Monte Carlo Simulation

Jayant K. Singh
Department of Chemical Engineering
IIT Kanpur
Overview

- To understand basic Molecular Simulation structure
- To understand basic MC code: NVT
- Modification for NPT, $\mu$VT
Molecular Simulation: System Size

Typical system size: 500-1000
Molecules at the surface $O(N^{-1/3})$
How do we mimic infinite bulk large system?

$$\langle U \rangle = \frac{1}{Z_N} \frac{1}{N!} \int dr^N U(r^N) e^{-\beta U(r^N)}$$
Periodic boundary conditions

Two –dimensional version of PBC

- Number density of the central box is conserved (and hence the entire system)
- It is not necessary to store the coordinates of all the images in a simulation; just the central box molecules.
PBC: Suppression of fluctuation

○ For cube of side $L$, the periodicity will suppress any density waves with a wavelength greater than $L$
  • *Thus not possible to simulate a liquid close to v-l critical point, where the range of critical fluctuation is macroscopic*

○ PBC has little effect on the equilibrium thermodynamic properties and structure of fluids away from phase transitions and where the interactions are short-ranged.

○ Check if this is true for each model studied.

○ Standard practice is to increase the number of molecules and the box to keep the same number density and rerun the simulations
PBC: Macroscopic vs. Microscopic

- Important to ask if the properties of a small infinitely periodic system and the macroscopic system which it represents are the same?
- Depends on the range of intermolecular potential and the phenomenon under investigation
- LJ fluid: possible to obtain bulk equilibrium properties with $L=6\sigma$
- If $U \sim r^{-\nu}$ where $\nu < d$ of the system
  - Substantial interaction between a particle and its own images in the neighbouring boxes
- Methods to treat long range interactions
  - $U \sim 1/r$ (charges) $U \sim 1/r^3$ (dipolar fluids)
Truncating the potential

- Most extensive calculation in MC/MD simulation is the calculation of $U$ of the configuration or $F$ acting on all molecules.
- Must include interaction between molecule $i$ with every other molecule $j$ (assuming pairwise additivity): $N-1$ terms.
- But, in principle, we must also include all interactions between molecule $I$ and images in the neighbouring boxes.
  - Impossible to calculate
- For a short range $U$, we may calculation this summation by making an approximation.
  - Truncation
Implementing Cubic Periodic Boundaries: Central-image codes

- Involved in most time-consuming part of simulation
- \((-1/2, 1/2)\), decision based
  - \(\text{if}(r(0) > 0.5) \quad r.x = r.x - 1.0\)
  - \(\text{if}(r(0) < -0.5) \quad r.x = r.x + 1.0; \quad \text{//only first shell}\)
  - examples: \(-0.2 \rightarrow -0.2; -1.4 \rightarrow -0.4; +0.4 \rightarrow +0.4; +0.6 \rightarrow -0.4; +1.5 \rightarrow +0.5\)

- \((0, bs)\), function based (aint ; rounding)
  - if\((xnew < 0.0)\) \(xnew = xnew + bs\)
  - If\((xnew > bs)\) \(xnew = xnew - bs\)
  - if\((xnew > bs)\) \(xnew = xnew - bs * \text{aint}(xnew / bs)\)
  - if\((xnew < 0.0)\) \(xnew = xnew - bs * \text{aint}(xnew / bs - 1.0)\)

\(\text{aint}(x) = 0\) if \(x < 1\) and if \(x > 1\) it returns the largest whole no
  that does not exceed its magnitude

\(\text{nint}(x)\) \textbf{rounds} its argument to the nearest whole number.
Implementing Cubic Periodic Boundaries: Nearest-image codes

- Simply apply \((-1/2,1/2)\) central-image code to raw difference!
  - \(dx_{ij} = x_j - x_i\) //unit box length
  - if\((dx_{ij} > 0.5)\) \(dx_{ij} = dx_{ij} - 1.0\)
  - if\((dx_{ij} < -0.5)\) \(dx_{ij} = dx_{ij} + 1.0\)
  - \(dx_{ij} *\) = \(bs\);

- Or…
  - \(dx_{ij} = x_j - x_i\); //true box length
    if\((dx_{ij} > bs-dx_{ij})\) \(dx_{ij} = dx_{ij} - bs\)
    if\((dx_{ij} < -bs-dx_{ij})\) \(dx_{ij} = dx_{ij} + bs\)

- Take care not to lose correct sign, if doing force calculation

- Nearest image for non-cubic boundary not always given simply in terms of a central-image algorithm
**Structure of Molecular Simulation 1**

**Initialization**

Initialize the lattice, read variables such as T, rho etc., initialize all other variables

**Perform MC Cycle**

Perform, MC move such as displacement move. During each cycle displacement for every atom is attempted. During equibriation period number of cycles (~5000 cycles) are performed to relax the structure (to “forget” artificial initial configuration)

**If production cycle, record average and write out**

Averages are accumulation only after equibriation period. Write out running average. Configuration output is also generated typically even during equibriation period for debugging/rerunning mode.
Structure of a Molecular Simulation 2

\[ \Delta t \]

MD time step or MC cycle

⇒ property value \( m_i \)

Progress of simulation →
Structure of a Molecular Simulation 2

Progress of simulation →

Δt

MD time step or MC cycle ⇒ property value \( m_i \)

Simulation block ⇒ block average

\[
\bar{m}_2 = \frac{1}{b} \sum_{i=1}^{b} m_i
\]
Structure of a Molecular Simulation 2

Progress of simulation

MD time step or MC cycle ⇒ property value $m_i$

Simulation block ⇒ block average $\overline{m} = \frac{1}{b} \sum_{i=1}^{b} m_i$

Complete simulation ⇒ simulation average

$\langle m \rangle = \frac{1}{nb} \sum_{i=1}^{nb} m_i$

⇒ simulation error bar

$\sigma_{\langle m \rangle} = \frac{\sigma_m}{\sqrt{nb - 1}}$; $\sigma_m = \sqrt{\frac{1}{nb} \sum_{k=1}^{nb} (\overline{m_k} - \langle m \rangle)^2}$
Initial Configuration

- Read from a File
- Placement on a lattice is a common choice
  - 2D; square lattice: \( N = 2n^2 \) (8, 18, 32, 50, 72, 98, 128, …)
  - 3D, face-center cubic: \( N = 4n^3 \) (32, 128, 256,…)
- Other options involve “simulation”
  - place at random, then move to remove overlaps
  - randomize at low density, then compress
  - other techniques invented as needed
- Orientations done similarly
  - lattice or random, if possible
Monte Carlo Move: generating new configuration

Monte Carlo Move

New configuration

Select type of trial move
each type of move has fixed probability of being selected

Perform selected trial move

Decide to accept trial configuration, or keep original
Basic MC structure

Program mc_nvt
Integer :: i, j, k
    call readinfo ! Input file
    call lattice ! Creating the lattice from scratch or reading from the file

    do k=1, 2
        ncycle=Nequil
        if(k .eq. 2) ncycle =Nprod
        do i=1, ncycle
            do j=1, npart
                call displace(success)
                natt =natt+1
                if(success) nacc=nacc+1
            end do
            if(k .eq. 1) then
                if( mod(i, nadjust) .eq. 0) call newMaxima
            else
                if( mod(i, nsample) .eq. 0) call sample
            end if
        end do
    End do
End
Metropolis Algorithm

Given a desired limiting probability distribution, for example, $\pi = \pi_{\text{NVT}}$, what transition probabilities will yield $\pi$.

Construct transition probabilities to satisfy detailed balance

Metropolis Algorithm

- with probability $\tau_{ij}$, choose a trial state $j$ for the move (note: $\tau_{ij} = \tau_{ji}$)
- if $\pi_j > \pi_i$, accept $j$ as the new state
- otherwise, accept state $j$ with probability $\pi_j/\pi_i$
  - generate a random number $R$ on $(0,1)$; accept if $R < \pi_j/\pi_i$
- if not accepting $j$ as the new state, take the present state as the next one in the Markov chain
Generating the desired distribution: Detailed balance

\[ \pi_i \pi_{ij} = \pi_j \pi_{ji} \]

\[ \pi_{ij} = \tau_{ij} \text{acc}(i \rightarrow j) = \tau_{ij} \min(1, \chi) \]

\[ \pi_{ji} = \tau_{ji} \text{acc}(j \rightarrow i) = \tau_{ji} \min\left(1, \frac{1}{\chi}\right) \]

\[ \frac{\text{acc}(i \rightarrow j)}{\text{acc}(j \rightarrow i)} = \frac{\pi_j \tau_{ji}}{\pi_i \tau_{ij}} \]
Implementation of Metropolis Method

✓ Necessary to specify the underlying stochastic matrix $\tau$
✓ Freedom to choose $\tau$ but $\tau_{mn} = \tau_{nm}$
✓ A useful but arbitrary definition of neighbouring state

✓ Displace one atom random from its position $r_i^m$
With equal probability to any point $r_i^n$ inside the square/cube $R$ of side $2\delta_{\text{max}}$ and is centered at $r_i^m$

- Large but finite no. of new position, $N_R$, for atom $i$ and
- $\tau_{mn} = 1/N_R$ if $r_i^n$ belongs to $R$
- $=0$ if $r_i^n$ does not belongs to $R$
- $\delta_{\text{max}}$: maximum displacement is adjustable parameter that governs the size of the region $R$ and controls the convergence of the Markov Chain.
Displacement Trial Move

- Gives new configuration of same volume and number of molecules
- Basic trial:
  - displace a randomly selected atom to a point chosen with uniform probability inside a cubic volume of edge $2\delta$ centered on the current position of the atom

Examine underlying transition probabilities to formulate acceptance criterion

Forward-step transition probability, $\tau_{ij} =$

\[
\tau_{ij} = \frac{1}{N} \frac{1}{(2\delta)^d} = \tau_{ji}
\]

Prob of selecting a molecule $X$ Prob of moving a new position, $r$ new
**NVT-ensemble**

Limiting probability distribution

\[ \pi_i \propto \exp[-\beta U(i)] \]

\[
\frac{\text{acc}(i \rightarrow j)}{\text{acc}(j \rightarrow i)} = \frac{\pi_j \tau_{ji}}{\pi_i \tau_{ij}}
\]

\[
\frac{\text{acc}(i \rightarrow j)}{\text{acc}(j \rightarrow i)} = \exp[-\beta (U(j) - U(i))]
\]

Acceptance probability

\[ \chi = e^{-\beta (U^{\text{new}} - U^{\text{old}})} \]
Subroutine displace move

Subroutine displace(success)
  mol=int(Nmol*rand(seed))+1
  call energy(mol, enmolOld)
  xold=X(mol)
  dx=(2.0*rand(seed) -1.0)*bs*ds
  Xnew=xold+dx
  If(xnew > bs) xnew=xnew-bs*aint(xnew/bs)
  If(xnew < 0) xnew=xnew-bs*aint(xnew/bs-1.0)
  X(mol)=xnew
  call energy(mol, enmolNew)
  lnpsi=-beta*(enmolNew-enmolOld)
  if(rand(seed) .lt. exp(-beta*(enmolNew-enmolOld)) then
    ! Success
  else
    ! Reject
      X(mol)=xold ! Note old conf is retained
  end if
End if
Need to consider old configuration again?

Transition probability:

\[ \pi_{ij} = \tau_{ij} \times acc(i \rightarrow j) \]

\[ \sum_{j} \pi_{ij} = 1 \]

Probability to accept the old configuration:

\[ \pi_{ii} = 1 - \sum_{j, j \neq i} \pi_{ij} \]
Keeping old configuration?
Displacement: not too small, not too big!
Displacement Trial Move: Tuning

- Size of step is adjusted to reach a target rate of acceptance of displacement trials
  - *typical target is 50%*
    - though there is no theoretical basis
  - *for hard potentials target may be lower (rejection is efficient)*
  - *Large step leads to less acceptance but bigger moves*
  - *Small step leads to less movement but more acceptance*
Subroutine: adjust

Subroutine newMaxima

tarRatio=0.5
If(natt > 0) then
    simRatio=nacc/natt
    if(simRatio > tarRatio) ds=ds*1.05
    if(simRatio < tarRatio) ds=ds*0.95
    ds=min(ds,0.5)
End if

nacc=0
natt=0
End subroutine
Lennard Jones potentials

• The Lennard-Jones potential

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

• The truncated Lennard-Jones potential

\[ u(r) = \begin{cases} 
  u^{LJ}(r) & r \leq r_c \\
  0 & r > r_c 
\end{cases} \]

• The truncated and shifted Lennard-Jones potential

\[ u(r) = \begin{cases} 
  u^{LJ}(r) - u^{LJ}(r_c) & r \leq r_c \\
  0 & r > r_c 
\end{cases} \]
Pair correlation function

Environment around a given molecule

\[ g(r) = \text{pair correlation function aka RDF} \]

\[ g(r) = \frac{\text{average number of particle in shell between } r, \ r + dr}{\text{number of particle in random system}} \]

\[ g(r) = \frac{\text{average number of particle in shell between } r, \ r + dr}{4\pi r^2 dr \rho} \]

\[ U/N = \frac{1}{2} \rho \int_0^\infty u(r)g(r)dr \bar{\rho} = 2\pi \rho \int_0^\infty u(r)g(r)r^2 dr \]

\[ P = \frac{\rho}{\beta} - \frac{1}{6} \rho^2 \int_0^\infty \frac{du(r)}{dr} g(r)dr \bar{\rho} = \frac{\rho}{\beta} - \frac{2}{3} \pi \rho^2 \int_0^\infty \frac{du(r)}{dr} g(r)r^3 dr \]
Correction to thermodynamic properties

\[ g(r) = 1, \ r > r_c : \text{uniform distribution beyond cut off} \]

\[ u(r) = \begin{cases} 
  u^{LJ}(r) & r \leq r_c \\
  0 & r > r_c 
\end{cases} \]

\[ u^{tail} = \frac{8}{3} \pi \rho \left[ \frac{1}{3} \left( \frac{1}{r_c} \right)^9 - \left( \frac{1}{r_c} \right)^3 \right] \]

\[ p = \rho kT + \frac{\text{vir}}{V} \]

\[ \text{vir} = \frac{1}{3} \sum_i \sum_{j > i} \vec{f}(r_{ij}) \cdot \vec{r}_{ij} \]

\[ p^{tail} = \frac{16}{3} \pi \rho^2 \left[ \frac{2}{3} \left( \frac{1}{r_c} \right)^9 - \left( \frac{1}{r_c} \right)^3 \right] \]

\[ \mu_{tail} = \rho \int_{r_{cut}}^{\infty} u(r) 4\pi r^2 \, dr = 2 \frac{U_{tail}}{N} \]

For \( r_c = 2.5\sigma \), these are about 5-10\% of total values.
Phase diagrams of Lennard Jones fluids
Energy Subroutine

Subroutine energy(mol, energ)
    do j=1,Nmol
        if(j .eq. mol) cycle
        dxij= X(j)-xi
        if(dxij > bs-dxij) dxij=dxij-bs
        if(dxij < -bs-dxij) dxij=dxij+bs
        ! Similar for y and z
        drij2 = dxij*dxij + dyij*dyij + dzij*dzij
        if(drij2 < rcut2) then
            r2 = 1.0 / rij2
            r6 = r2 * r2 * r2
            r12 = r6 * r6
            energ = eneg+4.0 * (r12 - r6)
        end if
    end if
    return
End
### Table III. Simulation results from series (c), (e), and (f). All quantities are given in Lennard-Jones units. \( T \) is the temperature (provided for convinience), \( P/n_c \) is the final value of the pressure as estimated by the correction formula extrapolation simulation average for the pressure, molar density, and molar energy is each phase. The small subscripts indicate the simulation error. \( \sigma \) is the standard deviation of the simulation, and \( \sigma \) is the standard deviation of the simulation error. The quantity \( \Delta \mu(p_T) \) is the change in chemical potential from \( \Delta(S) \) given by a series (c) simulation, and \( \Delta \) is determined from the simulation data of each phase by applying the Gibbs-Duhem equation as written \( \Delta(S) = \Delta(S) - \Delta(S) \). Entries with \( n \) considered "best" results for the temperature and are provided only for comparison, these data are not presented in Fig. 3, the critical properties.

<table>
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<th>( \beta )</th>
<th>( T )</th>
<th>( P/n_c )</th>
<th>( \rho )</th>
<th>( \mu )</th>
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<td>0.741</td>
<td>0.00229</td>
<td>0.00225, 0.02</td>
<td>0.03313, 0.835</td>
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<td>0.01224</td>
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<td>0.01151, 0.750</td>
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<td>1.250</td>
<td>0.0911</td>
<td>0.092, 0.009</td>
<td>0.118, 0.474</td>
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### The Lennard-Jones equation of state revisited

By J. KARL JOHNSON, JOHN A. ZOLLWEG and KEITH E. GUBBINS

School of Chemical Engineering, Cornell University, Ithaca, NY 14853, USA
Monte Carlo: other ensemble
**NPT Ensemble**

In the classical limit, the partition function becomes

\[
\Delta = \frac{1}{\Lambda^{3N}N!} \int dV \exp(-\beta PV) \int dr^N \exp[-\beta U(r^N)]
\]

\[
= \frac{1}{\Lambda^{3N}N!} \int dV \exp(-\beta PV) V^N \int ds^N \exp[-\beta U(s^N;L)]
\]

Probability density to find a particular configuration \((s^N)\)

\[
\pi_{NPT}(V,s^N) \propto V^N \exp[-\beta PV] \exp[-\beta U(s^N;L)]
\]

Sample a particular configuration by two kind of moves

- Change of volume (volume move)
- Change of particle coordinate (displacement move)

Acceptance rules: apply detailed balanced
Volume-change Trial Move

- Gives new configuration of different volume and same $N$ and $s^N$
- Basic trial:
Volume-change Trial Move

- Gives new configuration of different volume and same $N$ and $s_N$
- Basic trial:
  - Select a random value for volume change
  - $\text{by some amount within } \pm \delta V$
Volume-change Trial Move

- Gives new configuration of different volume and same $N$ and $s^N$
- Basic trial:
  - increase or decrease the total system volume by some amount within $\pm \delta V$,
Volume-change Trial Move

- Gives new configuration of different volume and same $N$ and $s^N$
- Basic trial:
  - *increase or decrease the total system volume by some amount within $\pm \delta V$, scaling all molecule centers-of-mass in proportion to the linear scaling of the volume*

*Scale all positions in proportion*
Volume-change Trial Move

- Gives new configuration of different volume and same $N$ and $s^N$
- Basic trial:
  - increase or decrease the total system volume by some amount within $\pm \delta V$, scaling all molecule centers-of-mass in proportion to the linear scaling of the volume

Consider acceptance of new configuration
Volume-change Trial Move

- Gives new configuration of different volume and same $N$ and $s^N$

- Basic trial:
  - *increase or decrease the total system volume by some amount within $\pm \delta V$, scaling all molecule centers-of-mass in proportion to the linear scaling of the volume*

- Limiting probability distribution
  - *isothermal-isobaric ensemble*

\[
\pi \left( (Vs)^N \right) = \frac{1}{\Delta} e^{-\beta U(Vs)^N - \beta PV} V^N ds^N dV
\]
Volume-change Trial Move
Analysis of Transition Probabilities

- Detailed specification of trial move and transition probabilities
  - First select $V_{\text{new}}$ and second accept the move
  - Forward-step transition probability $= \frac{1}{2\delta V} \times \min(1, \chi)$
  - Reverse step transition probability $= \frac{1}{2\delta V} \times \min(1, \frac{1}{\chi})$

$\chi$ is formulated to satisfy detailed balance
Volume-change Trial Move
Analysis of Detailed Balance

Forward-step transition probability:
\[ \frac{1}{2\delta V} \times \min(1, \chi) \]

Reverse-step transition probability:
\[ \frac{1}{2\delta V} \times \min(1, \frac{1}{\chi}) \]

Detailed balance:
\[ \pi_i \pi_{ij} = \pi_j \pi_{ji} \]

Limiting distribution:
\[ \pi \left( (Vs)^N \right) = \frac{1}{\Delta} e^{-\beta U \left( (Vs)^N \right) - \beta PV} V^N ds^N dV \]
Volume-change Trial Move
Analysis of Detailed Balance

Detailed balance

\[
\pi_i \pi_{ij} \frac{e^{-\beta (U^{\text{old}} + PV^{\text{old}})} (V^{\text{old}})^N}{\Delta N} \left[ \frac{1}{2\delta V} \times \min(1, \chi) \right] = \pi_j \pi_{ji} \frac{e^{-\beta (U^{\text{new}} + PV^{\text{new}})} (V^{\text{new}})^N}{\Delta N} \left[ \frac{1}{2\delta V} \times \min(1, \frac{1}{\chi}) \right]
\]

Detailed balance

\[
\pi_i \pi_{ij} \frac{e^{-\beta (U^{\text{old}} + PV^{\text{old}})} (V^{\text{old}})^N}{\Delta} \left[ \frac{1}{2\delta V} \times \min(1, \chi) \right] = \pi_j \pi_{ji} \frac{e^{-\beta (U^{\text{new}} + PV^{\text{new}})} (V^{\text{new}})^N}{\Delta} \left[ \frac{1}{2\delta V} \times \min(1, \frac{1}{\chi}) \right]
\]

\[e^{-\beta (U^{\text{old}} + PV^{\text{old}})} (V^{\text{old}})^N \chi = e^{-\beta (U^{\text{new}} + PV^{\text{new}})} (V^{\text{new}})^N\]

\[\chi = \exp \left[ -\beta (\Delta U + P\Delta V) + N \ln(V^{\text{new}} / V^{\text{old}}) \right]\]  

Acceptance probability
Volume-change Trial Move

- Step in ln(V) instead of V
  \[(\ln V)^{\text{new}} = (\ln V)^{\text{old}} + \delta(\ln V)\]
  - larger steps at larger volumes, smaller steps at smaller volumes

\[
\Delta(N,P,T) = \frac{1}{\Lambda^{3N} N!} \int dV \exp(-\beta PV) V^N \int ds^N \exp[-\beta U(s^N;L)]
\]
\[
= \frac{1}{\Lambda^{3N} N!} \int d(\ln V) \exp(-\beta PV) V^{N+1} \int ds^N \exp[-\beta U(s^N;L)]
\]

Probability density to find a particular configuration \((s^N)\)

\[
\pi(V; s^N) \propto V^{N+1} \exp(-\beta PV) \exp[-\beta U(s^N;L)]
\]

Acceptance probability \(\min(1, \chi)\)

\[
\chi = \exp[-\beta (\Delta U + P\Delta V) + (N + 1) \ln(V^{\text{new}} / V^{\text{old}})]
\]
Algorithm: NPT

- Randomly change the position of a particle
- Randomly change the volume
Basic NPT code

Subroutine npt
call readinfo
call lattice
do k=1, 2
   ncycle=Nequil
   if(k .eq. 2) ncycle =Nprod

do I =1, ncycle
do j=1, ndisp+nvol
   j=int(ndisp+nvol)+1
   if(j .le. ndisp) then
      call displace()
   else
      call volChange()
   end if
end do
if (mod(i,nsample) .eq. 0) call sample(i)
End do
End do
End
Volume change move

Subroutine VolChange
  call energy(enOld)
  vold=bs**3
  lnvn=log(vold)+(2.0*ran2()-1.0)*vmax
  vnew=exp(lnvn)
  bsnew=vnew**(1.0/3.0)
  do i=1, Nmol
      X(i)=X(i)*bsnew/bs ! scaling
  end do
  call energy(enNew)
  chi=exp(-beta*((enNew-enOld)+p*(vNew-vOld))+(Nmol+1)*log(vnew/vold))
  if(ran2() .gt. chi) then ! Reject
    ! Scale it back
    do i=1, Nmol
      X(i)=X(i)*bs/bsnew
    end do
  end if
return

End subroutine
MuVT Ensemble

In the classical limit partition function is:

$$\Xi = \sum_{N=0}^{N=\infty} \frac{\exp(\beta \mu N)}{\Lambda^{3N} N!} \int \exp\left(-\beta U(\vec{r}^N)\right) d\vec{r}^N$$

Probability to find a particular configuration:

$$\pi_{\mu VT} (V, s^N) \propto \frac{\exp(\beta \mu N) V^N}{\Lambda^{3N} N!} \exp \left[-\beta U (s^N; L)\right]$$

Sample a particular configuration:
- Change of the number of particles
- Displacement of particle
Basic GCMC subroutine

Subroutine GCMC

do I = 1, ncycle
    do j = 1, ndisp + nexch
        j = int(ndisp + nexch) + 1
        if (j .le. Ndisp) then
            call displace()
        else
            call addRemove()
        end if
    end do
    if (mod(I, nsample) .eq. 0) call sample
end do
End do

End
\textit{\(\mu VT\)-ensemble}

Insertion and removal of particles

\[ acc(N \rightarrow N + 1) = \min \left[ 1, \frac{V \exp(\beta \mu) \exp(-\beta \Delta U)}{\Lambda^3 (N + 1)} \right] \]

\[ acc(N \rightarrow N - 1) = \min \left[ 1, \frac{\Lambda^3 N \exp(-\beta \mu) \exp(-\beta \Delta U)}{V} \right] \]
Summary

✓ PBC: test different system size
✓ Extension to molecular system
  ✓ Rotation move
  ✓ Configuration bias move
  ✓ Reptation move
  ✓ Bias move: associating fluids, dense system
✓ Detailed balance for acceptance criteria
✓ Efficient algorithms
  ✓ Neighbor list, cell list
✓ Long range interaction
  ✓ Ewald sum
  ✓ Reaction field
✓ Phase Equilibria
  ✓ Gibbs Ensemble MC, Gibbs Duhem Integration