2.5 Monte Carlo moves for a simple bead-spring polymer chain

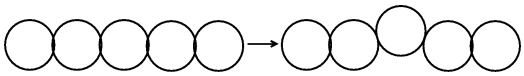
In the following we will discuss several Monte Carlo moves which are well-suited for the simulation of coarse-grained polymer models.

Phase behavior of single polymer chains

At high temperatures, the free energy (F=E-TS) is dominated by entropic contributions, i.e., the chain wants to explore as many configurations as possible. At low temperatures, the free energy is dominated by energetic contributions, i.e., the monomers in the chain want to be located in the minimum of the pair-potential. Therefore, the chain "collapses" to a globular state. The transition from the coil to the globular state is referred to as the Θ-transition.

2.5.1 Local Monte Carlo moves

Starting configuration
|: Move a particle



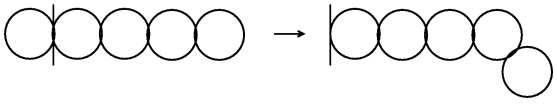
Determine the energy difference between old and new configuration
Energy lower? → Accept the move
Energy higher? → Accept with probability $\exp(-\beta\Delta E)$

[Draw random number $0<r<1$:
$r < \exp(-\beta\Delta E)$ → accept
else → reject move

Ex.: $\exp(-\beta\Delta E) = 0.1$, i.e. we would like to accept the move with 10% probability. We draw an evenly distributed number r between 0 and 1. The chance that $r < 0.1$ is 10%.

]
:|

2.5.2 Reptation / slithering snake moves

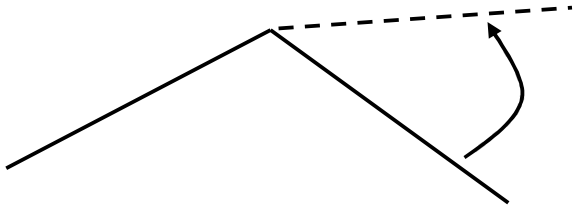


Recipe: Choose one end at random. Cut off one bead and attach it at the other end. Accept

with Metropolis. In the simplest implementation the bond length is not changed.

Adv.: Simple, faster than local displacements up to high densities, also works in melts.

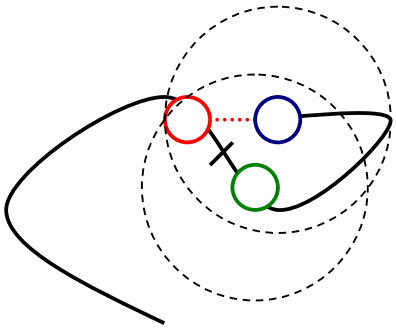
2.5.3 Pivot algorithm



Recipe: Choose a monomer at random which acts as a rotation center. Rotate one arm of the chain by an arbitrary angle. Accept with Metropolis.

Adv.: Most efficient scheme for dilute systems.
Disadv.: Doesn't work at high densities or in globular systems

2.5.4 Backbite move



Recipe:

|: 1. Choose one end at random (blue sphere).

2. Place a sphere around that end (radius should be larger than typical bond lengths). Choose an interaction partner (red sphere) within that sphere (among n_1 potential partners).

3. Backbite: The bond of the interaction partner to its successor (green sphere) is severed and the former successor becomes the new end. At the same time, a bond between the former end and the interaction partner is formed (red dotted line). The green sphere becomes the new end.

4. Place a sphere of the same size around the new end (green sphere) and count the number of beads within that sphere (n_2).

5. Accept with modified Metropolis criterion:
   Detailed balance:
   $w_{12}\ 0.5\ 1/n_1 \exp(-\beta E_{old}) = w_{21}\ 0.5\ 1/n_2 \exp(-\beta E_{new})$
   → Metropolis: min (1, n1/n2 exp(-$\beta\Delta$E))

:|

Adv.: Very efficient in globular systems (high densities)
Disadv.: Doesn't work in dilute systems (←→ pivot)

Comparison MC/MD

MD:
(-) efficiency of MD is comparable to local MC (with small step sizes), but at high densities there is often no clever MC move available
(+) dynamics is more realistic
(+) efficient (parallelized) implementations in standard software packages (even on GPUs)

MC:
(+) typically more efficient than MD for calculation of equilibrium properties
(-) non-physical dynamics
(-) MC algorithms are often tailored to the model under consideration
→ typically not implemented in standard software packages