Monte Carlo Simulation

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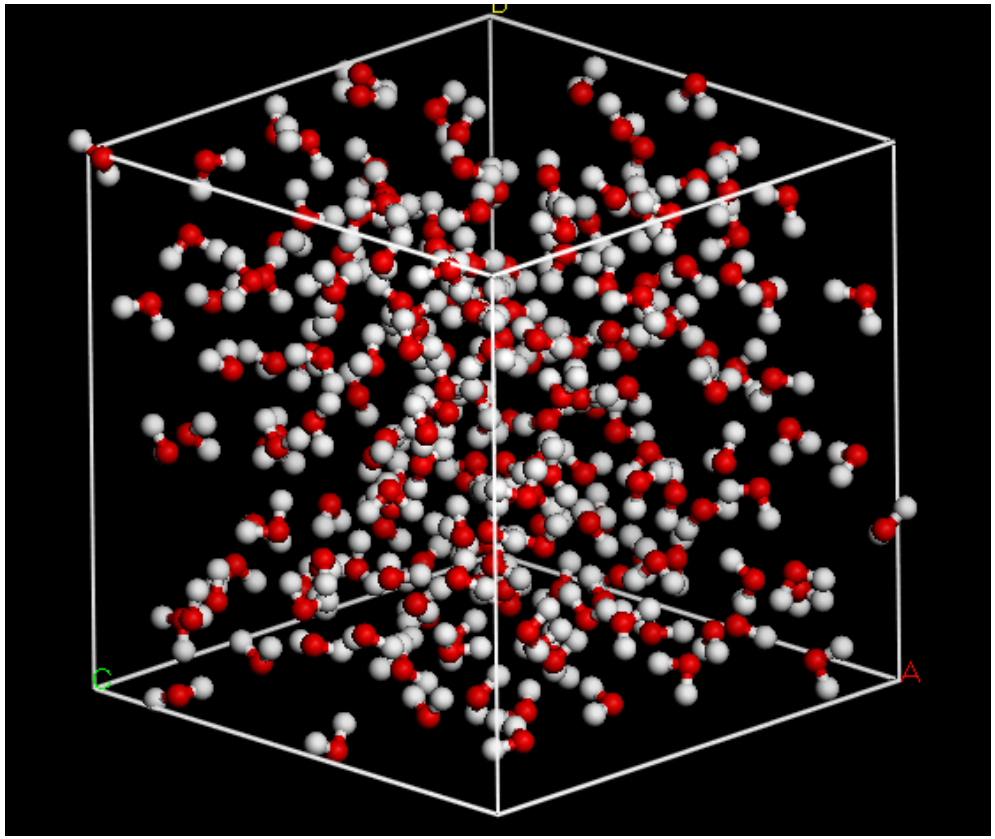
Overview

- To understand basic Molecular Simulation structure
- To understand basic MC code: NVT
- Modification for NPT, μVT

Molecular Simulation: System Size

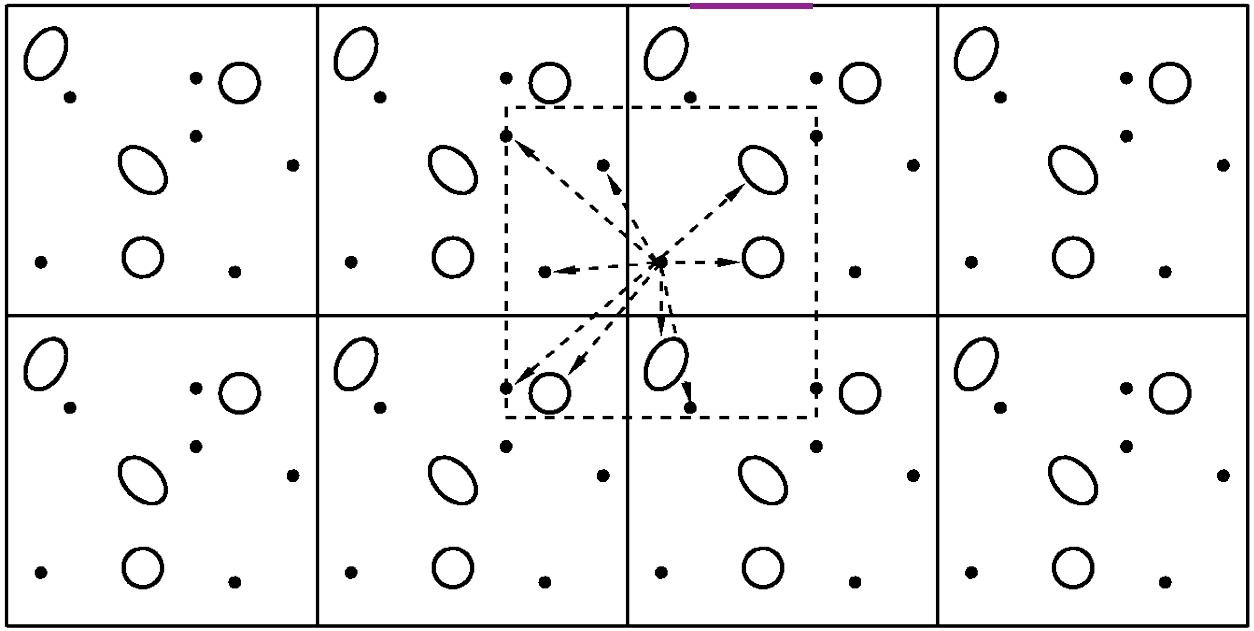


$$\langle U \rangle = \frac{1}{Z_N}\frac{1}{N!}\int dr^N U(r^N) e^{-\beta U(r^N)}$$

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

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

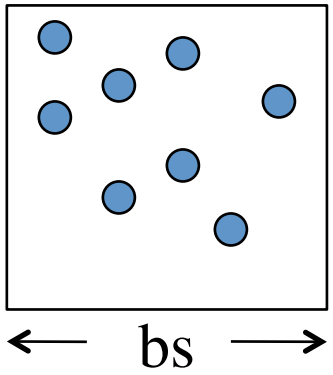
- Important to ask if the properties of a small infinitely periodic system and the macroscopic system which it represents are the same?
- Depends on the range of intermolecular potential and the phenomenon under investigation
- LJ fluid: possible to obtain bulk equilibrium properties with $L=6\sigma$
- If $U \sim r^{-v}$ where $v < d$ 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
  - `if(r(0) > 0.5) r.x =r.x- 1.0`
  - `if(r(0) < -0.5) r.x = r.x+1.0;  //only first shell`
  - *examples: -0.2 → -0.2; -1.4 → -0.4; +0.4 → +0.4; +0.6 → -0.4; +1.5 → +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 * aint(xnew / bs)

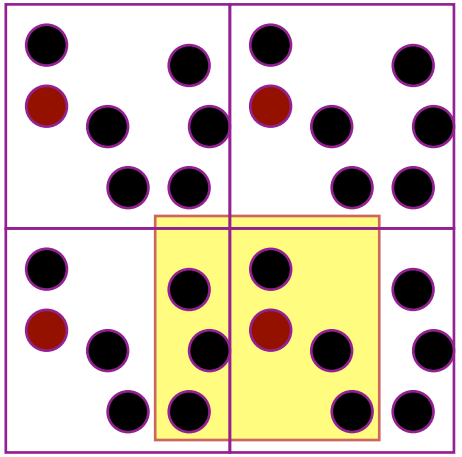
if(xnew < 0.0) xnew = xnew - bs * aint(xnew / bs - 1.0)

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

nint(x) **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!
  - `dxij = xj - xi //unit box length`
  - `if(dxij > 0.5) dxij =dxij -1.0`
  - `if(dxij < -0.5) dxij =dxij+ 1.0`
  - `dxij *= bs;`

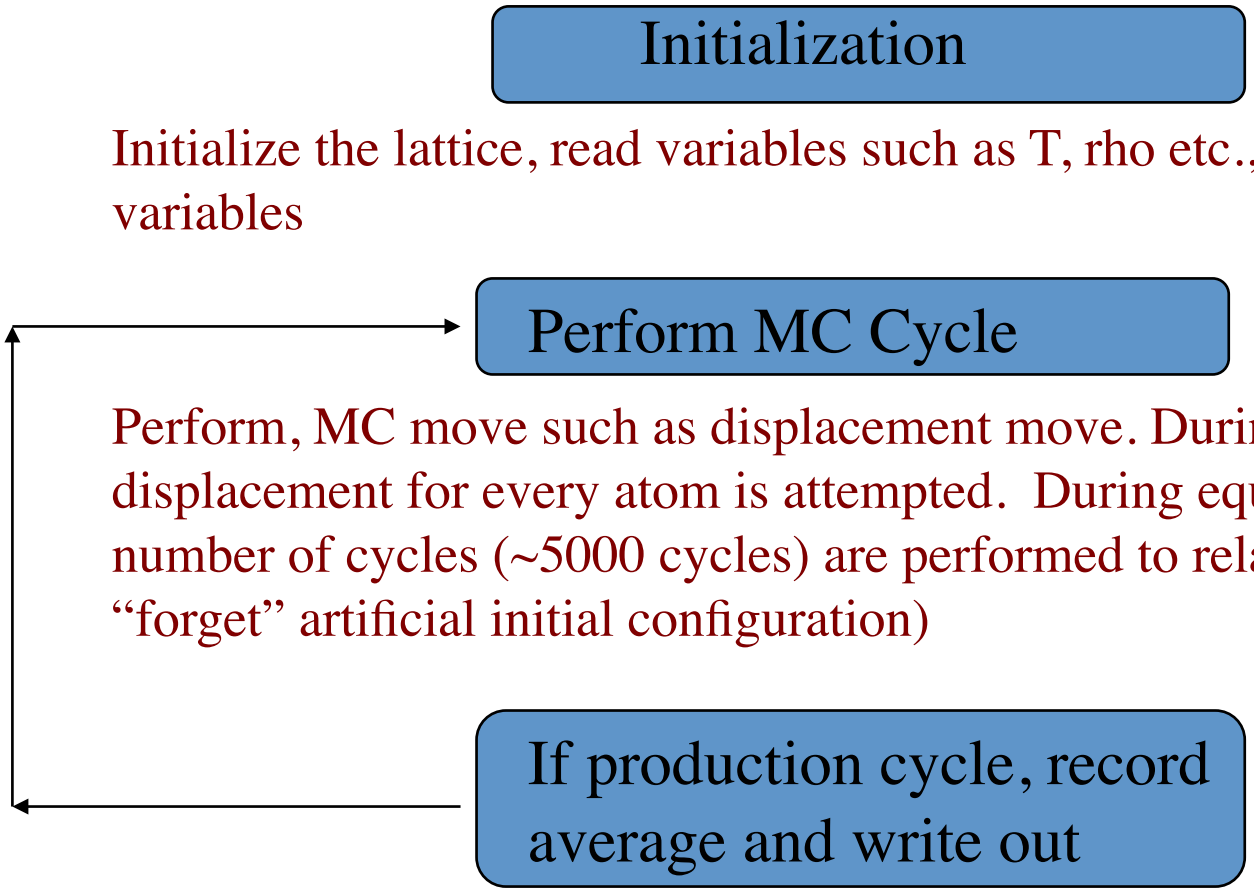


- Or…
  - `dxij = xj -xi; //true box length`

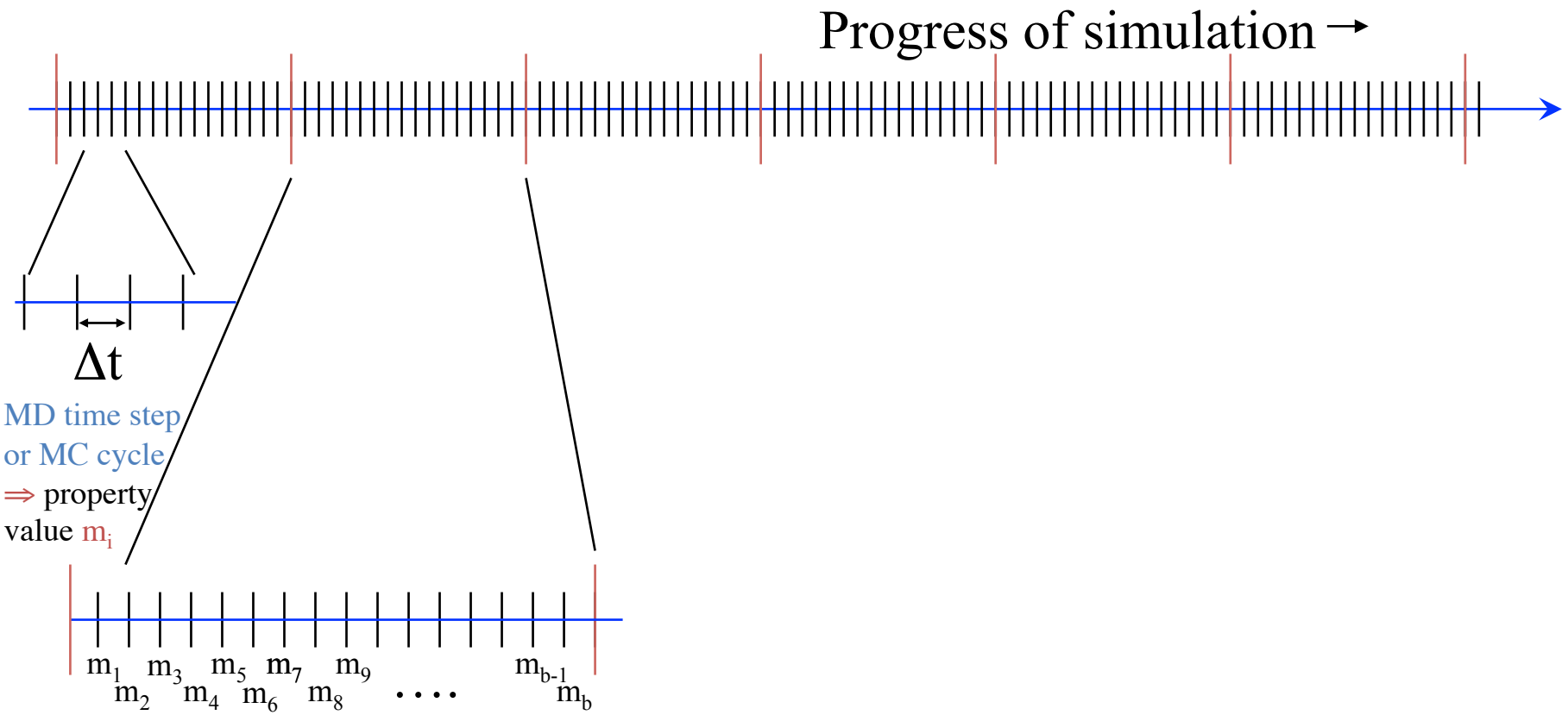
```
if(dxij > bs-dxij) dxij=dxij-bs
if(dxij <-bs-dxij) dxij=dxij+bs
```

- 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

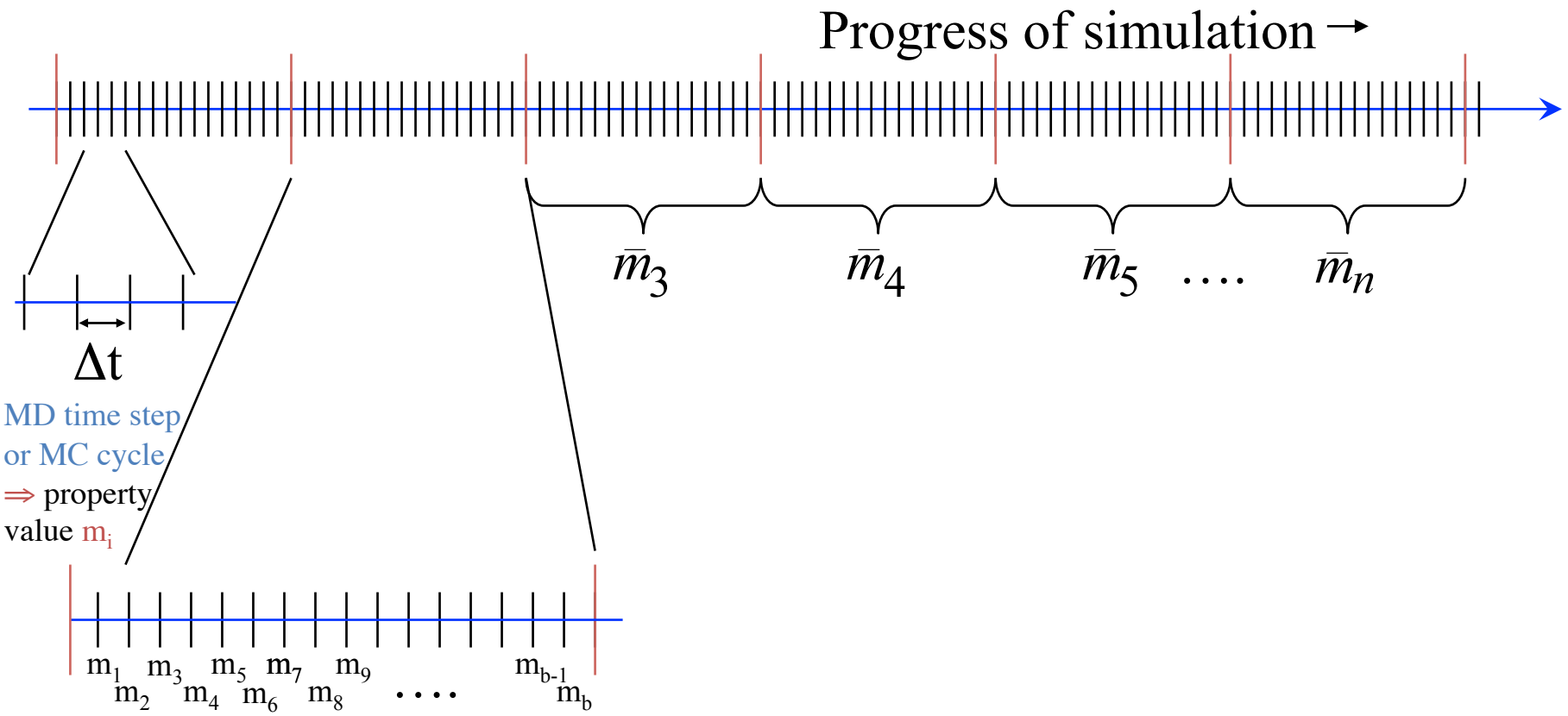
Structure of Molecular Simulation 1



Structure of a Molecular Simulation 2



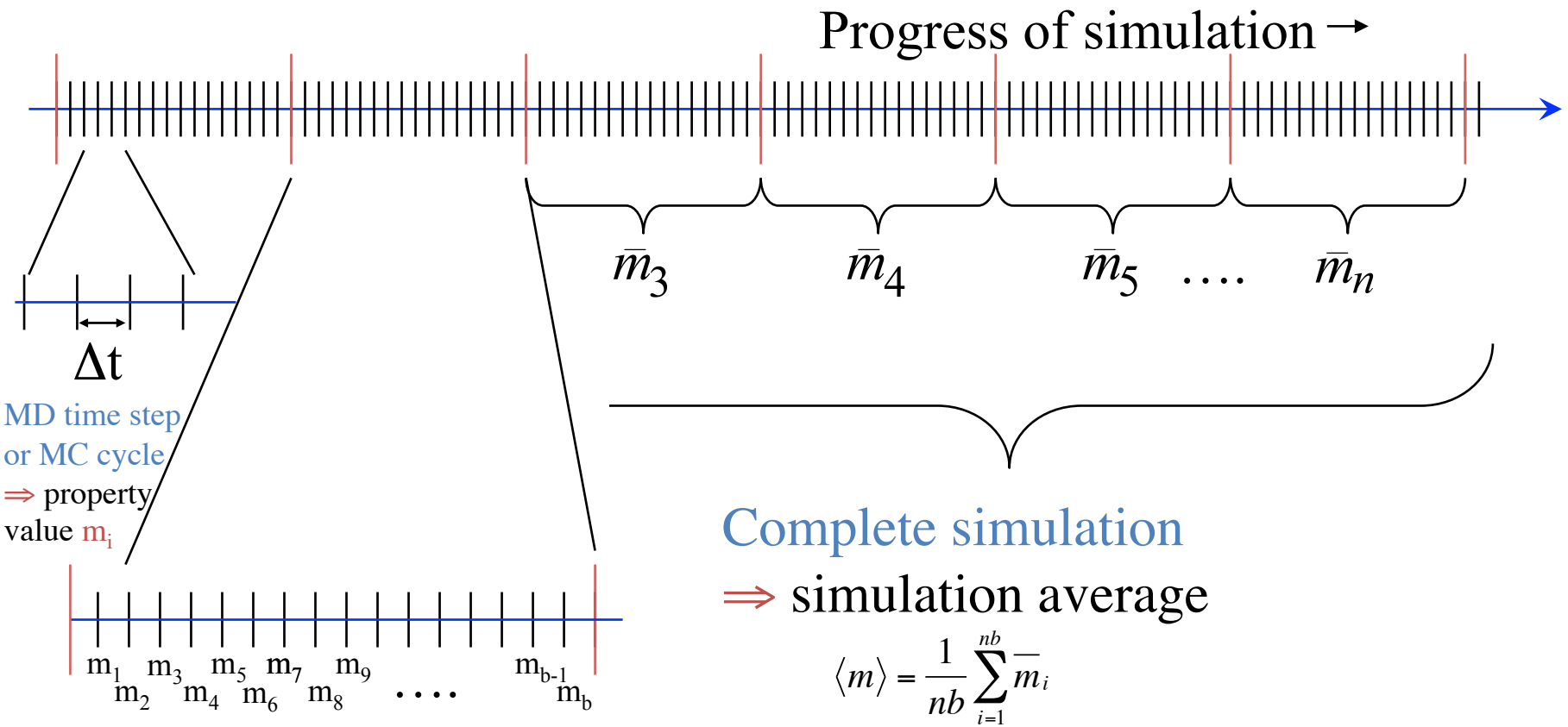
Structure of a Molecular Simulation 2



Simulation block

⇒ block average $\bar{m}_2 = \frac{1}{b}\sum_{i=1}^{b} m_i$

Structure of a Molecular Simulation 2



Simulation block

⇒ block average $\bar{m}_2 = \frac{1}{b}\sum_{i=1}^{b} m_i$

Complete simulation

⇒ simulation average

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

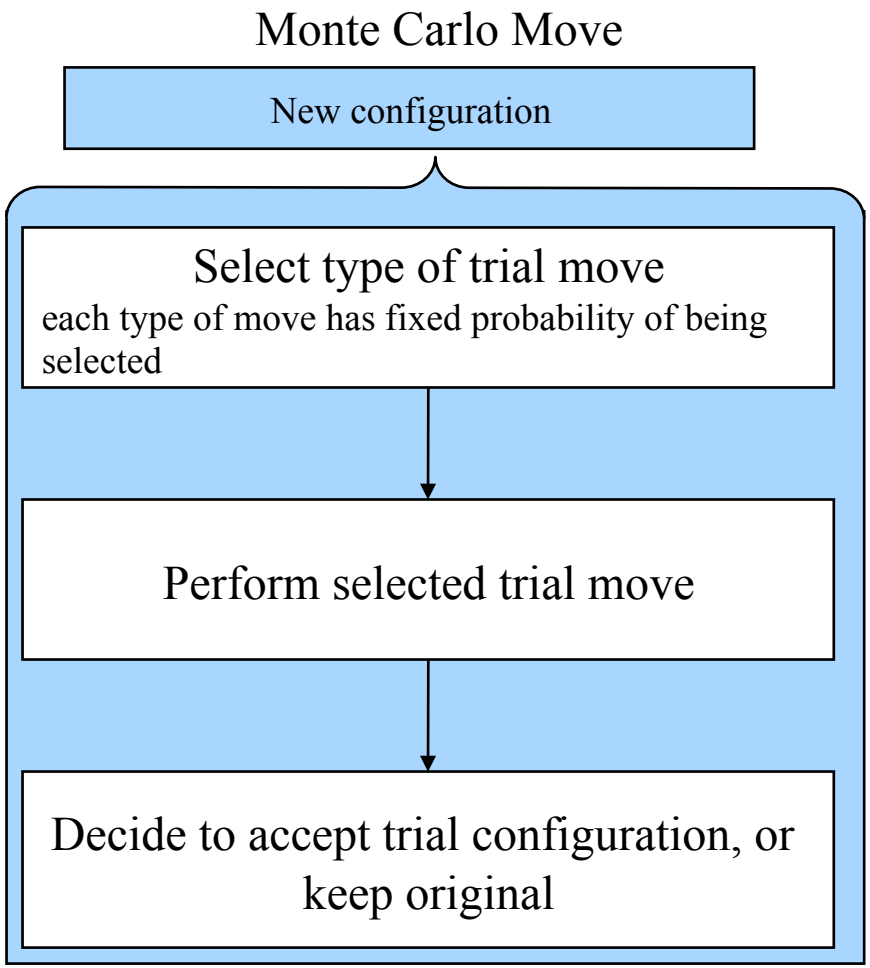
⇒ simulation error bar

$$\sigma_{\langle m \rangle} = \frac{\sigma_{\bar{m}}}{\sqrt{nb-1}}; \sigma_{\bar{m}} = \sqrt{\frac{1}{nb}\sum_{k=1}^{nb}\left(\bar{m}_k^2 - \langle m \rangle^2\right)}$$

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



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, $\pi=\pi_{NVT}$, what transition probabilities will yield π.

- Construct transition probabilities to satisfy detailed balance
- Metropolis Algorithm
  - with probability τ_{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 π_j/π_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

$$\pi_i \pi_{ij} = \pi_j \pi_{ji}$$

$$\pi_{ij} = \tau_{ij} acc(i \to j) = \tau_{ij} \min(1, \chi)$$

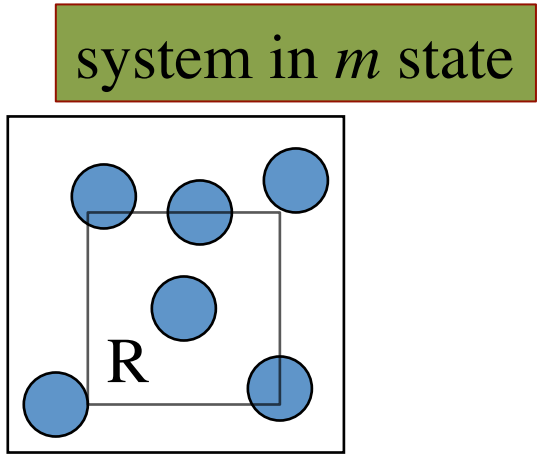
$$\pi_{ji} = \tau_{ji} acc(j \to i) = \tau_{ji} \min\left(1, \frac{1}{\chi}\right)$$

$$\frac{acc(i \to j)}{acc(j \to i)} = \frac{\pi_j \tau_{ji}}{\pi_i \tau_{ij}}$$

Implementation of Metropolis Method

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

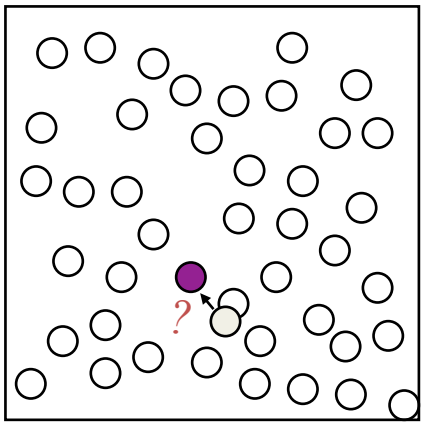
✓Displace one atom random from its position r_i^m
With equal probability to any point r_i^n inside the square/cube *R* of side $2\delta_{max}$ and is centered at r_i^m



-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
-δ_{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 2δ centered on the current position of the atom*



Examine underlying transition probabilities to formulate acceptance criterion

Forward-step transition probability, τ_{ij}=

Prob of selecting a molecule X Prob of moving a new position, *r* new

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

NVT-ensemble

Limiting probability distribution $\pi_i \propto \exp\left[-\beta U(i)\right]$

$$\frac{acc(i \to j)}{acc(j \to i)} = \frac{\pi_j \tau_{ji}}{\pi_i \tau_{ij}}$$

$$\frac{acc(i \to j)}{acc(j \to i)} = \exp\left[-\beta\left(U(j) - U(i)\right)\right]$$

Acceptance probability

$$\chi = e^{-\beta(U^{new} - U^{old})}$$

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:

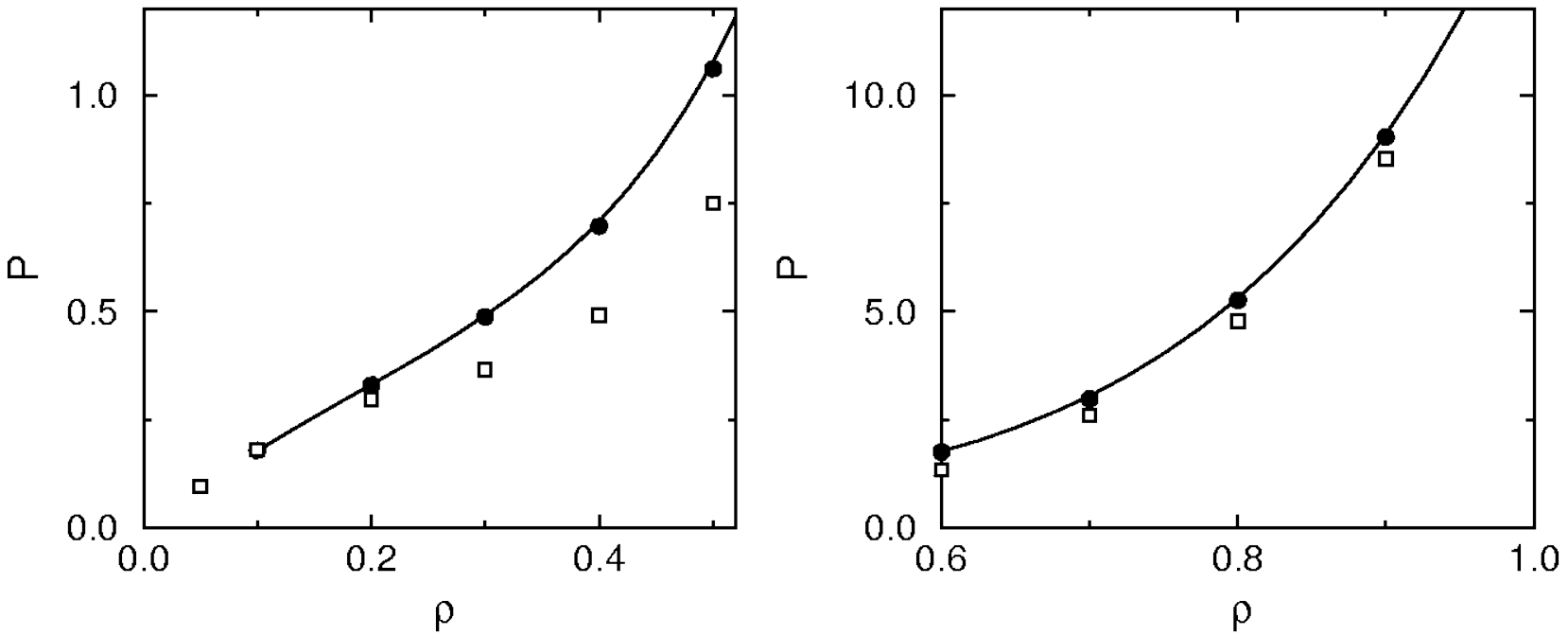
$$\pi_{ij} = \tau_{ij} \times acc(i \to j)$$

$$\sum_{j} \pi_{ij} = 1$$

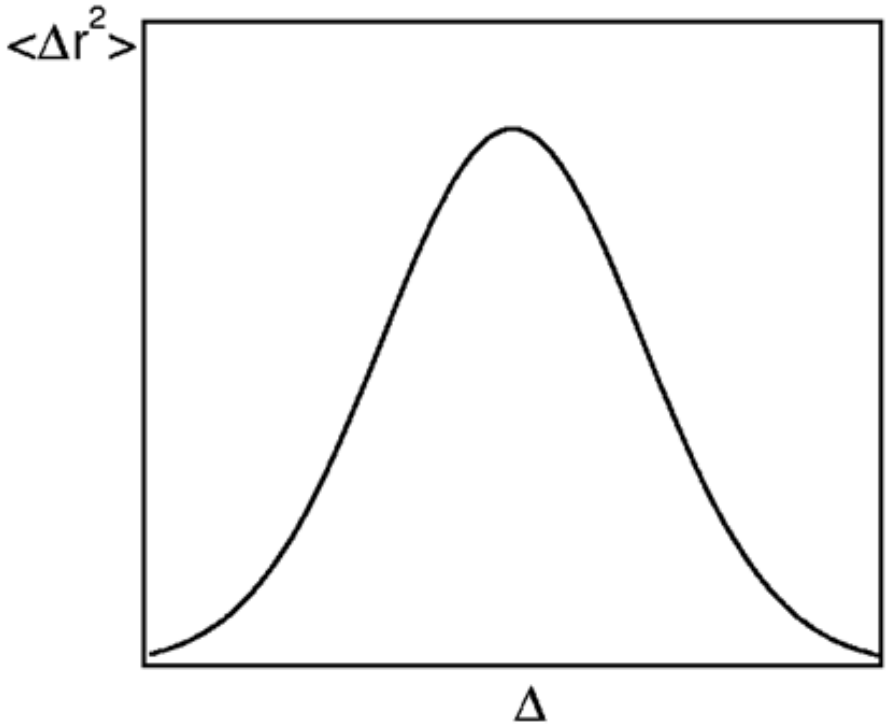
Probability to accept the old configuration:

$$\pi_{ii} = 1 - \sum_{j, j \neq i} \pi_{ij}$$

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

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

- The truncated Lennard-Jones potential

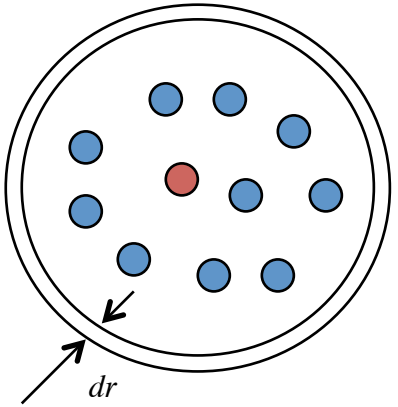
$$u(r) = \begin{cases} u^{LJ}(r) & r \le r_c \\ 0 & r > r_c \end{cases}$$

- The truncated and shifted Lennard-Jones potential

$$u(r) = \begin{cases} u^{LJ}(r) - u^{LJ}(r_c) & r \le r_c \\ 0 & r > r_c \end{cases}$$

Pair correlation function

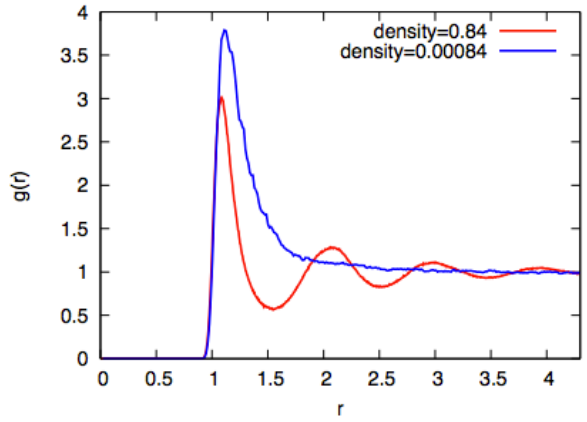
- Environment around a given molecule



g(r)=pair correlation function aka RDF

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

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



$$U/N = \frac{1}{2}\rho\int_0^\infty u(r)g(r)d\vec{r} = 2\pi\rho\int_0^\infty u(r)g(r)r^2 dr$$

$$P = \frac{\rho}{\beta} - \frac{1}{6}\rho^2\int_0^\infty \frac{du(r)}{dr}g(r)d\vec{r} = \frac{\rho}{\beta} - \frac{2}{3}\pi\rho^2\int_0^\infty \frac{du(r)}{dr}g(r)r^3 dr$$

Correction to thermodynamic properties

$g(\mathrm{r}) = 1, r > r_c$: uniform distribution beyond cut off

$$u(r) = \begin{cases} u^{LJ}(r) & r \le r_c \\ 0 & r > r_c \end{cases}$$

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

$$p = \rho kT + \frac{vir}{V}$$

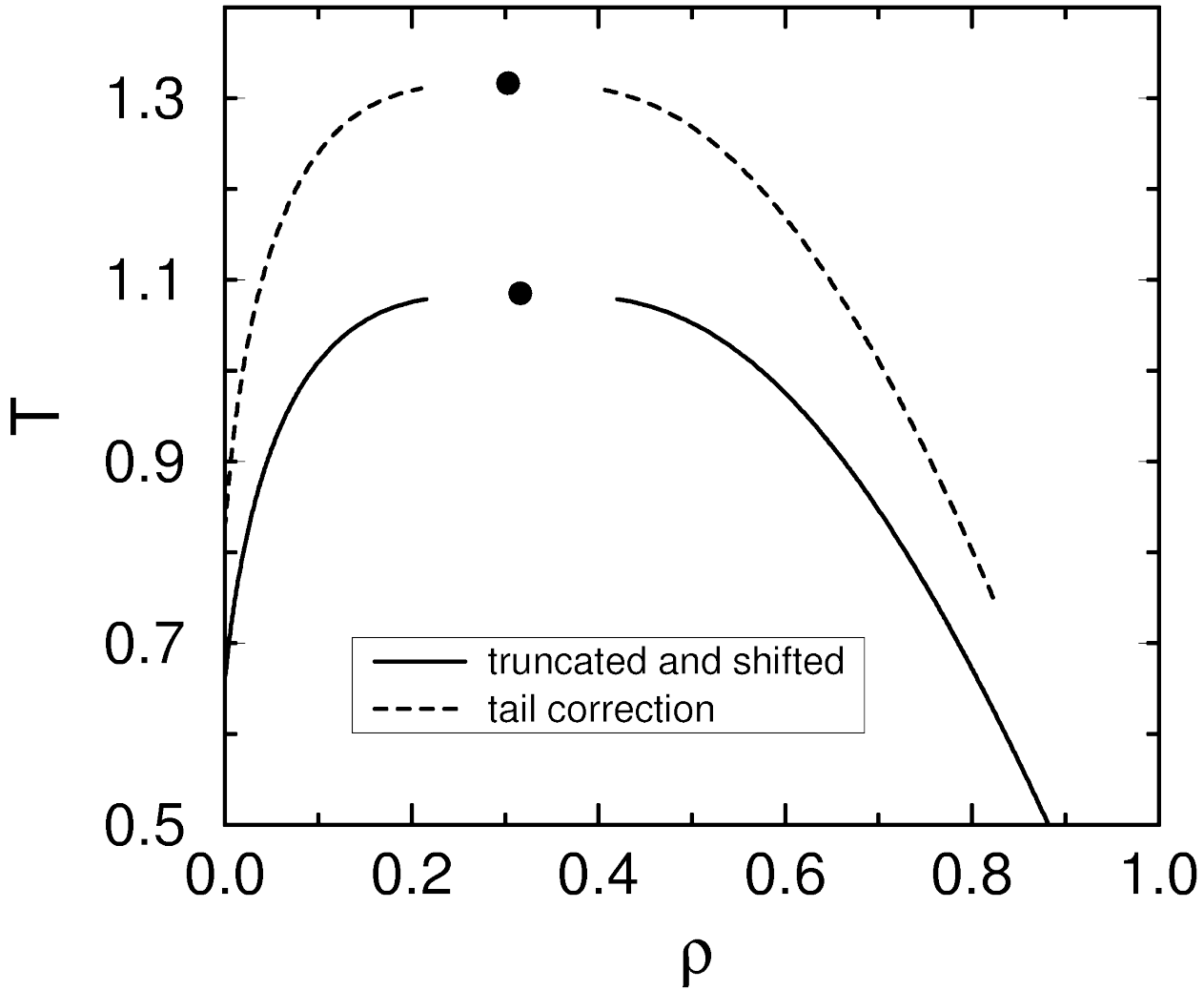
$$vir = \frac{1}{3}\sum_i \sum_{j>i} \vec{f}(r_{ij}) \bullet_{ij} \overline{r_{ij}}$$

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

$$\mu_{tail} = \rho\int_{rcut}^{\infty} u(r)4\pi r^2 dr = 2\frac{U_{tail}}{N}$$

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
return
End
```

Lennard-Jones EOS

Direct evaluation of phase coexistence by molecular simulation via integration along the saturation line

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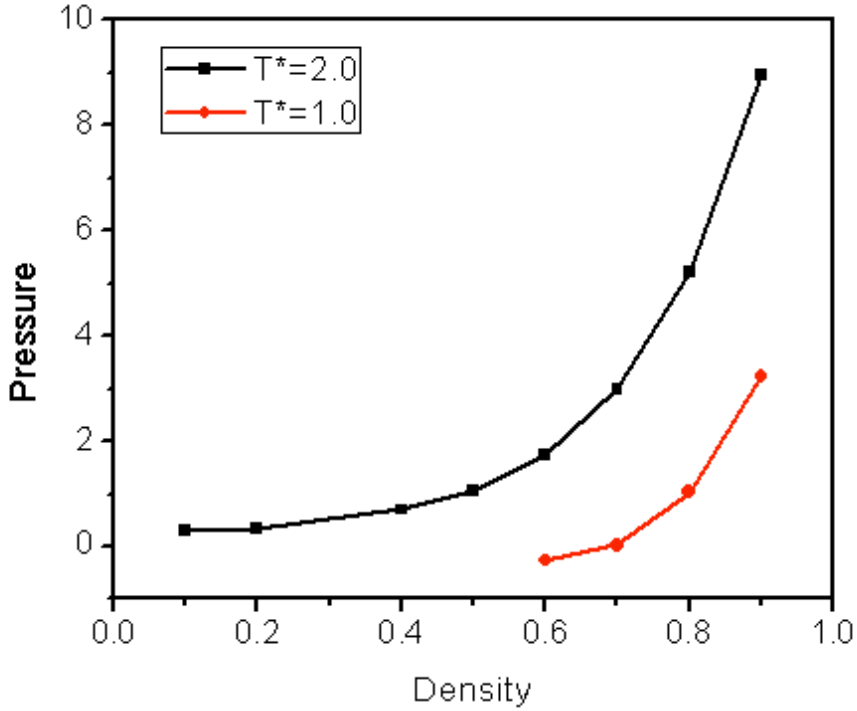
(Received 23 October 1992; accepted 4 December 1992)

TABLE III. Simulation results from series (o), (r), and (t). All quantities are given in Lennard-Jones units. β is the r temperature (provided for convenience), $P(\rho/c)$ is the final value of the pressure as estimated by the corrector formul report simulation averages for the pressure, molar density, and molar energy in each phase. The small subscripts indicat so 5.85_1 means 5.85 ± 0.01; this reflects only the statistical error of the simulations, and does not attempt to incorporate a result from the predictor–corrector integration method. The quantity $\Delta(\beta\mu)$ is the change in chemical potential from i $\beta = 1.35$ [given by a series (e) simulation], and it is determined from the simulation data of each phase by applying simp the Gibbs–Duhem equation as written $d(\beta\mu) = h\, d\beta + \beta P/\rho\, d \ln P$, where the molar enthalpy $h = u + P/\rho$. Entries with no considered "best" results for the temperature and are provided only for comparison; these data are not presented in Fig. 9 the critical properties.

			P(sim)		ρ		$-u$	
β	T	$P(\rho/c)$	vapor	liquid	vapor	liquid	vapor	liqu
Series (o)								
1.35	0.741	0.00229	0.00225_1	0.02_2	0.00313	0.835	0.0360	6.0
1.30	0.769	0.00321	0.00316_2	0.04_2	0.00433_3	0.815_1	0.0487_7	5.8
1.25	0.800	0.00452	0.00445_5	0.01_3	0.00591_4	0.801_2	0.064_1	5.7
1.20	0.833	0.00633	0.00627_5	0.02_3	0.00807_6	0.786_1	0.086_2	5.6
1.15	0.870	0.00886	0.00877_8	0.00_2	0.01101_7	0.769_1	0.113_2	5.4
1.10	0.909	0.0124	0.0124_1	-0.00_2	0.0151_1	0.750_2	0.151_2	5.2
1.05	0.952	0.0173	0.0174_3	-0.01_3	0.0207_2	0.726_1	0.200_3	5.0
1.00	1.000	0.0242	0.0246_2	0.04_3	0.0284_2	0.704_2	0.265_3	4.9
0.95	1.053	0.0338	0.0343_4	0.02_2	0.0395_3	0.672_2	0.360_4	4.6
0.90	1.111	0.0471	0.0475_6	0.06_2	0.0557_4	0.635_3	0.488_5	4.3
0.85	1.176	0.0659	0.0655_8	0.07_3	0.0810_6	0.578_4	0.689_9	3.9
0.80	1.250	0.0911	0.093_2	0.09_1	0.118_2	0.47_3	0.95_1	3.2



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The Lennard-Jones equation of state revisited

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Monte Carlo: other ensemble

NPT Ensemble

In the classical limit, the partition function becomes

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

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

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

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

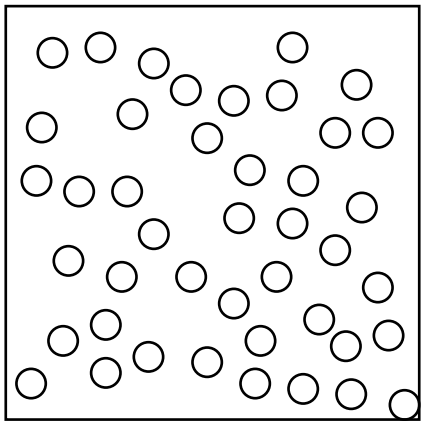
Sample a particular configuration by two kind of moves

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

Acceptance rules : apply detailed balanced

Volume-change Trial Move

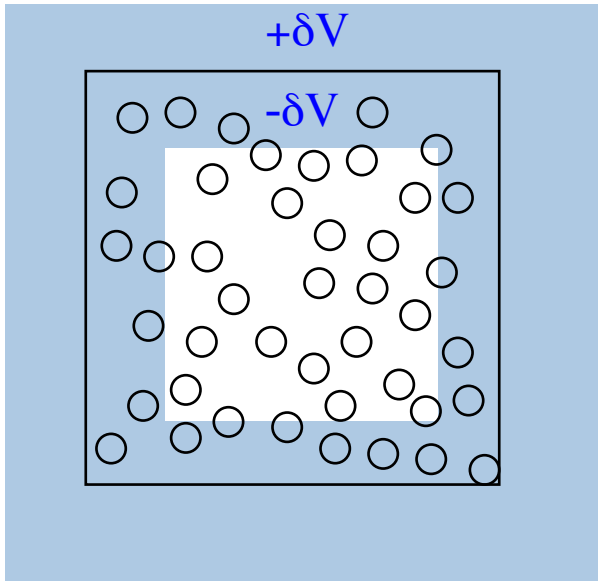
- Gives new configuration of different volume and same N and $\mathbf{s}^N$
- Basic trial:
  -



Volume-change Trial Move

- Gives new configuration of different volume and same N and $\mathbf{s}^N$
- Basic trial:
  - *by some amount within $\pm\delta V$*

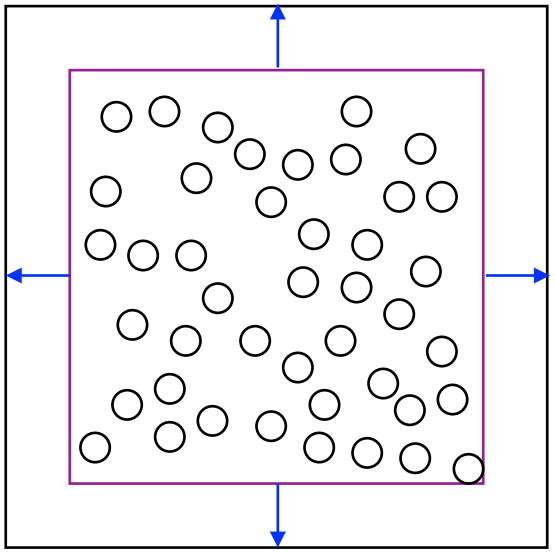
Select a random value for volume change



Volume-change Trial Move

- Gives new configuration of different volume and same N and $\mathbf{s}^N$
- Basic trial:
  - *increase or decrease the total system volume by some amount within* $\pm\delta V$,

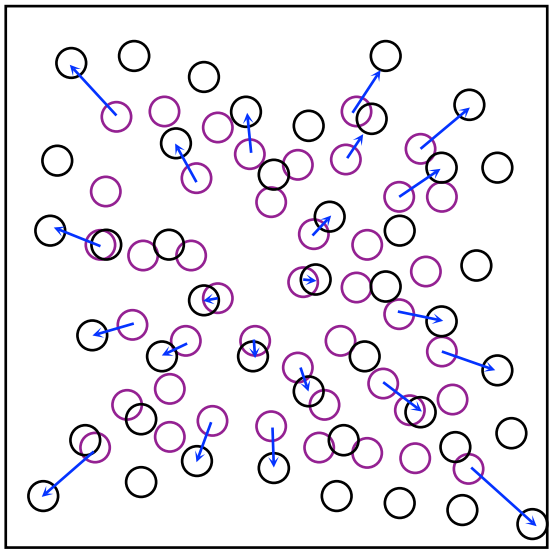
Perturb the total system volume



Volume-change Trial Move

- Gives new configuration of different volume and same N and $\mathbf{s}^N$
- 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*

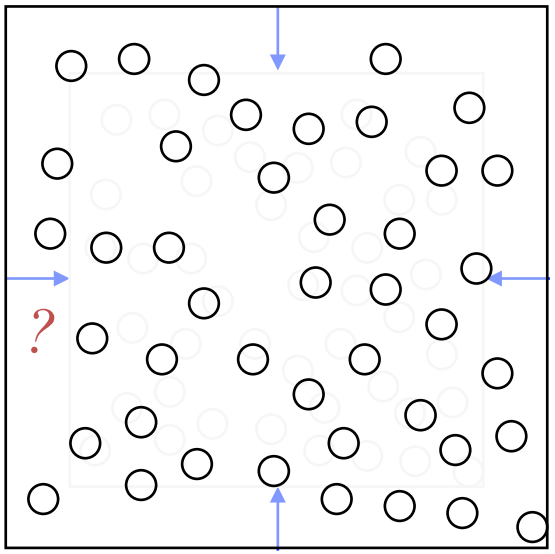
Scale all positions in proportion



Volume-change Trial Move

- Gives new configuration of different volume and same N and $\mathbf{s}^N$
- 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*

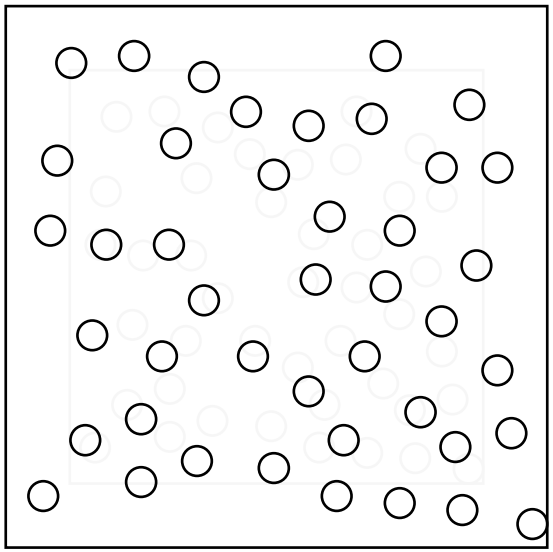
Consider acceptance of new configuration



Volume-change Trial Move

- Gives new configuration of different volume and same N and $\mathbf{s}^N$
- 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*

Examine underlying transition probabilities to formulate acceptance criterion



$$\pi\left((V\mathbf{s})^N\right) = \frac{1}{\Delta} e^{-\beta U\left((V\mathbf{s})^N\right) - \beta PV} V^N d\mathbf{s}^N dV$$

Volume-change Trial Move
Analysis of Transition Probabilities

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

χ 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

$\pi_i \quad \pi_{ij} \quad = \quad \pi_j \quad \pi_{ji}$

Limiting distribution

$$\pi\left((V\mathbf{s})^N\right) = \frac{1}{\Delta} e^{-\beta U\left((V\mathbf{s})^N\right) - \beta PV} V^N d\mathbf{s}^N dV$$

Volume-change Trial Move
Analysis of Detailed Balance

Detailed balance

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

Detailed balance

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

$$e^{-\beta(U^{old}+PV^{old})}\left(V^{old}\right)^{N}\chi=e^{-\beta(U^{new}+PV^{new})}\left(V^{new}\right)^{N}$$

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

Acceptance probability

Volume-change Trial Move

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

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

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

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

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

$$\chi = \exp\left[-\beta(\Delta U + P\Delta V) + (N+1)\ln(V^{new}/V^{old})\right]$$

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:

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

Probability to find a particular configuration:

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

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
```

μVT-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