Monte Carlo Simulation

Outline

- Basic statistical mechanics
- Why Monte Carlo technique?
- Random vs Importance Sampling
- Metropolis Method
- Basic Algorithm
- Simulating hard fluids
- Configurational bias Monte Carlo

The classical expression for the partition function is given by

$$Q = c \int dp^N dq^N \exp\left[-H(p^N q^N)/k_B T \right]$$

In general it is not possible to compute the above integral either through MC or MD. $H(p^N q^N)$ is the Hamiltonian of the system. C = 1/(h^{3N}N!)

The ensemble average of any quantity A is given by

$$\langle A \rangle = \frac{\int dp^N dq^N A(p^N q^N) \exp\left[-H(p^N q^N)/k_B T \right]}{\int dp^N dq^N \exp\left[-H(p^N q^N)/k_B T \right]}$$

Integration on p can be carried out easily as Hamiltonian has a quadratic dependence on p. The integration on q is hard to evaluate.

Review

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

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

- 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*

Markov Processes

- Stochastic process
  - *movement through a series of well-defined states in a way that involves some element of randomness*
  - *for our purposes,“states” are microstates in the governing ensemble*
- Markov process
  - *stochastic process that has no memory*
  - *selection of next state depends only on current state, and not on prior states*
  - *process is fully defined by a set of transition probabilities* π_{ij}

    π_{ij} = probability of selecting state j next, given that presently in state i.

    Transition-probability matrix Π collects all π_{ij}

Transition-Probability Matrix

○ Example

- *system with three states*

If in state 1, will stay in state 1 with probability 0.1

If in state 1, will move to state 3 with probability 0.4

$$\Pi \equiv \begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{13} \\ \pi_{21} & \pi_{22} & \pi_{23} \\ \pi_{31} & \pi_{32} & \pi_{33} \end{pmatrix} = \begin{pmatrix} \boxed{0.1} & 0.5 & \boxed{0.4} \\ 0.9 & 0.1 & \boxed{0.0} \\ 0.3 & 0.3 & 0.4 \end{pmatrix}$$

Never go to state 3 from state 2

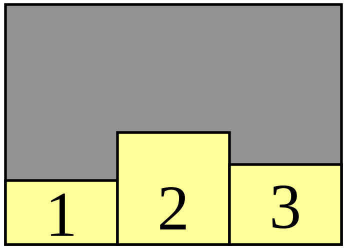
○ Requirements of transition-probability matrix

- *all probabilities non-negative, and no greater than unity*
- *sum of each row is unity*
- *probability of staying in present state may be non-zero*

Distribution of State Occupancies

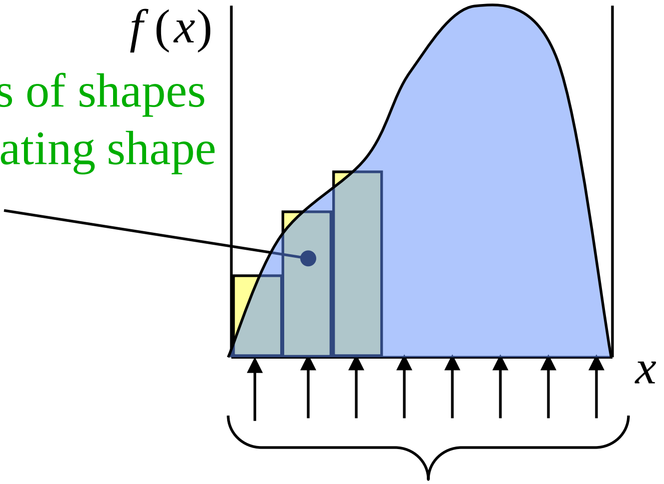
- Consider process of repeatedly moving from one state to the next, choosing each subsequent state according to Π
  - $1 \to 2 \to 2 \to 1 \to 3 \to 2 \to 2 \to 3 \to 3 \to 1 \to 2 \to 3 \to \mathit{etc.}$
- Histogram the occupancy number for each state

$$\left.\begin{array}{l} \bullet\quad n_1 = 3 \\ \bullet\quad n_2 = 5 \\ \bullet\quad n_3 = 4 \end{array}\right\} \qquad\qquad \begin{array}{l} \pi_1 = 0.25 \\ \pi_2 = 0.42 \\ \pi_3 = 0.33 \end{array}$$



- After very many steps, a limiting distribution emerges

Suppose we want to evaluate such integral by using numerical quadrature, for example using Simpson’s rule



Sum areas of shapes approximating shape of curve

n uniformly separated points

Evaluating the general integral $I = \int_a^b f(x)dx$

○ Quadrature formula

$$I \approx \Delta x \sum_{i=1}^{n} f(x_i) = \frac{b-a}{n} \sum_{i=1}^{n} f(x_i)$$

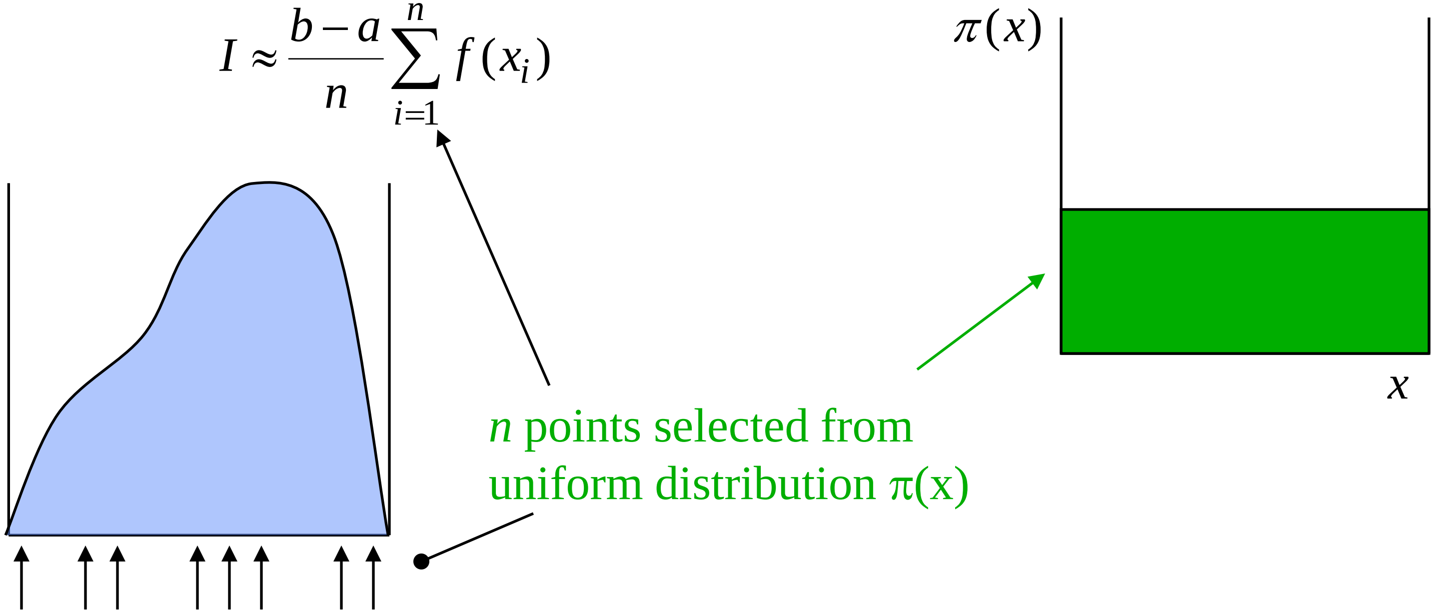
Suppose we want to carry out the qudrature by evaluating the integrand on a mesh of points in the DN dimensional configuration space (3N for 3-d system).

If we take n equidistant points along each coordinate axis, the total number of point at which the integrand needs to be evaluated is n^{DN}.

If we have 100 particles in in 3-d and if we take n = 5 (very small) then we have to evaluate 5^{300}, this is impossible to compute and also not desirable.

Monte Carlo Scheme (random sampling)

- Stochastic approach
- Same quadrature formula, different selection of points



$$I \approx \frac{b-a}{n}\sum_{i=1}^{n} f(x_i)$$

n points selected from uniform distribution π(x)

As n →∞ this will give the correct value of the integral. However, like the previous quadrature method this is of little use because most of the computing is spent on points where Boltzmann factor is negligible

Solution : Importance sampling

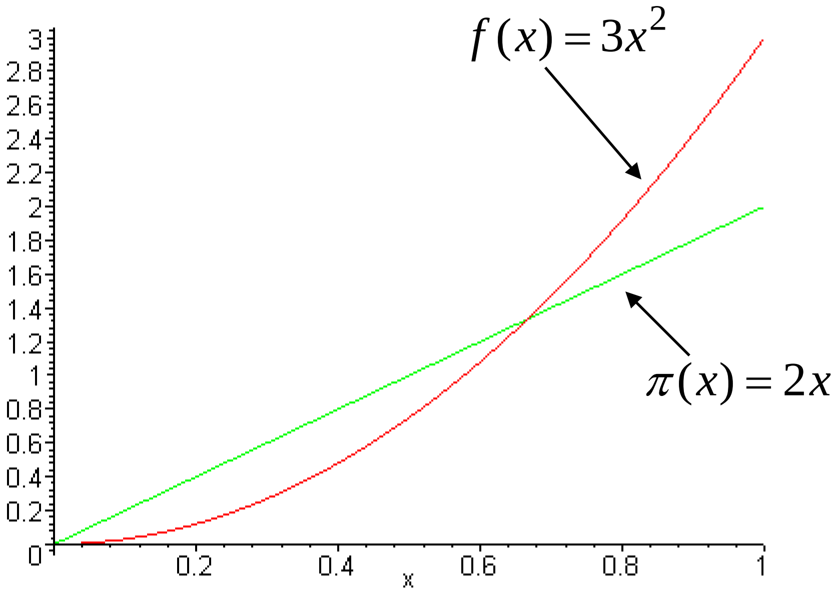
Sample many points where Boltzmann factor is large and fewer points in other regions: basic idea behind Importance sampling

Importance Sampling

- Put more quadrature points in regions where integral receives its greatest contributions
- Return to 1-dimensional example

$$I = \int_0^1 3x^2 dx$$

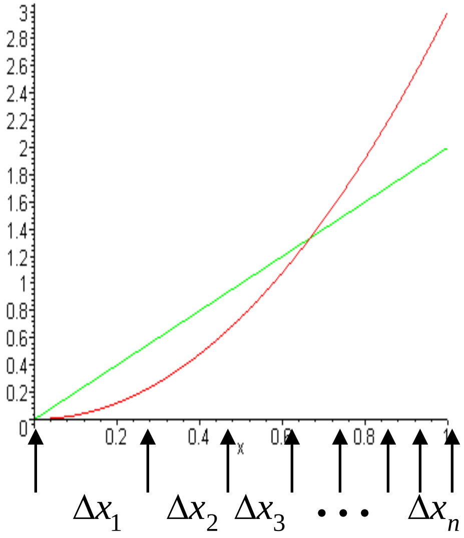
- Most contribution from region near x = 1
- Choose quadrature points not uniformly, but according to distribution $\pi(x)$
  - *linear form is one possibility*
- How to revise the integral to remove the bias?



The Importance-Sampled Integral

- Consider a rectangle-rule quadrature with unevenly spaced abscissas

$$I \approx \sum_{i=1}^{n} f(x_i)\Delta x_i$$



- Spacing between points
  - *reciprocal of local number of points per unit length*

$$\Delta x_i = \frac{b-a}{n}\frac{1}{\pi(x_i)}$$

Greater $\pi \rightarrow$ more points $\rightarrow$ smaller spacing

- Importance-sampled rectangle rule
  - *Same formula for MC sampling*

$$I \approx \frac{b-a}{n}\sum_{\substack{i=1 \\ \pi(x)}}^{n}\frac{f(x_i)}{\pi(x_i)}$$

choose x points according to π

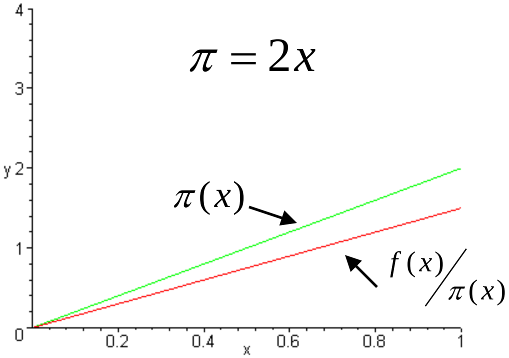
Choosing a Good Weighting Function

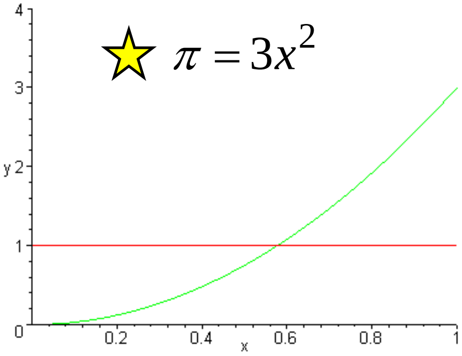
- MC importance-sampling quadrature formula

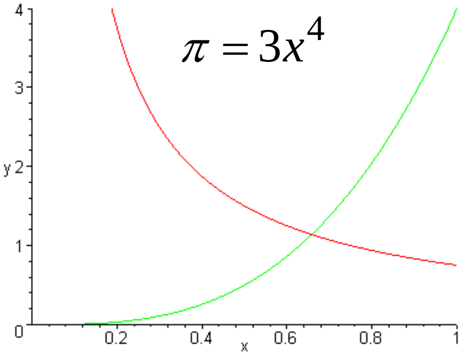
$$I \approx \frac{1}{n}\sum_{i=1}^{n}\frac{f(x_i)}{\pi(x_i)}$$

$\pi(x)$

- Do not want π(x) to be too much smaller or too much larger than f(x)
  - *too small leads to significant contribution from poorly sampled region*
  - *too large means that too much sampling is done in region that is not (now) contributing much*







Variance determines the choice of weighting function

$$\sigma_I^2 = \frac{1}{n^2}\sum_{i=1}^{n}\sum_{j=1}^{n}\left\langle\left(\frac{f(x_i)}{\pi(x_i)}-\left\langle\frac{f}{\pi}\right\rangle\right)-\left(\frac{f(x_j)}{\pi(x_j)}-\left\langle\frac{f}{\pi}\right\rangle\right)\right\rangle$$

$$= \frac{1}{n^2}\sum_{i=1}^{n}\left\langle\left(\frac{f(x_i)}{\pi(x_i)}-\left\langle\frac{f}{\pi}\right\rangle\right)^2\right\rangle$$

$$= \frac{1}{n}\left[\left\langle\left(\frac{f}{\pi}\right)^2\right\rangle-\left\langle\frac{f}{\pi}\right\rangle^2\right]$$

$$\left\langle\left(\frac{f}{\pi}\right)^2\right\rangle = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{f(x_i)}{\pi(x_i)}\right)^2$$

Variance still goes as 1/n, but the magnitude of this variance can be reduced dramatically by choosing π(x) such that f(x)/ π(x) is a smooth function of x.

Variance in Importance Sampling Integration

- Choose π to minimize variance in average

$$\sigma_I^2 = \frac{1}{n}\left\{\int\left[\frac{f(x)}{\pi(x)}\right]^2 \pi(x)dx - \left[\int\left[\frac{f(x)}{\pi(x)}\right]\pi(x)dx\right]^2\right\}$$

$f(x) = 3x^2$

$\pi(x)$	σ_I	n = 100	n = 1000
1	$2/\sqrt{5n}$	0.09	0.03
$2x$	$1/\sqrt{8n}$	0.04	0.01
$3x^2$	0	0	0
$4x^3$	$1/\sqrt{8n}$	0.04	0.01

- Smallest variance in average corresponds to π(x) = c × f(x)
  - *not a viable choice*
  - *the constant here is selected to normalize* π
  - *if we can normalize* π *we can evaluate* $\int \pi(x)dx$
  - *this is equivalent to solving the desired integral of f(x)*

The Metropolis Method

The classical expression for the partition function is given by

$$Q = c\int dp^N dq^N \exp\left[-H(p^N q^N)/k_B T\right]$$

In general it is not possible to compute the above integral either through MC or MD. The ensemble average of any quantity A is given by

$$\langle A\rangle = \frac{\int dp^N dq^N A(p^N q^N)\exp\left[-H(p^N q^N)/k_B T\right]}{\int dp^N dq^N \exp\left[-H(p^N q^N)/k_B T\right]}$$

This is the ratio of two integrals and Metropolis showed that Monte Carlo methods can be used to efficiently compute the ratio.

Let us define the probability density ρ of finding the system in a configuration (q^N)

$$\rho(p^N q^N) = \exp\left[-H(p^N q^N)/k_B T\right]/Q$$

In terms of this probability density the configuration average of any quantity A is given by

$$\langle A\rangle = \int dp^N dq^N A(p^N q^N)\,\rho(p^N q^N)$$

So if by some means we can generate points in the configuration space according the the above probability density we can evaluate the above average as

$$\langle A\rangle = \frac{1}{n}\sum_{i=1}^{n} k_i A(q_i^N)$$

k_i is the number of points generated per unit volume around a point q^N and is equal to nρ (n is the total number of points)

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This is the ratio of two integrals and Monte Carlo methods can be used to efficiently compute the ratio.

$$\rho(p^N q^N) = \exp\left[-H(p^N q^N)/k_B T\right]/Q$$

This the probability of the state with energy $H(p^N q^N)$

$$\langle A\rangle = \int dp^N dq^N A(p^N q^N)\,\rho(p^N q^N)$$

How to generate points in configuration space

Metropolis Algorithm 1.

- ○ Prescribes transition probabilities to satisfy detailed balance, given desired limiting distribution
- ○ Recipe:
  From a state *i*…
  - *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* $(\pi_{ii} \neq 0)$

Metropolis, Rosenbluth, Rosenbluth, Teller and Teller,
J. Chem. Phys., ***21*** *1087 (1953)*

$\pi(o\rightarrow n)$ is the transition probability to go from o (old) to n (new)
$\pi(n\rightarrow o)$ is the transition probability to go from n (new) to o (old)
$N(o)$ and $N(n)$ are the probability of finding the system in configuration o and n

Detailed balance requires

$$N(o)\,\pi(o\rightarrow n) = N(n)\,\pi(n\rightarrow o)$$

Denote the transition matrix that determines the probability of performing a trial move from o to n by $\alpha(o\rightarrow n)$ where α is the underlying matrix of the Markov chain. We also denote the probability of accepting a trial move from o to n by $\mathrm{acc}(o\rightarrow n)$.

$$\pi(o\rightarrow n) = \alpha(o\rightarrow n)\,\mathrm{acc}(o\rightarrow n)$$

In the original Metropolis scheme α was chosen to be symmetric : $\alpha(o\rightarrow n)= \alpha(n\rightarrow o)$. In terms of α we have

$$N(o)\,\mathrm{acc}(o\rightarrow n) = N(n)\,\mathrm{acc}(n\rightarrow o)$$

From the above equation we have

$$\frac{acc(o \rightarrow n)}{acc(n \rightarrow o)} = \frac{N(n)}{N(o)} = \exp(-\beta[U(n) - U(o)])$$

Various choices of the acceptance probability satisfy the above condition. Metropolis choose the following

$$\begin{aligned} acc(o \rightarrow n) &= N(n)/N(o) \quad && if \;\; N(n) < N(o) \\ &= 1 && if \; N(n) \geq N(o) \end{aligned}$$

So the transition probability for going from a state o to a state n is given by

$$\begin{aligned} \pi(o \rightarrow n) &= \alpha(o \rightarrow n) && N(n) \geq N(o) \\ &= \alpha(o \rightarrow n)\,[N(n)/N(o)] \quad && N(n) < N(o) \end{aligned}$$

$$\pi(o \rightarrow n) = 1 - \textstyle\sum_{n \neq o} \pi(o \rightarrow n)$$

The Algorithm

- Select a particle at random and calculate its energy $U(r^N)$
- Give the particle a random displacement $r' = r + dr$ and rotation if (linear and non-linear molecule and compute the new energy $U(r'^N)$
- Accept the move from r^N to r'^N with probability

$$acc(o \rightarrow n) = \min(1, \exp\{-\beta[U(r'^N) - U(r^N)]\})$$

Generating trial displacement

```
for (j = 0; j < NDIM; ++j) {
      dr[j] = (2.0 * ran3(i_ran) - 1.0) * dr_max;
      mol_coords_trial[j] += dr[j];
    }
```

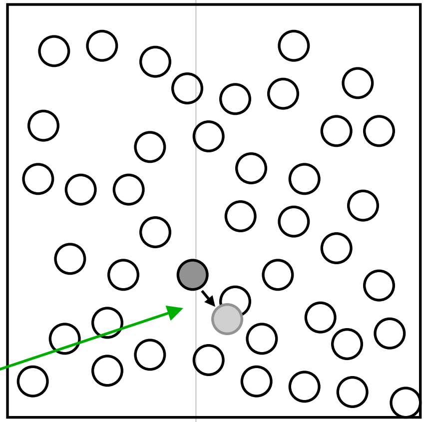
Generating trial rotation

```
  do {
      mag2 = 0.0;
      for (i = 1; i < 4; ++i){
         q[i] = (2.0 * ran3(i_ran) - 1.0) * du_max;
         mag2 += SQR(q[i]);
         } } while (mag2 > 1.0);
   q[0] = sqrt(1 - mag2);
/* Compute the elements of the rotation matrix. */
   a11 = SQR(q[0]) + SQR(q[1]) - SQR(q[2]) - SQR(q[3]);
   a12 = 2.0 * q[1] * q[2] + 2.0 * q[0] * q[3];
   a13 = 2.0 * q[1] * q[3] - 2.0 * q[0] * q[2];
   a21 = 2.0 * q[1] * q[2] - 2.0 * q[0] * q[3];
   a22 = SQR(q[0]) - SQR(q[1]) + SQR(q[2]) - SQR(q[3]);
   a23 = 2.0 * q[2] * q[3] + 2.0 * q[0] * q[1];
   a31 = 2.0 * q[1] * q[3] + 2.0 * q[0] * q[2];
   a32 = 2.0 * q[2] * q[3] - 2.0 * q[0] * q[1];
   a33 = SQR(q[0]) - SQR(q[1]) - SQR(q[2]) + SQR(q[3]);
```

Monte Carlo Simulation

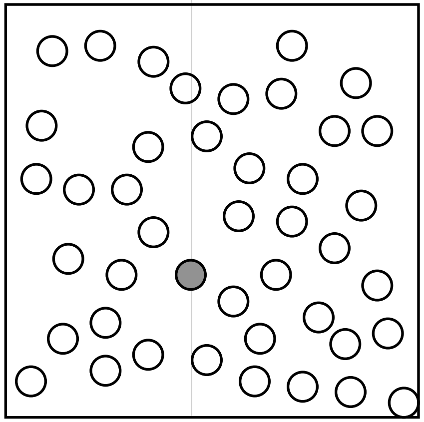
- MC techniques applied to molecular simulation
- Almost always involves a Markov process
  - *move to a new configuration from an existing one according to a well-defined transition probability*
- Simulation procedure
  - *generate a new "trial" configuration by making a perturbation to the present 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*

State k



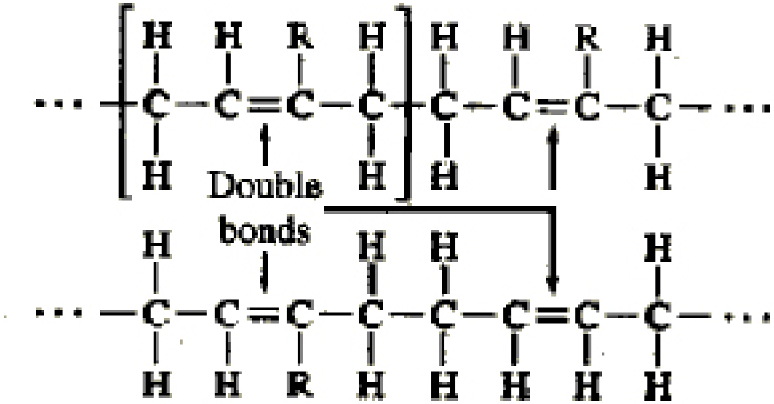
$$\frac{e^{-\beta U^{new}}}{e^{-\beta U^{old}}}$$

State k+1



Polymers are long molecular chains with chemically connected atomic groups (“monomers”)

Some of the common polymer chains

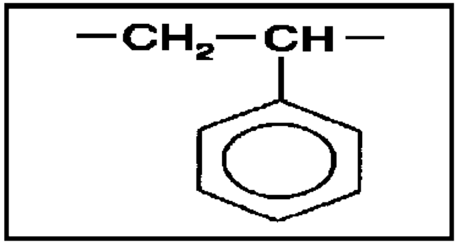


Number of monomer units in a chain is very large: N >>1

For laboratory synthesized polymer $N=10^2\text{-}10^4$

For biological polymer such as DNA $N = 10^9\text{-}10^{10}$

Poly(ethylene)



Structure of Polystyrene

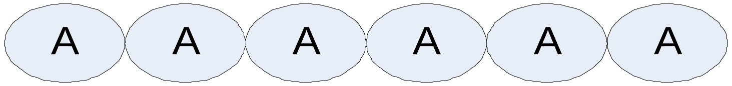
Some fundamental properties of polymeric systems

- ❑The chain structure of constituent molecules
- ❑The monomer units do not have freedom of independent translational motion and hence polymers do not have translational entropy (“poor in entropy)
- ❑Polymer chains are flexible (this is one of the main reasons for their special properties). This also make their study difficult as they can adopt various conformations.

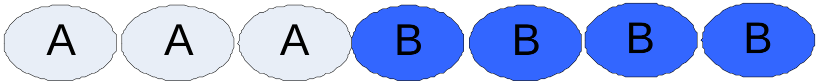
Various kind of polymer architecture

Linear polymer:

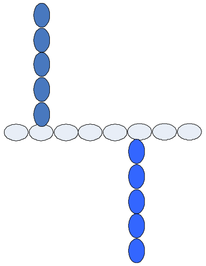
- Homopolymer: linking together N monomers of only one chemically distinct type



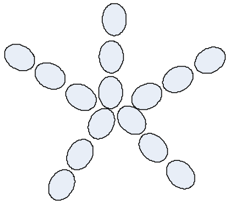
Copolymer: linking together N monomers of two or more chemically distinct types



Branched Polymer:



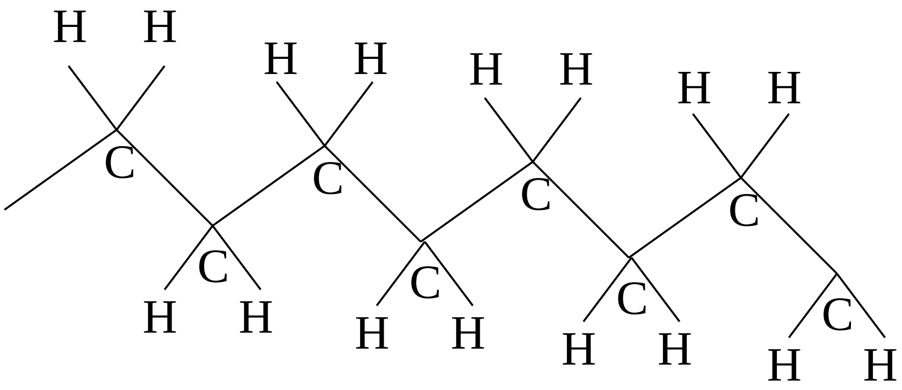
Star Polymer :



Hyper branched Polymer : Dendrimer

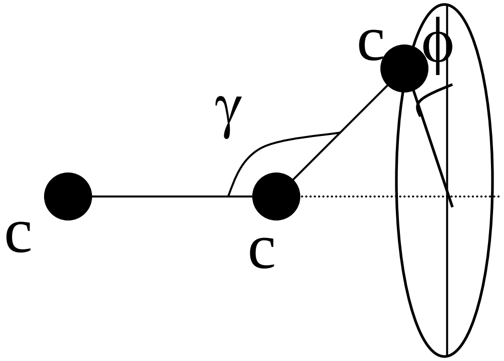
Flexibility mechanism of a polymer chain

Rotational-isomeric flexibility mechanism



At T=0 all the monomers will have trans conformation

Trans conformation of PE chain



At non-zero temperature rotation with fixed γ by changing the angle of internal rotation ϕ is possible. Any non zero ϕ ngives gives conformations other than trans. This kind of flexibility is called rotational isomeric flexibility mechanism. Different ϕ corresponds to different rotational isomers.

Persistence flexibility mechanism

When rotational isomers are not allowed thermal vibrations around the equilibrium conformation play important role

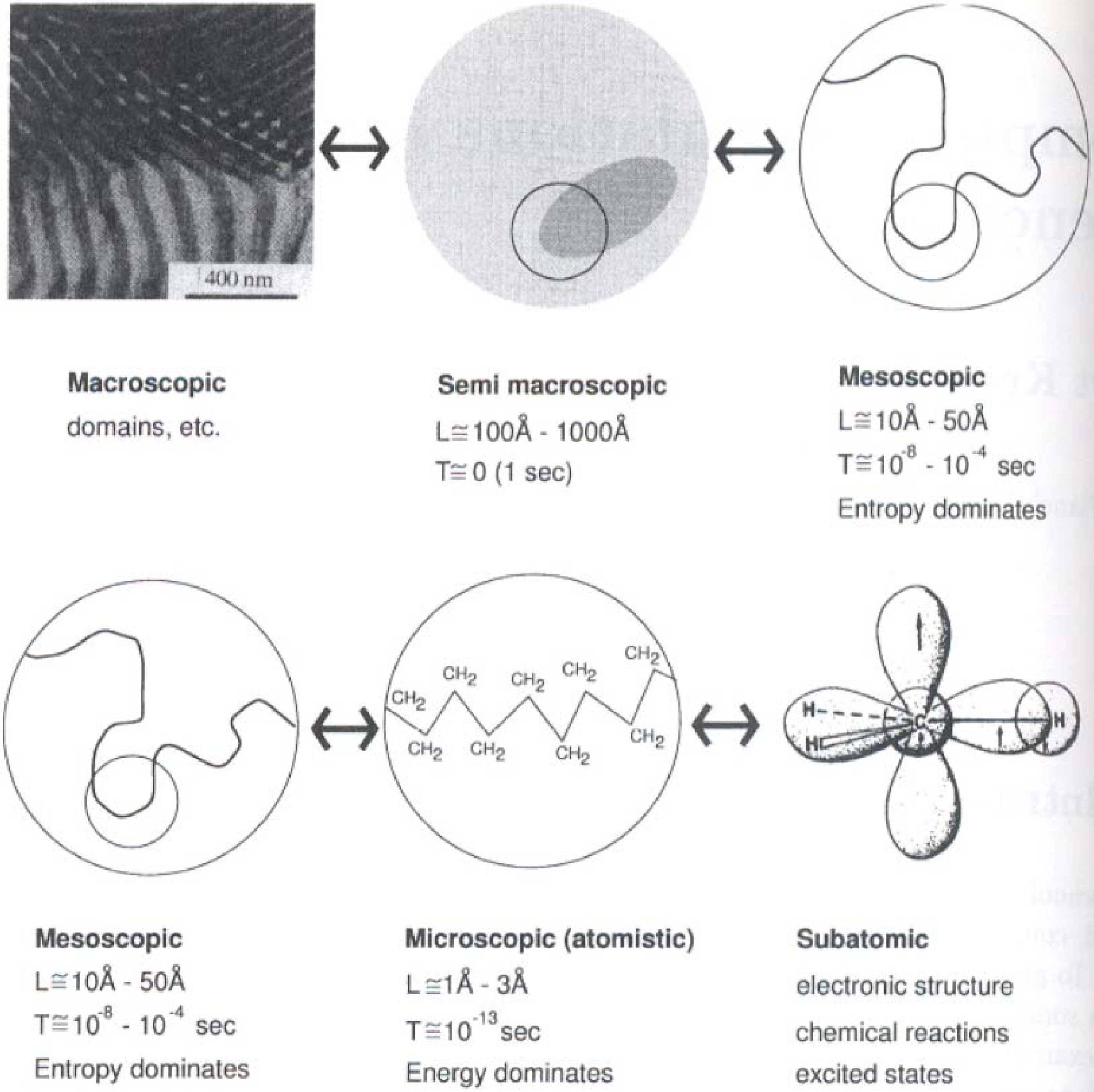
For poly-peptide and DNA molecules their conformation are stabilized by hydrogen bonds and internal rotation is not possible. In such case thermal vibrations around the equilibrium conformation gives rise to the persistence flexibility mechanism.

Freely-jointed flexibility mechanism

In this case flexibility arises from the free rotation of the junction points. Angle can take any value. Not very realistic , good for model theoretical calculations

Different length and time scale in polymeric systems (similar to many other soft-matter systems)

Kremer, NATO ASI School 1999



Macroscopic
domains, etc.

Semi macroscopic
$L \cong 100Å - 1000Å$
$T \cong 0$ (1 sec)

Mesoscopic
$L \cong 10Å - 50Å$
$T \cong 10^{-8} - 10^{-4}$ sec
Entropy dominates

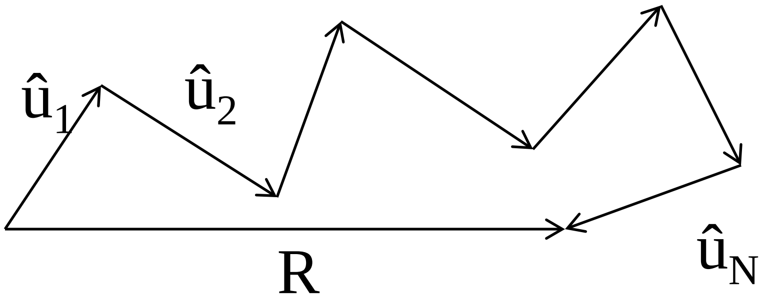
Mesoscopic
$L \cong 10Å - 50Å$
$T \cong 10^{-8} - 10^{-4}$ sec
Entropy dominates

Microscopic (atomistic)
$L \cong 1Å - 3Å$
$T \cong 10^{-13}$ sec
Energy dominates

Subatomic
electronic structure
chemical reactions
excited states

Simplest model of polymer: Random walk model

The simplest model of a polymer is a chain of like monomers, of length *a*, where each link is completely free to rotate in any direction.



Model of freely jointed chain

A polymer of *N* such links is equivalent to a random walk of *N* steps of length *a*.

In one dimension the probability distribution of arriving at X after N steps starting from the origin is given by the binomial distribution

$$P(X, N) = P_{bin}(m, N)$$

with $X = (2m - N)a$ (m forward steps minus $N - m$ backwards steps). Using the properties of the binomial distribution we have

$$\langle X \rangle = 0, \qquad \langle X^2 \rangle = Na^2.$$

End-end distance Root mean square End-end distance

The probability density $p(X)$ (such that $p(X)dX$ gives the probability of ending between X and $X+dX$) is

$$p(X) = \frac{1}{\sqrt{2\pi\sigma_1^2}} \exp\left(-\frac{X^2}{2\sigma_1^2} \right)$$

with $\sigma_1^2 = Na^2$. The large N results also follow from the central limit theorem. Since $X = \sum_{i=1}^{N} x_i$ is the sum of N independent random variables, for large N the distribution is Gaussian, with variance Na^2.

In 3-d we have

$$\vec{R}=(X,Y,Z)=\sum\vec{x}_i$$

Probability distribution function that the end-to-end vector of a chain of N-link is $\vec{R}$ is given by (see Reif Sec. 1.10)

$$p(\vec{R})=\frac{\int\cdots\int d^2x_1 d^2x_2\cdots d^2x_N\,\delta\left(\sum_i x_i-\vec{R}\right)}{\int\cdots\int d^2x_1 d^2x_2\cdots d^2x_N}$$

The distribution looks like

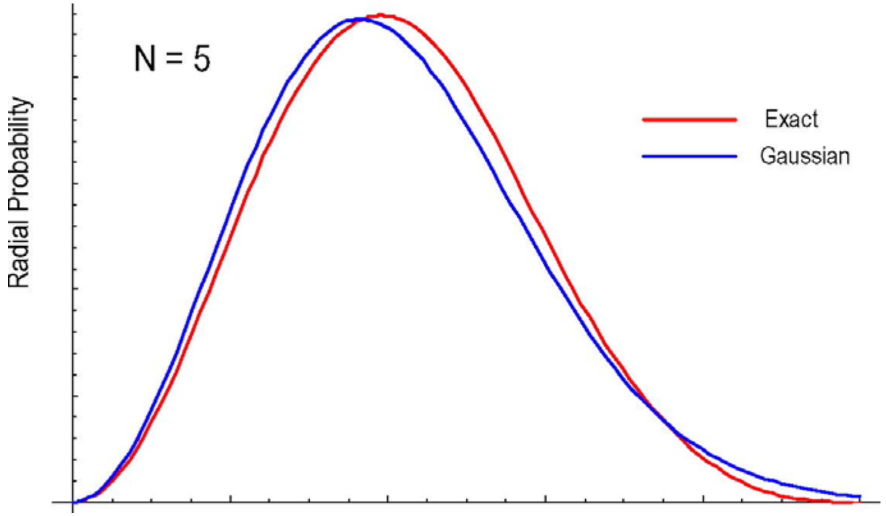
$$p(R)=\frac{1}{2\pi^2a^3}\int\frac{\sin(NQR/L)}{NQR/L}\left[\frac{\sin Q}{Q}\right]^N dQ,\quad where\ we\,have\,Q=qa\,and\ L=Na$$

Using large N limit and using the Gaussian approximation

$$\left[\frac{\sin ka}{ka}\right]^N = \left(1 - \frac{k^2a^2}{6}\right)^N = \exp\left(-\frac{Nk^2a^2}{6}\right)$$

The distribution becomes

$$p(\vec{R}) = \left(\frac{3}{2\pi Na^2}\right)^{3/2} \exp\left[-\frac{3R^2}{2Na^2}\right]$$



Some important definition before we proceed further

Kuhn length

For an ideal chain $<R^2> \sim N \sim L$

Kuhn length of a polymer chain is defined as

$$l = \frac{< R^2 >}{L} \qquad \text{at large L}$$

Persistence length

The orientational correlations of the chain as a function of the contour distance obey

$$\langle \cos\theta \rangle \sim \exp(-s / l_p)$$

θ is the angle between unit vectors u(0) and u(s). l_p is the persistence length

More realistic model (including the bond stiffness)

The freely jointed chain is an oversimplified model for a polymer. Two effects we might want to include are the stiffness against bond bending and the hard-core repulsion of the atomic cores.

Stiff polymers To model the stiffness of a polymer chain we restrict the free rotation of each bond by assuming there is an energy cost for a nonzero angle between successive bonds. The simplest model is to assume the energy depends on the angle between the bonds, but not on the orientation of the plane formed by the bonds. The *Kratky-Porod* model supposes the energy for each bond pair is proportional to ,

with the direction of the *j* th link (a unit vector). The Hamiltonian of this model is (for a polymer of *N*+1 monomers)

$$\vec{t}_j \bullet \vec{t}_{j+1}$$

Kratky Porod Hamiltonian

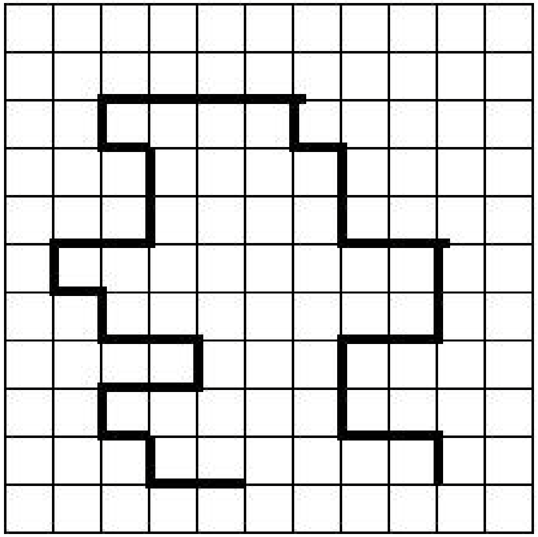
$$H = -K \sum_{j=1}^{N} \vec{t}_j \bullet \vec{t}_{j+1} = -K \sum_{j=1}^{N} \cos\theta_j$$

The model can be exactly solved to give the following expression for root mean-square end-to-end distance

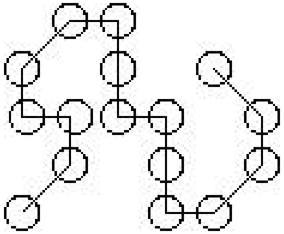
$$\left\langle \vec{R}^2 \right\rangle = a^2 \left\langle \left(\sum \vec{t}_j^{\,2} \right) \right\rangle = a^2 \sum_{ij} \left\langle \vec{t}_i \bullet \vec{t}_j \right\rangle$$

$$\left\langle \vec{R}^2 \right\rangle \approx N a^2 \left(1 + \frac{2c}{1-c} \right) = N a^2 \frac{1+c}{1-c}$$

Different coarse-grained models of polymer

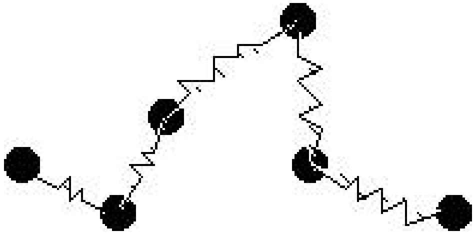


SAW on lattice



Pearl necklace

Pearl-necklace model is the direct generalization of the SAW for the continuous space. The chain consists of hard sphere of diameter and fixed bond length.

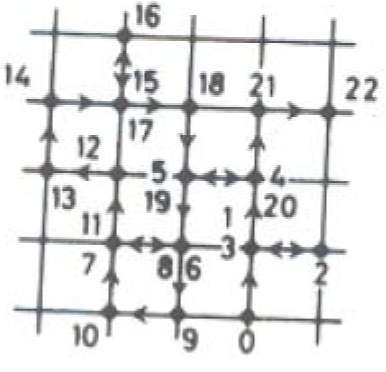


Bead spring model

Most widely used model is the self-avoiding walk (SAW) on lattice. Each lattice site can be occupied only once. It is possible to introduce nearest-neighbor interaction and other generalization.

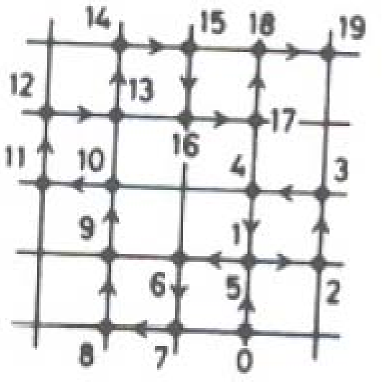
Kremer and Binder Comp. Phys. Reports, 7, 259 (1988)

Random Walk (RW)

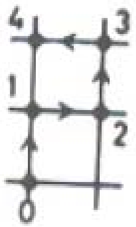


Construction of 22-step random walk (RW) on square lattice. Sites are labeled in the order in which they are visited starting from the origin. At each step we add at random an elementary lattice vector denoted by arrows.

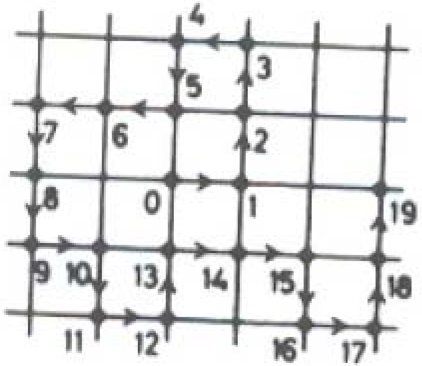
Non-reversible RW



NRRW is same as RW, but immediate reversal is forbidden



Self-avoiding Walk (SAW)



Visiting any lattice site more than once is not allowed

Why lattice model: Lack of self-averaging

Remember end-end distribution is Gaussian in 3-d for freely joined chain

$$p(\vec{R}) = \left(\frac{3}{2\pi N a^2}\right)^{3/2} \exp\left[-\frac{3R^2}{2Na^2}\right]$$

We have mean square end-to-end distance $<R^2> = Na^2$

So the mean square fluctuation in R^2 is

$$\Delta_R^2 \equiv \frac{\left\langle (R^2)^2 \right\rangle - \left\langle R^2 \right\rangle^2}{\left\langle R^2 \right\rangle^2} = \frac{2}{3}$$

This is constant! Which imply lack of self-averaging

Remember from your statmech: relative mean square fluctuation of thermodynamic quantities approaches zero when the number of degrees of freedom approach infinity. Like mean square fluctuation in average energy E = <H>,

$$\Delta_E^2 \equiv \frac{<H^2> - <H>^2}{<H>^2} \propto \frac{1}{N} \rightarrow 0 \quad as\ N \propto \infty$$

A large number of independent samples to be generated in simulation

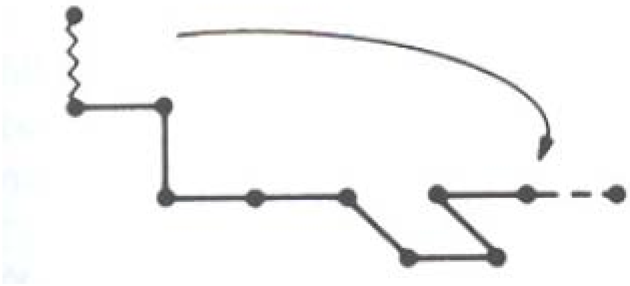
Various examples of Dynamic Monte Carlo Algorithm

The sampling of equilibrium conformations of polymer is usually time consuming because dynamics are dominated by topological constraints. Many “unphysical” trial moves are used for enhanced sampling and equilibration.

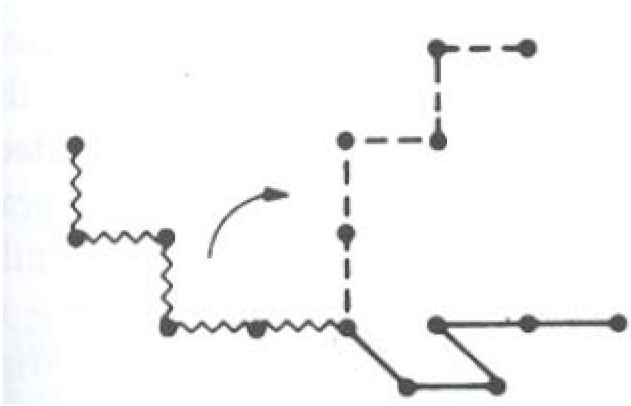
end bond

Bonds indicated as wavy lines are moved to new positions (broken lines), other bonds are not moved

Kink-jump crankshaft



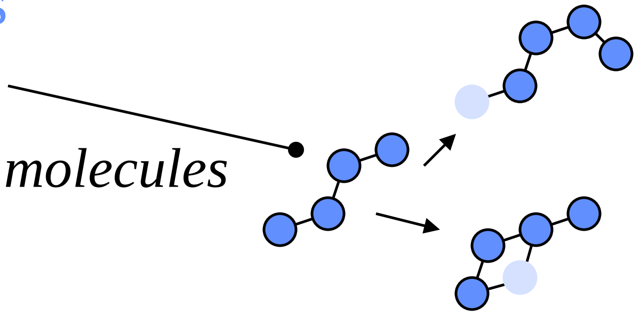
Reptation (Slithering snake) algorithm



Pivot (wiggle) algorithm

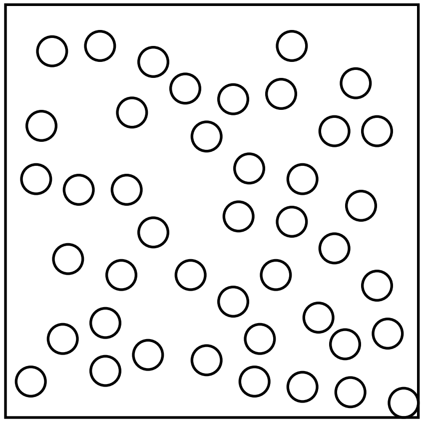
Trial Moves

- 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*



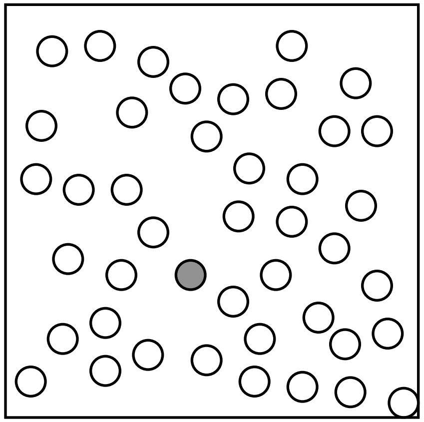
Displacement Trial Move
1. Specification

- 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*



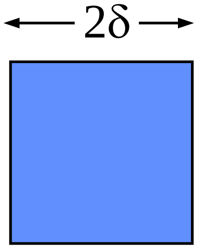
Select an atom at random

Displacement Trial Move

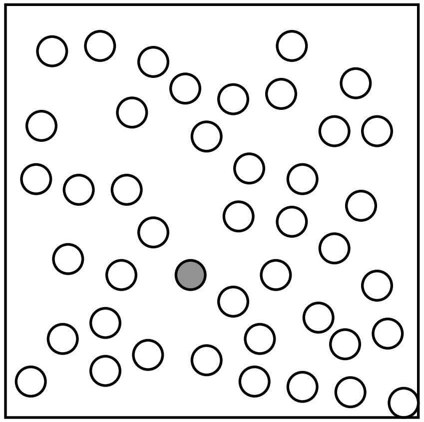
1. Specification

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

    a cubic volume of edge 2δ



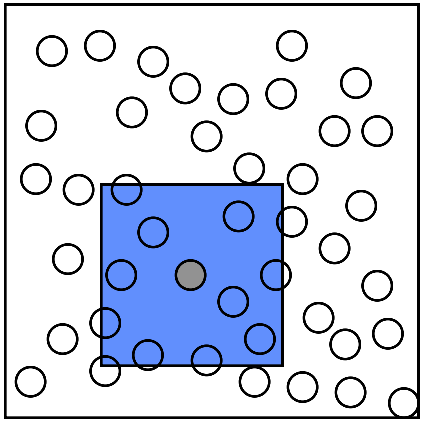
Consider a region about it



Displacement Trial Move
1. Specification

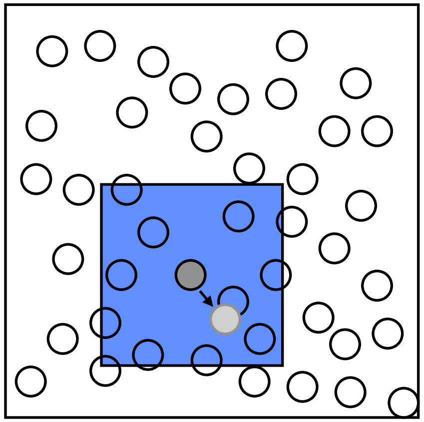
- Gives new configuration of same volume and number of molecules
- Basic trial:
  - *a randomly selected atom*
    a cubic volume of edge 2δ *centered on the current position of the atom*

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*

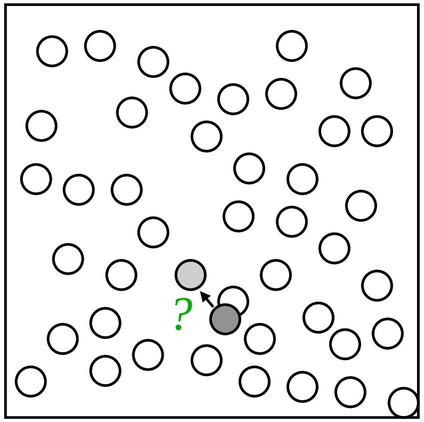


Move atom to point chosen uniformly in region

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

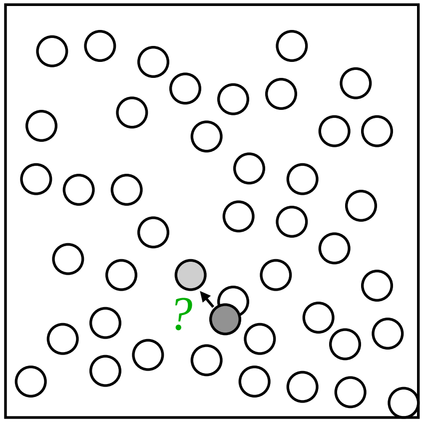


Displacement Trial Move
1. Specification

- 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 Transition Probabilities

○ Detailed specification of trial move and transition 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}]	1/v [1/v]
Accept move [accept move]	min(1,χ) [min(1,1/χ)]

$v = (2\delta)^d$ → 1/v

Forward-step transition probability

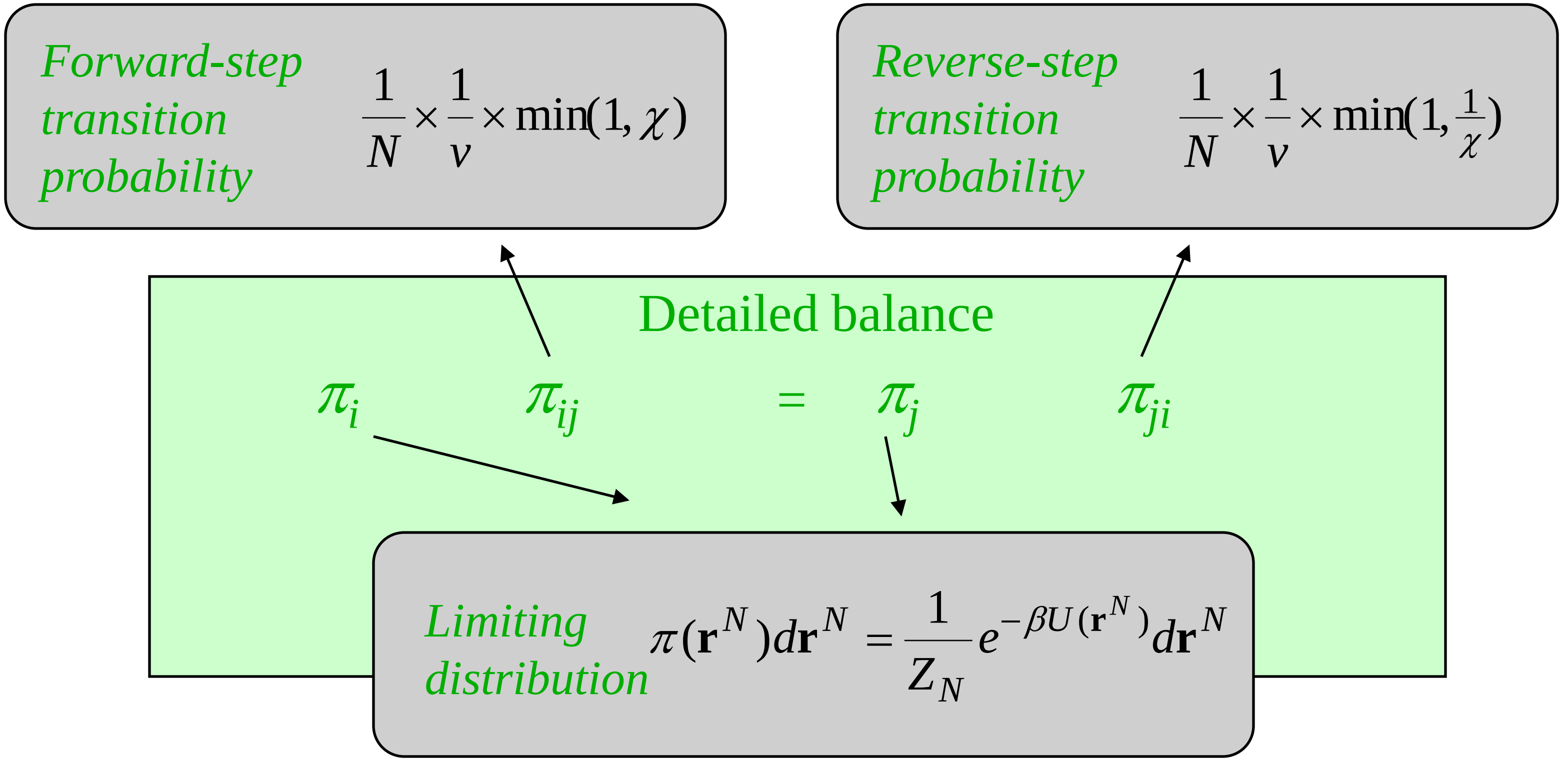
$$\frac{1}{N} \times \frac{1}{v} \times \min(1, \chi)$$

Reverse-step transition probability

$$\frac{1}{N} \times \frac{1}{v} \times \min(1, \frac{1}{\chi})$$

min(1,χ) ← *χ is formulated to satisfy detailed balance*

Displacement Trial Move
3. Analysis of Detailed Balance



Forward-step transition probability

$$\frac{1}{N}\times\frac{1}{v}\times\min(1,\chi)$$

Reverse-step transition probability

$$\frac{1}{N}\times\frac{1}{v}\times\min(1,\tfrac{1}{\chi})$$

Detailed balance

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

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 transition probability

$$\frac{1}{N}\times\frac{1}{v}\times\min(1,\chi)$$

Reverse-step transition probability

$$\frac{1}{N}\times\frac{1}{v}\times\min(1,\tfrac{1}{\chi})$$

Detailed balance

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

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

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 transition probability

$$\frac{1}{N}\times\frac{1}{v}\times\min(1,\chi)$$

Reverse-step transition probability

$$\frac{1}{N}\times\frac{1}{v}\times\min(1,\tfrac{1}{\chi})$$

Detailed balance

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

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

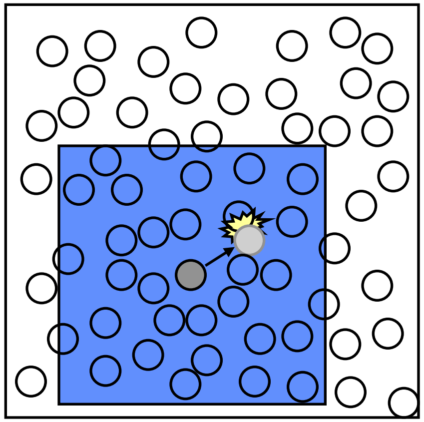
$$e^{-\beta U^{old}}\chi = e^{-\beta U^{new}}$$

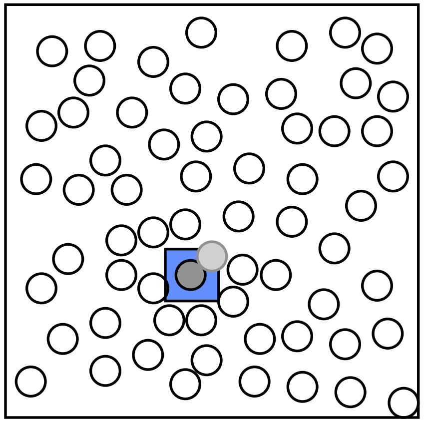
$$\boxed{\chi = e^{-\beta(U^{new}-U^{old})}}$$

Acceptance probability

Displacement Trial Move
5. Tuning

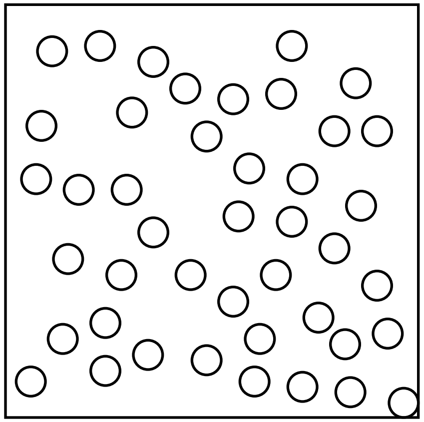
- Size of step is adjusted to reach a target rate of acceptance of displacement trials
  - *typical target is 50%*
  - *for hard potentials target may be lower (rejection is efficient)*


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:
  -

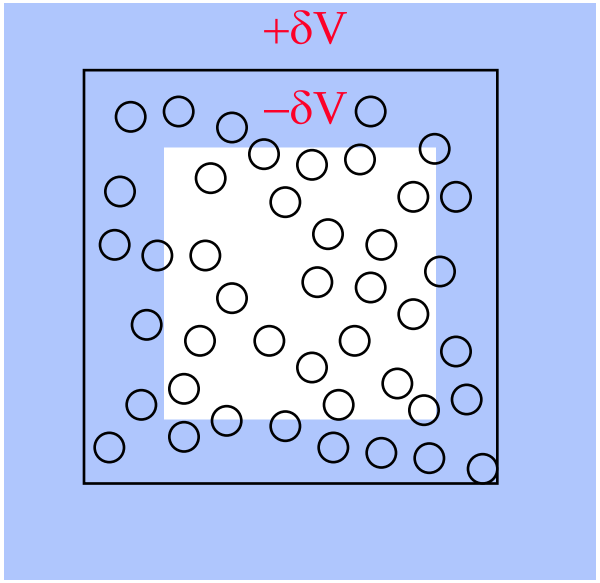


Volume-change Trial Move

1. Specification

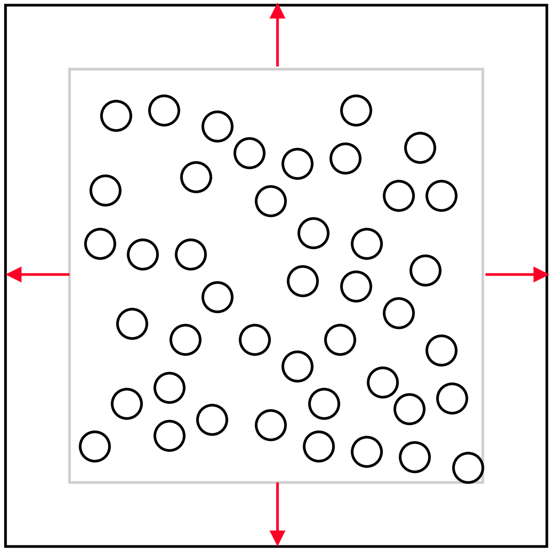
- Gives new configuration of different volume and same N and $\mathbf{s}^N$
- Basic trial:
  - *by some amount within* $\pm\delta V$

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 ±δV,*



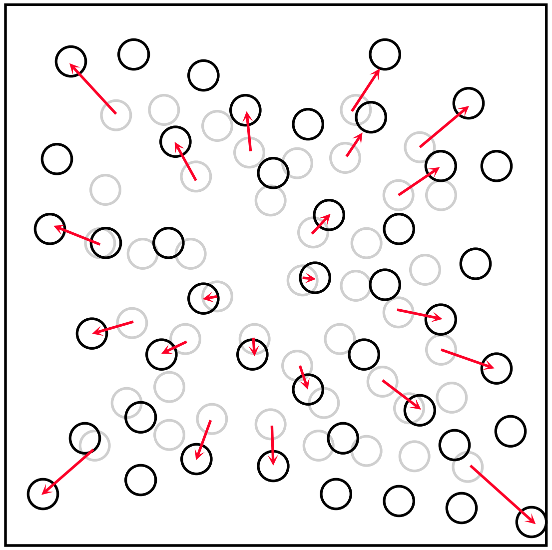
Perturb the total system volume

Volume-change Trial Move

1. Specification

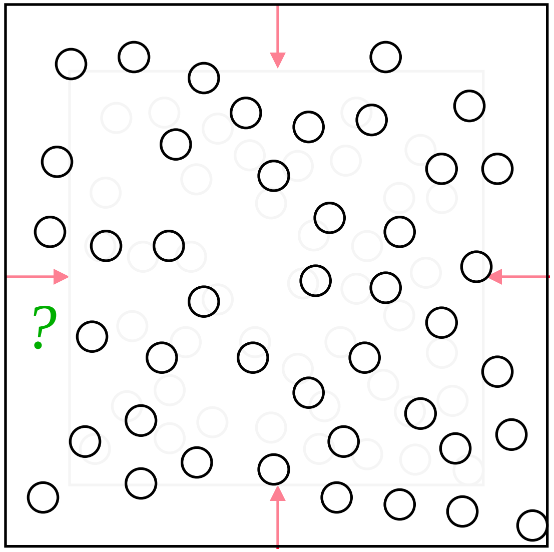
- ○ Gives new configuration of different volume and same N and $\mathbf{s}^N$
- ○ Basic trial:
  - *increase or decrease the total system volume by some amount within ±δV, scaling all molecule centers-of-mass in proportion to the linear scaling of the volume*

Scale all positions in proportion



Volume-change Trial Move
1. Specification

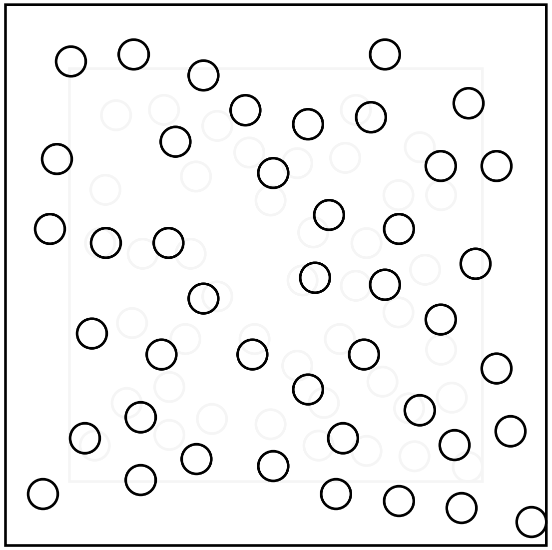
- Gives new configuration of different volume and same N and $\mathbf{s}^N$
- Basic trial:
  - *increase or decrease the total system volume by some amount within ±δV, scaling all molecule centers-of-mass in proportion to the linear scaling of the volume*



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 ±δV, 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 Transition Probabilities

- Detailed specification of trial move and transition 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 transition probability

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

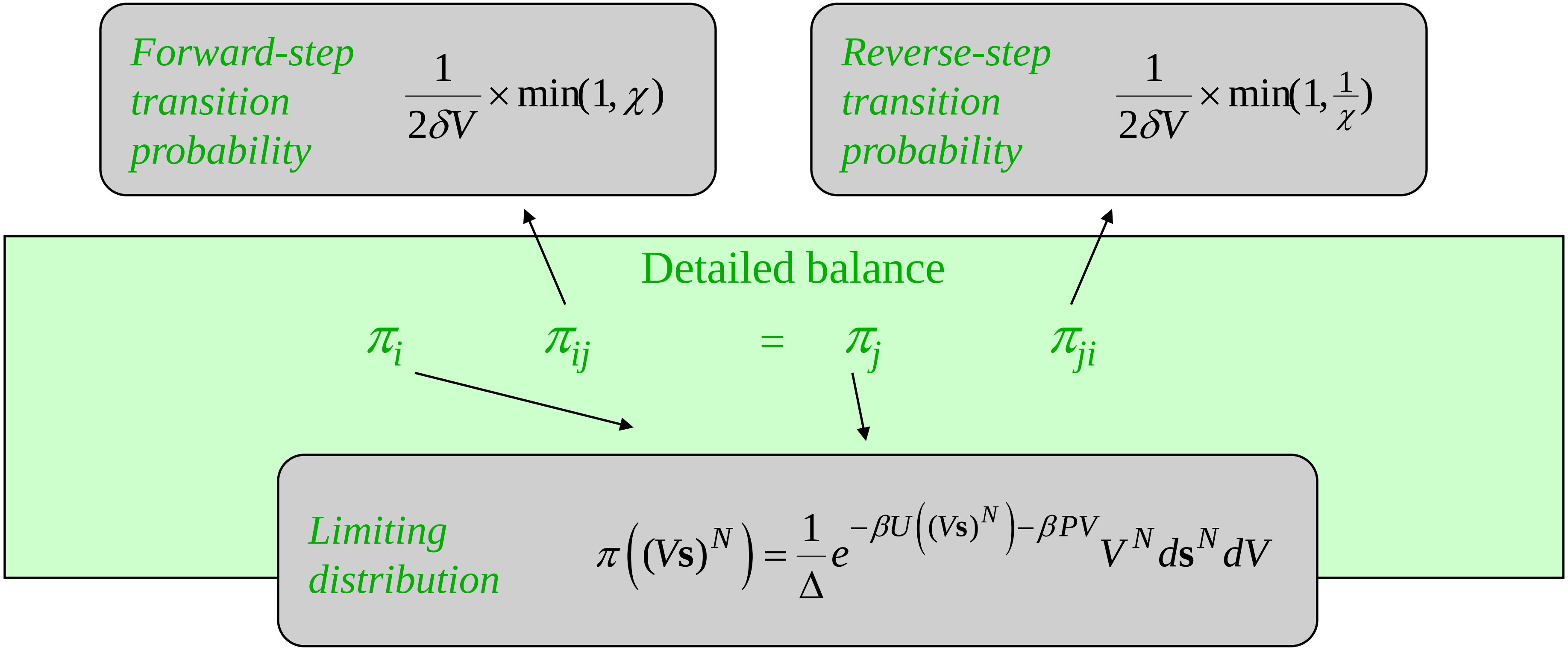
Reverse-step transition probability

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

χ is formulated to satisfy detailed balance

Volume-change Trial Move

3. Analysis of Detailed Balance



Forward-step transition probability

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

Reverse-step transition probability

$$\frac{1}{2\delta V}\times\min\left(1,\frac{1}{\chi}\right)$$

Detailed balance

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

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 transition probability

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

Reverse-step transition probability

$$\frac{1}{2\delta V} \times \min(1, \tfrac{1}{\chi})$$

Detailed balance

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

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

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 transition probability

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

Reverse-step transition probability

$$\frac{1}{2\delta V}\times\min(1,\tfrac{1}{\chi})$$

Detailed balance

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

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

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

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

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

Acceptance probability
min(1,χ)

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

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*

In terms of the probability density we can write the free energy also

$$F = -k_B T \ln Q = k_B T \ln\left(\frac{N! h^{3N}}{\int dp^N dq^N \exp(-H(p^N q^N)/k_B T)} \right)$$

Use the following identity

$$1 = \frac{1}{(8\pi^2 V)^N} \int \, dp^N dq^N \exp(-H(p^N q^N)/k_B T) \exp(H(p^N q^N)/k_B T)$$

To get

$$F = k_B T \ln(\int dp^N dq^N \exp\left[H(p^N q^N)/k_B T \right] \rho\left(p^N q^N \right))$$

The configuration with high energy make a significant contribution to the integral (to free energy) due to exponential term. A MC or MD preferentially samples lower-energy regions of phase space. An Ergodic trajectory would of course visit all the phase space, but in practice will never be adequately sampled by real simulation. So Computed free energy will be poorly converged and inaccurate

Metropolis Algorithm 2.

- What are the transition probabilities for this algorithm?
  - *Without loss of generality, define* i *as the state of greater probability*

$$\pi_i > \pi_j$$

$$\pi_{ij} = \tau_{ij} \times \frac{\pi_j}{\pi_i}$$

$$\left(\text{in general: } \pi_{ij} = \tau_{ij} \min\left(\frac{\pi_j}{\pi_i}, 1\right)\right)$$

$$\pi_{ji} = \tau_{ji}$$

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

- Do they obey detailed balance?

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

$$\pi_i \tau_{ij} \frac{\pi_j}{\pi_i} \overset{?}{=} \pi_j \tau_{ji}$$

$$\tau_{ij} = \tau_{ji}$$

- Yes, as long as the *underlying matrix* T of the Markov chain is symmetric
  - *this can be violated, but acceptance probabilities must be modified*