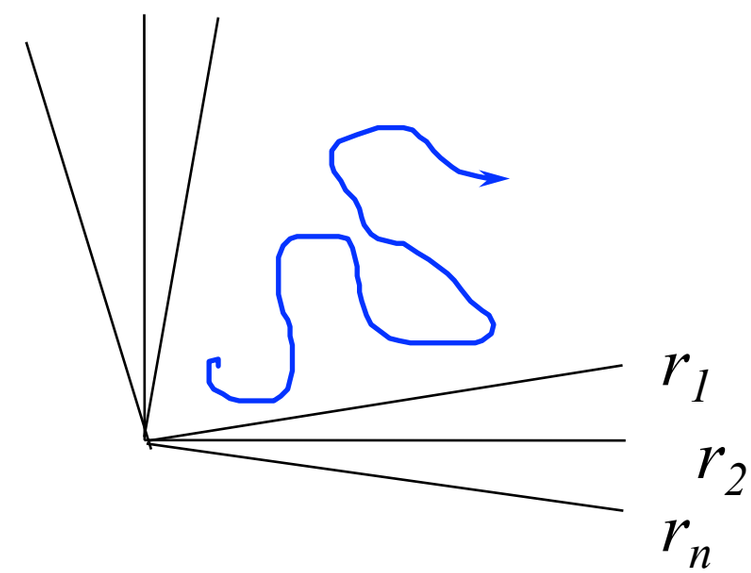
# 3. Monte Carlo Simulations

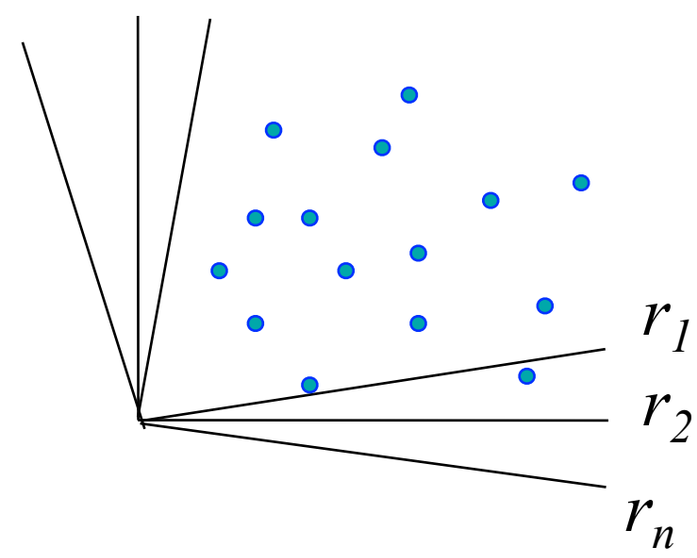
Understanding Molecular Simulation

# Molecular Simulations

➡ **Molecular dynamics**: solve equations of motion




➡ **Monte Carlo**: importance sampling



# Monte Carlo Simulations


3. Monte Carlo

3.1. Introduction

3.2. Statistical Thermodynamics (recall)

3.3. Importance sampling

3.4. Details of the algorithm

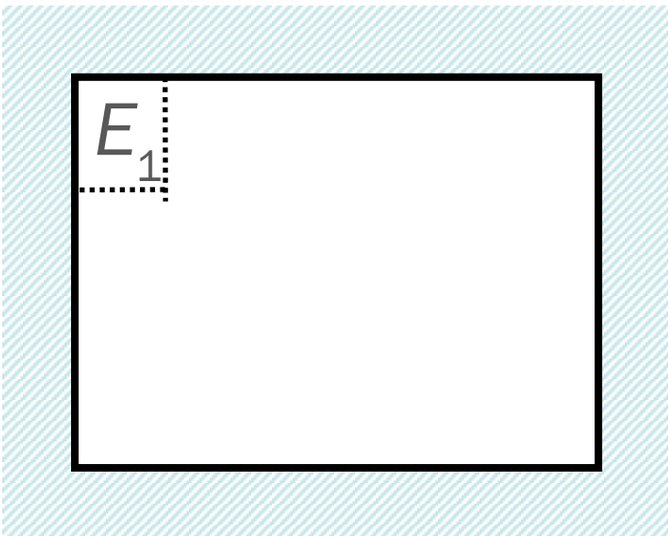
3.5. Non-Boltzmann sampling

3.6. Parallel Monte Carlo

# 3. Monte Carlo Simulations

## 3.2 Statistical Thermodynamics

# Canonical ensemble: statistical mechanics




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

$$\ln\Omega\left(E_1, E-E_1\right) = \ln\Omega\left(E\right) - \left(\frac{\partial \ln\Omega}{\partial E}\right)E_1 + \cdots$$

$=1/k_BT$

If the reservoir is very big we can ignore the higher order terms:

$$\frac{\ln\Omega\left(E_1, E-E_1\right)}{\ln\Omega\left(E\right)} = -\frac{E_1}{k_BT}$$

Hence, the probability to find $E_1$:

$$P\left(E_1\right) = \frac{\Omega\left(E_1, E-E_1\right)}{\sum_i \Omega\left(E_i, E-E_i\right)} = \frac{\Omega\left(E_1, E-E_1\right)/\Omega\left(E\right)}{\sum_i \Omega\left(E_i, E-E_i\right)/\Omega\left(E\right)} = C\frac{\Omega\left(E_1, E-E_1\right)}{\Omega\left(E\right)}$$

$$P\left(E_1\right) \propto \exp\left[-\frac{E_1}{k_BT}\right] \propto \exp\left[-\beta E_1\right]$$

$\beta=1/k_BT$

# Summary: Canonical ensemble (N,V,T)

Partition function:

$$Q_{N,V,T} = \frac{1}{\Lambda^{3N} N!} \int e^{-\frac{U(r)}{k_B T}} dr^{3N}$$

Probability to find a particular configuration:

$$P\left(r^{3N}\right) \propto e^{-\frac{U\left(r^{3N}\right)}{k_B T}}$$

Ensemble average:

$$\left\langle A \right\rangle_{N,V,T} = \frac{\frac{1}{\Lambda^{3N} N!} \int A(r) e^{-\beta U(r)} dr^{3N}}{Q_{N,V,T}} = \frac{\int A(r) e^{-\beta U(r)} dr^{3N}}{\int e^{-\beta U(r)} dr^{3N}}$$

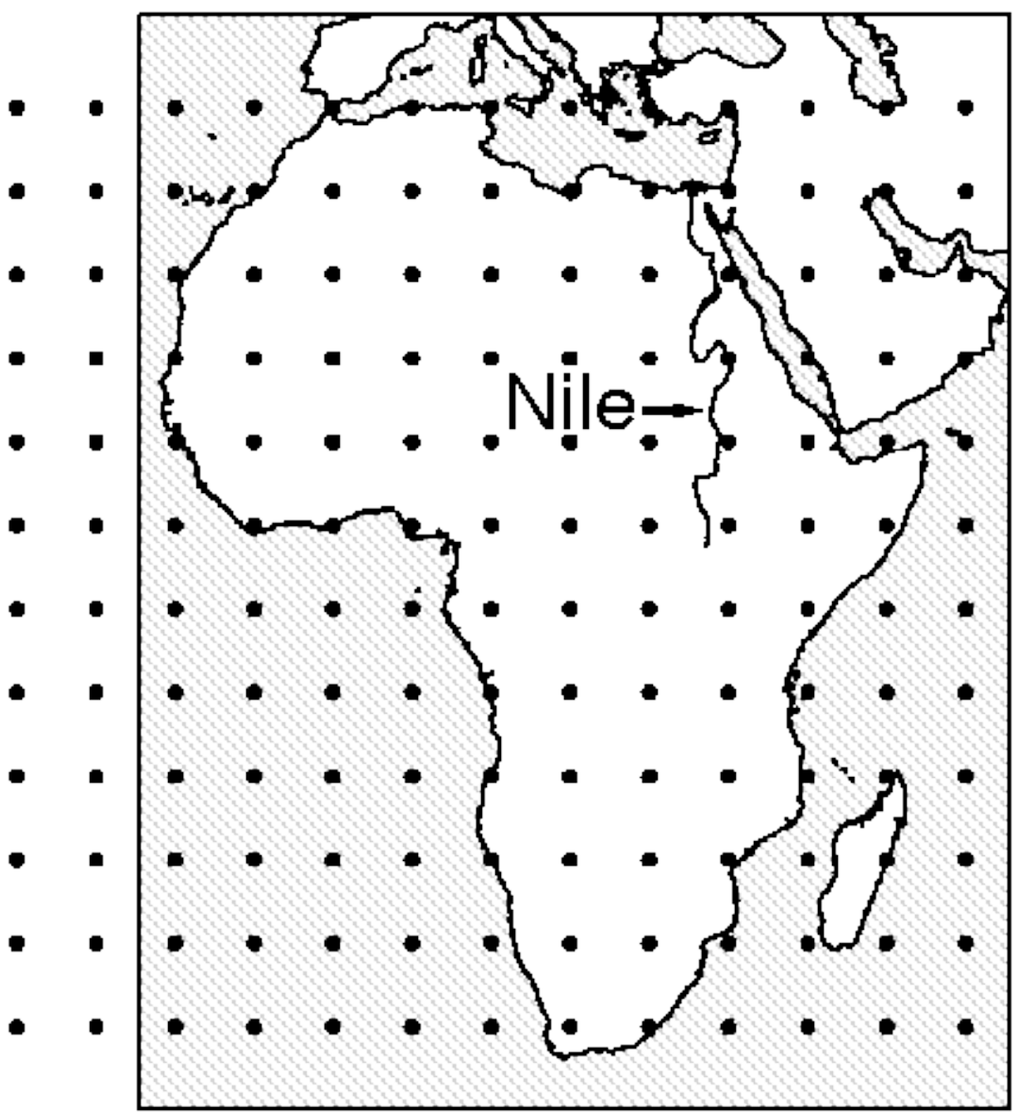
Free energy:

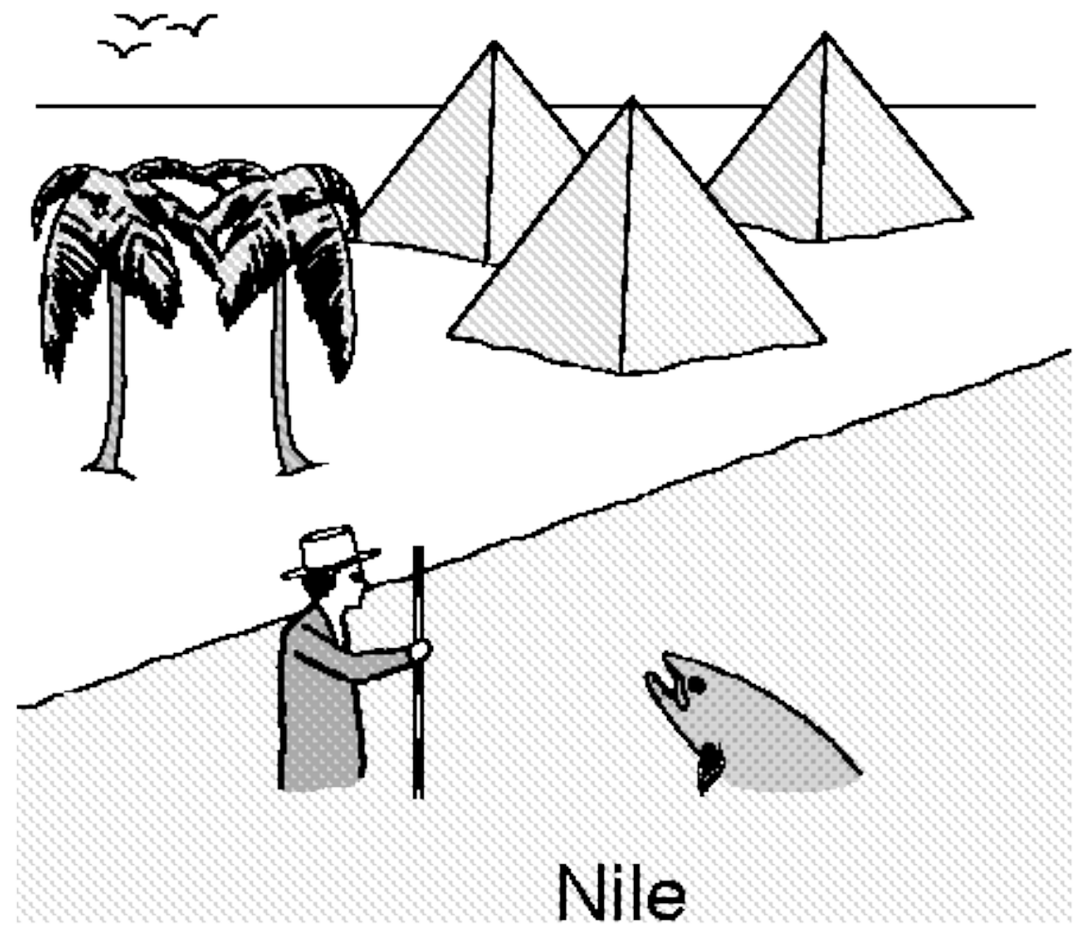
$$\beta F = -\ln Q_{NVT}$$

# 3.Monte Carlo Simulations

## 3.3 Importance Sampling

# Numerical Integration



# Monte Carlo simulations

Generate M configurations using Monte Carlo moves:

$$\left\{r_1^{3N}, r_2^{3N}, r_3^{3N}, r_4^{3N}, \cdots, r_M^{3N}\right\}$$

We can compute the average:

$$\bar{A} = \sum_{i=1}^{M} A\left(r_i^{3N}\right)$$

The probability to generate a configuration in our MC scheme: $P^{MC}$

$$\bar{A} = \frac{\int A\left(r^{3N}\right) P^{MC}\left(r^{3N}\right) dr^{3N}}{\int P^{MC}\left(r^{3N}\right) dr^{3N}}$$

Question: how to chose $P^{MC}$ such that we sample the canonical ensemble?

# Ensemble Average

$$\langle A \rangle_{NVT} = \frac{1}{Q_{NVT}} \frac{1}{N!\Lambda^{3N}} \int A\left(r^{3N}\right) e^{-\beta U\left(r^{3N}\right)} dr^{3N}$$

We can rewrite this using the probability to find a particular configuration

$$\langle A \rangle_{NVT} = \int A\left(r^{3N}\right) P\left(r^{3N}\right) dr^{3N}$$

with

$$P\left(r^{3N}\right) = \frac{e^{-\beta U\left(r^{3N}\right)}}{\Lambda^{3N} N! Q_{NVT}}$$

$$\langle A \rangle_{NVT} = \int A\left(r^{3N}\right) P\left(r^{3N}\right) dr^{3N} = \frac{\int A\left(r^{3N}\right) e^{-\beta U\left(r^{3N}\right)} dr^{3N}}{\int e^{-\beta U\left(r^{3N}\right)} dr^{3N}}$$

# Monte Carlo - canonical ensemble

Canonical ensemble:

$$\langle A \rangle_{NVT} = \int A\left(r^{3N}\right) P\left(r^{3N}\right) dr^{3N} = \frac{\int A\left(r^{3N}\right) e^{-\beta U\left(r^{3N}\right)} dr^{3N}}{\int e^{-\beta U\left(r^{3N}\right)} dr^{3N}}$$

with

$$P\left(r^{3N}\right) = \frac{e^{-\beta U\left(r^{3N}\right)}}{\Lambda^{3N} N! Q_{NVT}}$$

2. No need to know the partition function

Monte Carlo:

$$\bar{A} = \sum_{i=1}^{M} A\left(r_i^{3N}\right)$$

$$\bar{A} = \frac{\int A\left(r^{3N}\right) P^{MC}\left(r^{3N}\right) dr^{3N}}{\int P^{MC}\left(r^{3N}\right) dr^{3N}}$$

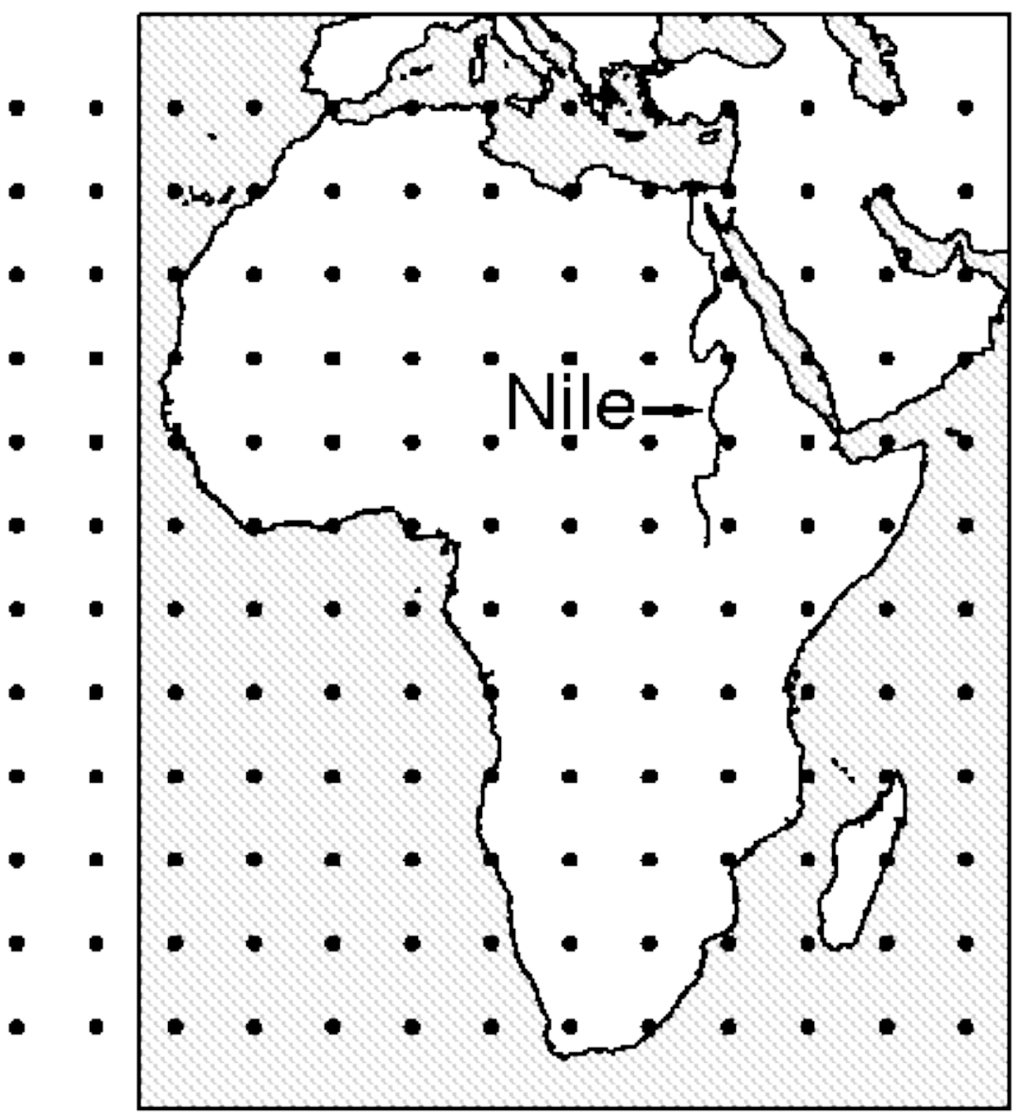
Hence, we need to sample:

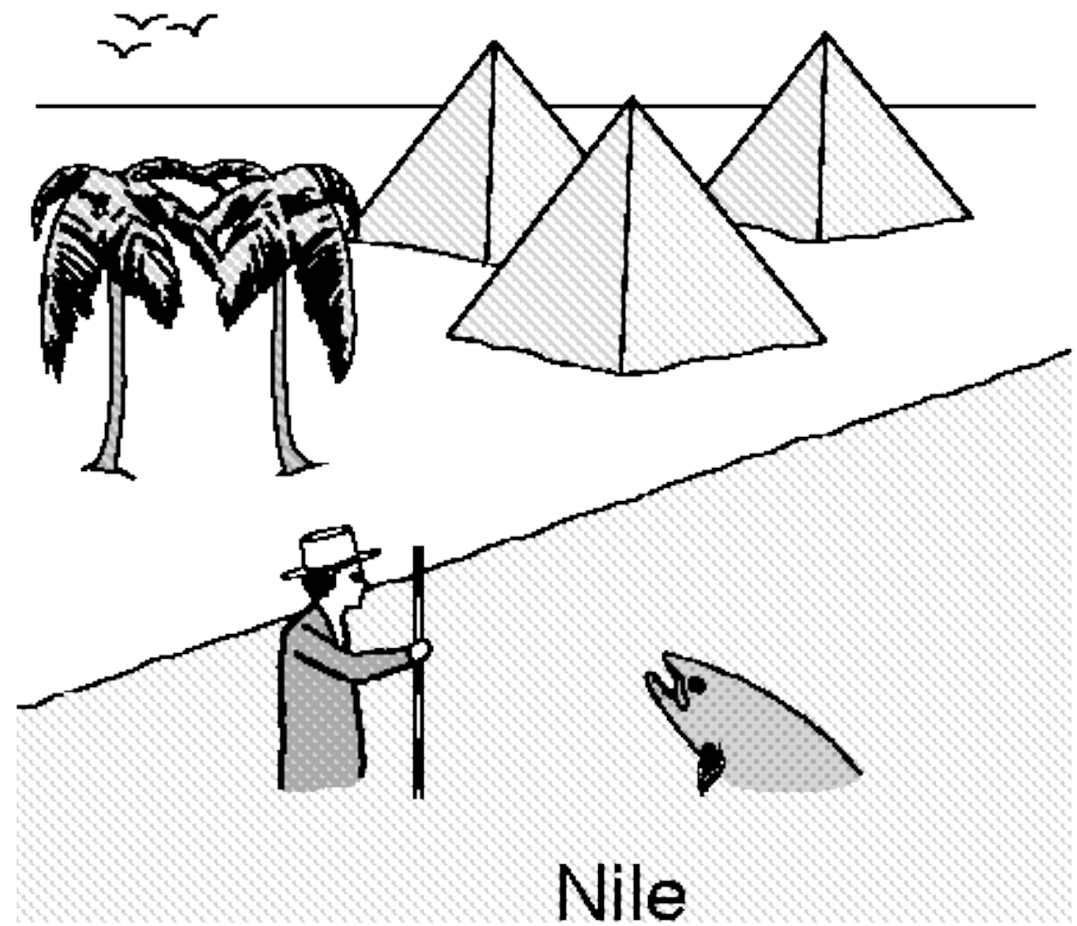
$$P^{MC}\left(r^{3N}\right) = C e^{-\beta U\left(r^{3N}\right)}$$

1. No need to know C

$$\bar{A} = \frac{C \int A\left(r^{3N}\right) e^{-\beta U\left(r^{3N}\right)} dr^{3N}}{C \int e^{-\beta U\left(r^{3N}\right)} dr^{3N}} = \frac{\int A\left(r^{3N}\right) e^{-\beta U\left(r^{3N}\right)} dr^{3N}}{\int e^{-\beta U\left(r^{3N}\right)} dr^{3N}} = \langle A \rangle_{NVT}$$

# Importance Sampling: what got lost?



# 3.Monte Carlo Simulation

## 3.4 Details of the algorithm

## Algorithm 1 (Basic Metropolis Algorithm)

```
 PROGRAM mc                                  basic Metropolis algorithm

 do icycl=1,ncycl                            perform ncycl MC cycles
   call mcmove                               displace a particle
   if (mod(icycl,nsamp).eq.0)
+    call sample                            sample averages
 enddo
 end
```

*Comments to this algorithm:*

1. *Subroutine* `mcmove` *attempts to displace a randomly selected particle (see Algorithm 2).*
2. *Subroutine* `sample` *samples quantities every* `nsamp`*th cycle.*

## Algorithm 2 (Attempt to Displace a Particle)

```
  SUBROUTINE mcmove                    attempts to displace a particle

  o=int(ranf()*npart)+1                select a particle at random
  call ener(x(o),eno)                  energy old configuration
  xn=x(o)+(ranf()-0.5)*delx            give particle random displacement
  call ener(xn,enn)                    energy new configuration
  if (ranf().lt.exp(-beta              acceptance rule (2.2.1)
+    *(enn-eno)) x(o)=xn              accepted: replace x(o) by xn
  return
  end
```

*Comments to this algorithm:*

1. *Subroutine* `ener` *calculates the energy of a particle at the given position.*
2. *Note that, if a configuration is rejected, the old configuration is retained.*
3. *The* `ranf()` *is a random number uniform in* $[0, 1]$.

# 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`?

# 3.Monte Carlo Simulations

## 3.4.1 Detailed balance

# 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`?

canonical ensembles

# Markov Processes

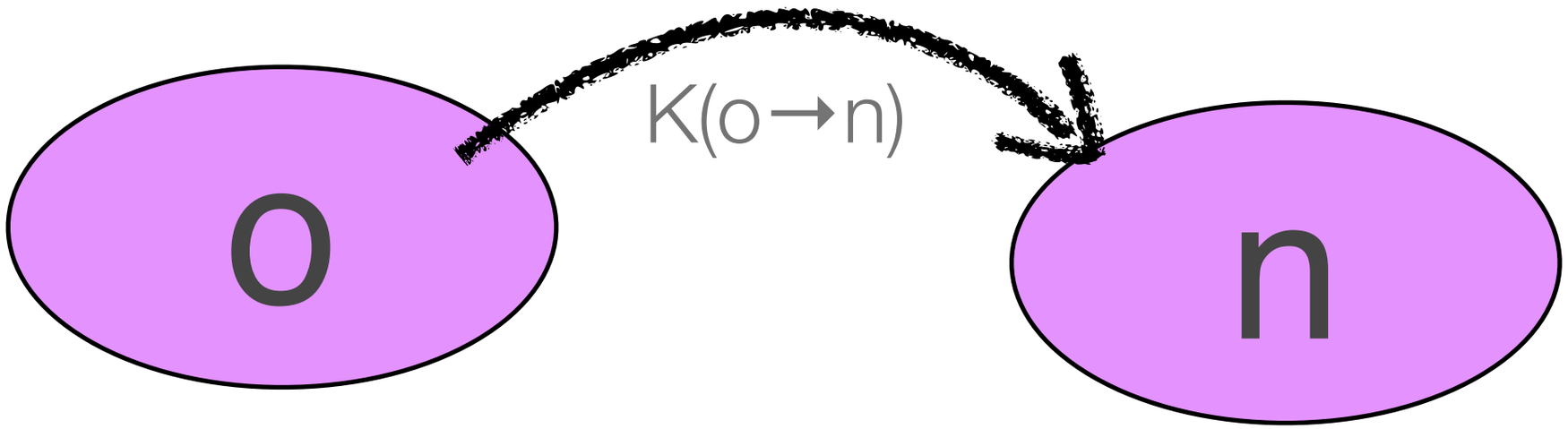
## Markov Process

- Next step only depends on the current state
- Ergodic: all possible states can be reached by a set of single steps
- Detailed balance
- * Process will approach a limiting distribution

# Ensembles versus probability

- *P(o)*: probability to find the state *o*
- Ensemble: take a very large number (*M*) of identical systems: *N(o) = M x P(o)*; the total number of systems in the state o

# Markov Processes - Detailed Balance

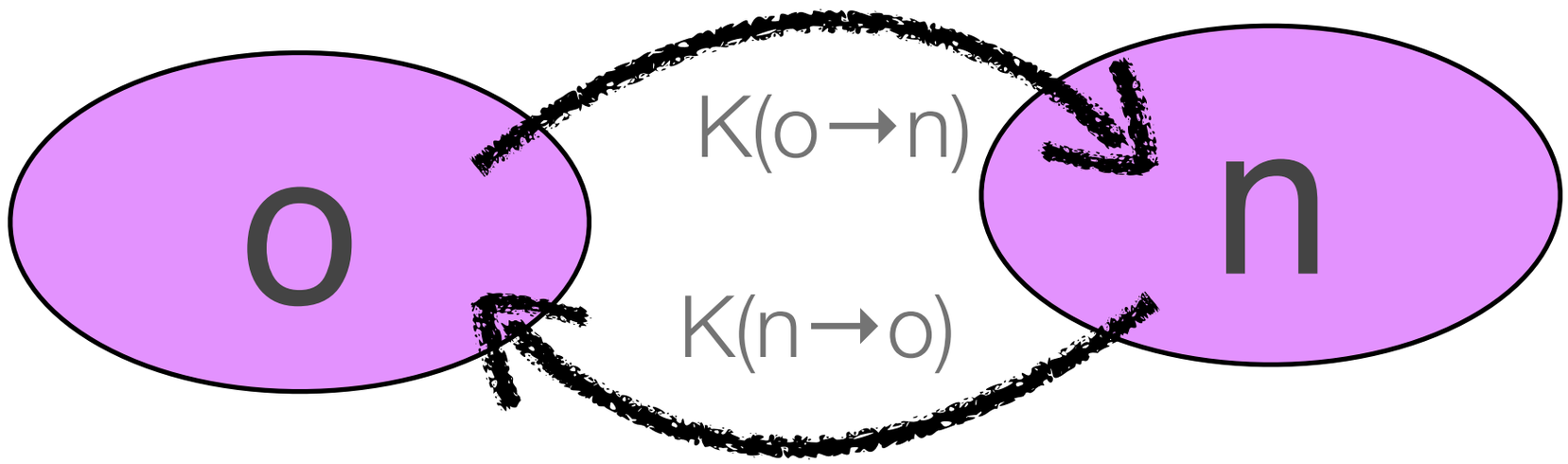



*K(o → n)*: total number of systems in our ensemble that move *o* → *n*

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

- *N(o)* : total number of systems in our ensemble in state o
- *α(o → n)*: a priori probability to generate a move *o* → *n*
- *acc(o → n)*: probability to accept the move *o* → *n*

# Markov Processes - Detailed Balance




Condition of detailed balance:

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

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

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

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

# NVT-ensemble

In the canonical ensemble the number of configurations in state *n* is given by:

$$N(n) \propto e^{-\beta U(n)}$$

We assume that in our Monte Carlo moves the a priori probability to perform a move is independent of the configuration:

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

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

Which gives as condition for the acceptance rule:

$$\boxed{\frac{\mathrm{acc}(o \rightarrow n)}{\mathrm{acc}(n \rightarrow o)} = \frac{e^{-\beta U(n)}}{e^{-\beta U(o)}}}$$

## Algorithm 2 (Attempt to Displace a Particle)

```
SUBROUTINE mcmove                    attempts to displace a particle

o=int(ranf()*npart)+1                select a particle at random
call ener(x(o),eno)                  energy old configuration
xn=x(o)+(ranf()-0.5)*delx            give particle random displacement
call ener(xn,enn)                    energy new configuration
if (ranf().lt.exp(-beta              acceptance rule (3.2.1)
+    *(enn-eno)) x(o)=xn             accepted: replace x(o) by xn
return
end
```

*Comments to this algorithm:*

1. *Subroutine* `ener` *calculates the energy of a particle at the given position.*
2. *Note that, if a configuration is rejected, the old configuration is retained.*
3. *The* `ranf()` *is a random number uniform in* $[0, 1]$.

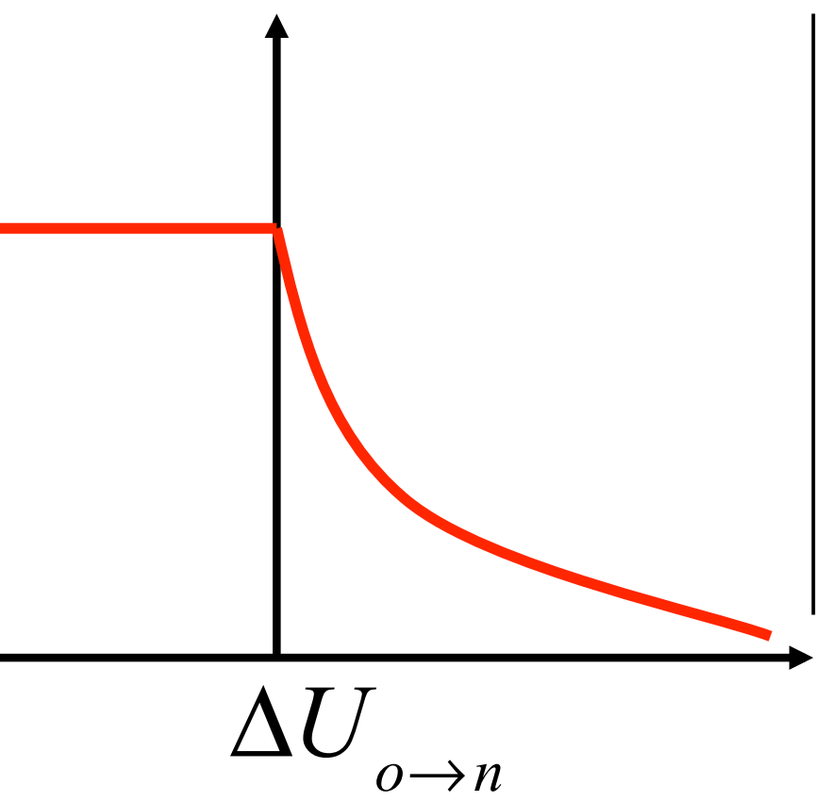
# Metropolis et al.

Many acceptance rules that satisfy:

$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \frac{e^{-\beta U(n)}}{e^{-\beta U(o)}}$$

Metropolis *et al.* introduced:

$$\mathrm{acc}(o \to n) = \min\left(1, e^{-\beta[U(n)-U(o)]}\right) = \min\left(1, e^{-\beta \Delta U}\right)$$




If: $\Delta U < 0 \quad \mathrm{acc}(o \to n) = 1$

accept the move

If: $\Delta U > 0 \quad \mathrm{acc}(o \to n) = e^{-\beta \Delta U}$

draw a uniform random number [0;1] and accept the new configuration if:

$$ranf < e^{-\beta \Delta U}$$

# 3.Monte Carlo Simulation

## 3.4.2 Particle selection

# 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

# 3.Monte Carlo Simulation

## 3.4.3 Selecting the 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`?

## Algorithm 2 (Attempt to Displace a Particle)

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  SUBROUTINE mcmove                    attempts to displace a particle

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  call ener(xn,enn)                    energy new configuration
  if (ranf().lt.exp(-beta              acceptance rule (3.2.1)
+    *(enn-eno)) x(o)=xn              accepted: replace x(o) by xn
  return
  end
```

*Comments to this algorithm:*

1. *Subroutine* `ener` *calculates the energy of a particle at the given position.*
2. *Note that, if a configuration is rejected, the old configuration is retained.*
3. *The* `ranf()` *is a random number uniform in* $[0, 1]$.

# Mathematical

Transition probability from *o* → *n:*

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

As by definition we make a transition:

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

The probability we do not make a move:

$$\pi(o \to o) = 1 - \sum_{n \neq 0} \pi(o \to n)$$

This term ≠ 0

# Model

Let us take a spin system:

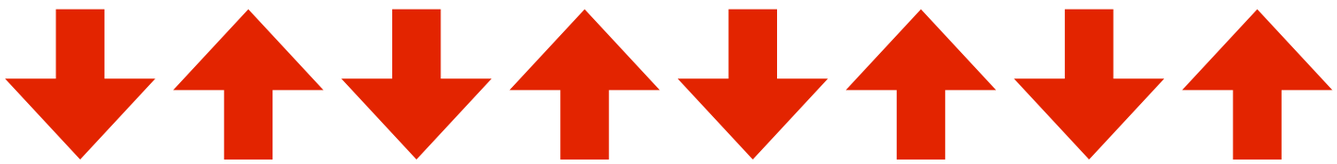
(with energy U↑ = +1 and U↓ = -1)

Probability to find↑:

$$P(\uparrow) = e^{-\beta U(\uparrow)}$$

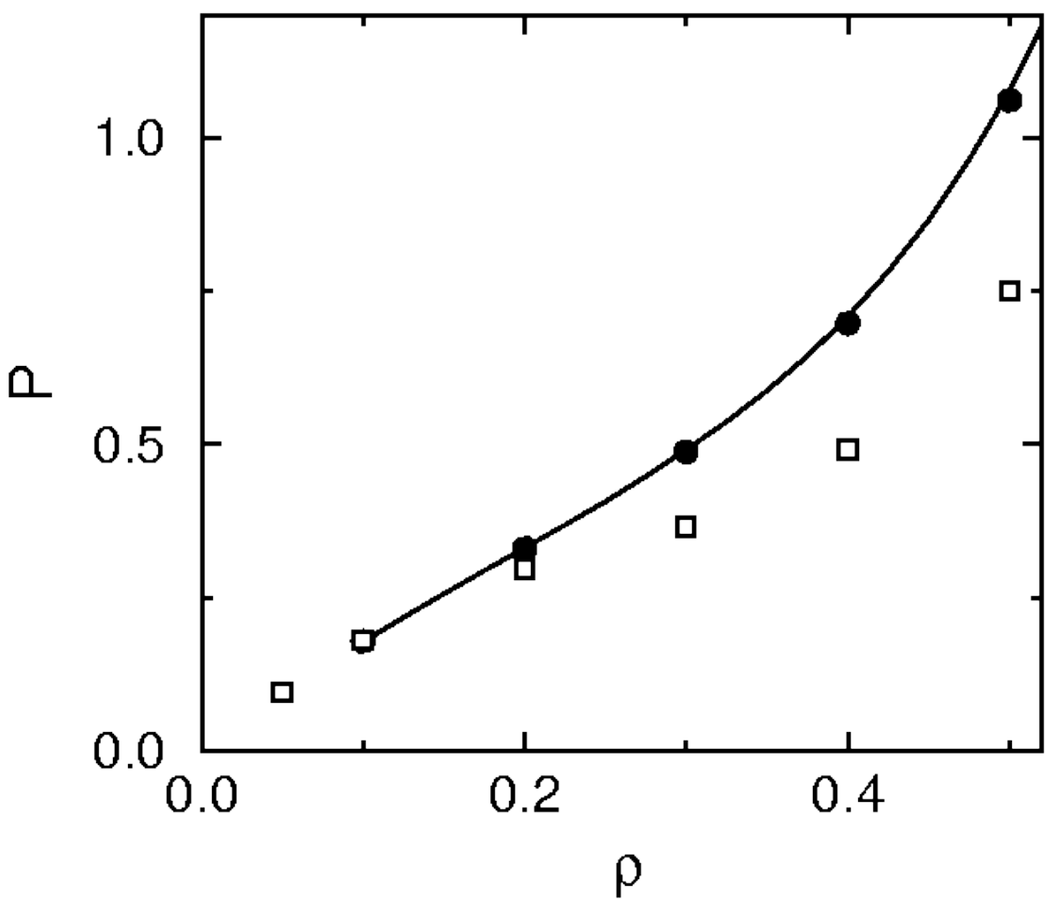
A possible configuration:

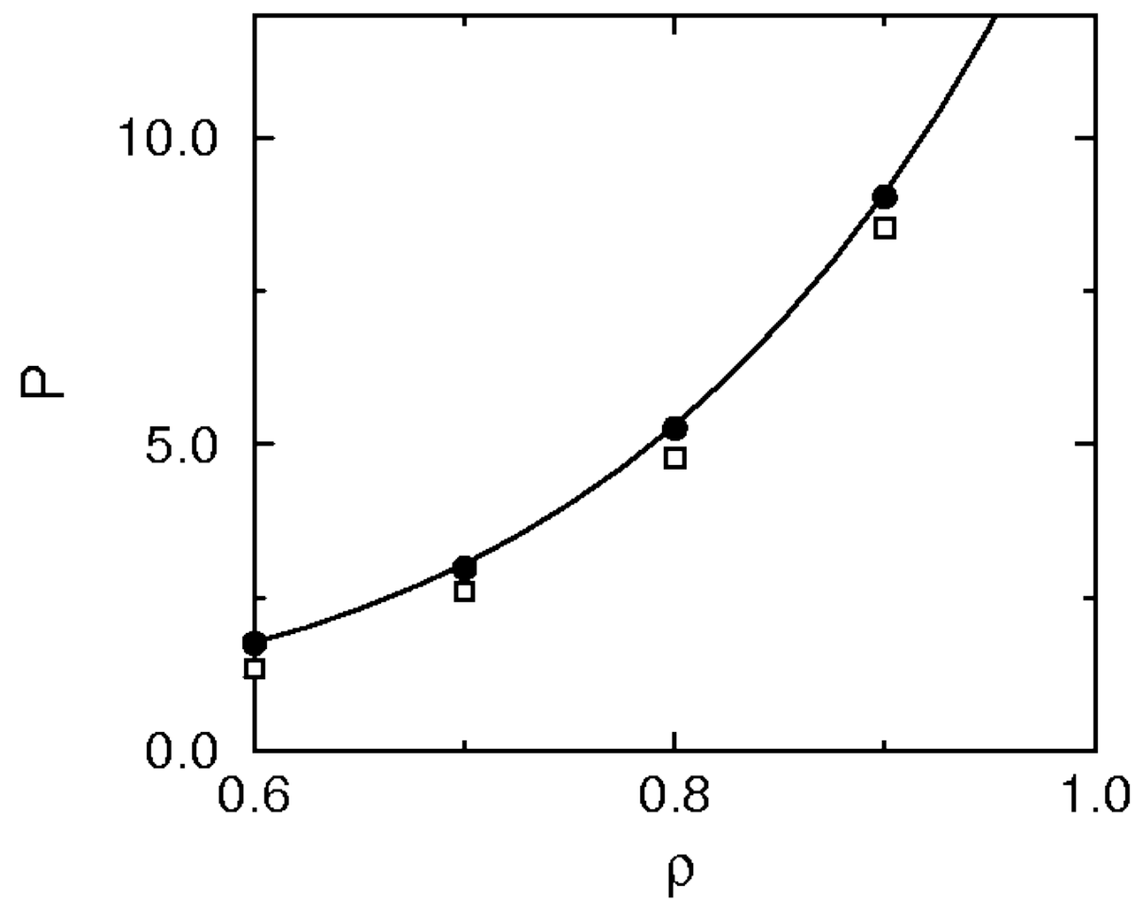
If we do not keep the old configuration:



(independent of the temperature)

# Lennard Jones fluid



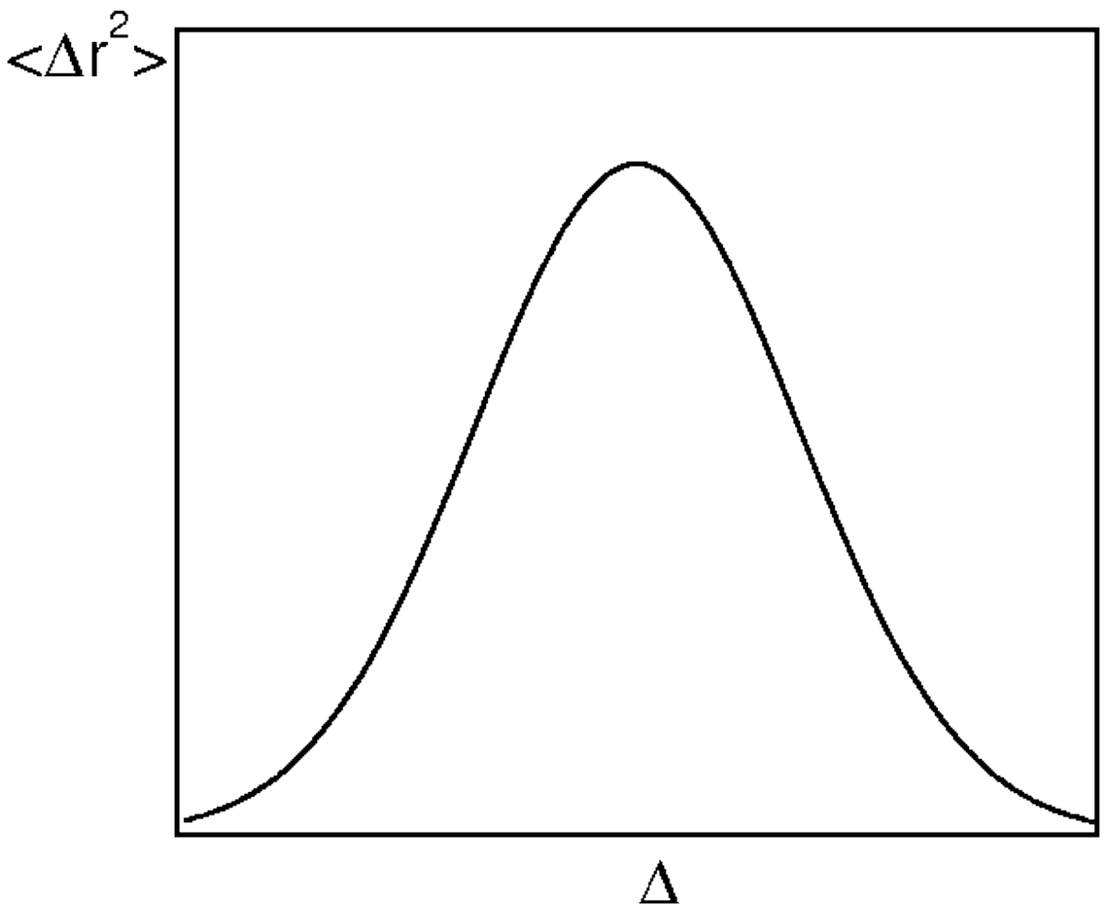
# 3.Monte Carlo Simulation

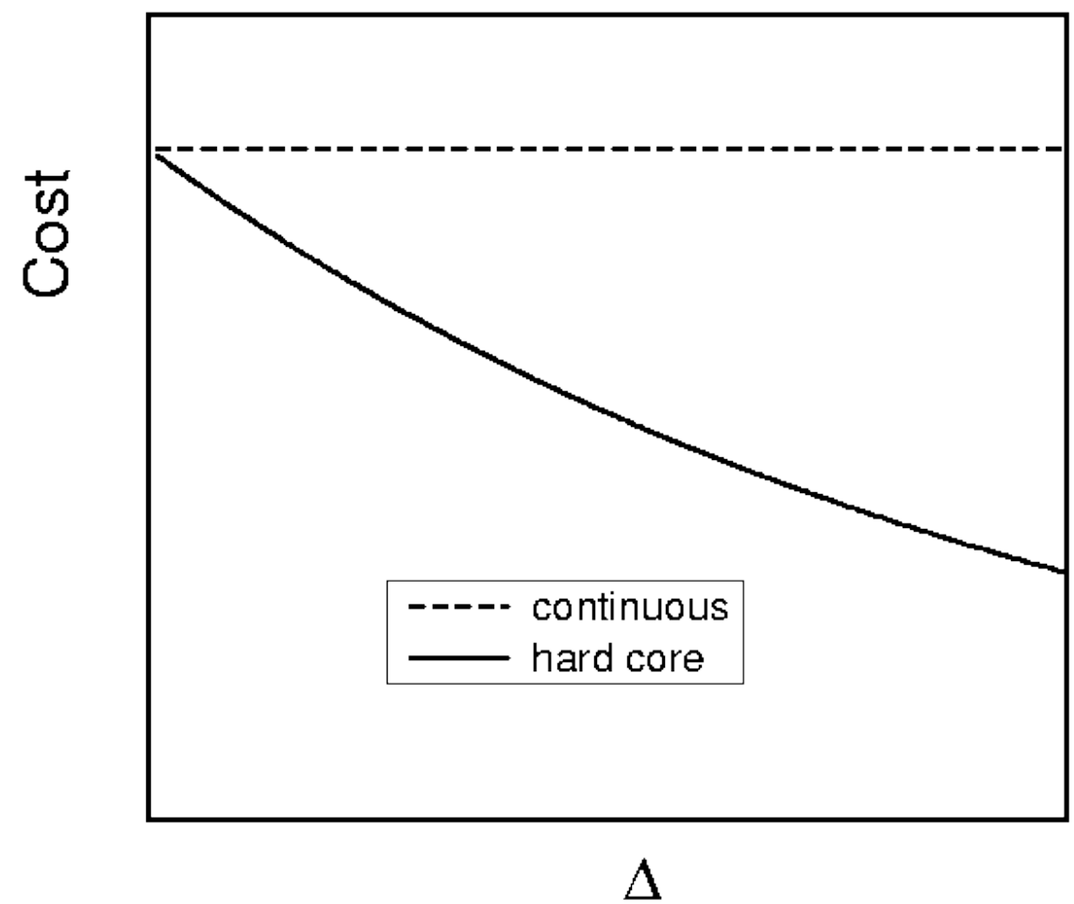
## 3.4.4 Particle displacement

# 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 big Not too small



# 3.Monte Carlo Simulation

## 3.5 Non-Boltzmann sampling

# Non-Boltzmann sampling

$\beta_1 = 1/k_B T_1$

Ensemble average of A at temperature $T_1$:

$$\langle A \rangle_{NVT_1} = \frac{\int A(r) e^{-\beta_1 U(r)} dr}{\int e^{-\beta_1 U(r)} dr} \times \frac{1}{1}$$

with

$$\langle A \rangle_{NVT_1} = \frac{\int A(r) e^{-\beta_1 U(r)} dr}{\int e^{-\beta_1 U(r)} dr}$$

$$1 = e^{-\beta_2 [U(r) - U(r)]}$$

$$\langle A \rangle_{NVT_1} = \frac{\int A(r) e^{-\beta_1 U(r)} e^{-\beta_2 [U(r) - U(r)]} dr}{\int e^{-\beta_1 U(r)} e^{-\beta_2 [U(r) - U(r)]} dr}$$

$$\langle A \rangle_{NVT_1} = \frac{\int A(r) e^{-[\beta_1 U(r) - \beta_2 U(r)]} e^{-\beta_2 U(r)} dr}{\int e^{-[\beta_1 U(r) - \beta_2 U(r)]} e^{-\beta_2 U(r)} dr}$$

again multiply with 1/1:

$$= \frac{\int e^{-\beta_2 U(r)} dr \int A(r) e^{-[\beta_1 U(r) - \beta_2 U(r)]} e^{-\beta_2 U(r)} dr}{\int e^{-[\beta_1 U(r) - \beta_2 U(r)]} e^{-\beta_2 U(r)} dr \int e^{-\beta_2 U(r)} dr}$$

This gives us:

$$\langle A \rangle_{NVT_1} = \frac{\left\langle A e^{-(\beta_1 - \beta_2) U} \right\rangle_{NVT_2}}{\left\langle e^{-(\beta_1 - \beta_2) U} \right\rangle_{NVT_2}}$$

# Non-Boltzmann sampling

Ensemble average of A at temperature $T_1$:

$$\langle A \rangle_{NVT_1} = \frac{\int A(r) e^{-\beta_1 U(r)} dr}{\int e^{-\beta_1 U(r)} dr}$$

**Why are we not using this?**

$T_1$ is arbitrary, we can use any value

$$\langle A \rangle_{NVT_1} = \frac{\int A(r) e^{-\beta_1 U(r)} e^{-\beta_2 [U(r)-U(r)]} dr}{\int e^{-\beta_1 U(r)} e^{-\beta_2 [U(r)-U(r)]} dr}$$

again multiply with 1/1:

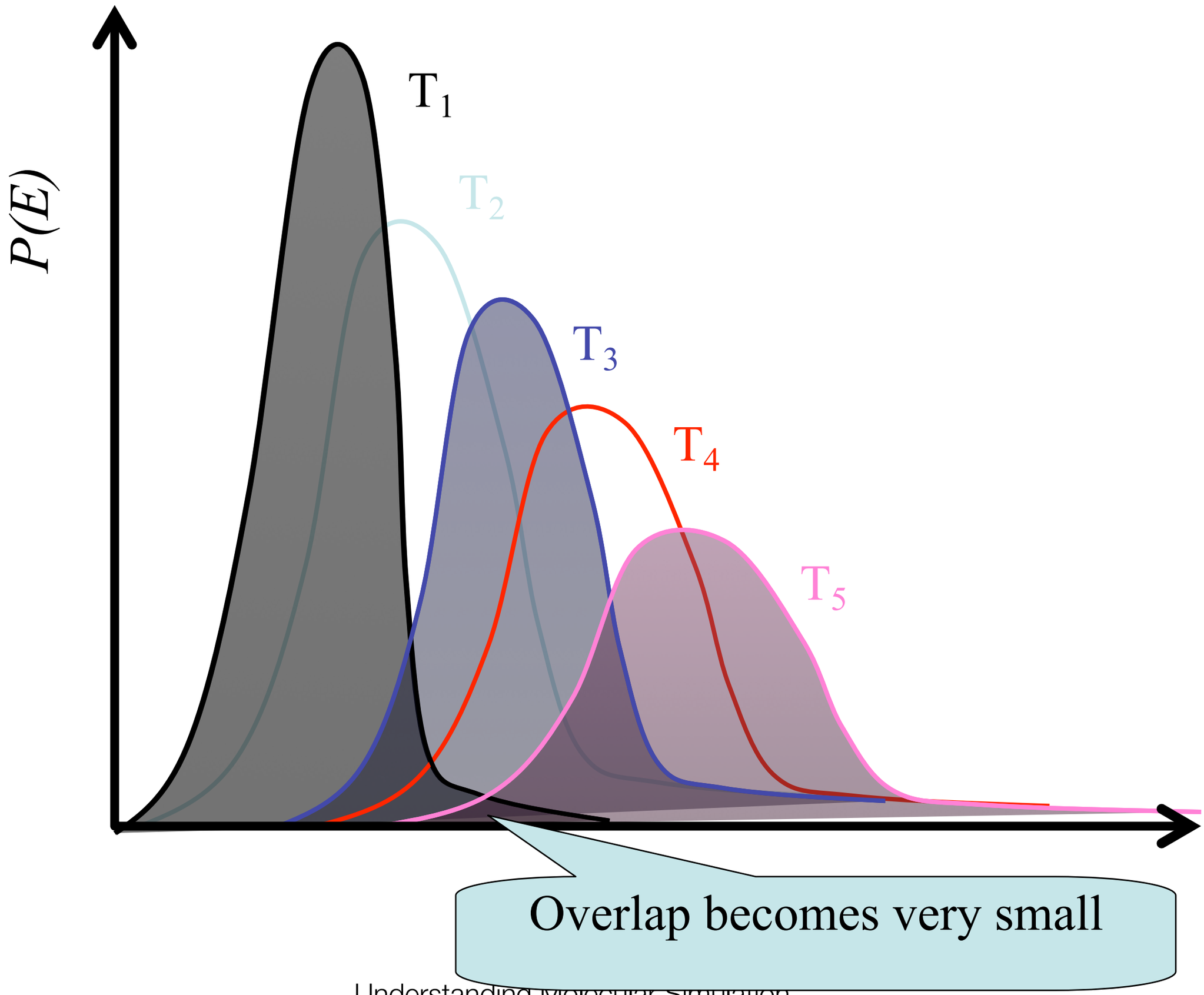
$$\langle A \rangle_{NVT_1} = \frac{\int A(r) e^{-[\beta_1 U(r)-\beta_2 U(r)]} e^{-\beta_2 U(r)} dr}{\int e^{-[\beta_1 U(r)-\beta_2 U(r)]} e^{-\beta_2 U(r)} dr} = \frac{\int e^{-\beta_1 U(r)} dr \int A(r) e^{-[\beta_1 U(r)-\beta_2 U(r)]} e^{-\beta_2 U(r)} dr}{\int e^{-[\beta_1 U(r)-\beta_2 U(r)]} e^{-\beta_2 U(r)} dr}$$

We perform a simulation at $T_2$

and only 1 simulation …

$$\langle A \rangle_{NVT_1} = \frac{\langle A e^{-(\beta_1-\beta_2)U} \rangle_{NVT_2}}{\langle e^{-(\beta_1-\beta_2)U} \rangle_{NVT_2}}$$

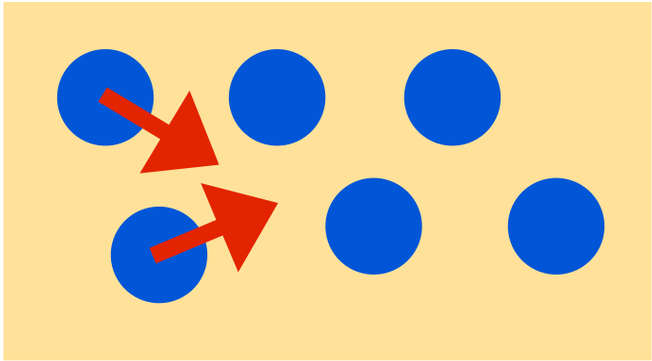
But obtain an ensemble average at $T_1$


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

# 3. Monte Carlo Simulation

## 3.6 Parallel Monte Carlo

# Parallel Monte Carlo



How to do a Monte Carlo simulation in parallel?

- (trivial but works best) Use an ensemble of systems with different seeds for the random number generator
- 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

Naive (and wrong)

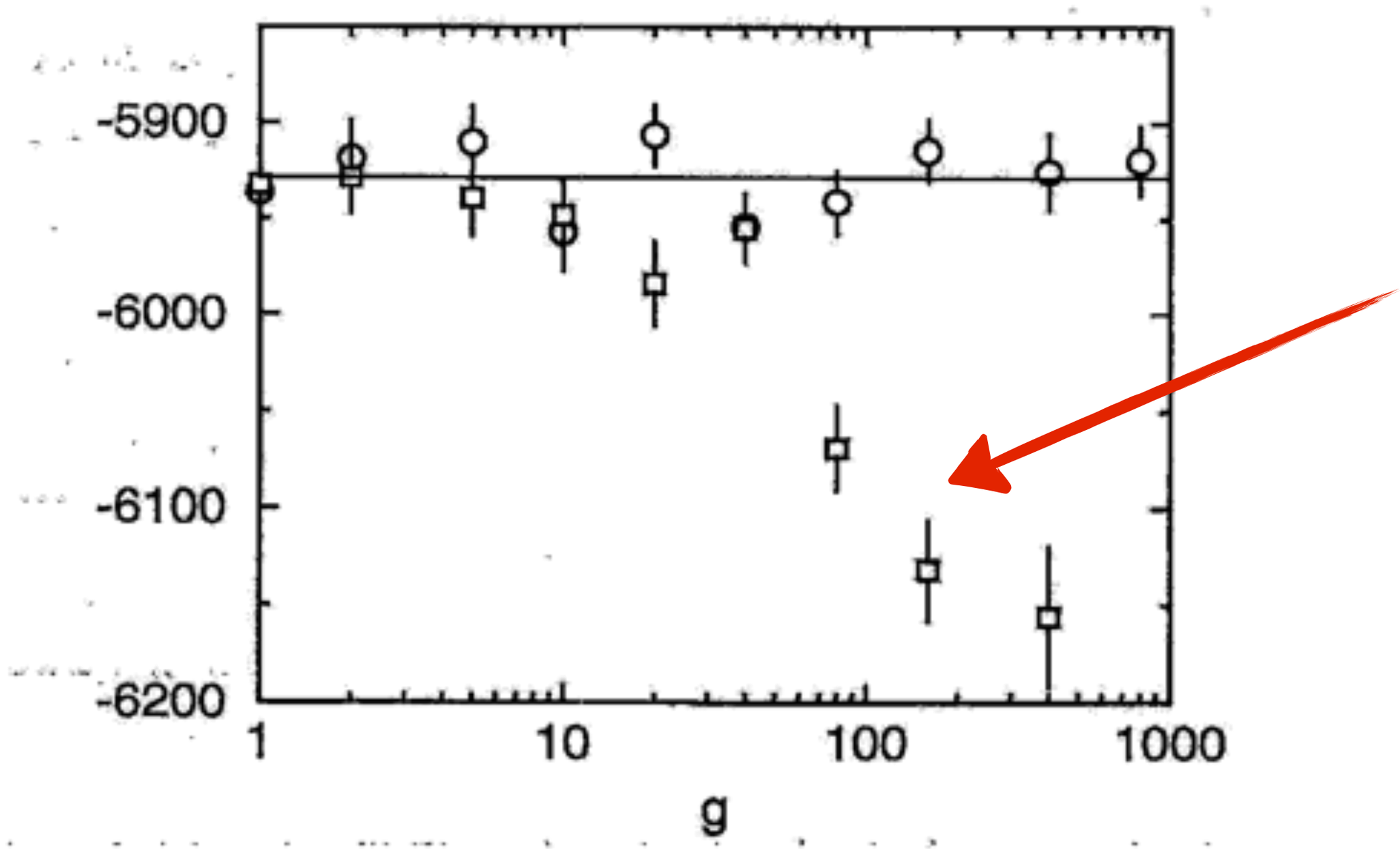
1. Generate k trial configurations in parallel
2. Select out of these the one with the lowest energy

$$P(n) = \frac{e^{-\beta U(n)}}{\sum_{j=1}^{g} e^{-\beta U(j)}}$$

3. Accept and reject using normal Monte Carlo rule:

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

# Conventional acceptance rules




The conventional acceptance rules give a bias

# What went wrong?

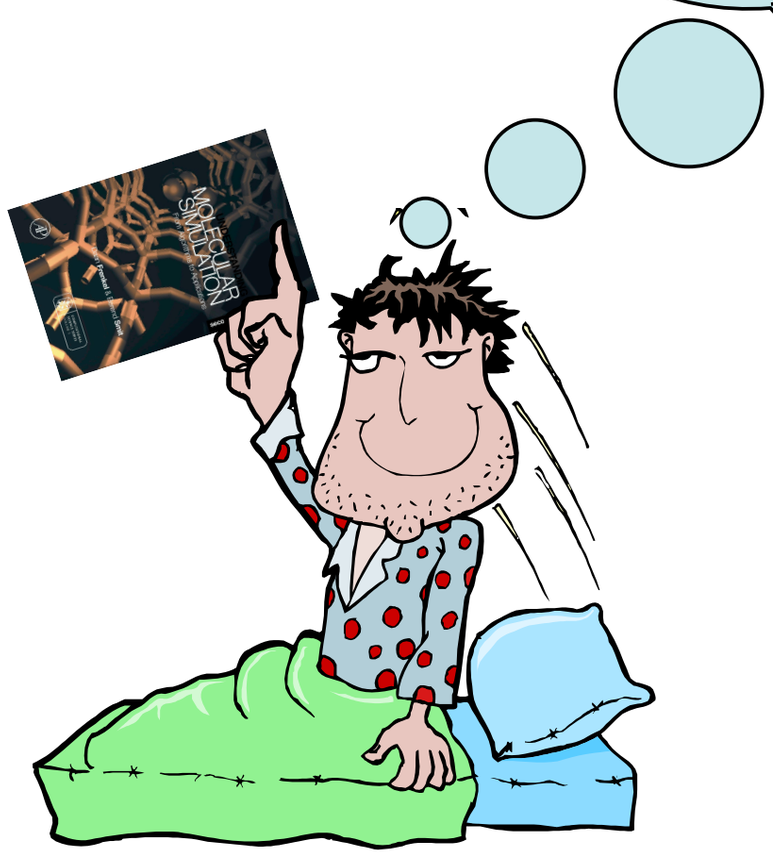
## Detailed balance!

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

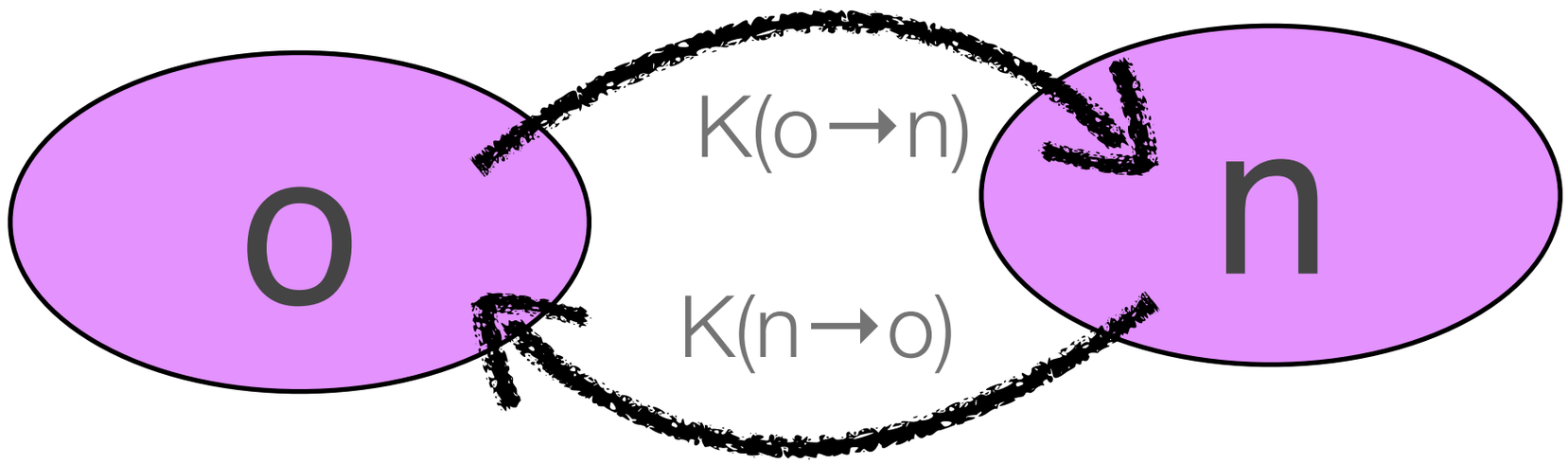
$$K(o \rightarrow n) = N(o) \times \alpha(o \rightarrow n) \times \mathrm{acc}(o \rightarrow n)$$

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

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



# Markov Processes - Detailed Balance




Condition of detailed balance:

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

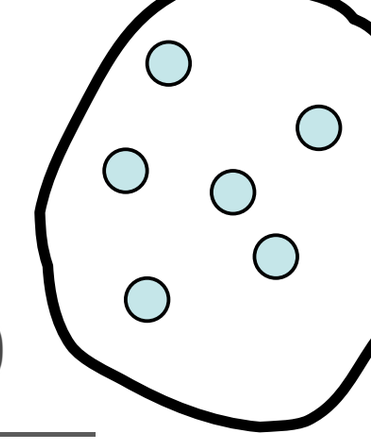
$$K(o \to n) = N(o) \times \alpha(o \to n) \times \mathrm{acc}(o \to n)$$

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

$$\boxed{\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \frac{N(n) \times \cancel{\alpha(n \to o)}}{N(o) \times \cancel{\alpha(o \to n)}} = \frac{N(n)}{N(o)}}$$

?

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



A priori probability to generate configuration n:

$$\alpha(o \to n) = \frac{e^{-\beta U(n)}}{\sum_{j=1}^{g} e^{-\beta U(j)}}$$

Rosenbluth factor configuration n:

$$W(n) = \sum_{j=1}^{g} e^{-\beta U(j)}$$

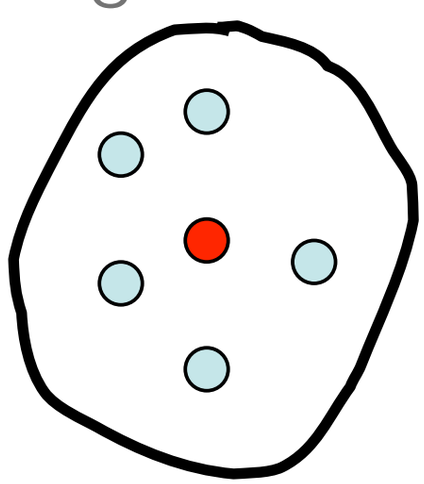
$$\alpha(o \to n) = \frac{e^{-\beta U(n)}}{W(n)}$$

A priori probability to generate configuration o:

$$\alpha(n \to o) = \frac{e^{-\beta U(o)}}{\sum_{j=1}^{g} e^{-\beta U(j)}}$$

Rosenbluth factor configuration o:

$$W(o) = e^{-\beta U(o)} + \sum_{j=1}^{g-1} e^{-\beta U(j)}$$



$$\alpha(n \to o) = \frac{e^{-\beta U(o)}}{W(o)}$$

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

Now with the correct a priori probabilities to generate a configuration:

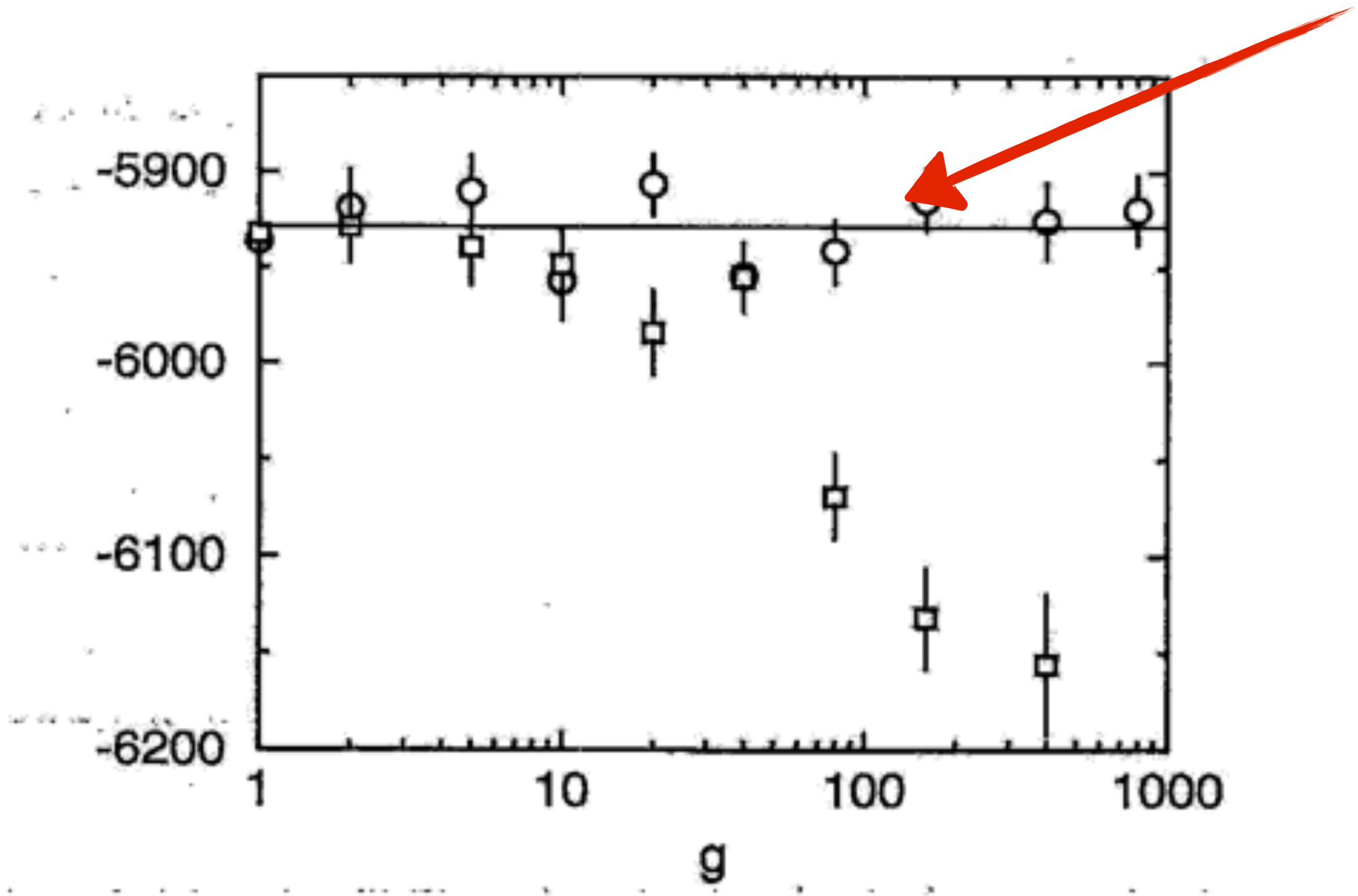
$$\alpha(o \to n) = \frac{e^{-\beta U(n)}}{W(n)}$$

$$\alpha(n \to o) = \frac{e^{-\beta U(o)}}{W(o)}$$

This gives as acceptance rules:

$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \frac{e^{-\beta U(n)} \times \frac{e^{-\beta U(o)}}{W(o)}}{e^{-\beta U(o)} \times \frac{e^{-\beta U(n)}}{W(n)}} = \frac{W(n)}{W(o)}$$

# Conventional acceptance rules




Modified acceptance rules remove the bias exactly