

## "Biased" Monte Carlo (Ch. 13 in F+S)

Why we Monte Carlo at all?

- Possibility for unphysical moves (e.g. Gibbs Ensemble GCMC) for rapid equilibration
- Design of special algorithms, e.g. for polymers

"Biased" Monte Carlo moves cannot, of course, be biased in the ensemble averages they generate (that would be incorrect). Instead, we work with an asymmetric a priori transition matrix to favor sampling of specific conformations and then correct (unbias) our results through appropriately modified acceptance criteria.

→ Analogy to Rosenbluth sampling of "static" conformations

### Beyond Metropolis

In standard Monte Carlo, we use a symmetric probability  $\alpha(o \rightarrow n) = \alpha(n \rightarrow o)$  for moving between states. Now let us select

$$\alpha(o \rightarrow n) = f(n) \neq \alpha(n \rightarrow o) = f(o)$$

We can still satisfy detailed balance

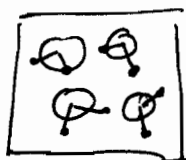
$$N(o) \cdot \alpha(o \rightarrow n) \cdot \text{accept}(o \rightarrow n) = N(n) \alpha(n \rightarrow o) \cdot \text{accept}(n \rightarrow o)$$

$$\frac{N(n)}{N(o)} = \exp(-\beta U(n) + \beta U(o)) \quad \text{in NVT ensemble}$$

By choosing  $\frac{\text{accept}(o \rightarrow n)}{\text{accept}(n \rightarrow o)} = \frac{g(o)}{g(n)} e^{-\beta U(n) + \beta U(o)}$  ①

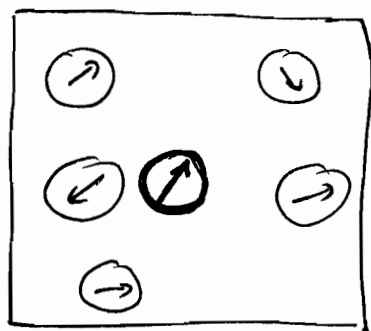
If we could select  $g(o)/g(n)$  to balance out the Boltzmann factor, we could have 10% acceptance of generated configurations! This is hard, because it requires careful selection of "new" states (but it is automatically done in MD).

Example: Orientational Bias

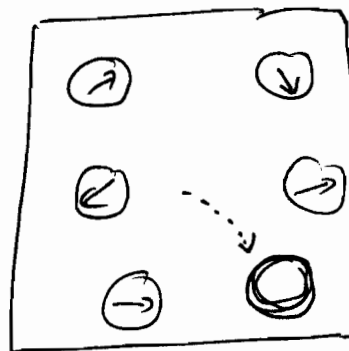


For polar molecules such as water, orientation (H-bonding) is very important.

Consider move to new position



old



new

How do we select favorable new orientation?

Pick  $k$  possible new orientations

$$\{\vec{b}\}_k = \{\vec{b}_1, \vec{b}_2, \dots, \vec{b}_k\}$$





and select "best" direction w/ probability

$$P(\vec{b}_n) = \frac{\exp(-\beta U_n^{or})}{\sum_{i=1}^k \exp(-\beta U_i^{or})} = f(n) \quad U^{or}: \text{orientational energy of interaction}$$

Sum over new =  $W_n$

Now, to satisfy detailed balance (eq. 1 on previous page), we need  $f(o)$ . Even though only one old configuration is given, we need a "virtual" reverse move:

{  + set of  $(k-1)$  virtual <sup>old</sup> orientations  }

old,  $\vec{b}_o$

Probability of picking actual "old" configuration would have been

$$P(\vec{b}_o) = \frac{\exp(-\beta U_o^{or})}{\sum_{i=1}^k \exp(-\beta U_i^{or})} = f(o)$$

Sum over "old" orientations =  $W_o$

$U = \text{total energy} = U^{pos} + U^{or}$

Detailed balance:  $\frac{\text{accept}(o \rightarrow n)}{\text{accept}(n \rightarrow o)} = \frac{f(o)}{f(n)} \frac{e^{-\beta U_n}}{e^{-\beta U_o}} =$

$$= \frac{e^{-\beta U_o^{or}}}{W_o} \frac{W_n}{e^{-\beta U_n^{or}}} \frac{e^{-\beta U_n}}{e^{-\beta U_o}} = \frac{W_n}{W_o} \frac{e^{-\beta U_n^{pos}}}{e^{-\beta U_o^{pos}}}$$

Final Metropolis's condition:

$$P_{acc} = \min \left\{ 1, \frac{w_n}{w_o} \exp(-\beta[u_n^{pos} - u_o^{pos}]) \right\}$$

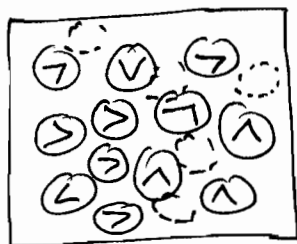
$$w = \sum_{i=1}^K \exp(-\beta u_i^{or}) \quad \text{"Rosenbluth weights" of old + new orientations}$$

Does this save time?

If the costs of calculating  $u^{pos}$ ,  $u^{or}$  are comparable, not too much CPU time is saved; One needs  $K$  calculations of  $u^{or}$  at both old + new positions. (Only efficient if  $t(pos) \gg t(or)$ )

Example - GCMC for water

For water  $t(pos) \ll t(or)$  because the orientational interactions involve electrostatics, which have to be performed by special methods (e.g. Ewald Sums)



○ LJ  $U^{LJ}$   
 ↗ electrostatics  $U^{el}$

Attempt  $K$  insertions of LJ core

select "best" from  $P_n = \frac{e^{-\beta u_n^{LJ}}}{\sum_{i=1}^K e^{-\beta u_i^{LJ}}} = w_n \cdot K$

Select random orientation, calculate  $U^{el}$

Accept/reject  $P_{acc} = \min \left\{ 1, w_n \cdot \frac{V}{N+1} e^{-\beta \Delta U^e + \beta \mu} \right\}$

Removals: select random molecule,  $k-1$  other random positions  $P_0 = \frac{e^{-\beta U_0^{i_0}}}{\sum_{i=1}^k e^{-\beta U_i^{i_0}}} = w_0 \cdot k$

Accept/reject  $P_{acc} = \min \left\{ 1, \frac{1}{w_0} \frac{N}{V} e^{-\beta \Delta U^e - \beta \mu} \right\}$

(If the factor  $k$  was omitted from  $w = \frac{1}{k} \sum_{i=1}^k e^{-\beta U_i^{i_0}}$  we would have had a shift of the chemical potential by a trivial  $\beta \ln k$  amount)

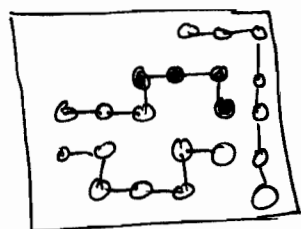
## Chains / Configurational Bias MC

Stepmann + Frenkel Mol. Phys. 75:59 (1992)

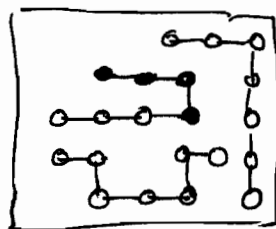
Frenkel, Mooij + Smit, J. Phys. Condens. Matter. 4:3053 (1992)

Laso, de Pablo, Suter JCP 97:2817 (1992)

- \* Inspired by Rosenbluth method for static configurations
- \* Makes possible MC simulations of chains, [equilibration of  $\sim C_{500}$  possible]



old



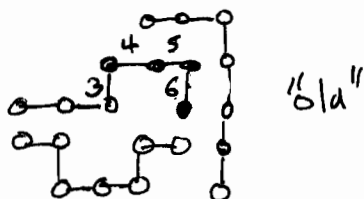
new

"Cut" section of chain  
"regrow" into new conformation

Same as for orientational bias:

$$\frac{\text{accept}(o \rightarrow n)}{\text{accept}(n \rightarrow o)} = \frac{f(o)}{f(n)} \frac{e^{-B u(n)}}{e^{-B u(o)}}$$

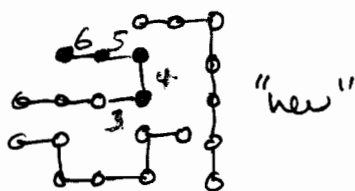
For simple (athermal) Rosenbluth sampling



$$w_i = \frac{\# \text{ of unoccupied positions}}{\# \text{ of total positions}}$$

$$w_6 = \frac{1}{4} \quad w_5 = \frac{2}{4} \quad w_4 = \frac{3}{4} \quad w_3 = \frac{3}{4}$$

$$w_o = \prod w_i = \frac{1}{4} \cdot \frac{2}{4} \cdot \frac{3}{4} \cdot \frac{3}{4} = \frac{9}{128}$$

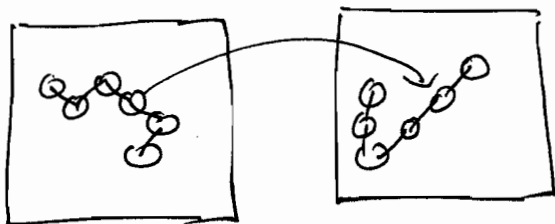


$$w_3 = \frac{3}{4} \quad w_4 = \frac{2}{4} \quad w_5 = \frac{2}{4} \quad w_6 = \frac{2}{4}$$

$$w_n = \prod w_i = \frac{3}{4} \cdot \frac{2}{4} \cdot \frac{2}{4} \cdot \frac{2}{4} = \frac{3}{32}$$

$$P_{acc} = \min \left\{ 1, \frac{w_n}{w_o} \exp(-B \Delta u) \right\}$$

Q: Should non-reversal of chains be taken into account? (e.g.  $w_o = \frac{1}{3} \cdot \frac{2}{3} \cdot \frac{3}{3} \cdot \frac{3}{3} = \frac{2}{9}$ ?)



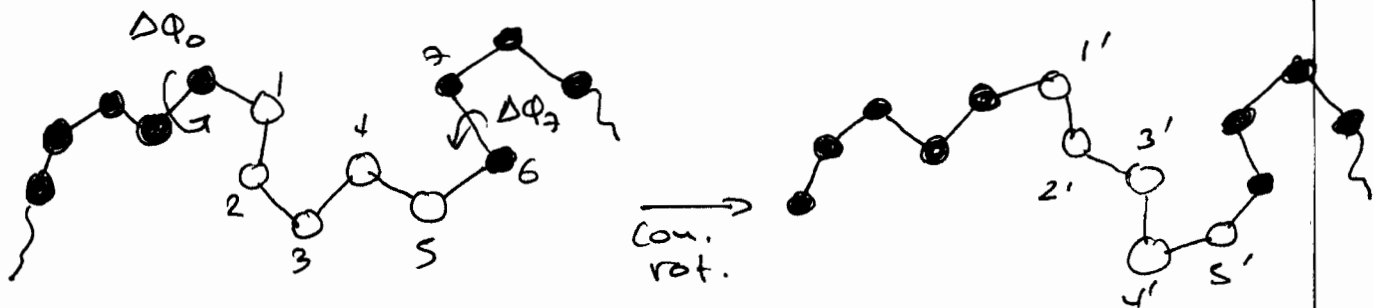
Similarly: transfers for Gibbs ensemble

## Complex Moves for Polymers

- High MW polymers are hard to equilibrate: entanglements, slow dynamics
- "Local" moves (e.g. displacements of single beads) constrained by bond connectivity, torsional + angle potentials

Theodorou + group:  
de Pablo + group

- \* Concerted Rotation (1993)
- \* End-Bridging (1999)
- \* Double-Bridging (2003)



- rotate bonds to get atoms  $1 \rightarrow 1'$   
 $5 \rightarrow 5'$

- rebridge atoms 2, 3, 4 to close chain

\* need Jacobian of coordinate transformation for  $\Delta\phi_0, \Delta\phi_3 \rightarrow$  cartesian

\* need possible number of rebridging solutions for new + old positions of atoms 1, 5

