Physical Sampling I: Equilibrium

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Ensembles

System

in a quantum state

Equilibrium

allow heat to flow between the system and a bath

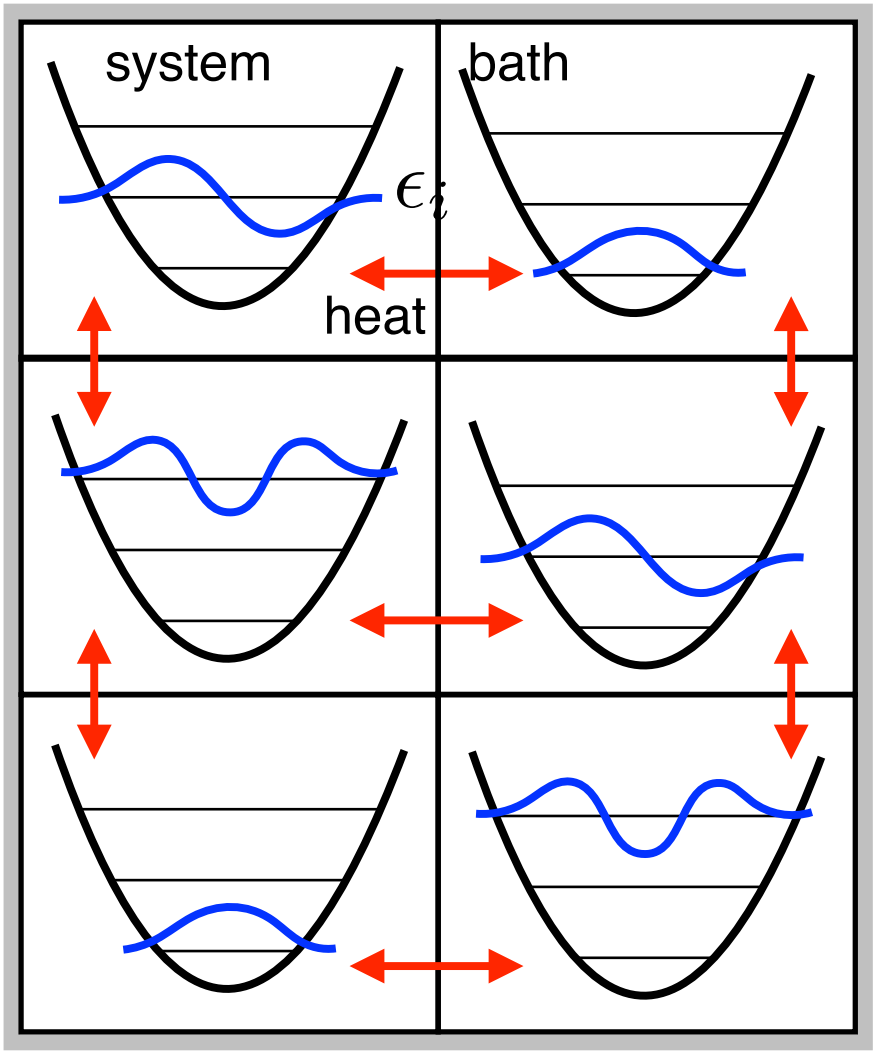
Ensemble 'trick'

replace the bath with replicas of the system

Ensemble properties

isolated with total energy **E**

arbitrarily large number of system replicas, **N**



Equilibrium ensemble state

Description of the ensemble state

$\{n_i\}$ number of replicas in quantum level i with energy ϵ_i

$\Omega(\{n_i\}) = \dfrac{N!}{\prod n_i!}$ number of microstates consistent with $\{n_i\}$

Equilibrium

defined by the most likely state of the ensemble with the most microstates:

$\max\left[\ln \Omega(\{n_i\})\right]$ subject to constraints $\alpha : \sum n_i = \mathbf{N}$

$\beta : \sum \epsilon_i n_i = \mathbf{E}$

Optimize with Lagrange multipliers

$$\frac{\partial}{\partial n_j}\left[\ln \Omega(\{n_i\}) - \alpha(\sum n_i - \mathbf{N}) - \beta(\sum \epsilon_i n_i - \mathbf{E})\right] = 0$$

Boltzmann distribution

… after some math:

$$n_i = e^{-\alpha} e^{-\beta \epsilon_i}$$

Solve for $\alpha : \sum n_i = \mathbf{N} \quad \Longrightarrow \quad e^{-\alpha} = \dfrac{N}{\sum e^{-\beta \epsilon_i}}$

Probability distribution

$$p_i = \frac{n_i}{N} = \frac{e^{-\beta \epsilon_i}}{\sum e^{-\beta \epsilon_j}}$$

Solve for β **?** no, β characterizes the distribution better than **E**, and was already coined previously by Boltzmann as $1/k_B T$

Boltzmann distribution:

$$p_i = \frac{e^{-\epsilon_i / k_\mathrm{B} T}}{q}$$

Partition function:

$$q = \sum e^{-\epsilon_i / k_\mathrm{B} T}$$

Thermal energy:

$$k_\mathrm{B} T = 1/\beta$$

Partition function

$$q = \sum e^{-\epsilon_i / k_\mathrm{B} T}$$

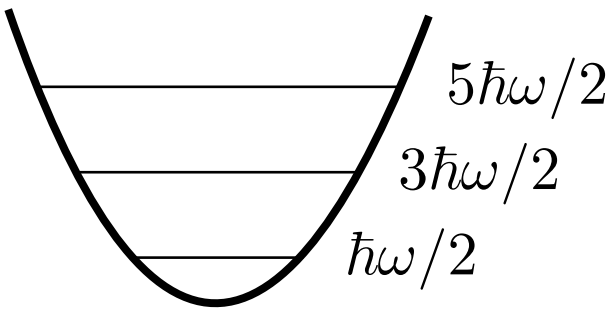
- normalizes the Boltzmann probability distribution
- is the number of thermally accessible states
- derivatives contain all thermodynamic functions

E.g.: the average energy

$$\langle E \rangle = \frac{\sum_i \epsilon_i e^{-\beta \epsilon_i}}{\sum_j e^{-\beta \epsilon_j}} = -\frac{1}{q} \frac{\partial q}{\partial \beta} = -\frac{\partial \ln q}{\partial \beta}$$

Harmonic oscillator

$$q_\mathrm{HO}^\mathrm{qm} = \sum_i e^{-\beta \hbar \omega (i + \frac{1}{2})} = \frac{e^{-\beta \hbar \omega / 2}}{1 - e^{-\beta \hbar \omega}}$$

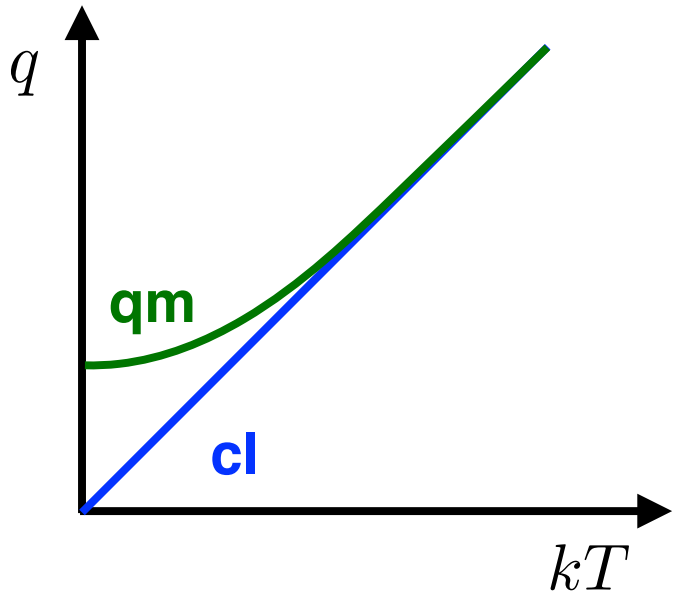


$$E_i = (1/2 + i)\hbar\omega$$

Harmonic oscillator partition function

Quantum

$$q_{\mathrm{HO}}^{\mathrm{qm}} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

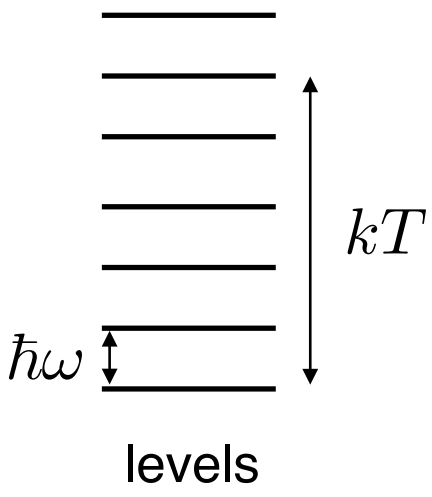


Classical limit:

$$\lim_{\beta\hbar\omega<0} q_{\mathrm{HO}}^{\mathrm{qm}} \rightarrow \frac{1}{\beta\hbar\omega} = \frac{kT}{\hbar\omega}$$

Interpretation:

number of thermally accessible states: $\dfrac{kT}{\hbar\omega}$



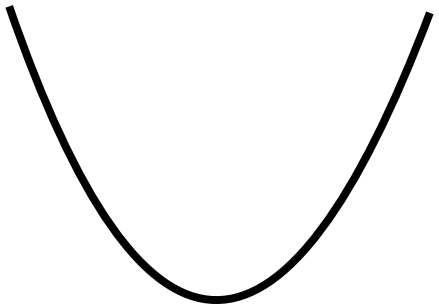
Classical partition function

Proposed changes	quantum		classical
energy of a state	ϵ_i	$\Longrightarrow$	$H(x,p)$
sum over states	$\sum_i$	$\Longrightarrow$	$\int_x \int_p$

Try $$q^{\mathrm{cl}} \stackrel{?}{=} \int_x \int_p e^{-H(x,p)/kT}$$

Harmonic oscillator

$$q^{\mathrm{cl}}_{\mathrm{HO}} \stackrel{?}{=} \int_x e^{-\beta\kappa x^2/2} dx \int_p e^{-\beta p^2/(2m)} dp$$



$V(x) = \kappa x^2/2$

classical / quantum comparison

$$q_{\mathrm{HO}}^{\mathrm{cl}} \stackrel{?}{=} \sqrt{\frac{2\pi kT}{\kappa}}\sqrt{2\pi mkT}$$
$$= (2\pi kT)\sqrt{\frac{m}{\kappa}}$$
$$= 2\pi\frac{kT}{\omega}$$

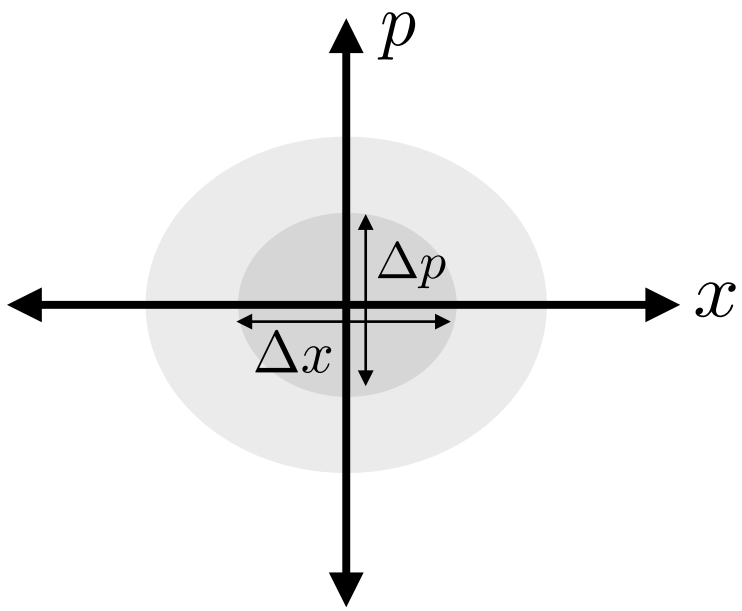
$\xrightarrow{1/h}$

$$q_{\mathrm{HO}}^{\mathrm{cl}} = \frac{1}{h}\sqrt{\frac{2\pi kT}{\kappa}}\sqrt{2\pi mkT}$$
$$= \frac{1}{h}(2\pi kT)\sqrt{\frac{m}{\kappa}}$$
$$= \frac{2\pi}{h}\frac{kT}{\omega} = \frac{kT}{\hbar\omega}$$

Missing normalization

the size of a state
in phase space

$$\Delta x \Delta p \sim h$$



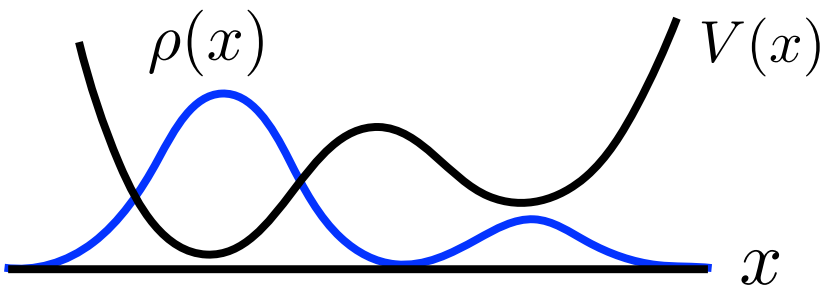
Classical partition function

Separable

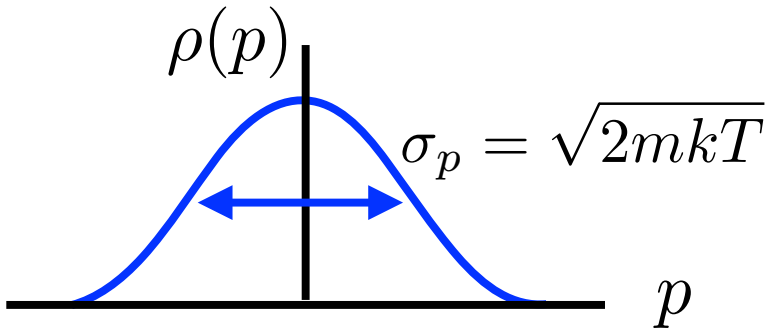
configuration momentum

$$q^{\mathrm{cl}} = \frac{1}{h} \int_x e^{-V(x)/kT} dx \int_p e^{-p^2/2mkT} dp$$

Configurational distribution



Momentum distribution



Many dimensions

$$q^{\mathrm{cl}} = Z_N \left[\frac{2\pi mkT}{h^2} \right]^{3N/2}$$

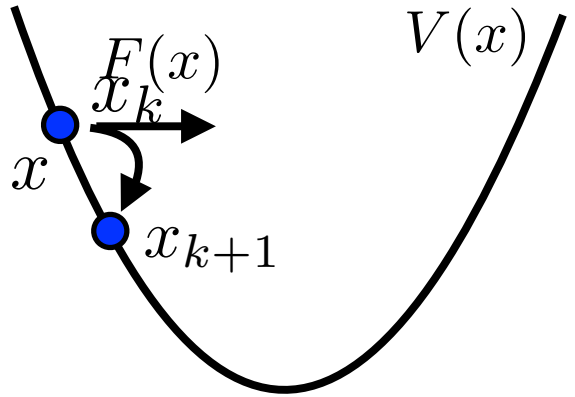
$$Z_N = \int_{x_1} \ldots \int_{x_{3N}} e^{-\beta V(x_1,\ldots,x_{3N})} dx_1 \ldots dx_{3N}$$

configurational partition function

Sampling with molecular dynamics

Newton's equation

$$F(x) = m\frac{\partial^2 x}{\partial t^2}$$



Velocity Verlet algorithm

Given x_k *and* v_k *and an expression for* $F(x)$

Step 1: calculate $x_{k+1} = x_k + hv_k + h^2 F(x_k)/2m$

Step 2: evaluate $F(x_{k+1})$

Step 3: calculate $v_{k+1} = v_k + \frac{h}{2m}[F(x_k) + F(x_{k+1})]$

Now all quantities for the new step, $k+1$*, have been found, go back to step 1.*

Average observables over trajectory

e.g.

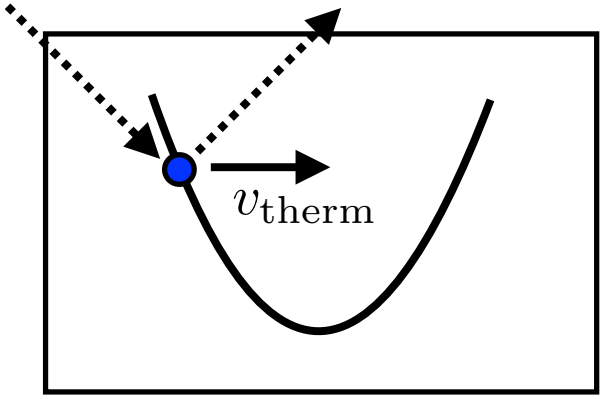
$$\langle A \rangle = \frac{\int_x A(x) e^{-V(x)/kT} dx}{\int_x e^{-V(x)/kT} dx} = \frac{1}{N}\sum_{k=1}^{N} A(x_k)$$

Thermostats

Andersen

fictitious particles instantaneously ‘collide’ with the atoms in the system and replace their velocity with a thermal distribution

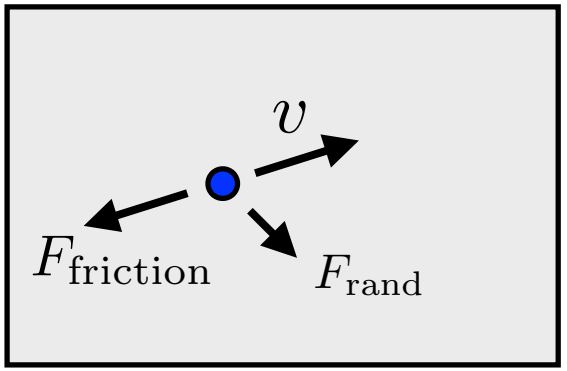
$$v \leftarrow v_{\text{therm}} \qquad \sigma_v = \sqrt{\frac{2kT}{m}}$$



Langevin

atoms are embedded in a 'sea' of fictitious thermal particles

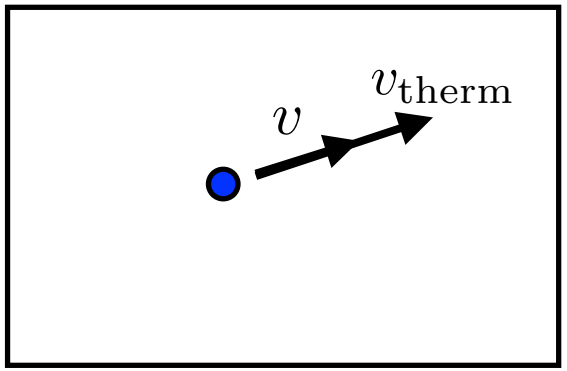
$$F = ma - \alpha v + F_{\text{random}}$$



~~Berendsen~~

velocity rescaling $v \leftarrow |v_{\text{therm}}|\hat{v}$

never use this



Metropolis Monte Carlo

Goal

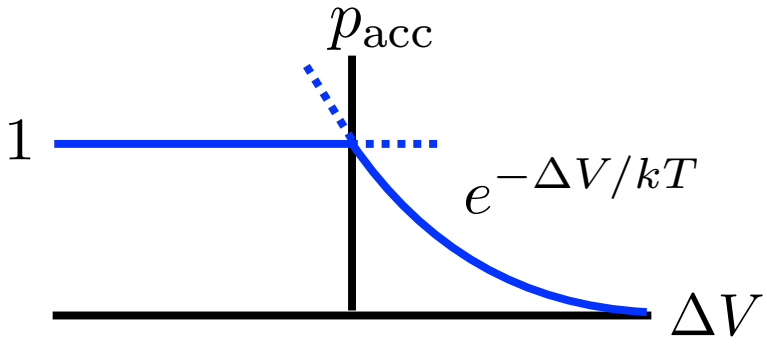
to avoid $$\langle A \rangle = \frac{\int_x A(x) e^{-V(x)/kT} dx}{\int_x e^{-V(x)/kT} dx}$$ (no momentum)

and replace with $$\langle A \rangle = \frac{1}{N} \sum_{k=1}^{N} A(x_k)$$

but how to draw x_k from the Boltzmann distribution, $\rho(x) \propto e^{-V(x)/kT}$

Metropolis algorithm

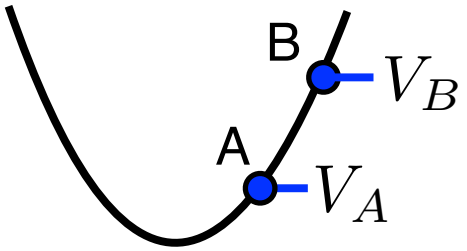
1. consider an unbiased trial move Δx
2. accept the move according to
$$p_{\mathrm{acc}} = \min[1, e^{-\Delta V/kT}]$$
3. repeat until convergence



Metropolis Monte Carlo

Proof that MC gives the Boltzmann distribution

consider two generic points on a potential landscape



if sampled until steady state $p_A p_{A\to B} = p_B p_{B\to A}$

$$\frac{p_B}{p_A} = \frac{p_{A\to B}}{p_{B\to A}} \qquad \frac{p_B}{p_A} = \frac{\min[1, e^{-(V_B - V_A)/kT}]}{\min[1, e^{-(V_A - V_B)/kT}]}$$

Two cases

I. $V_B \geq V_A$ $\qquad \dfrac{p_B}{p_A} = \dfrac{e^{-(V_B - V_A)/kT}}{1} = e^{-(V_B - V_A)/kT}$

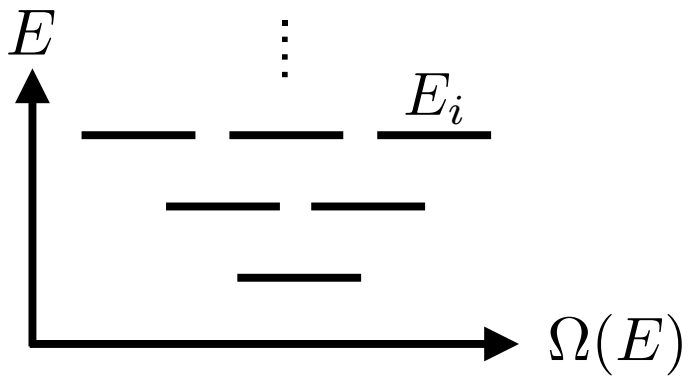
II. $V_B < V_A$ $\qquad \dfrac{p_B}{p_A} = \dfrac{1}{e^{-(V_A - V_B)/kT}} = e^{-(V_B - V_A)/kT}$

since A and B are arbitrary, $\dfrac{p_B}{p_A} = e^{-(V_B - V_A)/kT}$ for all points

Free energy

Separate degeneracy and energy

$$Q = \sum_i e^{-E_i/kT} = \sum_E \Omega(E) \underbrace{e^{-E/kT}}_{p(E)}$$



Equilibrium

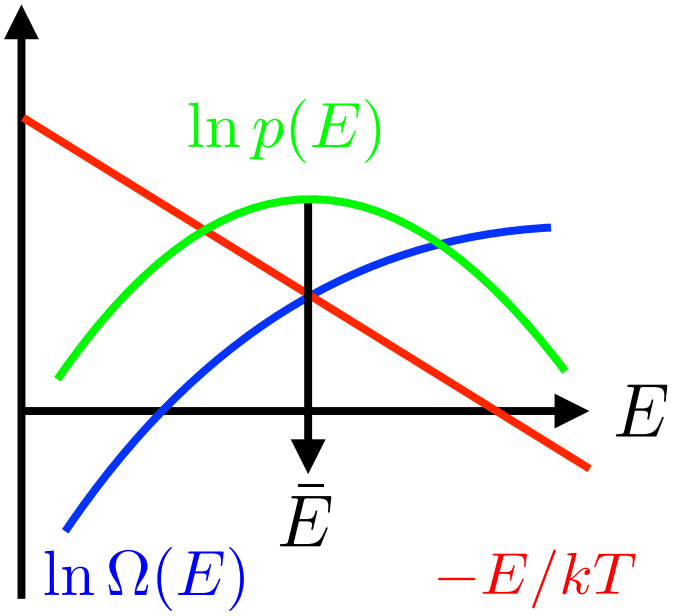
maximizes $p(E)$ at $\bar{E}$

$$\ln Q = \ln \Omega(\bar{E}) - \bar{E}/kT \quad \text{(max term)}$$

$$-kT \ln Q = \bar{E} - kT \ln \Omega(\bar{E}) \quad \text{(minimized)}$$

$$= E - TS \qquad E \leftarrow \bar{E}$$

$$= A \qquad \text{free energy}$$



Free energy

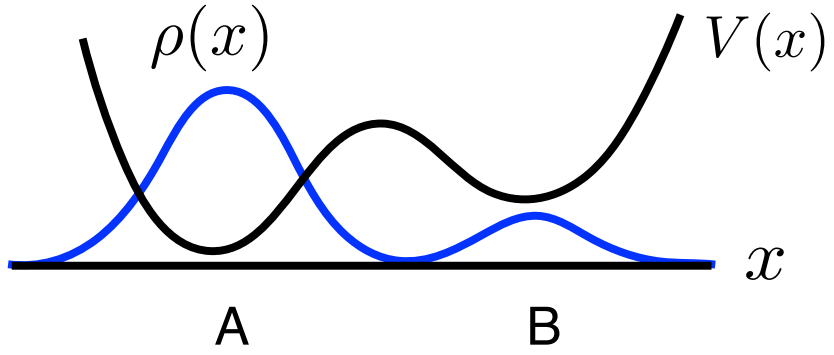
A is minimized at equilibrium

A defines equilibrium in the canonical ensemble

Free energy differences

Probability of being in a state

$$\frac{p_B}{p_A} = \frac{q_B}{q_A} = e^{-(A_B - A_A)/kT}$$

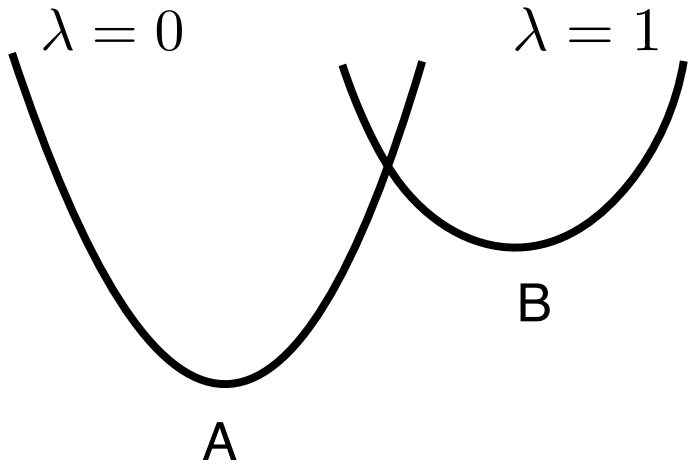


For relative probabilities, need free energy differences

Thermodynamic integration

$$\Delta A = \int_{\lambda=0}^{1} \left\langle \frac{\partial H_\lambda}{\partial \lambda} \right\rangle_\lambda d\lambda$$

$$\left\langle \frac{\partial H_\lambda}{\partial \lambda} \right\rangle_\lambda = \frac{\int_x \frac{\partial H_\lambda}{\partial \lambda} e^{-V(x)/kT} dx}{\int_x e^{-V(x)/kT} dx}$$

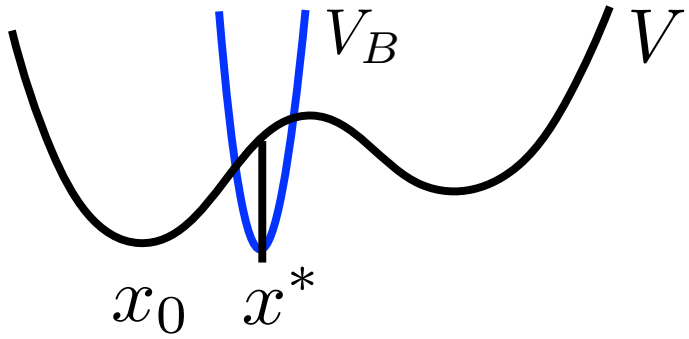


calculate average with MC/MD; path independent

Importance sampling

Umbrella sampling

we are interested in some property around x^*, e.g. which is unlikely



$$\langle A \rangle = \frac{\int A e^{-V/kT}}{\int e^{-V/kT}} \qquad V(x^*) > V(x_0)$$

add a bias potential V_B in the region of interest

$$\langle A \rangle = \frac{\int A e^{-(V+V_B)/kT} e^{V_B/kT}}{\int e^{-(V+V_B)/kT} e^{V_B/kT}}$$

$$= \frac{\int A e^{-(V+V_B)/kT} e^{V_B/kT}}{\int e^{-(V+V_B)/kT}} \frac{\int e^{-(V+V_B)/kT}}{\int e^{-(V+V_B)/kT} e^{V_B/kT}} = \boxed{\frac{\left\langle A e^{V_B/kT} \right\rangle_B}{\left\langle e^{V_B/kT} \right\rangle_B}}$$

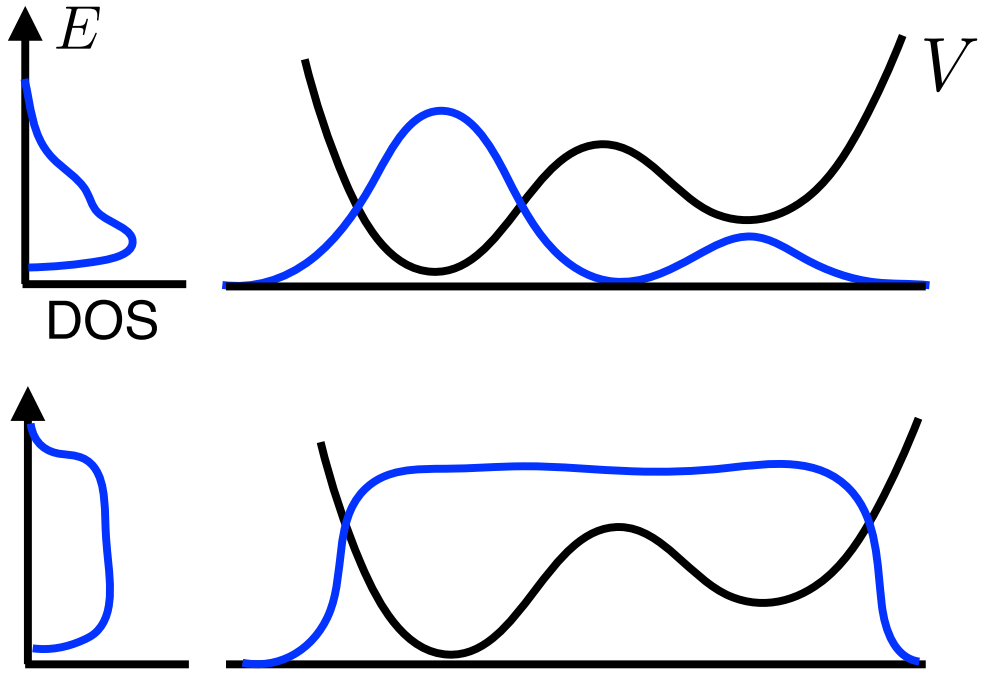
which is sampled on the biased potential

Importance sampling

Wang Landau

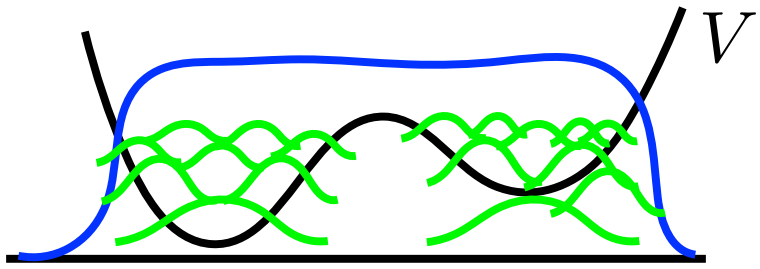
sample density of states

reweight the sampling
based upon 1/DOS
until a flat density of
states is obtained



Metadynamics

bias sampling with a history
dependent bias potential constructed
from Gaussian potentials; continue
until a flat distribution is obtained



Global optimization I

Parallel tempering /

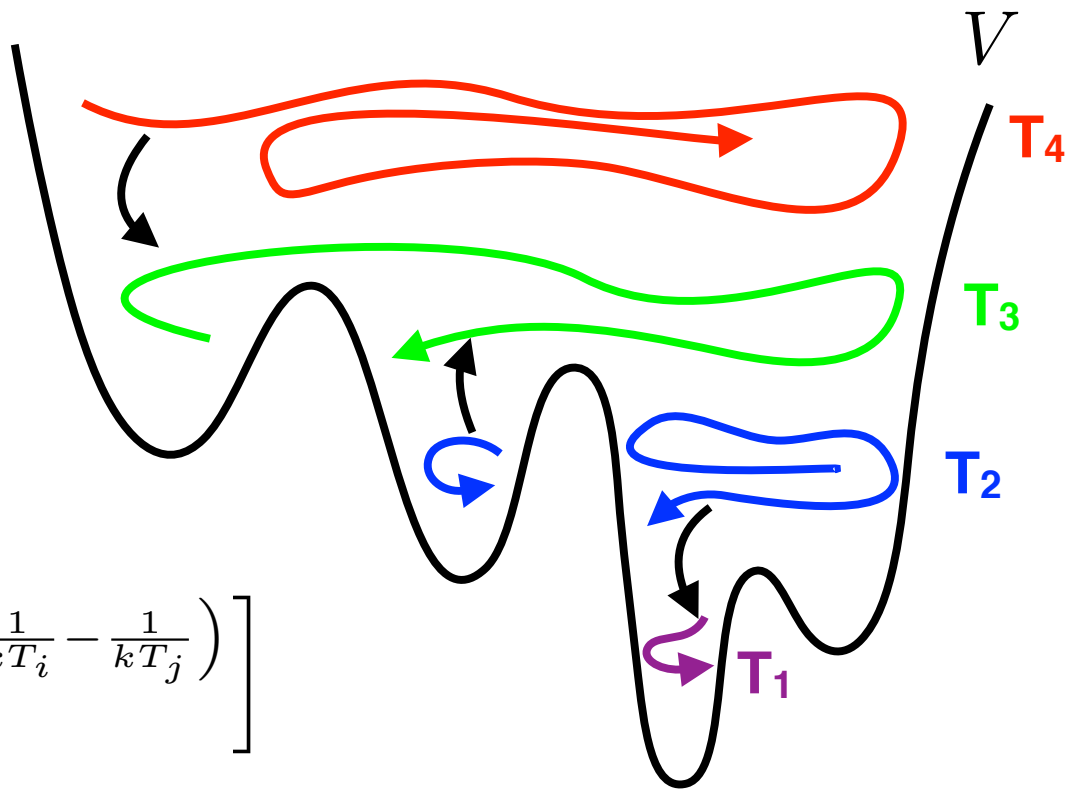
Replica exchange

run molecular dynamics
at a set of temperatures

accept trial moves
between trajectories with
probability

$$p_{\mathrm{acc}} = \min\left[1, e^{(E_i - E_j)\left(\frac{1}{kT_i} - \frac{1}{kT_j}\right)}\right]$$

gives an equilibrium
distribution, not dynamics



Global optimization II

Basin hopping

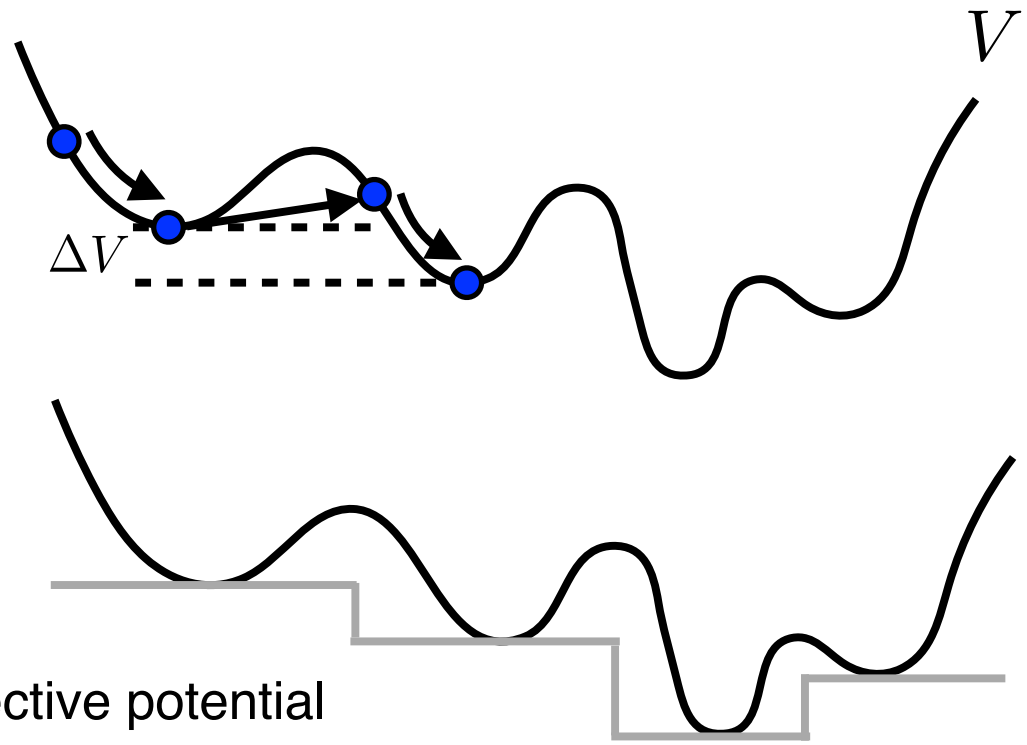
local optimization

make a random trial move
and minimize

accept based upon the
Metropolis criterion

$$p_{\mathrm{acc}} = \min[1, e^{-\Delta V/kT}]$$

repeat



effective potential
has reduced barriers

Other strategies

genetic algorithms

swarm optimization

minima hopping

Discussion / questions?