CE 530 Molecular Simulation

Lecture 9

Monte Carlo Simulation

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Review

- We want to apply Monte Carlo simulation to evaluate the configuration integrals arising in statistical mechanics

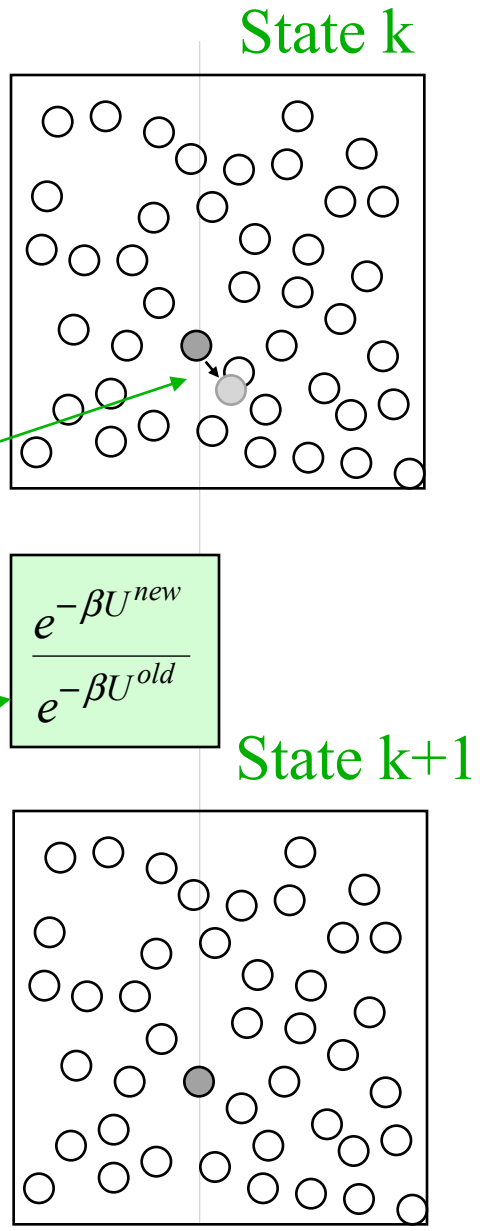
$$\langle U \rangle = \frac{1}{N!}\int dr^N U(r^N)\frac{e^{-\beta U(r^N)}}{Z_N}$$

$\pi(r^N)$

- Importance-sampling Monte Carlo is the only viable approach
  - *unweighted sum of U with configurations generated according to distribution* $e^{-\beta U}/Z_N$
- Markov processes can be used to generate configurations according to the desired distribution $\pi(r^N)$.
  - *Given a desired limiting distribution, we construct single-step transition probabilities that yield this distribution for large samples*
  - *Construction of transition probabilities is aided by the use of detailed balance:* $\pi_i \pi_{ij} = \pi_j \pi_{ji}$
  - *The Metropolis recipe is the most commonly used method in molecular simulation for constructing the transition probabilities*

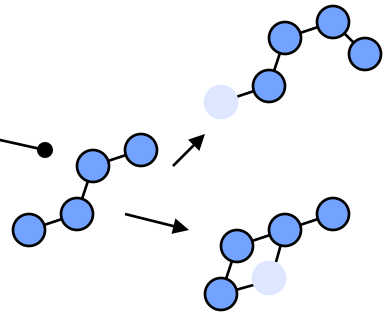
Monte Carlo Simulation

- MC techniques applied to molecular simulation
- Almost always involves a Markov process
  - *move to a new configuration from an existing one according to a well-defined transition probability*
- Simulation procedure
  - *generate a new "trial" configuration by making a perturbation to the present configuration*
  - *accept the new configuration based on the ratio of the probabilities for the new and old configurations, according to the Metropolis algorithm*
  - *if the trial is rejected, the present configuration is taken as the next one in the Markov chain*
  - *repeat this many times, accumulating sums for averages*

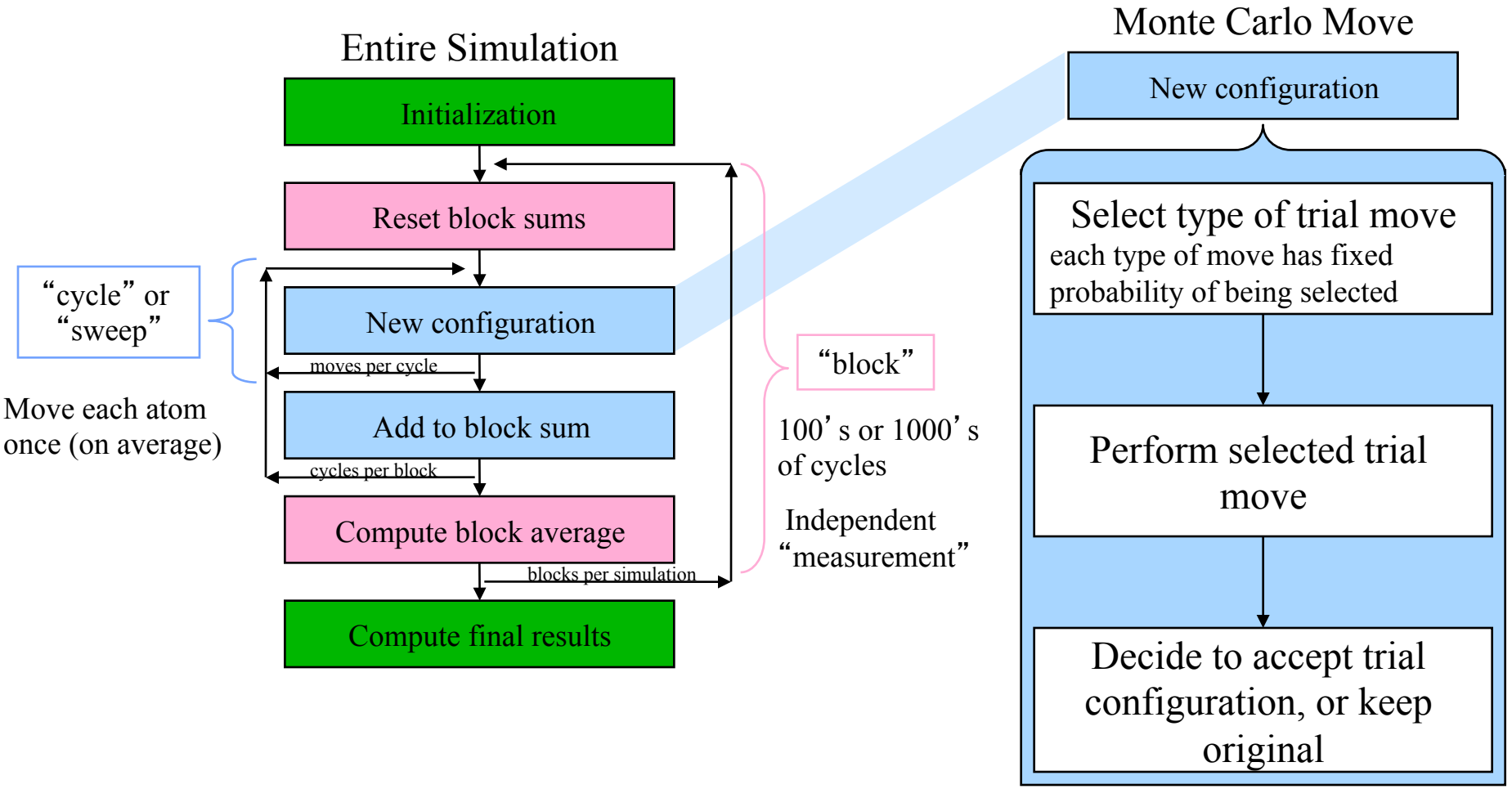


Trial Moves

- A great variety of trial moves can be made
- Basic selection of trial moves is dictated by choice of ensemble
  - *almost all MC is performed at constant T*
    - no need to ensure trial holds energy fixed
  - *must ensure relevant elements of ensemble are sampled*
    - all ensembles have molecule displacement, rotation; atom displacement
    - isobaric ensembles have trials that change the volume
    - grand-canonical ensembles have trials that insert/delete a molecule
- Significant increase in efficiency of algorithm can be achieved by the introduction of clever trial moves
  - *reptation, crankshaft moves for polymers*
  - *multi-molecule movements of associating molecules*
  - *many more*



General Form of Algorithm



Simulation API: Integrator

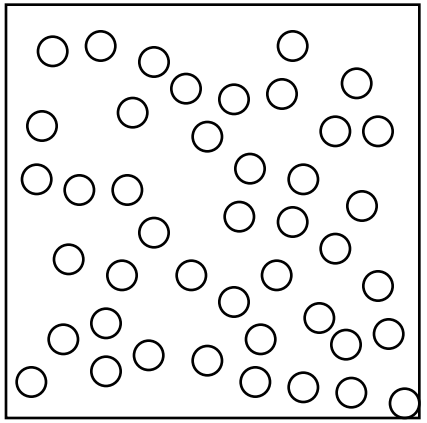
- Integrator
  - *repeatedly changes configuration to follow a sampling algorithm*
  - *public void doStep()*
  - *deploys subclass-specific agent to each atom*
  - *only one integrator acts on a given box*
  - *some integrators act on multiple boxes*
    - IntegratorGEMC (Gibbs ensemble Monte Carlo)
    - IntegratorPT (Parallel tempering)
- IntegratorMD
  - *IntegratorVelocityVerlet*
  - *IntegratorHard*
    - discontinuous molecular dynamics
- IntegratorMC

Simulation API: IntegratorMC

- IntegratorMC
  - *Monte Carlo sampling*
  - *Selects trial move, performs trial, decides acceptance, notifies move and other listeners*
- MCMove
  - *Performs Monte Carlo trial*
  - *Reports information needed to determine acceptance*
    - $\ln(\pi_{new}/\pi_{old})$, $\ln(\tau_{ij}/\tau_{ji})$
    - Holds fields needed for evaluation
  - *Does appropriate update for acceptance or rejection*
  - *For example*
    - MCMoveAtom
    - MCMoveInsertDelete
    - MCMoveRotateMolecule
    - MCMoveVolume
  - *Sampled ensemble is determined by set of MCMoves added to integrator*

Displacement Trial Move
1. Specification

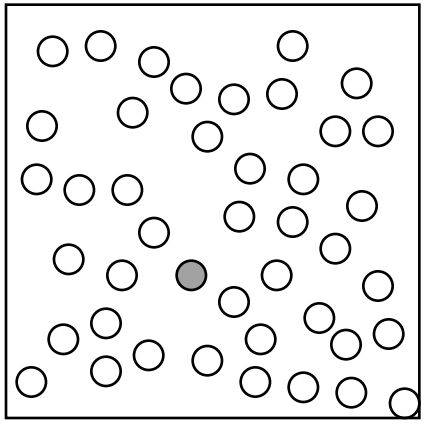
- Gives new configuration of same volume and number of molecules
- Basic trial:
  -



Displacement Trial Move
1. Specification

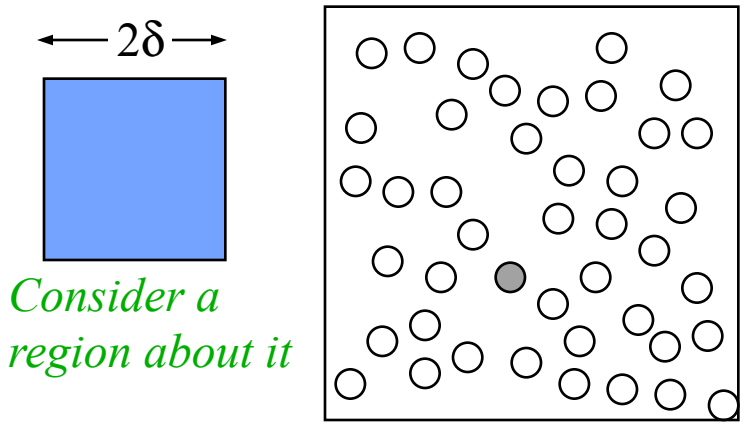
- Gives new configuration of same volume and number of molecules
- Basic trial:
  - *a randomly selected atom*

Select an atom at random



Displacement Trial Move
1. Specification

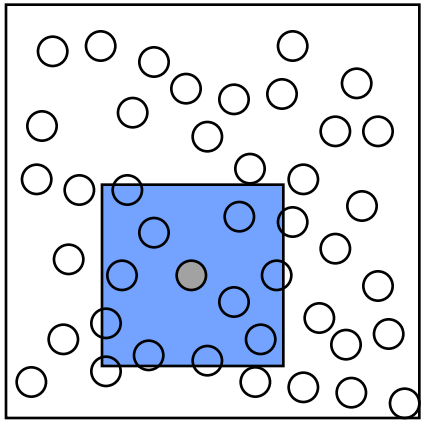
- Gives new configuration of same volume and number of molecules
- Basic trial:
  - *a randomly selected atom*
    a cubic volume of edge 2δ



Displacement Trial Move
1. Specification

- Gives new configuration of same volume and number of molecules
- Basic trial:
  - *a randomly selected atom*
    a cubic volume of edge 2δ *centered on the current position of the atom*

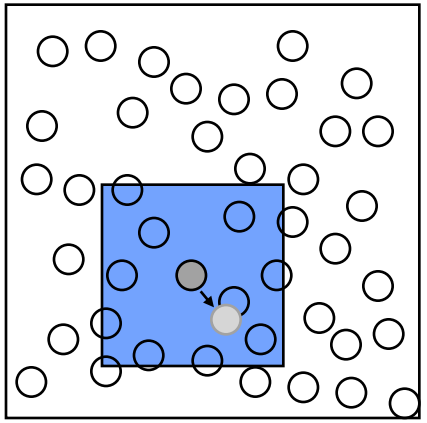
Consider a region about it



Displacement Trial Move
1. Specification

- 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*

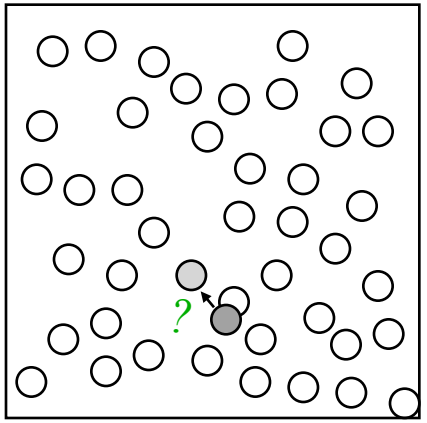
Move atom to point chosen uniformly in region



Displacement Trial Move
1. Specification

- 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*

Consider acceptance of new configuration

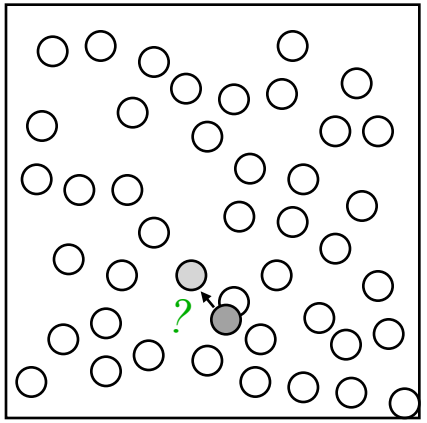


Displacement Trial Move
1. Specification

- 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*
- Limiting probability distribution
  - *canonical ensemble*

$$\pi(\mathbf{r}^N)d\mathbf{r}^N = \frac{1}{Z_N} e^{-\beta U(\mathbf{r}^N)} d\mathbf{r}^N$$

Examine underlying transition probabilities to formulate acceptance criterion



  - *for this trial move, probability ratios are the same in other common ensembles, so the algorithm described here pertains to them as well*

Displacement Trial Move
2. Analysis of Trial Probabilities

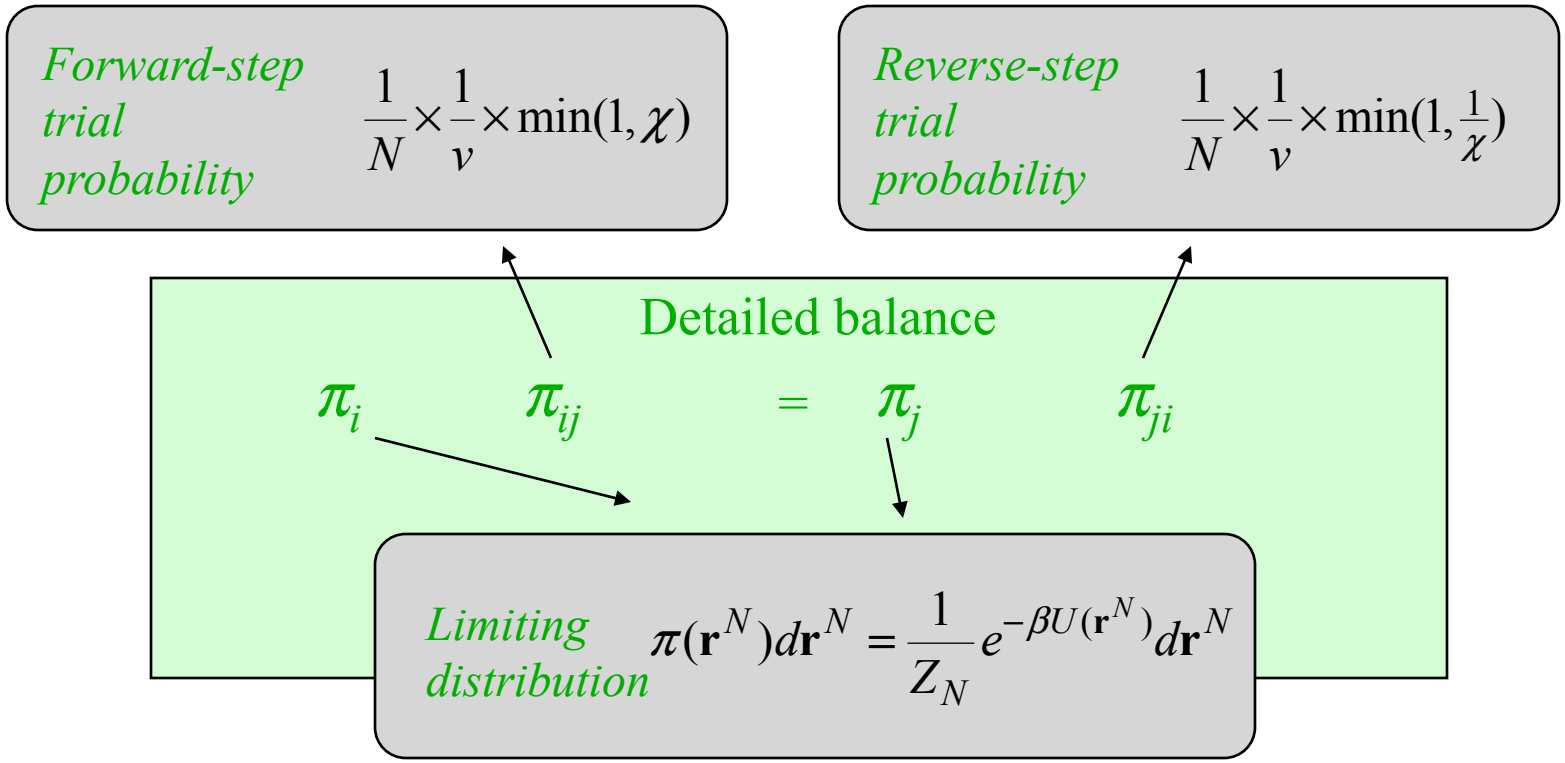
- Detailed specification of trial moves and probabilities

Event [reverse event]	Probability [reverse probability]
Select molecule k [select molecule k]	1/N [1/N]
Move to r^{new} [move back to r^{old}]	$v = (2\delta)^d$ → 1/v [1/v]
Accept move [accept move]	min(1,χ) ← *χ is formulated to satisfy detailed balance* [min(1,1/χ)]

Forward-step trial probability $\frac{1}{N} \times \frac{1}{v} \times \min(1, \chi)$

Reverse-step trial probability $\frac{1}{N} \times \frac{1}{v} \times \min(1, \frac{1}{\chi})$

Displacement Trial Move
3. Analysis of Detailed Balance



Displacement Trial Move
3. Analysis of Detailed Balance

Forward-step trial probability $\frac{1}{N}\times\frac{1}{v}\times\min(1,\chi)$

Reverse-step trial probability $\frac{1}{N}\times\frac{1}{v}\times\min(1,\frac{1}{\chi})$

Detailed balance

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

$$\frac{e^{-\beta U^{old}}d\mathbf{r}^N}{Z_N}\left[\frac{1}{N}\times\frac{1}{v}\times\min(1,\chi)\right]=\frac{e^{-\beta U^{new}}d\mathbf{r}^N}{Z_N}\left[\frac{1}{N}\times\frac{1}{v}\times\min(1,\frac{1}{\chi})\right]$$

Limiting distribution $\pi(\mathbf{r}^N)d\mathbf{r}^N=\frac{1}{Z_N}e^{-\beta U(\mathbf{r}^N)}d\mathbf{r}^N$

Displacement Trial Move
3. Analysis of Detailed Balance

Forward-step trial probability $\frac{1}{N}\times\frac{1}{v}\times\min(1,\chi)$

Reverse-step trial probability $\frac{1}{N}\times\frac{1}{v}\times\min(1,\frac{1}{\chi})$

Detailed balance

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

$$\frac{e^{-\beta U^{old}}}{Z_N}d\mathbf{r}^N\left[\frac{1}{N}\times\frac{1}{v}\times\min(1,\chi)\right]=\frac{e^{-\beta U^{new}}}{Z_N}d\mathbf{r}^N\left[\frac{1}{N}\times\frac{1}{v}\times\min(1,\frac{1}{\chi})\right]$$

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

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

Acceptance probability

Displacement Trial Move
4. Simulation Example

Have a look at a simple MC simulation applet

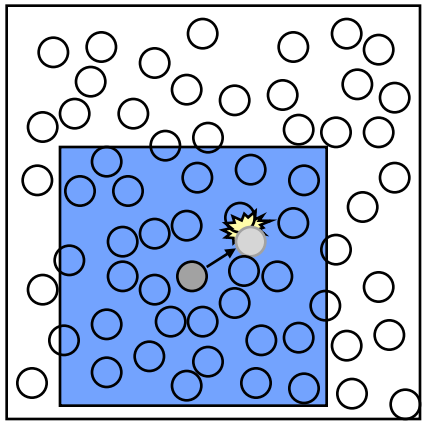
If the link doesn't work, enter this URL in your browser:

http://www.eng.buffalo.edu/~kofke/applets/SimpleMC.html

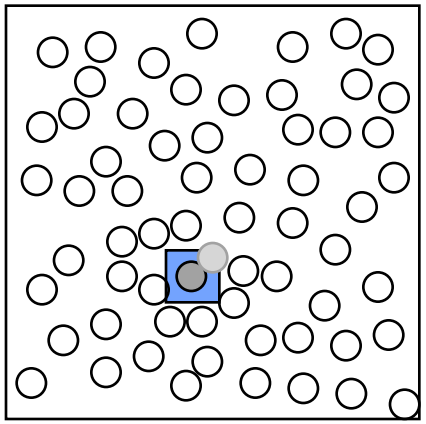
Displacement Trial Move
5. Tuning

- Size of step is adjusted to reach a target rate of acceptance of displacement trials
  - *typical target is 50%*
  - *for hard potentials target may be lower (rejection is efficient)*

Large step leads to less acceptance but bigger moves

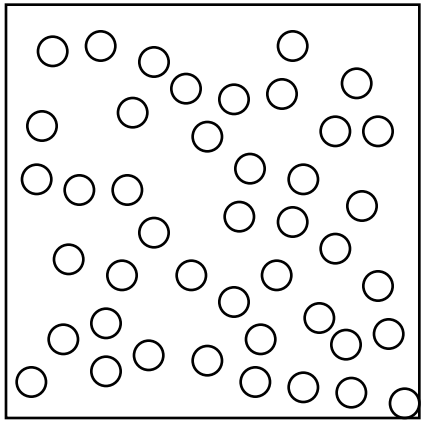


Small step leads to less movement but more acceptance



Volume-change Trial Move
1. Specification

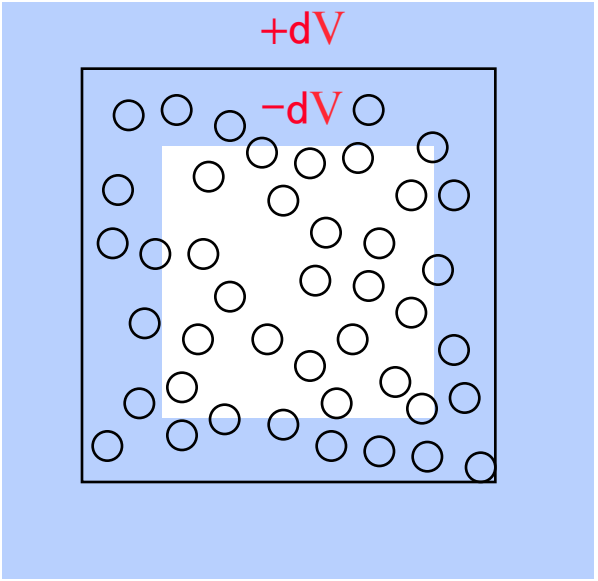
- Gives new configuration of different volume and same N and $\mathbf{s}^N$
- Basic trial:
  -



Volume-change Trial Move
1. Specification

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

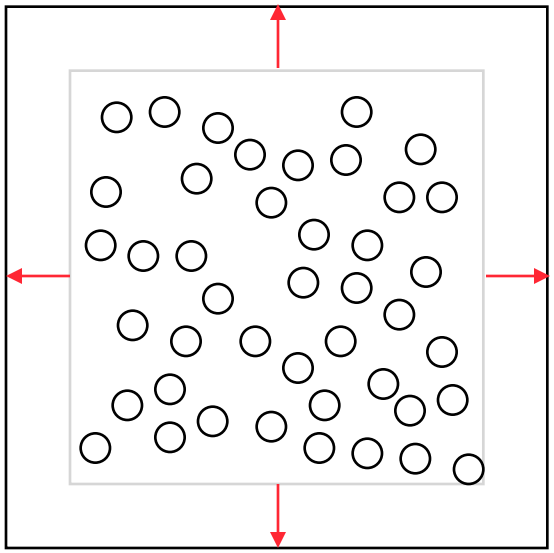
Select a random value for volume change



Volume-change Trial Move
1. Specification

- 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* $\pm\delta V$,

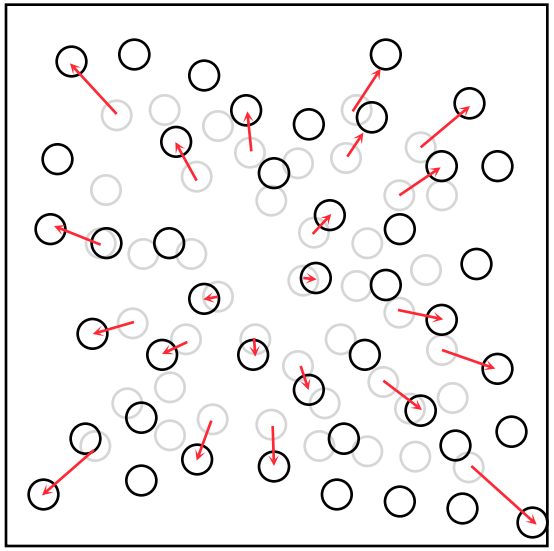
Perturb the total system volume



Volume-change Trial Move
1. Specification

- 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*

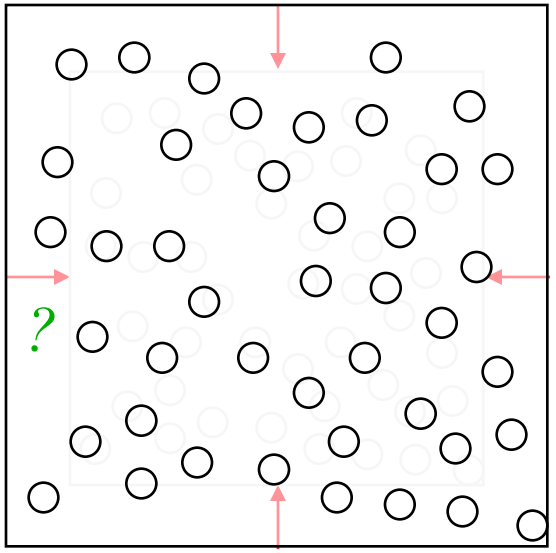
Scale all positions in proportion



Volume-change Trial Move
1. Specification

- 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*

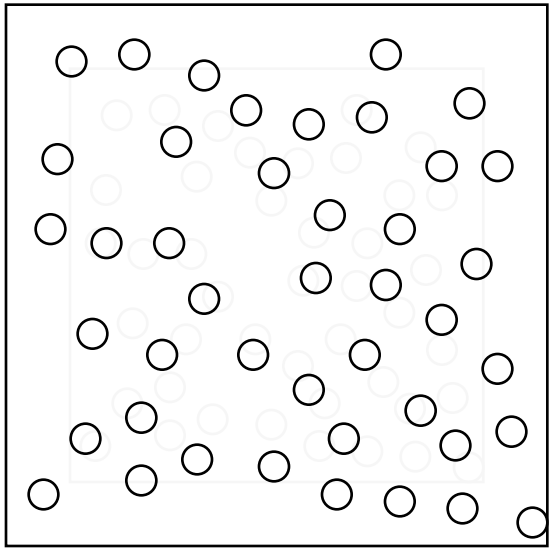
Consider acceptance of new configuration



Volume-change Trial Move
1. Specification

- 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



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

Remember how volume-scaling was used in derivation of virial formula

Volume-change Trial Move
2. Analysis of Trial Probabilities

- Detailed specification of trial moves and probabilities

Event [reverse event]	Probability [reverse probability]
Select V^{new} [select V^{old}]	$1/(2\ \delta V)$ $[1/(2\ \delta V)]$
Accept move [accept move]	$\mathrm{Min}(1,\chi)$ $[\mathrm{Min}(1,1/\chi)]$

Forward-step trial probability $\frac{1}{2\delta V}\times\min(1,\chi)$

Reverse-step trial probability $\frac{1}{2\delta V}\times\min(1,\frac{1}{\chi})$

χ is formulated to satisfy detailed balance

Volume-change Trial Move
3. Analysis of Detailed Balance

Forward-step trial probability $\frac{1}{2\delta V} \times \min(1, \chi)$

Reverse-step trial 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
3. Analysis of Detailed Balance

Forward-step trial probability $\frac{1}{2\delta V}\times\min(1,\chi)$

Reverse-step trial probability $\frac{1}{2\delta V}\times\min(1,\frac{1}{\chi})$

Detailed balance

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

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

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
3. Analysis of Detailed Balance

Forward-step trial probability $\frac{1}{2\delta V}\times\min(1,\chi)$

Reverse-step trial probability $\frac{1}{2\delta V}\times\min(1,\frac{1}{\chi})$

Detailed balance

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

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

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

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

Acceptance probability

Volume-change Trial Move
4. Alternative Formulation

- Step in ln(V) instead of V
  - *larger steps at larger volumes, smaller steps at smaller volumes*

Limiting distribution

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

Trial move

$$V^{new} = V^{old} e^{\delta(\ln V)} \qquad (\ln V)^{new} = (\ln V)^{old} + \delta(\ln V)$$

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

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

Volume-change Trial Move
5. Simulation Example

Have a look at a simple NPT MC simulation applet

If the link doesn't work, here's the URL:

http://www.eng.buffalo.edu/~kofke/applets/nptMCLJ.html

Summary

- Monte Carlo simulation is the application of MC integration to molecular simulation
- Trial moves made in MC simulation depend on governing ensemble
  - *many trial moves are possible to sample the same ensemble*
- Careful examination of underlying transition matrix and limiting distribution give acceptance probabilities
  - *particle displacement*
  - *volume change*
- Next up: simple biasing methods