Basic Monte Carlo (part 2)

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Convergence

Here, we will indicate that a system which is subject to the Metropolis algorithm will eventually move towards equilibrium.

Metropolis criterion: $W_{ij} = \min(1, P_j/P_i)$, where P_j and P_i are the equilibrium distributions of state j and i. In our case P_j and P_i are given by the Boltzmann distribution.

Let's consider $0 < P_j/P_i < 1$.
The net flux $Flux_{ij}$ from state i to j is given by:

$Flux_{ij} = P_i(t)\, W_{ij} - P_j(t)\, W_{ji} = P_i(t)\, P_j/P_i - P_j\,(t) = P_i(t)\,(P_j/P_i - P_j(t)/P_i(t))$.

If $P_j(t)/P_i(t) < P_j/P_i \rightarrow Flux_{ij} > 0 \rightarrow P_j(t)$ and $P_j(t)/P_i(t)$ increases
$\rightarrow$ system moves towards equilibrium.

If $P_j(t)/P_i(t) > P_j/P_i \rightarrow Flux_{ij} < 0 \rightarrow P_i(t)$ increases and $P_j(t)/P_i(t)$ decreases
$\rightarrow$ system moves towards equilibrium.

Selection probabilities:

In most cases in the canonical ensemble we do not need to consider selection probabilities as moves are symmetrical. If we, e.g., choose an Ising-Spin at random for a single spin flip the probability for selecting a particular spin is $a_i=1/N$ (N being the total number of spins). The selection probability for the reverse move (flip the same spin back) is also $a_j=a_i=1/N$ so the two cancel out and need not be considered. Sometimes, however, selection probabilities differ and detailed balance (and acceptance rule) are adjusted:

$$\frac{W_{ij}}{W_{ji}} = \frac{a_j}{a_i} e^{-\beta \Delta E}$$

Markov chains

In mathematics, a Markov chain, named after Andrey Markov, is a random process where all information about the future is contained in the present state (i.e. one does not need to examine the past to determine the future). To be more exact, the process has the Markov property, meaning that future states depend only on the present state, and are independent of past states. In other words, the description of the present state fully captures all the information that could influence the future evolution of the process. Being a stochastic process means that all state transitions are probabilistic

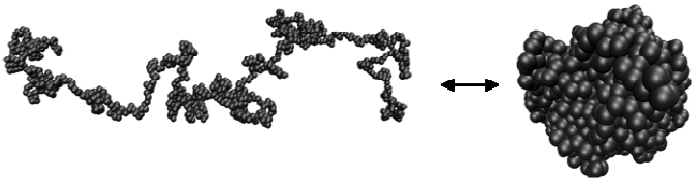
(determined by random chance and thus unpredictable in detail, though likely predictable in its statistical properties). (From wikipedia).

Monte Carlo simulations fulfill these criteria and form a Markov chain.

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.

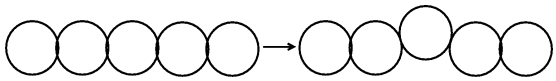
Phase behavior of single polymer chains



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.

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%.

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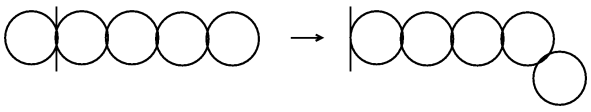
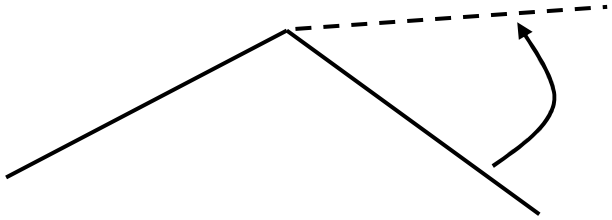
Reptation / slithering snake moves



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.

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