Review

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

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

- 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

Entire Simulation
- Initialization
- Reset block sums
- New configuration
- Add to block sum
- Compute block average
- Compute final results

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

“cycle” or “sweep”
Move each atom once (on average)

“block”
100’ s or 1000’ s of cycles
Independent “measurement”
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*
    \[ \ln(\pi_{\text{new}}/\pi_{\text{old}}), \ln(\tau_{ij}/\tau_{ji}) \]
    Hold 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:
  .

![Diagram of molecule configurations]
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 $2\delta$

Consider a region about it
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 $2\delta$ 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 $2\delta$ 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 $2\delta$ 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 $2\delta$ centered on the current position of the atom
- Limiting probability distribution
  - canonical ensemble
    \[ \pi(r^N)dr^N = \frac{1}{Z_N} e^{-\beta U(r^N)} dr^N \]
- 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

<table>
<thead>
<tr>
<th>Event</th>
<th>Probability</th>
<th>Forward-step trial probability</th>
<th>Reverse-step trial probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Select molecule k</td>
<td>1/N</td>
<td>$\frac{1}{N} \times \frac{1}{v} \times \min(1, \chi)$</td>
<td>$\frac{1}{N} \times \frac{1}{v} \times \min(1, \frac{1}{\chi})$</td>
</tr>
<tr>
<td>[select molecule k]</td>
<td>[1/N]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Move to $r^{\text{new}}$</td>
<td>$v = (2\delta)^d$</td>
<td>1/v</td>
<td>$\frac{1}{N} \times \frac{1}{v} \times \min(1, \chi)$</td>
</tr>
<tr>
<td>[move back to $r^{\text{old}}$]</td>
<td></td>
<td>[1/v]</td>
<td></td>
</tr>
<tr>
<td>Accept move</td>
<td>$\min(1, \chi)$</td>
<td>$\min(1, \chi)$</td>
<td>$\chi$ is formulated to satisfy detailed balance</td>
</tr>
<tr>
<td>[accept move]</td>
<td>[min(1, $1/\chi$)]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\chi$ is formulated to satisfy 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:
\[ \pi_i \pi_{ij} = \pi_j \pi_{ji} \]

Limiting distribution:
\[ \pi(r^N)dr^N = \frac{1}{Z_N} e^{-\beta U(r^N)}dr^N \]
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

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

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

Limiting distribution

\[
\pi(r^N) dr^N = \frac{1}{Z_N} e^{-\beta U(r^N)} dr^N
\]
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**

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

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

\[e^{-\beta U^{\text{old}}} \chi = e^{-\beta U^{\text{new}}}\]

**Acceptance probability**

\[\chi = e^{-\beta (U^{\text{new}} - U^{\text{old}})}\]
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
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 $s^N$
- Basic trial:
Volume-change Trial Move

1. Specification

- Gives new configuration of different volume and same $N$ and $s^N$
- Basic trial:
  - Select a random value for volume change by some amount within $\pm \delta V$
Volume-change Trial Move
1. Specification

- 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

1. Specification

- 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*
Volume-change Trial Move

1. Specification

- 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

1. Specification

- 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*

\[
\pi \left( (Vs)^N \right) = \frac{1}{\Delta} e^{-\beta U((Vs)^N) - \beta PV} V^N ds^N dV
\]

Examine underlying transition probabilities to formulate acceptance criterion

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

<table>
<thead>
<tr>
<th>Event [reverse event]</th>
<th>Probability [reverse probability]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Select ( V^{\text{new}} ) [select ( V^{\text{old}} )]</td>
<td>( \frac{1}{2\delta V} ) [( \frac{1}{1/2\delta V} )]</td>
</tr>
<tr>
<td>Accept move [accept move]</td>
<td>Min(1,( \chi )) [Min(1,1/( \chi ))]</td>
</tr>
</tbody>
</table>

**Forward-step trial probability**

\[
\frac{1}{2\delta V} \times \min(1, \chi)
\]

**Reverse-step trial probability**

\[
\frac{1}{2\delta V} \times \min(1, \frac{1}{\chi})
\]

\( \chi \) 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
\[ \pi_i \pi_{ij} = \pi_j \pi_{ji} \]

Limiting distribution
\[ \pi \left( (Vs)^N \right) = \frac{1}{\Delta} e^{-\beta U (Vs)^N} - \beta PV \cdot V^N ds^N dv \]
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
\[
\begin{bmatrix}
\pi_i \\
\pi_{ij}
\end{bmatrix} = \begin{bmatrix}
\pi_j \\
\pi_{ji}
\end{bmatrix} = \frac{1}{\Delta_N} \begin{bmatrix}
\frac{1}{2\delta V} \times \min(1, \chi) \\
\frac{1}{2\delta V} \times \min(1, \frac{1}{\chi})
\end{bmatrix}
\]

Limiting distribution
\[
\pi \left( (Vs)^N \right) = \frac{1}{\Delta} e^{-\beta(U + PV) - \beta PV} V^N ds^N dV
\]
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
\[
\begin{bmatrix}
\pi_i \\
\pi_{ij}
\end{bmatrix}
\begin{bmatrix}
\frac{1}{2\delta V} \times \min(1, \chi)
\end{bmatrix}
= 
\begin{bmatrix}
\pi_j \\
\pi_{ji}
\end{bmatrix}
\begin{bmatrix}
\frac{1}{2\delta V} \times \min(1, \frac{1}{\chi})
\end{bmatrix}
\]

\[
e^{-\beta(U_{old} + PV_{old})} (V_{old})_N
\Delta
= 
e^{-\beta(U_{new} + PV_{new})} (V_{new})_N
\Delta
\]

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

\[
\pi((Vs)^N) = \frac{1}{\Delta} e^{-\beta_U ((Vs)^N) - \beta PV N + 1} d s^N d \ln V
\]

\[
V^{\text{new}} = V^{\text{old}} e^{\delta(\ln V)} \quad (\ln V)^{\text{new}} = (\ln V)^{\text{old}} + \delta(\ln V)
\]

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

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