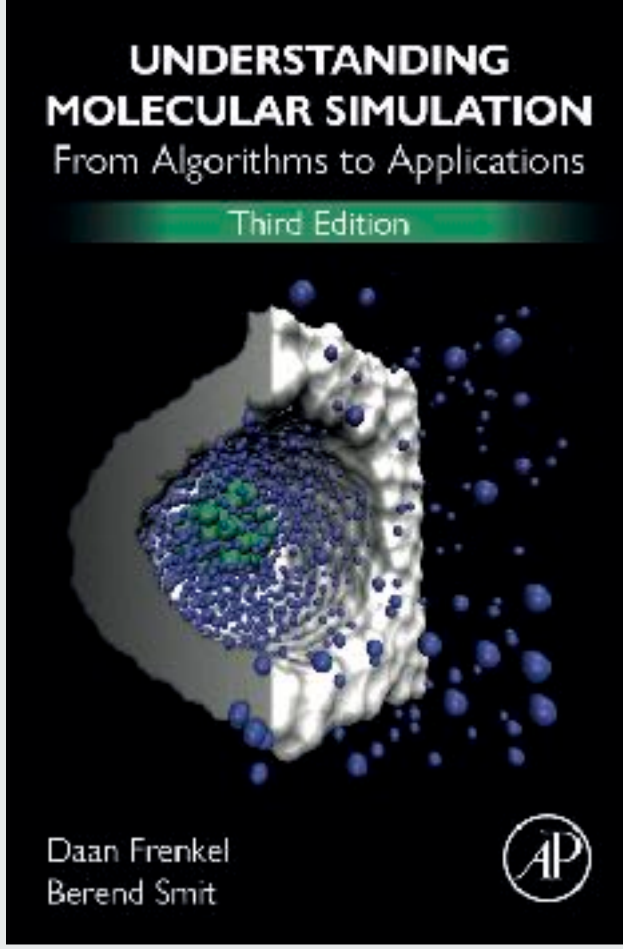
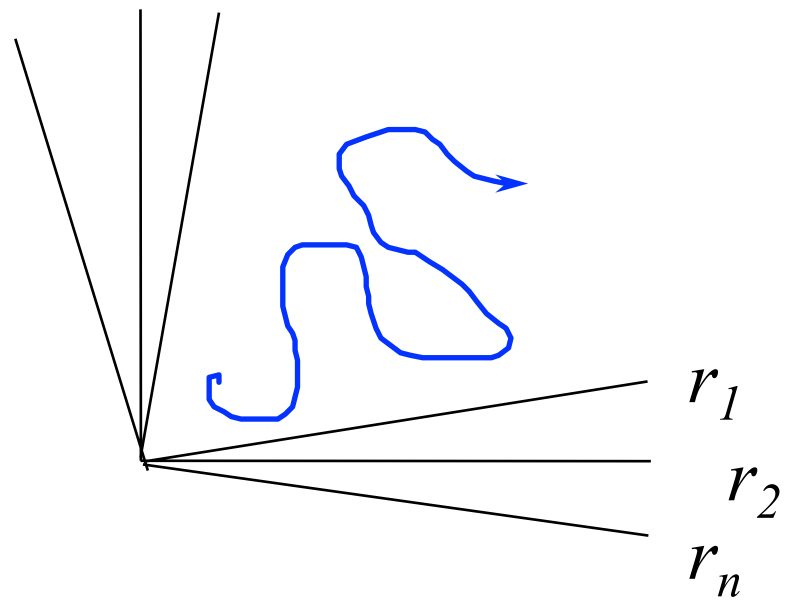


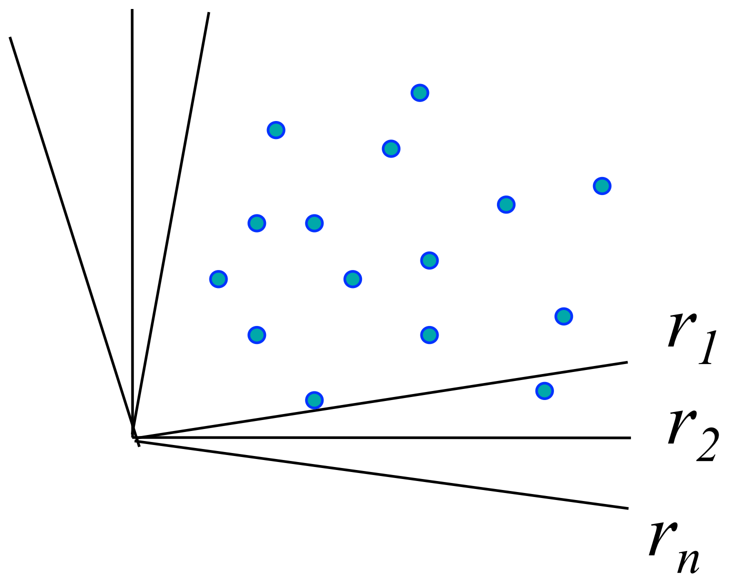
3. Monte Carlo Simulations

Molecular Simulations

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



- **Monte Carlo**: importance sampling

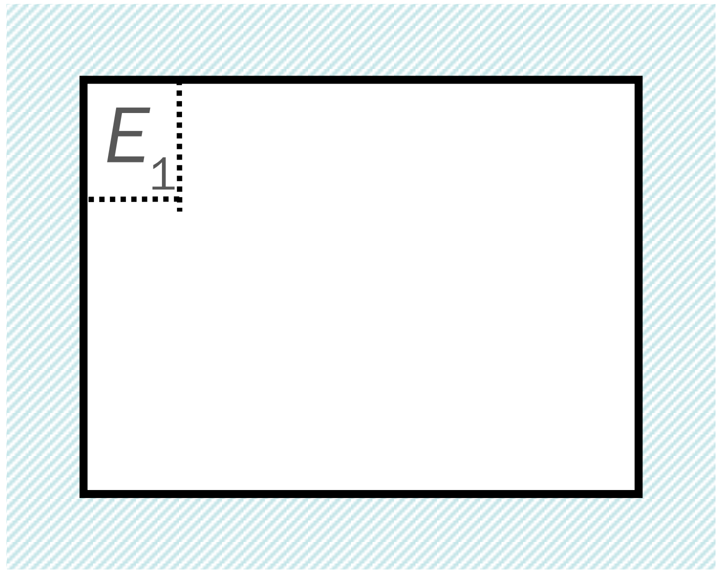


Monte Carlo Simulations

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$_B$T

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

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

Hence, the probability to find E_1:

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

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

β=1/k$_B$T

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:

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

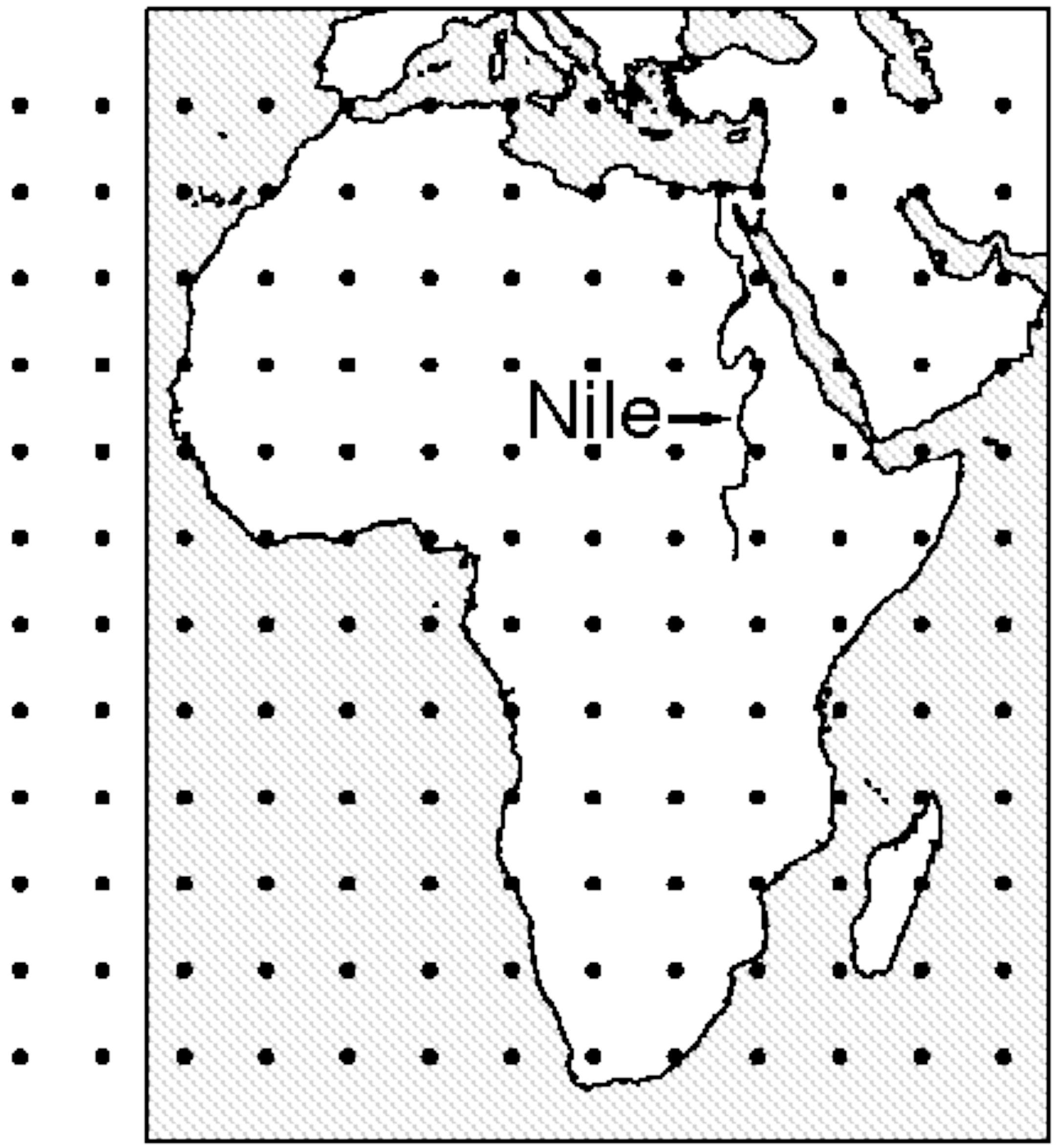
Free energy:

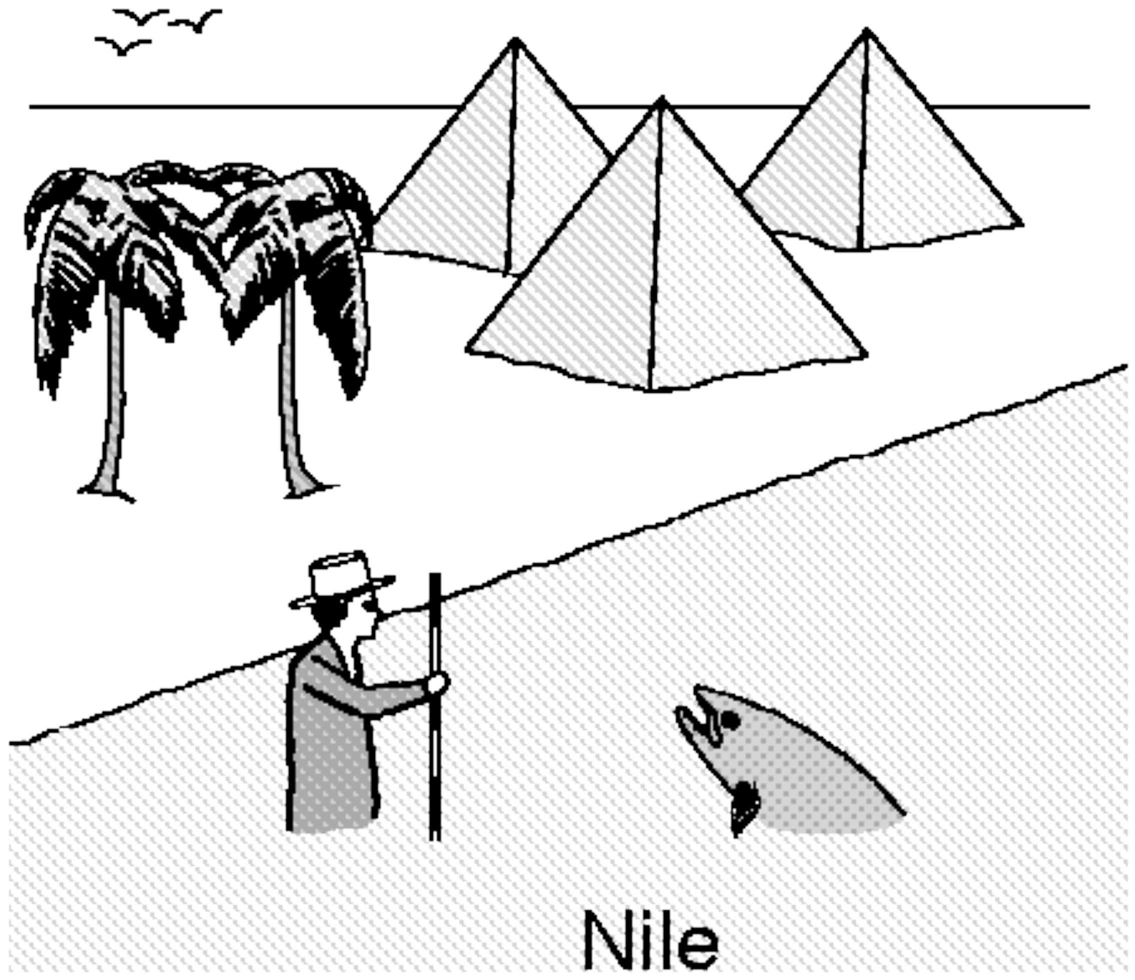
$$\beta F = -\ln Q_{NVT}$$

3.Monte Carlo Simulations

3.3 Importance Sampling

Numerical Integration





Understanding Molecular Simulation

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:

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

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

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

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

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

with

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

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

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:

$$\bar{A} = \sum_{i=1}^{M} A\left(r_i^{3N}\right) \qquad \bar{A} = \frac{\int A\left(r^{3N}\right) P^{MC}\left(r^{3N}\right) dr^{3N}}{\int P^{MC}\left(r^{3N}\right) dr^{3N}}$$

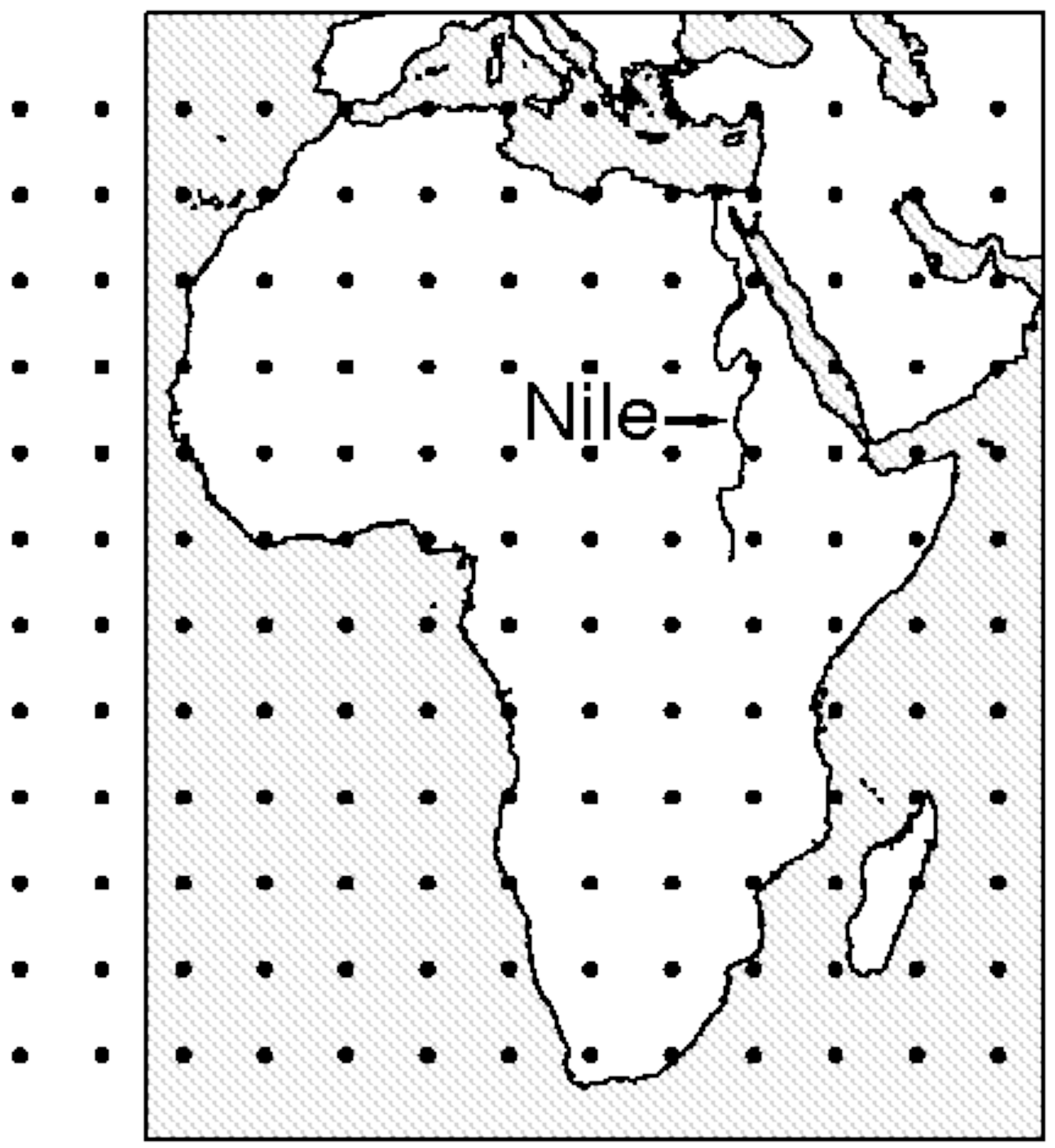
Hence, we need to sample:

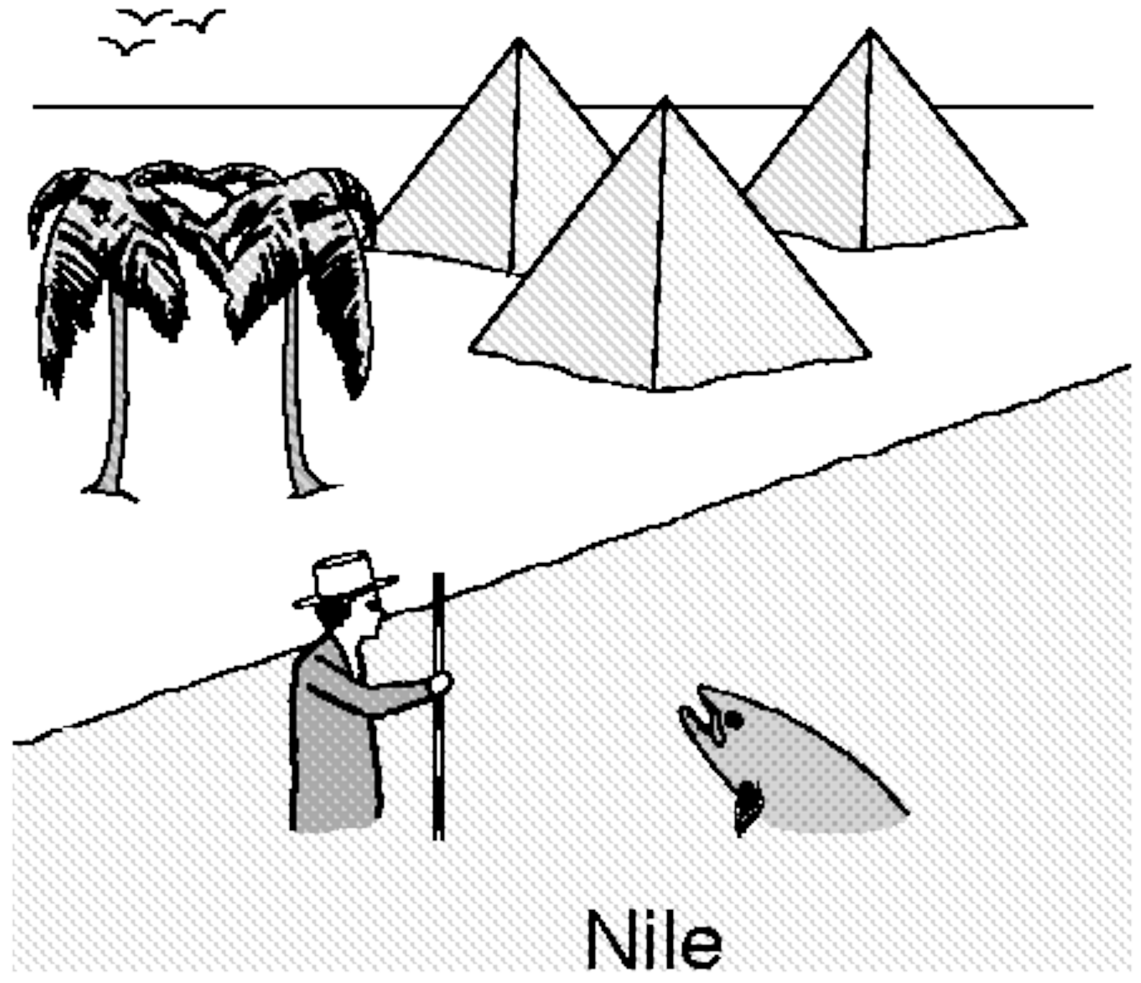
$$P^{MC}\left(r^{3N}\right) = C e^{-\beta U\left(r^{3N}\right)}$$

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 (Core of Metropolis MC code)

```
program MC                                  basic Metropolis algorithm
    for 1 ≤ itrial ≤ ntrial do              perform ntrial MC trial moves
      mcmove                                trial move procedure
      if (itrial % nsamp) == 0 then         % denotes the Modulo operation
        sample                              sample procedure
      endif
    enddo
end program
```

Specific Comments *(for general comments, see p. 7)*

1. *Function* **mcmove** *attempts to displace a randomly selected particle (see Algorithm 2).*
2. *Function* **sample** *samples observables every* `nsample`*-th trial move.*

Algorithm 2 (Monte Carlo trial displacement)

```
function mcmove                                  Metropolis MC trial move
    i=int($\mathcal{R}$*npart)+1                 select random particle with
                                                 $1 \leq$ i $\leq$ npart
    eno = ener(x(i),i)                           eno: energy particle i at
                                                 "old" position x(i)
    xn=x(i)+($\mathcal{R}$-0.5)*delx             trial position xn for particle i
    enn = ener(xn,i)                             enn: energy of i at xn
    if $\mathcal{R}$ < exp[-β*(enn-eno)] then    Metropolis criterion Eq. (3.3.1)
      x(i)=xn                                    if accepted, x(i) becomes xn
    endif
end function
```

Specific Comments *(for general comments, see p. 7)*

1. npart*: number of particles.* x(npart) *position array.* $T = 1/\beta$*, maximum steps size* $=$ 0.5*delx
2. *The function* **ener**(x)*: computes the interaction energy of a particle at position x, using the approach shown in Algorithm 5.*
3. $\mathcal{R}$ *generates a random number uniformly between 0 and 1*
4. int(z) *returns the integer part of* z
5. *Note that, if a configuration is rejected, the old configuration is retained.*

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

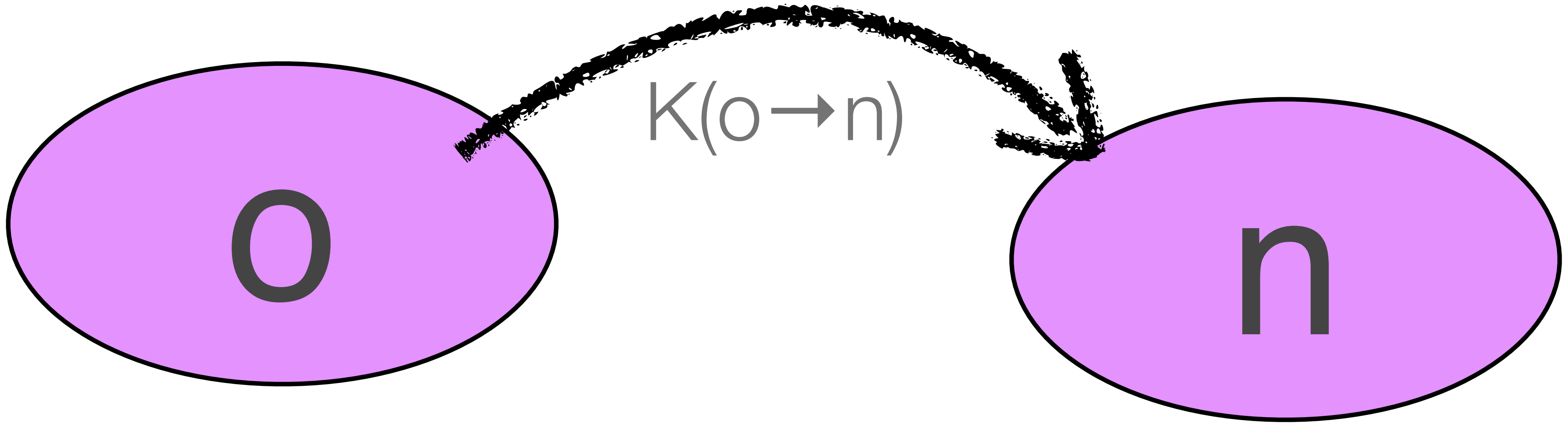
- Next step only depends on the current state
- Ergodic: all possible states can be reached by a set of single steps
- Detailed balance

* 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

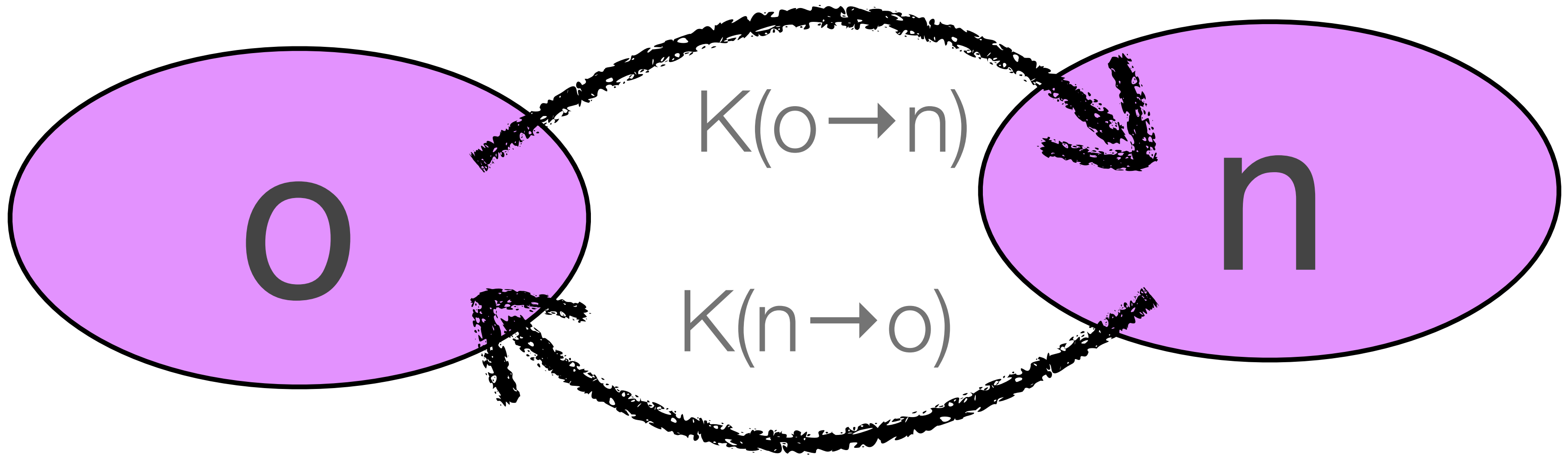


K(o → n): total number of systems in our ensemble that move *o* → *n*

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

- *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:

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

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

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

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

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:

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

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

Which gives as condition for the acceptance rule:

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

Algorithm 2 (Monte Carlo trial displacement)

```
function mcmove                                Metropolis MC trial move

    i=int($\mathcal{R}$*npart)+1                    select random particle with
                                               $1 \le$ i $\le$ npart
    eno = ener(x(i),i)                         eno: energy particle i at
                                               "old" position x(i)
    xn=x(i)+($\mathcal{R}$-0.5)*delx                trial position xn for particle i
    enn = ener(xn,i)                           enn: energy of i at xn
    if $\mathcal{R}$ < exp[-$\beta$*(enn-eno)] then        Metropolis criterion Eq. (3.3.1)
      x(i)=xn                                  if accepted, x(i) becomes xn
    endif
end function
```

Specific Comments *(for general comments, see p. 7)*

1. npart*: number of particles.* x(npart) *position array. $T = 1/\beta$, maximum steps size* $=$ 0.5*delx
2. *The function* **ener**(x)*: computes the interaction energy of a particle at position x, using the approach shown in Algorithm 5.*
3. *$\mathcal{R}$ generates a random number uniformly between 0 and 1*
4. int(z) *returns the integer part of* z
5. *Note that, if a configuration is rejected, the old configuration is retained.*

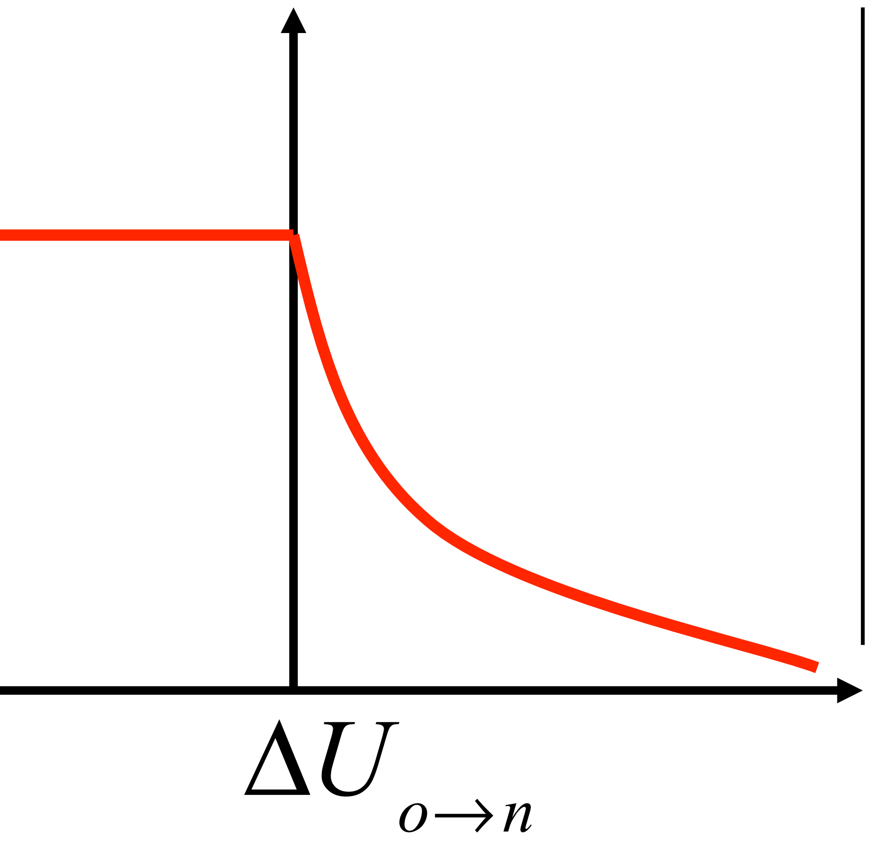
Metropolis et al.

Many acceptance rules that satisfy:

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

Metropolis *et al.* introduced:

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



If:

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

accept the move

If:

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

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 (Monte Carlo trial displacement)

```
function mcmove                          Metropolis MC trial move

    i=int($\mathcal{R}$*npart)+1                select random particle with
                                         $1 \leq$ i $\leq$ npart
    eno = ener(x(i),i)                   eno: energy particle i at
                                         "old" position x(i)
    xn=x(i)+($\mathcal{R}$-0.5)*delx            trial position xn for particle i
    enn = ener(xn,i)                     enn: energy of i at xn
    if $\mathcal{R} <$ exp[-$\beta$*(enn-eno)] then     Metropolis criterion Eq. (3.3.1)
        x(i)=xn                          if accepted, x(i) becomes xn
    endif
end function
```

Specific Comments *(for general comments, see p. 7)*

1. npart*: number of particles.* x(npart) *position array.* $T = 1/\beta$*, maximum steps size* = 0.5*delx
2. *The function* **ener**(x)*: computes the interaction energy of a particle at position x, using the approach shown in Algorithm 5.*
3. $\mathcal{R}$ *generates a random number uniformly between 0 and 1*
4. int(z) *returns the integer part of* z
5. *Note that, if a configuration is rejected, the old configuration is retained.*

Mathematical

Transition probability from $o \rightarrow n$:

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

As by definition we make a transition:

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

The probability we do not make a move:

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

This term $\neq 0$

Model

Let us take a spin system: ↑ ↓

(with energy U↑ = +1 and U↓ = -1)

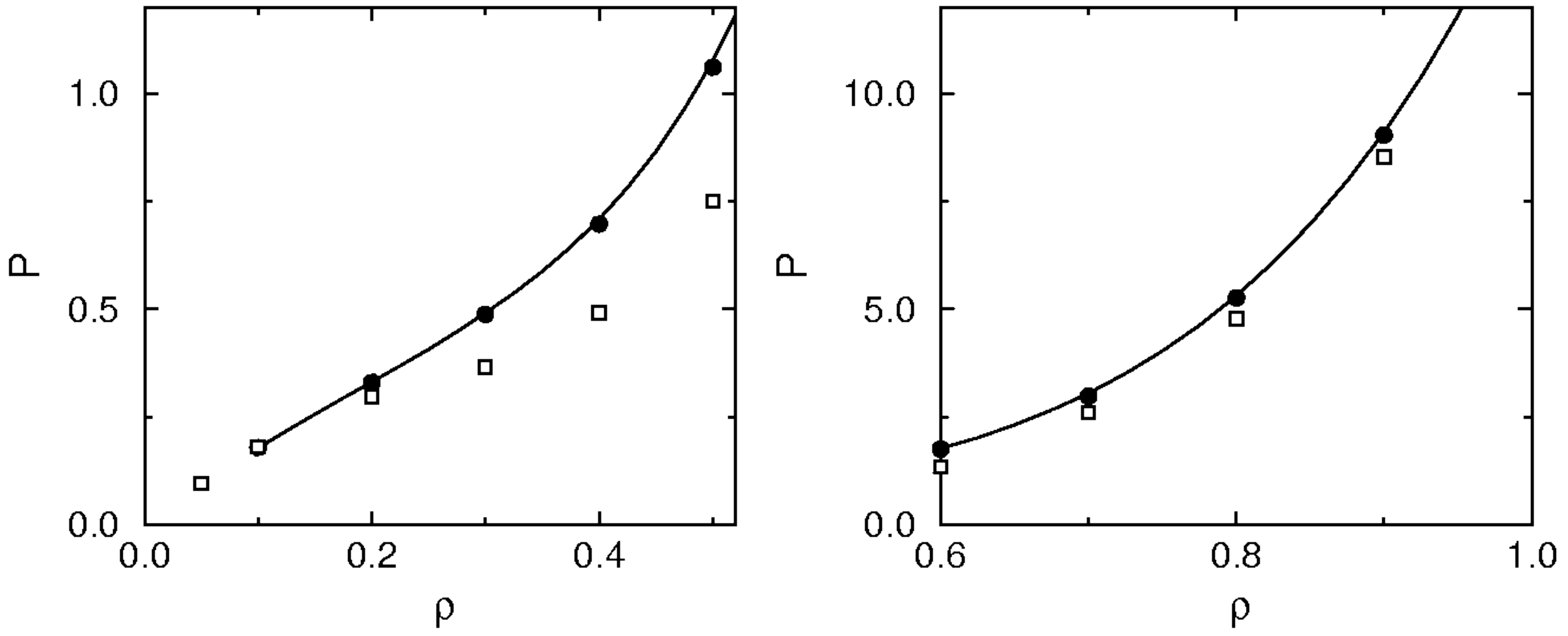
Probability to find ↑: $P(\uparrow) = e^{-\beta U(\uparrow)}$

A possible configuration: ↓ ↓ ↑ ↓ ↑ ↓ ↓ ↓

If we do not keep the old configuration: ↓ ↑ ↓ ↑ ↓ ↑ ↓ ↑

(independent of the temperature)

Lennard Jones fluid



Understanding Molecular Simulation

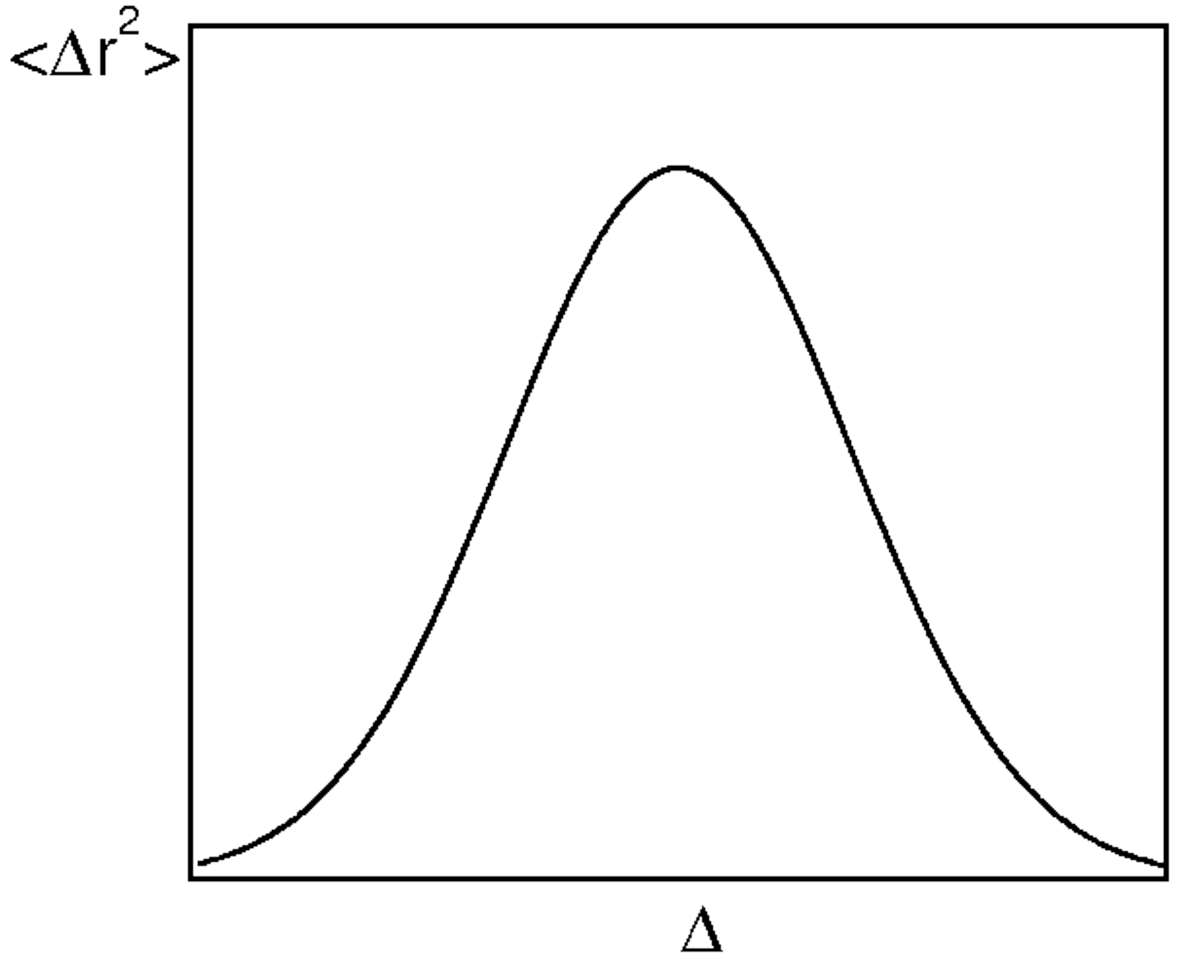
3.Monte Carlo Simulation

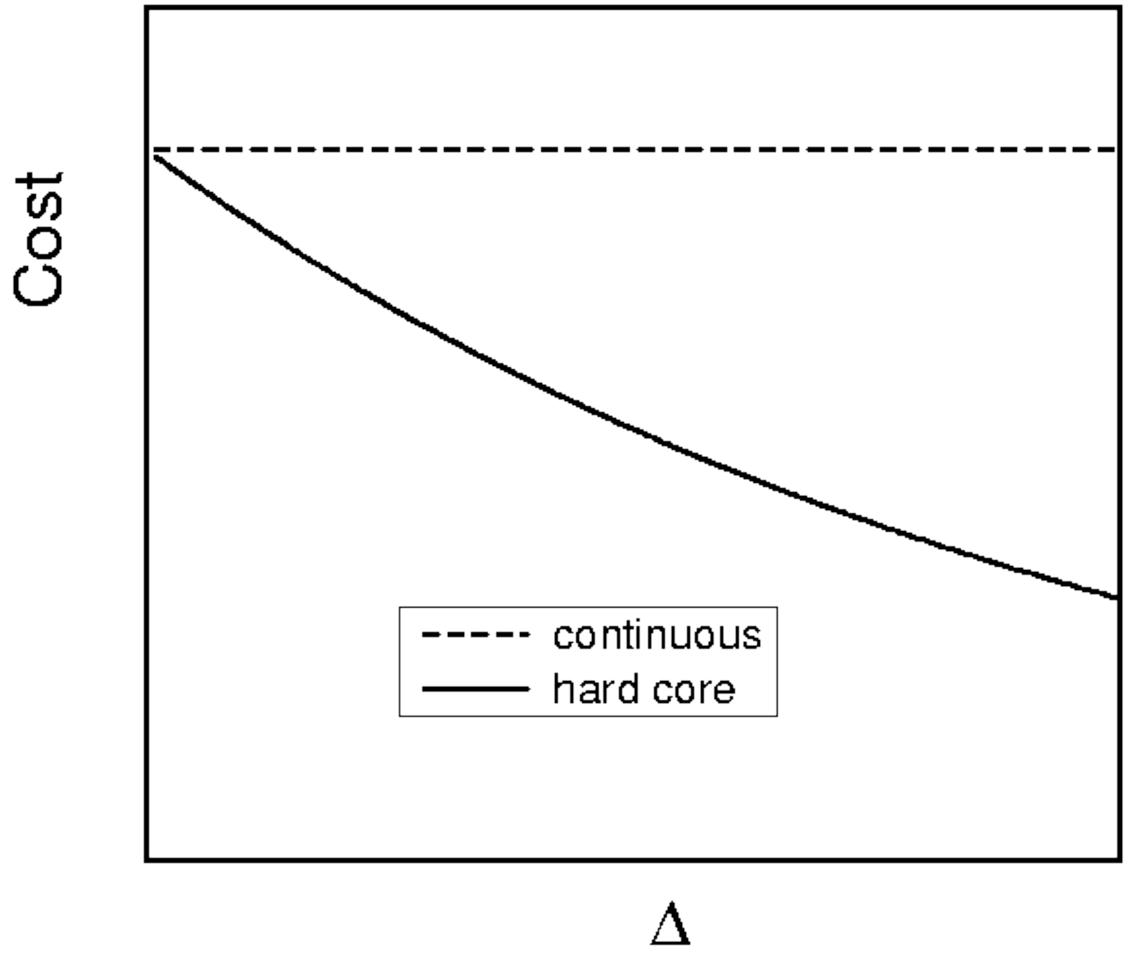
3.4.4 Particle displacement

Questions

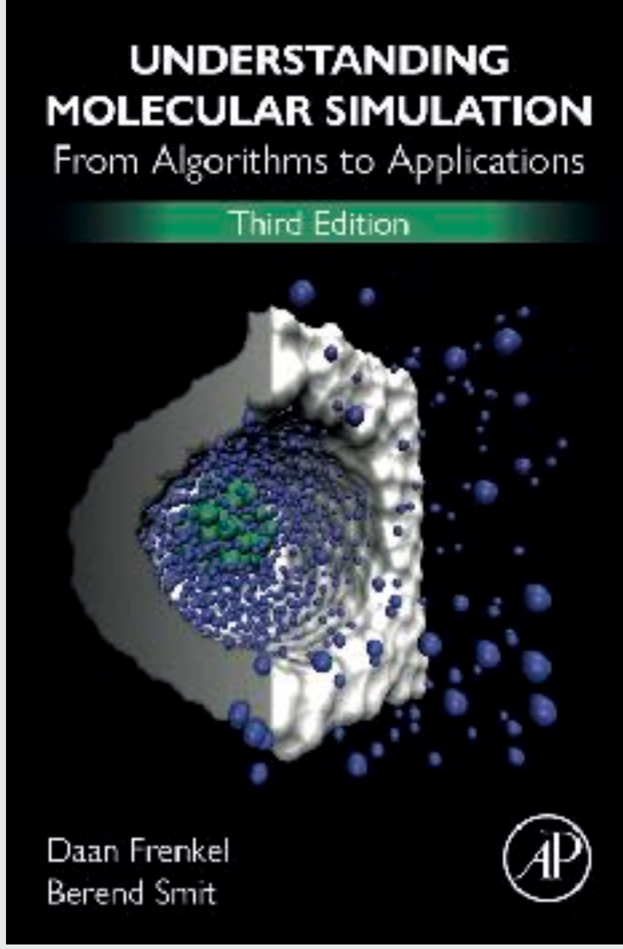
- How can we prove that this scheme generates the desired distribution of configurations?
- Why make a random selection of the particle to be displaced?
- Why do we need to take the old configuration again?
- **How large should we take: `delx`?**

Not too big Not too small





Understanding Molecular Simulation



3.Monte Carlo Simulation

3.5 Non-Boltzmann sampling

Non-Boltzmann sampling

$\beta_1 = 1/k_B T_1$

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

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

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

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

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

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 T₁:

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

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

Why are we not using this?

T₁ is arbitrary, we can use any value

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

ag in multiply with 1/1:

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

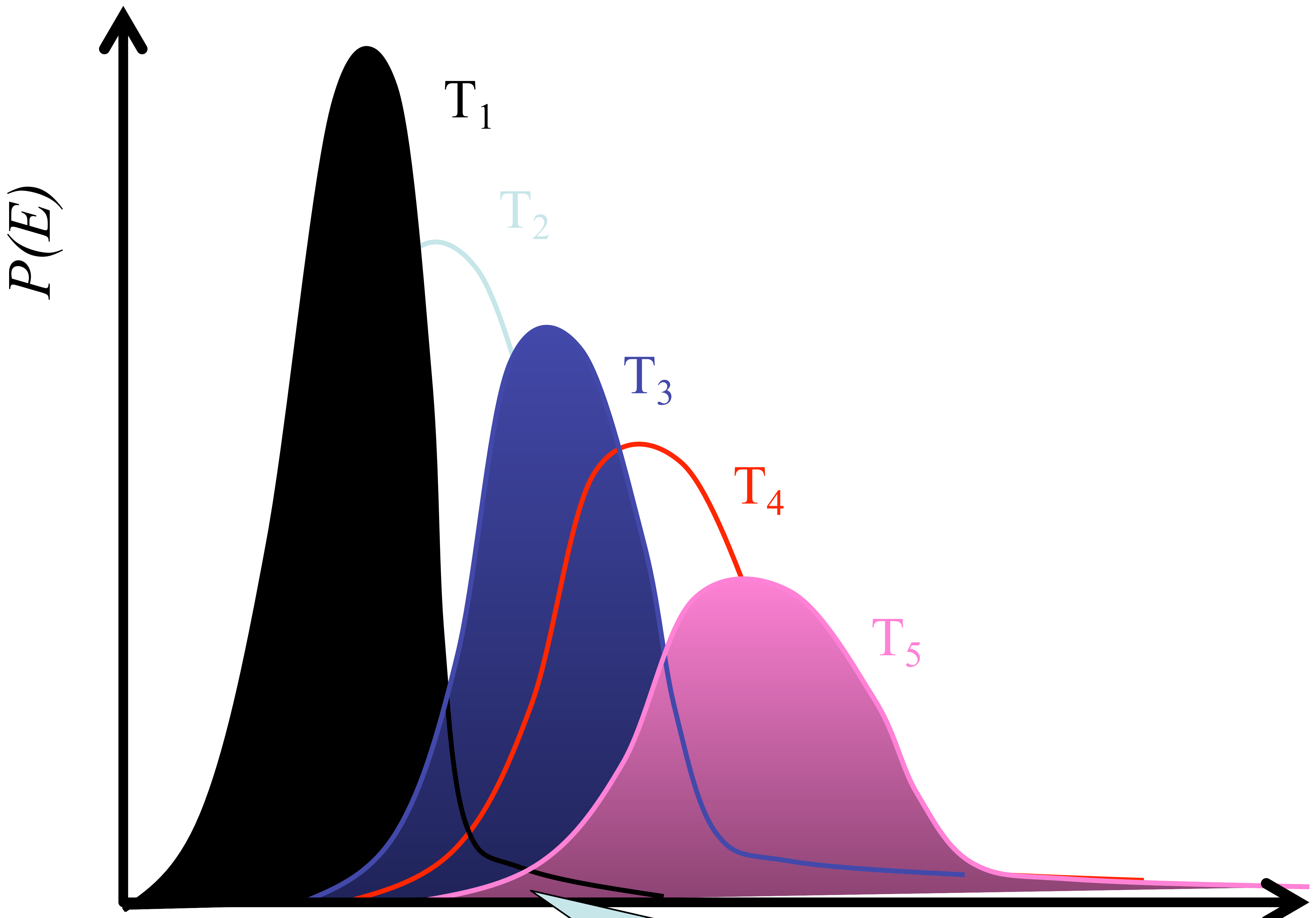
$$= \frac{\int e^{\beta_2 U(r)}dr \int A(r)e^{-[\beta_1 U(r)-\beta_2 r)]}e^{-\beta_2 U(r)}dr}{\int e^{-[\beta_1 U(r)-\beta_2 U(r)]}e}$$

We perform a simulation at T₂

and only 1 simulation …

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

But obtain an ensemble average at T₁

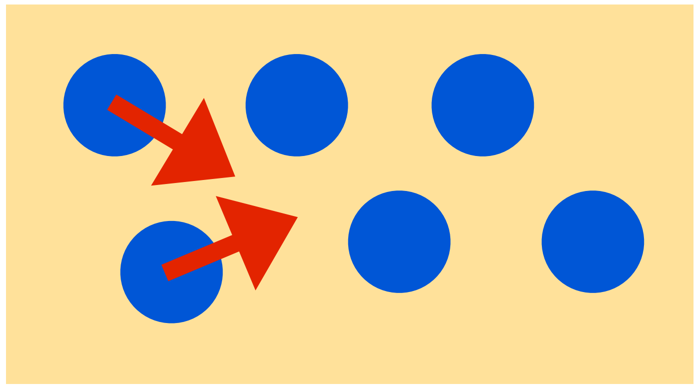


Overlap becomes very small

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)

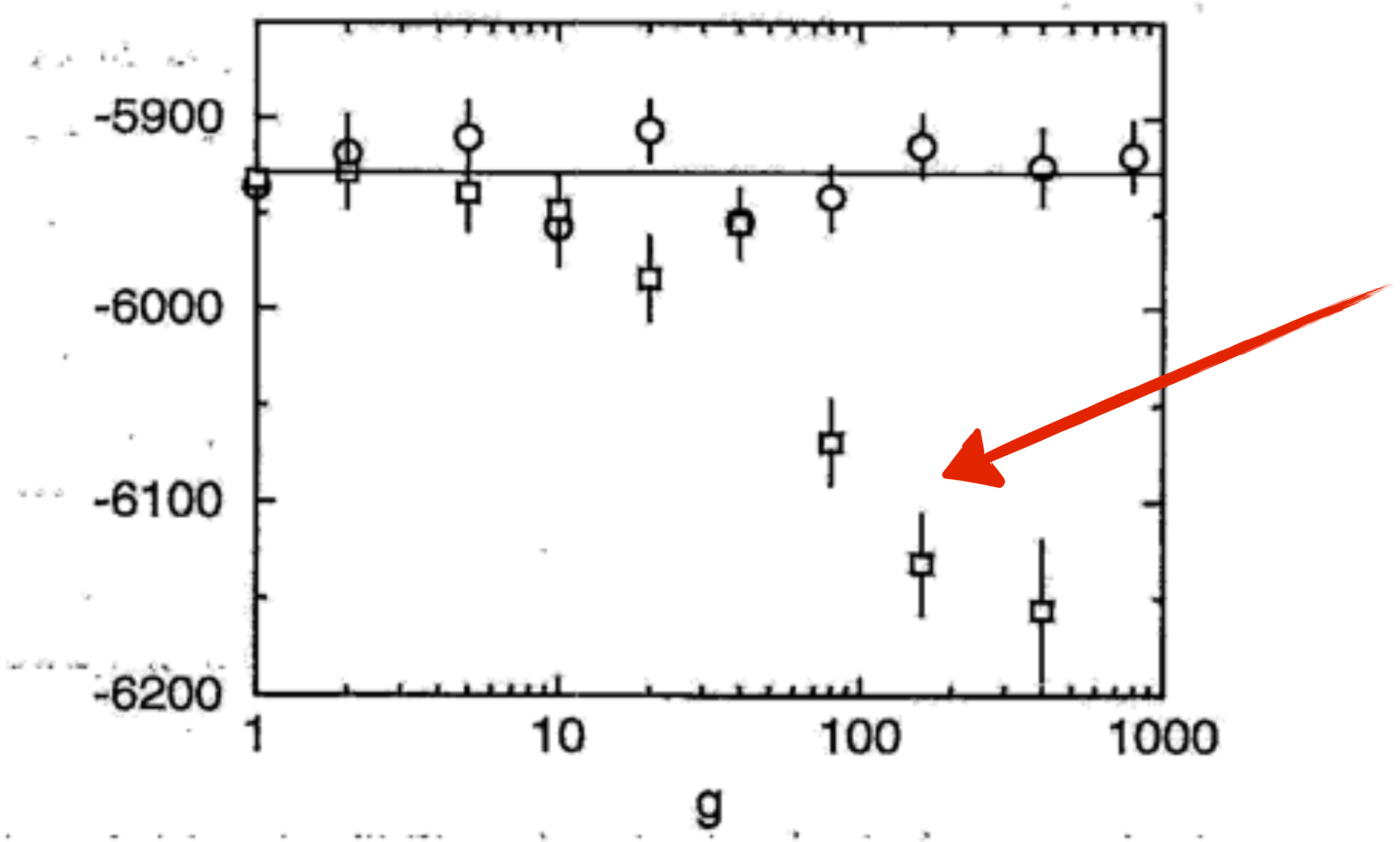
1. Generate k trial configurations in parallel
2. Select out of these the one with the lowest energy

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

3. Accept and reject using normal Monte Carlo rule:

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

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

$$\begin{tikzcd}
o \arrow[r, bend left, "K(o\to n)"] & n \arrow[l, bend left, "K(n\to o)"]
\end{tikzcd}$$

Condition of detailed balance:

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

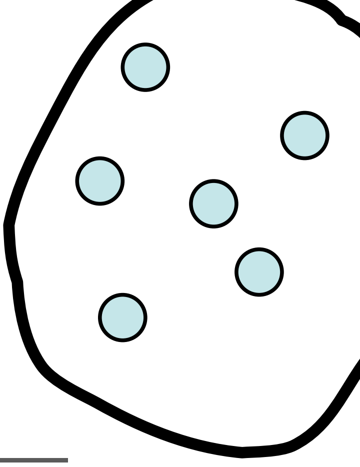
$$K(o \to n) = N(o) \times \alpha(o \to n) \times \mathrm{acc}(o \to n)$$

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

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

?

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



A priori probability to generate configuration n:

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

Rosenbluth factor configuration n:

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

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

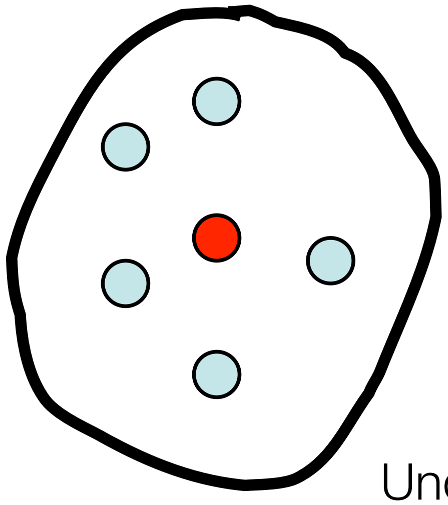
A priori probability to generate configuration o:

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

Rosenbluth factor configuration o:

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

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



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

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

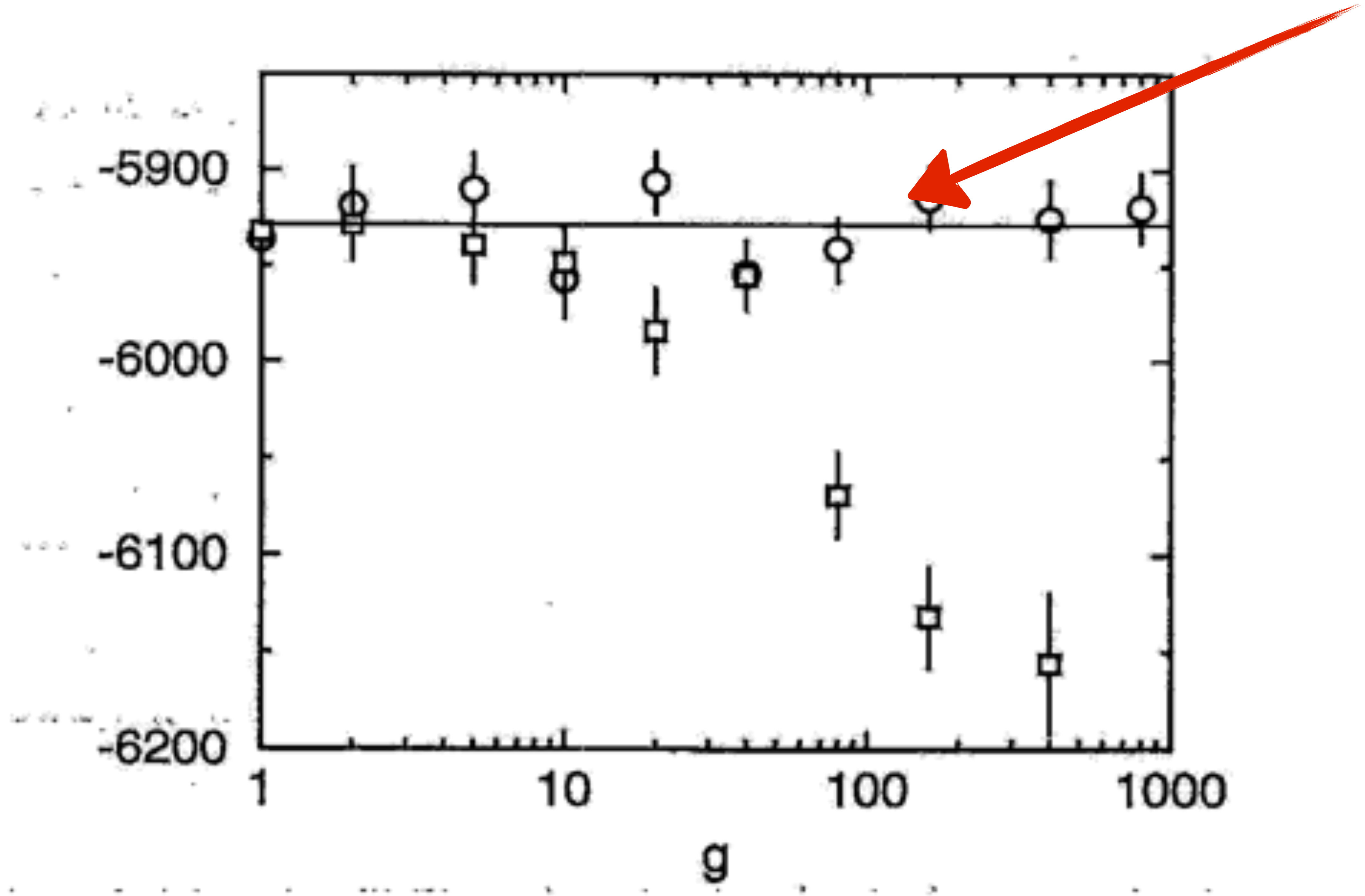
$$\alpha(o \to n) = \frac{e^{-\beta U(n)}}{W(n)}$$

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

This gives as acceptance rules:

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

Conventional acceptance rules



Modified acceptance rules remove the bias exactly