Basic Monte Carlo
(chapter 3)

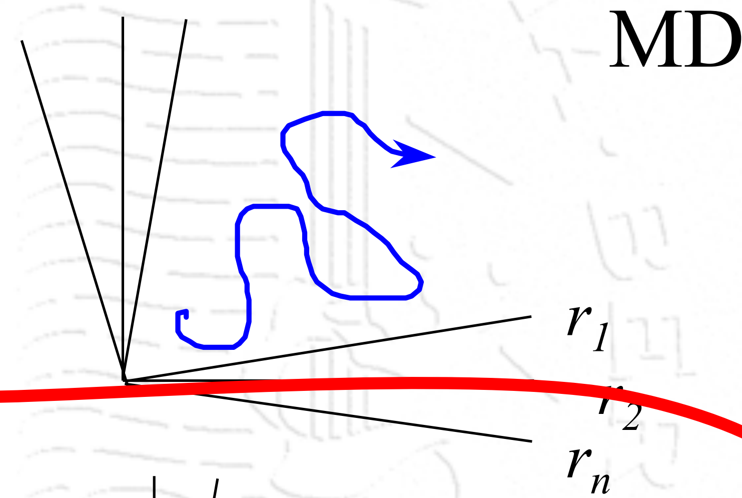
Algorithm

Detailed Balance

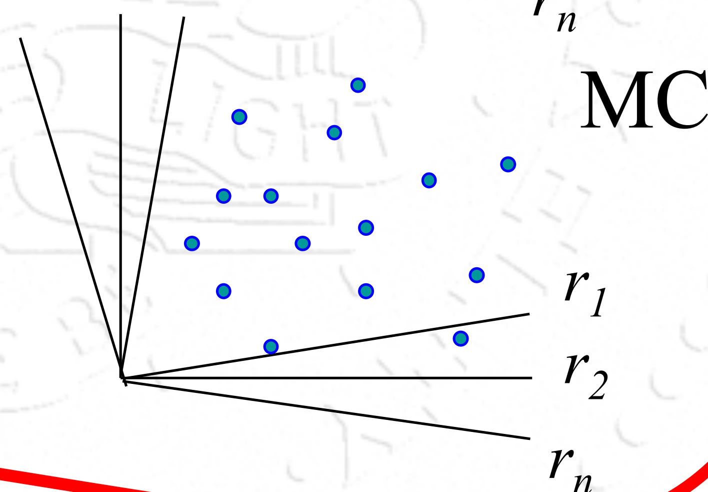
Other points

Molecular Simulations

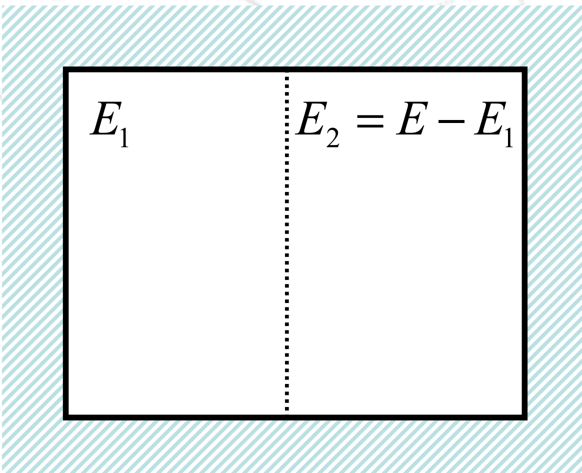
- Molecular dynamics: solve equations of motion



- Monte Carlo: importance sampling



Does the basis assumption lead to something that is consistent with classical thermodynamics?



Systems 1 and 2 are weakly coupled such that they can exchange energy.

What will be E_1?

$$\Omega\left(E_1, E - E_1\right) = \Omega_1\left(E_1\right) \times \Omega_2\left(E - E_1\right)$$

BA: each configuration is equally probable; but the number of states that give an energy E_1 is not know.

$$\Omega\left(E_1, E - E_1\right) = \Omega_1\left(E_1\right) \times \Omega_2\left(E - E_1\right)$$

$$\ln\Omega\left(E_1, E - E_1\right) = \ln\Omega_1\left(E_1\right) + \ln\Omega_2\left(E - E_1\right)$$

$$\left(\frac{\partial \ln\Omega\left(E_1, E - E_1\right)}{\partial E_1}\right)_{N_1,V_1} = 0$$

Energy is conserved!
dE_1=-dE_2

$$\left(\frac{\partial \ln\Omega_1\left(E_1\right)}{\partial E_1}\right)_{N_1,V_1} + \left(\frac{\partial \ln\Omega_2\left(E - E_1\right)}{\partial E_1}\right)_{N_2,V_2} = 0$$

$$\left(\frac{\partial \ln\Omega_1\left(E_1\right)}{\partial E_1}\right)_{N_1,V_1} = \left(\frac{\partial \ln\Omega_2\left(E - E_1\right)}{\partial E_2}\right)_{N_2,V_2}$$

This can be seen as an equilibrium condition

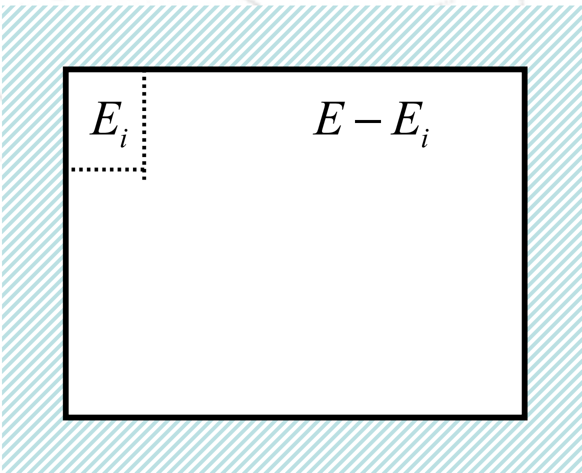
$$\beta \equiv \left(\frac{\partial \ln\Omega\left(E\right)}{\partial E}\right)_{N,V}$$

$$\beta_1 = \beta_2$$

Canonical ensemble

$1/k_BT$

Consider a small system that can exchange heat with a big reservoir



$$\ln\Omega(E-E_i)=\ln\Omega(E)-\frac{\partial\ln\Omega}{\partial E}E_i+\cdots$$

$$\ln\frac{\Omega(E-E_i)}{\Omega(E)}=-\frac{E_i}{k_BT}$$

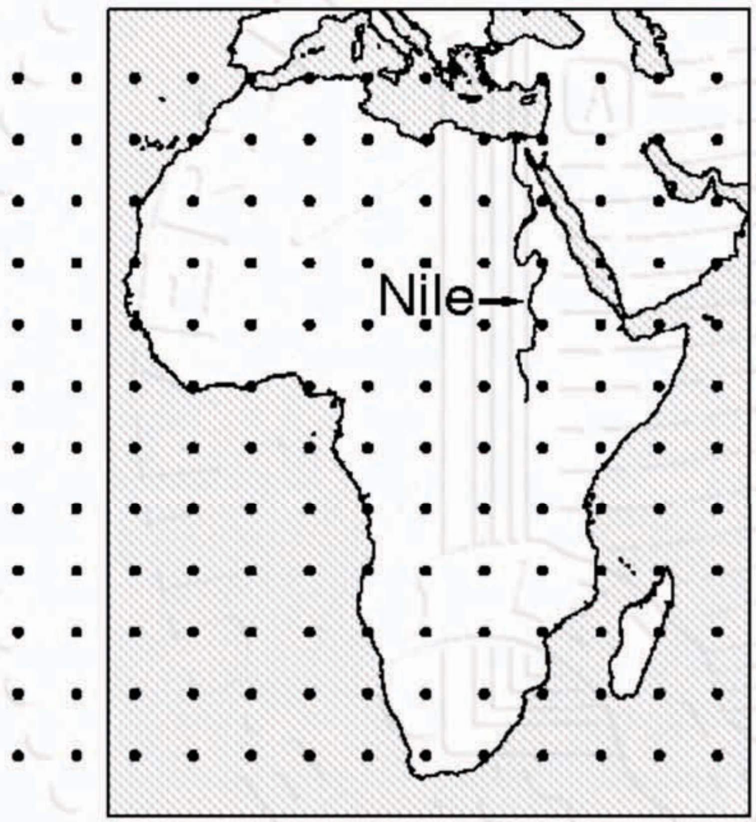
Hence, the probability to find E_i:

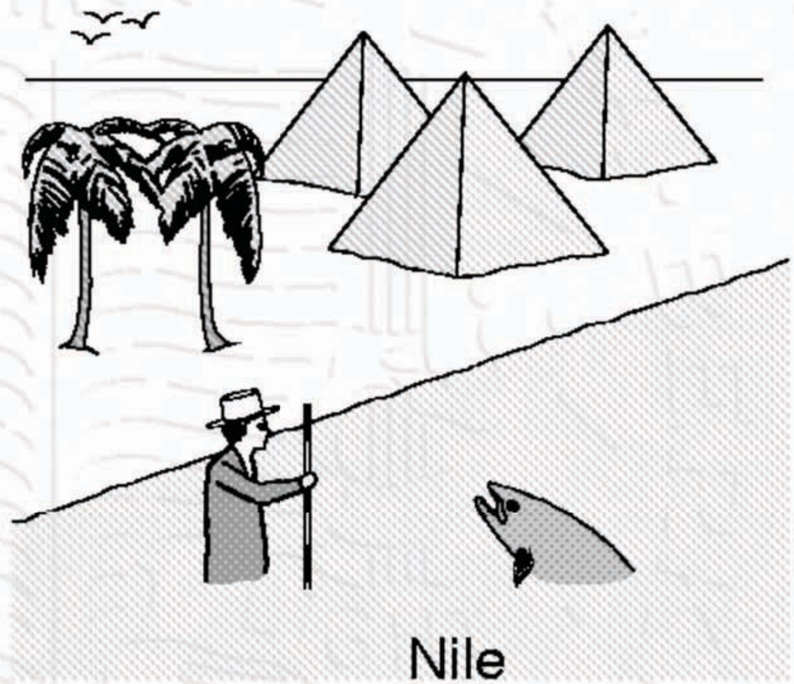
$$P(E_i)=\frac{\Omega(E-E_i)}{\sum_j\Omega(E-E_j)}=\frac{\exp(-E_i/k_BT)}{\sum_j\exp(-E_j/k_BT)}$$

$$P(E_i)\propto\exp(-E_i/k_BT)$$

Boltzmann distribution

Monte Carlo simulation

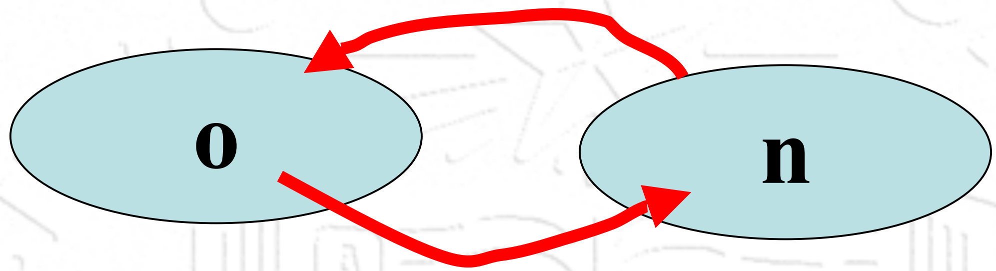




Questions

- How can we prove that this scheme generates the desired distribution of configurations?
- Why make a random selection of the particle to be displaced?
- Why do we need to take the old configuration again?
- How large should we take: `delx`?

Detailed balance



$$K(o \rightarrow n) = K(n \rightarrow o)$$

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$$\frac{\mathrm{acc}(o \rightarrow n)}{\mathrm{acc}(n \rightarrow o)} = \frac{N(n) \times \alpha(n \rightarrow o)}{N(o) \times \alpha(o \rightarrow n)} = \frac{N(n)}{N(o)}$$

NVT-ensemble

$$N(n) \propto \exp\left[-\beta U\left(n\right)\right]$$

$$\frac{\mathrm{acc}(o \rightarrow n)}{\mathrm{acc}(n \rightarrow o)} = \frac{N(n)}{N(o)}$$

$$\frac{\mathrm{acc}(o \rightarrow n)}{\mathrm{acc}(n \rightarrow o)} = \exp\left[-\beta\left[U\left(n\right) - U\left(o\right)\right]\right]$$

Questions

- How can we prove that this scheme generates the desired distribution of configurations?
- Why make a random selection of the particle to be displaced?
- Why do we need to take the old configuration again?
- How large should we take: `delx`?

Mathematical

Transition probability:

$$\pi(o \to n) = \alpha(o \to n) \times \mathrm{acc}(o \to n)$$

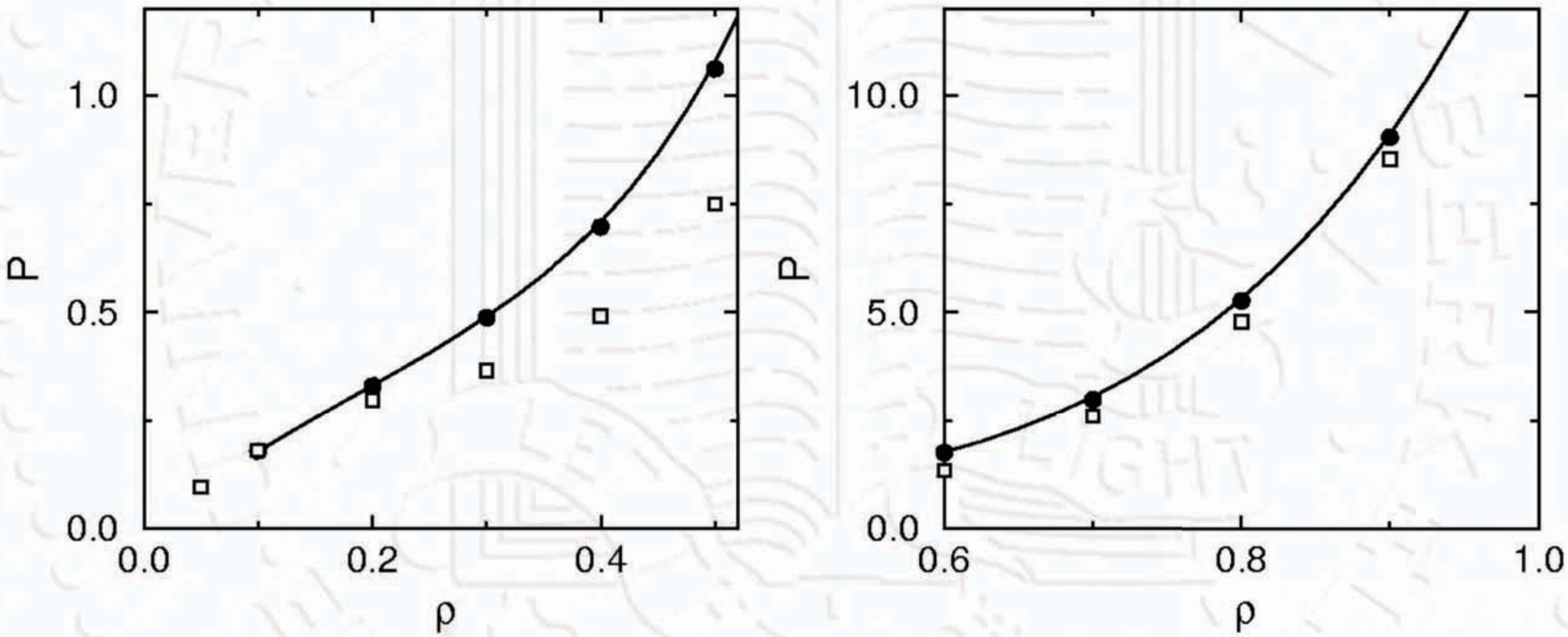
$$\sum_n \pi(o \to n) = 1$$

Probability to accept the old configuration:

$\neq 0$

$$\pi(o \to o) = 1 - \sum_{n \neq o} \pi(o \to n)$$

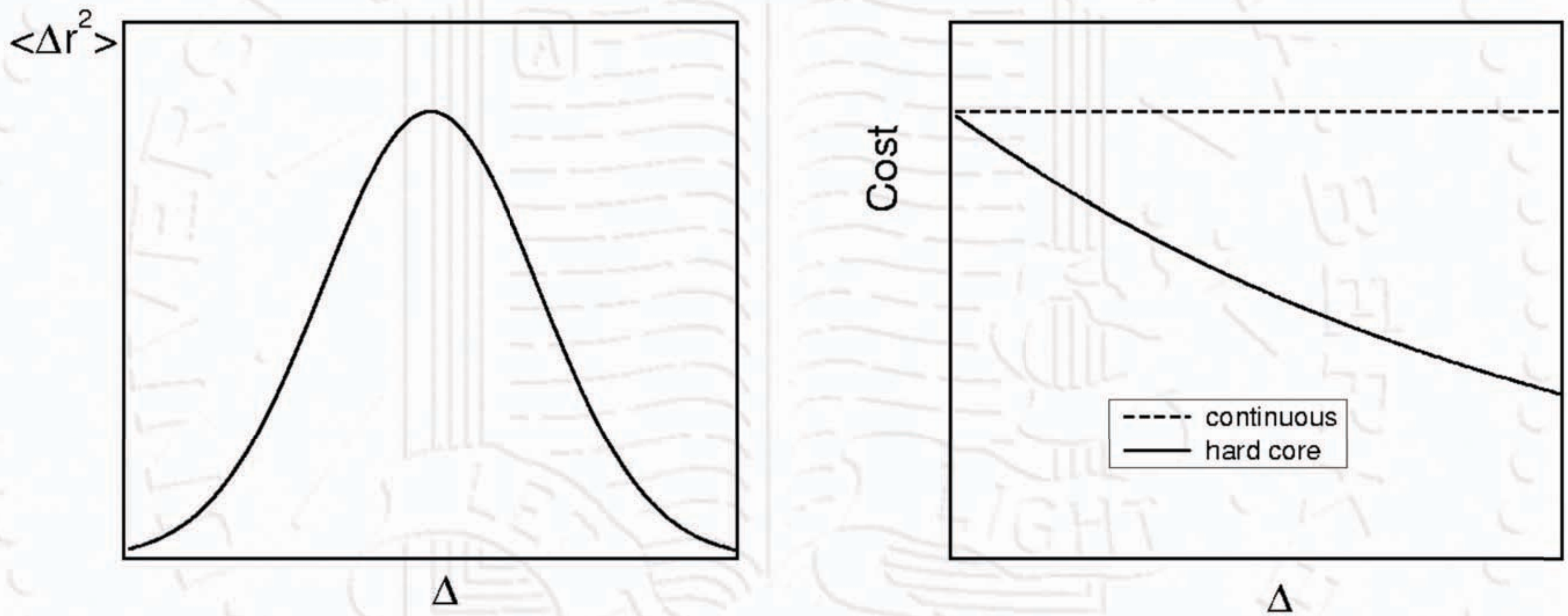
Keeping old configuration?



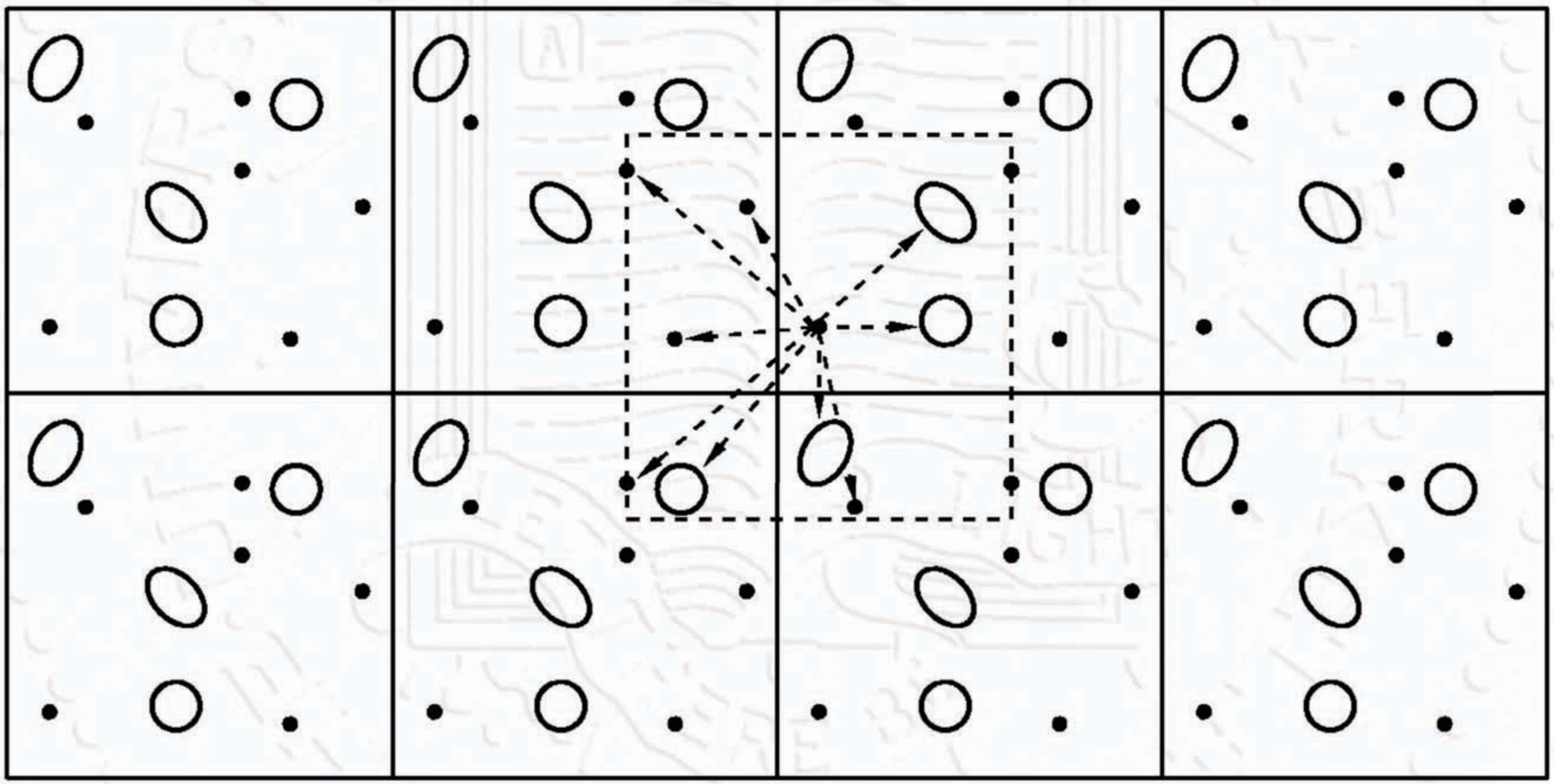
Questions

- How can we prove that this scheme generates the desired distribution of configurations?
- Why make a random selection of the particle to be displaced?
- Why do we need to take the old configuration again?
- How large should we take: `delx`?

Not too small, not too big!



Periodic boundary conditions



Lennard Jones potentials

•The Lennard-Jones potential

$$u^{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

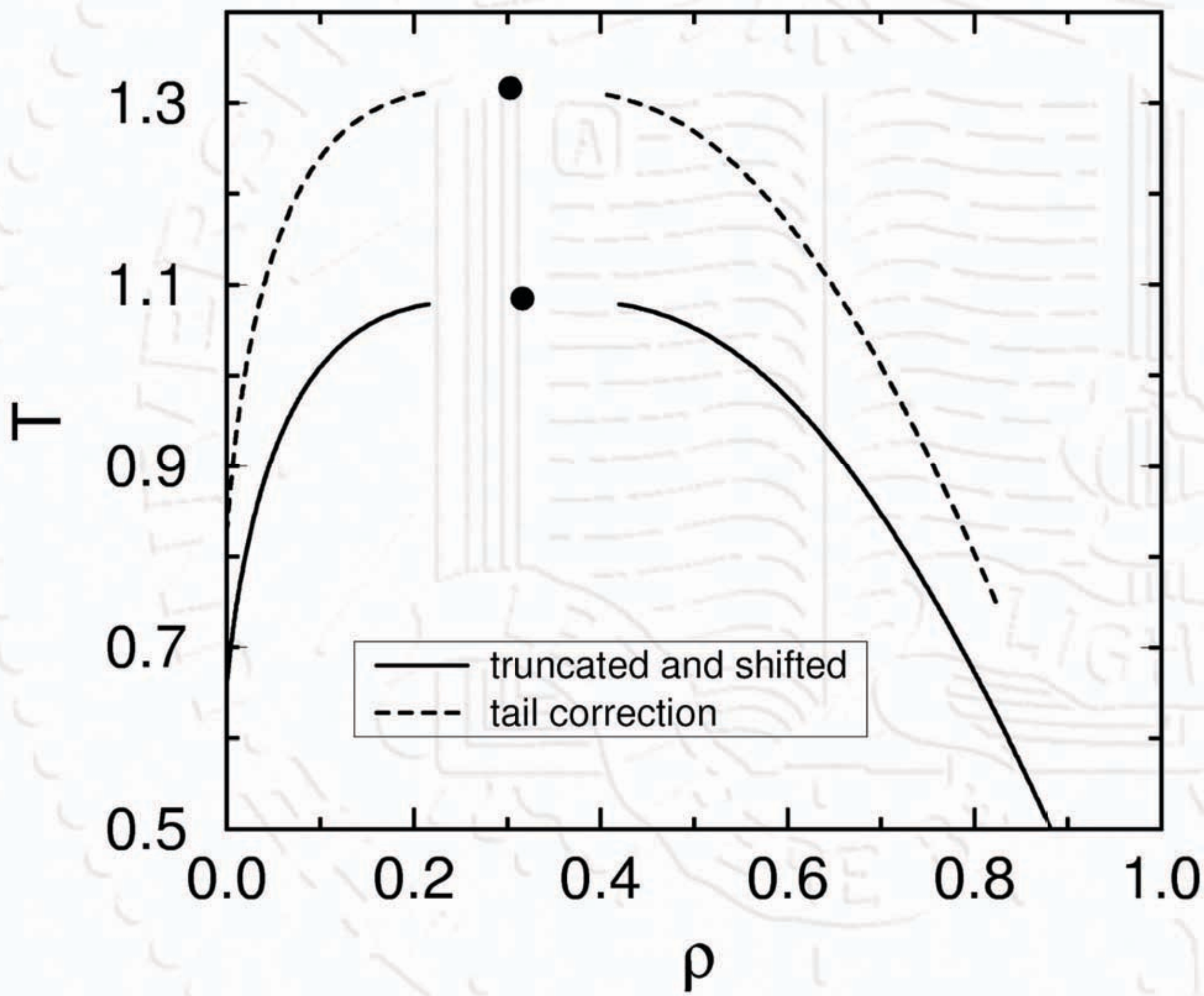
•The truncated Lennard-Jones potential

$$u(r) = \begin{cases} u^{LJ}(r) & r \le r_c \\ 0 & r > r_c \end{cases}$$

•The truncated and shifted Lennard-Jones potential

$$u(r) = \begin{cases} u^{LJ}(r) - u^{LJ}(r_c) & r \le r_c \\ 0 & r > r_c \end{cases}$$

Phase diagrams of Lennard Jones fluids



Non-Boltzmann sampling

$$\langle A \rangle_{NVT_1} = \frac{1}{Q_{NVT_1}} \frac{1}{\Lambda^{3N} N!} \int \mathrm{d}\mathrm{r}^N A(\mathrm{r}^N) \exp\left[-\beta_1 U(\mathrm{r}^N)\right]$$

$$= \frac{\int \mathrm{d}\mathrm{r}^N A(\mathrm{r}^N) \exp\left[-\beta_1 U(\mathrm{r}^N)\right]}{\int \mathrm{d}\mathrm{r}^N \exp\left[-\beta_1 U(\mathrm{r}^N)\right]}$$

$$= \frac{\int \mathrm{d}\mathrm{r}^N A(\mathrm{r}^N) \exp\left[-\beta_1 U(\mathrm{r}^N)\right] \exp\left[\beta_2 U(\mathrm{r}^N) - \beta_2 U(\mathrm{r}^N)\right]}{\int \mathrm{d}\mathrm{r}^N \exp\left[-\beta_1 U(\mathrm{r}^N)\right] \exp\left[\beta_2 U(\mathrm{r}^N) - \beta_2 U(\mathrm{r}^N)\right]}$$

$$= \frac{\int \mathrm{d}\mathrm{r}^N A(\mathrm{r}^N) \exp\left[\beta_2 U(\mathrm{r}^N) - \beta_1 U(\mathrm{r}^N)\right] \exp\left[-\beta_2 U(\mathrm{r}^N)\right]}{\int \mathrm{d}\mathrm{r}^N \exp\left[\beta_2 U(\mathrm{r}^N) - \beta_1 U(\mathrm{r}^N)\right] \exp\left[-\beta_2 U(\mathrm{r}^N)\right]}$$

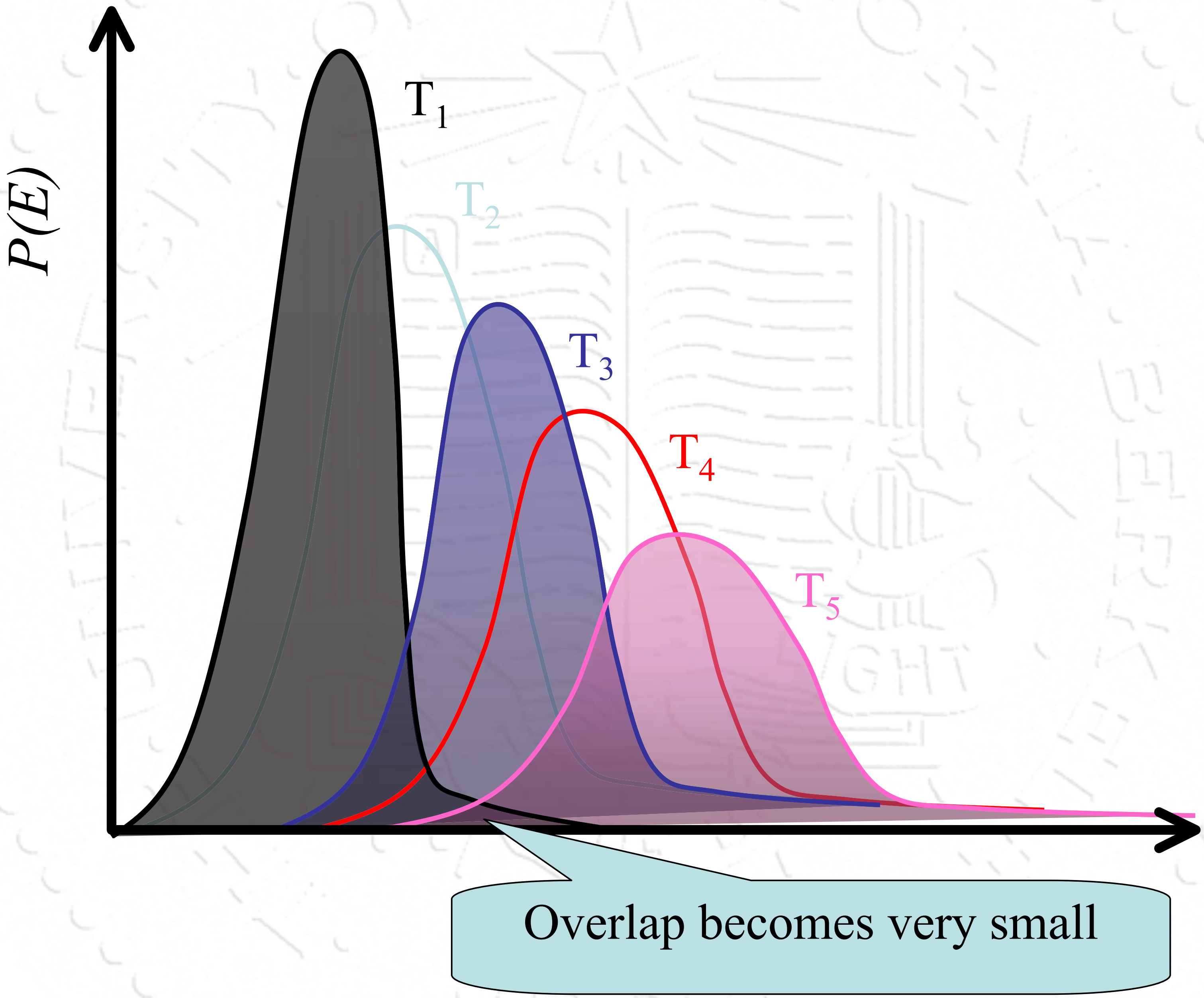
$$= \frac{\left\langle A \exp\left[(\beta_2 - \beta_1) U\right]\right\rangle_{NVT_2}}{\left\langle \exp\left[(\beta_2 - \beta_1) U\right]\right\rangle_{NVT_2}}$$

T_1 is arbitrary!

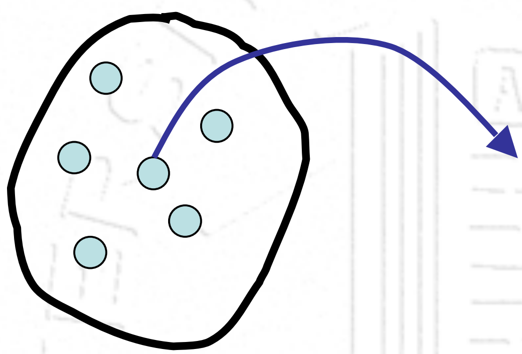
Why are we not using this?

We only need a *single* simulation!

We perform a simulation at $T=T_2$ and we determine A at $T=T_1$


P(E)
T1
T2
T3
T4
T5
Overlap becomes very small

How to do *parallel* Monte Carlo



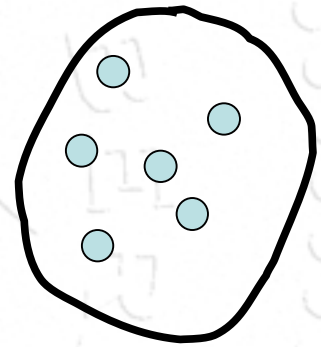
- Is it possible to do Monte Carlo in parallel
  - Monte Carlo is sequential!
  - We first have to know the fait of the current move before we can continue!

Parallel Monte Carlo

Algorithm (*WRONG*):

1. Generate *k* trial configurations in parallel
2. Select out of these the one with the lowest energy

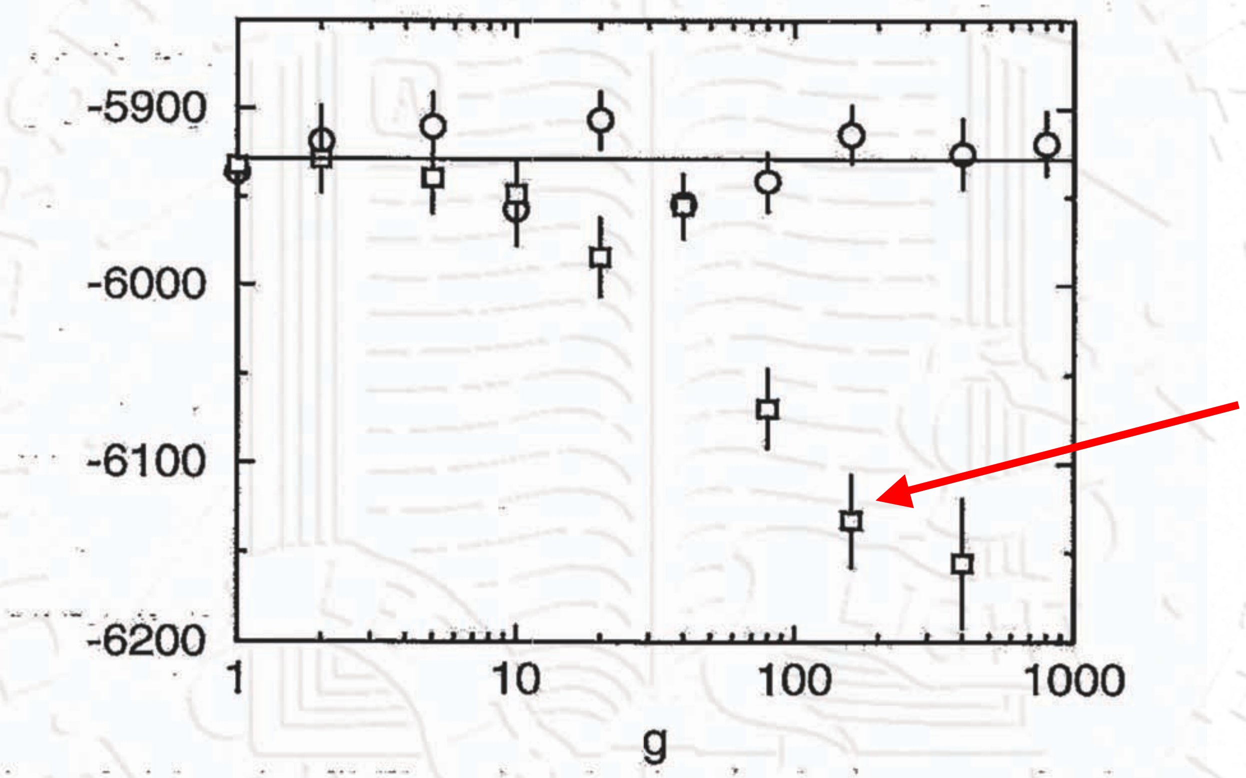
$$P(n) = \frac{\exp\left[-\beta\left(U_n\right)\right]}{\sum_{j=1}^{g} \exp\left[-\beta\left(U_j\right)\right]}$$



3. Accept and reject using normal Monte Carlo rule:

$$\mathrm{acc}\left(o \rightarrow n\right) = \exp\left[-\beta\left(U_n - U_o\right)\right]$$

Conventional acceptance rule



Conventional acceptance rules leads to a ***bias***

W

Detailed balance!

$$K(o \to n) = K(n \to o)$$

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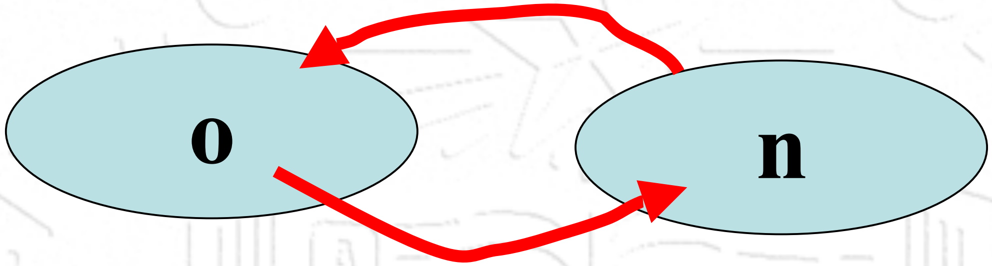
Detailed balance



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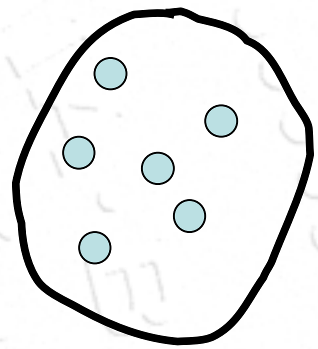
?

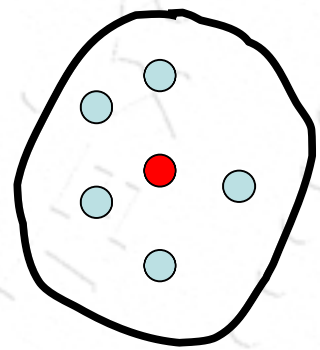
$$K(o \to n) = N(o) \times \alpha(o \to n) \times \mathrm{acc}(o \to n)$$

$$\alpha(o \to n) = \frac{\exp\left[-\beta\left(U_n\right)\right]}{\sum_{j=1}^{g} \exp\left[-\beta\left(U_j\right)\right]}$$



$$\alpha(o \to n) = \frac{\exp\left[-\beta\left(U_n\right)\right]}{W\left(n\right)}$$

$$\alpha(n \to o) = \frac{\exp\left[-\beta\left(U_o\right)\right]}{\sum_{j=1}^{g} \exp\left[-\beta\left(U_j\right)\right]}$$



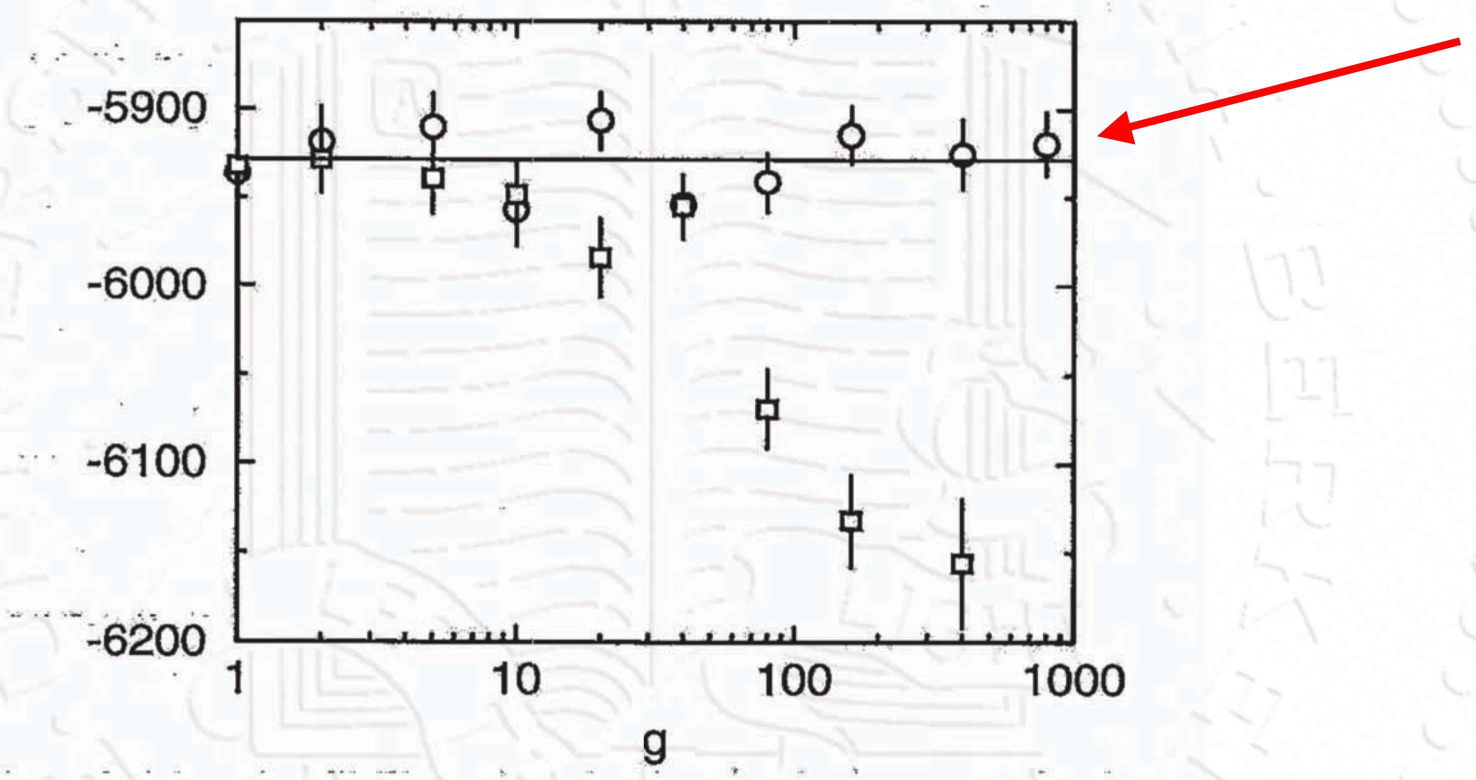
$$\alpha(n \to o) = \frac{\exp\left[-\beta\left(U_o\right)\right]}{W\left(o\right)}$$

$$\frac{\text{acc}(o \rightarrow n)}{\text{acc}(n \rightarrow o)} = \frac{N(n) \times \alpha(n \rightarrow o)}{N(o) \times \alpha(o \rightarrow n)}$$

$$\alpha(o \rightarrow n) = \frac{\exp\left[-\beta\left(U_n\right)\right]}{W\left(n\right)} \quad \alpha(n \rightarrow o) = \frac{\exp\left[-\beta\left(U_o\right)\right]}{W\left(o\right)}$$

$$\frac{\text{acc}(o \rightarrow n)}{\text{acc}(n \rightarrow o)} = \frac{N(n) \times \dfrac{\exp\left[-\beta\left(U_o\right)\right]}{W\left(o\right)}}{N(o) \times \dfrac{\exp\left[-\beta\left(U_n\right)\right]}{W\left(n\right)}} = \frac{W(n)}{W(o)}$$

Modified acceptance rule

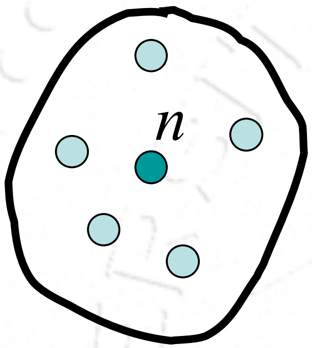


Modified acceptance rule remove the ***bias*** exactly!

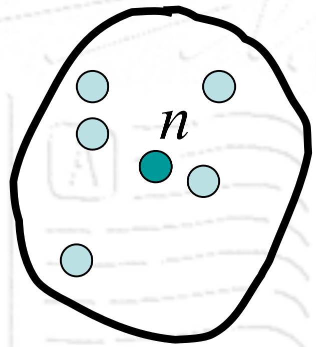
But is there not a problem …?

Detailed balance

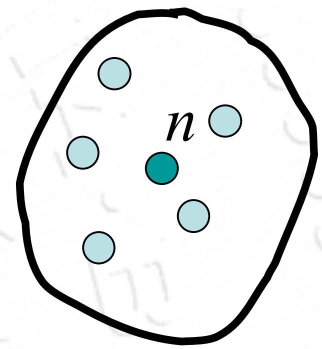
We imposed detailed balance.



$\left\{\mathbf{b}_n \middle| \mathbf{b}_{1b}, \mathbf{b}_{2b}, \mathbf{b}_{3b}, \cdots, \mathbf{b}_{kb}\right\}$

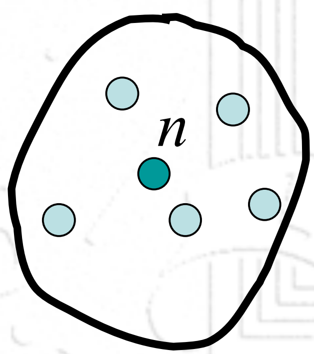


$\left\{\mathbf{b}_n \middle| \mathbf{b}_{1c}, \mathbf{b}_{2c}, \mathbf{b}_{3c}, \cdots, \mathbf{b}_{kc}\right\}$



$\left\{\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3, \cdots, \mathbf{b}_n, \cdots, \mathbf{b}_k\right\}$

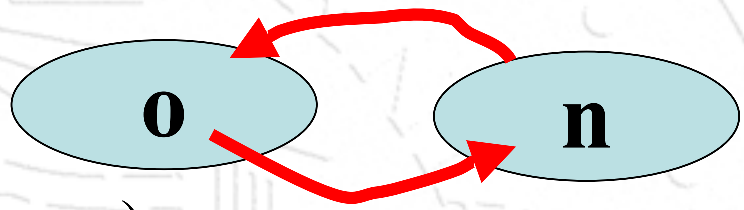
$\left\{\mathbf{b}_n \middle| \mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3, \cdots, \mathbf{b}_k\right\}$



$\left\{\mathbf{b}_n \middle| \mathbf{b}_{1a}, \mathbf{b}_{2a}, \mathbf{b}_{3a}, \cdots, \mathbf{b}_{ka}\right\}$

But there are many sets of trial orientations that $o \rightarrow n$

Detailed Balance?



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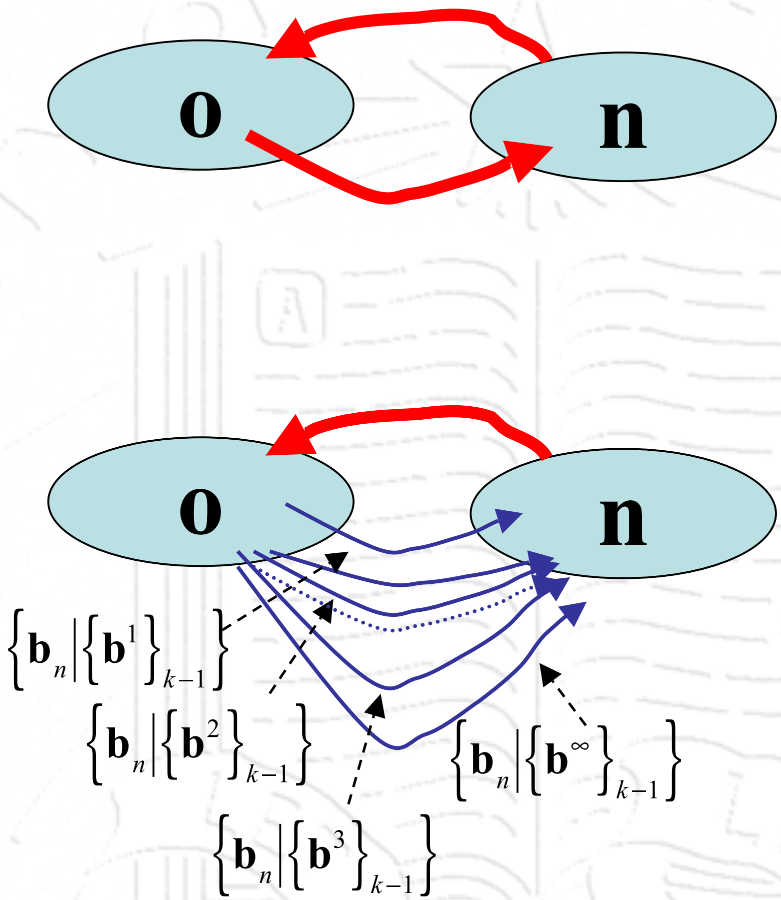
$$K(o \to n) = N(o) \times \alpha(o \to n) \times \text{acc}(o \to n)$$

$$\alpha(o \to n) = \sum_{\{\mathbf{b}\}_{k-1}} \frac{\exp\left[-\beta\left(U_n\right)\right]}{\sum_{j=1}^{k} \exp\left[-\beta\left(U_j\right)\right]}$$

$$\left\{\mathbf{b}_n \middle| \mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3, \cdots, \mathbf{b}_k\right\} = \left\{\mathbf{b}_n \middle| \left\{\mathbf{b}\right\}_{k-1}\right\}$$

$$\alpha(o \to n) = \sum_{\{\mathbf{b}\}_{k-1}} \frac{\exp\left[-\beta\left(U_n\right)\right]}{\sum_{j=1}^{k} \exp\left[-\beta\left(U_j\right)\right]}$$

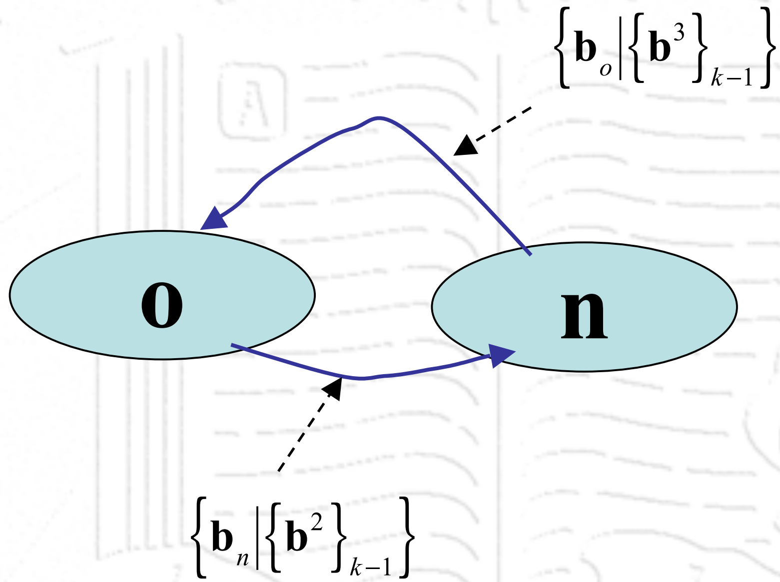
$$\left\{\mathbf{b}_o \middle| \mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3, \cdots, \mathbf{b}_k\right\} = \left\{\mathbf{b}_o \middle| \left\{\mathbf{b}\right\}_{k-1}\right\}$$

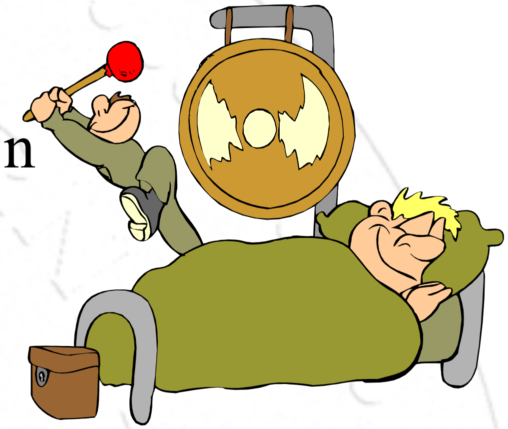


Detail balance: summation over **all possible** path from *o* to *n*

$$K(o \to n) = K(n \to o)$$

Super-detailed balance: detailed balance should hold for any two sets of paths that connect o and n and n and o





$$K\left(o \rightarrow n \middle| \left\{ \mathbf{b} \right\}_{k-1}\right) = K\left(n \rightarrow o \middle| \left\{ \mathbf{b}' \right\}_{k-1}\right)$$

Super detailed balance!

Detailed balance?

Summation over all possible paths

$$K(o \to n) = \sum_{\{\mathbf{b}\}_{k-1}} K\left(o \to n \middle| \{\mathbf{b}\}_{k-1}\right) \qquad K(n \to o) = \sum_{\{\mathbf{b}\}_{k-1}} K\left(n \to o \middle| \{\mathbf{b}\}_{k-1}\right)$$

$$K(o \to n) - K(n \to o) = \sum_{\{\mathbf{b}\}_{k-1}} K\left(o \to n \middle| \{\mathbf{b}\}_{k-1}\right) - \sum_{\{\mathbf{b}'\}_{k-1}} K\left(n \to o \middle| \{\mathbf{b}'\}_{k-1}\right)$$

Super detailed balance

$$K\left(o \to n \middle| \{\mathbf{b}\}_{k-1}\right) = K\left(n \to o \middle| \{\mathbf{b}'\}_{k-1}\right)$$

Every single term in the first summation is equal to any term in the second

$$K(o \to n) - K(n \to o) = 0$$