CE 530 Molecular Simulation

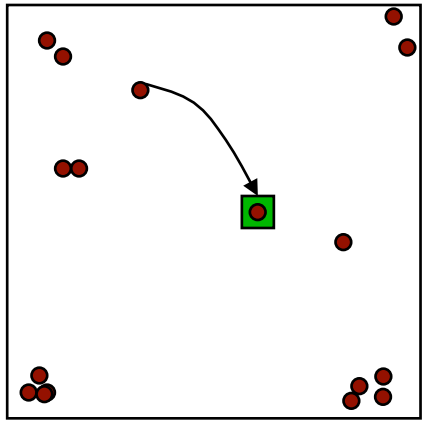
Lecture 22

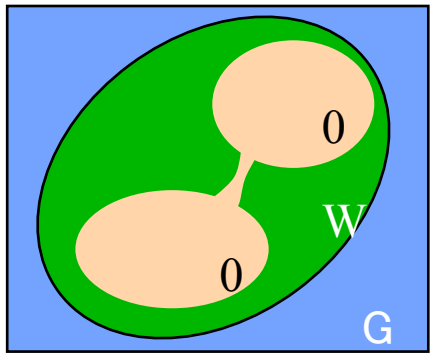
Chain-Molecule Sampling Techniques

David A. Kofke
Department of Chemical Engineering
SUNY Buffalo
kofke@eng.buffalo.edu

Monte Carlo Sampling

- MC method permits great flexibility in developing improved sampling methods
- Biasing methods improve sampling without changing the limiting distribution
  - *Modification of trial probabilities compensated by changes in acceptance and reverse-trial probabilities*
- Non-Boltzmann sampling methods modify the limiting distribution
  - *Desired ensemble average obtained by taking a weighted average over the non-Boltzmann sample*

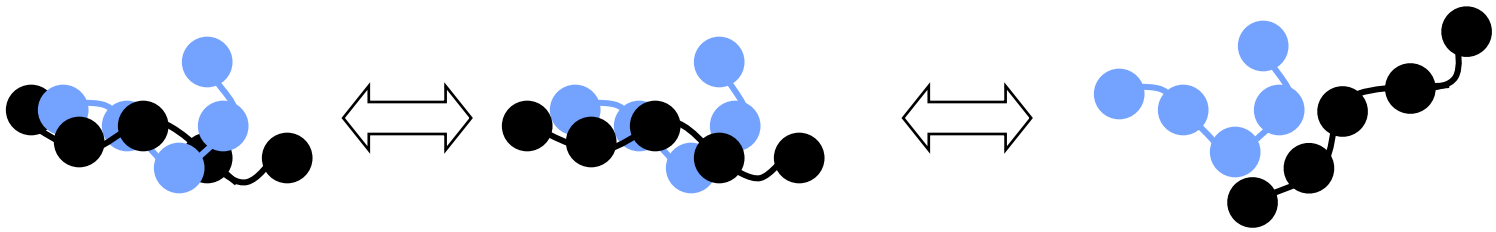




$$\langle M \rangle_0 = \frac{\left\langle M e^{-\beta(U_0 - U_W)} \right\rangle_W}{\left\langle e^{-\beta(U_0 - U_W)} \right\rangle_W}$$

Simulating Chain Molecules

- Slow to explore different parts of phase space
- Concerted moves needed to detangle chains



- Algorithms based solely on single-atom moves may be non-ergodic

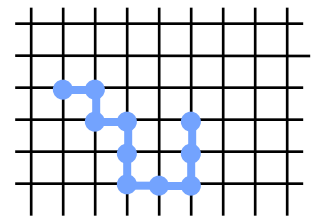
Modeling Chain Molecules

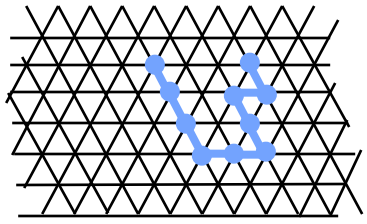
- Detailed models use full array of potentials discussed previously
  - *LJ atoms, with torsion, bend, stretch intramolecular potentials*
- Other models try to explain qualitative features of polymer behavior
  - *hard- or soft-sphere atoms, only stretch*

    bead-spring; tangent spheres; finitely-extensible nonlinear elastic (FENE)
  - *each unit of model might represent a multi-unit segment of the true polymer*
  - *the only feasible approach for very long chains*

    $>10^3$ units
- Lattice models are very helpful
  - *discretize space*

    various choices for lattice symmetry
  - *chain occupies contiguous sites on lattice*
  - *one chain unit per site*



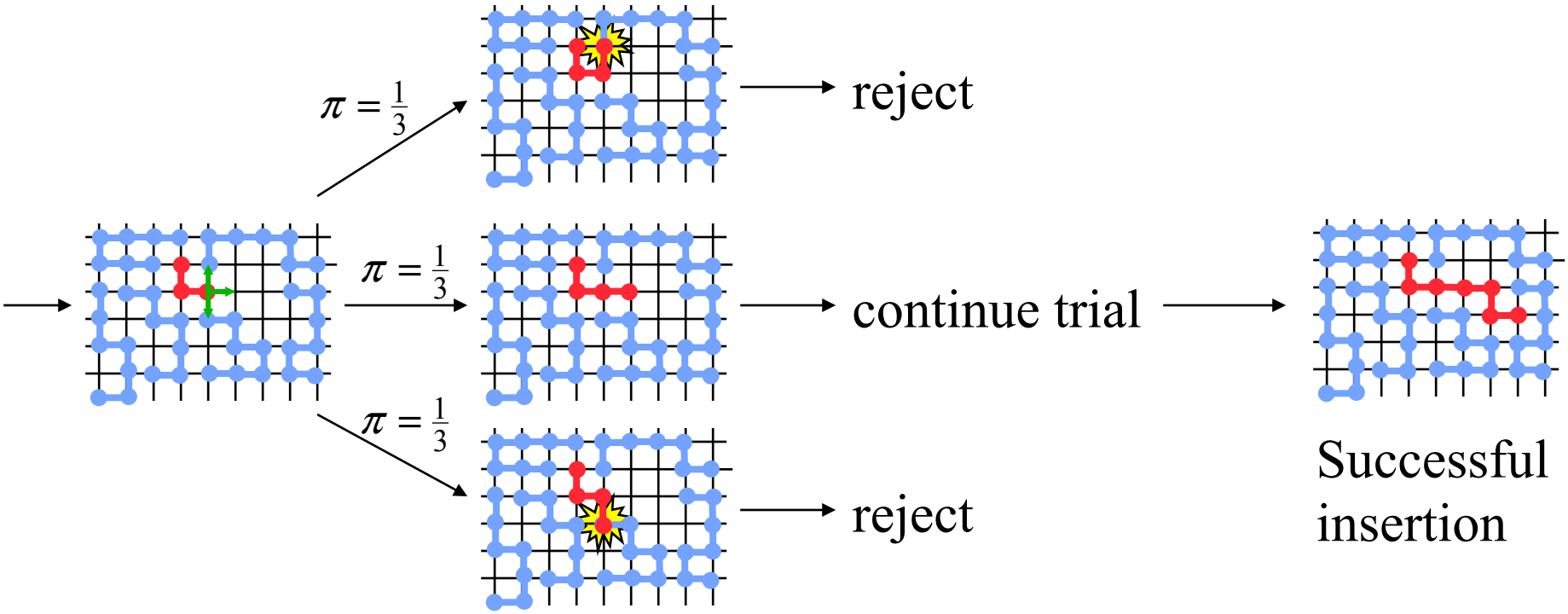


Generating Configurations of Chains

- Open ensembles (grand-canonical) often preferred
  - *insertion and removal of chains enhances sampling of configurations*
- Insertions and removals are difficult!
- We'll examine three approaches
  - *Simple sampling*
  - *Configurational bias*
  - *Pruned-enriched sampling*
- Consider methods in the context of a simple hard-exclusion model (no attraction, no bending energy)
  - *All non-overlapping chain configurations are weighted uniformly*

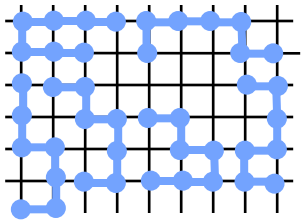
Simple Sampling

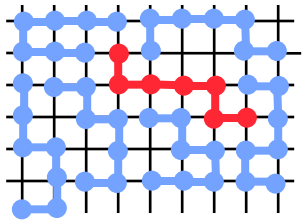
- Molecules are inserted and deleted in an unbiased fashion
  - *Stepwise insertion: after j segments have been inserted, the (j +1)th segment is placed at random at one of the sites adjoining the last segment*
  - *Any attempt that leads to an overlap with an existing segment causes the whole trial to be immediately discarded*



Simple Sampling: Insertion Likelihood

- What is the probability that this trial will occur using simple insertion?

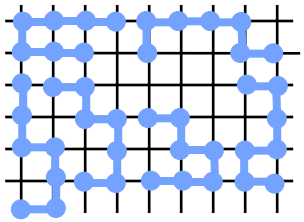




63 sites

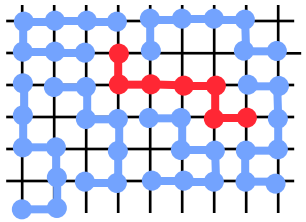
- *In-class assignment 1*
  - figure it out

Simple Sampling: Insertion Likelihood



63 sites

- What is the probability that this trial will occur using simple insertion?

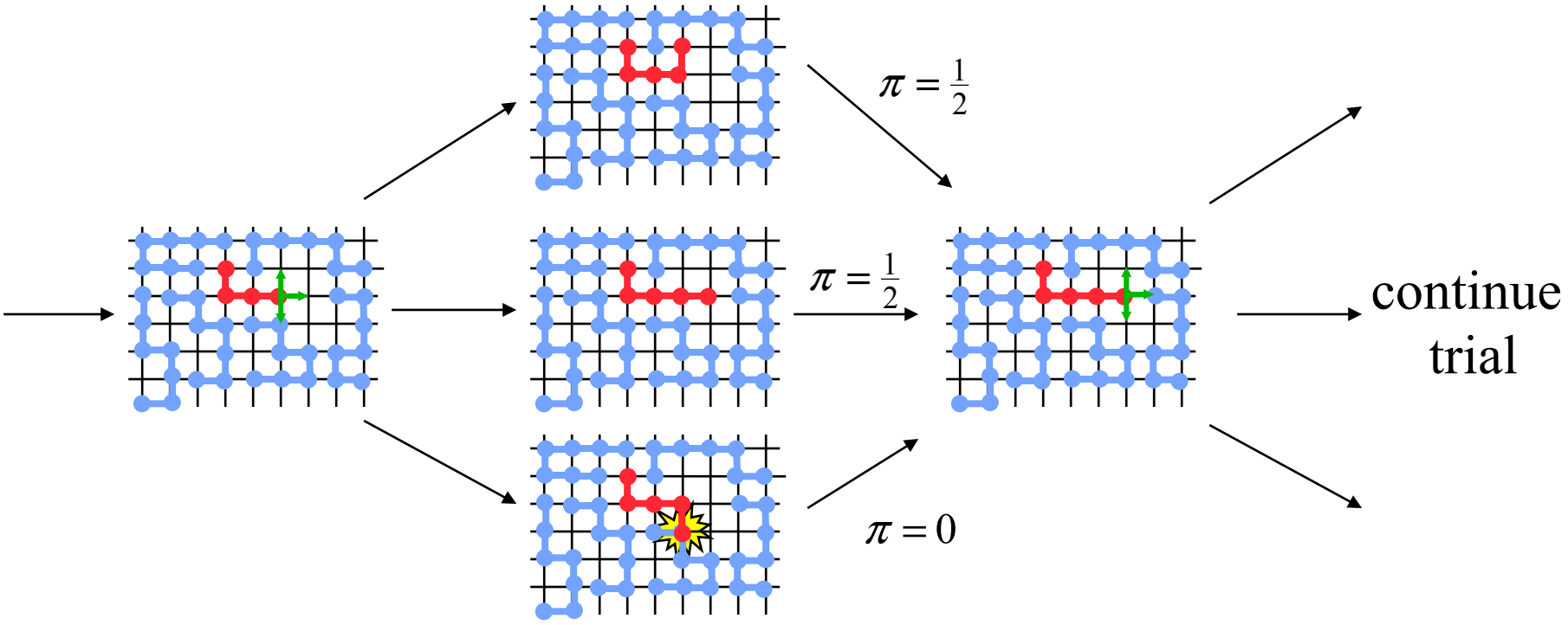


- Insertion probability for first unit
  - *1/63*
- Insert six more units, each with probability 1/3 going in the "right" spot
  - $1/3^6$
- Could begin on either end of chain
  - *multiply by 2*
- Total probability is product $\tau_{ij} = \frac{1}{63} \times \frac{1}{3^6} \times 2 = 0.000044$

$$= 4.4 \times 10^{-5}$$

Configurational Bias Monte Carlo

- Based on 1955 idea of Rosenbluth & Rosenbluth
- Apply bias during growth of chain, so that overlaps do not lead to rejection of entire trial
- Remove bias during acceptance of complete trial
  - *Accumulate "Rosenbluth weight" during course of trial*



Configurational-Bias Insertion/Deletion Trial. Analysis of Trial Probabilities

- Detailed specification of trial moves and and probabilities

Event [reverse event]	Probability [reverse probability]
Select insertion trial [select deletion trial]	½ [½]
Place molecule at {**r**} [delete molecule N+1]	1/W({**r**}) [1/(N+1)]
Accept move [accept move]	min(1,χ) [min(1,1/χ)]

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

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

We'll work this out later

Configurational-Bias Insertion/Deletion Trial. Analysis of Detailed Balance

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

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

Detailed balance

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

Limiting distribution $\pi\left(\mathbf{r}^N\right)=\frac{1}{\Xi}q(T)e^{-\beta U\left(\mathbf{r}^N\right)+\beta\mu N}$

Configurational-Bias Insertion/Deletion Trial. Analysis of Detailed Balance

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

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

Detailed balance

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

$$\frac{e^{-\beta U^{old}+\beta\mu N}}{\Xi q^{-N}}\left[\frac{1}{2}\times\frac{1}{W}\times\min(1,\chi)\right]=\frac{e^{-\beta U^{new}+\beta\mu(N+1)}}{\Xi q^{-(N+1)}}\left[\frac{1}{2}\times\frac{1}{N+1}\times\min(1,\frac{1}{\chi})\right]$$

Energy is zero in both configurations

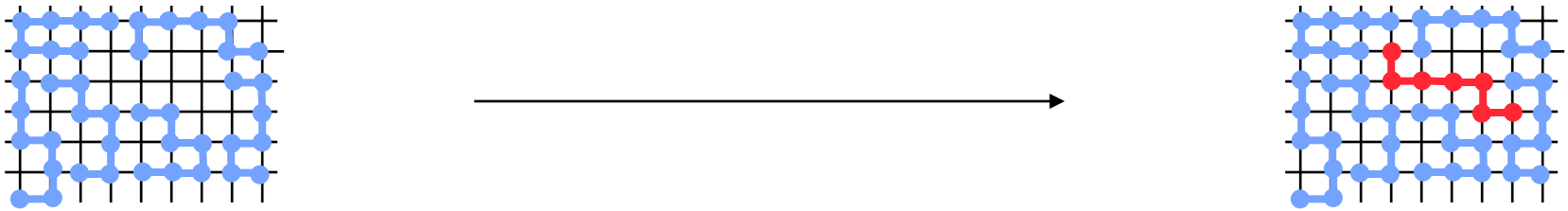
$$\frac{1}{W}\chi=\frac{q(T)}{N+1}e^{+\beta\mu}$$

$$\chi=\frac{q(T)}{N+1}We^{+\beta\mu}$$

Acceptance probability

Rosenbluth Weight

- What is W?
- 1/W is the probability that the chain would be inserted into the given position



- *Each placement of a unit in the chain is selected with probability*

$$\pi_j = \frac{1}{w_i}$$

where w_i *is the number of non-overlap "sibling" alternatives available at generation* i *of the overall insertion*

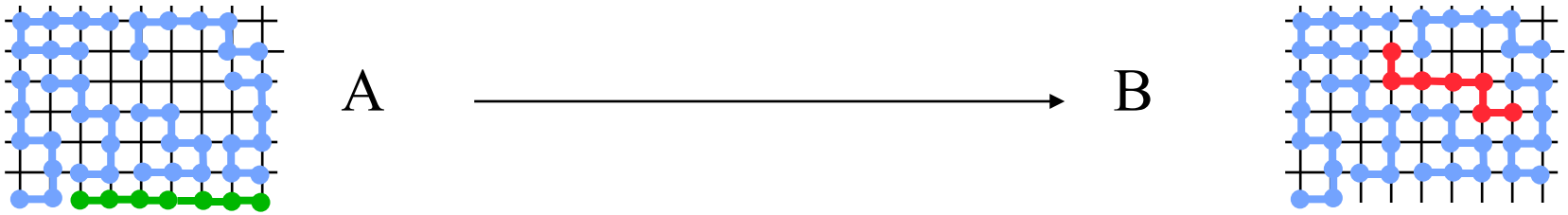
- *Probability of making this particular insertion is*

$$\tau = \tfrac{1}{63}\times\tfrac{1}{1}\times\tfrac{1}{1}\times\tfrac{1}{1}\times\tfrac{1}{2}\times\tfrac{1}{2}\times\tfrac{1}{1} = 0.004$$

$$W = 63\times1\times1\times1\times2\times2\times1 = 252$$

NVT Configuration Sampling

- CBMC is also used to generate new configurations of present molecules

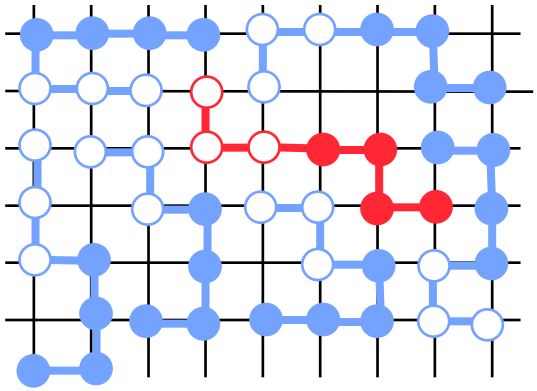


- Acceptance of any move is based on Rosenbluth weight for given move and the reverse move
  - $W_A = 63$
  - $W_B = 252$
  - *The move A → B is accepted with probability 1*
  - *The move B → A is accepted with probability 63/252 = 1/4*

Attractive Interactions

- Molecules with attraction
  - *Generalization uses Boltzmann factor to formulate Rosenbluth weight*
  - *At each step weight is* $w_i = \sum_{j=1}^{k} e^{-\beta u_i(j)}$

    Before, this was a sum of terms either zero or one
  - *And probability of selecting site* j *is* $\pi_j = \frac{e^{-\beta u_j}}{w_i}$

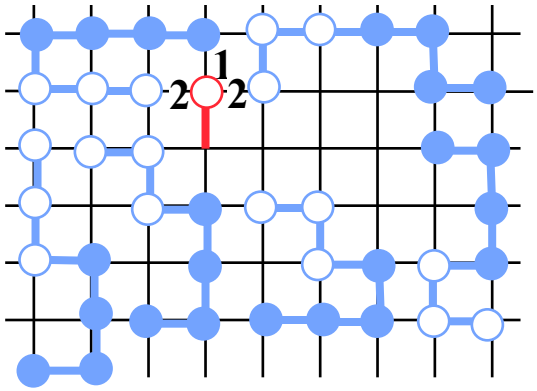


$e^{-\beta u} = \begin{cases} 2 & \circ\circ \\ 1 & \circ\bullet \\ 2 & \bullet\bullet \end{cases}$ (for example)

$\tau =$

Attractive Interactions

- Molecules with attraction
  - *Generalization uses Boltzmann factor to formulate Rosenbluth weight*
  - *At each step weight is* $w_i = \sum_{j=1}^{k} e^{-\beta u_i(j)}$
  - *And probability of selecting site* j *is* $\pi_j = \frac{e^{-\beta u_j}}{w_i}$



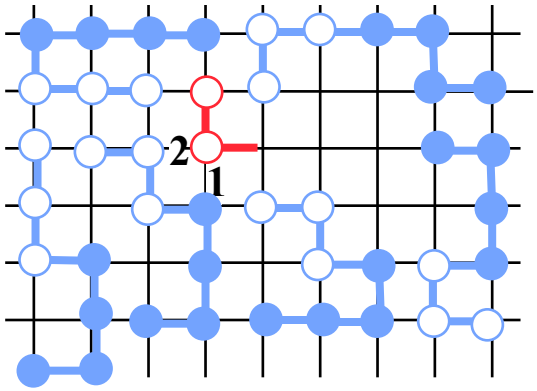
$$e^{-\beta u} = \begin{cases} 2 & \text{○ ○} \\ 1 & \text{○ ●} \\ 2 & \text{● ●} \end{cases}$$

$$\tau = \frac{1 \times 2 \times 2}{63}$$

$$W = 63$$

Attractive Interactions

- Molecules with attraction
  - *Generalization uses Boltzmann factor to formulate Rosenbluth weight*
  - *At each step weight is* $w_i = \sum_{j=1}^{k} e^{-\beta u_i(j)}$
  - *And probability of selecting site* j *is* $\pi_j = \frac{e^{-\beta u_j}}{w_i}$



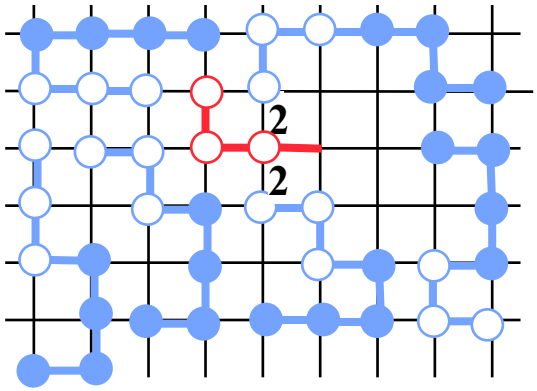
$$e^{-\beta u} = \begin{cases} 2 & \text{○ ○} \\ 1 & \text{○ ●} \\ 2 & \text{● ●} \end{cases}$$

$$\tau = \frac{4}{63} \times \frac{2 \times 1}{2+0+0}$$

$$W = 63 \times 2$$

Attractive Interactions

- Molecules with attraction
  - *Generalization uses Boltzmann factor to formulate Rosenbluth weight*
  - *At each step weight is* $w_i = \sum_{j=1}^{k} e^{-\beta u_i(j)}$
  - *And probability of selecting site* j *is* $\pi_j = \frac{e^{-\beta u_j}}{w_i}$



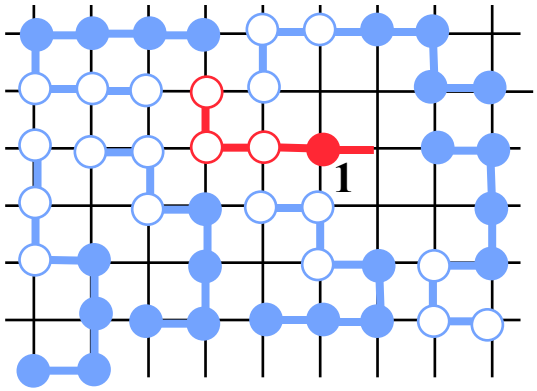
$$e^{-\beta u} = \begin{cases} 2 & \text{○ ○} \\ 1 & \text{○ ●} \\ 2 & \text{● ●} \end{cases}$$

$$\tau = \frac{4}{63} \times \frac{2}{2} \times \frac{2\times 2}{4+0+0}$$

$$W = 63 \times 2 \times 4$$

Attractive Interactions

- Molecules with attraction
  - *Generalization uses Boltzmann factor to formulate Rosenbluth weight*
  - *At each step weight is* $w_i = \sum_{j=1}^{k} e^{-\beta u_i(j)}$
  - *And probability of selecting site* j *is* $\pi_j = \frac{e^{-\beta u_j}}{w_i}$



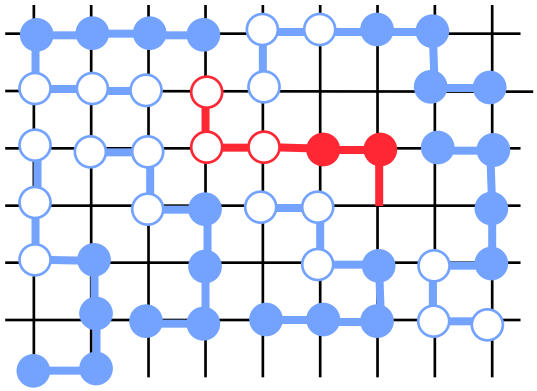
$$e^{-\beta u} = \begin{cases} 2 & \text{○ ○} \\ 1 & \text{○ ●} \\ 2 & \text{● ●} \end{cases}$$

$$\tau = \frac{4}{63} \times \frac{2}{2} \times \frac{4}{4} \times \frac{1}{1+0+0}$$

$$W = 63 \times 2 \times 4 \times 1$$

Attractive Interactions

- Molecules with attraction
  - *Generalization uses Boltzmann factor to formulate Rosenbluth weight*
  - *At each step weight is* $w_i = \sum_{j=1}^{k} e^{-\beta u_i(j)}$
  - *And probability of selecting site* j *is* $\pi_j = \frac{e^{-\beta u_j}}{w_i}$



$$e^{-\beta u} = \begin{cases} 2 & \circ\ \circ \\ 1 & \circ\ \bullet \\ 2 & \bullet\ \bullet \end{cases}$$

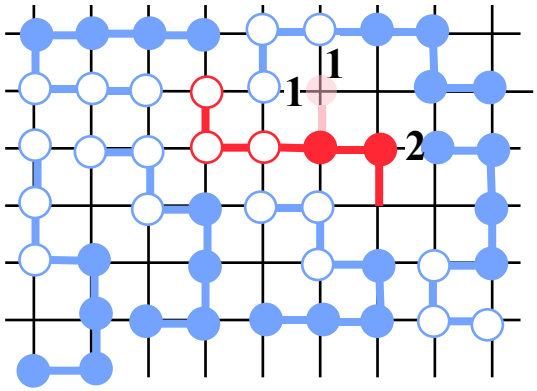
$$\tau = \frac{4}{63} \times \frac{2}{2} \times \frac{4}{4} \times \frac{1}{1} \times ?$$

$$W = 63 \times 2 \times 4 \times 1 \times ?$$

In-class assignment 2
Get the next term

Attractive Interactions

- Molecules with attraction
  - *Generalization uses Boltzmann factor to formulate Rosenbluth weight*
  - *At each step weight is* $w_i = \sum_{j=1}^{k} e^{-\beta u_i(j)}$
  - *And probability of selecting site* j *is* $\pi_j = \frac{e^{-\beta u_j}}{w_i}$



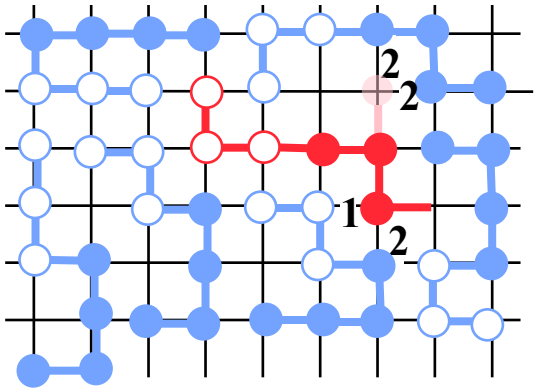
$$e^{-\beta u} = \begin{cases} 2 & \text{○ ○} \\ 1 & \text{○ ●} \\ 2 & \text{● ●} \end{cases}$$

$$\tau = \frac{4}{63} \times \frac{2}{2} \times \frac{4}{4} \times \frac{1}{1} \times \frac{2}{2+1\times1+0}$$

$$W = 63 \times 2 \times 4 \times 1 \times 3$$

Attractive Interactions

- Molecules with attraction
  - *Generalization uses Boltzmann factor to formulate Rosenbluth weight*
  - *At each step weight is* $w_i = \sum_{j=1}^{k} e^{-\beta u_i(j)}$
  - *And probability of selecting site* j *is* $\pi_j = \frac{e^{-\beta u_j}}{w_i}$



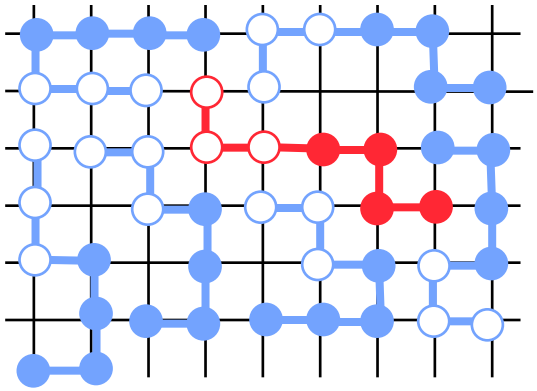
$$e^{-\beta u} = \begin{cases} 2 & \text{○ ○} \\ 1 & \text{○ ●} \\ 2 & \text{● ●} \end{cases}$$

$$\tau = \frac{4}{63} \times \frac{2}{2} \times \frac{4}{4} \times \frac{1}{1} \times \frac{2}{3} \times \frac{2\times1}{2+2\times2+0}$$

$$W = 63 \times 2 \times 4 \times 1 \times 3 \times 6$$

Attractive Interactions

- Molecules with attraction
  - *Generalization uses Boltzmann factor to formulate Rosenbluth weight*
  - *At each step weight is* $w_i = \sum_{j=1}^{k} e^{-\beta u_i(j)}$
  - *And probability of selecting site* j *is* $\pi_j = \frac{e^{-\beta u_j}}{w_i}$



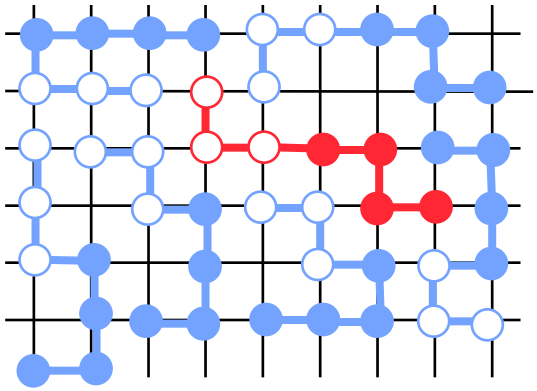
$$e^{-\beta u} = \begin{cases} 2 & \text{○ ○} \\ 1 & \text{○ ●} \\ 2 & \text{● ●} \end{cases}$$

$$\tau = \frac{4}{63} \times \frac{2}{2} \times \frac{4}{4} \times \frac{1}{1} \times \frac{2}{3} \times \frac{2}{6} \times \frac{4}{4+0+0}$$

$$W = 63 \times 2 \times 4 \times 1 \times 3 \times 6 \times 4$$

Attractive Interactions

- Molecules with attraction
  - *Generalization uses Boltzmann factor to formulate Rosenbluth weight*
  - *At each step weight is* $w_i = \sum_{j=1}^{k} e^{-\beta u_i(j)}$
  - *And probability of selecting site* j *is* $\pi_j = \frac{e^{-\beta u_j}}{w_i}$



$$e^{-\beta u} = \begin{cases} 2 & \text{○ ○} \\ 1 & \text{○ ●} \\ 2 & \text{● ●} \end{cases}$$

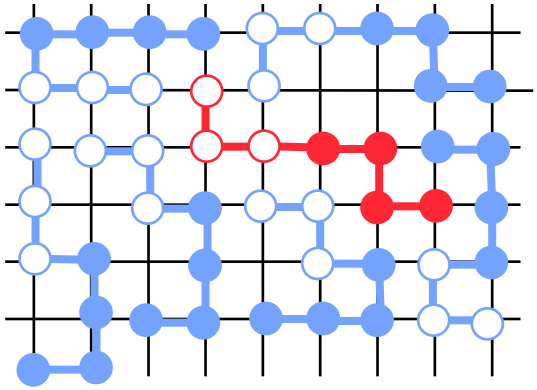
$$\tau = \frac{4}{63} \times \frac{2}{2} \times \frac{4}{4} \times \frac{1}{1} \times \frac{2}{3} \times \frac{2}{6} \times \frac{4}{4} = 0.014$$

$$W = 63 \times 2 \times 4 \times 1 \times 3 \times 6 \times 4 = 36288$$

Attractive Interactions

Molecules with attraction

- *Generalization uses Boltzmann factor to formulate Rosenbluth weight*
- *At each step weight is* $w_i = \sum_{j=1}^{k} e^{-\beta u_i(j)}$
- *And probability of selecting site* j *is* $\pi_j = \frac{e^{-\beta u_j}}{w_i}$



$$e^{-\beta u} = \begin{cases} 2 & \circ\circ \\ 1 & \circ\bullet \\ 2 & \bullet\bullet \end{cases}$$

$$\tau = \frac{4}{63}\times\frac{2}{2}\times\frac{4}{4}\times\frac{1}{1}\times\frac{2}{3}\times\frac{2}{6}\times\frac{4}{4} = 0.014$$

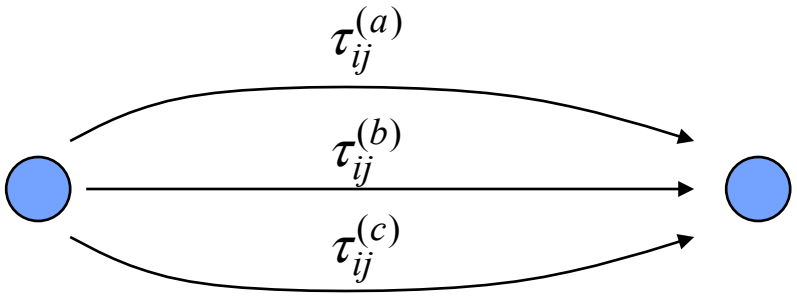
$$W = 63\times 2\times 4\times 1\times 3\times 6\times 4 = 36288$$

W is used just as before: accept with proby min[1, W_{new}/W_{old}]

- *energy contribution is built-in:* $\prod \tau_i = \prod \frac{e^{-\beta u_i}}{w_i} = \frac{e^{-\beta U}}{W}$

A General Result for Markov Processes 1.

- Consider a process in which there are several ways to generate each trial i → j



- To enforce detailed balance, all routes should be considered in formulating acceptance probability

$$\pi_i \left[\tau_{ij}^{(a)} + \tau_{ij}^{(b)} + \tau_{ij}^{(c)} \right] \min[1, \chi] = \pi_j \left[\tau_{ji}^{(a)} + \tau_{ji}^{(b)} + \tau_{ji}^{(c)} \right] \min[1, 1/\chi]$$

- If there are many ways to generate the trial, this can pose difficulties

A General Result for Markov Processes 1.

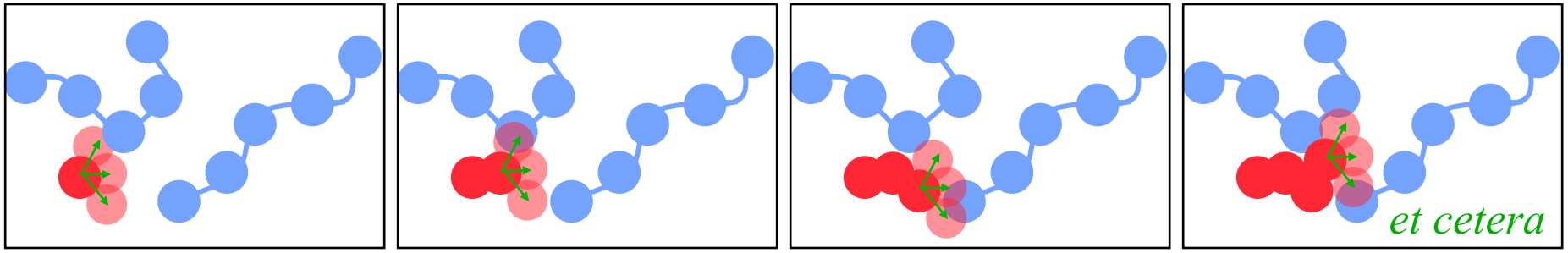
- Consider the following recipe for a single-step trial
  - *Generate the trial i → j via route (a), with probability* $\tau_{ij}^{(a)}$
  - *Choose a reverse trial j → i via one of the routes, say (b)*
    Choose it with probability that it would occur as the j → i route
    Probability = $\tau_{ji}^{(b)}/\tau_{ji}$
  - *Accept the (forward) trial as if (a) and (b) were the only routes*

$$\pi_i \tau_{ij}^{(a)} \min[1, \chi^{ab}] = \pi_j \tau_{ji}^{(b)} \min[1, 1/\chi^{ab}]$$

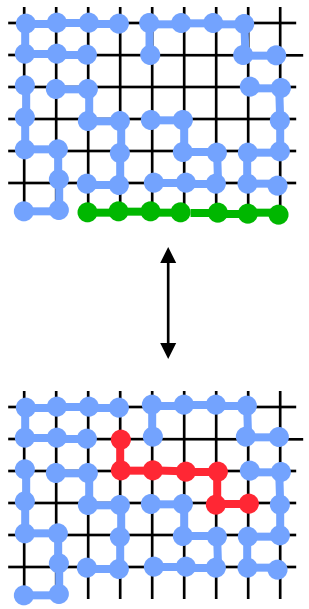
- This recipe satisfies detailed balance for the overall transition i → j

Off the Lattice

- CBMC can be extended to off-lattice models
- Choose a set of trial orientations at random for each atom insertion

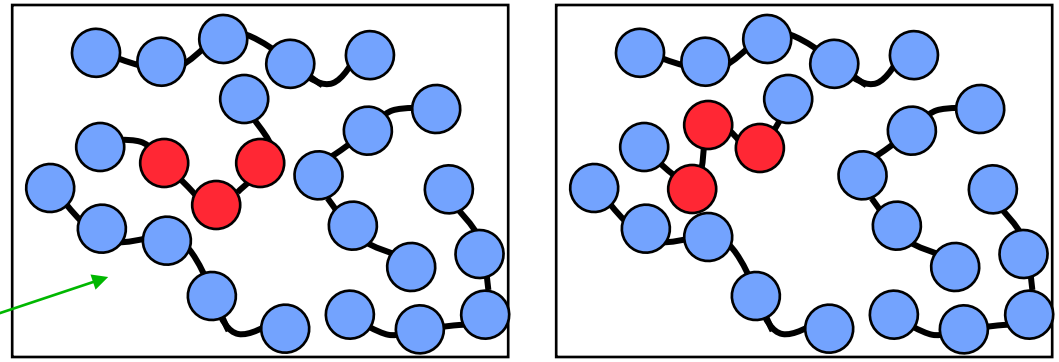


- Once a chain is generated in new position, perform same operation tracing out its original location
- Compile Rosenbluth weight for new and original chains to use in acceptance $W = \prod_{\substack{\text{atoms} \\ i}} \sum_{\substack{\text{trials} \\ j}} e^{-\beta u_i(j)}$
- Note that each insertion may be accomplished via multiple routes, differing in the discarded atom trials



CBMC General Comments

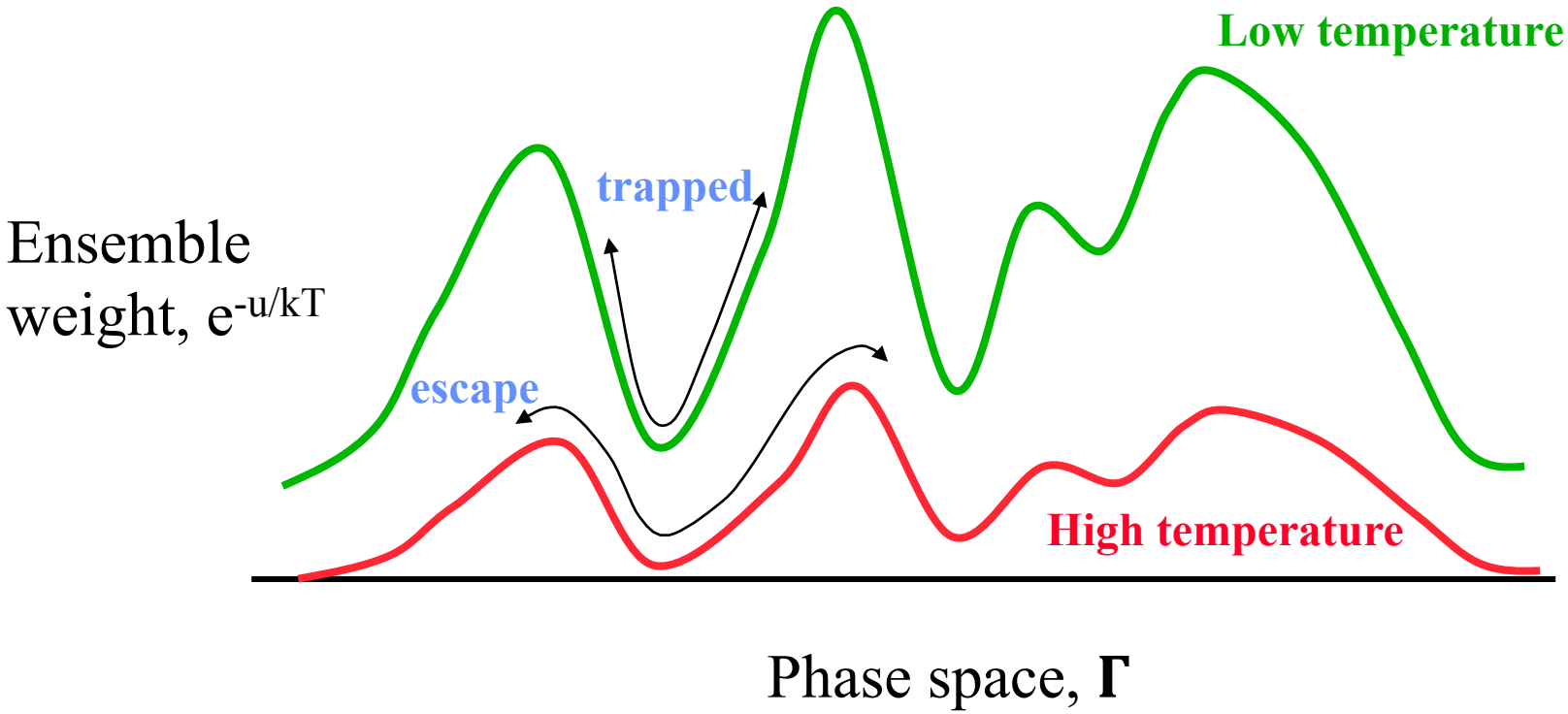
- Method begins to fail for sufficiently long chains
  - *maybe as few as 10 atoms*
- Extensions of method
  - *Gibbs ensemble*
  - *Branched polymers*
  - *Partial chain regrowth*
  - *Chemical-potential calculation*



- General idea can be applied in other ways
  - *Multi-step trial broken into smaller decisions, with acceptance including consideration of the choices not taken*

Parallel Tempering 1.

- At high temperature a broader range of configurations is sampled
- Barriers to transitions are lowered

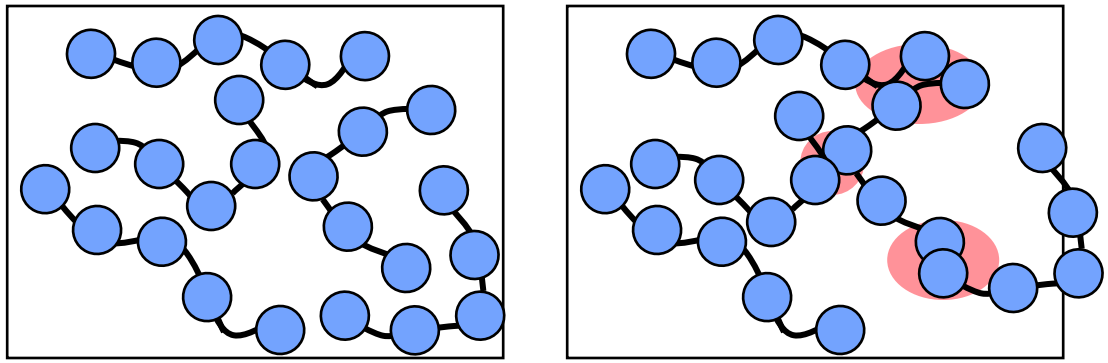


- How to simulate a low-temperature system with high-temperature barrier removal?

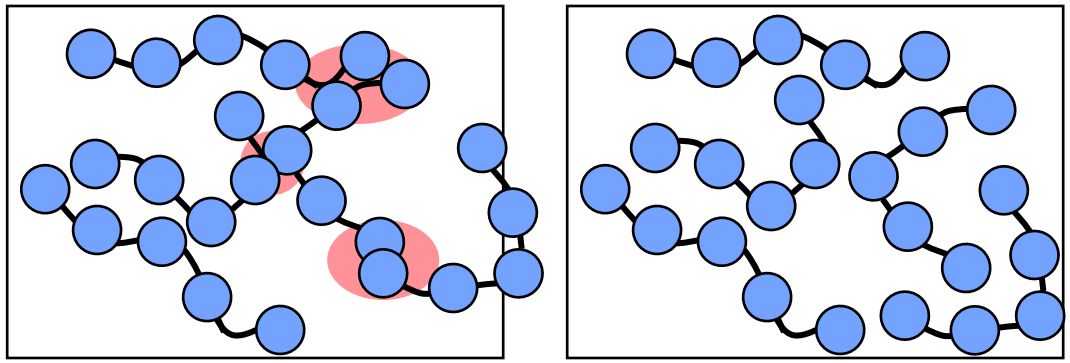
Parallel Tempering 2.

- Simulate loosely coupled high- and low-temperature systems in parallel

Low temperature **High temperature**



- Perform moves in which two systems swap configurations



- Accept based on $e^{-\beta_H(U_2-U_1)}e^{-\beta_L(U_1-U_2)} = e^{-(\beta_H-\beta_L)(U_2-U_1)} = e^{-\Delta\beta\Delta U}$

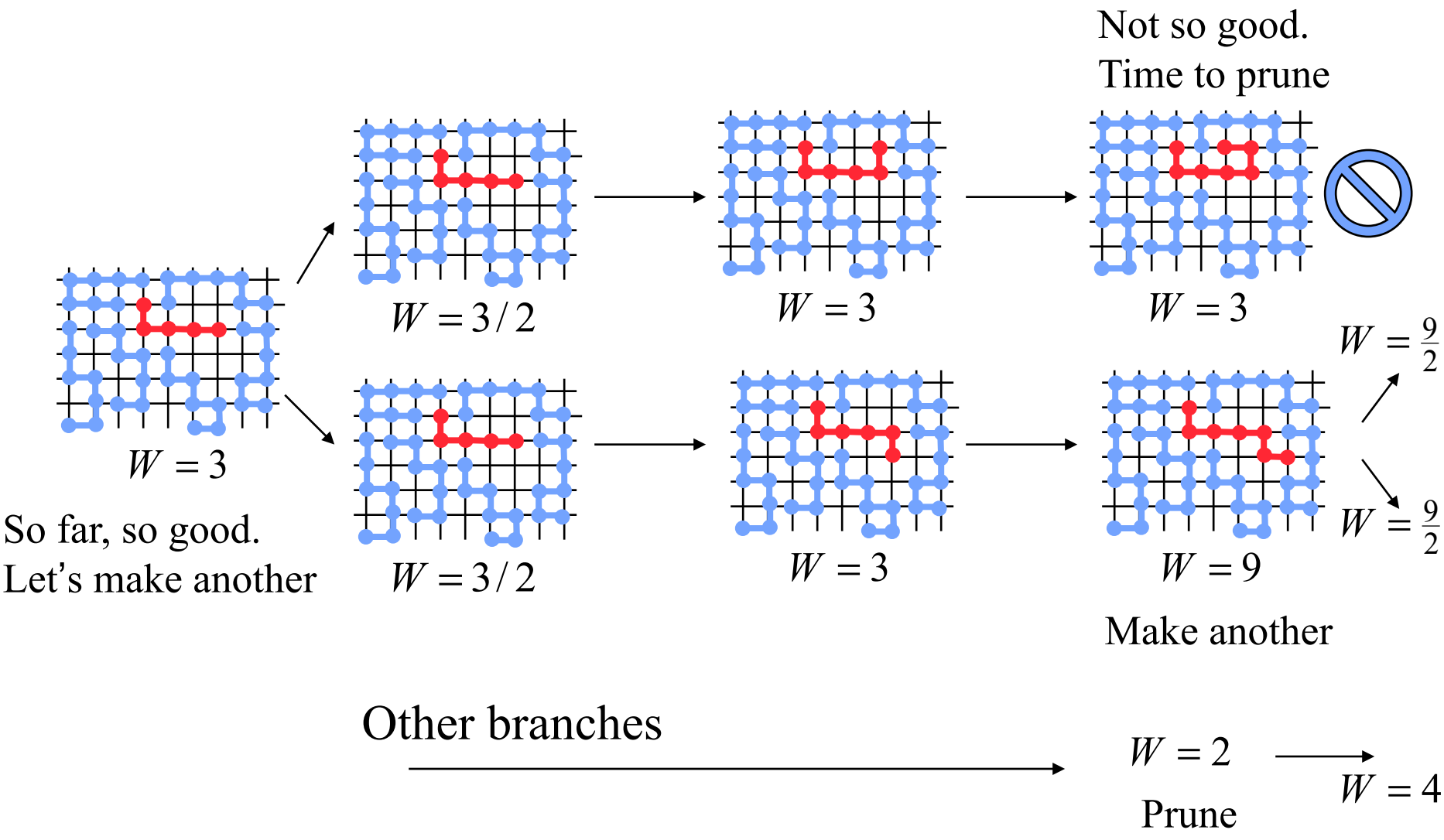
Parallel Tempering 3.

- To get reasonable acceptance rate, temperatures should not be too different
- Can be extended to include any number of systems simulated in parallel
- Can be extended to do “tempering” in other variables, such as the chemical potential
- Very well suited for use in conjunction with histogram reweighting

Pruned-Enriched Rosenbluth Method

- At some point along the growth process it may become clear that
  - *the chain is doomed, or*
  - *the chain is really doing well*
- We'd like to enrich the presence of the good ones, while pruning out the ones that look bad
- Use a criterion based on partial Rosenbluth weight

Pruned-Enriched Rosenbluth Method



Pruned-Enriched Rosenbluth Method

- Set cutoffs for intermediate Rosenbluth weights
  - *duplicate any configuration having* $W > W^{>}$, *halving weights of new duplicates*
  - *prune configurations having* $W < W^{<}$, *taking every-other such configuration, and doubling the weight of those not taken*