# CE 530 Molecular Simulation

## Lecture 10

## Simple Biasing Methods

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# Review

- Monte Carlo simulation
  - *Markov chain to generate elements of ensemble with proper distribution*
- Metropolis algorithm
  - *relies on microscopic reversibility* $\pi_i \pi_{ij} = \pi_j \pi_{ji}$
  - *two parts to a Markov step*
    - ➔ generate trial move (underlying transition probability matrix)
    - ➔ decide to accept move or keep original state
- Determination of acceptance probabilities
  - *detailed analysis of forward and reverse moves*
  - *we examined molecule displacement and volume-change trials*

# Performance Measures

- How do we improve the performance of a MC simulation?
  - *characterization of performance*
  - *means to improve performance*
- Return to our consideration of a general Markov process
  - *fixed number of well defined states*
  - *fully specified transition-probability matrix*
  - *use our three-state prototype*
- Performance measures
  - *rate of convergence*
  - *variance in occupancies*

$$\Pi \equiv \begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{13} \\ \pi_{21} & \pi_{22} & \pi_{23} \\ \pi_{31} & \pi_{32} & \pi_{33} \end{pmatrix}$$

# Rate of Convergence 1.

- What is the likely distribution of states after a run of finite length?
  - *Is it close to the limiting distribution?*

*Probability of being in state 3 after n moves, beginning in state 1*

$$\pi_1^{(n)} = \pi_1^{(0)}\Pi^n \equiv \begin{pmatrix}1 & 0 & 0\end{pmatrix}\begin{pmatrix}\pi_{11}^{(n)} & \pi_{12}^{(n)} & \pi_{13}^{(n)} \\ \pi_{21}^{(n)} & \pi_{22}^{(n)} & \pi_{23}^{(n)} \\ \pi_{31}^{(n)} & \pi_{32}^{(n)} & \pi_{33}^{(n)}\end{pmatrix} = \begin{pmatrix}\pi_{11}^{(n)} & \pi_{12}^{(n)} & \boxed{\pi_{13}^{(n)}}\end{pmatrix}$$

  - *We can apply similarity transforms to understand behavior of* $\Pi^n$
    - ➙ eigenvector equation $\Pi\Phi = \Phi\Lambda \Rightarrow \Pi = \Phi\Lambda\Phi^{-1}$

eigenvalue matrix: $\Lambda = \begin{pmatrix}\lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3\end{pmatrix}$

eigenvector matrix $\Phi = \begin{pmatrix}\begin{pmatrix}\\ \phi_1 \\ \\ \end{pmatrix} & \begin{pmatrix}\\ \phi_2 \\ \\ \end{pmatrix} & \begin{pmatrix}\\ \phi_3 \\ \\ \end{pmatrix}\end{pmatrix}$

# Rate of Convergence 1.

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  - *We can apply similarity transforms to understand behavior of* $\Pi^n$
    - ➙ eigenvector equation $\Pi\Phi = \Phi\Lambda \Rightarrow \Pi = \Phi\Lambda\Phi^{-1}$

$$\Pi^n = \left(\Phi\Lambda\Phi^{-1}\right)\left(\Phi\Lambda\Phi^{-1}\right)\ldots\text{(n times)}\ldots\Phi^{-1}$$

$$= \Phi\Lambda\left(\Phi^{-1}\Phi\right)\Lambda\left(\Phi^{-1}\Phi\right)\ldots$$

$$= \Phi\Lambda^n\Phi^{-1}$$

$$\Lambda^n = \begin{pmatrix}\lambda_1^n & 0 & 0 \\ 0 & \lambda_2^n & 0 \\ 0 & 0 & \lambda_3^n\end{pmatrix}$$

# Rate of Convergence 2.

- Likely distribution after finite run

$$\pi_i^{(n)} = \pi_i^{(0)} \Pi^n = \pi_i^{(0)} \Phi \Lambda^n \Phi^{-1}$$

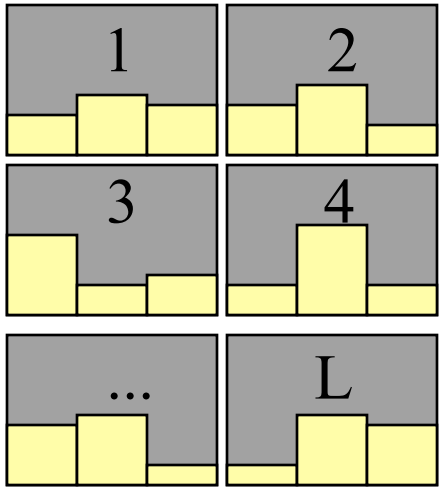
$$\Lambda^n = \begin{pmatrix} \lambda_1^n & 0 & 0 \\ 0 & \lambda_2^n & 0 \\ 0 & 0 & \lambda_3^n \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \lambda_2^n & 0 \\ 0 & 0 & \lambda_3^n \end{pmatrix} \underset{n \to \infty}{=} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

- Convergence rate determined by magnitude of other eigenvalues
  - *very close to unity indicates slow convergence*

# Occupancy Variance 1.

- Imagine repeating Markov sequence many times (L→∞), each time taking a fixed number of steps, *M*
  - *tabulate histogram for each sequence;* $p_i^{(k)} = \frac{m_i^{(k)}}{M}$
  - *examine variances in occupancy fraction*

$$\overline{\sigma_i^2} = \sum_{k=1}^{L} \left( p_i^{(k)} - \pi_i \right)^2 \qquad \overline{\sigma_i \sigma_j} = \sum_{k=1}^{L} \left( p_i^{(k)} - \pi_i \right)\left( p_j^{(k)} - \pi_j \right)$$




  - *through propagation of error, the occupancy (co)variances sum to give the variances in the ensemble averages; e.g. (for a 2-state system)*

$$\sigma_U^2 = U_1^2 \overline{\sigma_1^2} + U_2^2 \overline{\sigma_2^2} + 2U_1 U_2 \overline{\sigma_1 \sigma_2}$$

  - *we would like these to be small*

# Occupancy Variance 2.

- A formula for the occupancy (co)variance is known

$$M\overline{\sigma_i^2} = \pi_i^2 + 2\pi_i s_{ii} - 1 \qquad \text{variance}$$

$$M\overline{\sigma_i \sigma_j} = \pi_i \pi_j + \pi_i s_{ij} + \pi_j s_{ji} \qquad \text{covariance}$$

$$S = (\mathbf{I} - \Pi + \Phi)^{-1} - \Phi$$

- *right-hand sides independent of M*
- *standard deviation decreases as* $1/\sqrt{M}$

# Example Performance Values

*Limiting distribution* $\pi = (0.25 \quad 0.5 \quad 0.25)$

*Inefficient*

$$\Pi = \begin{pmatrix} 0.97 & 0.02 & 0.01 \\ 0.01 & 0.98 & 0.01 \\ 0.01 & 0.02 & 0.97 \end{pmatrix} \quad \lambda = \begin{pmatrix} 1 & 0.96 & 0.96 \end{pmatrix} \quad \Sigma = \begin{pmatrix} 9.2 & -6.1 & -3.1 \\ -6.1 & 12.2 & -6.1 \\ -3.1 & -6.1 & 9.2 \end{pmatrix}$$

*Barker*

$$\Pi = \begin{pmatrix} 0.42 & 0.33 & 0.25 \\ 0.17 & 0.66 & 0.17 \\ 0.25 & 0.33 & 0.42 \end{pmatrix} \quad \lambda = \begin{pmatrix} 1 & 0.33 & 0.17 \end{pmatrix} \quad \Sigma = \begin{pmatrix} 0.30 & -0.25 & -0.05 \\ -0.25 & 0.50 & -0.25 \\ -0.05 & -0.25 & 0.30 \end{pmatrix}$$

*Most efficient*

$$\Pi = \begin{pmatrix} 0 & 1 & 0 \\ 0.5 & 0 & 0.5 \\ 0 & 1 & 0 \end{pmatrix} \quad \lambda = \begin{pmatrix} 1 & 0 & -1 \end{pmatrix} \quad \Sigma = \begin{pmatrix} 0.125 & 0 & -0.125 \\ 0 & 0 & 0 \\ -0.125 & 0 & 0.125 \end{pmatrix}$$

*Metropolis*

$$\Pi = \begin{pmatrix} 0.0 & 0.5 & 0.5 \\ 0.25 & 0.5 & 0.25 \\ 0.5 & 0.5 & 0.0 \end{pmatrix} \quad \lambda = \begin{pmatrix} 1 & 0 & -0.5 \end{pmatrix} \quad \Sigma = \begin{pmatrix} 0.10 & -0.125 & 0.02 \\ -0.125 & 0.25 & -0.125 \\ 0.02 & -0.125 & 0.10 \end{pmatrix}$$

# Example Performance Values

$$\Pi = \begin{pmatrix} 0 & 0.99 & 0.01 & 0 \\ 0.99 & 0 & 0 & 0.01 \\ 0 & 0.01 & 0 & 0.99 \\ 0 & 0.01 & 0.99 & 0 \end{pmatrix}$$

Lots of movement 1 → 2; 3 → 4

Little movement (1,2) → (3,4)

$$\pi = (0.25 \quad 0.25 \quad 0.25 \quad 0.25)$$

*Limiting distribution*

$$\lambda = (1 \quad 0.98 \quad -0.99 \quad -0.99)$$

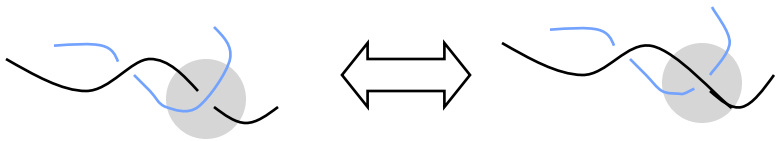
*Eigenvalues*

$$\Sigma = \begin{pmatrix} 6.2 & 6.2 & -6.2 & -6.2 \\ 6.2 & 6.2 & -6.2 & -6.2 \\ -6.2 & -6.2 & 6.2 & 6.2 \\ -6.2 & -6.2 & 6.2 & 6.2 \end{pmatrix}$$

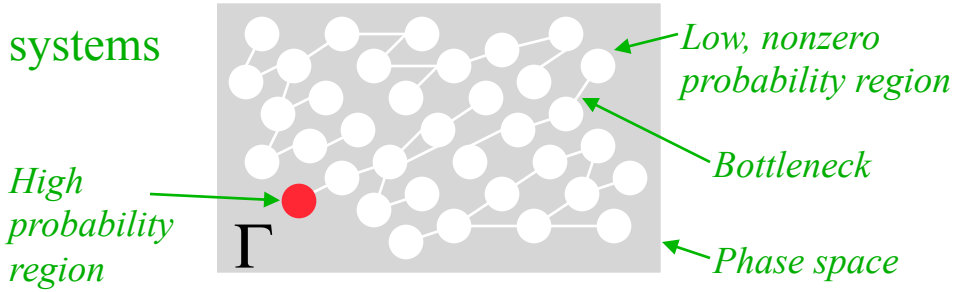
*Covariance matrix*

# Heuristics to Improve Performance

- Keep the system moving
  - *minimize diagonal elements of probability matrix*
  - *avoid repeated transitions among a few states*
- Typical physical situations where convergence is poor
  - *large number of equivalent states with poor transitions between regions of them*
    - ➔ entangled polymers



  - *large number of low-probability states and a few high-probability states*
    - ➔ low-density associating systems



# Biasing the Underlying Markov Process

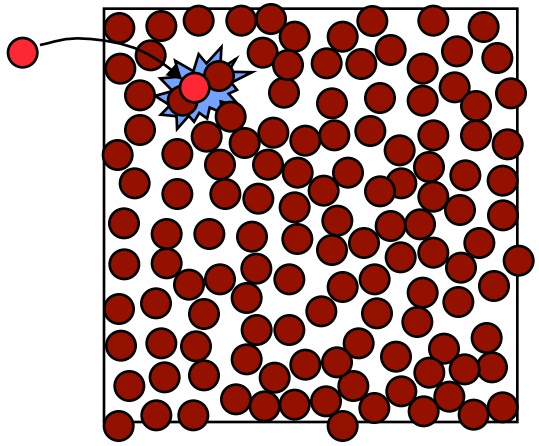
- Detailed balance for trial/acceptance Markov process
  - $\pi_i \tau_{ij} \min(1, \chi) = \pi_j \tau_{ji} \min(1, 1/\chi)$
- Often it happens that $\tau_{ij}$ is small while $\chi$ is large (or vice-versa)
  - *even if product is of order unity, $\pi_{ij}$ will be small because of* min()
- The underlying TPM can be adjusted (biased) to enhance movement among states
  - *bias can be removed in reverse trial probability, or acceptance*
  - *require in general*

$$\chi = \frac{\pi_j \tau_{ji}}{\pi_i \tau_{ij}}$$

  - *ideally, $\chi$ will be unity (all trials accepted) even for a "large" change*
    - ➙ rarely achieve this level of improvement
  - *requires coordination of forward and reverse moves*

# Example: Biased Insertion in GCMC

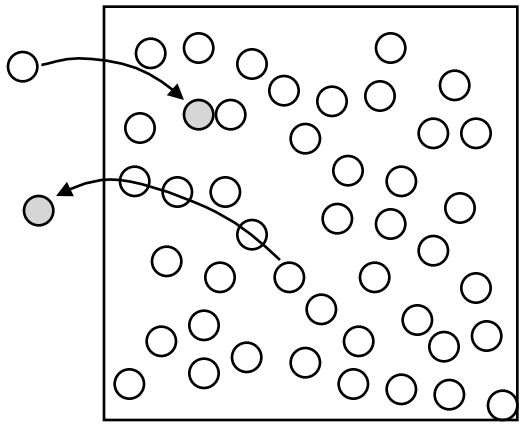
- Grand-canonical Monte Carlo (μVT)
  - *fluctuations in N require insertion/deletion trials*
  - *at high density, insertions may be rarely accepted*
    - ➙ $\tau_{ij}$ is small for *j* a state having additional but non-overlapping molecule
  - *at high chemical potential, limiting distribution strongly favors additional molecules* $\pi \propto e^{\beta\mu N}$
    - ➙ $\chi$ is large for (N+1) state with no overlap
  - *apply biasing to improve acceptance*
  - *first look at unbiased algorithm*



# Insertion/Deletion Trial Move
# 1. Specification

- Gives new configuration of same volume but different number of molecules
- Choose with equal probability:
  - *insertion trial: add a molecule to a randomly selected position*
  - *deletion trial: remove a randomly selected molecule from the system*
- Limiting probability distribution
  - *grand-canonical ensemble*

$$\pi\left(\mathbf{r}^N\right) = \frac{1}{\Xi}\frac{1}{\Lambda^{dN}} e^{-\beta U\left(\mathbf{r}^N\right)+\beta\mu N} d\mathbf{r}^N$$



# Insertion/Deletion Trial Move
# 2. Analysis of Trial Probabilities

- Detailed specification of trial moves and and probabilities

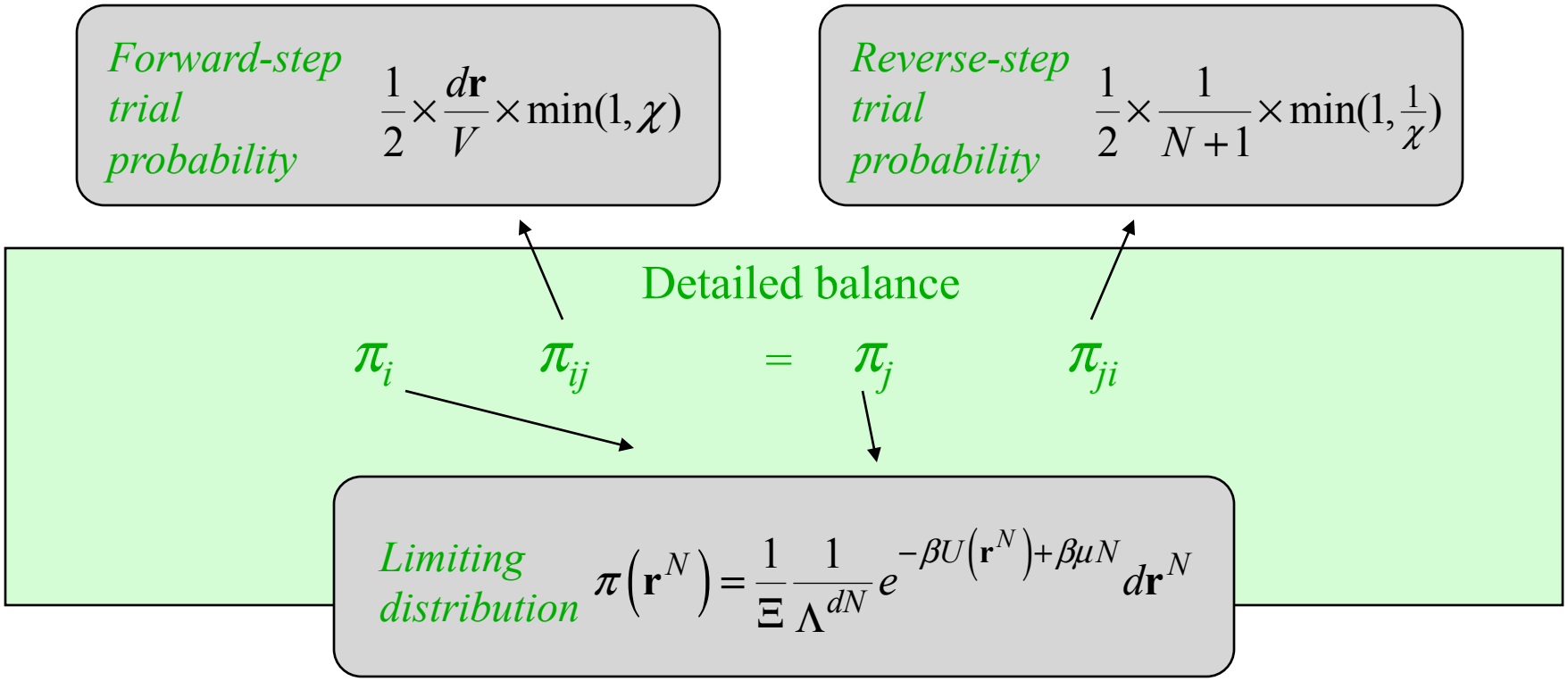
| Event<br>[reverse event] | Probability<br>[reverse probability] |
|---|---|
| Select insertion trial<br>[select deletion trial] | ½<br>[½ ] |
| Place molecule at $\mathbf{r}_{N+1}$<br>[delete molecule N+1] | d**r**/V<br>[1/(N+1)] |
| Accept move<br>[accept move] | min(1,$\chi$)<br>[min(1,1/$\chi$)] |

*Forward-step trial probability* $\frac{1}{2}\times\frac{d\mathbf{r}}{V}\times\min(1,\chi)$

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

*$\chi$ is formulated to satisfy detailed balance*

# Insertion/Deletion Trial Move
# 3. Analysis of Detailed Balance



# Insertion/Deletion Trial Move
# 3. Analysis of Detailed Balance

*Forward-step trial probability* $\frac{1}{2}\times\frac{d\mathbf{r}}{V}\times\min(1,\chi)$

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

Detailed balance

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

$$\frac{e^{-\beta U^{old}+\beta\mu N}d\mathbf{r}^N}{\Xi\Lambda^{dN}}\left[\frac{1}{2}\times\frac{d\mathbf{r}}{V}\times\min(1,\chi)\right]=\frac{e^{-\beta U^{new}+\beta\mu(N+1)}d\mathbf{r}^{N+1}}{\Xi\Lambda^{d(N+1)}}\left[\frac{1}{2}\times\frac{1}{N+1}\times\min(1,\frac{1}{\chi})\right]$$

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

# Insertion/Deletion Trial Move
# 3. Analysis of Detailed Balance

*Forward-step trial probability* $\frac{1}{2}\times\frac{d\mathbf{r}}{V}\times\min(1,\chi)$

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

Detailed balance

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

$$\frac{e^{-\beta U^{old}+\beta\mu N}d\mathbf{r}^N}{\Xi\Lambda^{dN}}\left[\frac{1}{2}\times\frac{d\mathbf{r}}{V}\times\min(1,\chi)\right]=\frac{e^{-\beta U^{new}+\beta\mu(N+1)}d\mathbf{r}^{N+1}}{\Xi\Lambda^{d(N+1)}}\left[\frac{1}{2}\times\frac{1}{N+1}\times\min(1,\frac{1}{\chi})\right]$$

$$\frac{1}{V}e^{-\beta U^{old}}\chi=\frac{1}{\Lambda(N+1)}e^{-\beta U^{new}-\beta\mu}$$

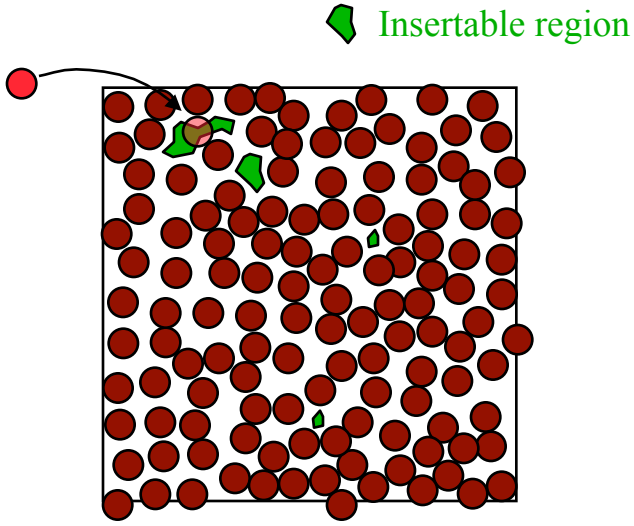
$$\chi=\frac{V}{\Lambda(N+1)}e^{-\beta(U^{new}-U^{old})+\beta\mu}$$

Acceptance probability

Remember
insert: (N+1) = $N_{old}$+1
delete: (N+1) = $N_{old}$

# Biased Insertion/Deletion Trial Move
# 1. Specification

- Trial-move algorithm. Choose with equal probability:
  - *Insertion*
    - ➙ identify region where insertion will not lead to overlap
    - ➙ let the volume of this region be εV
    - ➙ place randomly somewhere in this region
  - *Deletion*
    - ➙ select any molecule and delete it



# Biased Insertion/Deletion Trial Move
# 2. Analysis of Trial Probabilities

- Detailed specification of trial moves and and probabilities

| Event<br>[reverse event] | Probability<br>[reverse probability] |
|---|---|
| Select insertion trial<br>[select deletion trial] | ½<br>[½ ] |
| Place molecule at $\mathbf{r}_{N+1}$<br>[delete molecule N+1] | $d\mathbf{r}/(\varepsilon V)$<br>[1/(N+1)] |
| Accept move<br>[accept move] | $\min(1,\chi)$<br>[$\min(1,1/\chi)$] |

*Forward-step trial probability* $\frac{1}{2}\times\frac{d\mathbf{r}}{\varepsilon V}\times\min(1,\chi)$

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

Only difference from unbiased algorithm

# Biased Insertion/Deletion Trial Move
# 3. Analysis of Detailed Balance

Detailed balance

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

$$\frac{e^{-\beta U^{old}+\beta\mu N}\,d\mathbf{r}^N}{\Xi\Lambda^{dN}}\left[\frac{1}{2}\times\frac{d\mathbf{r}}{\varepsilon V}\times\min(1,\chi)\right]=\frac{e^{-\beta U^{new}+\beta\mu(N+1)}\,d\mathbf{r}^{N+1}}{\Xi\Lambda^{d(N+1)}}\left[\frac{1}{2}\times\frac{1}{N+1}\times\min(1,\frac{1}{\chi})\right]$$

Remember
insert: (N+1) = $N_{old}$+1
delete: (N+1) = $N_{old}$

$$\chi=\frac{\varepsilon V}{\Lambda(N+1)}e^{-\beta(U^{new}-U^{old})+\beta\mu}$$

Acceptance probability

- *ε must be computed even when doing a deletion, since χ depends upon it*
  - ➜ for deletion, ε is computed for configuration after molecule is removed
  - ➜ for insertion, ε is computed for configuration before molecule is inserted

# Biased Insertion/Deletion Trial Move
# 4. Comments

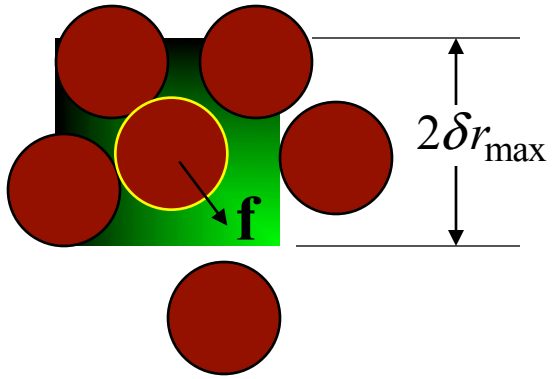
- Advantage is gained when ε is small and $e^{\beta\mu}$ is large
  - *for hard spheres near freezing*
    - → $\beta\mu + \ln(V/\Lambda N)$ : 16 (difficult to accept deletion without bias)
    - → $\varepsilon$ : $10^{-7}$ (difficult to find acceptable insertion without bias)
    - → $\chi$ : 1

$$\chi = \varepsilon e^{\beta\mu} \frac{V}{\Lambda(N+1)} e^{-\beta\Delta U}$$

- Identifying and characterizing (computing ε) the non-overlap region may be difficult

# Force-Bias Trial Move
# 1. Specification

- Move atom in preferentially in direction of lower energy
  - *select displacement* $\delta\mathbf{r}$ *in a cubic volume centered on present position*
  - *within this region, select with probability*




$$p(\delta\mathbf{r}) = \frac{\exp[+\lambda\beta\mathbf{f}\cdot\delta\mathbf{r}]}{C(\mathbf{f})} = \frac{e^{\lambda\beta f_x \delta r_x} e^{\lambda\beta f_y \delta r_y}}{c_x c_y}$$

*Favors* $\delta r_y$ in same direction as $f_y$

  - $C = c_x c_y$ *is a normalization constant*

$$c_x = \int_{-\delta r_{\max}}^{+\delta r_{\max}} e^{\lambda\beta f_x \delta r_x} d(\delta r_x) = \frac{\sinh(\lambda\beta f_x \delta r_{\max})}{\lambda\beta f_x}$$

*Pangali, Rao, and Berne, Chem. Phys. Lett. 47 413 (1978)*

# An Aside: Sampling from a Distribution

- Rejection method for sampling from a complex distribution p(x)
  - *write* $p(x) = Ca(x)b(x)$
    - a(x) is a simpler distribution
    - b(x) lies between zero and unity
  - *recipe*
    - generate a uniform random variate $U$ on (0,1)
    - generate a variate $X$ on the distribution a(x)
    - if $U <$ b(X) then keep X
    - if not, try again with a new $U$ and $X$
- We wish to sample from $p(x) = e^{qx}$ for $x = (-\delta,+\delta)$
  - *we know how to sample on* $e^{q(x-x0)}$ for $x = (x_0,\infty)$
    - $x = x_0 - q \ln[U(0,1)]$
  - *use rejection method with*
    - $a(x) = e^{q(x-\delta)}$
    - b(x) = 0 for $x < -\delta$ or $x > +\delta$; 1 otherwise
      - i.e., sample on a(x) and reject values outside desired range

# Force-Bias Trial Move
# 2. Analysis of Trial Probabilities

- Detailed specification of trial moves and and probabilities

| Event<br>[reverse event] | Probability<br>[reverse probability] |
|---|---|
| Select molecule k<br>[select molecule k] | 1/N<br>[1/N] |
| Move to $\mathbf{r}^{new}$<br>[move back to $\mathbf{r}^{old}$] | $p^{old}(\delta\mathbf{r})$<br>$[p^{new}(-\delta\mathbf{r})]$ |
| Accept move<br>[accept move] | $\min(1,\chi)$<br>$[\min(1,1/\chi)]$ |

*Forward-step trial probability* $\dfrac{p^{old}(\delta\mathbf{r})d\mathbf{r}}{N}\times\min(1,\chi)$

*Reverse-step trial probability* $\dfrac{p^{new}(-\delta\mathbf{r})d\mathbf{r}}{N}\times\min(1,\frac{1}{\chi})$

# Force-Bias Trial Move
# 3. Analysis of Detailed Balance

*Forward-step trial probability* $\dfrac{p^{old}(\delta\mathbf{r})d\mathbf{r}}{N}\times\min(1,\chi)$

*Reverse-step trial probability* $\dfrac{p^{new}(-\delta\mathbf{r})d\mathbf{r}}{N}\times\min(1,\frac{1}{\chi})$

$$p(\delta\mathbf{r})=\frac{\exp\left[+\lambda\beta\mathbf{f}\cdot\delta\mathbf{r}\right]}{C(\mathbf{f})}=\frac{e^{\lambda\beta f_x\delta r_x}e^{\lambda\beta f_y\delta r_y}}{c_x c_y}$$

Detailed balance

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

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

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

# Force-Bias Trial Move
# 3. Analysis of Detailed Balance

*Forward-step trial probability* $\dfrac{p^{old}(\delta\mathbf{r})d\mathbf{r}}{N}\times\min(1,\chi)$

*Reverse-step trial probability* $\dfrac{p^{new}(-\delta\mathbf{r})d\mathbf{r}}{N}\times\min(1,\frac{1}{\chi})$

$$p(\delta\mathbf{r})=\frac{\exp\left[+\lambda\beta\mathbf{f}\cdot\delta\mathbf{r}\right]}{C(\mathbf{f})}=\frac{e^{\lambda\beta f_x\delta r_x}e^{\lambda\beta f_y\delta r_y}}{c_x c_y}$$

Detailed balance

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

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

$$\frac{1}{C\left(\mathbf{f}^{old}\right)}e^{-\beta U^{old}+\lambda\beta\mathbf{f}^{old}\cdot\delta\mathbf{r}}\chi=\frac{1}{C\left(\mathbf{f}^{new}\right)}e^{-\beta U^{new}-\lambda\beta\mathbf{f}^{new}\cdot\delta\mathbf{r}}$$

$$\chi=\frac{C\left(\mathbf{f}^{old}\right)}{C\left(\mathbf{f}^{new}\right)}e^{-\beta(U^{new}-U^{old})-\lambda\beta(\mathbf{f}^{new}+\mathbf{f}^{old})\cdot\delta\mathbf{r}}$$

Acceptance probability

# Force-Bias Trial Move
# 4. Comments

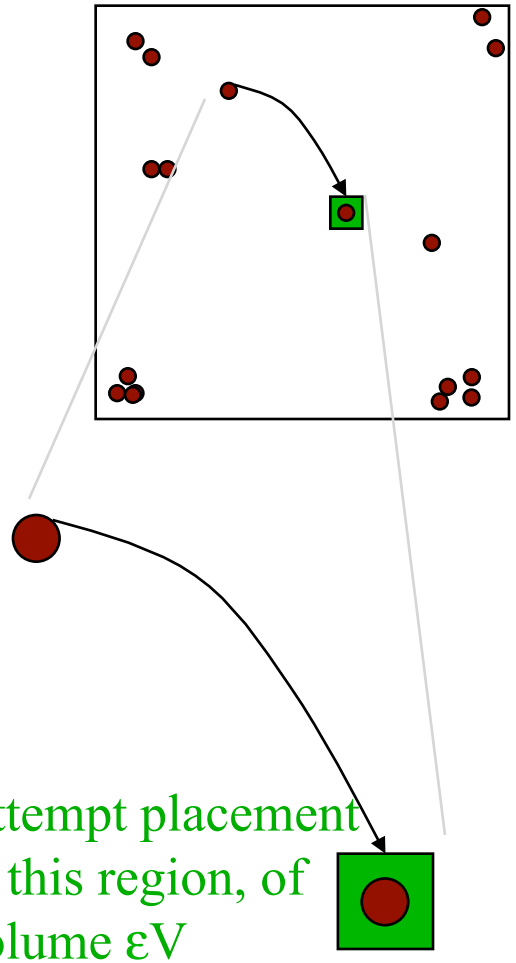
- Necessary to compute force both before and after move

$$\chi = \frac{C\left(\mathbf{f}^{old}\right)}{C\left(\mathbf{f}^{new}\right)} e^{-\beta(U^{new}-U^{old})-\lambda\beta(\mathbf{f}^{new}+\mathbf{f}^{old})\cdot\delta\mathbf{r}}$$

- From definition of force $\mathbf{f} = -\nabla U$
  - $U^{new} \approx U^{old} - \frac{1}{2}(\mathbf{f}^{new} + \mathbf{f}^{old}) \cdot \delta\mathbf{r}$
  - *$\lambda$ = 1/2 makes argument of exponent nearly zero*
  - *$\lambda$ = 0 reduces to unbiased case*
- Force-bias makes Monte Carlo more like molecular dynamics
  - *example of hybrid MC/MD method*
- Improvement in convergence by factor or 2-3 observed
  - *worth the effort?*

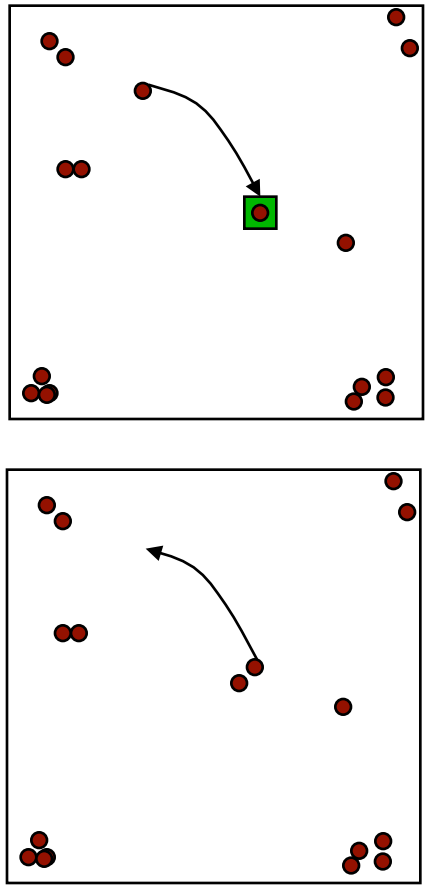
# Association-Bias Trial Move
# 1. Specification

- Low-density, strongly attracting molecules
  - *when together, form strong associations that take long to break*
  - *when apart, are slow to find each other to form associations*
  - *performance of simulation is a problem*
- Perform moves that put one molecule preferentially in vicinity of another
  - *suffer overlaps, maybe 50% of time*
  - *compare to problem of finding associate only 1 time in (say) 1000*
- Must also preferentially attempt reverse move



# Association-Bias Trial Move
# 1. Specification

- With equal probability, choose a move:
  - *Association*
    - ➔ select a molecule that is not associated
    - ➔ select another molecule (associated or not)
    - ➔ put first molecule in volume $eV$ in vicinity of second
  - *Dis-association*
    - ➔ select a molecule that is associated
    - ➔ move it to a random position anywhere in the system



# Association-Bias Trial Move
# 2. Analysis of Trial Probabilities

- Detailed specification of trial moves and and probabilities

| Event<br>[reverse event] | Probability<br>[reverse probability] |
|---|---|
| Select molecule k<br>[select molecule k] | $1/N_{un}$<br>$[1/(N_{assoc}+1)]$ |
| Move to $\mathbf{r}^{new}$<br>[move back to $\mathbf{r}^{old}$] | $1/(N_{assoc}\varepsilon V)$ (*)<br>$[1/V]$ |
| Accept move<br>[accept move] | $\min(1,\chi)$<br>$[\min(1,1/\chi)]$ |

*Forward-step trial probability* $\dfrac{1}{N_u N_a \varepsilon V} \times \min(1, \chi)$

*Reverse-step trial probability* $\dfrac{1}{(N_a+1)V} \times \min(1, \dfrac{1}{\chi})$

(*) incorrect

# Association-Bias Trial Move
# 3. Analysis of Detailed Balance

*Forward-step trial probability* $\frac{1}{N_u N_a \varepsilon V} \times \min(1, \chi)$

*Reverse-step trial probability* $\frac{1}{(N_a+1)V} \times \min(1, \frac{1}{\chi})$

Detailed balance

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

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

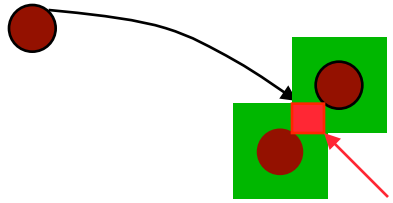
$$\chi = \frac{N_a}{(N_a+1)} N_u \varepsilon e^{-\beta(U^{new} - U^{old})}$$

Acceptance probability

# Association-Bias Trial Move
# 4. Comments

- This is incorrect! $\chi = \frac{N_a}{N_a+1} N_u \varepsilon e^{-\beta(U^{new}-U^{old})}$

- Need to account for full probability of positioning in $\mathbf{r}^{new}$



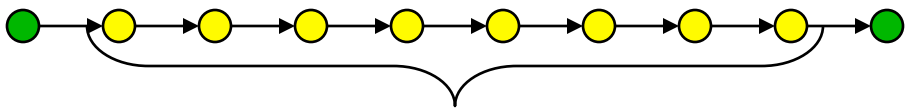
This region has extra probability of being selected (in vicinity of two molecules)

  - *must look in local environment of trial position to see if it lies also in the neighborhood of other atoms*
    - ➔ add a $1/\varepsilon V$ for each atom

- Algorithm requires to identify or keep track of number of associated/unassociated molecules

# Using an Approximation Potential
# 1. Specification

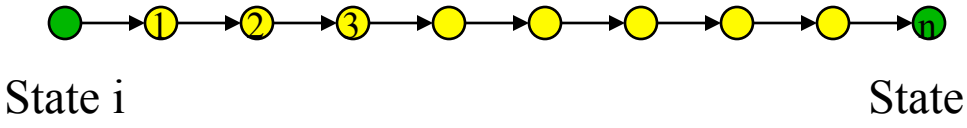
- Evaluating the potential energy is the most time-consuming part of a simulation
- Some potentials are especially time-consuming, e.g.
  - *three-body potentials*
  - *Ewald sum*
- Idea:
  - *move system through Markov chain using an approximation to the real potential (cheaper to compute)*
  - *at intervals, accept or reject entire subchain using correct potential*



True potential Approximate True potential

# Approximation Potential
# 2. Analysis of Trial Probabilities

- What are $\pi_{ij}$ and $\pi_{ji}$?




- Given that each elementary Markov step obeys detailed balance for the approximate potential…
  - *…one can show that the "super-step"* i → j *also obeys detailed balance (for the approximate potential)*
  - $\pi_i^a \pi_{ij}^{(n)} = \pi_j^a \pi_{ji}^{(n)}$
  - *very hard to analyze without this result*
    - ➥ would have to consider all paths from i to j to get transition probability

# Approximation Potential
# 3. Analysis of Detailed Balance

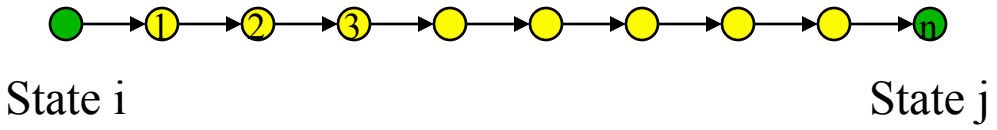
- Formulate acceptance criterion to satisfy detailed balance for the real potential

$$\pi_i \pi_{ij}^{(n)} \min(1, \chi) = \pi_j \pi_{ji}^{(n)} \min(1, 1/\chi)$$

$$\pi_i \left( \frac{\pi_j^a}{\pi_i^a} \pi_{ji}^{(n)} \right) \min(1, \chi) = \pi_j \pi_{ji}^{(n)} \min(1, 1/\chi)$$

Approximate-potential detailed balance

$$\pi_i^a \pi_{ij}^{(n)} = \pi_j^a \pi_{ji}^{(n)}$$



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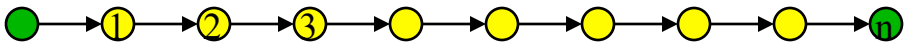
Approximate-potential detailed balance

$$\pi_i^a \pi_{ij}^{(n)} = \pi_j^a \pi_{ji}^{(n)}$$




State i State j

# Approximation Potential
# 3. Analysis of Detailed Balance

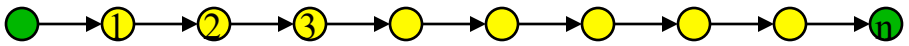
- Formulate acceptance criterion to satisfy detailed balance for the real potential

$$\pi_i \pi_{ij}^{(n)} \min(1, \chi) = \pi_j \pi_{ji}^{(n)} \min(1, 1/\chi)$$

$$\pi_i \left( \frac{\pi_j^a}{\pi_i^a} \cancel{\pi_{ji}^{(n)}} \right) \min(1, \chi) = \pi_j \cancel{\pi_{ji}^{(n)}} \min(1, 1/\chi)$$

$$\chi = \frac{\pi_j}{\pi_j^a} \times \frac{\pi_i^a}{\pi_i}$$

Close to 1 if approximate potential is good description of true potential




State i State j

# Summary

- Good Monte Carlo keeps the system moving among a wide variety of states
- At times sampling of wide distribution is not done well
  - *many states of comparable probability not easily reached*
  - *few states of high probability hard to find and then escape*
- Biasing the underlying transition probabilities can remedy problem
  - *add bias to underlying TPM*
  - *remove bias in acceptance step so overall TPM is valid*
- Examples
  - *insertion/deletion bias in GCMC*
  - *force bias*
  - *association bias*
  - *using an approximate potential*