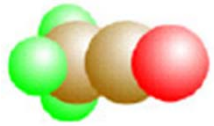
Applied Statistical Mechanics
Lecture Note - 11



고려대학교

Molecular Monte Carlo Method

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강정원

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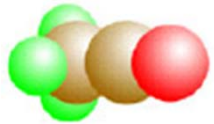

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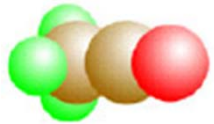
I-1. Introduction



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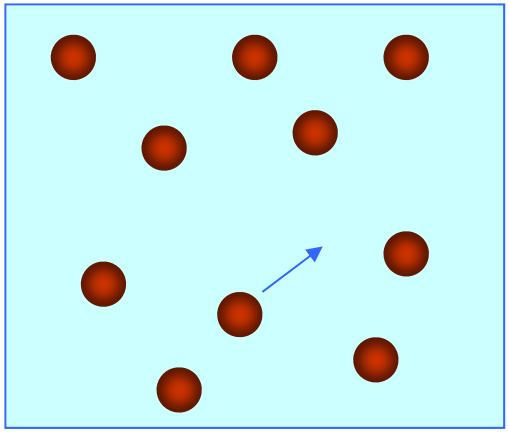
■ Overview of Molecular Monte Carlo Method

Objective
Calculation of Macroscopic Properties from Microscopic Properties (intermolecular forces…)

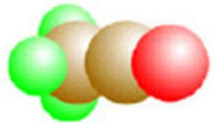
Averaging Method
Ensemble Averages *NVT* Ensemble *NPT* Ensemble *μPT* Ensemble



Generation of Random Configurations
Use of Random Number Importance Sampling Markov Chain Metropolis Algorithm

Approximations
Periodic Boundary Condition Minimum Image Convention Long Range Correction Neighborhood List

I-2. Averaging Method



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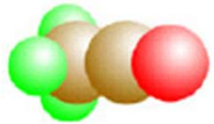
- Statistical Mechanics : Theoretical Basis for derivation of macroscopic behavior from microscopic properties
- Configuration : position and momenta ($\boldsymbol{r}^N$ and $\boldsymbol{p}^N$)
- Configurational Variable : $A(\boldsymbol{r}^N, \boldsymbol{p}^N)$
- Ensemble average
  - Weighted sum over all possible members of ensemble
  - Using classical mechanics

$$< A >= \frac{1}{Q}\frac{1}{h^{3N}N!}\int dp^N \int dr^N A(p^N, r^N)\exp\{-\beta E(r^N, p^N)\}$$

$$Q = \frac{1}{h^{3N}N!}\int dp^N \int dr^N \exp\{-\beta E(p^N, r^N)\}$$

I-2. Averaging Method



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- Separation of Energy
  - Total energy is sum of kinetic and potential parts

$$E(r^N, p^N) = K(p^N) + U(r^N)$$

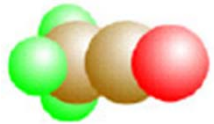
  - Kinetic parts can be treated separately from potential parts

$$Q = \frac{1}{h^{3N} N!} \int dp^N \exp(-\beta \sum_i p_i^2 / 2m_i) \int dr^N \exp\{-\beta U(r^N)\}$$

$$= \frac{1}{\Lambda^{3N}} \boxed{\frac{1}{N!} \int dr^N \exp\{-\beta U(r^N)\}} \quad Z_N$$

$$= \frac{1}{\Lambda^{3N}} \frac{1}{Z_N}$$

I-2. Averaging Method



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■ Ensemble Average of a property

$$\langle A \rangle = \frac{1}{Z_N N!} \int dr^N A(r^N, p^N) \exp\{-\beta U(r^N)\} = \frac{\int dr^N A(r^N, p^N) \exp\{-\beta U(r^N)\}}{\int dr^N \exp\{-\beta U(r^N)\}}$$

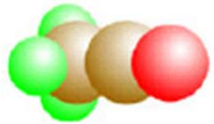
- Monte Carlo Simulation calculates excess thermodynamic properties that result in deviation from ideal gas behavior

■ Metropolis Monte Carlo Method

$$\langle A \rangle = \int \frac{\exp\{-\beta U(r^N)\}}{Z_N(r^N)} A(r^N) dr^N = \int \boxed{\mathcal{N}(r^N)} A(r^N) dr^N = \langle A \rangle_{trials, \mathcal{N}(r^N)}$$

probability of a given configuration r^N

I-3. General MMMC Scheme



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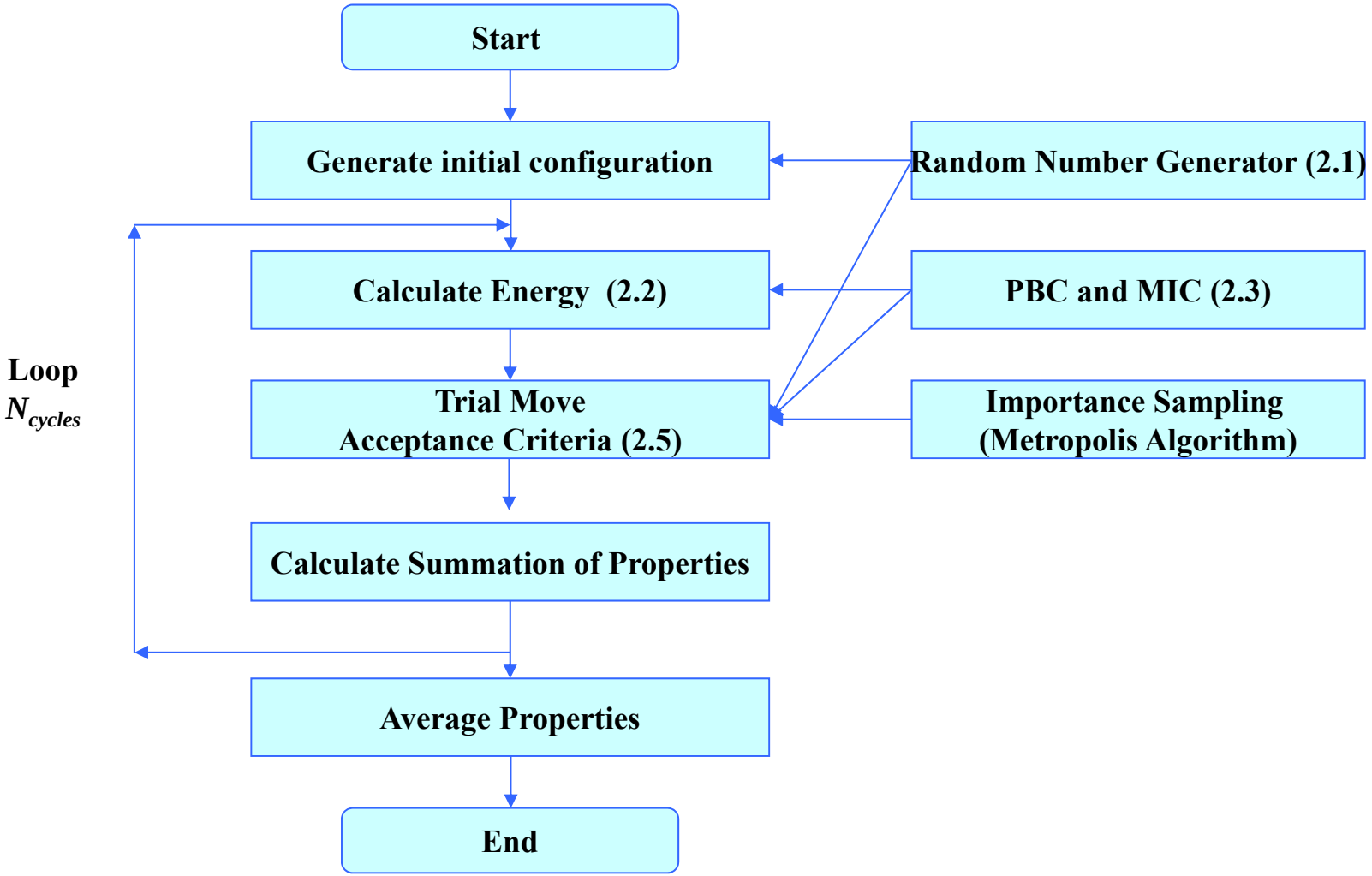
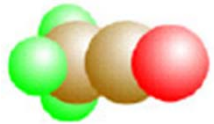


II-1. Random Number Generation



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- There is nothing like “Random number generator “
  - “*Pseudo Random Number Generator* “
  - Most of the pseudo random number generator repeats “sequence”
  - It is important to know *how long is the sequence*

- Most FORTRAN, C compiler supplies random number generator based on **Linear Congruental Method**
  - The relationship will repeat when n greater than 32767

$$I_{n+1} = (aI_n + c) \bmod (m)$$

$$a, c > 0, m > l_0, a, c$$

Ex) Digital FORTRAN
RANDOM_NUMBER subroutine
Period = 10**18

II-1. Random Number Generation

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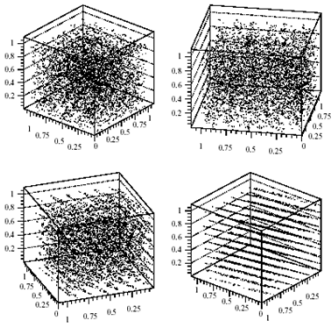


- RANDU Algorithm
  - 1960's , IBM

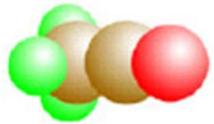
$$I_{n+1} = (65539 \times I_n) \bmod (2^{31})$$

  - This generator was found to have serious problem : *"The Marsaglia Effect"*

- Improving the behavior of random number generator
  - Two initial seed can extend the period grater than m

$$I_n = (a \times I_{n-1} + b \times I_{n-2}) \bmod (m)$$

II-1. Random Number Generation



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- Using Random number generators
  - Check the period
  - Serial Test : *(x,y) or (x,y,z)*
  - Be careful about dummy argument
    - Use different dummy argument for two different set of random numbers
    - Compiler's optimizer is trying to remove multiple calls to random number generator

```
X = RAND(IDUM) + RAND(IDUM)
```

↓

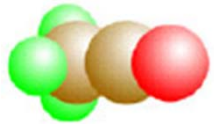
```
X = 2.0 * RAND(IDUM)
```

```
    DO 1 I = 1,100
          X = RAND(IDUM)
1   CONTINUE
```

↓ → You have to change dummy argument each calls

Not evaluating every steps
Evaluated only once

II-1. Random Number Generation



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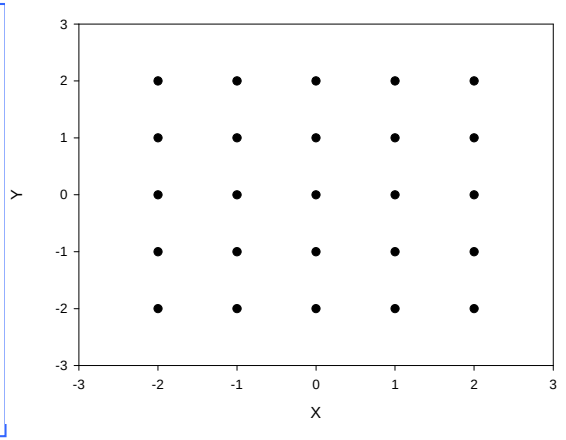
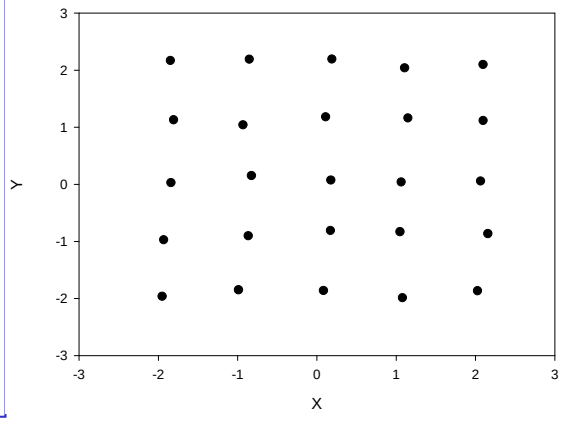
■ Initializing Configuration (Example : 2D Space)

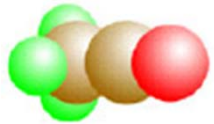
```
bx = rLx/float(nx)
by = rLy/float(ny)
do  60  ip= 1, np
              x(ip) = ( 0.5*(1.-float(nx)) +
             float(mod( ip-1, nx )) )*bx
              y(ip) = ( 0.5*(1.-float(ny)) +
              float((ip-1)/nx) )*by
60 continue
```




```
bx = rLx/float(nx)
by = rLy/float(ny)
do  60  ip= 1, np
              x(ip) = ( 0.5*(1.-float(nx)) +
             float(mod( ip-1, nx ))+0.1*r2() )*bx
              y(ip) = ( 0.5*(1.-float(ny)) +
              float((ip-1)/nx) +0.1*r2())*by
60 continue
```



II-2. Calculating Potential Energy



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■ Potential Energy of *N*-interacting particles

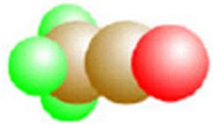
$$U = \sum_i u_1(r_i) + \sum_i \sum_{j>i} u_2(r_i, r_j) + \sum_i \sum_{j>i} \sum_{k>j>i} u_3(r_i, r_j, r_k) + \ldots$$

Three-body interaction

Two-body interaction

Effect of external field

II-2. Calculating Potential Energy



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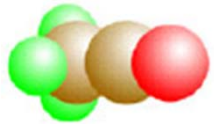
- Typically, effect of external field is zero
- Two body interaction is the most important term in the calculations
  - Truncated after second term
- For some cases, three body interactions may be important
- Including three body interactions imposes a very large increase in computation time $t \propto N^m$
- Short range and long range interactions
  - Short range : Dispersion and Repulsion
  - Long range : Ionic interaction
    - Special methods are required for long range interactions due to limited size of simulation box

II-2. Calculating Potential Energy



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■ Naïve calculation

Summations are chosen to avoid duplicated evaluation and "self" interaction

$$U = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} u_2(r_{ij})$$

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

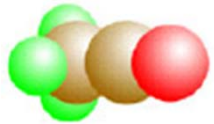
Pseudo Code

```
Loop i = 1, N-1
   Loop j = i+1,N
            Evaluate r_ij
            Evaulate U_ij
            Accumulate Energy
   End j Loop
End j Loop
```

FORTRAN Code

```
      DO 10 I = 1, N
      DO 20 J = I+1, N
            DX = X(I)-X(J)
            DY = Y(I)-Y(J)
            RIJ2 = DX*DX + DY*DY
            RIJ6 = RIJ2*RIJ2*RIJ2
            RIJ12 = RIJ6*RIJ6
           UTOT = UTOT + 1/RIJ12 - 1/RIJ6
20    CONTINUE
10    CONTINUE
```

II-3. Periodic Boundary Condition and Minimum Image Convention



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- Problems
  - Simulations are performed typically with a few hundred molecules arranged in a cubic lattice → computational limitation
    - Large fraction of the molecules can be expected in a surface rather than in the bulk
  - Simulation require summation over almost infinite interactions
  - PBC (Periodic Boundary Condition) and MIC (Minimum Image Convention) are used to avoid this problems

II-3. Periodic Boundary Condition and Minimum Image Convention

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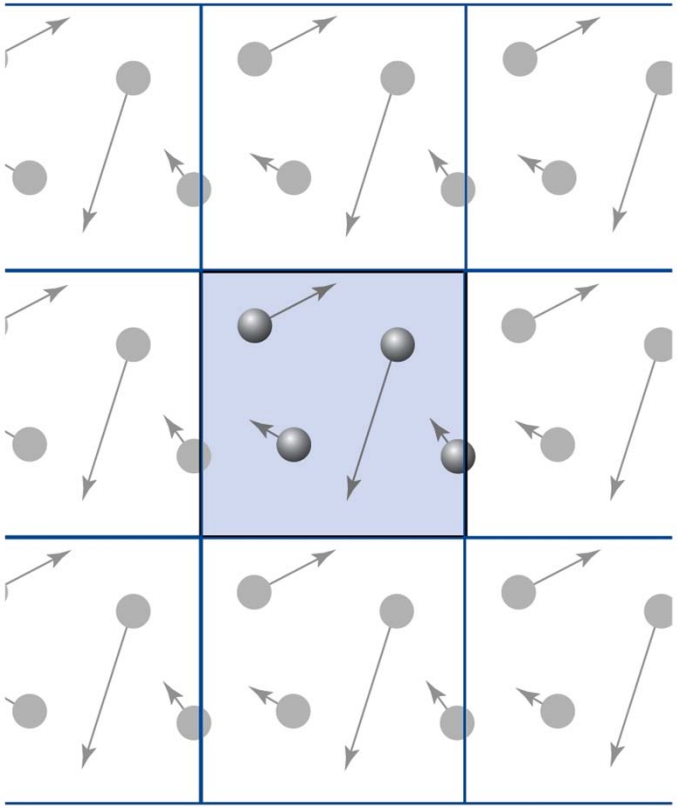
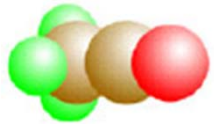
- Periodic Boundary Condition
  - Infinite replica of the simulation box
  - Molecules on any lattice have mirror image counter parts in all the other boxes
  - Changes in one box are matched exactly in the other box → surface effects are eliminated



II-3. Periodic Boundary Condition and Minimum Image Convention



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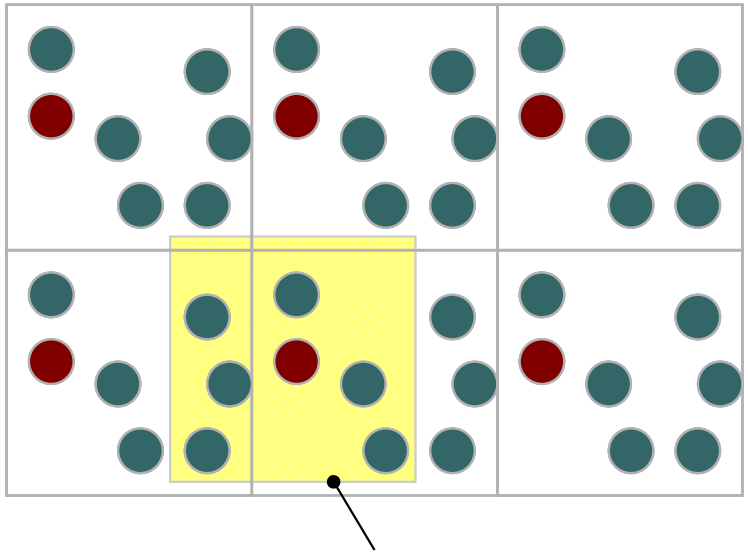
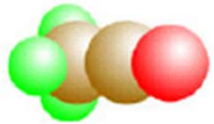
■ Minimum Image Convention

- Summation over infinite array of periodic image → impossible
- For a given molecule, we position the molecule at the center of a box with dimension identical to simulation box
- Assume that the central molecules only interacts with all molecules whose center fall within this region



Nearest images of colored sphere

II-3. Periodic Boundary Condition and Minimum Image Convention



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- Implementing PBC
  - Decision based : IF statement
  - Function based : rounding , truncation, modulus

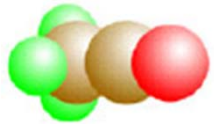
Decision

```
BOXL2 = BOXL/2.0
IF(RX(I).GT.BOXL2) RX(I)=RX(I)-BOXL
IF(RX(I).LT.-BOXL2) RX(I) = RX(I) + BOXL
```

Function

```
RX(I) = RX(I) - BOXL * AINT(RX(I)/BOXL)
```

II-3. Periodic Boundary Condition and Minimum Image Convention



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■ Implementing PBC and MIC

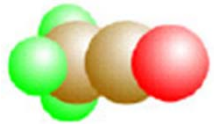
Pseudo CODE

```
Loop i = 1, N −1
   Loop j = I + 1, N
      Evaluate r_ij
      Convert r_ij to its periodic image (r_ij')
       if (r_ij' < cutOffDistance)
              Evaluate U(r_ij)
              Accumulate Energy
       End if
   End j Loop
End i Loop
```

FORTRAN CODE

```
   do  10  ip= 1, Np−1
    xip = x(ip)
    yip = y(ip)
    do  20  jp= ip+1, Np
     xx = xip − x(jp)
     dx = dble( xx − rLx*anint( xx/rLx ) )
     yy = yip − y(jp)
     dy = dble( yy − rLy*anint( yy/rLy ) )
     rij2 = dx*dx + dy*dy
     if  ( rij2 .lt. dcut2 )  then
        rij6  = 1.d0/(rij2*rij2*rij2)
        rij12 = rij6*rij6
        ham = ham +      rij12 − rij6
        pre = pre + 2.d0*rij12 − rij6
     endif
20   continue
10 continue
```

II-3. Periodic Boundary Condition and Minimum Image Convention



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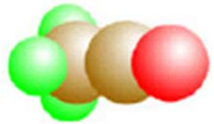
- Features due to PBC and MIC
  - Accumulated energies are calculated for the periodic separation distance
  - Only molecules within cut-off distance contributed to calculated energy
  - Caution : Cut-off distance should be smaller than the size of simulation box → if not, violation to MIC
  - Calculated potential = truncated potential
- Long range correction

$$X_{full} = X_c + X_{lrc}$$

$$E_{lrc} = 2\pi N\rho \int_{r_c}^{\infty} r^2 u(r) dr$$

  - For NVT ensemble No. of particle and density (V) are const.
    - LRC can be added after simulation
  - For other ensembles, LRC must be added during the simulation

II-4. Neighborhood List



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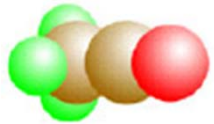
- In 1967, *Verlet* proposed a new algorithm to reduce computation time
- Instead of searching for neighboring molecules, the neighbors of the molecules are stored and used for the calculation
- Variable *d* is used to encompass slightly outside the cut-off distance
- Update of the list
  - update of the list / 10-20 steps
  - Largest displacement exceed *d* value

II-5. Metropolis Sampling Algorithm



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- Average of a property

$$\langle A \rangle = \int \frac{\exp\{-\beta U(r^N)\}}{Z_N(r^N)} A(r^N) dr^N = \int \mathcal{N}(r^N) A(r^N) dr^N = \langle A \rangle_{trials, \mathcal{N}(r^N)}$$

- There are a lot of choice to make Markov process that follows a given PDF

$$\boldsymbol{\rho\pi = \rho} \qquad \sum_m \rho_m \pi_{mn} = \rho_n$$

$$\sum_n \pi_{mn} = 1$$

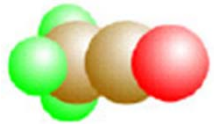
This condition is not sufficient :
more conditions are required to setup transition matrix

→

"Microscopic reversibiltiy"
Sufficient, but not necessary condition

$$\rho_m \pi_{mn} = \rho_n \pi_{nm}$$

II-5. Metropolis Sampling Algorithm



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- In 1953, Metropolis showed a transition probability matrix exists than ensures that the PDF is obeyed

$$\pi_{mn} = \alpha_{mn} \qquad \rho_n \geq \rho_m, m \neq n$$

$$\pi_{mn} = \alpha_{mn}\left(\frac{\rho_n}{\rho_m}\right) \qquad \rho_n < \rho_m, m \neq n$$

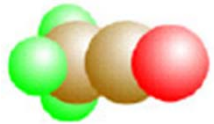
$$\pi_{mm} = 1 - \sum_{n \neq m} \pi_{mn}$$

- Other choice can also satisfies condition of microscopic reversibility (Barker , 1965)

$$\pi_{mn} = \alpha_{mn}\left(\frac{\rho_n}{\rho_n + \rho_m}\right) \qquad m \neq n$$

$$\pi_{mm} = 1 - \sum_{n \neq m} \pi_{mn}$$

II-5. Metropolis Sampling Algorithm



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- Metropolis Recipe
  - with probability π_{mn} a trial state j for the move
  - if $\rho_n > \rho_m$ accept n as new state
  - Otherwise, accept n as the new state with probability $\rho_n > \rho_m$
    - Generate a random number R on (0,1) and accept if $R < \rho_n / \rho_m$
  - If not accepting n as new state, take the present state as the next one in Markov chain ($\pi_{mn} \neq 0$)

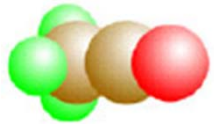
- What is the value of α ?

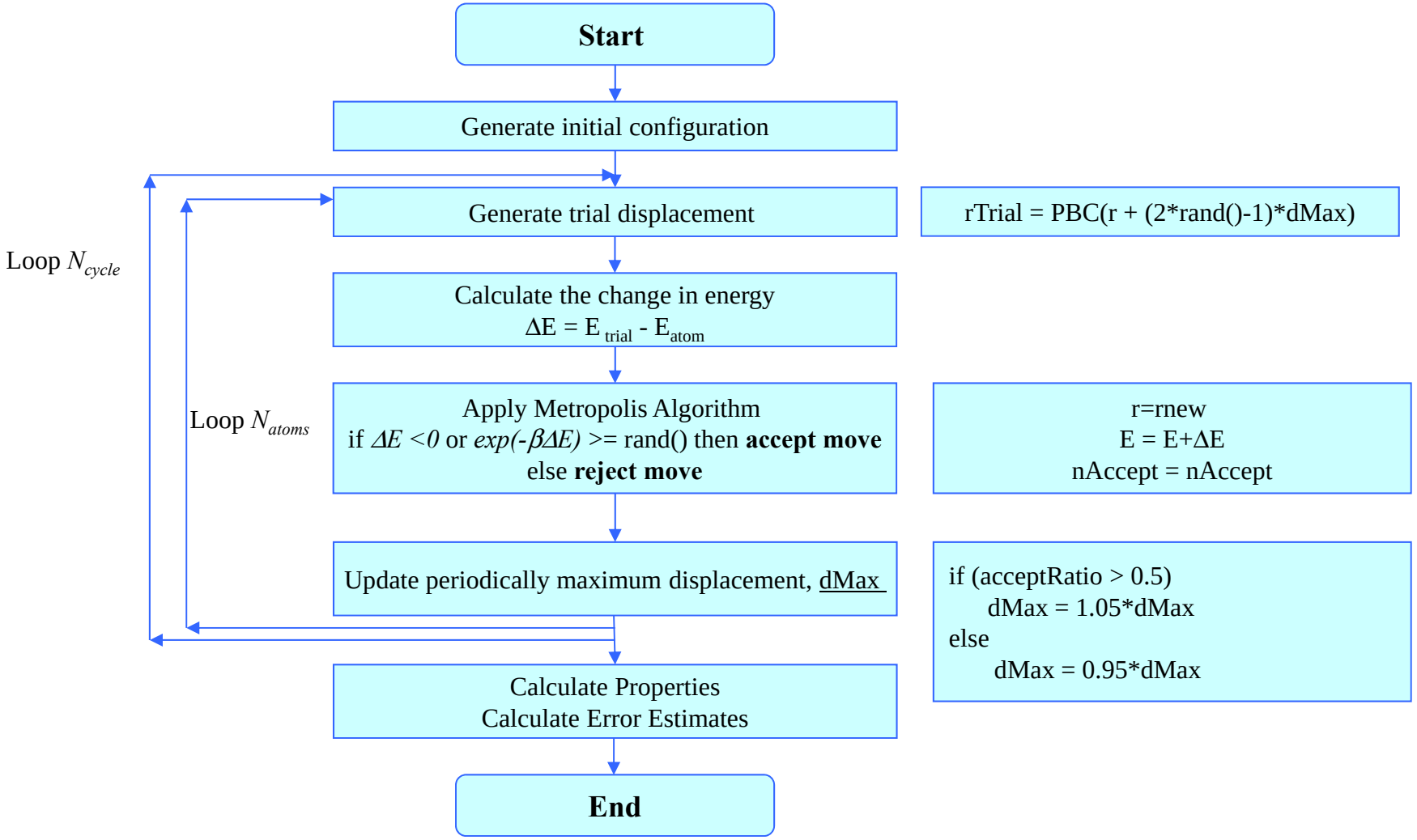
$$\alpha_{mn} = 1/N_R \qquad \text{if accepting}$$

$$\alpha_{mn} = 0 \qquad \text{if not accepting}$$

N_R : Number of accepted trials

II-6. Implementation





II-6. Implementation

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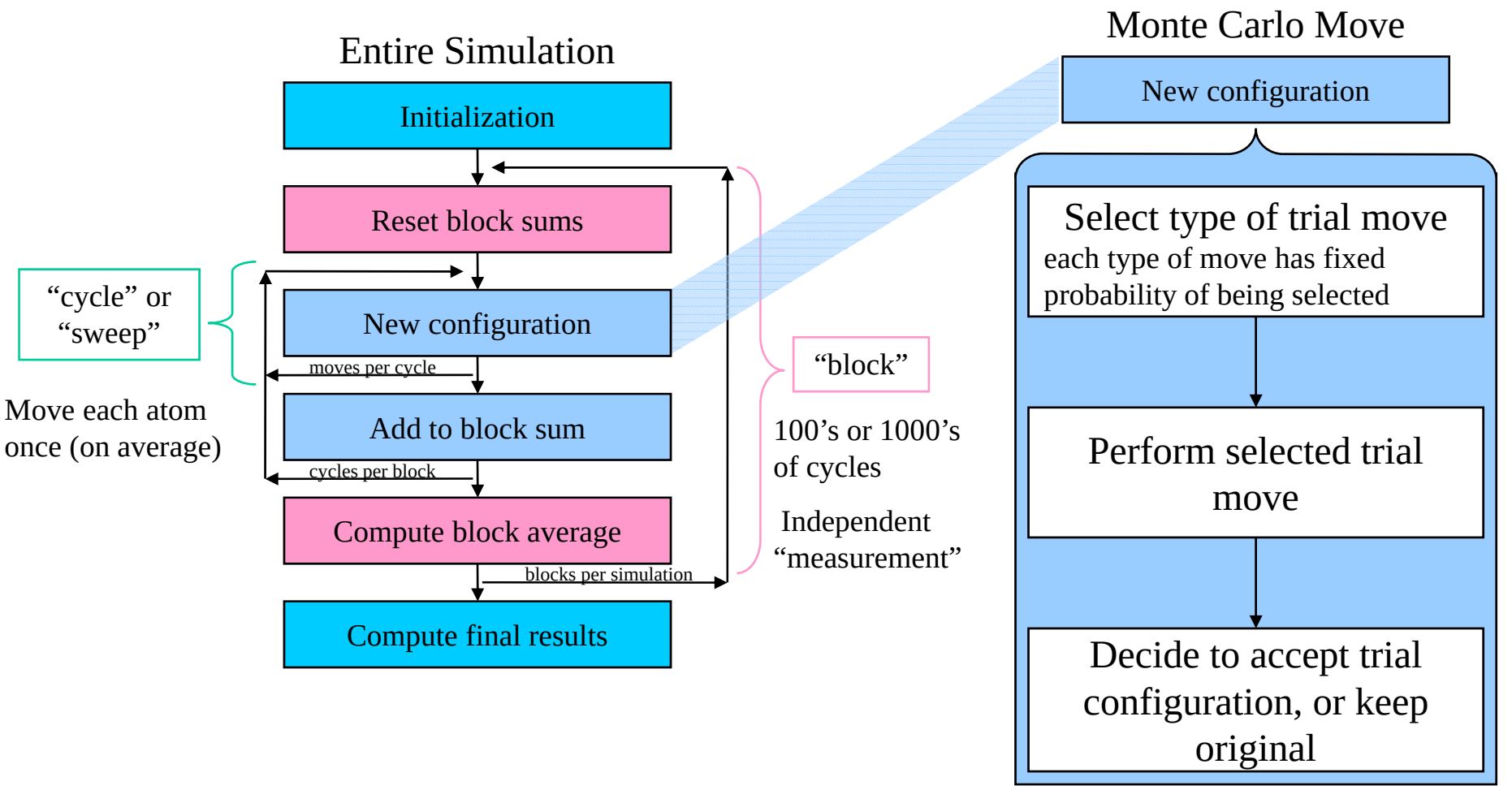
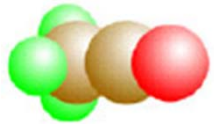


II-7. Averages and Error Estimates



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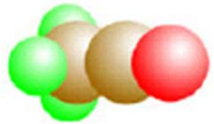
- Equilibration period
  - The averages are evaluated after “equilibration period”
  - The equilibration period must be tested : cycle vs. properties
    - Ex) 20 000 run :
      - 1 to 10 000 : equilibration period
      - 10 001 to 20 000 : averages are accumulated
- Error estimation
  - Error estimation based on different simulation runs (with different initial configurations)
  - Error estimation dividing total simulation runs into several blocks

    →common method

II-7. Averages and Error Estimates



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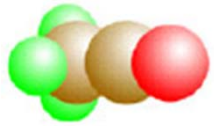
- Average and Error Estimates

$$\langle A \rangle_{run} = \frac{1}{N - N_{equil} - 1} \sum_{i > N_{equil}} A_i$$

$$\langle A \rangle_b = \frac{1}{l} \sum_{i=1}^{N_b} A_i$$

$$\sigma = \sqrt{\frac{1}{N_b} \sum_{b=1}^{n_b} \left(\langle A \rangle_b - \langle A \rangle_{run} \right)^2}$$

III-1. Introduction



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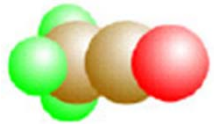
- MMC in different ensembles
  - A very large number of systems for convenient calculation of time average macroscopic properties
  - Common macroscopic attributes
    - *(N, V, E)* : Microcanonical ensemble
    - *(N, V, T)* : Canonical ensemble
    - *(N, P, T)* : NPT ensemble

    → No change in N , Closed system
    - *(μ, V, T)* : Grand canonical ensemble

    → Change in N , Open system
  - Microcanonical ensemble cannot be used in MMC because constant-kinetic energy constraint cannot be assumed
  - In thermodynamic limit all ensembles are equivalent and it is also possible to transform between ensembles. The choice of ensemble is completely a matter of convenience (which property ?)

III-1. Introduction



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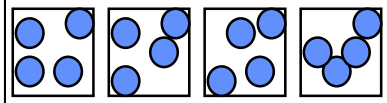
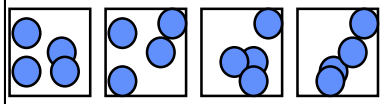
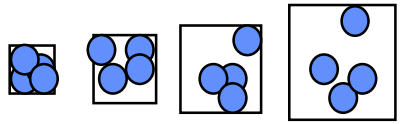
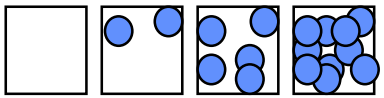
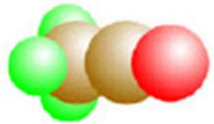
- Commonly encountered ensemble

Name	All states of:	Probability distribution	Schematic
Microcanonical (EVN)	given EVN	$\pi_i = \frac{1}{\Omega}$	
Canonical (TVN)	all energies	$\pi(E_i) = \frac{1}{Q} e^{-\beta E_i}$	
Isothermal-isobaric (TPN)	all energies and volumes	$\pi(E_i, V_i) = \frac{1}{\Delta} e^{-\beta(E_i + PV_i)}$	
Grand-canonical (TVμ)	all energies and molecule numbers	$\pi(E_i, N_i) = \frac{1}{\Xi} e^{-\beta(E_i + \mu N_i)}$	

III-1. Introduction



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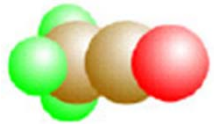
- Partition functions and bridge equation

Ensemble	Thermodynamic Potential	Partition Function	Bridge Equation
Microcanonical	Entropy, S	$\Omega = \sum 1$	$S/k = \ln \Omega(E,V,N)$
Canonical	Helmholtz, A	$Q = \sum e^{-\beta E_i}$	$-\beta A = \ln Q(T,V,N)$
Isothermal-isobaric	Gibbs, G	$\Delta = \sum e^{-\beta(E_i + PV_i)}$	$-\beta G = \ln \Delta(T,P,N)$
Grand-canonical	Hill, L = –PV	$\Xi = \sum e^{-\beta(E_i + \mu N_i)}$	$\beta PV = \ln \Xi(T,V,\mu)$

III-2. NVT Ensemble



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- Ensemble average : Boltzmann distribution as weighting factor

$$\langle A \rangle = \int \frac{\exp\{-\beta U(r^N)\}}{Z_N(r^N)} A(r^N) dr^N = \frac{\sum_i A(i)\exp(E(i))}{\sum_i \exp(E(i))}$$

- Weighted average

$$W(i) = \exp(-\beta E(i))$$

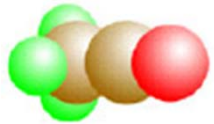
$$\langle A \rangle = \frac{1}{N}\sum_i A(i)$$

- For Other ensembles ? → Tricky technique used : “Pseudo Boltzmann Factor”

$$W(i) = \exp(-\beta Y)$$

for NVT ensemble , $Y = E(i)$

III-3. NPT Ensemble



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- Thermodynamic properties

$$\langle A \rangle = \frac{\int_0^\infty \exp(-\beta pV)dV \int_V A(r^N, V)\exp\{-\beta U(r^N)\}dr^N}{\int_0^\infty \exp(-\beta pV)dV \int_V \exp\{-\beta U(r^N)\}dr^N}$$

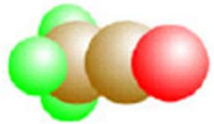
- V can change
  - Particles are confined in fluctuating length L
  - Scaled coordinate :

$$\boldsymbol{\alpha}_i = \mathbf{r}_i / L$$

  - integration over total volume → integration over unit cube Ω

$$\langle A \rangle = \frac{\int_0^\infty \exp(-\beta pV)dV \int_\Omega A((L\alpha)^N, V)\exp\{-\beta U((L\alpha)^N, V)\}d\alpha^N}{\int_0^\infty \exp(-\beta pV)dV \int_\Omega \exp\{-\beta U((L\alpha)^N, V)\}d\alpha^N}$$

III-3. NPT Ensemble



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- Pesude Boltzmann Factor

$$Y = pV + E((L\alpha)^N, L) - NkT \ln V$$

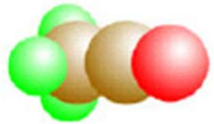
- Simple modification of NVT ensemble →Use ΔY instead of ΔU
- Volume fluctuation
  - NVT ensemble
    - Move 1 molecule at a time
    - Calculate energies of remaining N-1 molecules
  - NPT ensemble
    - Change in V affects the coordinates of all atoms
    - N*N calculations are required
    - Effective strategy : “Scaling Method”

$$E = 4\varepsilon \sum\sum \left(\frac{\sigma_{ij}}{L\alpha_{ij}} \right)^{12} - 4\varepsilon \sum\sum \left(\frac{\sigma_{ij}}{L\alpha_{ij}} \right)^{6}$$

$$E = E(12) + E(6)$$

$$E_{trial} = E(12)\left(\frac{L_{trial}}{L} \right)^{12} + E(6)\left(\frac{L_{trial}}{L} \right)^{6}$$

III-3. NPT Ensemble



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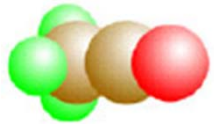
- "Scaling method" only applicable to relatively simple model potential → Scalable potential
  - if not, N*(N-1) calculations are required for each volume fluctuation
- Trial moves : Displacement and volume fluctuation
  - Displacement on each atoms
  - Volume change
- When V change is attempted, long range correction must be re-evaluated

III-3. μVT Ensemble



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- Property average

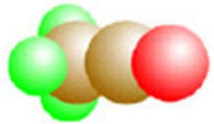
$$\langle A \rangle = \frac{\sum_{n-0}^{\infty} \frac{\Lambda^{-3N}}{N!} \exp(\beta N\mu) \int_V A(r^N) \exp\{-\beta U(r^N)\} dr^N}{Z_{\mu VT}}$$

$$\beta\mu^{ideal} = \log(N/V) + 3\log\Lambda$$

$$\langle A \rangle = \frac{\sum_{n-0}^{\infty} \exp(\beta N\mu^* - \ln N!) \int_V A(r^N) \exp\{-\beta U(r^N)\} dr^N}{Z_{\mu VT}}$$

$$\mu^* = \mu^{ex} + kT \ln\langle N \rangle$$

III-3. μVT Ensemble



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- The Pseudo Boltzmann Factor

$$Y = -N\mu^* + kT \ln N! + E(r^N)$$

- Attempted Trial Moves
  - Particle displacement
  - Particle insertion
  - Particle deletion