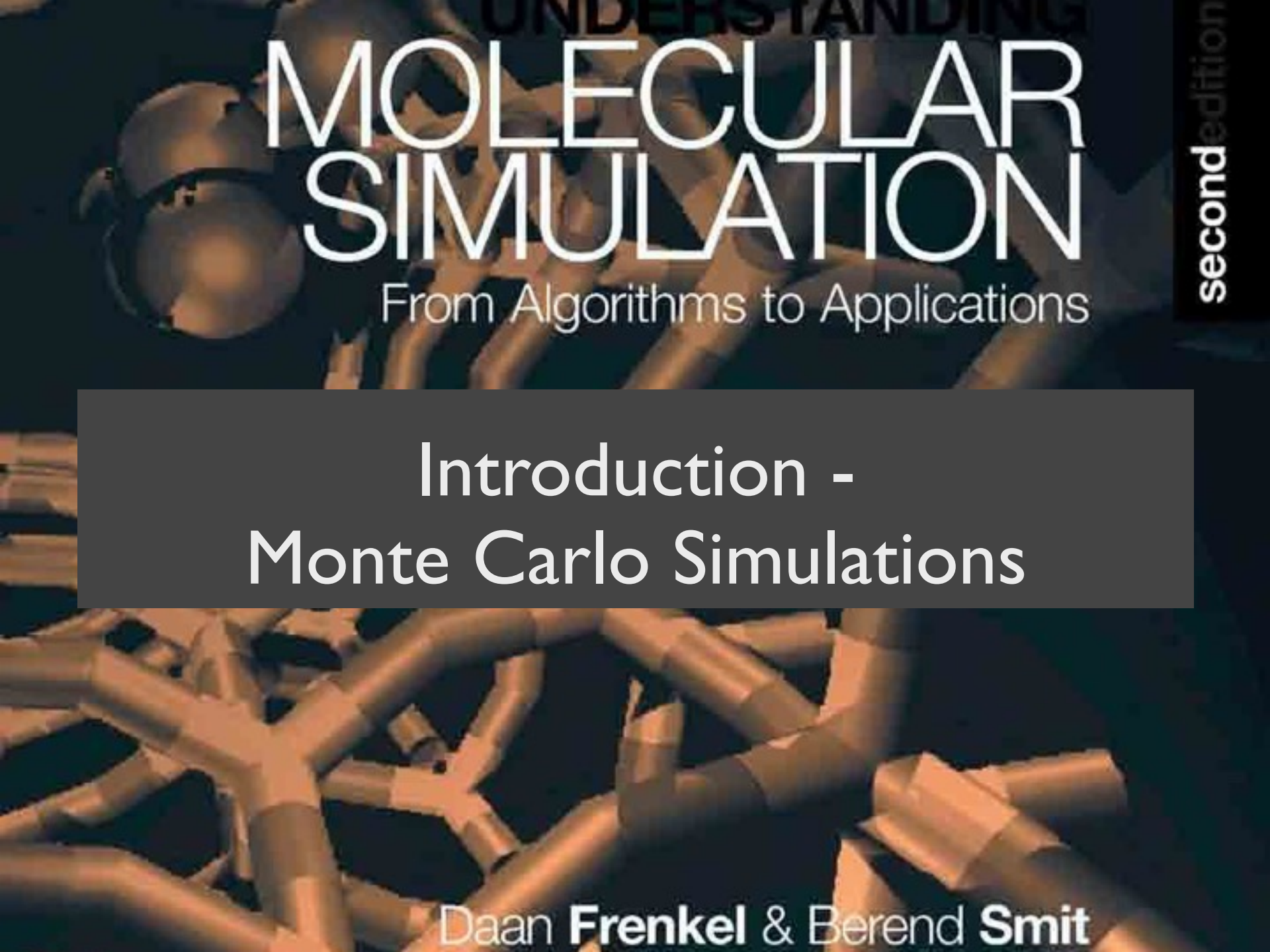
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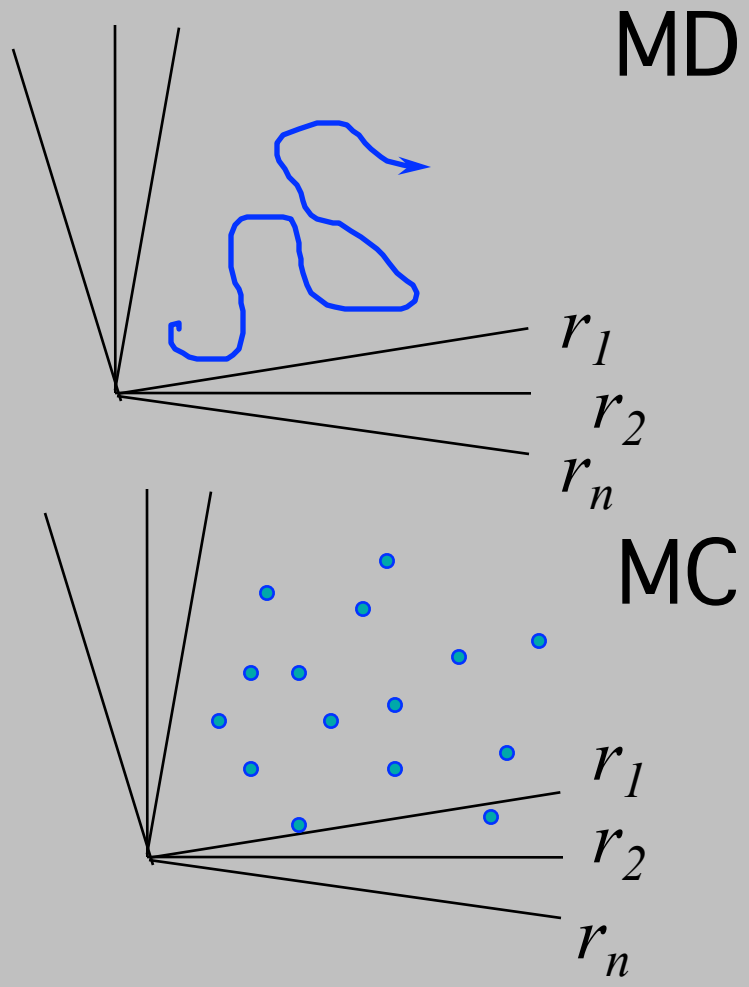
Introduction -
Monte Carlo Simulations
Daan Frenkel & Berend Smit

Molecular Simulations

- Molecular dynamics: solve equations of motion

- Monte Carlo: importance sampling



Molecular Simulations

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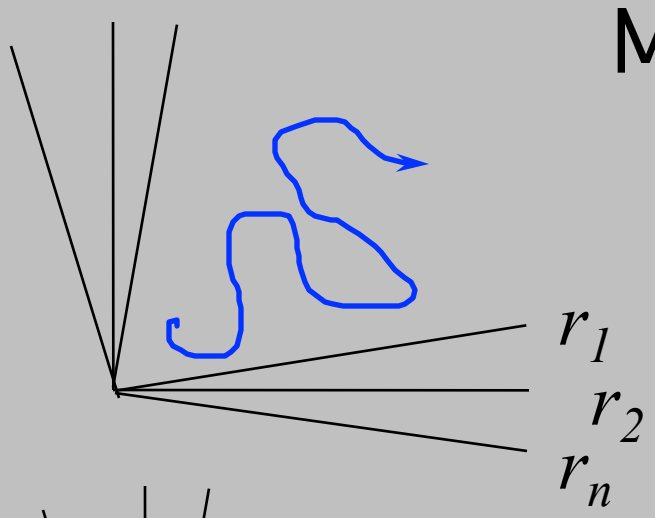

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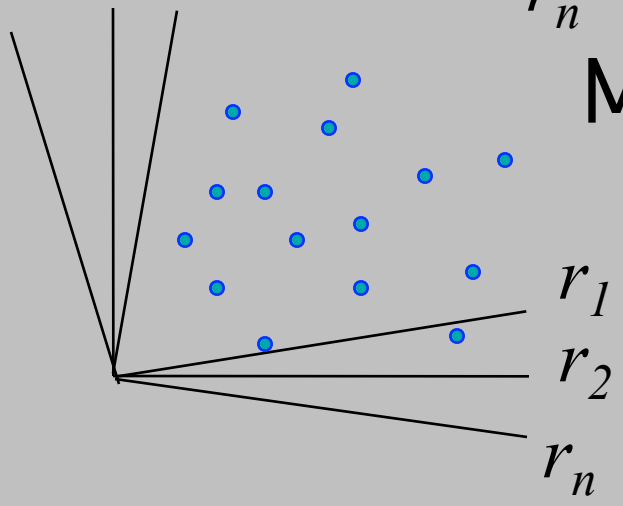

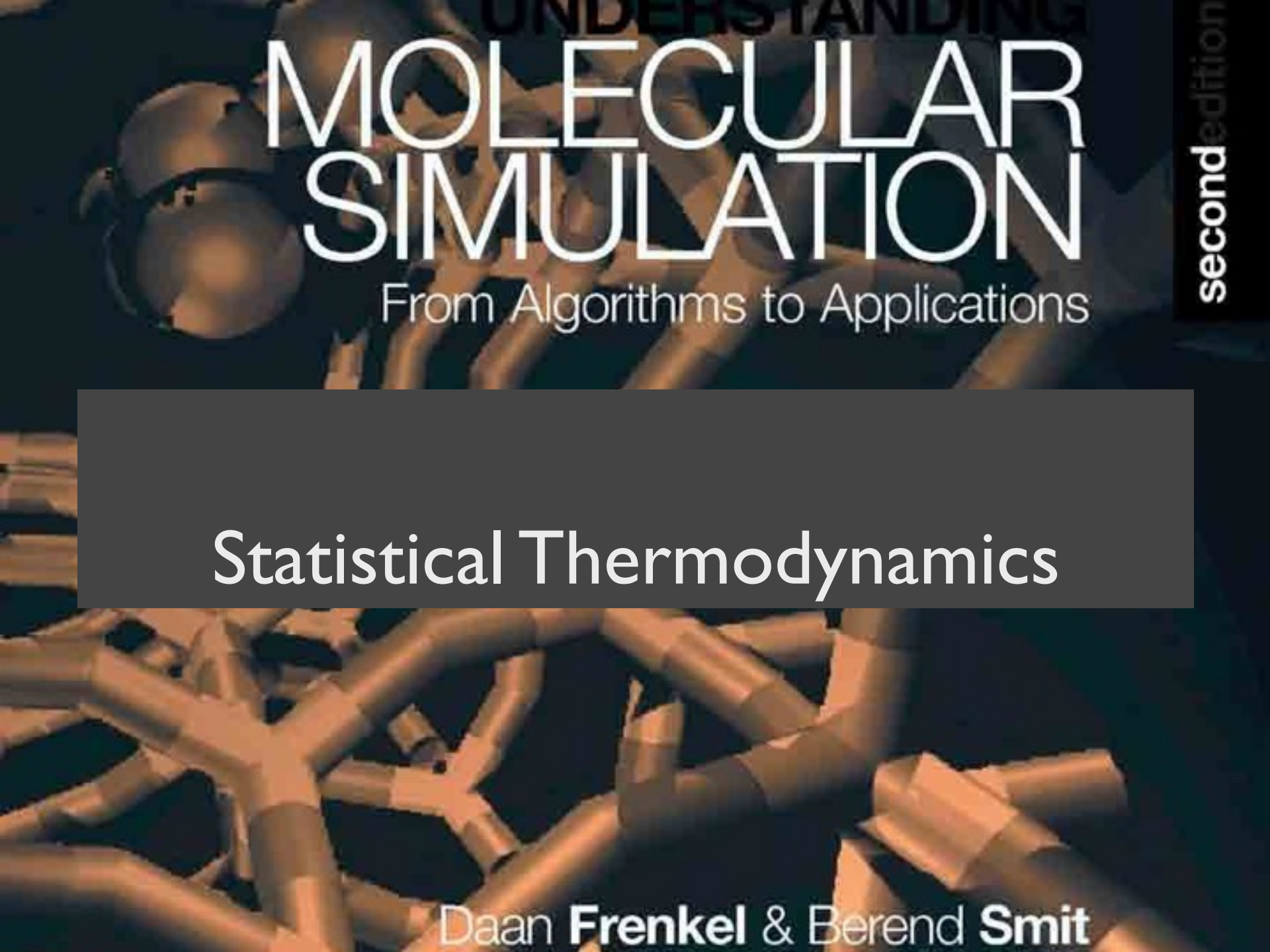
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Statistical Thermodynamics
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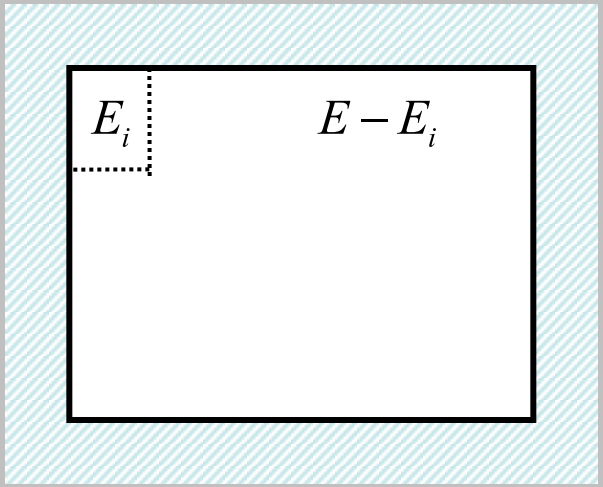
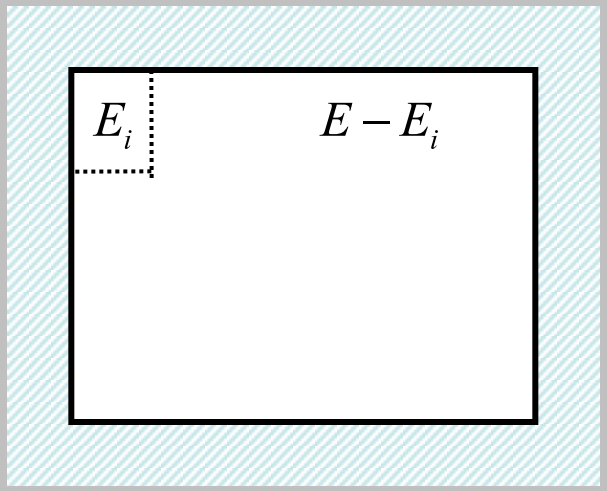
Canonical ensemble



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

Canonical ensemble



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

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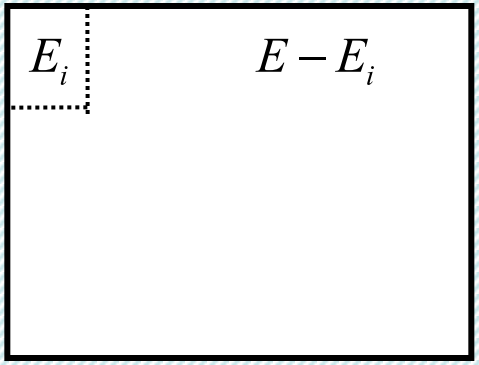

$1/k_B T$

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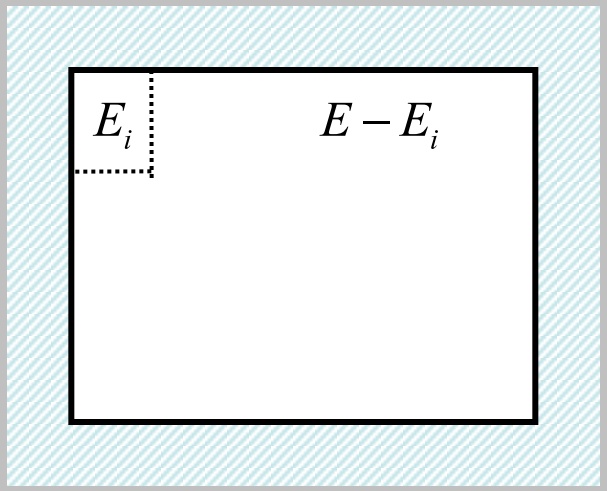

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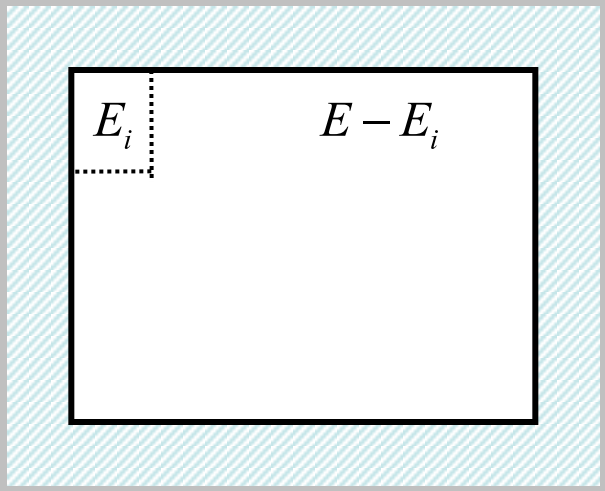

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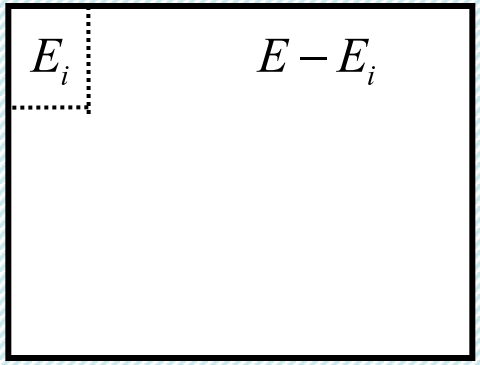

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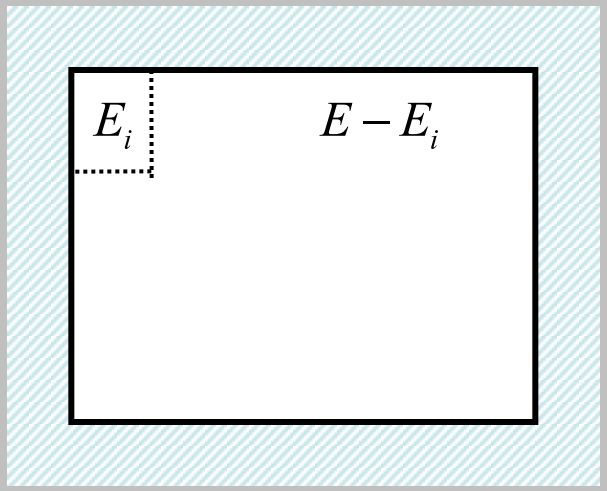

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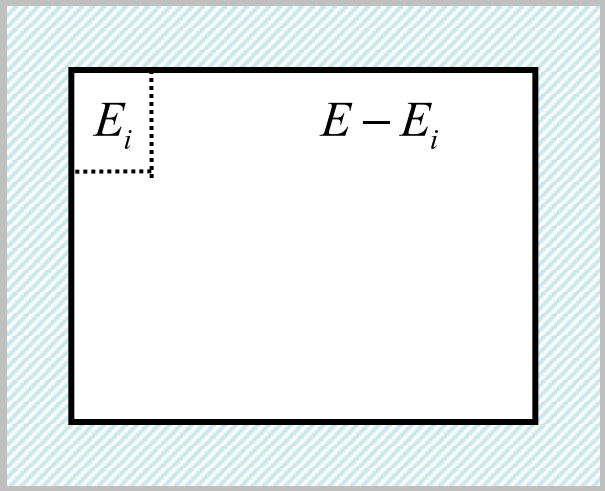

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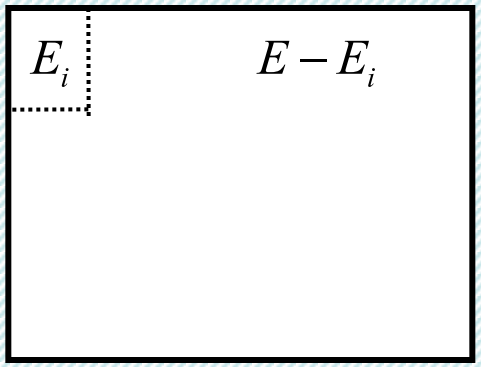

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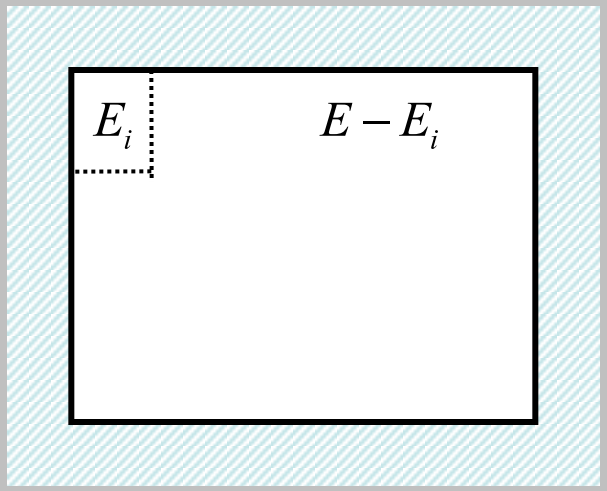
Boltzmann distribution

Canonical ensemble



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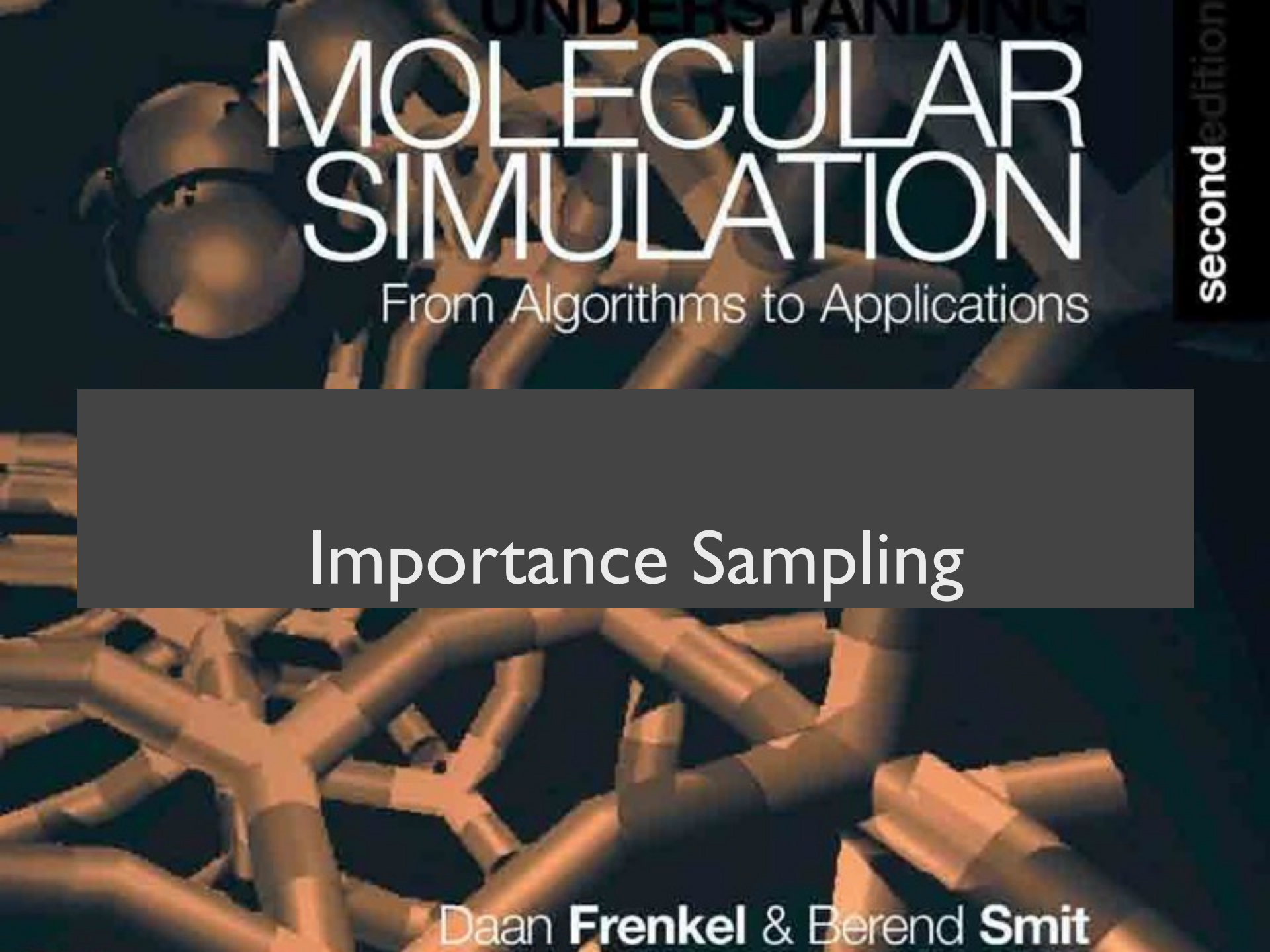
Free energy:

$$\beta F=-\ln Q_{N,V,T}$$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Importance Sampling
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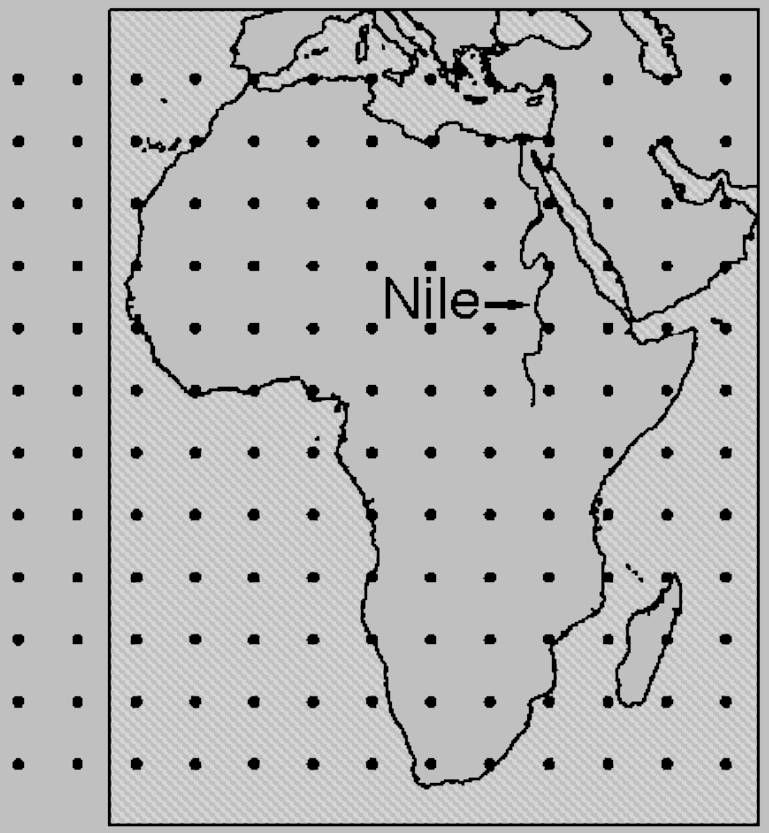
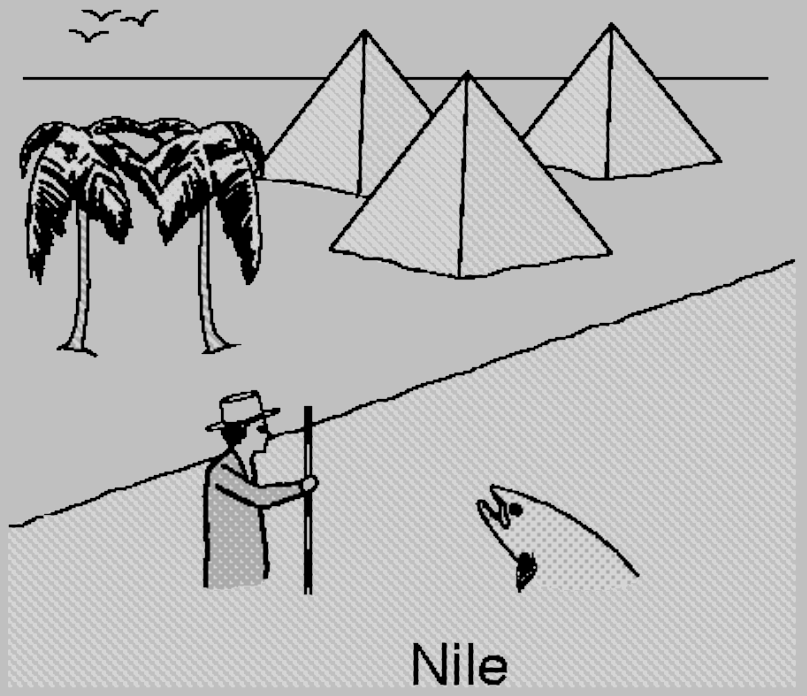
Numerical Integration





Ensemble Average

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Generate configurations using Monte Carlo moves

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Generate configurations using Monte Carlo moves

$$\left\{\mathrm{r}_1^N, \mathrm{r}_2^N, \mathrm{r}_3^N, \mathrm{r}_4^N \cdots, \mathrm{r}_M^N\right\} \qquad \bar{A} = \frac{1}{M} \sum_{i=1}^{M} A(\mathrm{r}_i^N) = \frac{\int \mathrm{d}\mathrm{r}^N A(\mathrm{r}^N) P^{MC}(\mathrm{r}^N)}{\int \mathrm{d}\mathrm{r}^N P^{MC}(\mathrm{r}^N)}$$

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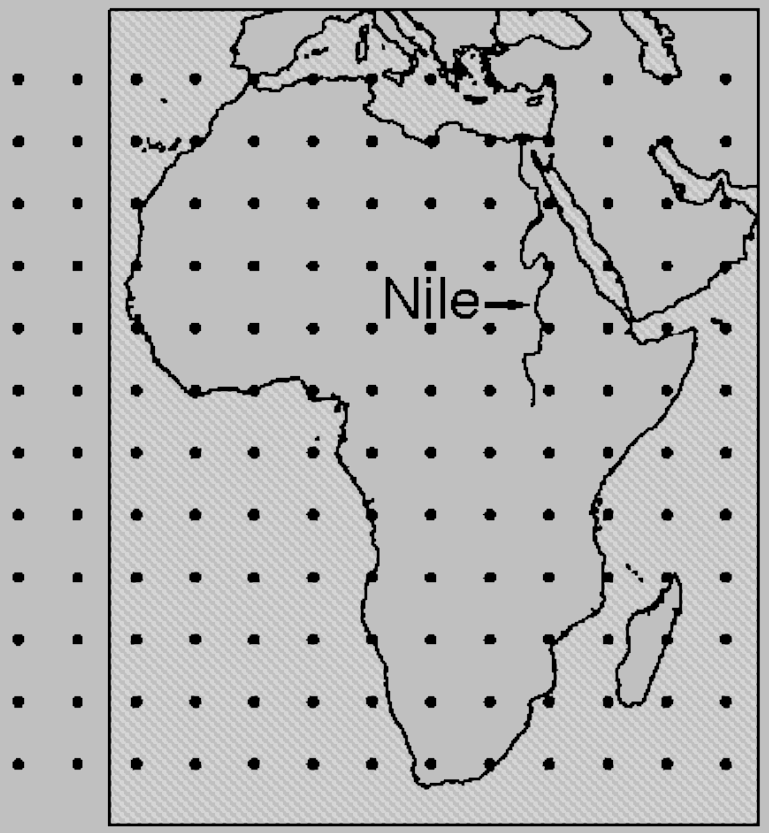
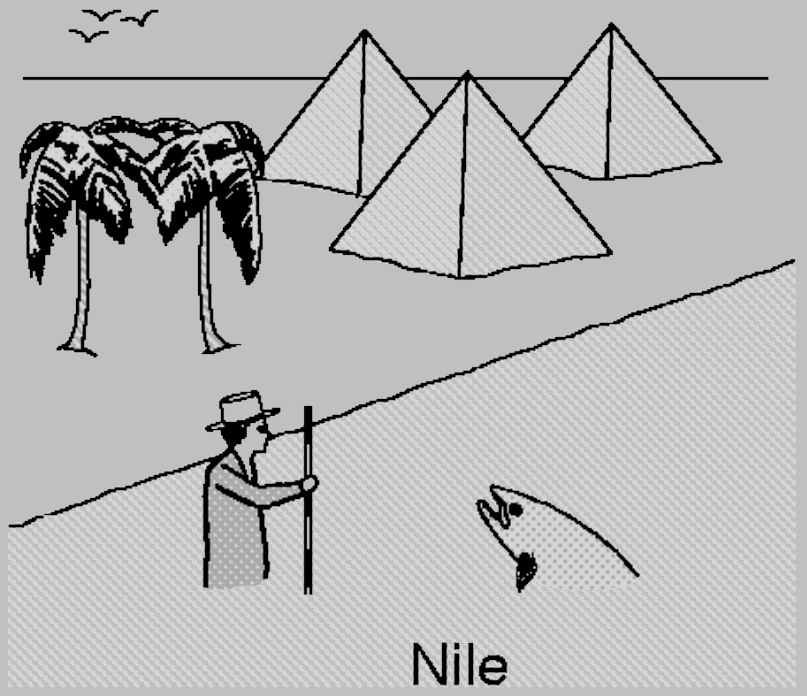
Importance Sampling





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* `nsampth` *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 (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* $[0, 1]$.

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Desired distribution: NVT ensemble

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Markov Processes

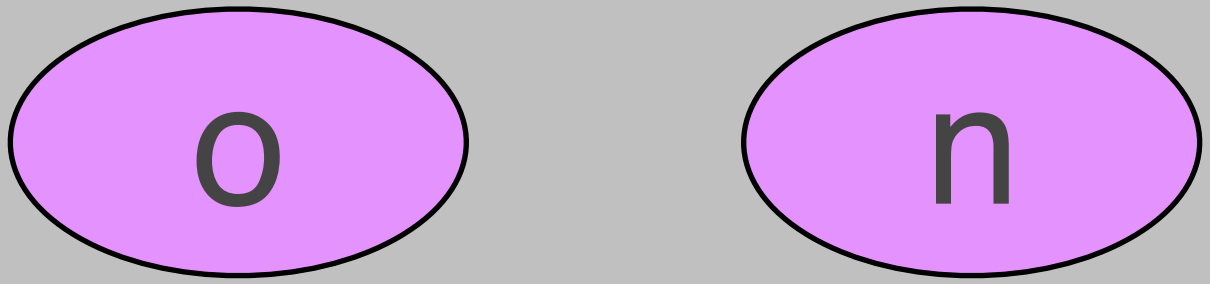
Markov Process

- 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

Ensemble - 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



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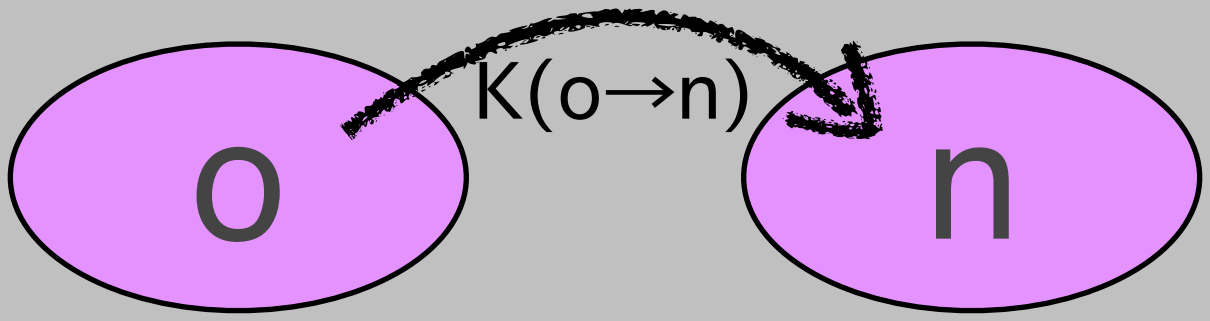

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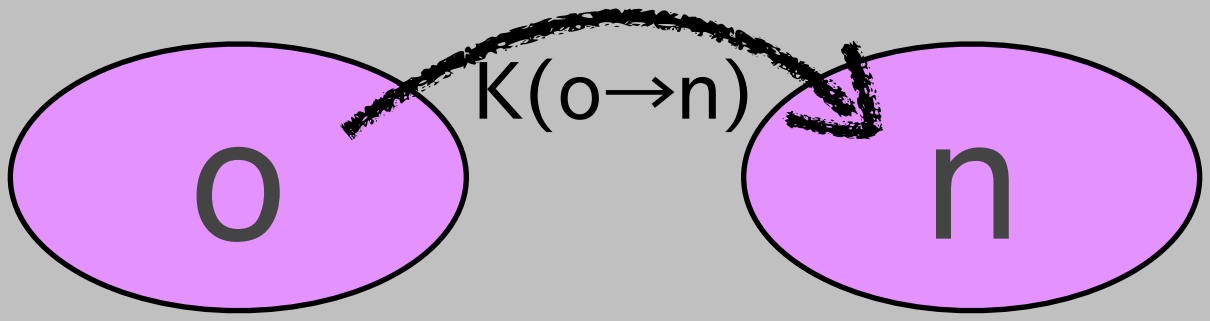
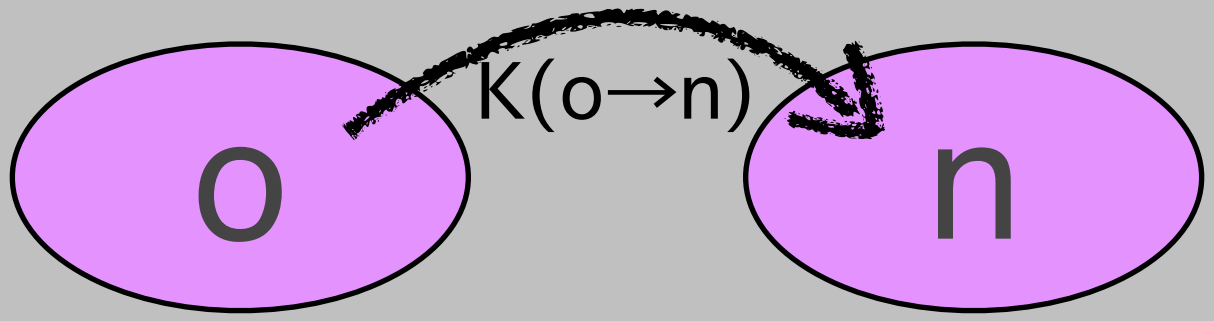


K(o → n): total number of systems in our ensemble that move *o* → *n*

Markov Processes - Detailed Balance



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

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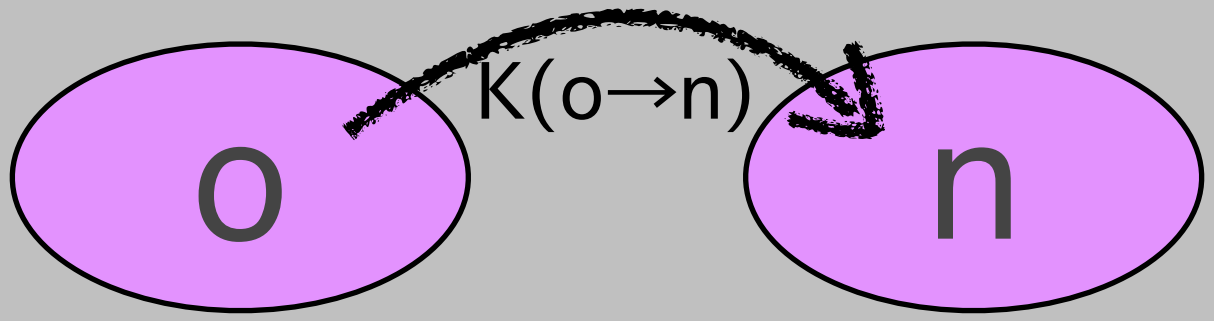

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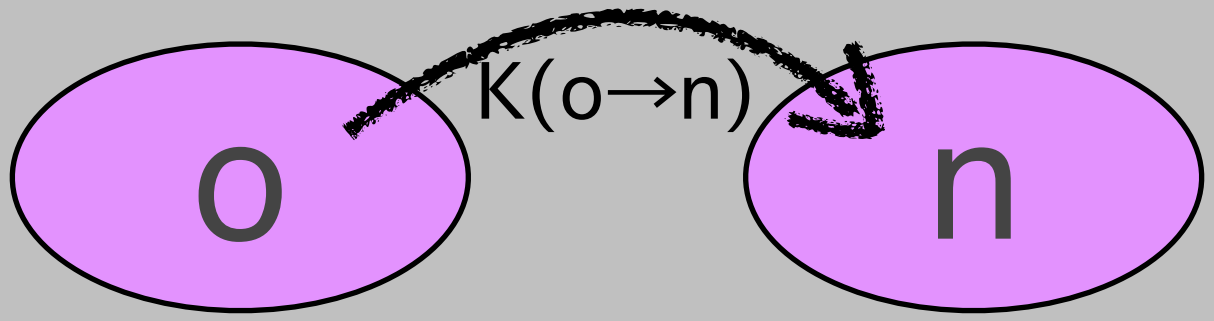

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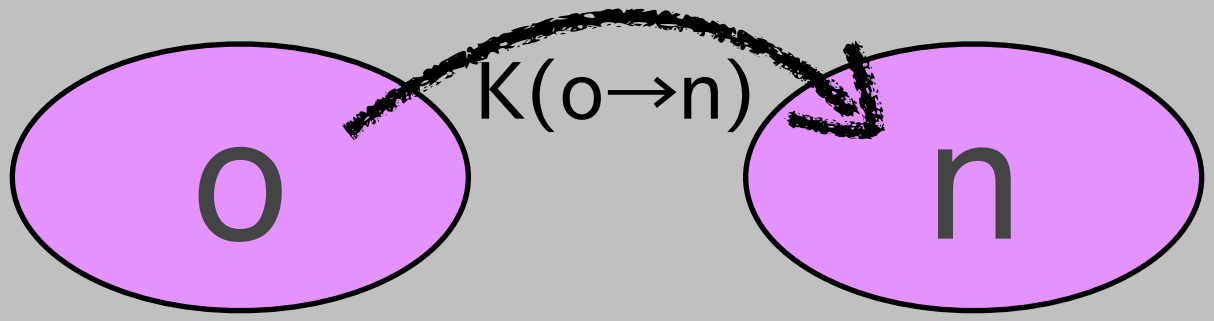

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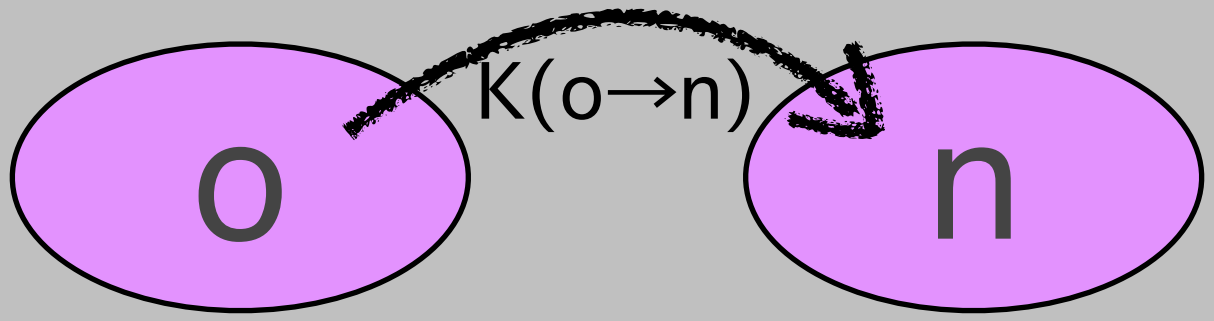

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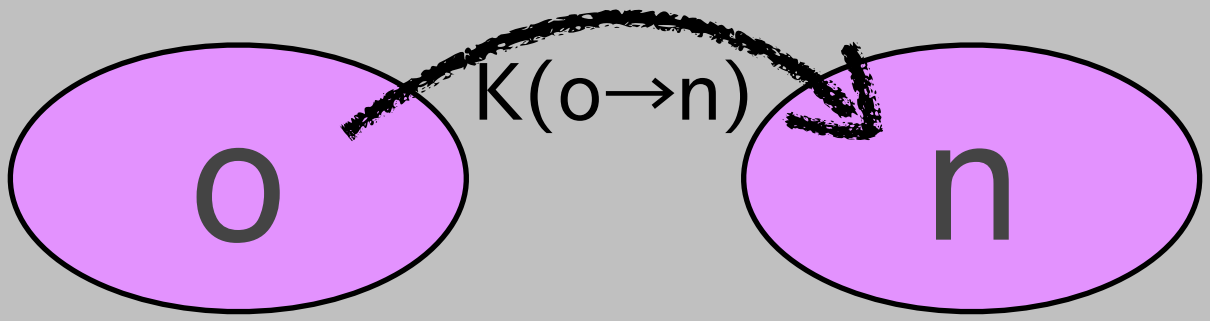

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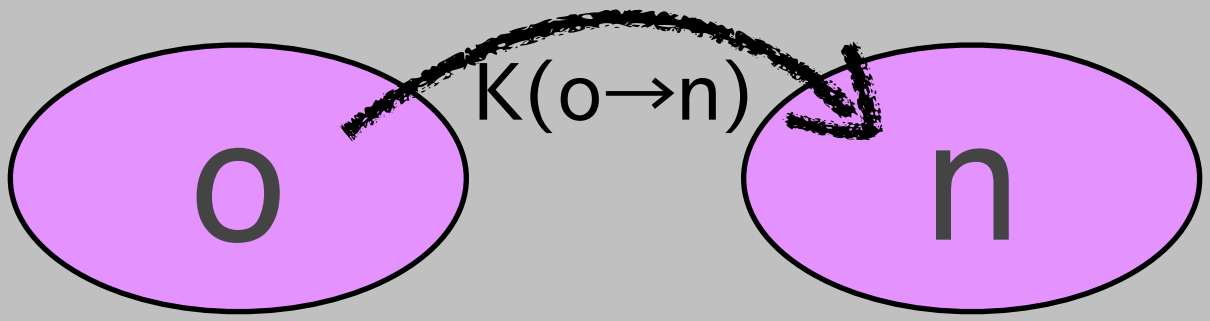
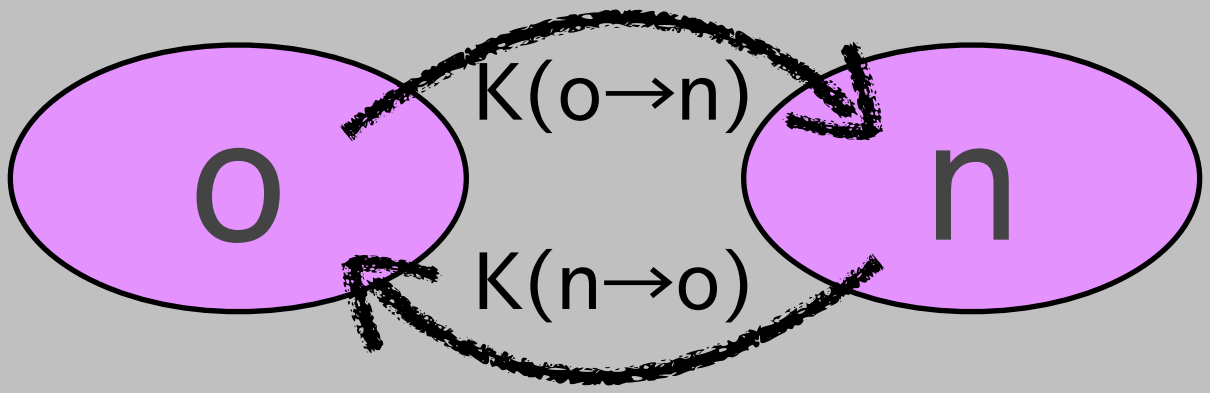


Condition of detailed balance:

Markov Processes - Detailed Balance



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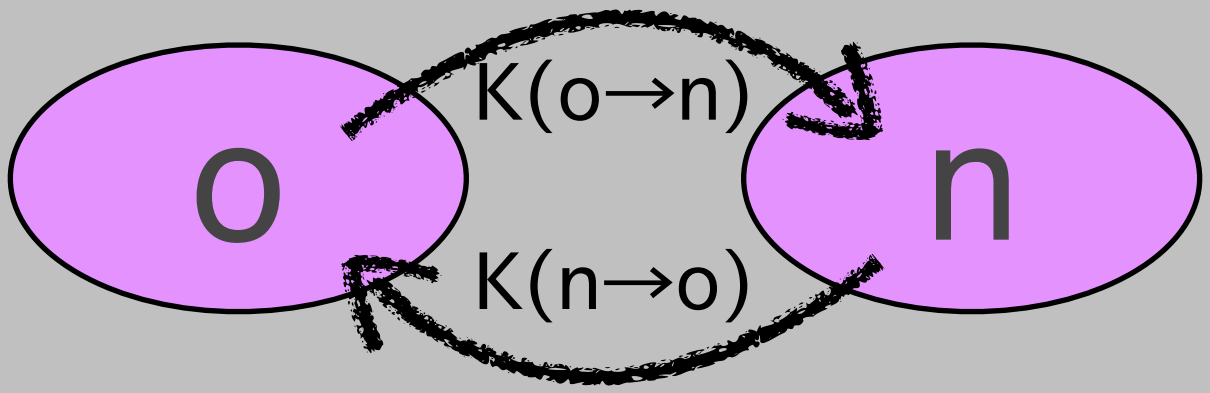

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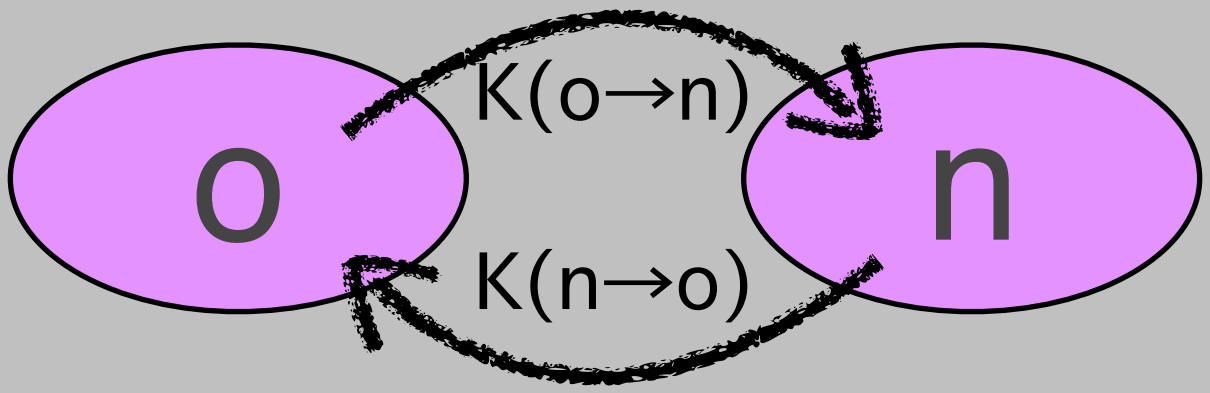

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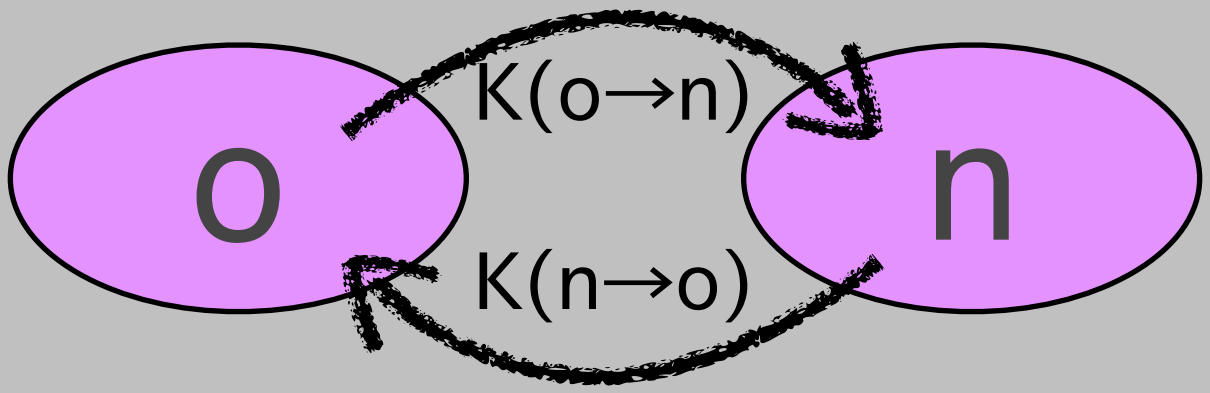

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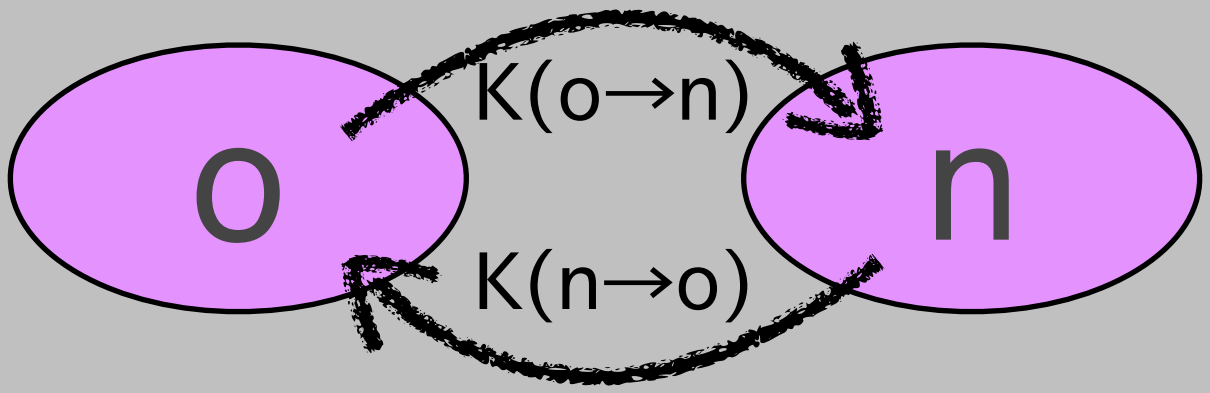

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Which gives as condition for the acceptance rule:

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Metropolis et al.

Many acceptance rules that satisfy:

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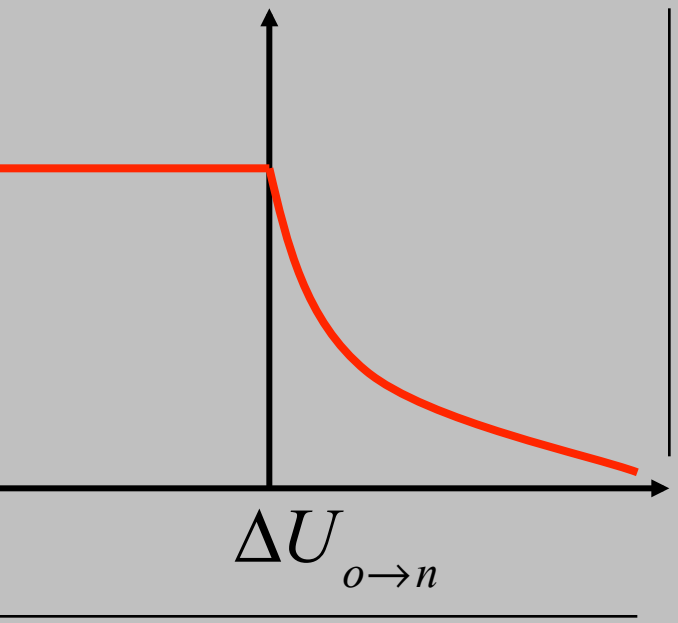

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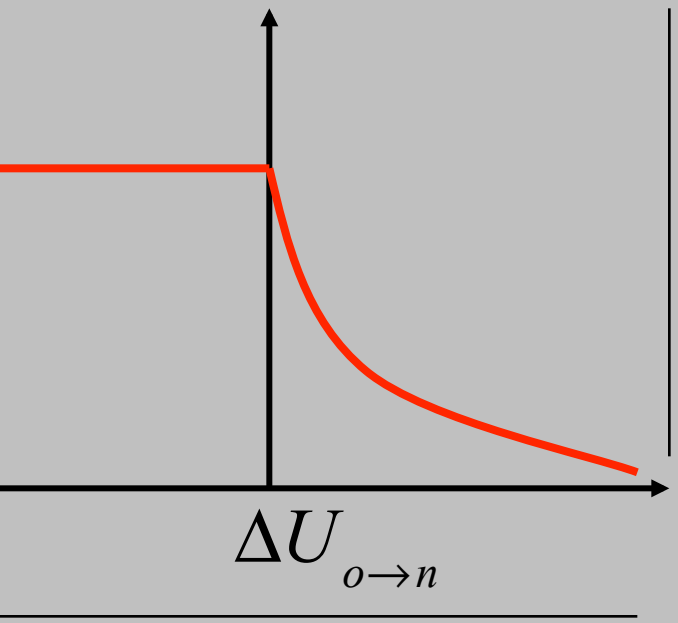

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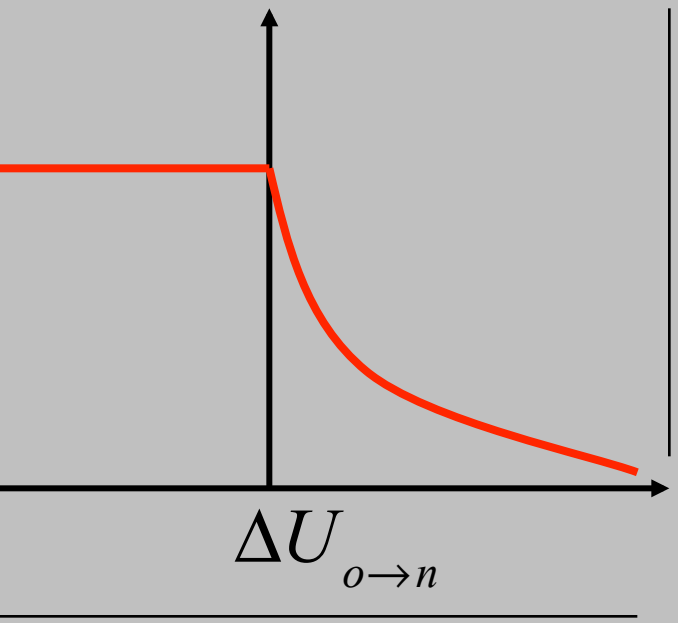

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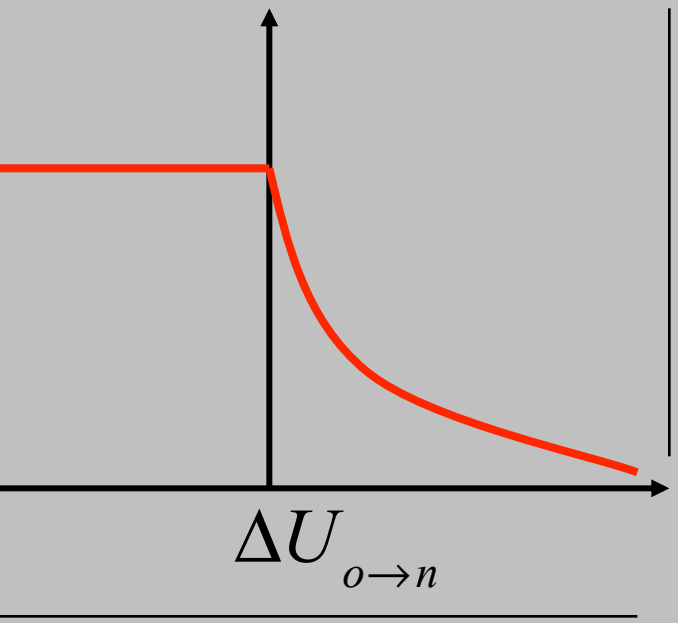

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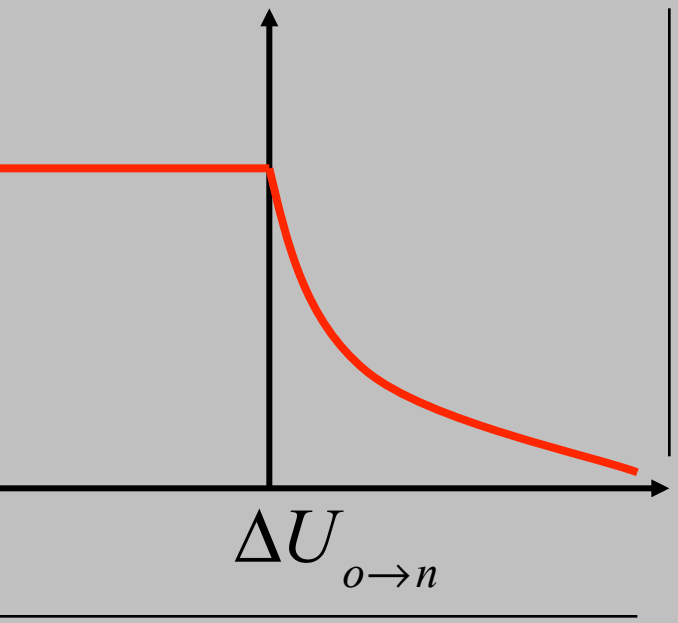

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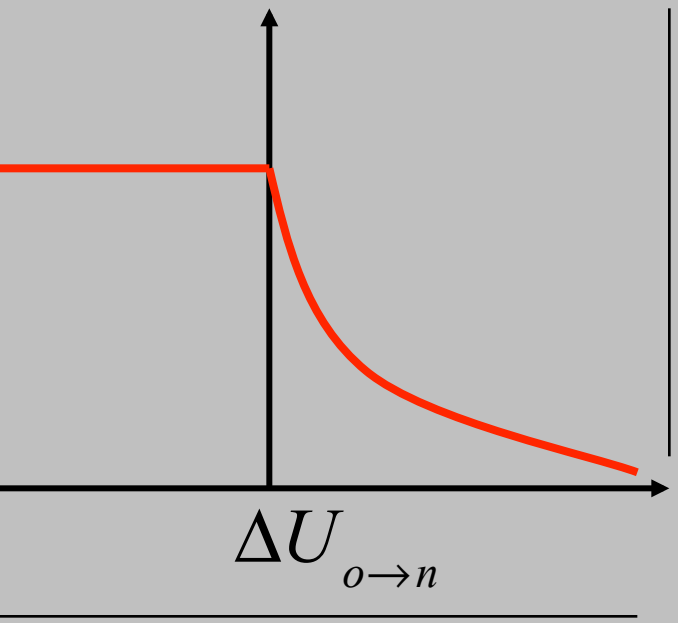

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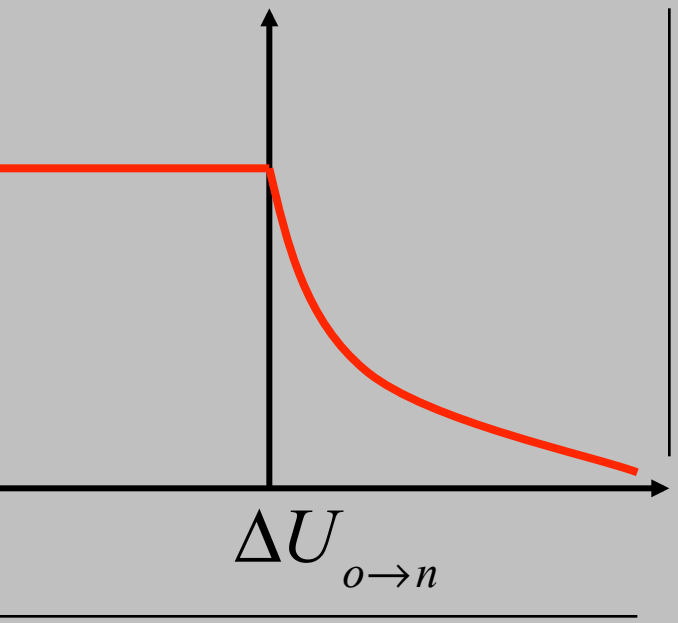

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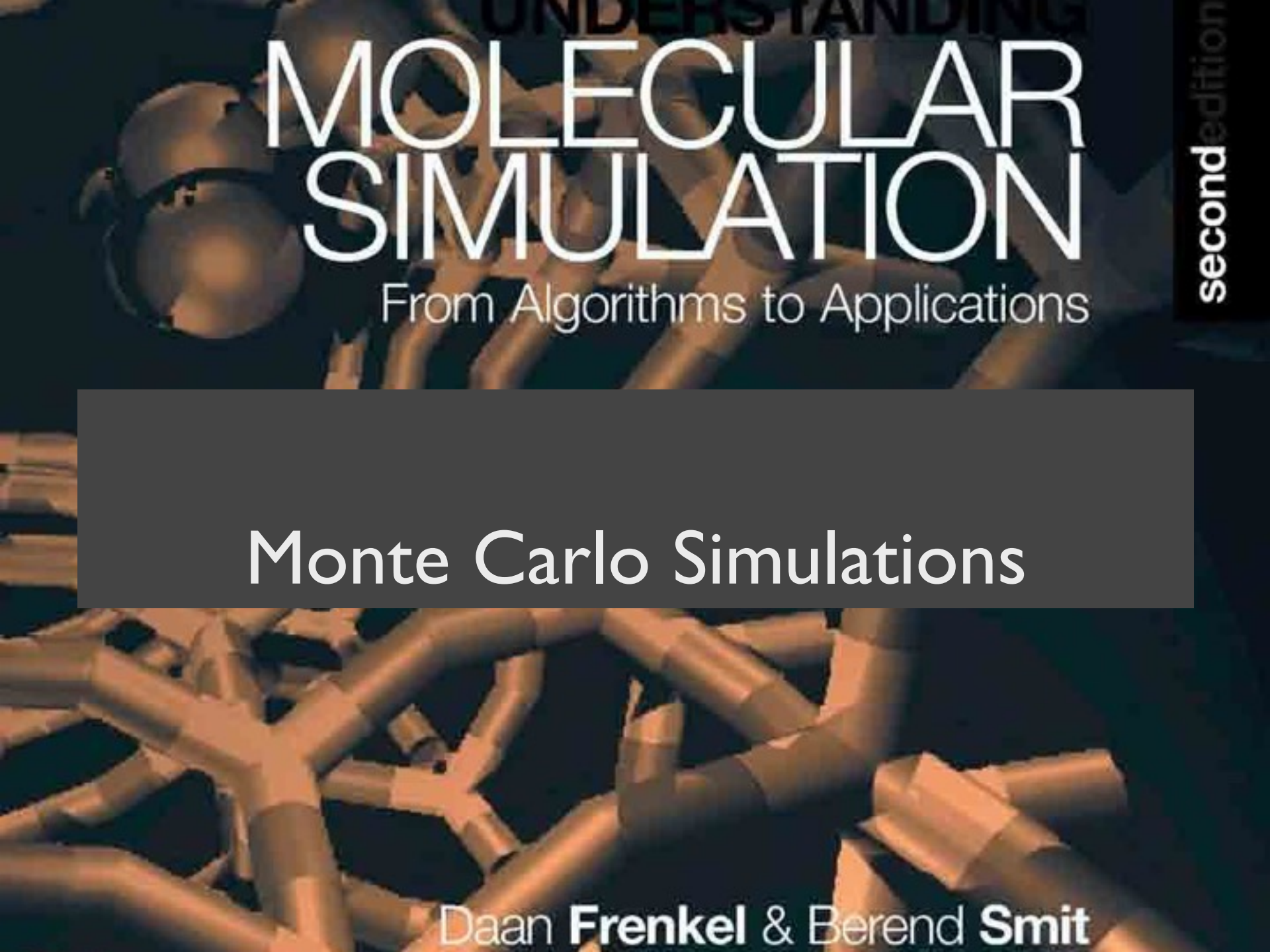
UNDERSTANDING
MOLECULAR
SIMULATION
From Algorithms to Applications
second edition
Monte Carlo Simulations
Daan Frenkel & Berend Smit

Questions

- How can we prove that this scheme generates the desired distribution of configurations?
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- How large should we take: `delx`?

Algorithm 2 (Attempt to Displace a Particle)

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SUBROUTINE mcmove                    attempts to displace a particle

o=int(ranf()*npart)+1                select a particle at random
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+    *(enn-eno)) x(o)=xn             accepted: replace x(o) by xn
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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.*
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Detailed Balance

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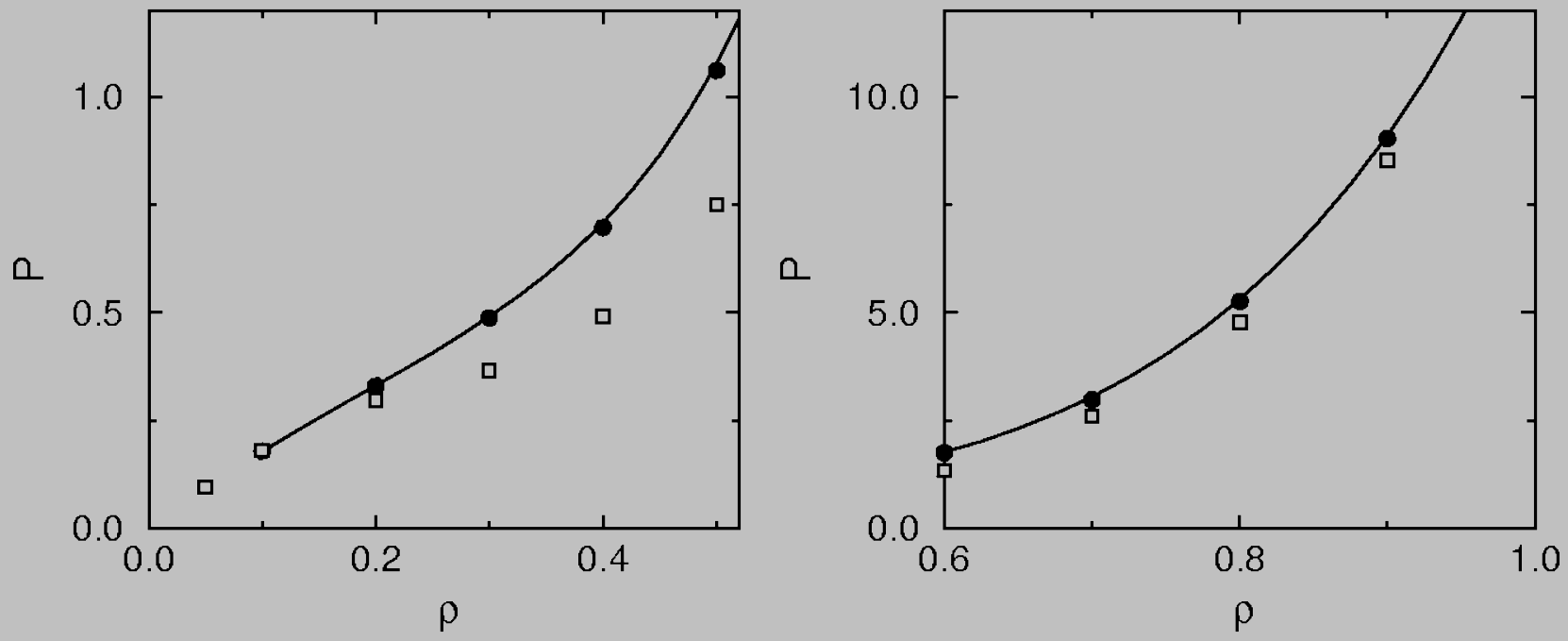
If we do not keep the old configuration:

Independent of the temperature

Lennard Jones fluid



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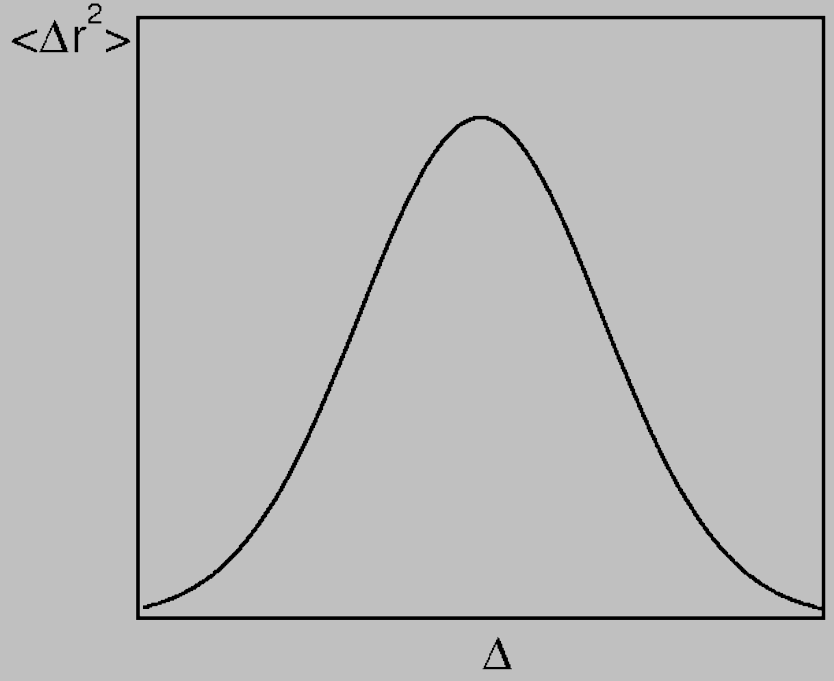
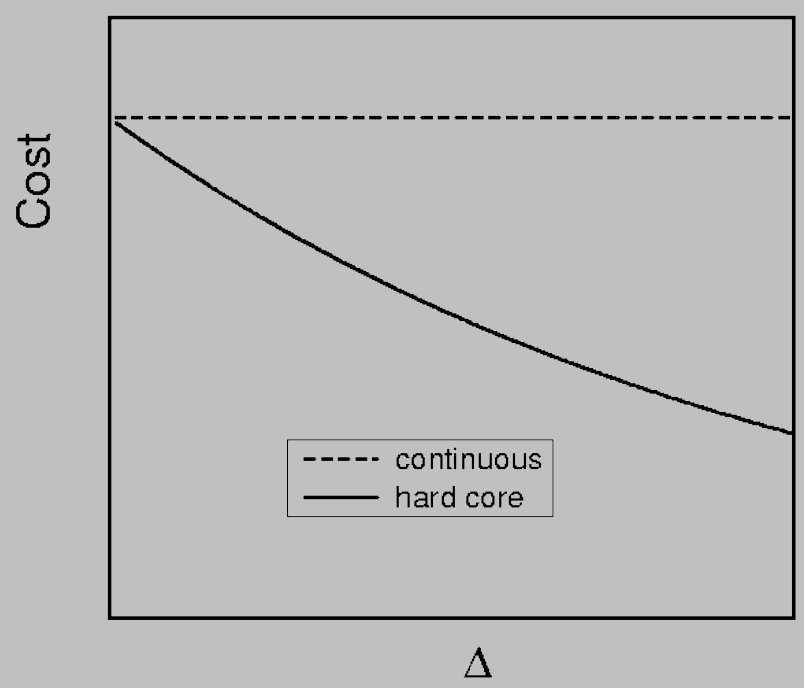
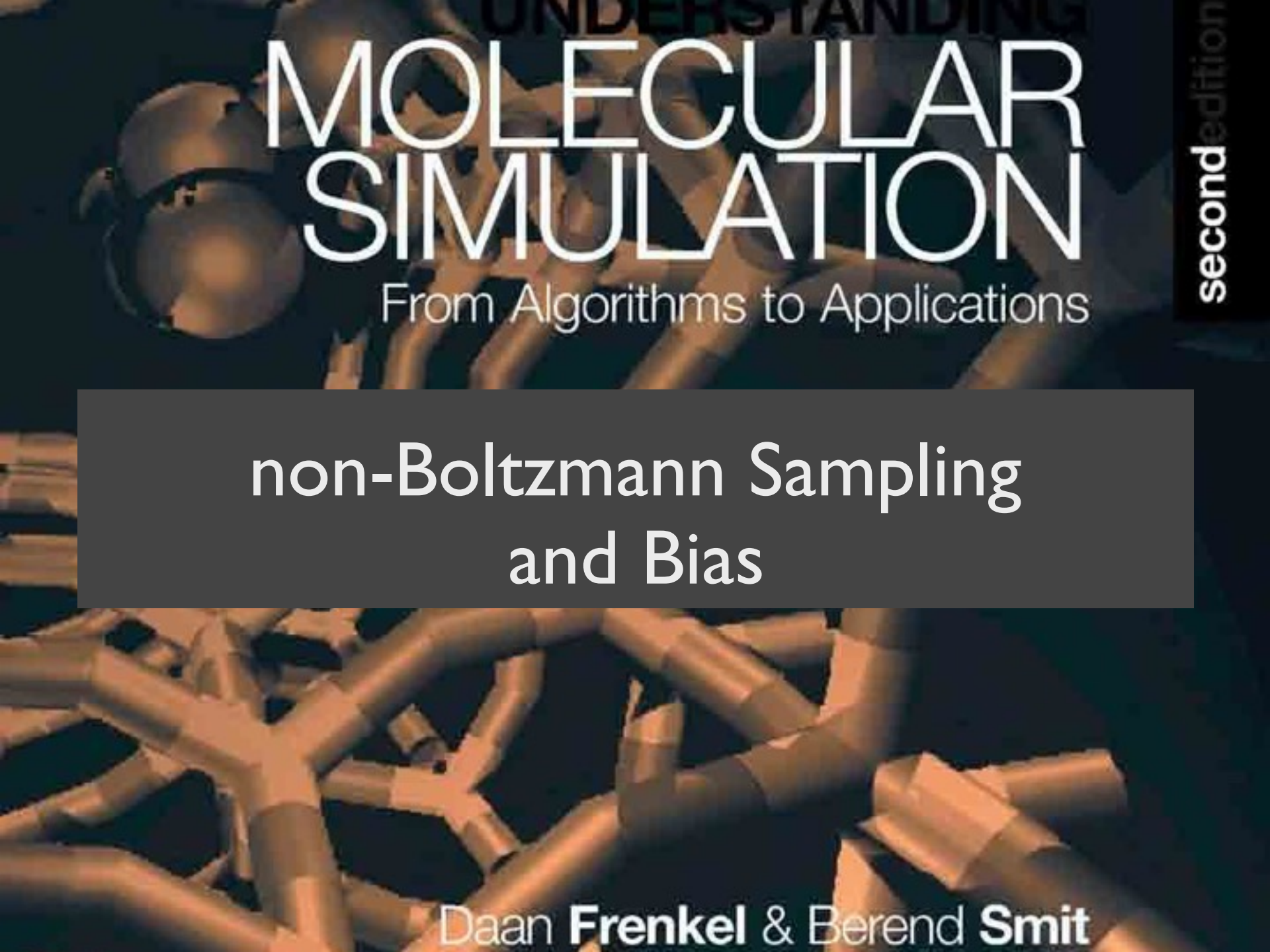
Not too big Not too small







non-Boltzmann Sampling and Bias

Non-Boltzmann sampling

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

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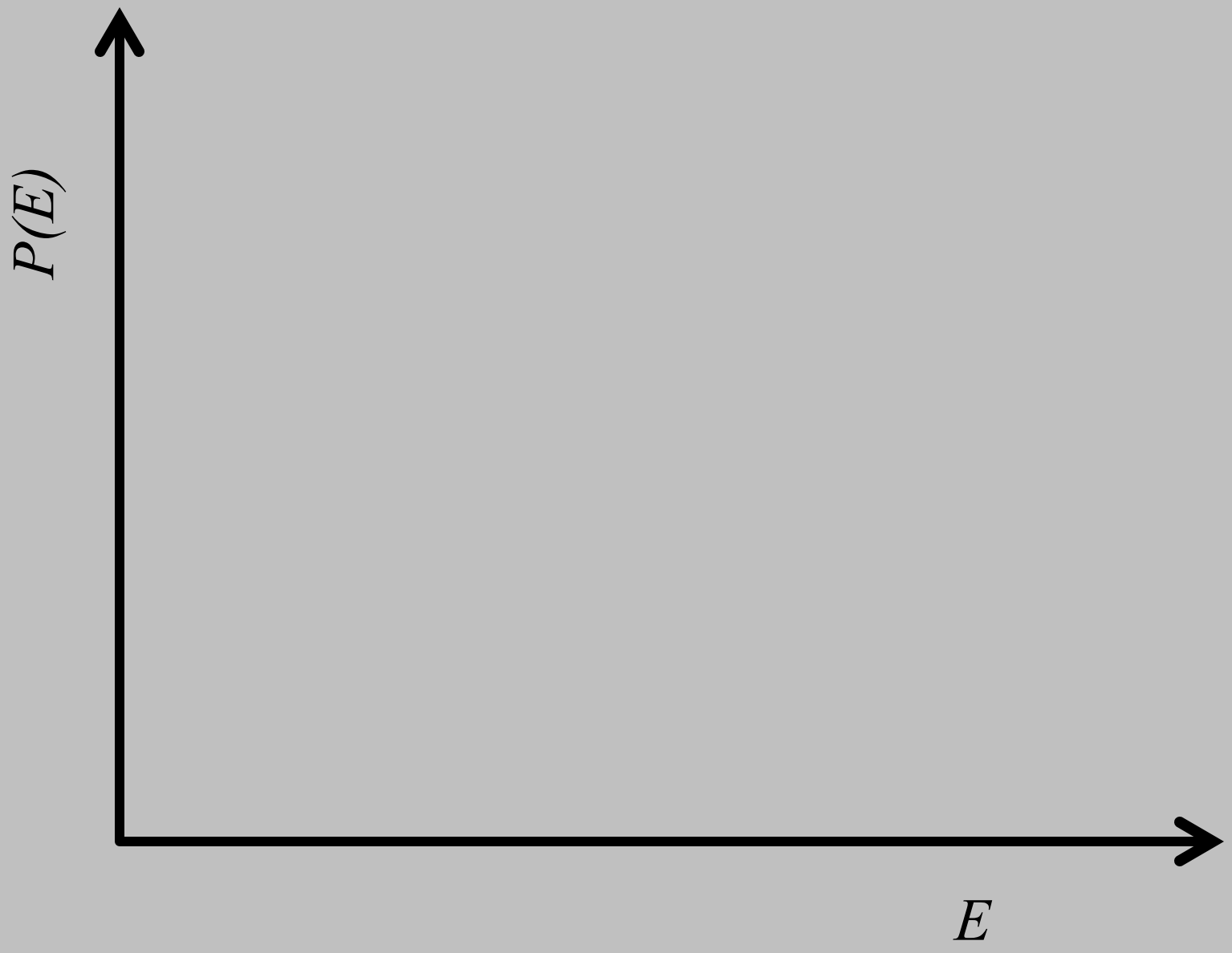
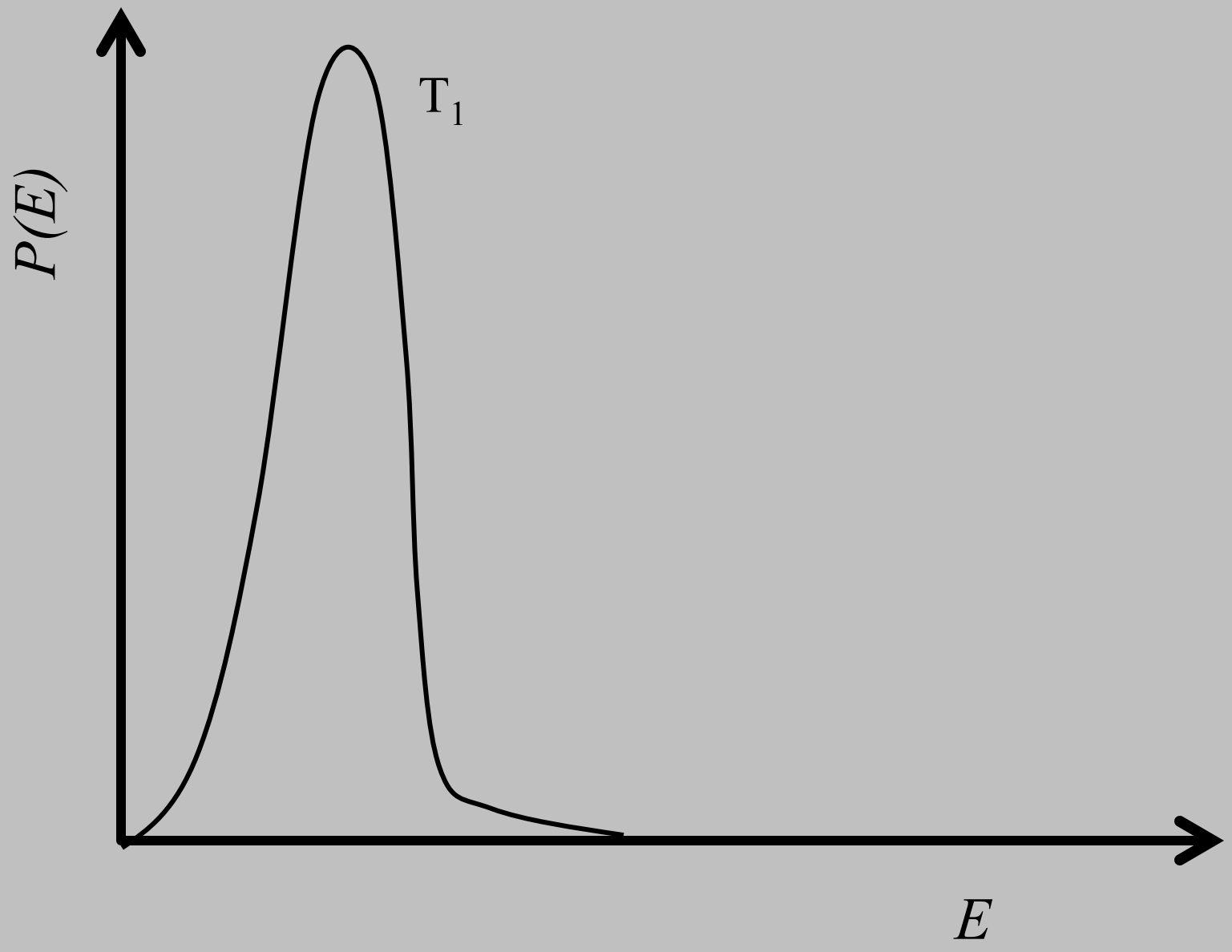
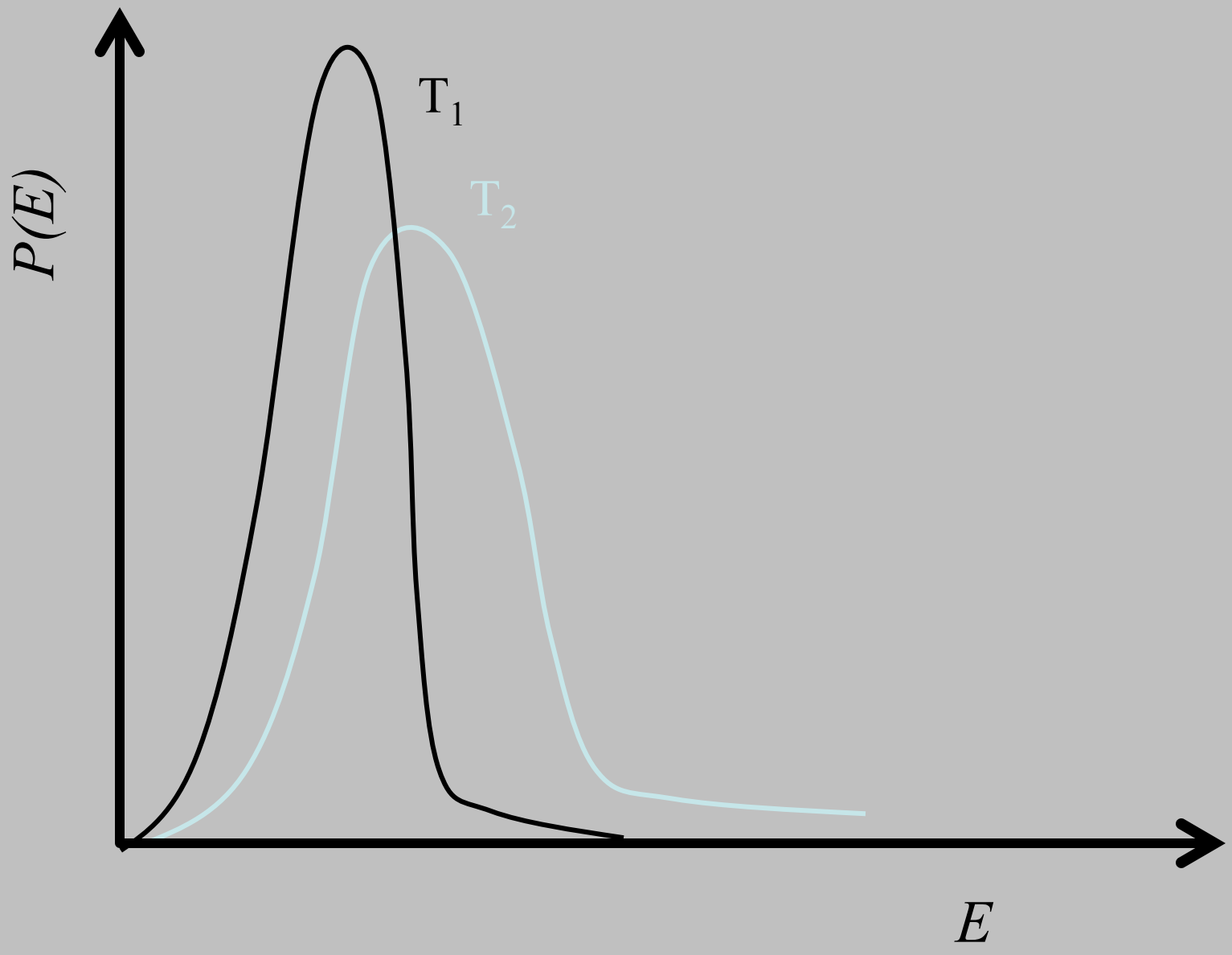
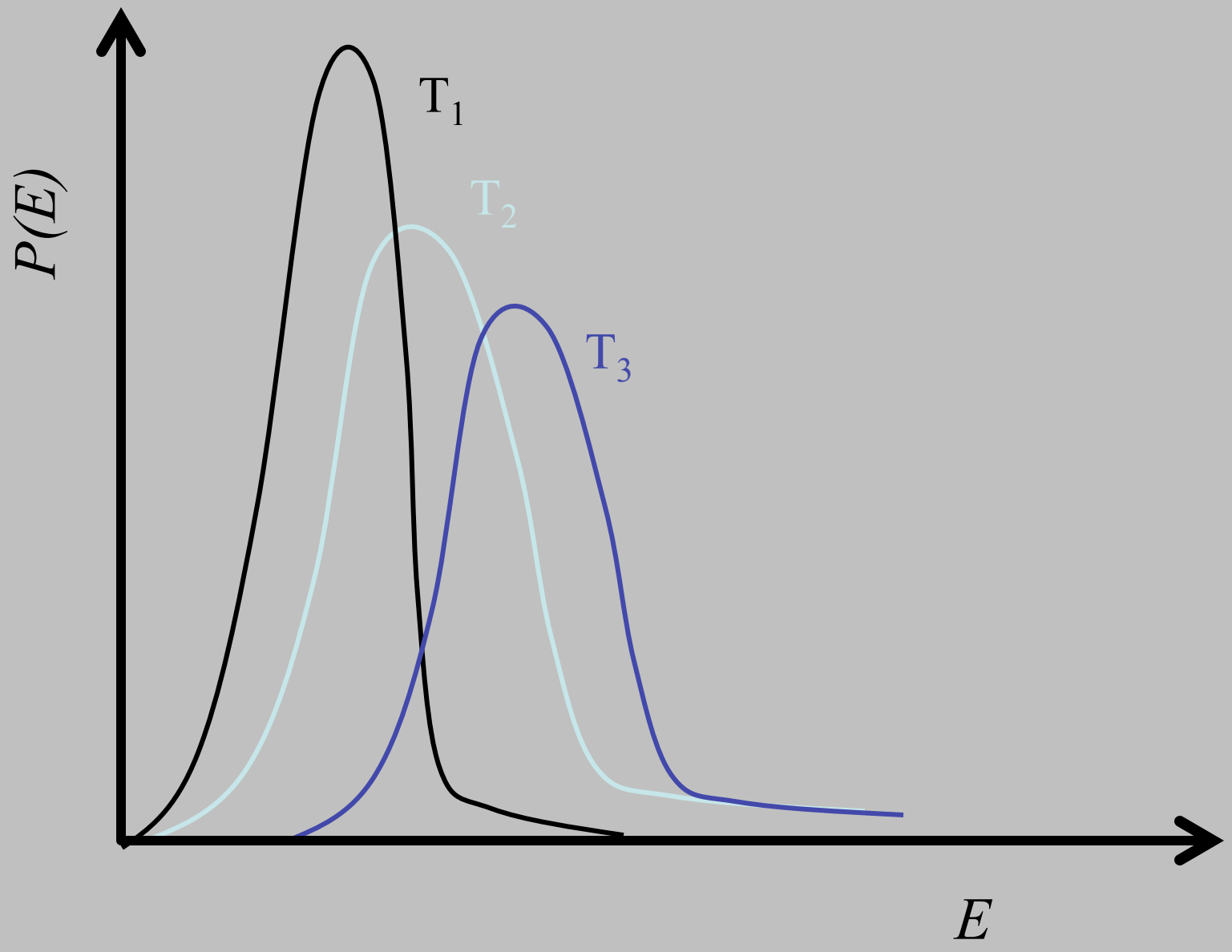
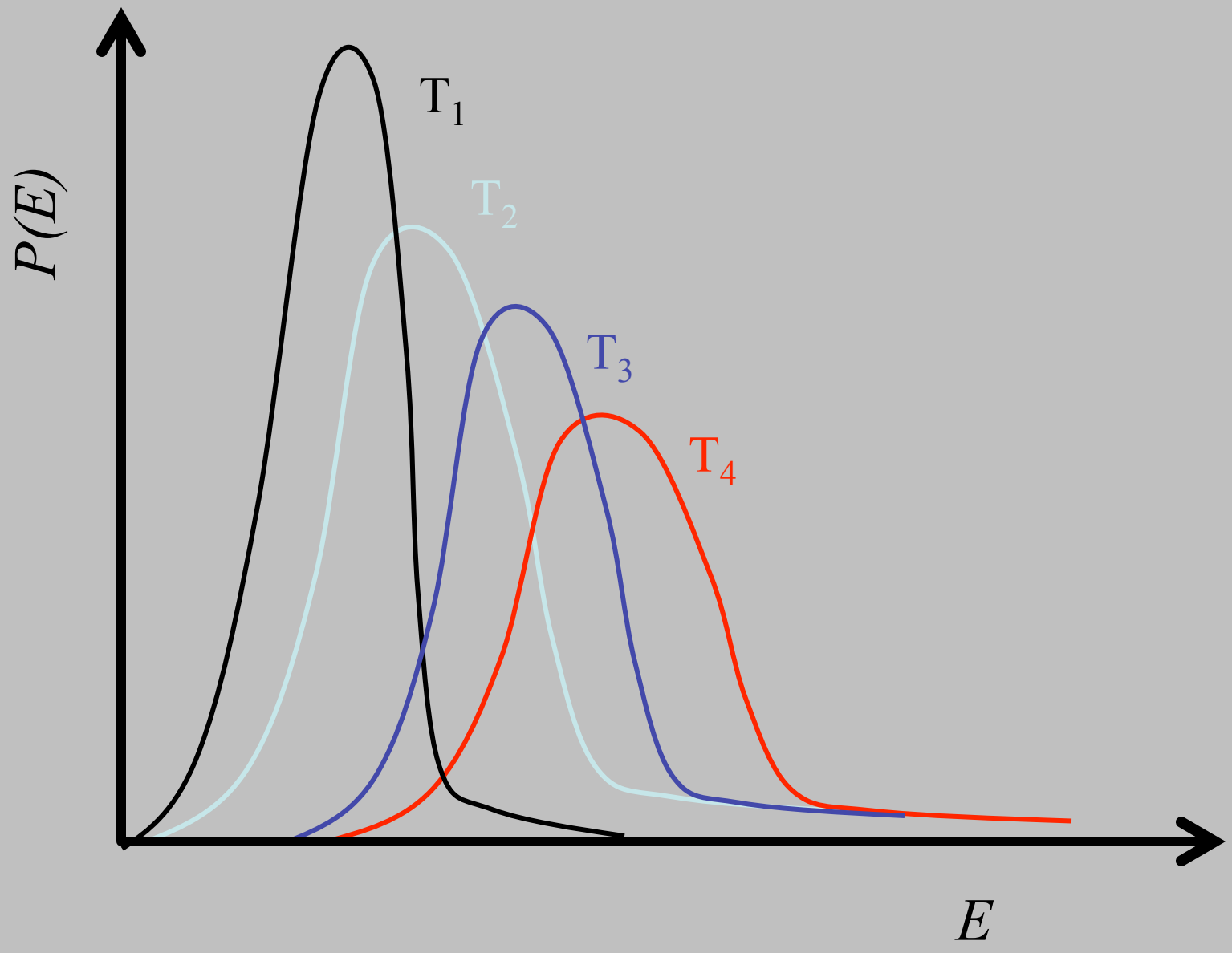
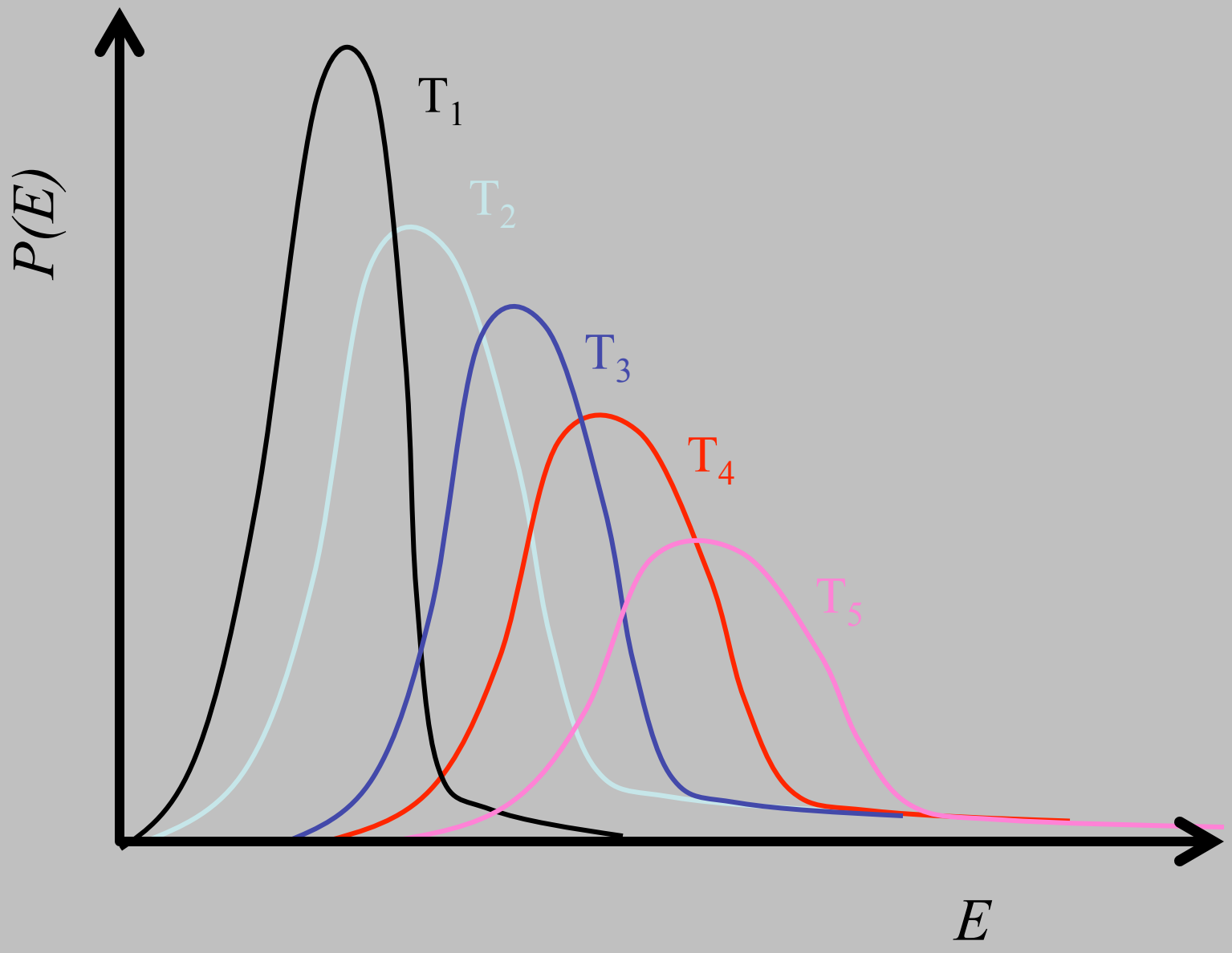

P(E)
E

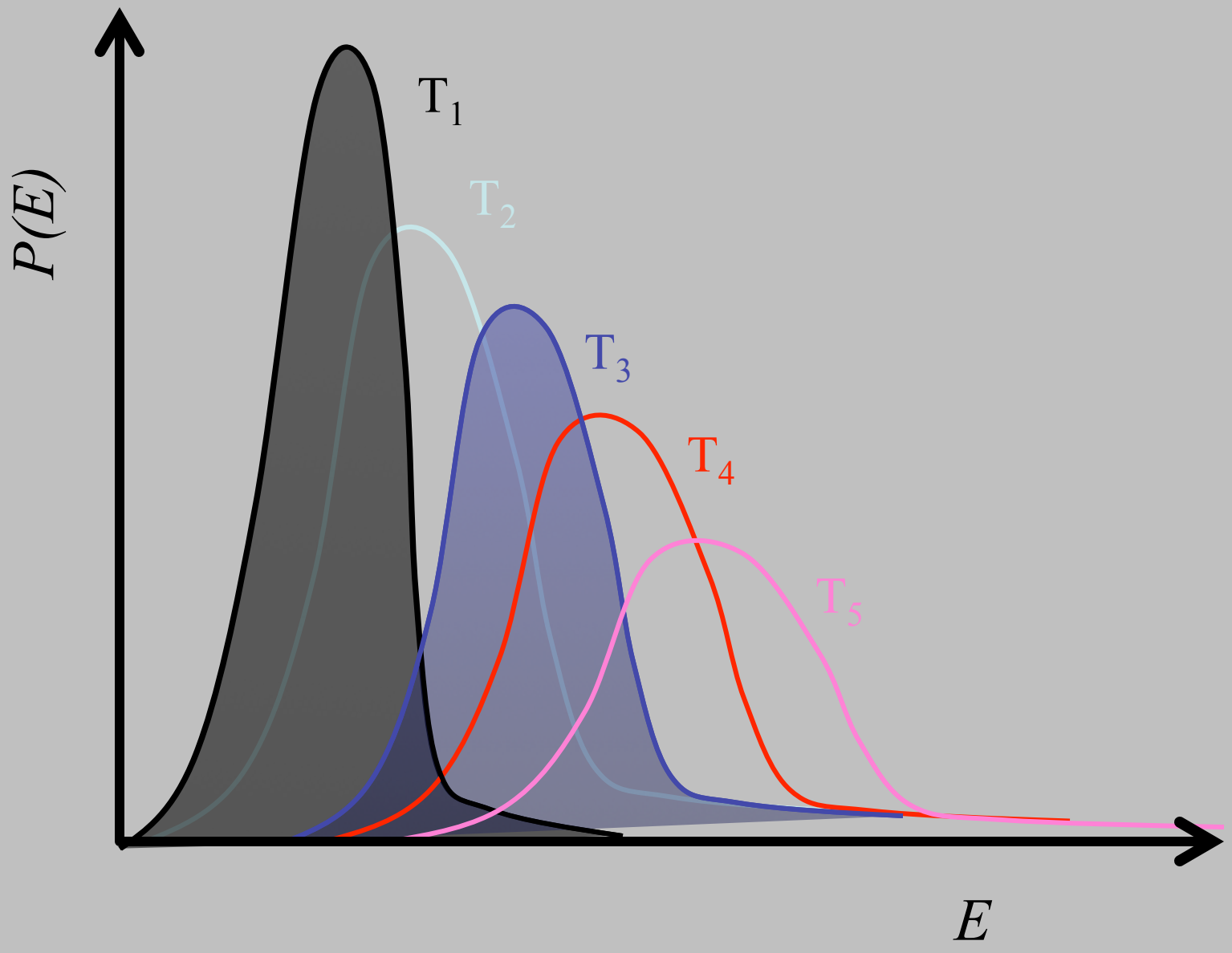

P(E)
T1
E

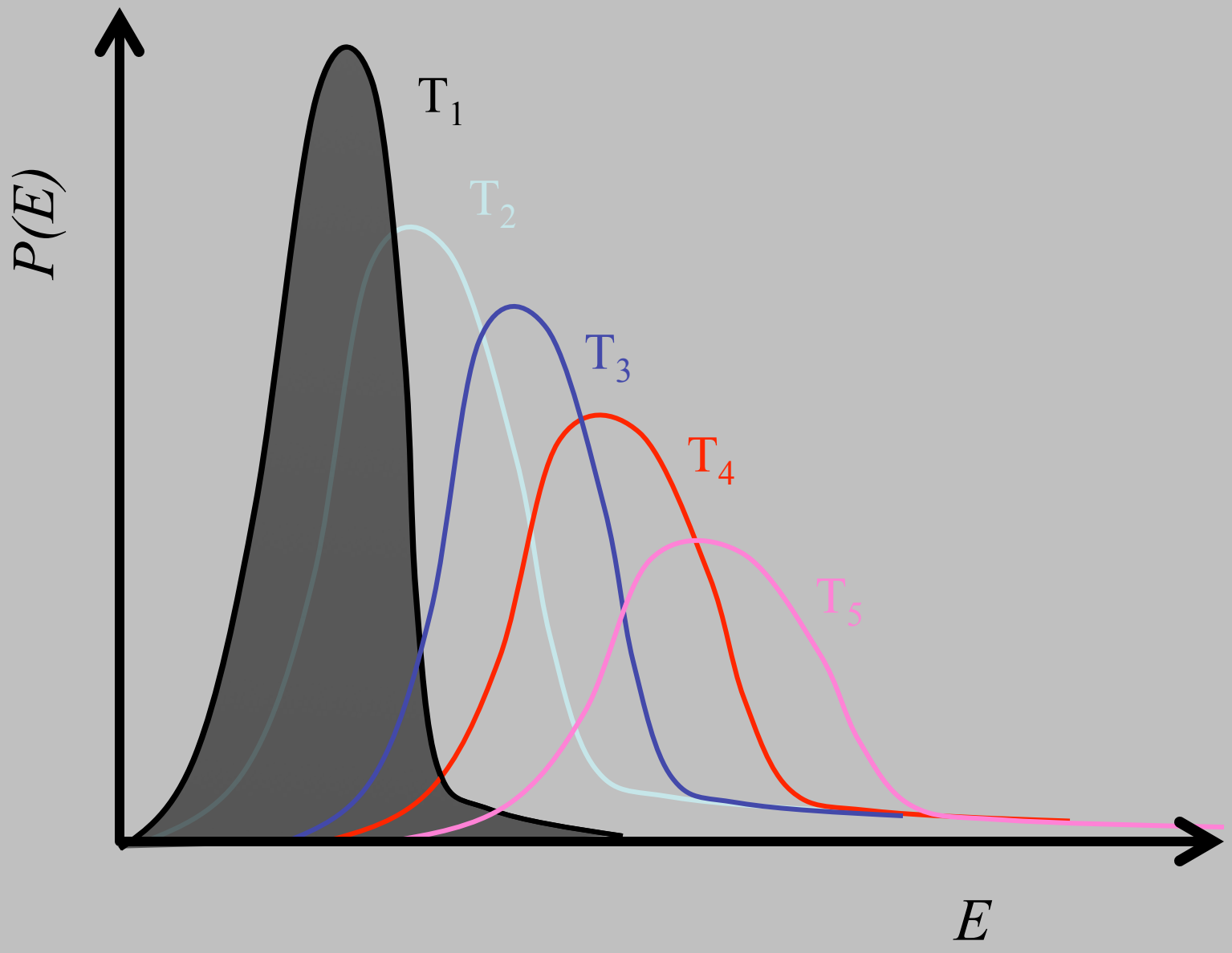

P(E)
T1
T2
E

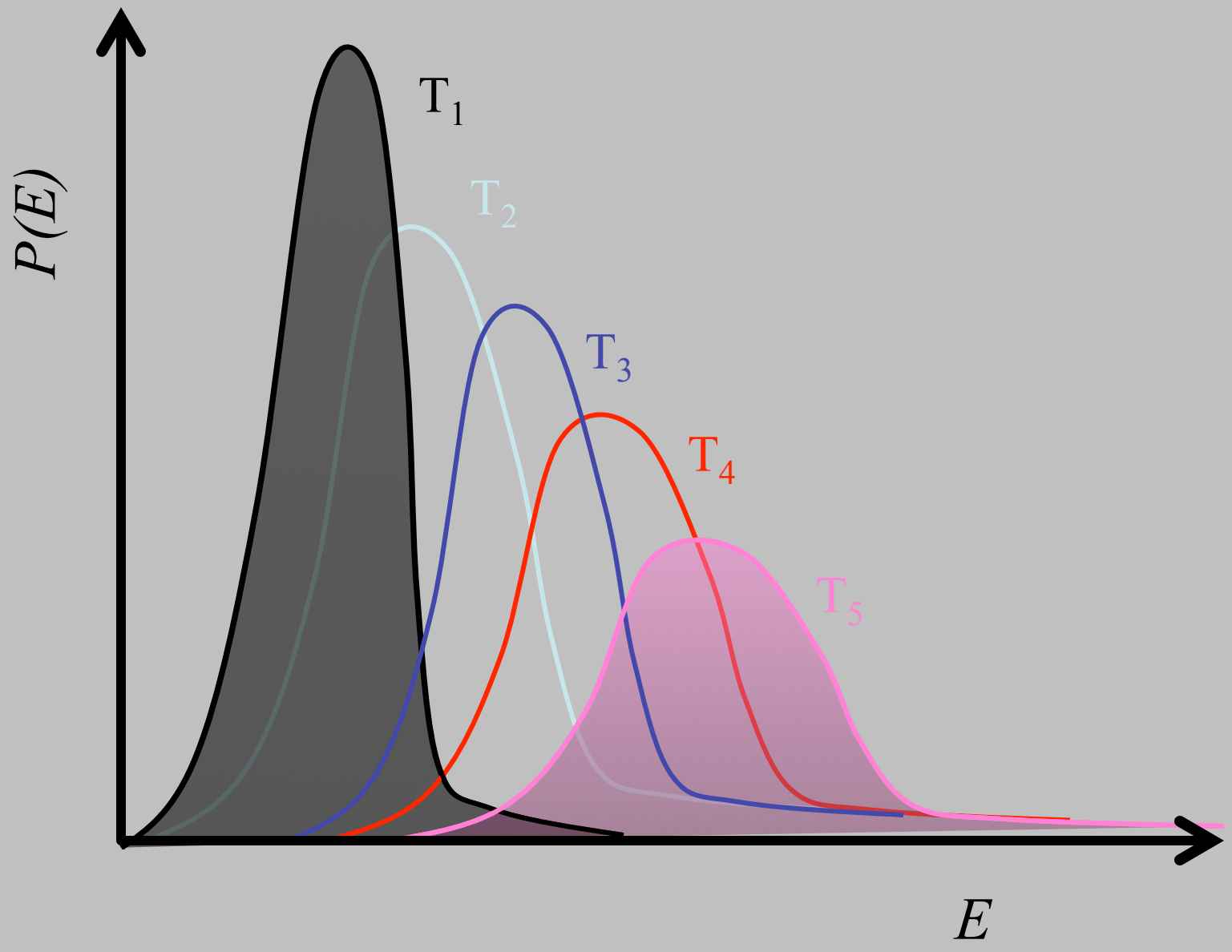

P(E)
T1
T2
T3
E

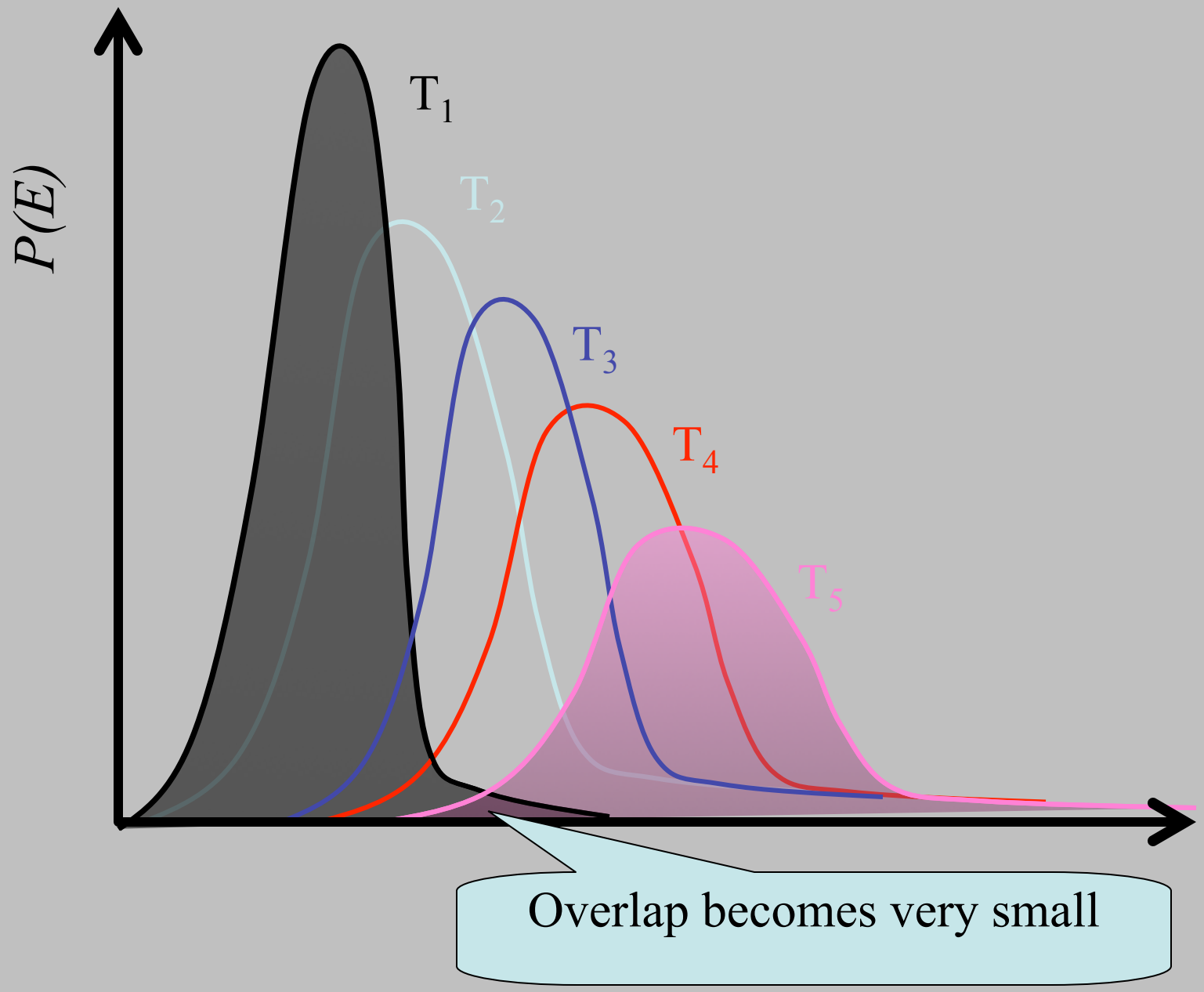

P(E)
T1
T2
T3
T4
E


P(E)
T1
T2
T3
T4
T5
E

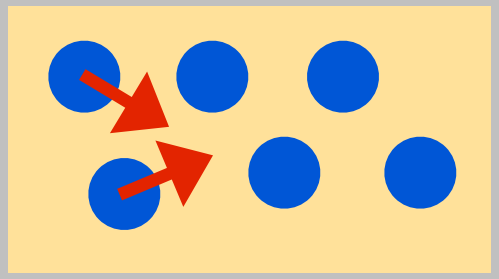

P(E)
T1
T2
T3
T4
T5
E


P(E)
T1
T2
T3
T4
T5
E

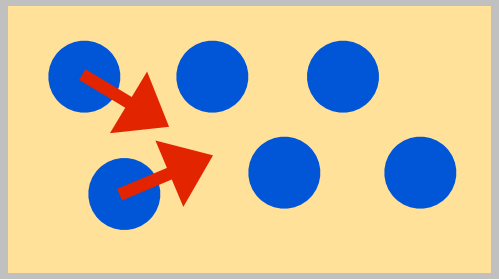

P(E)
T1
T2
T3
T4
T5
E


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

Parallel Monte Carlo

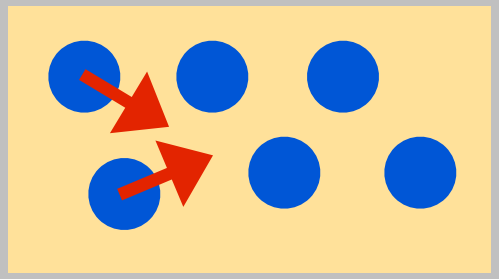


Parallel Monte Carlo



How to do a Monte Carlo simulation in parallel?

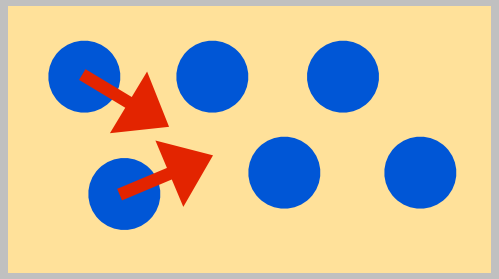
Parallel Monte Carlo



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

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

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Naive (and wrong)

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1. Generate k trial configurations in parallel

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Parallel Monte Carlo - algorithm

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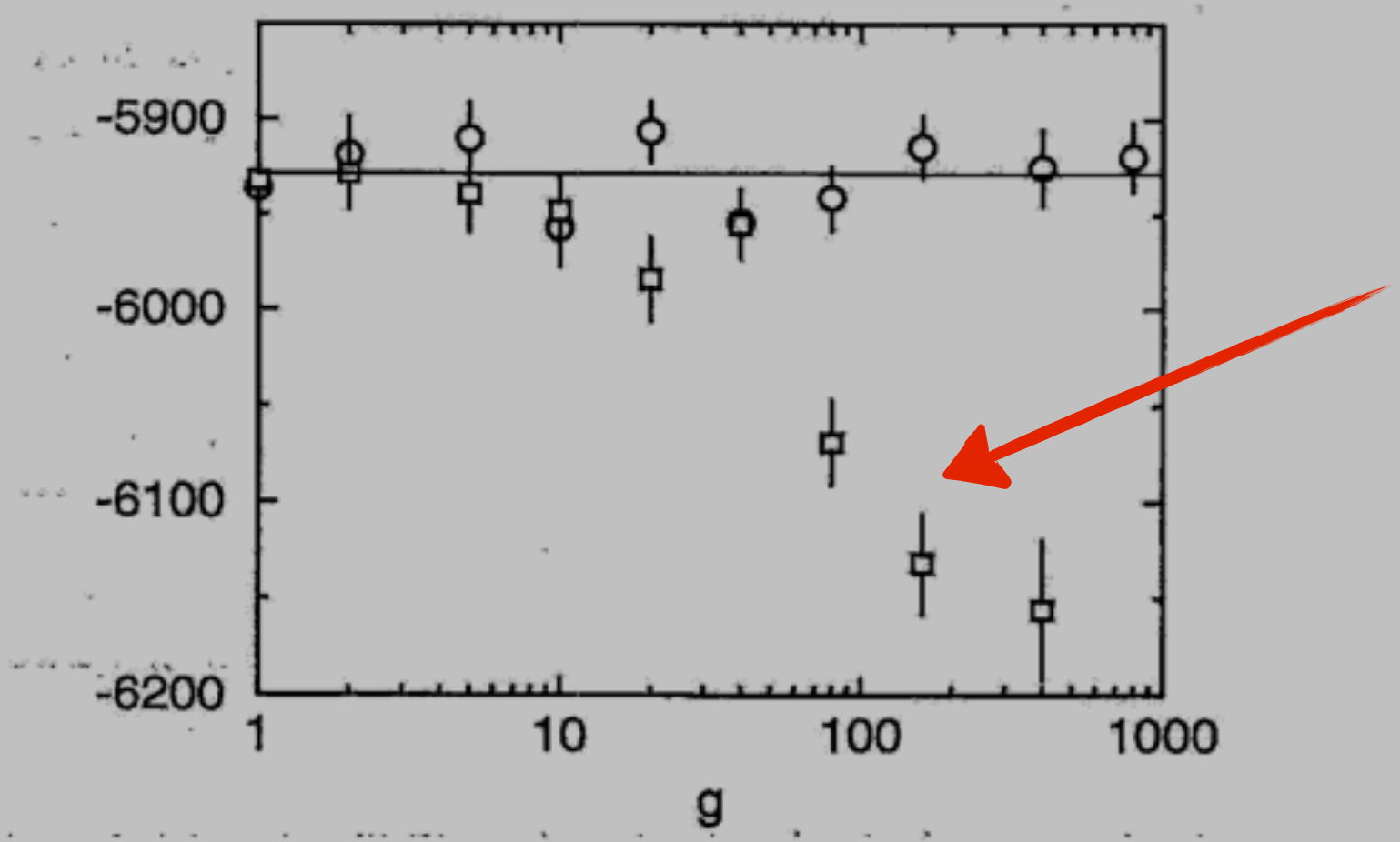
$$P(n) = \frac{\exp\left[-\beta\left(U_n\right)\right]}{\sum_{j=1}^{g} \exp\left[-\beta\left(U_j\right)\right]}$$

3. Accept and reject using normal Monte Carlo rule:

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

Conventional acceptance rules



The conventional acceptance rules give a bias

What went wrong?

Detailed balance!

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

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

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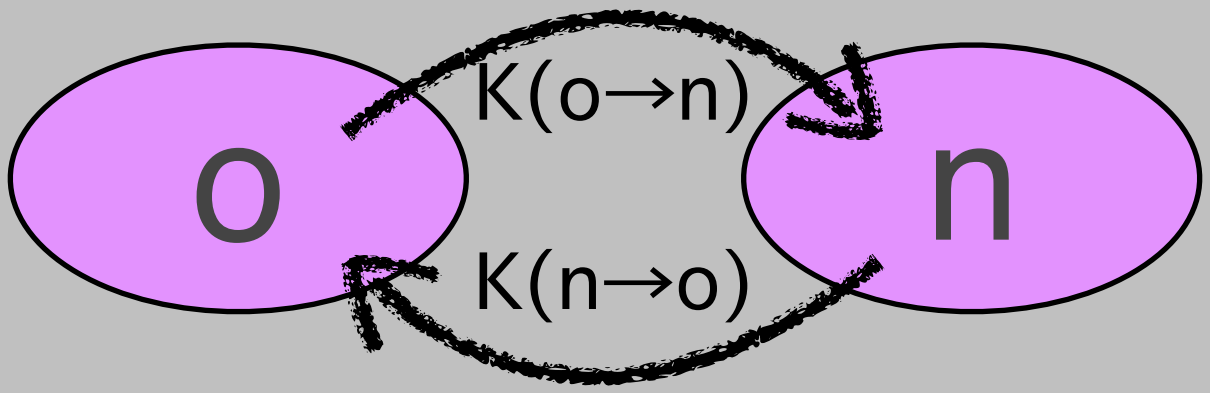
$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \frac{N(n) \times \alpha(n \to o)}{N(o) \times \alpha(o \to n)} = \frac{N(n)}{N(o)}$$

Markov Processes - Detailed Balance



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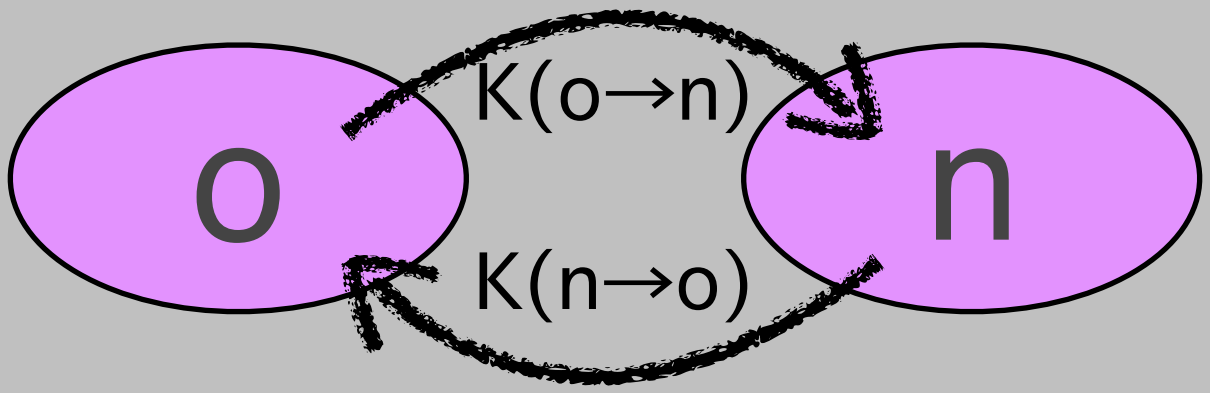

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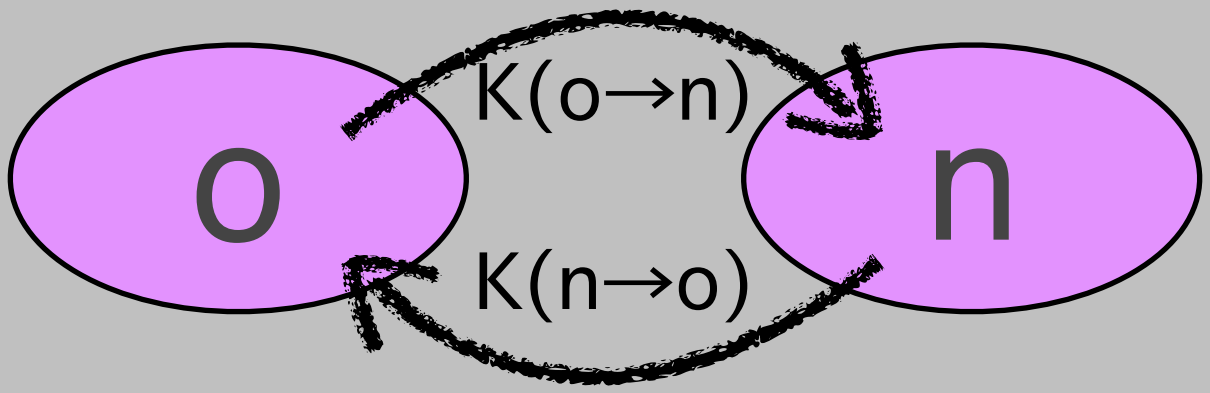

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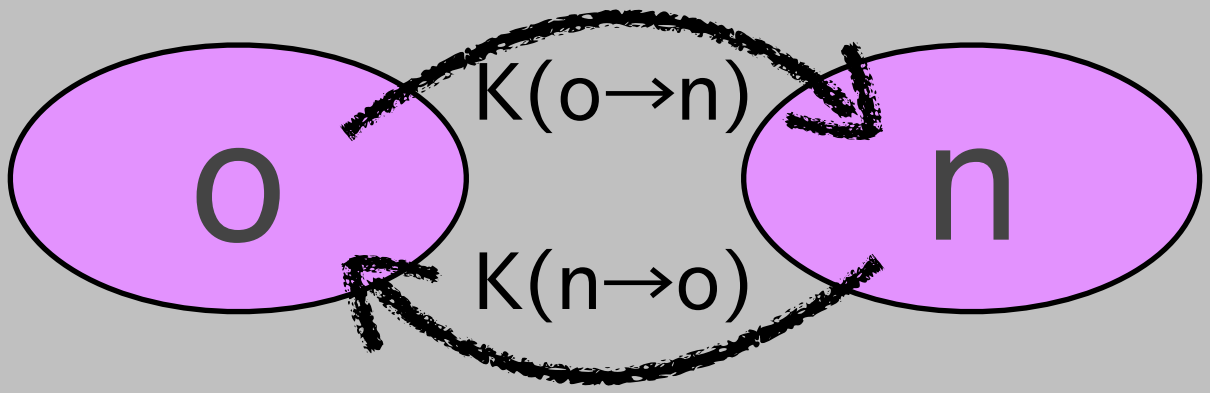

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?

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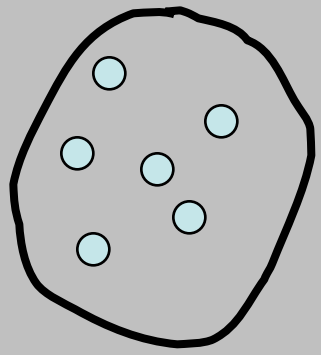

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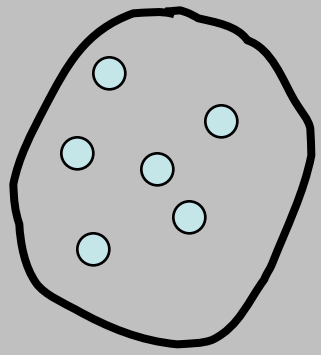

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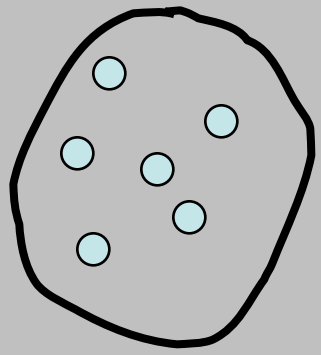

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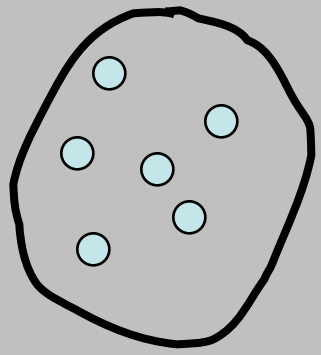

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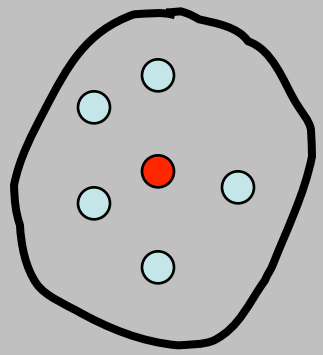

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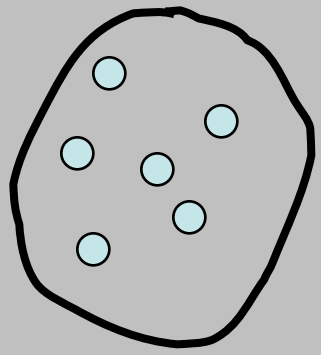

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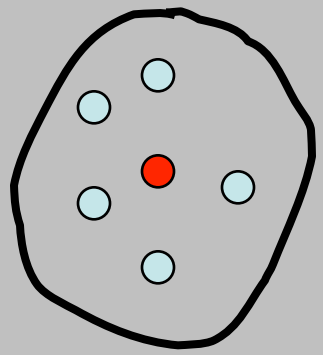

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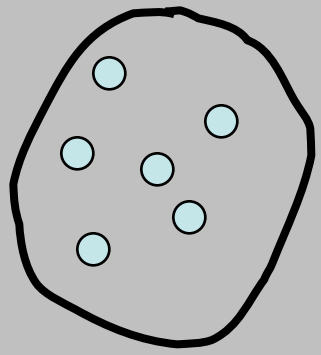

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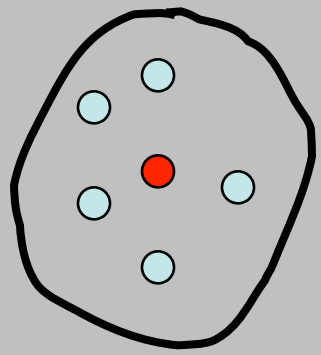

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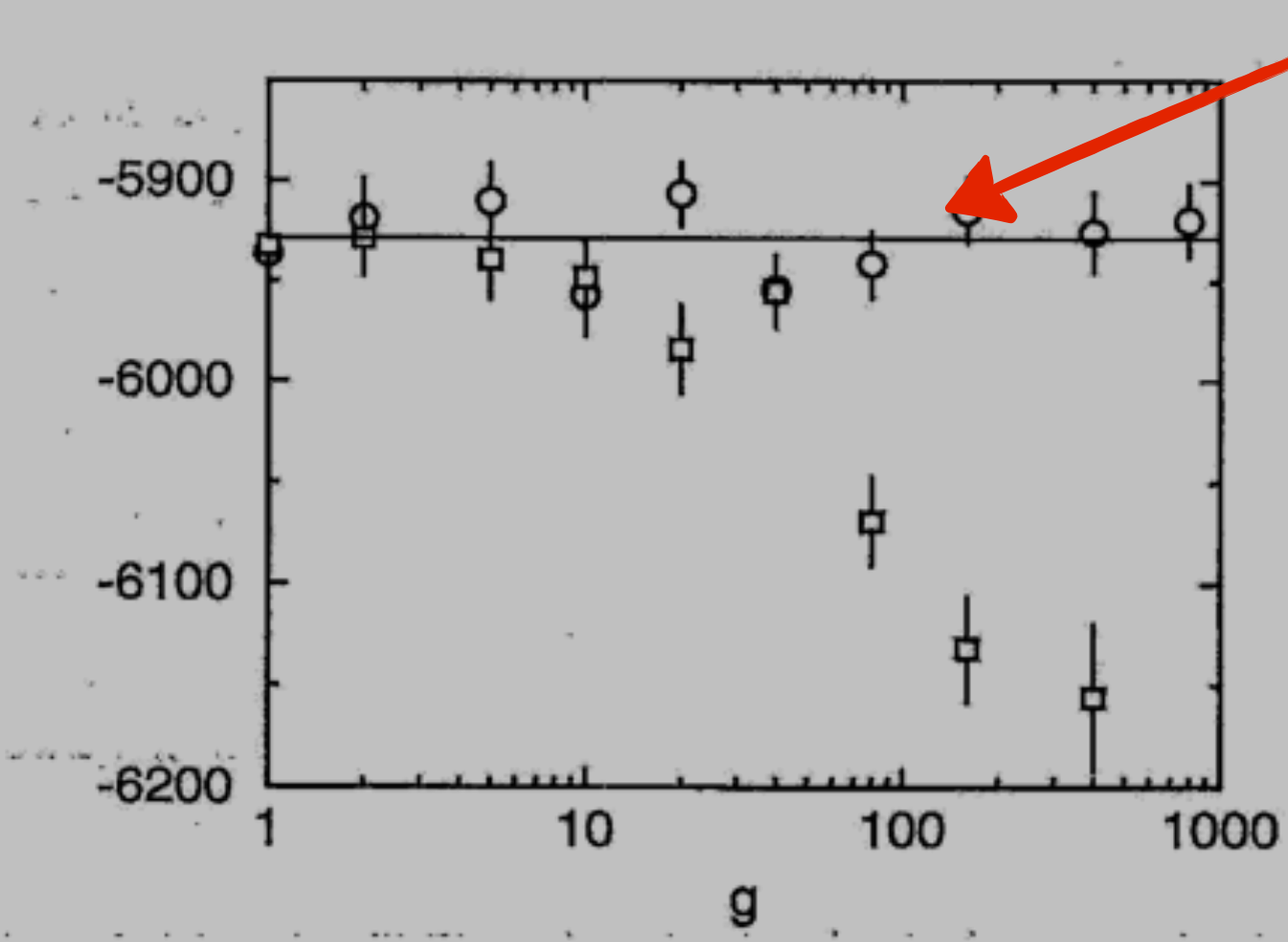
Conventional acceptance rules



Modified acceptance rules remove the bias exactly