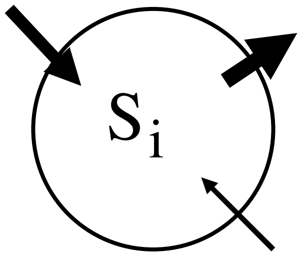
# Recap: Canonical Monte Carlo (Importance Sampling)

Peter Virnau, 18.12.2007

Master equation (in equilibrium)




$$\sum_j P_i(t)W_{ij} = \sum_j P_j(t)W_{ji}$$

"Flow out of state i = Flow into state i"

This equation is fulfilled by any means, if

$$P_i(t)W_{ij} = P_j(t)W_{ji}$$ Detailed balance

$$\frac{W_{ij}}{W_{ji}} = e^{-\beta(E_j-E_i)}$$

Choose $W_{ij}$ such that detailed balance is fulfilled.
Metropolis: min(1,exp(-$\beta\Delta$E)) or Glauber ...

**Caution:** $W_{ij}$ should consider the way we select particles for our Monte Carlo move→ $W_{ij} = a_{ij}\, w_{ij}$ ,where $a_{ij}$ is the contribution from how we chose particles.

Example 1: Local displacement
Chose a particle at random, displace it
$W_{ij} = a_{ij}\, w_{ij} = 1/N\, w_{ij}$ ; $W_{ji} = a_{ji}\, w_{ji} = 1/N\, w_{ji}$ → $W_{ij} / W_{ji} = w_{ij} / w_{ji}$
→ $a_{ij}$ need not be considered!

Example 2: Slithering snake move
Chose a particle at random, chose one side, attach particle from other side
$W_{ij} = a_{ij}\, w_{ij} = 1/N\ ½\ w_{ij}$ ; $W_{ji} = a_{ji}\, w_{ji} = 1/N\ ½\ w_{ji}$ → $W_{ij} / W_{ji} = w_{ij} / w_{ji}$
→ $a_{ij}$ need not be considered

In the canonical ensemble we usually do not need to consider $a_{ij}$. In other ensembles, however, this is no longer true!

# Grandcanonical simulations ($\mu$VT ensembe)

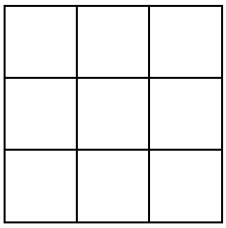
Example: Insertion and deletion of a Lennard-Jones particle

$$P_i(N) = \frac{e^{-\beta E_i(N)+\beta\mu N}}{Z_{gk}} \qquad P_j(N+1) = \frac{e^{-\beta E_j(N+1)+\beta\mu(N+1)}}{Z_{gk}}$$

Detailed balance:

$$\frac{1}{2}\frac{c}{V}P_i(N)w_{ij}(N \to N+1) = \frac{1}{2}\frac{1}{N+1}P_j(N+1)w_{ji}(N+1 \to N)$$

c/V: probability for choosing a particular position



Idea: subdivide volume small subboxes. Chance of choosing any of the subboces = volume of subbox (c) / total volume → 1/V dependence.
Constant c can be absorbed into chemical potential, which is only defined up to a constant.

1/(N+1): probability of selecting one out of (N+1) particles

$$\frac{w_{ij}(N \rightarrow N+1)}{w_{ji}(N+1 \rightarrow N)} = \frac{V}{c(N+1)} e^{-\beta(E_j(N+1)-E_i(N))+\beta\mu}$$

<u>Metropolis:</u>

Insertion: $w_{ij}(N \rightarrow N+1)$ $=\min(1, V/(N+1) \exp(-\beta\Delta E+\beta\mu))$
Deletion: $w_{ji}(N+1 \rightarrow N)$ $=\min(1, (N+1)/V \exp(+\beta\Delta E-\beta\mu))$

Verification: $V/(N+1) \exp(-\beta\Delta E+\beta\mu) > 1$

$$\frac{w_{ij}(N \rightarrow N+1)}{w_{ji}(N+1 \rightarrow N)} = \frac{V}{(N+1)} e^{-\beta(\Delta E)+\beta\mu}$$

$V/(N+1) \exp(-\beta\Delta E+\beta\mu) < 1$ homework

<u>"Numerical Recipe"</u>

Starting configuration

50% 50%

|: insert delete

Update configuration
Calculate energy
Pick random number

$r<V/(N+1)\exp(-\beta\Delta E+\beta\mu)$ $r<(N+1)/V \exp(+\beta\Delta E-\beta\mu)$

Yes: accept new configuration
No: restore old configuration :|