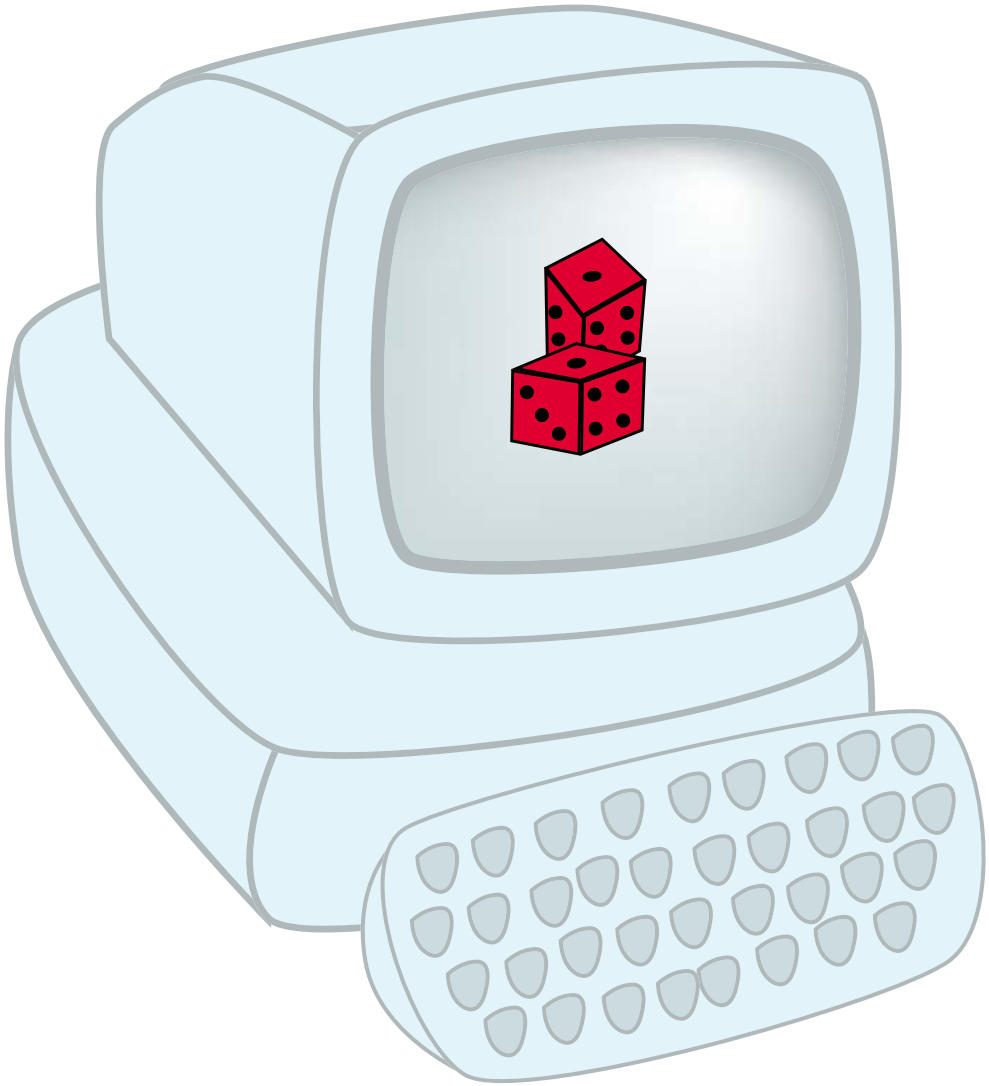
3.320 Lecture 18 (4/12/05)



Monte Carlo Simulation II and free energies

Figure by MIT OCW.

References

General Statistical Mechanics

- *D. Chandler, "Introduction to Modern Statistical Mechanics"*
- *D.A. McQuarrie, "Statistical Thermodynamics" OR "Statistical Mechanics"*

Monte Carlo

- D. Frenkel and B. Smit, "Understanding Molecular Simulation", Academic Press.

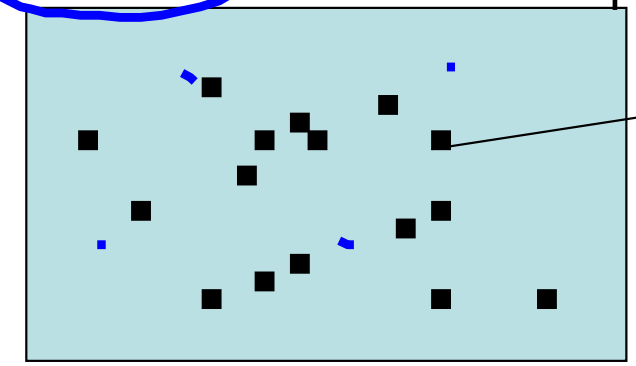
  Fairly recent book. Very good background and theory on MD, MC and Stat Mech. Applications are mainly on molecular systems.

- *M.E.J. Newman and G.T. Barkema, "Monte Carlo Methods in Statistical Physics"*

- *K. Binder and D.W. Heerman, "Monte Carlo Simulation in Statistical Physics"*

Monte Carlo is Efficient Sampling of Ensemble

Ensemble is collection of possible microscopic states



$$P_\nu = \frac{\exp(-\beta H_\nu)}{Q}$$

$$U = \sum_{\nu \in e} P_\nu E_\nu$$

$$V = \sum_{\nu \in e} P_\nu V_\nu$$

Simple Sampling

Pick states ν randomly and weigh their property proportional to P_ν

$$< A > = \sum_{\nu=1}^{M} P_\nu A_\nu \qquad P_\nu = \frac{\exp(-\beta H_\nu)}{\sum_{\nu=1}^{M} \exp(-\beta H_\nu)}$$

Importance Sampling

Pick states with a frequency proportional to their probability P_ν

$$< A > = \sum_{\nu=1}^{M} A_\nu$$

Probability weighted sample

Metropolis Algorithm

Put it all together: The Metropolis Monte Carlo Algorithm

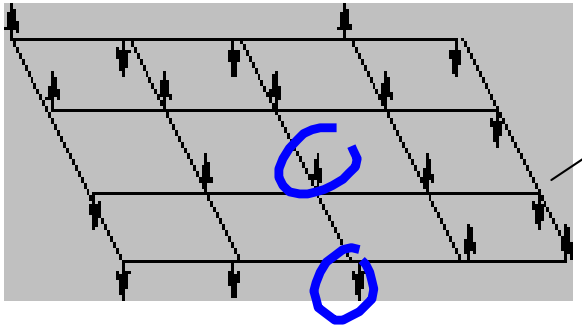
1. Start with some configuration
2. Choose perturbation of the system
3. Compute energy for that perturbation
4. If $\Delta E < 0$ –> accept perturbation
   If $\Delta E > 0$ –> accept perturbation, accept perturbation with probability $\exp\left[\frac{-\Delta E}{k\mathrm{T}}\right]$
5. Choose next perturbation

Property will be average over these states

Metropolis, Rosenbluth, Rosenbluth, Teller and Teller, The Journal of Chemical Physics, **21**, 1087 (1953).

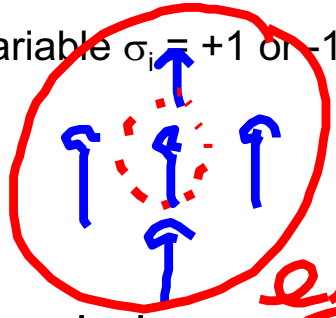
Ising Model

But first, a model system: The Ising Model



At every lattice site i, a spin variable σ_i = +1 or -1

$$H = -\frac{1}{2}\sum_{i,j} J\sigma_i\sigma_j$$



$\Delta E = 8J$

$\exp(-\beta\Delta E)$

Also used for other "two-state" systems: e.g. alloy ordering

Which perturbation ? Pick spin and flip over

1. Start with some spin configuration
2. Randomly pick a site and consider flipping the spin over on that site
3. Compute energy for that perturbation
4. If $\Delta E < 0$ –> accept perturbation
   If $\Delta E > 0$ –> accept perturbation, accept perturbation with probability $\exp\left[\frac{-\Delta E}{kT}\right]$
5. Go back to 2

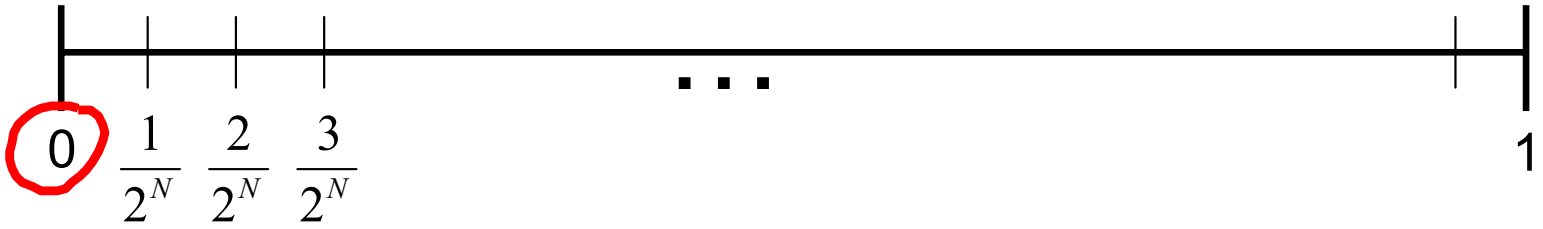
Implemented by random numbers

Random Numbers

Most random number generators generate integers between 0 and $2^N - 1$

To generate real numbers in interval [0,1], division by 2^N is performed

rand() < exp(−βΔE) → execute.

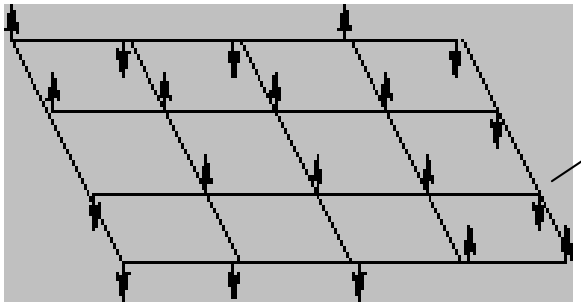


The probability that "0" is given for the random number is $1/2^N$

When rand = 0, any excitation occurs, since exp (-β ΔE) > 0, for any ΔE

What exactly is the quantity in the exponential ?

E.g. Ising Model



At every lattice site i, a spin variable σ_i = +1 or -1

$$H = -\frac{1}{2}\sum_{i,j} J\sigma_i\sigma_j + \mu_i\sum_i \sigma_i$$

If average spin of system is not conserved, then probability need to be weighted by $\exp\left[-\beta\left(-\frac{1}{2}\sum_{i,j} J\sigma_i\sigma_j + \mu_i\sum_i \sigma_i\right)\right]$

Legendre Transform of Energy and Entropy

Energy formulation

$$dU = TdS + (-pdV) + \mu dN + \ldots$$

Legendre transforms

$$\begin{cases} F = U - TS \\ G = U - TS + pV \end{cases}$$

Different variables F(V,N,T), G(P,N,T)

Entropy formulation

$$dS = \frac{1}{T}dU + (-\frac{p}{T}dV) + \frac{\mu}{T}dN + \ldots$$

$$A(\frac{1}{T}, V, N) = S - \frac{1}{T}U$$

$$K(\frac{1}{T}, \frac{p}{T}, N) = S - \frac{1}{T}U + \frac{p}{T}V$$

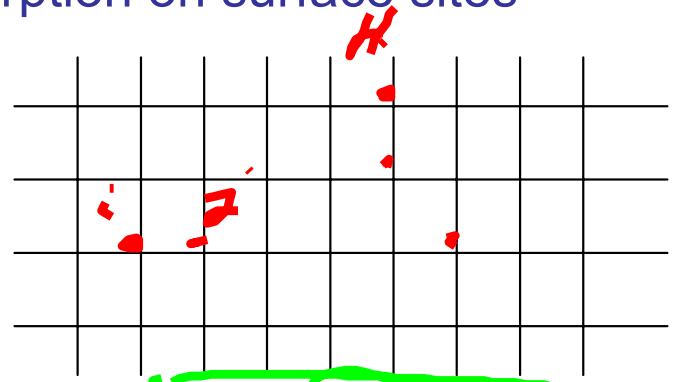
$$L(\frac{1}{T}, V, \frac{\mu}{T}) = S - \frac{1}{T}U - \frac{\mu}{T}N$$

These are the form of the Hamiltonians !

Lab problem: H adsorption phase diagram on Pd (100)

Simple transformation to a lattice model -> spin can be used to indicate whether a lattice site is occupied or not. E.g. Adsorption on surface sites

$$H = \frac{1}{2}\sum_{i,j} W_1 p_i p_j + E_a \sum_i p_i$$



p_i = 1 when site is occupied by H, =0 when not

Can be transformed to:

$$H = \frac{1}{2}\sum_{i,j} V_1 \sigma_i \sigma_j + \mu_i \sum_i \sigma_i \qquad \text{with}$$

$$V_1 = \frac{W_1}{4}$$

$$\mu = \frac{E_a}{2} + \frac{zW_1}{4}$$

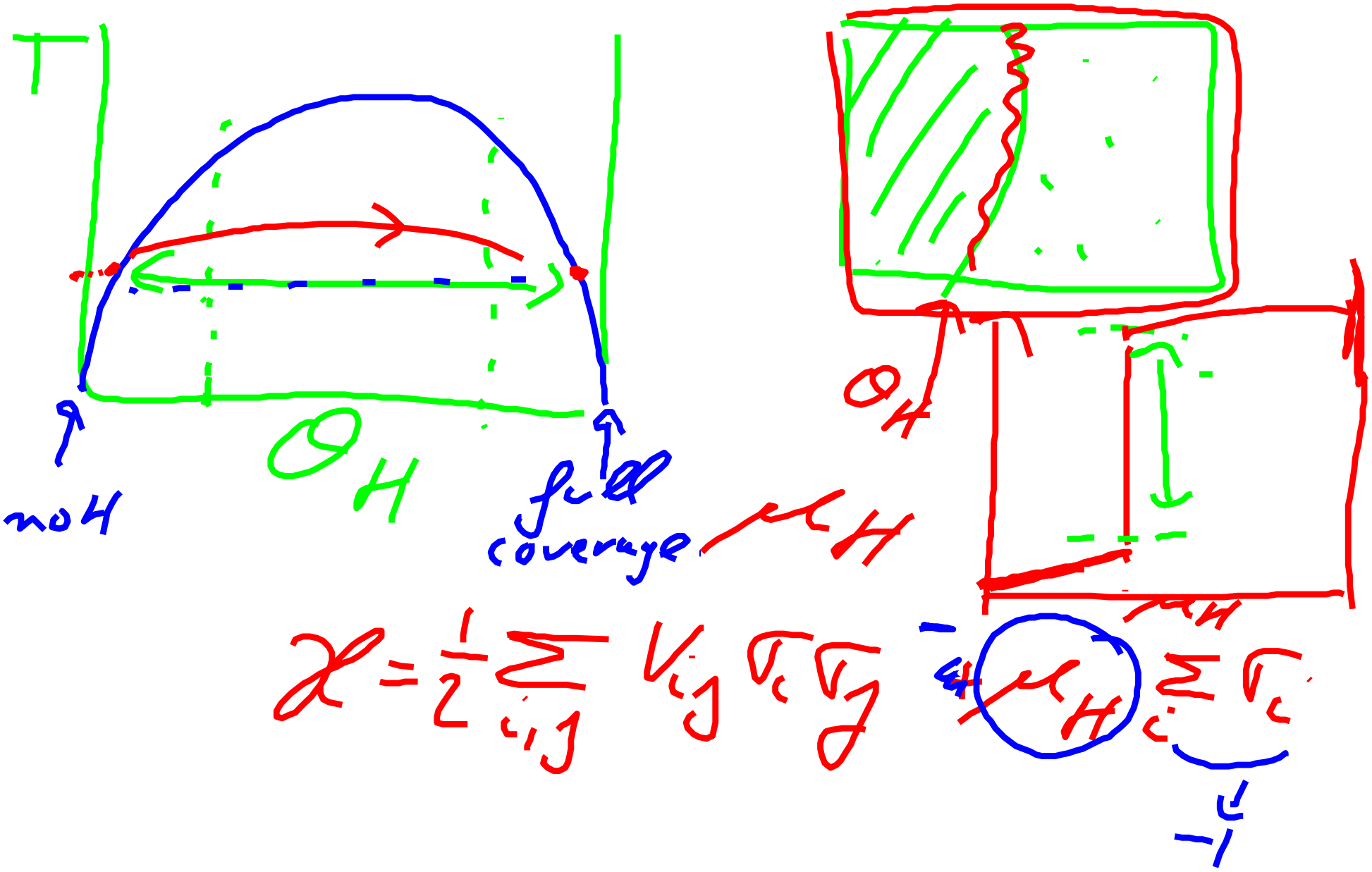
$$\sigma_i = 2p_i - 1 \qquad p_i = \frac{1+\sigma_i}{2}$$

$p_i = 1 \rightarrow \sigma_i = 1$

$p_i = 0 \rightarrow \sigma_i = -1$

Can use canonical or grand-canonical ensemble to get H/Pd(100) phase diagram

Why work grand canonical instead of canonical ?



Accuracy of Monte Carlo to obtain Ensemble Properties

Not worry about accuracy of model or Hamiltonian. Only ask question:
Given H, how good is Monte Carlo sampling to get properties of ensemble ?

As good as you want !

Sources of error: Finite sample (time in MC); Finite Size (Periodic Boundaries)

Sampling Error

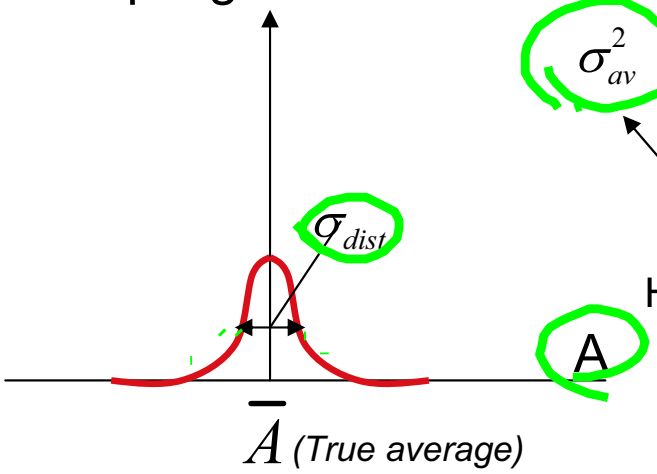
error on the average for random sampling ?

"A" is quantity being sampled

$$\sigma_{av}^2 = \overline{\left(\langle A \rangle - \bar{A}\right)^2} = \frac{\sigma_{dist}^2}{m} \approx \frac{\langle A^2 \rangle - \langle A \rangle^2}{m}$$

Sample size

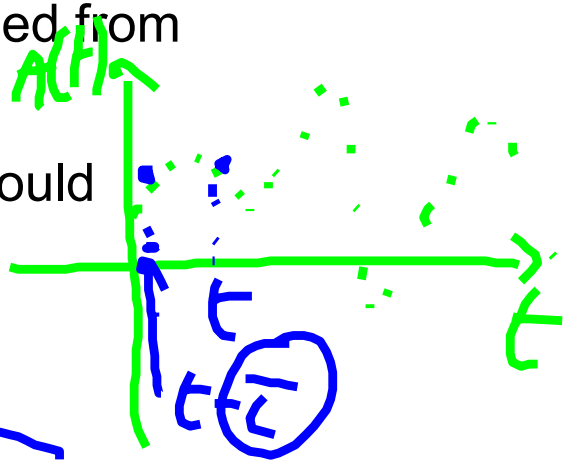
How accurate is the average ?



But sample is correlated

States in Markov chain are not independent. State is obtained from previous state through some perturbation mechanism !

Convergence is not as good as random sampling formula would indicate.



Correlation Time

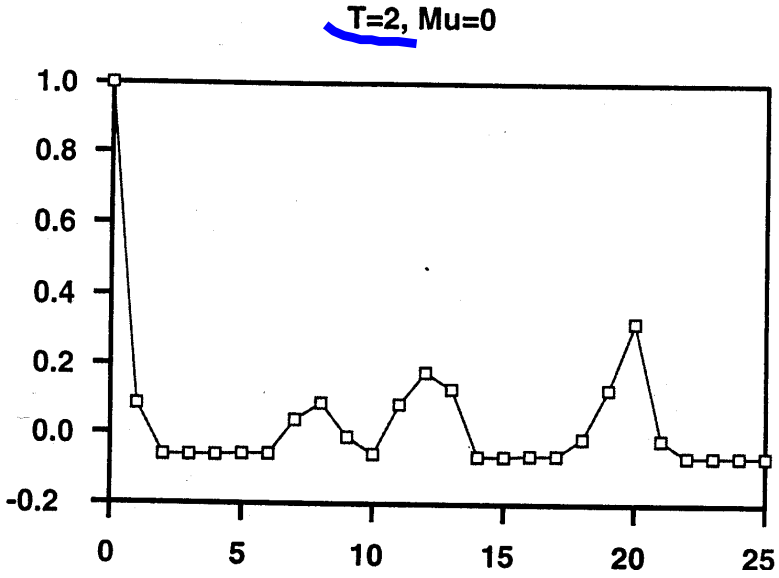
Correlation function $C_A(\tau) = \lim_{t->\infty} \frac{1}{t}\int_0^t \frac{(A(t)-<A>)(A(t+\tau)-<A>)}{<A^2>-<A>^2} dt$

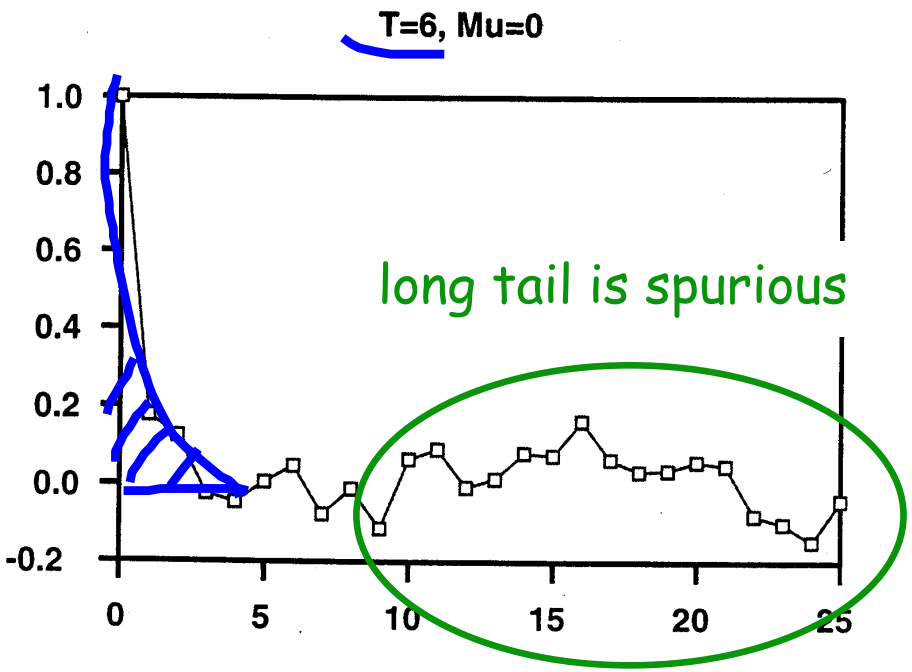
e.g. velocity in harmonic oscillator

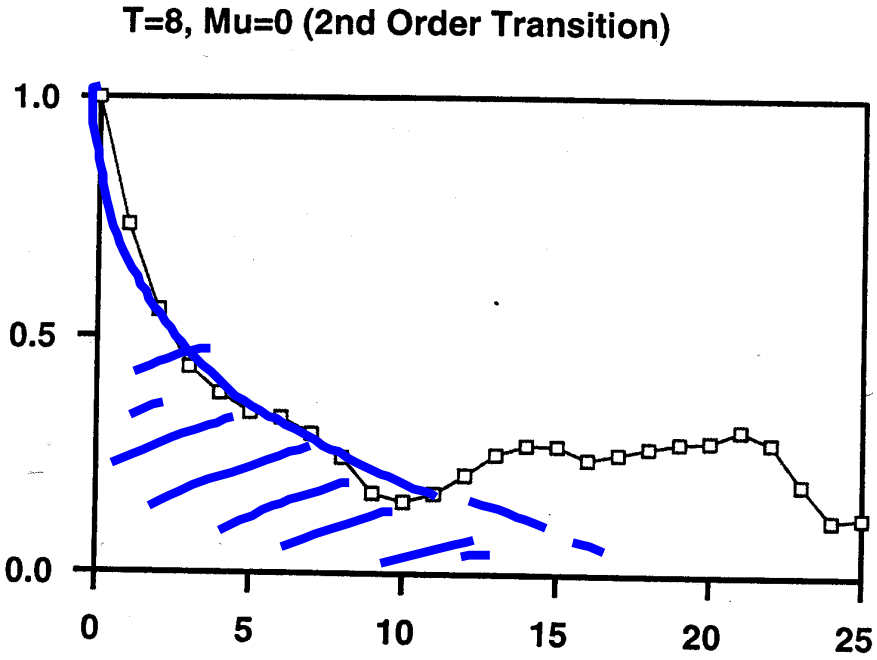
Correlation time $\tau_A = \int_0^\infty C_A(\tau) d\tau$

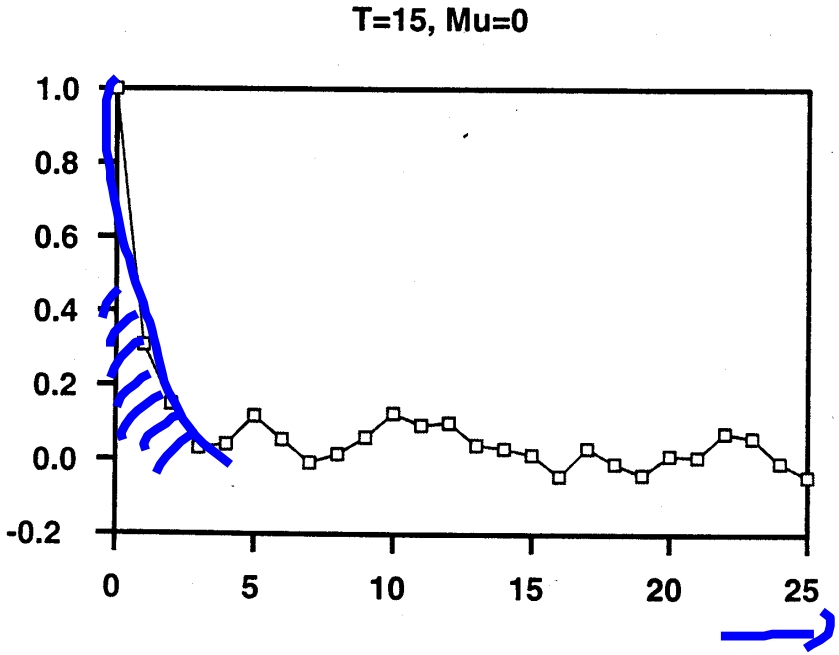
Quality of average gets diluted by correlation time $\sigma_{av}^2 = \frac{<A^2>-<A>^2}{m}(1+2\tau_A)$

Correlation time in Ising models









Size effects

Only important near second order transitions and for phases to "fit" within the periodic boundary conditions

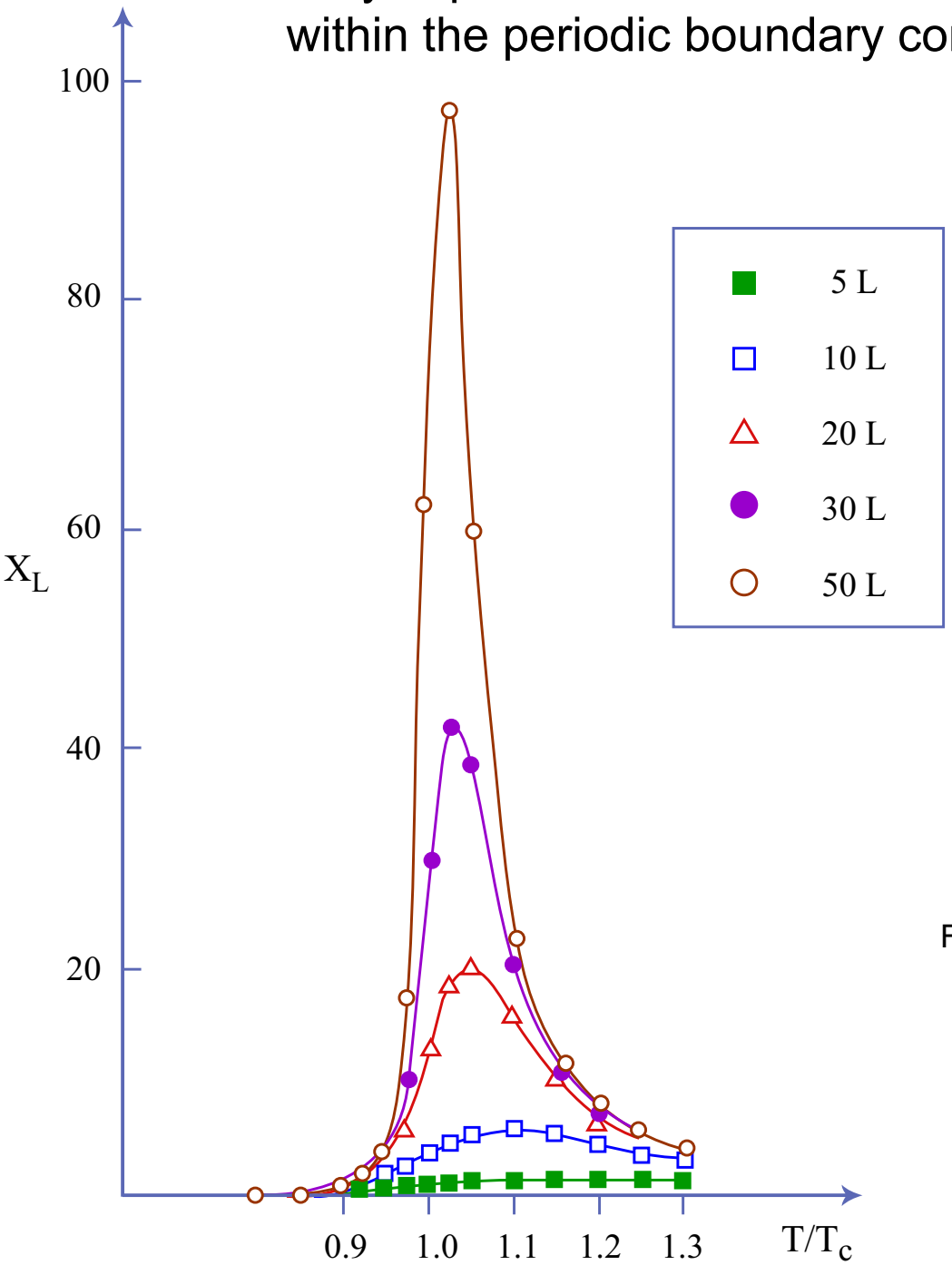


Figure by MIT OCW.

It is your move !

"Dynamics" in Monte Carlo is not real, hence you can pick any "perturbations" that satisfy the criterion of detailed balance and a priori probabilities.

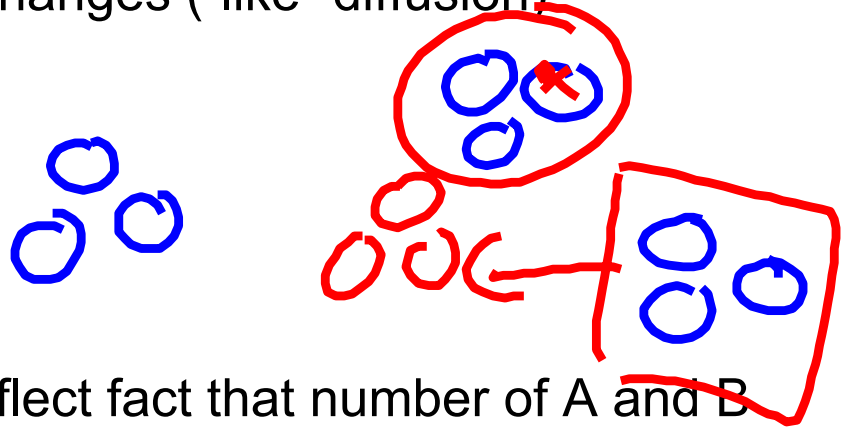
e.g. mixing of A and B atoms on a lattice (cfr. regular and ideal solution in thermodynamics)

Could pick nearest neighbor A-B interchanges ("like" diffusion)

-> Glauber dynamics

Could "exchange" A for B

-> Kawasaki dynamics



For Kawasaki dynamics Hamiltonian needs to reflect fact that number of A and B atoms can change (but A+B number remains the same) -> add chemical potential term in the Hamiltonian

$$H = \frac{1}{2}\sum_{i,j}\left(V^{AB}\left(p_i^A p_j^B + p_i^B p_j^A\right) + V^{AA}\, p_i^A p_j^A + V^{BB}\, p_i^B p_j^B\right) + (\mu_A - \mu_B)\sum_i p_i^A$$

With more difficult system, algorithms that can easily access the low energy states are most efficient

Example: Heisenberg Model: continuously rotating magnetic moment

$$\vec{S}_i = S_i^x \hat{e}_x + S_i^y \hat{e}_y + S_i^z \hat{e}_z.$$

$$\hat{H}_{\text{Heisenberg}} = -\frac{1}{2}\sum_{i \neq j} J_{ij} \vec{S}_i \cdot \vec{S}_j - \sum_i \vec{H} \cdot \vec{S}_i.$$

Coordinates

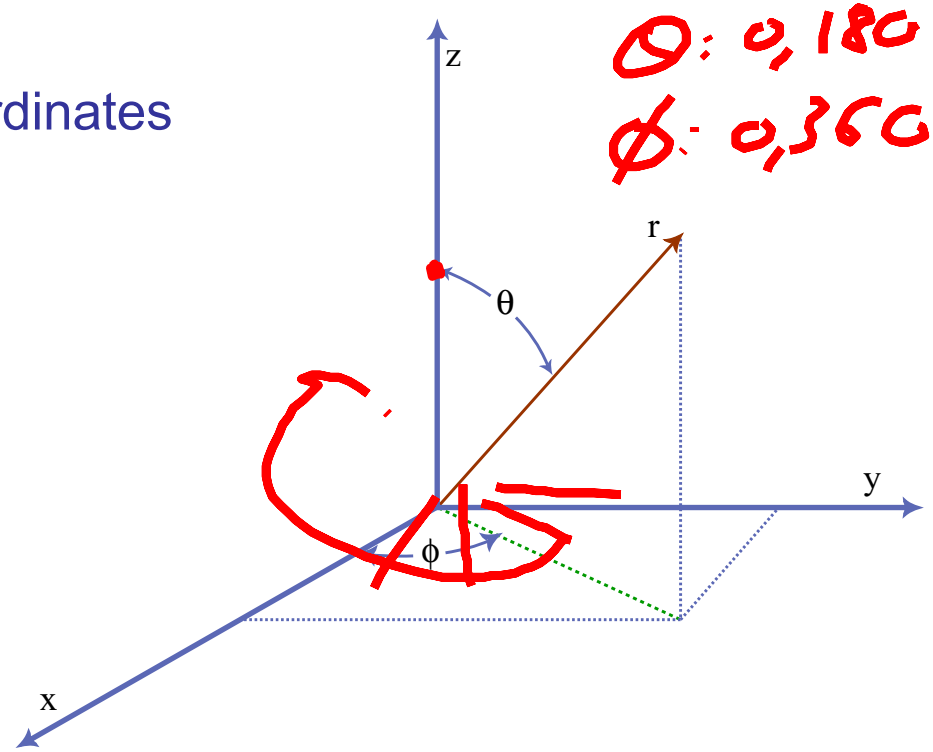
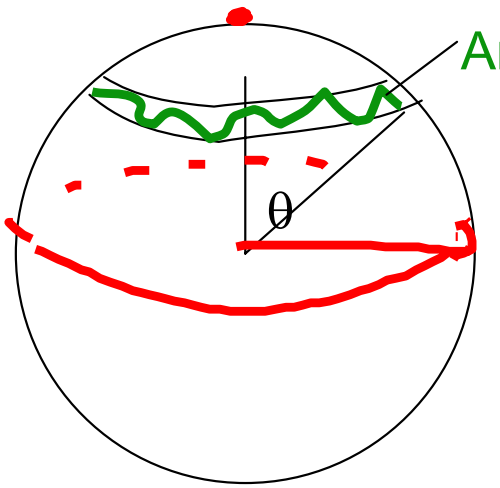


Figure by MIT OCW.

Should I pick θ and ϕ randomly ?

Proper distribution of θ and ϕ

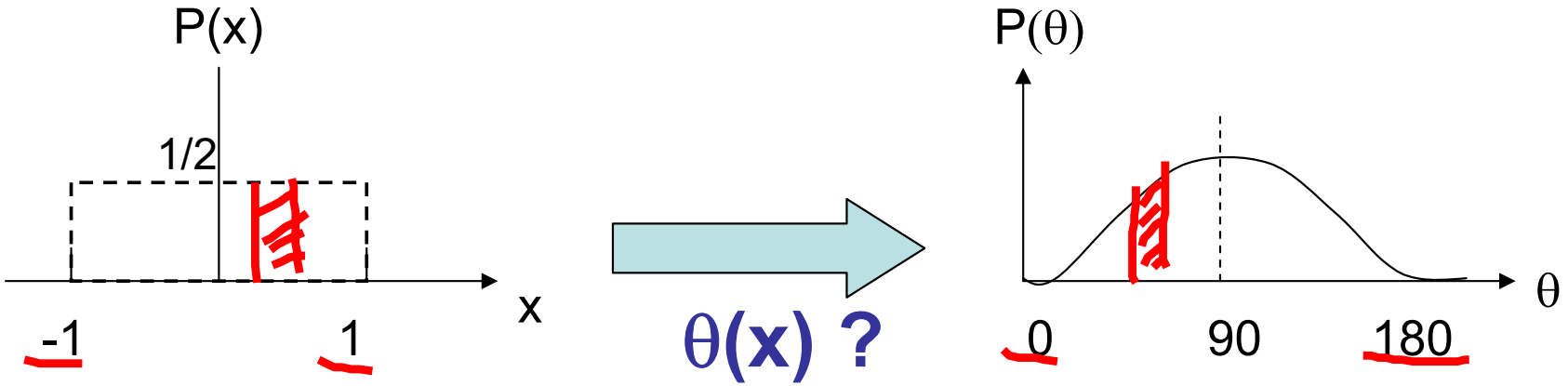
Random distribution of θ and ϕ does not give random distribution of vector orientation in space. For small θ, all ϕ give spin oriented along the z-axis



Area is proportional to $2\pi\sin(\theta)\,d\theta$

Need to pick θ proportional to $\sin(\theta)\,d\theta$

Sampling variables that are not homogeneously distributed in phase space



Homogeneous distribution of random numbers

$\theta = \cos^{-1}(-x)$

Distribute θ as 1/2 sin(θ)

$$P(\theta)\,d\theta = P(x)\,dx$$

$$\tfrac{1}{2}\sin\theta\,d\theta = \tfrac{1}{2}\,dx$$

$$\frac{d\theta}{dx} = \frac{dx}{d\theta} = \sin\theta$$

$$x = -\cos\theta$$

Low Temperature Spin Waves

More efficient to perturb spins slightly by picking their new orientation from a narrow cone around the old orientation

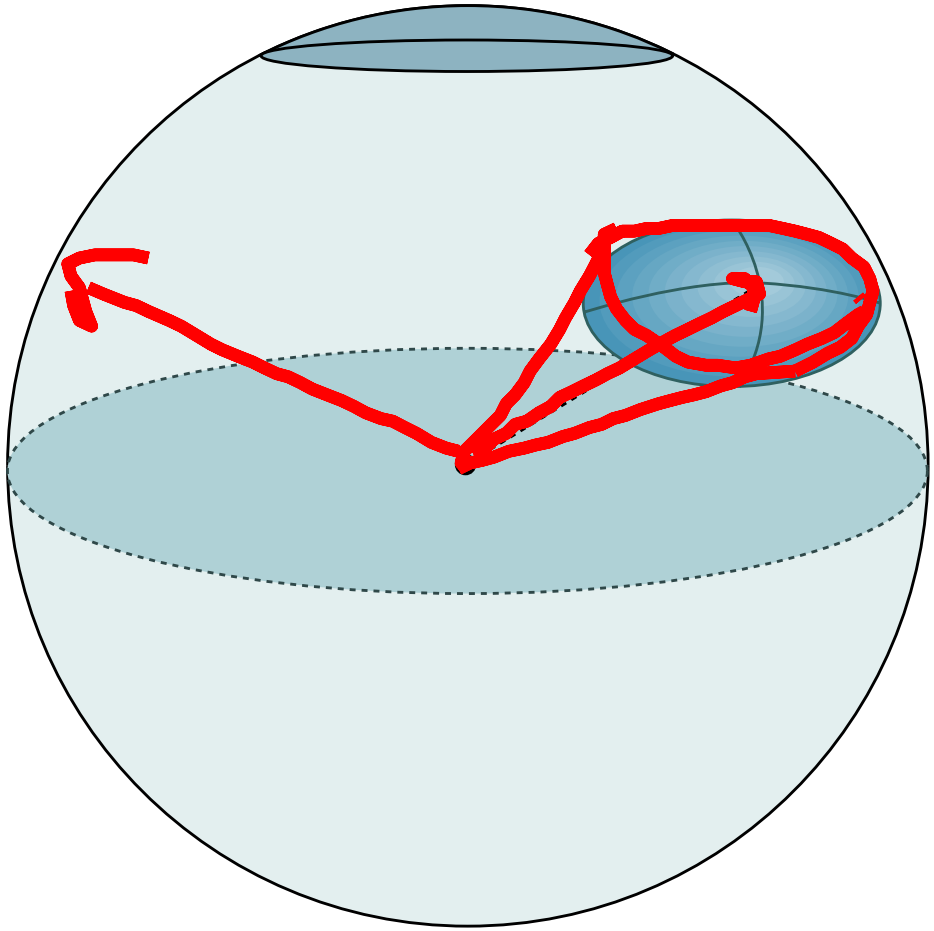
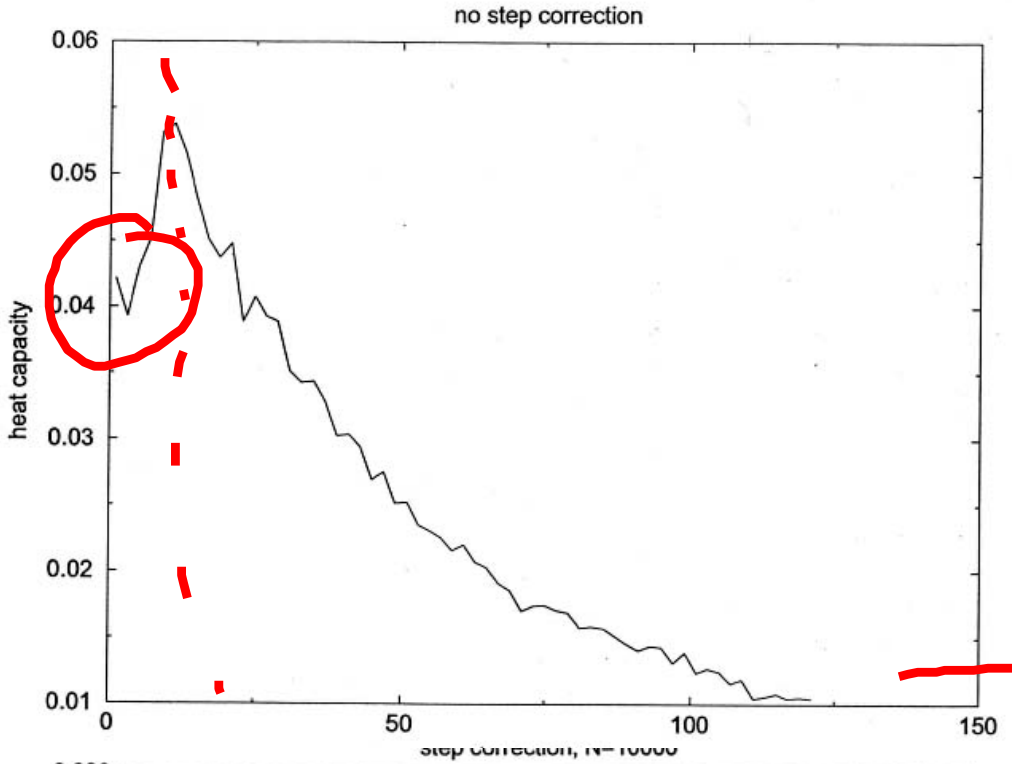
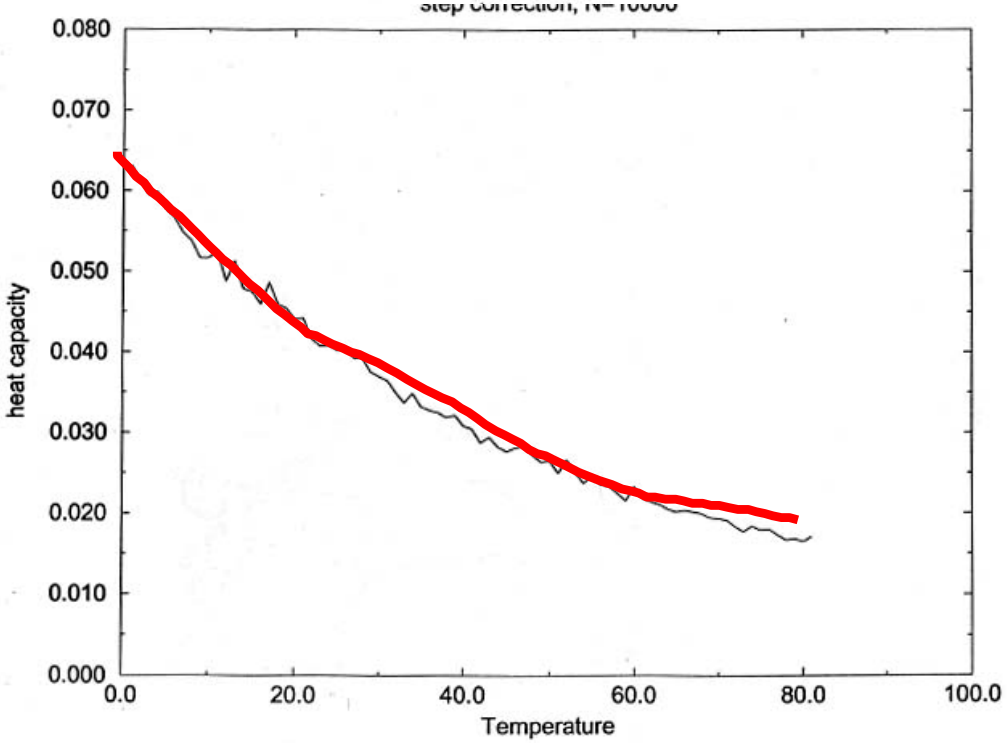


Figure by MIT OCW.


no step correction
heat capacity
0.06
0.05
0.04
0.03
0.02
0.01
0
50
100
150


heat capacity
0.080
0.070
0.060
0.050
0.040
0.030
0.020
0.010
0.000
0.0
20.0
40.0
60.0
80.0
100.0
Temperature

Long chain molecules

Fixed dihedral angle, but still rotation possible

Sample configuration space by sampling possible values of free rotations. Often only small perturbations possible

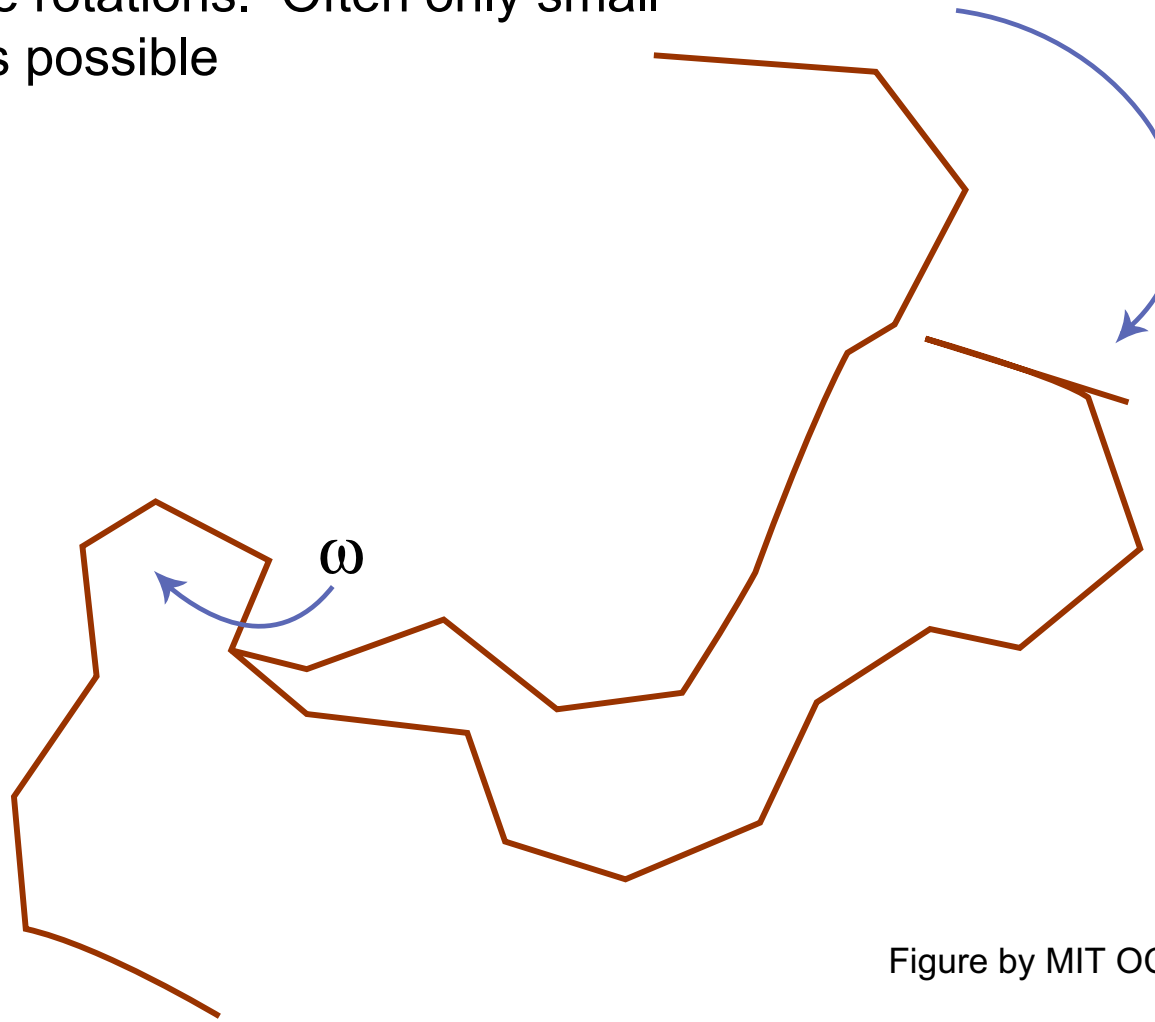
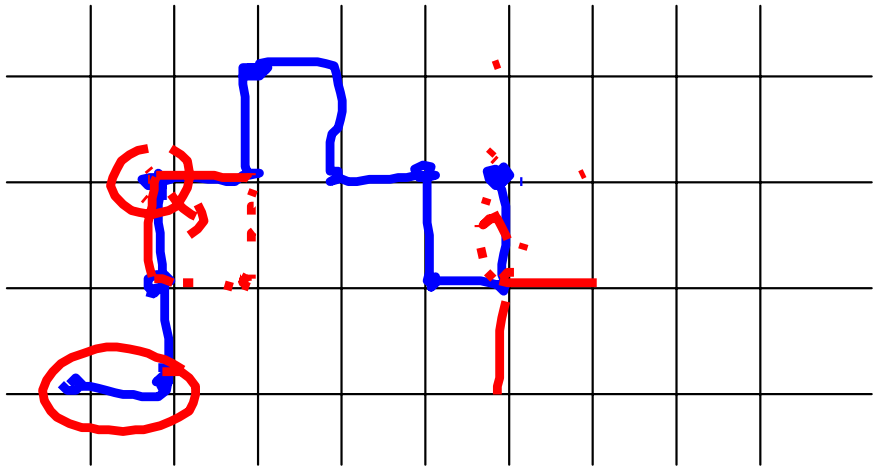
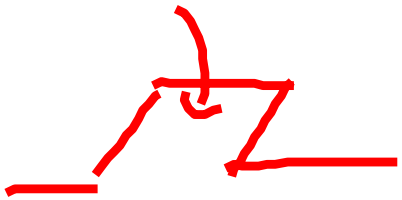


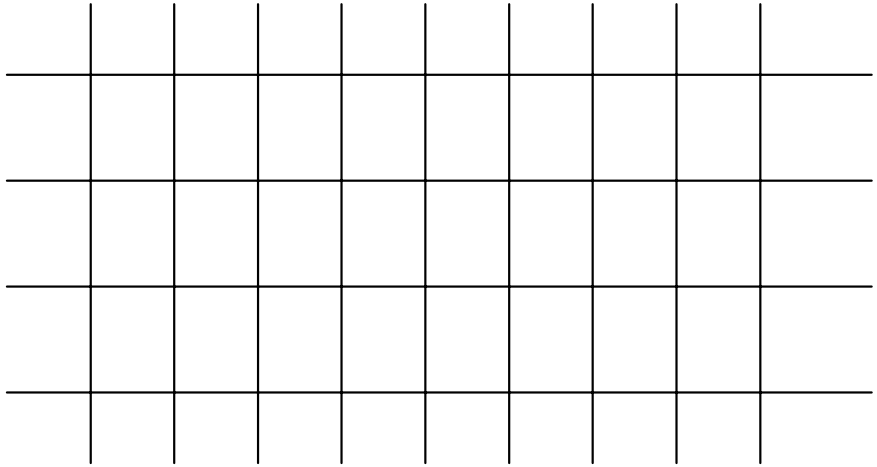
Figure by MIT OCW.

Polymers on a lattice





Possible algorithms ?



Non-Boltzmann sampling and Umbrella sampling

Simple Sampling

Sample randomly

$$< A > \;=\; \sum_{\nu=1}^{M} \frac{\exp(-\beta H_\nu)}{\sum_{\nu=1}^{M} \exp(-\beta H_\nu)} \; A_\nu$$

Importance Sampling

Sample with Boltzmann weight

$$< A > \;=\; \sum_{\nu=1}^{M} A_\nu$$

Non Boltzmann Sampling

Sample with some Hamiltonian H^o

$$< A > \;=\; \frac{\sum_{\nu=1}^{M} \exp(-\beta(H_\nu - H_\upsilon^o)) \; A_\nu}{\sum_{\nu=1}^{M} \exp(-\beta(H_\nu - H_\upsilon^o))}$$

$\Delta H = H - H^o$

[end of this day's lecture…to be continued next lecture.]

Monte Carlo

Advantages

- Conceptually simple
- Easy to implement
- Can Equilibrate any degree of freedom/No Dynamics needed
- Accurate Statistical Mechanics

Disadvantages

- No Kinetic Information
- Requires many Energy Evaluations
- Stochastic nature gives noise in data
- Not easy to get entropy/free energy

References

D. Frenkel and B. Smit, "Understanding Molecular Simulation", Academic Press.

Fairly recent book. Very good background and theory on MD, MC and Stat Mech. Applications are mainly on molecular systems.

M.E.J. Newman and G.T. Barkema, "Monte Carlo Methods in Statistical Physics"

K. Binder and D.W. Heerman, "Monte Carlo Simulation in Statistical Physics"