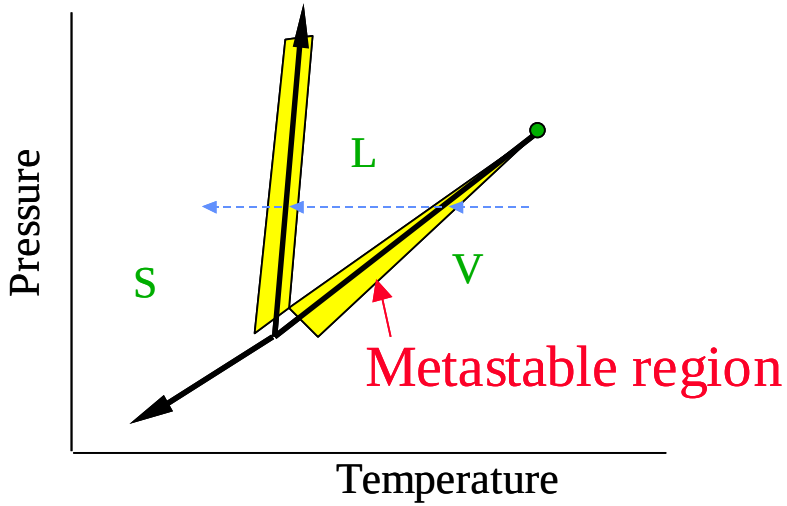
- Gibbs Phase Rule
  - $F = 2 + C - P$
    - *F : Degree of Freedom*
    - *C : Number of Components*
    - *P : Number of Phases*

Straightforward Simulation

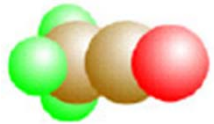
고려대학교

- Change *T* or *P* for given model system and wait for a phase transformation occur
  - Major Drawbacks
    - Hysterisis : Irreversible phase transformation
    - Large free energy barrier at interface → Depends on the size of the interface → Depends on the choice of simulation system





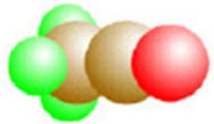
Alternative Methods



고려대학교

- Gibbs Ensemble Method (Panagiotopoulos, 1987)
- Gibbs – Duhem Integration Method (Kofke, 1993)

Why free energies are important in Phase Coexistence ?



고려대학교

- From 2nd Law of Thermodynamics
  - At equilibrium, *S* is maximum for (N,V,E)
  - (N,V,E) System : A is minimum

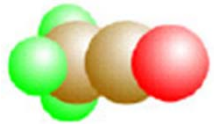
    $A = U - TS$ *(Helmholtz Free Energy)*
  - (N,P,T) System : G is Minimum

    $G = H - TS$ (*Gibbs Free Energy*)
- Equilibrium Condition

$$A^{\alpha} = A^{\beta}$$

$$G^{\alpha} = G^{\beta}$$

Free energy cannot be directly measured in simulation



고려대학교

- Helmholtz free energy

$$A = -kT \ln Q(N,V,T) = -kT \left(\frac{\int dp^N dr^N \exp(-\beta H(p^N, r^N))}{\Lambda^{dN} N!} \right)$$

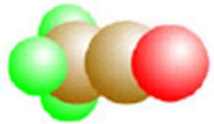
  - Not the form of canonical average over phase space
  - Depends directly on the available volume in the phase space
  - Cannot be directly measured in real experiment, too.

- Derivatives of free energy

$$\left(\frac{\partial A}{\partial V} \right)_{N,T} = -p \qquad \left(\frac{\partial A/T}{\partial 1/T} \right)_{V,T} = -E$$

→ **Find a reversible path in V,T plane and perform integration**

Kirkwood's coupling parameter method



고려대학교

- Assume U depends on the coupling parameter λ :

$$U(\lambda) = (1-\lambda)U_I + \lambda U_{II} = U_I + \lambda(U_{II} - U_I)$$

- Partition function for potential energy function

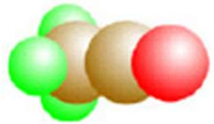
$$Q(N,V,T,\lambda) = \frac{1}{\Lambda^{3N} N!}\int dr^N \exp(-\beta U(\lambda))$$

$$\left(\frac{\partial A(\lambda)}{\partial \lambda}\right)_{N,V,T} = -\frac{1}{\beta}\frac{\partial}{\partial \lambda}\ln Q(N,V,T,\lambda) = -\frac{1}{\beta Q(N,V,T,\lambda)}\frac{\partial Q(N,V,T,\lambda)}{\partial \lambda}$$

$$= \frac{\int dr^N \left(\frac{\partial U(\lambda)}{\partial \lambda}\right)\exp(-\beta U(\lambda))}{\int dr^N \exp(-\beta U(\lambda))} = \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_\lambda$$

→ Ensemble average of with potential function U(λ)

Kirkwood's coupling parameter method



고려대학교

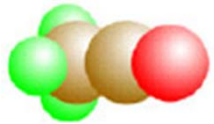
- Free energy difference

$$A(\lambda=1)-A(\lambda=0)=\int_{\lambda=0}^{\lambda=1}d\lambda\left\langle\frac{\partial U(\lambda)}{\partial\lambda}\right\rangle$$

- All free energy methods are based on calculation of free energy differences
- Example :
  - Volume of R can be measured as a fraction of total volume
    - Sample the reference system
    - keep an average of the fraction of time occupying the target system

$$\frac{\Omega_R}{\Omega_\Gamma}=\langle s(\Gamma)\rangle_\Gamma \qquad S_R-S_\Gamma=k\ln\left(\Omega_R/\Omega_\Gamma\right)$$

Chemical Potentials



고려대학교

- Chemical Potentials

$$\mu_a = \left(\frac{\partial G}{\partial N_a}\right)_{T,P,N_{b\neq a}} = \left(\frac{\partial A}{\partial N_a}\right)_{T,V,N_{b\neq a}} = -T\left(\frac{\partial S}{\partial N_a}\right)_{V,E,N_{b\neq a}}$$

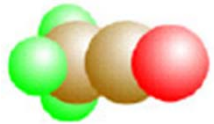
$$Q(N,V,T) = \frac{V^N}{\Lambda^{dN} N!}\int_0^1 \ldots \int_0^1 ds^N \exp(-\beta U(s^N;L))$$

$$s^N = r^N / L$$

$$A(N,V,T) = -kT\ln Q = -kT\ln\left[\frac{V^N}{\Lambda^{dN} N!}\right] - kT\ln\left\{\int_0^1 \ldots \int_0^1 ds^N \exp(-\beta U(s^N;L))\right\}$$

$$= A_{id}(N,V,T) + A_{ex}(N,V,T)$$

Chemical Potentials



고려대학교

- For sufficiently large N,

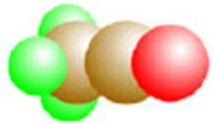
$$\mu = -kT \ln(Q_{N+1} / Q_N)$$

$$\mu = -kT \ln(Q_{N+1} / Q_N) = -kT \ln\left[\frac{V / \Lambda^d}{N+1}\right] - kT \ln\left\{\frac{\int_0^1 \ldots \int_0^1 ds^{N+1} \exp(-\beta U(s^{N+1}))}{\int_0^1 \ldots \int_0^1 ds^{N} \exp(-\beta U(s^{N}))}\right\}$$

$$= \mu_{id}(\rho) + \mu_{ex}$$

$$\mu_{ex} = -kT \ln \int ds^{N+1} \left\langle \exp(-\beta \Delta U) \right\rangle_N$$

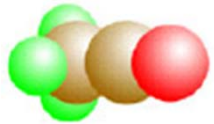
Widom's Test Particle Insertion Method



고려대학교

- Widom (1963)
- A "ghost particle" is randomly inserted into the ensemble and calculating the energy of its interaction
- The test particle is a "ghost", it does not affect the properties of real molecule
- In principle , this method can be used in any simulation system for the calculation of chemical potential

Implementation of Widom's Method



고려대학교

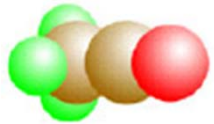
- Carry out conventional NVT or NPT Monte Carlo Simulation of N particles
- At frequent interval during simulation, randomly generate a coordinate, s_{N+1} uniformly over unit cube
- For given s_{N+1}, compute :

$$\mu_{ex} = -kT \ln\left\langle \exp(-\beta \Delta U) \right\rangle \longrightarrow \text{NVT ensemble}$$

$$\mu_{ex} = -kT \ln\left[\frac{\left\langle V \exp(-\beta \Delta U) \right\rangle}{\left\langle V \right\rangle} \right] \longrightarrow \text{NPT ensemble}$$

- Average → chemical potential

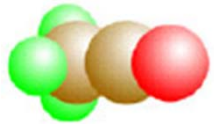
Note on Widom's Method



고려대학교

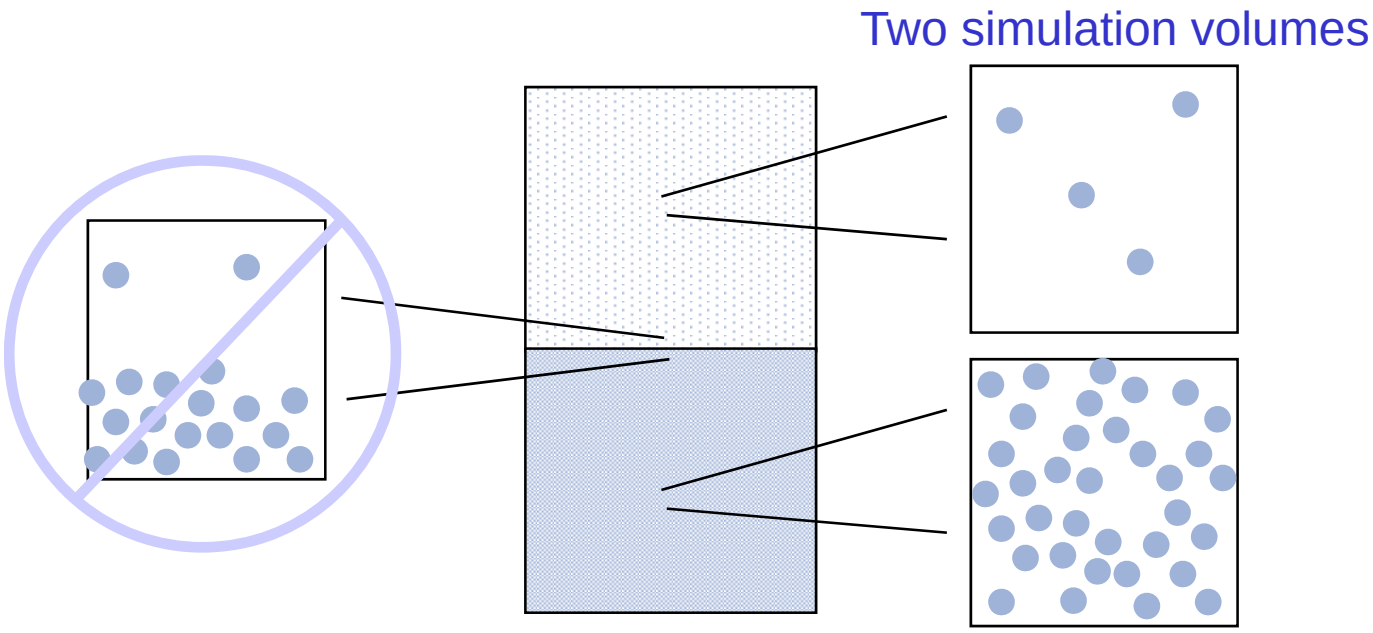
- Widom's method can be used as a verification that equilibrium has been attained
- At high density, some difficulties are encountered
  - Difficult to insert a particle at given location

Gibbs Ensemble Method

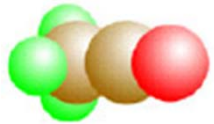


고려대학교

- Proposed by Panagiotopoulos (1987,1988)
- Simulation method without interface
- Thermodynamic contact without physical contact



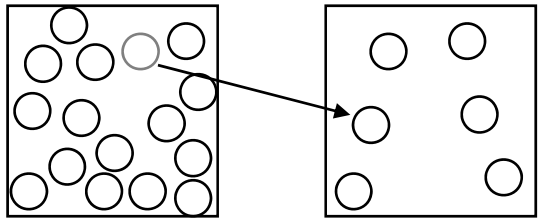
Gibbs Ensemble Method



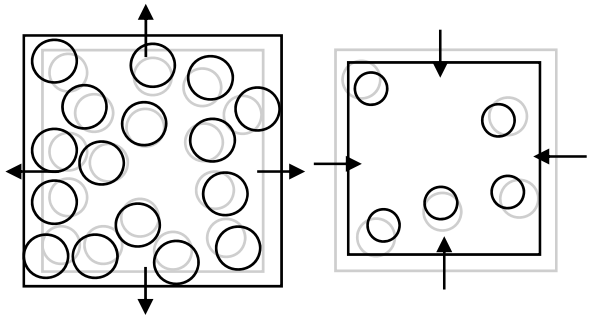
고려대학교

- MC simulation includes moves that couples two simulation volumes

Particle exchange equilibrates chemical potential



Volume exchange equilibrates pressure



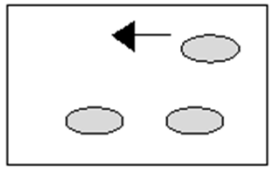
Incidentally, the coupled moves enforce mass and volume balance

Gibbs Ensemble Method

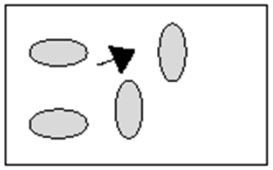
고려대학교

(1) Attempt molecular displacement

Box 1: N_1, V_1, T

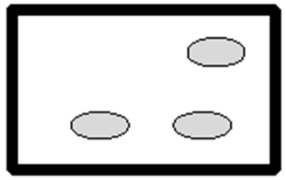


Box 2: N_2, V_2, T

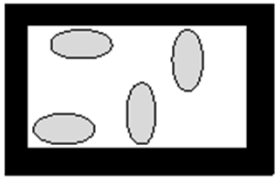


(2) Attempt volume fluctuation

Box 1: N_1, $V_1 + \Delta V$, T

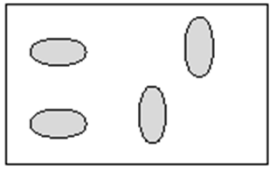


Box 2: N_2, $V_2 - \Delta V$, T

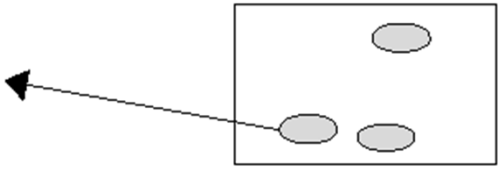


(3) Attempt molecular transfer

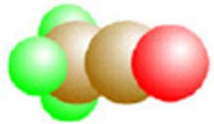
Box 1: $N_1 + 1$, V_1, T



Box 2: $N_2 - 1$, V_2, T



Gibbs Ensemble Method



고려대학교

- Acceptance of three moves → Governed by Pseudo Boltzman Factor
  - Displacement movement

$$\Delta Y_{disp} = \Delta E_{\alpha} + \Delta E_{\beta}$$

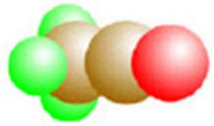
  - Volume change

$$\Delta Y_{disp} = \Delta E_{\alpha} + \Delta E_{\beta} - N_{\alpha} kT \ln \frac{V_{\alpha} + \Delta V_{\alpha}}{V_{\alpha}} - N_{\beta} kT \ln \frac{V_{\beta} + \Delta V_{\beta}}{V_{\beta}} + P(\Delta V_{\alpha} + \Delta V_{\beta})$$

  - Molecular transfer

$$\Delta Y_{disp} = \Delta E_{\alpha} + \Delta E_{\beta} - kT \ln \frac{V_{\beta}(N_{\alpha} + 1)}{V_{\alpha} N_{\beta}}$$

Gibbs Ensemble - Algorithm



고려대학교

Part 1 Initialisation:
Specify the number of cycles (*nCycles*), number of particles in the boxes (*nBox1*, *nBox2*), number of volume (*nVol*), transfer attempts (*nTrans*), and the total number of moves (*nTotal* = *nBox1* + *nBox2* + *nVol* + *nTrans*).

Part 2 Generate Markov chain:

loop $i \leftarrow 1 \ldots nCycles$

loop $j \leftarrow 1 \ldots nTotal$

if (rand() ≤ *nBox1*/*nTotal*) //Decide which move to perform

Part 2.1 Displace particle in box 1.

else if(rand() ≤ (*nBox1* + *nBox2*)/*nTotal*)

Displace particle in box 2.

else if(rand() ≤ (*nBox1* + *nBox2* + *nVol*)/*nTotal*)

Part 2.2 Change volume.

else if(*rand()* ≤ (*nBox1* + *nBox2* + *nVol* + 0.5*nTrans*)/*nTotal*)

Part 2.3 Transfer particle from box 1 to box 2.

else

Transfer particle from box 2 to box 1.

end if

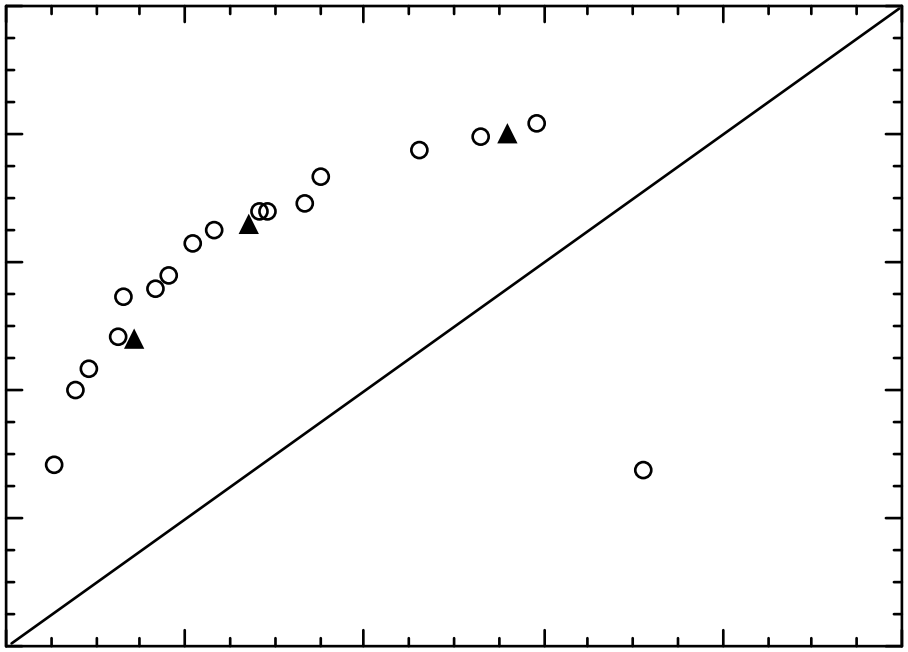
end *j* **loop**

end *i* **loop**

Gibbs Ensemble – Result

고려대학교

- Water + Methanol Mixture



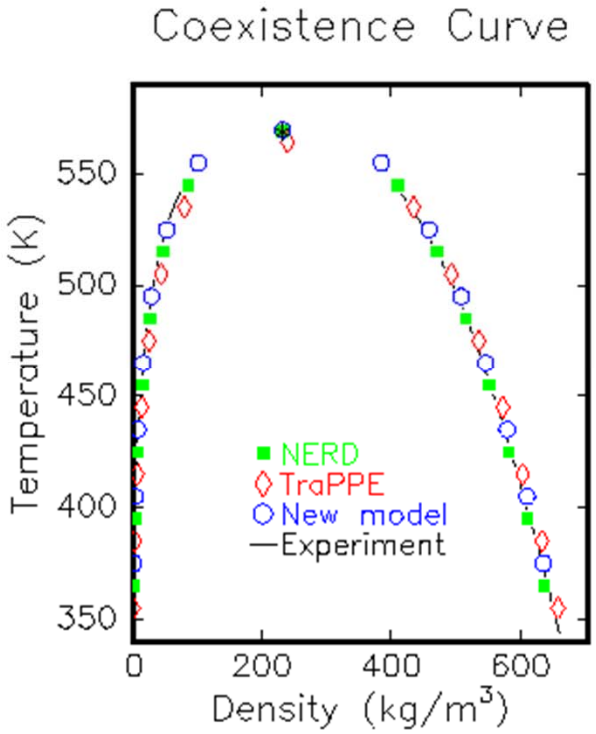
•*Strauch and Cummings, Fluid Phase Equilibria,* ***86*** *(1993) 147-172;*

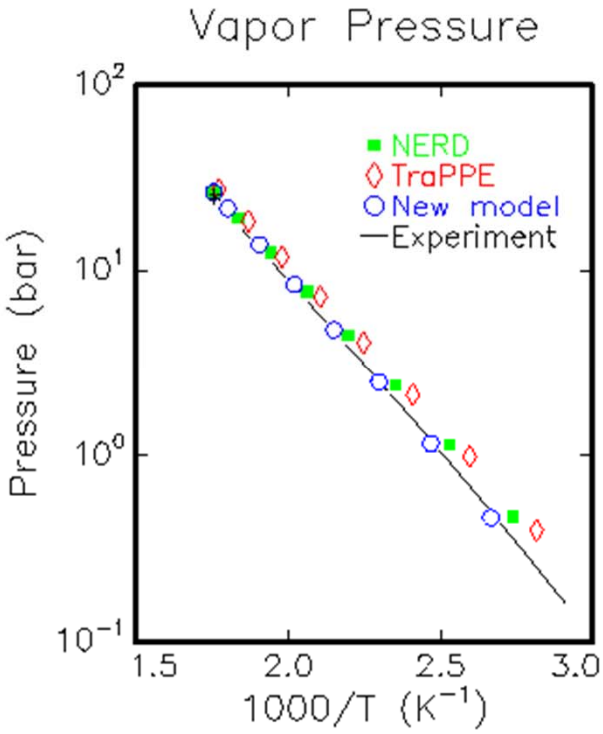
• *Chialvo and Cummings, Molecular Simulation,* ***11*** *(1993) 163-175.*

Gibbs Ensemble – Result

고려대학교

- Panagiotopoulos Group

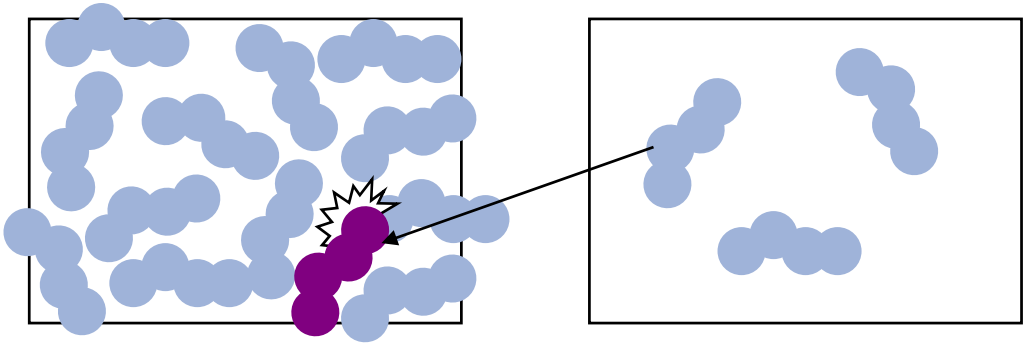




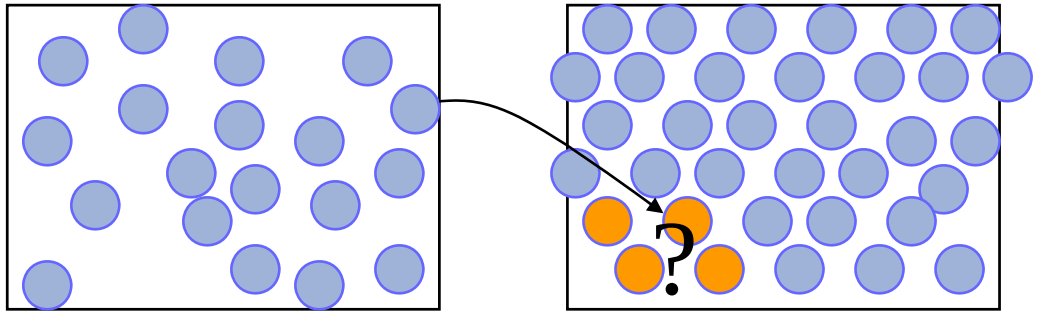
Gibbs Ensemble Limitation

고려대학교

- Limitation arise from particle-exchange requirements

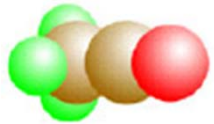


Dense phase or Complex molecules



Solid phases

Gibbs-Duhem Integration



고려대학교

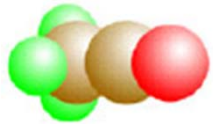
- David Kofke (1993)
- Basis : Numerical Integration of Cluisus – Clapeyron Equation

$$\mu_\alpha - \mu_\beta = -(S_\alpha - S_\beta)dT - (V_\alpha - V_\beta)dP$$

$$\frac{dP}{dT} = \frac{S_\alpha - S_\beta}{V_\alpha - V_\beta} = \frac{\Delta H}{T\Delta V}$$

$$\frac{d\ln P}{d1/T} = -\frac{\Delta H}{P\Delta V/T} \longrightarrow \left(\frac{\partial \ln p}{\partial \beta}\right)_\sigma = -\frac{\Delta h}{\Delta Z}$$

Gibbs – Duhem Integration

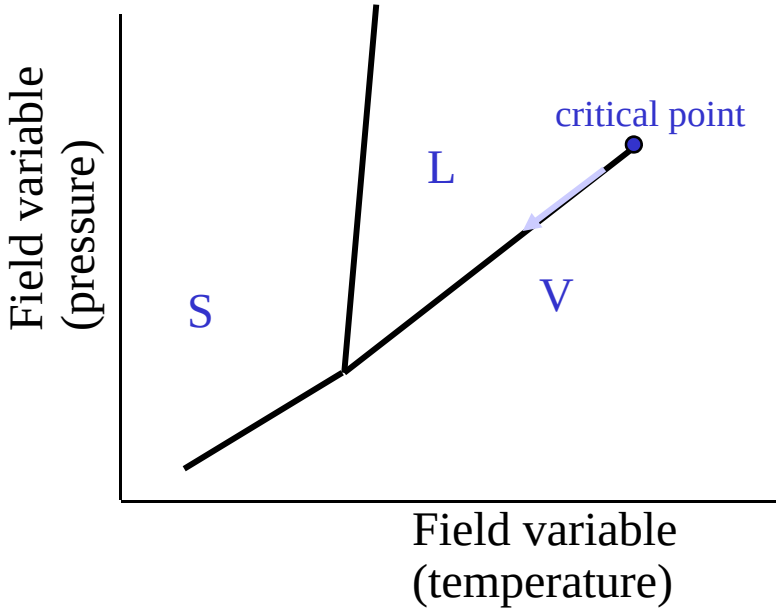


고려대학교

- GE equation

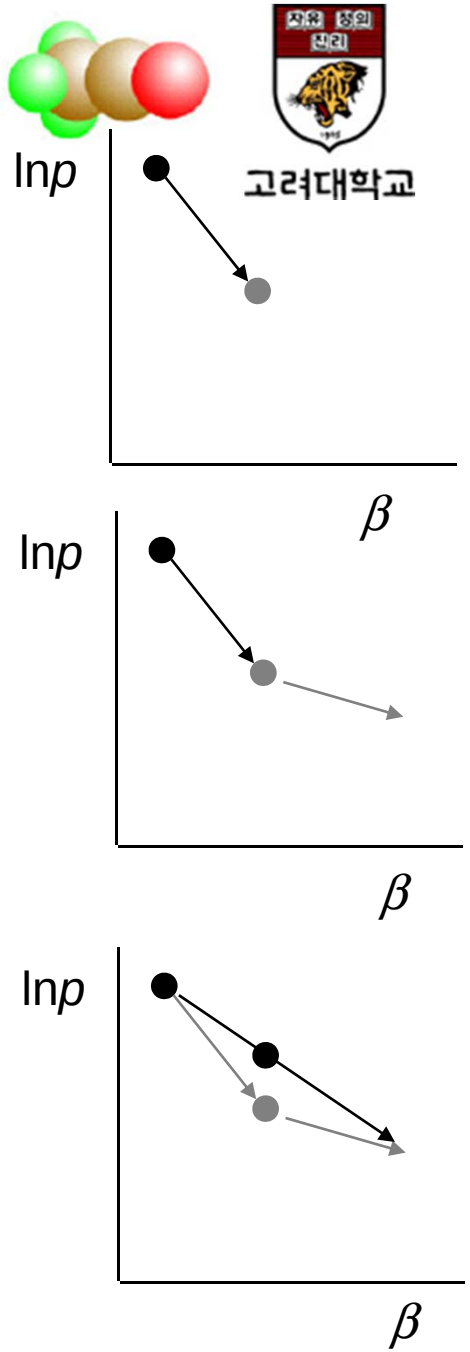
$$\left(\frac{\partial \ln p}{\partial \beta}\right)_{\sigma} = -\frac{\Delta h}{\Delta Z}$$

- Treat as nonlinear first order ODE
  - Use (NPT) simulation to obtain ΔH/Δz

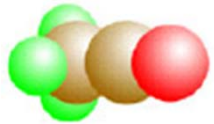


Predictor-Corrector Algorithm Implementation

- Given initial condition and slope (= $-\Delta h/\Delta Z$), predict new (p,T) pair.
- Evaluate slope at new state condition…
- …and use to correct estimate of new (p,T) pair



Gibbs Duhem Integration



고려대학교

- Potentially very efficient algorithm
  - Coexistence curves for solid-liquid systems
  - Coexistence curves for complex molecules
- Algorithm is not robust
- No built-in diagnostics

- Additional free energy calculation may be required to check the result