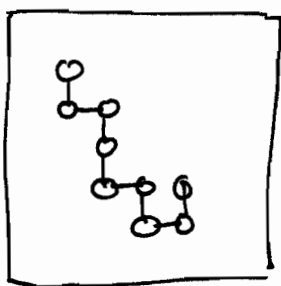


Rosenbluth Sampling (Ch. 11 in FTS)

This is the first of a large number of "biased" sampling schemes. Because it is particularly simple, we will explore this in detail first, and then present variations of it and extensions to other systems.

In the original Rosenbluth + Rosenbluth sampling method (JCP, 23, 356 (1955)), one is interested in conformational properties of a simple homopolymer model:



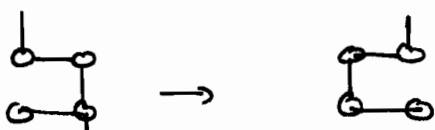
Model: \rightarrow Connected chain of monomers, degree of polymerization = r

\rightarrow Excluded-volume interactions between beads

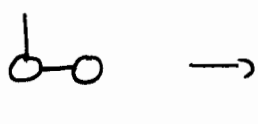
\rightarrow athermal or "thermal" version, with nearest-neighbor attractions

For athermal system, how do we generate a representative ensemble of configurations of one chain?

1) Metropolis MC sampling by local moves:



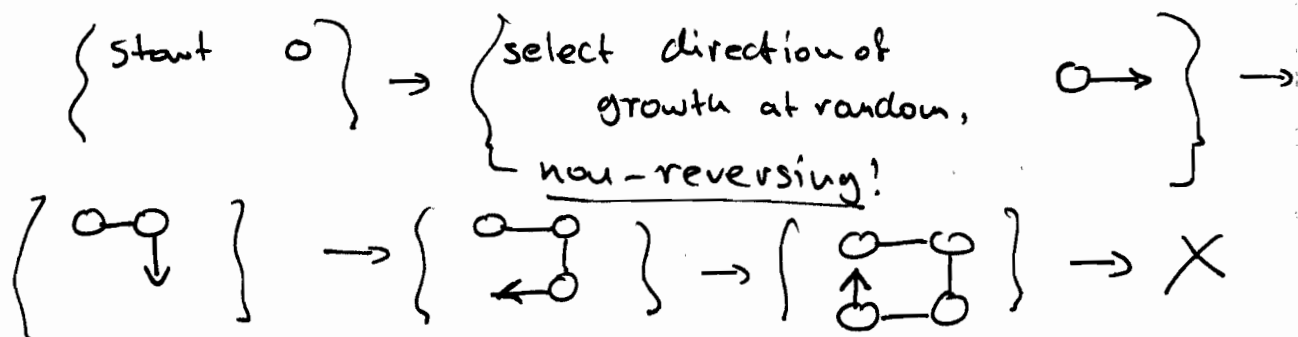
"Crankshaft"



"end flip"

} slow for large r

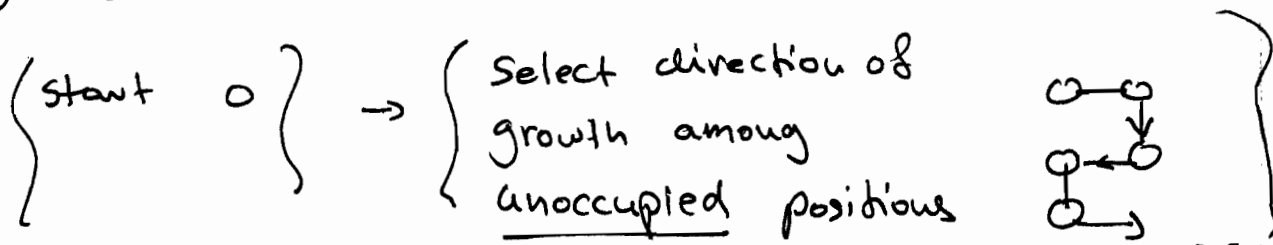
2) generate configurations "at random"



For chain of length r , there are (in 3 dimensions) $z \cdot (z-1)^{r-2}$ possible configurations.
 $z = \text{coordination number}$

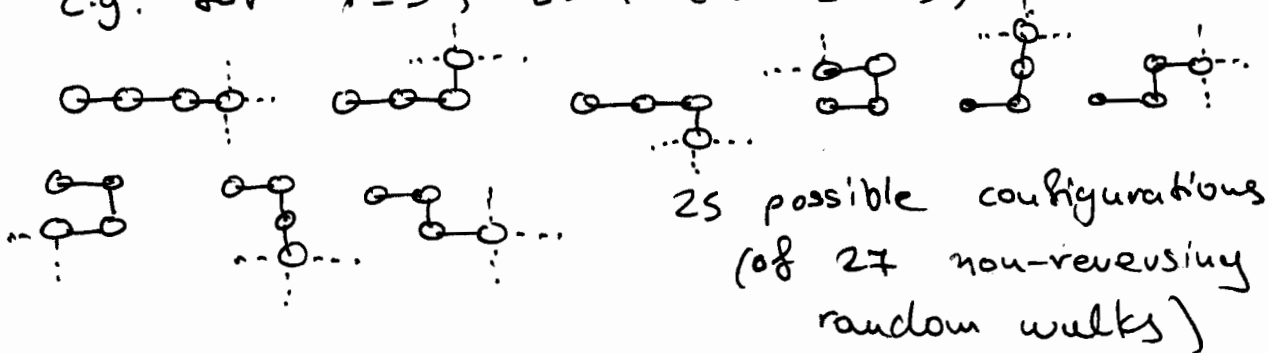
However, for large r , the "random" scheme will frequently result in a chain that does not satisfy the excluded volume constraint, and thus is not a valid conformation. (for $r=100$, 99.8% rejection)

3) Rosenbluth method -

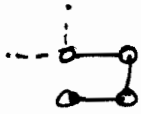


If nothing else is done, the Rosenbluth method would result in a biased (incorrect) sample.

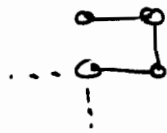
E.g. for $r=5$, $z=4$ (in 2-D), fixed first bond



In Rosenbluth method, configurations



and



take a weight of $2/3$, to compensate for the fact that they appear in the sample $\frac{3}{2} = 1.50$ times as frequently as in the correct unbiased sample.

In general, the Rosenbluth weight w is

$$w = \prod_{\text{growth steps}} \frac{\# \text{ of available growth directions in a step}}{\text{total } \# \text{ of growth directions}}$$

when properties are calculated, the weight of each configuration is used:

$$\langle F_i \rangle = \left(\sum_i F_i w_i \right) / \sum_i w_i$$

Calculation of the Chemical Potential via Rosenbluth sampling

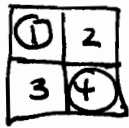
In the previous section we were interested in properties of a single chain - now we consider what happens when we wish to determine the chemical potential in a multiparticle system.

Widom insertions: $B\mu^{\text{ex}} = \ln \left(\left\langle \exp(-B\psi) \right\rangle \right)$

ψ : test particle energy

Rosenbluth Sampling ②

Consider a simple system ^{of monomers} with just four positions:



positions ① and ④ are occupied,

$$\text{So } \exp(-\beta\psi_1) = \emptyset = \exp(-\beta\psi_4)$$

$$\exp(-\beta\mu^{\text{ex}}) = \langle \exp(-\beta\psi) \rangle = \frac{\exp(-\beta\psi_2) + \exp(-\beta\psi_3)}{4}$$

In the Rosenbluth implementation, we only insert in unoccupied positions, with weight $w = \frac{2}{4} = \frac{1}{2}$

$$\langle w_i \exp(-\beta\psi) \rangle_R = \frac{1}{2} \cdot \frac{2}{4} \cdot (\exp(-\beta\psi_2) + \exp(-\beta\psi_3))$$

Alternatively, we could implement a "thermal" version of Rosenbluth sampling, in which the position to be sampled is picked with probability proportional to the Boltzmann weight:

$$P_2 = \frac{e^{-\beta\psi_2}}{e^{-\beta\psi_2} + e^{-\beta\psi_3}}$$

$$P_3 = \frac{e^{-\beta\psi_3}}{e^{-\beta\psi_2} + e^{-\beta\psi_3}}$$

$$P_1 = P_4 = \emptyset$$

In this case, the chemical potential is just the ensemble average of the Rosenbluth weights, which are now defined as

$$w_i = \frac{1}{k} \sum_{j=1}^k \exp(-\beta\psi_j) \quad \text{k is the number of trial positions}$$

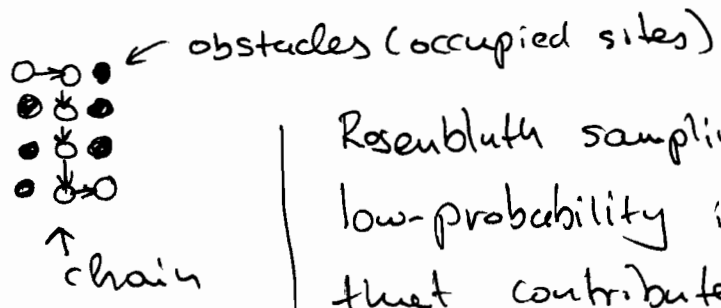
In the example above, every attempted insertion has the same Rosenbluth weight, $w = \frac{1}{4} (e^{-\beta\psi_2} + e^{-\beta\psi_3})$

The chemical potential is

$$\exp(-\beta \mu^{ex}) = \langle w_i \rangle = \frac{1}{4} (e^{-\beta \psi_2} + e^{-\beta \psi_3})$$

The concept of "including the Boltzmann weight while sampling" is quite general, as will be shown in the section on configurational-bias methods.

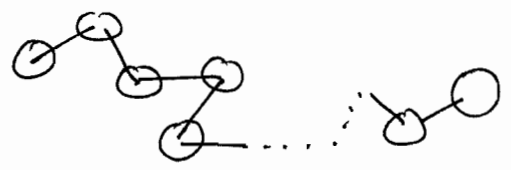
Does this save time? In the case of single-site systems, the effort required to compute the energy at each "trial" site is equal to the effort that would be needed for direct calculation of $e^{\beta \mu^{ex}}$ from $\langle \exp(-\beta U_{test}) \rangle$; However, for a multisegment molecule:



Rosenbluth sampling quickly finds low-probability inserted configurations that contribute greatly to the ensemble average.

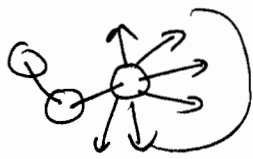
Extension to Continuous Space

Consider a chain in continuous space with a torsional, bond bending and bead-bead interactions



l beads
 $U = U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_l)$

We can apply Rosenbluth sampling to compute configurational properties as follows.



k directions of possible growth at each step i

$$w_i = \frac{1}{k} \sum_{j=1}^k \exp(-\beta U_i(j)) \quad \text{step } i$$

↳ total energy of bead i

Chose one of these directions w/ probability proportional to $\exp(-\beta U_i(j))$

Weight of completed chain $W = \prod_{i=1}^L w_i$

Properties of the chain (e.g. R_g) calculated

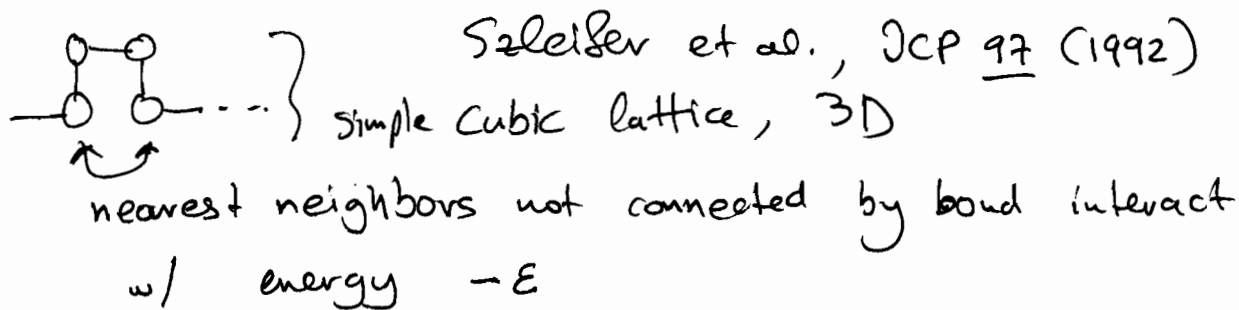
from $\langle f \rangle = \frac{\sum_{\text{samples}} W_r F_r}{\# \text{ of samples}}$

Note that the Boltzmann factor of the energy does not enter in $\langle f \rangle$, since it has been included during the growth step

Limitations of Rosenbluth Sampling

Once more, sampling issues can crop up when the region of conformational space sampled is significantly different from the region that contributes heavily to the properties

E.g. for original problem of conformations of a lattice polymer chain

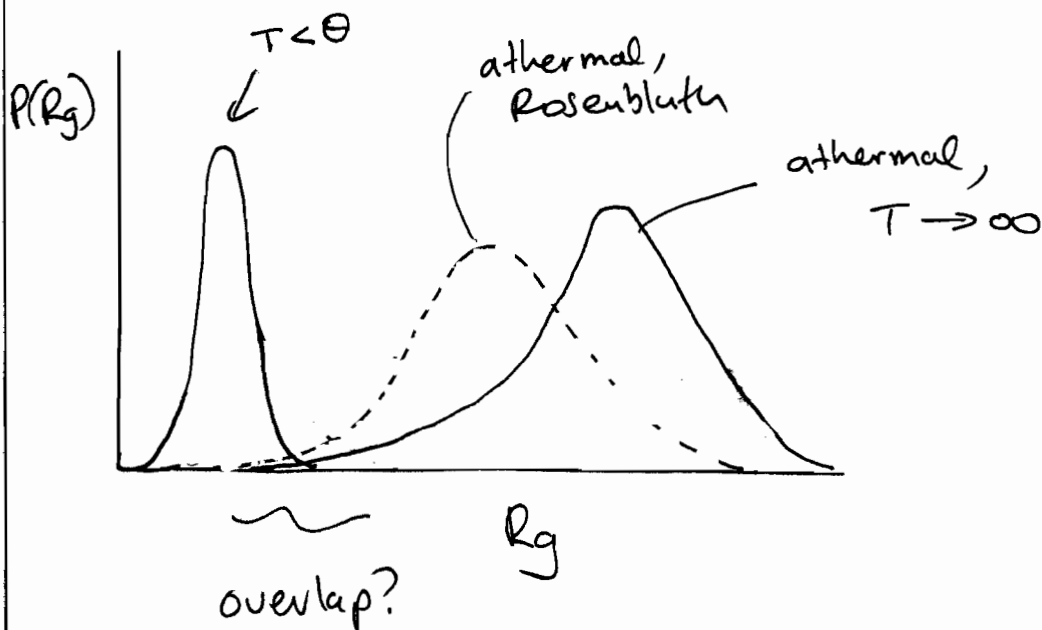


$$T^* = KT/E \simeq 2.97 : \Theta \text{ temperature,}$$

$$R_g \propto \sqrt{r} \text{ as } r \rightarrow \infty$$

$$T^* \gg \Theta : \text{good solvent } R_g \propto r^{0.6}$$

$$T^* \ll \Theta : \text{poor solvent } R_g \propto r^{1/3}$$



"Athermal" Rosenbluth samples slightly more compact states than the true (unbiased) distribution at $T \rightarrow \infty$, but does not sample the compact states characteristic of $T < \Theta$