3.320: Lecture 17 (4/7/05)

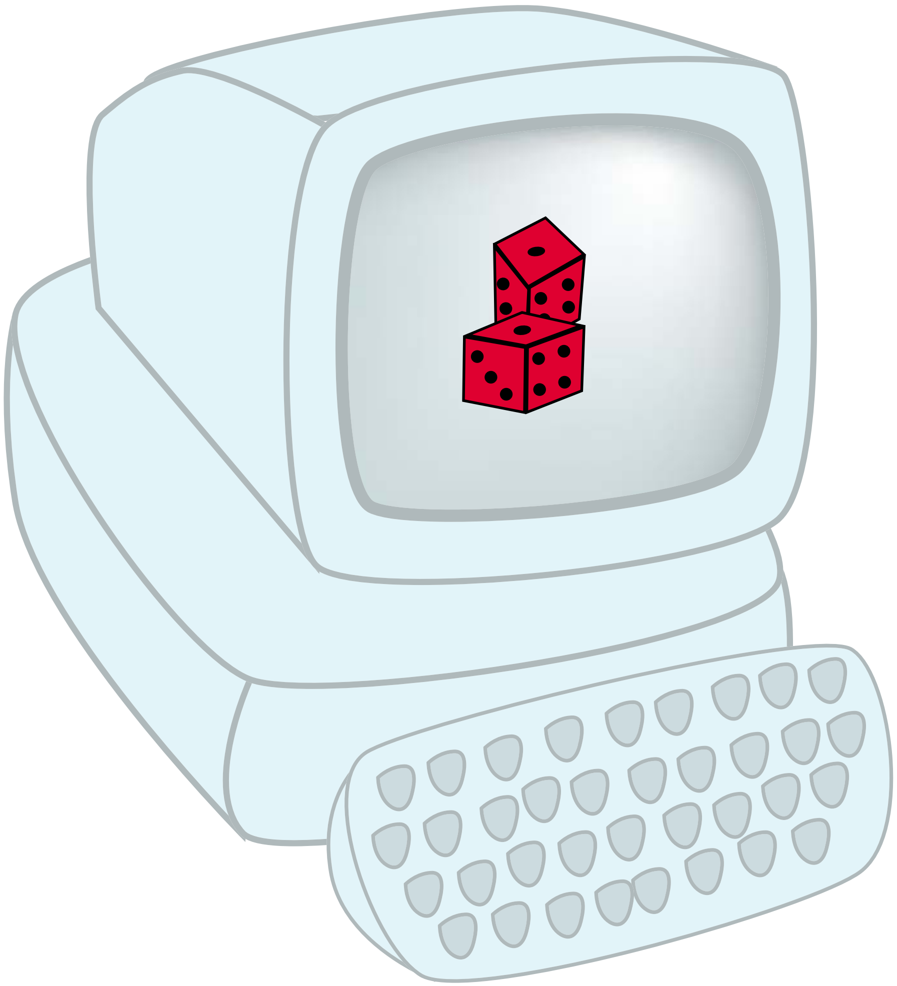


Figure by MIT OCW.

Monte Carlo Simulation, and some Statistical Mechanics to entertain …

Thurs, 31 Mar	Molecular Dynamics III.
Tues, 5 Apr	**Lab 4**: Molecular Dynamics.
Thurs, 7 Apr	Monte Carlo simulations: Application to lattice models, sampling errors, metastability.
Tues, 12 Apr	Coarse graining: Alloy theory.
Thurs, 14 Apr	Alloy Theory II, free energy integration. Show different ways of integration (lambda, temperature, field, particle, potentials).
Tues, 19 Apr	**Patriots Day: MIT Vacation**
Thurs, 21 Apr	Case Studies Nanotubes and High Pressure
Tues, 26 Apr	**Lab 5:** Monte Carlo (offline)
Thurs, 28 Apr	Hyperdynamics and Case Studies
Tues, 3 May	Green Kubo
Thurs, 5 May	Modeling in industry (Chris Wolverton from Ford Motor Company)
Tues, 10 May	Case Studies III
Thurs, 12 May	Conclusions (G C)

Time or (Phase) Space

In MD system is followed in time

$$U = \frac{1}{t}\int_0^t E(\tau)\,d\tau$$

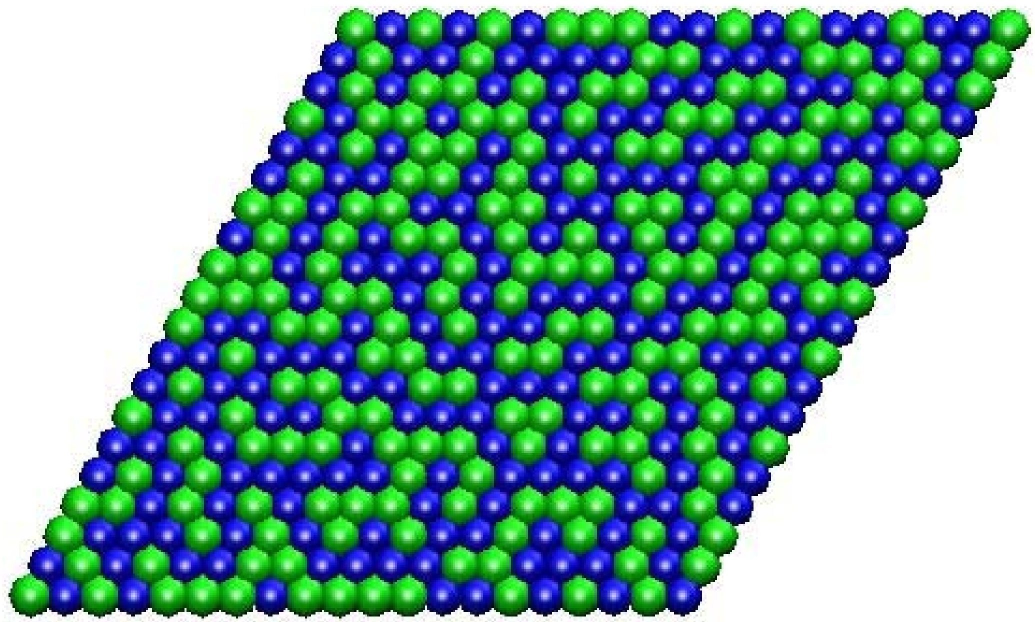
$$V = \frac{1}{t}\int_0^t V(\tau)\,d\tau$$

Macroscopic properties such as energy and volume can be calculated as averages over the simulation

Average only includes phenomena that occur in the time scale of the MD simulation.

If we want averaged properties over long-time, statistical sampling may be more efficient.

Example of Time Scale Problem: Intermixing



To average the energy, system would have to go through many configurations in the simulation

-> Diffusion required

Estimate Diffusion constant required to get significant number of atom exchanges

$$\frac{\partial}{\partial t}\left\langle \underbrace{r^2(t)}_{Na^2} \right\rangle = 2dD$$

Assume random walk

$$\frac{\partial N a^2}{\partial t} = 2dD$$

$$\Gamma a^2 = 2dD$$

$$D = \frac{\Gamma a^2}{2d}$$

What does this mean for the activation barrier ?

$$\boxed{\Gamma \approx \nu \exp\left(\frac{-E_a}{kT}\right)}$$

Assume ν is vibrational frequency ≈ 10^{13} Hz

To get Γ of 10^{10} Hz:

$$\exp\left(\frac{-E_a}{kT}\right) > 10^{-3}$$

$$-E_a > kT\ln(10^{-3})$$

$$\boxed{E_a < 6.9kT}$$

T = 300 K	6.9kT = 180 meV
T = 1000K	6.9kT = 590 meV

Thermal averaging rather than dynamics

If long-time averages is all you care about, and excitations of the system are beyond the time scale of Molecular Dynamics, it may be better to use statistical sampling methods such as Monte Carlo

IDEA

Try to obtain a sample of microscopic states that is statistically significant for the long-time averages

A short review of statistical mechanics and its relation to thermodynamics …

A short review of statistical mechanics and thermodynamics

Questions to be answered

- *How to go from microscopic description to macroscopic behavior/variables ?*
- *How do macroscopic constraints/environments relate to simulation approach ?*

This is important, because certain macroscopic conditions, correspond to fixing the averages of microscopic quantities

Example: role of H in catalysis on Pd

Does H sit on the surface of Pd or subsurface ? How investigate ?

A short review of statistical mechanics and thermodynamics

Ensemble.

MICROSCOPIC (atoms, electrons, …)	Statistical Mechanics ⟷	MACROSCOPIC Thermodynamics
Sample with certain constraints		Fixed Thermodynamic Variables

Macroscopic conditions (constant volume, temperature, number of particles, …) translate to the microscopic world as boundary conditions (constraints).

Microscopic system is defined by the extensive variables that are constant in the macroscopic world. E.g. (E,V,N), (V,N) …

The probability distribution for the microscopic system and its Hamiltonian are related to the macroscopic free energy function

Conjugate Variables. Do you prefer Energy or Entropy ?

In the **energy** formulation, the conjugate variable pairs can be identified from the work terms in the first Law of thermodynamics: (T,S), (-p,V), (μ,N), …

There is one **Extensive** variable and one **Intensive** variable

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

Always need to specify one of these !

In statistical mechanics it is sometimes easier to use the **entropy** formulation, simply obtained by rearranging the first law. In this formulation the conjugate pairs are (1/T, U), (-p/T, V), …

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

Thermodynamic quantities are averages over relevant set of microscopic states

Ensemble is the collection of all possible microscopic states the system can be in, given the thermodynamic (macroscopic) boundary conditions.

E(E,V,N) -> micro canonical: *e.g. Newtonian system in box with elastic walls.*

E(T,V,N) -> canonical ensemble: *e.g. Newtonian system in a box with non-elastic walls (walls equilibrated at temperature T)*

E(T,V,μ) -> grand canonical ensemble: *e.g. open system*

…

…get ready for the grand moment

How to average over the ensemble ?

Average (i.e. macroscopic) quantities can be obtained by suitable averaging of the properties of the microscopic states in the ensemble, rather than as a time average over a dynamic trajectory.

Of course, the key is to average with the correct weights:
Probability that a system is in particular microstate

$\beta = \frac{1}{kT}$

$$P_\nu = \frac{\exp(-\beta H_\nu)}{\sum_{\nu \in e} \exp(-\beta H_\nu)}$$

$$Q = \sum_{\nu \in e} \exp(-\beta H_\nu)$$

Hamiltonian is relevant Legendre transform of the entropy

$$F = -\frac{1}{\beta} \ln(Q)$$

Example: Fixed N,V,T: -F/T = S – <E>/T

$$P_\nu = \frac{\exp(-\beta E_\nu)}{\sum_{\nu \in \varepsilon} \exp(-\beta E_\nu)}$$

Example: Fixed μ,V,T: -F/T = S – <E>/T + μ /T

$$P_\nu = \frac{\exp(-\beta(E_\nu - \mu N))}{\sum_{\nu \in \varepsilon} \exp(-\beta(E_\nu - \mu N))}$$

Summary: In case you can't see the trees anymore …

Macroscopic Boundary Conditions

Constant Thermodynamic Variables

Relevant Ensemble

$$P_\nu = \frac{\exp(-\beta H_\nu)}{\sum_{\nu \in e} \exp(-\beta H_\nu)}$$

Averages

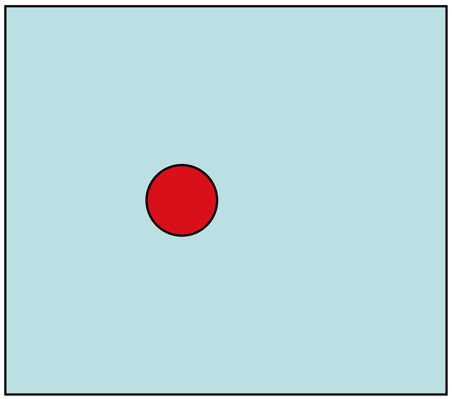
$$U = \sum_{\nu \in e} P_\nu E_\nu$$

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

$$\textbf{magnetic moment} = \sum_{\nu \in e} P_\nu \textbf{magnetic moment}_\nu$$

Can get averages without need for dynamics !

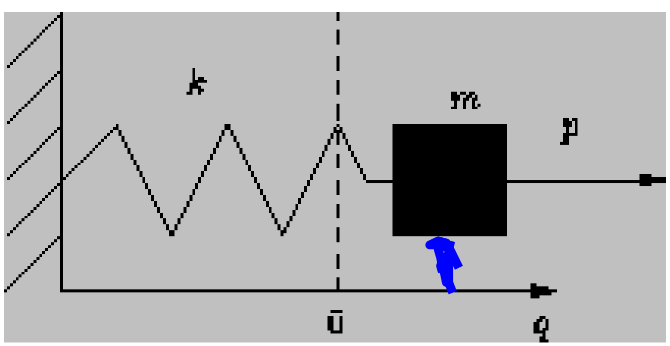
The catch: Ergodicity and time scales

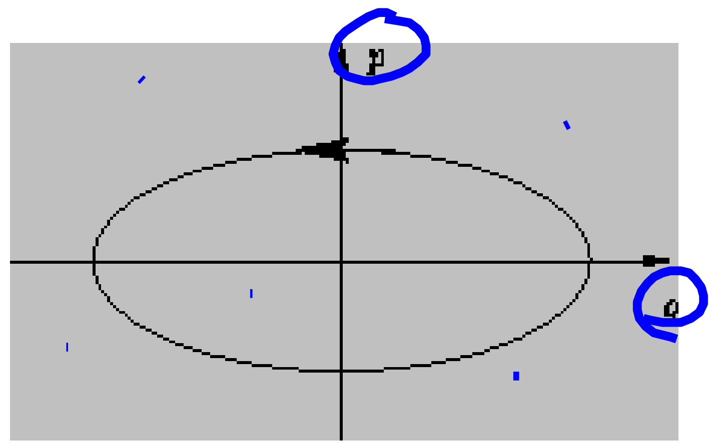


Coordinates: r and p

-> integrate over its phase space ?

But if …





Coordinates and Ergodicity

Harmonic oscillator is not ergodic in phase space of (r,p).

Of course, we know there is only one coordinate when system is quantized -> amplitude of normal mode (n)

Some systems are "not ergodic" on normal time scales, but would be if one waited long enough (eons). E.g. glasses.

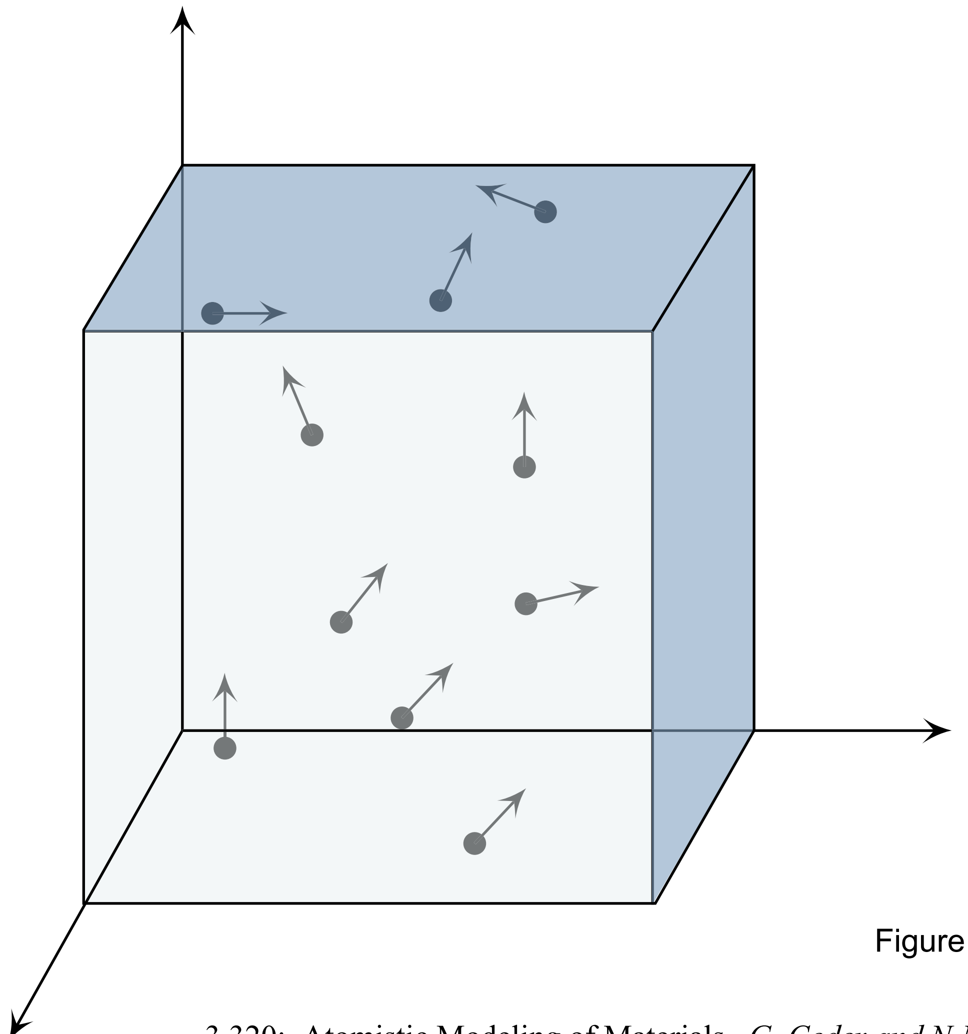
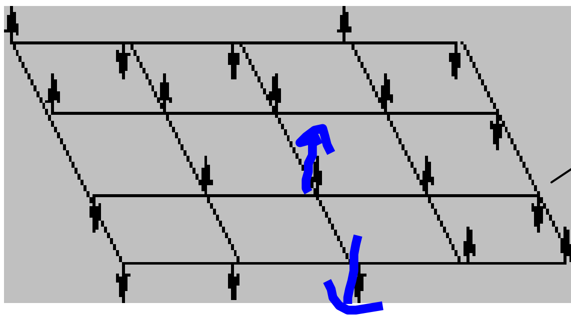


Figure by MIT OCW.

By now, you must be quite anxious: Monte Carlo Simulation (Finally …)

But first, a model system: The Ising Model



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

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

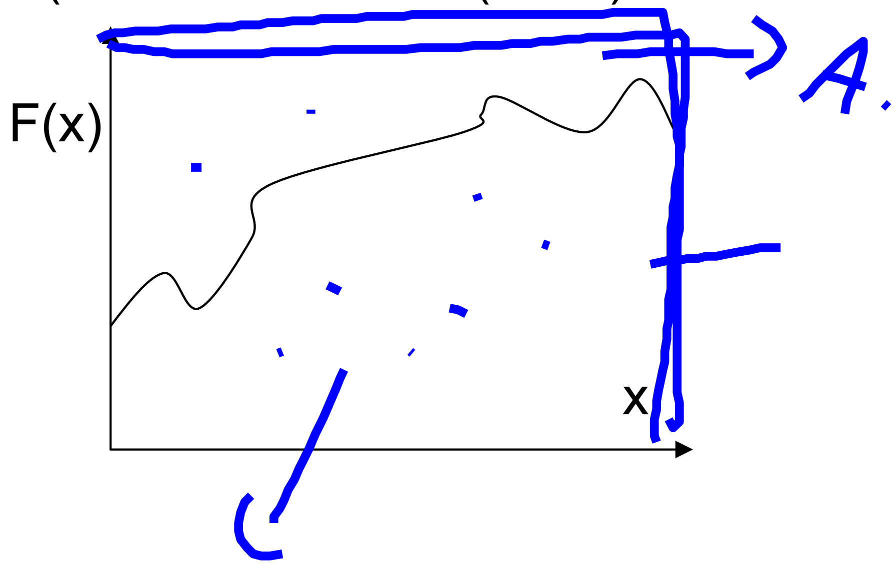
When J > 0, ferromagnetic behavior; when J < 0 Anti-ferro

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

The Monte Carlo Method: Do you take it *simple* or *important* ?

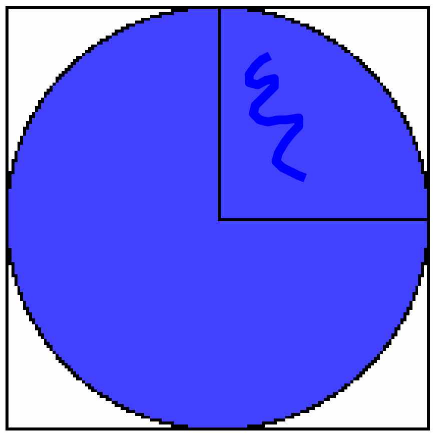
Modern form originated with Ulam and Segré in Los Alamos and the ENIAC computer (but really goes back to Fermi)

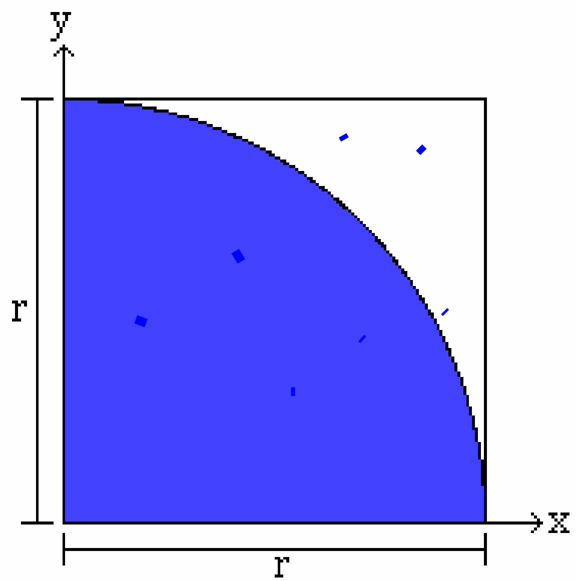
Before that “sampling” was used a method for integration of functions (Comte de Buffon (1777).



N times below curve = $\frac{I}{\text{total area}}$.

How about some Pi(e) ?





$$\frac{\#\ \text{darts hitting shaded area}}{\#\ \text{darts hitting inside square}} = \frac{\frac{1}{4}\pi r^2}{r^2} = \frac{1}{4}\pi$$

or

$$\pi = 4\,\frac{\#\ \text{darts hitting shaded area}}{\#\ \text{darts hitting inside square}}$$

Simple sampling for materials

A suggestion:

Pick M states randomly from ensemble, and calculate average property as:

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

$$P_\nu = \frac{\exp(-\beta H_\nu)}{\sum_{\nu=1}^{M} \exp(-\beta H_\nu)}$$

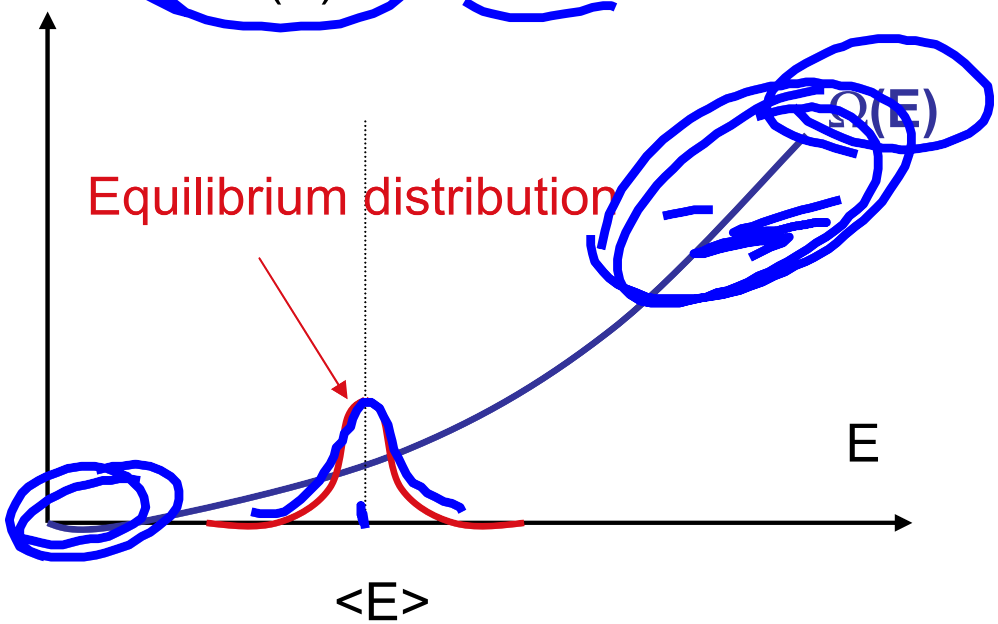
Simple sampling (i.e. economists use it sometimes)

Simple sampling does not work, because one picks mainly states with low weight in the true partition function. (i.e. states with high energy).

Simple sampling for the Ising model

Energies occur proportional to their multiplicity: $S(E)/k = \ln(\Omega(E))$,

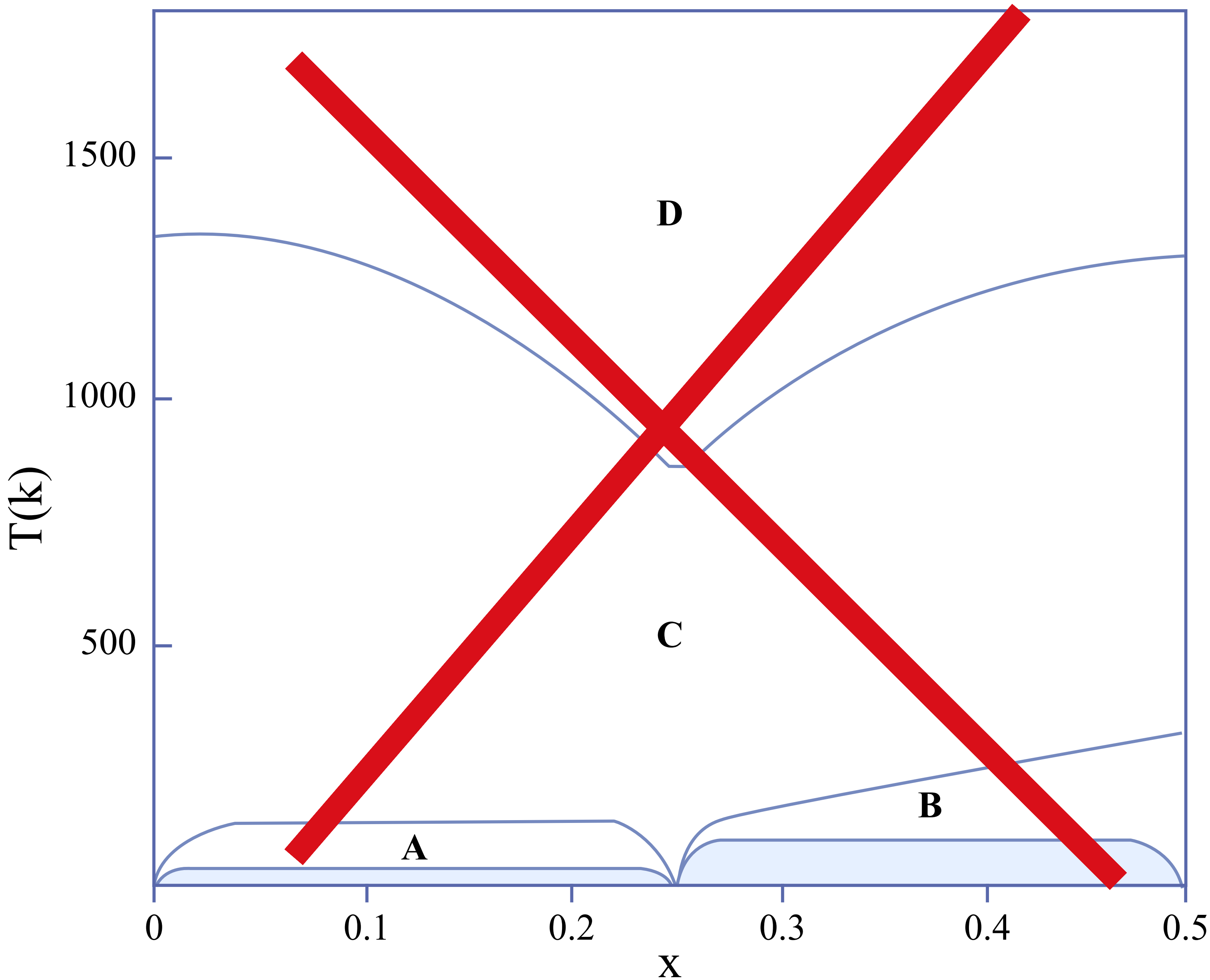
and $d\ln\Omega(E)/dE = 1/kT > 0$



In lattice model all states would have almost no net magnetization …

Even smart people make mistakes

Images removed for copyright reasons.
Portions of paper published in Physical Review B, 1998.



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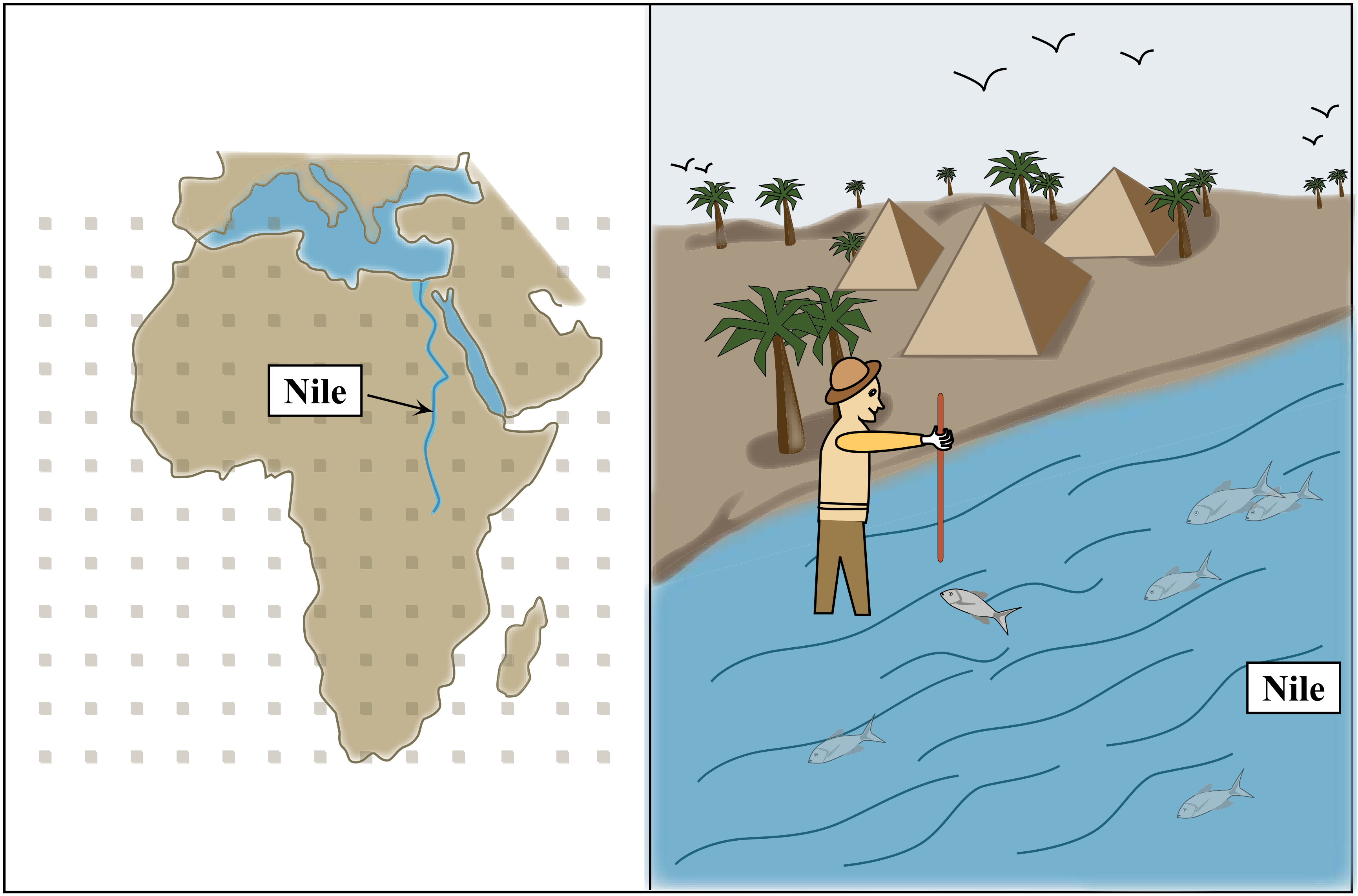


Figure by MIT OCW.

Source: Frenkel, D., and B. Smith. *Understanding Molecular Simulation.* Academic Press.

And now for the *Important* part: Picking states with a biased probability: Importance Sampling

Can we pick states from the ensemble with a probability proportional to exp (-βE) ? Rather than picking random and later weighing them by a probability.

Random sample

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

Probability weighted sample

How to construct probability-weighted sample ?

Metropolis algorithm

"walks" through phase space (Markov chain of states) visiting each state with proper probability (in the infinite time limit)

- Random starting state i
- Pick trial state j from i with some rate $W^o_{i\to j}$
- Accept j with some probability $P_{i\to j}$

Conditions for generating proper probability distribution

*Equal a-priori probabilities: $W^o_{i\to j} = W^o_{j\to i}$

*Detailed Balance: $\boxed{P_i W_{i\to j} = P_j W_{j\to i}}$ $\frac{W_{i\to j}}{W_{j\to i}} = \frac{P_j}{P_i}$

When $W^o_{i\to j}$ and $P_{i\to j}$ satisfy the above criteria, the Metropolis algorithm will produce an equilibrium distribution.

PROOF

Ensemble of systems. To have stable (equilibrium) proportion of number of systems in each state, need:

$$\sum_j P_i P_{i\to j} = \sum_j P_j P_{j\to i}$$

A typical Metropolis algorithm (but not at all the only possible one)

$w_{i \to j}$

$$P_{i\to j} = 1 \quad \textbf{when} \quad E_j < E_i$$

$$P_{i\to j} = \exp(-\beta(E_j - E_i)) \quad \textbf{when} \quad E_j > E_i$$

Downhill moves always accepted, uphill moves with some "thermal-like" probability

$P_i P_{i\to j} = P_j P_{j\to i} \quad \| \quad \frac{\exp(-\beta E_i)}{Z} \cdot 1 = \frac{\exp(-\beta E_j)}{Z} \, \mathrm{ex}$

$\exp(-\beta(E_i - \cancel{E_j}))$

Put it all together: A Monte Carlo Algorithm

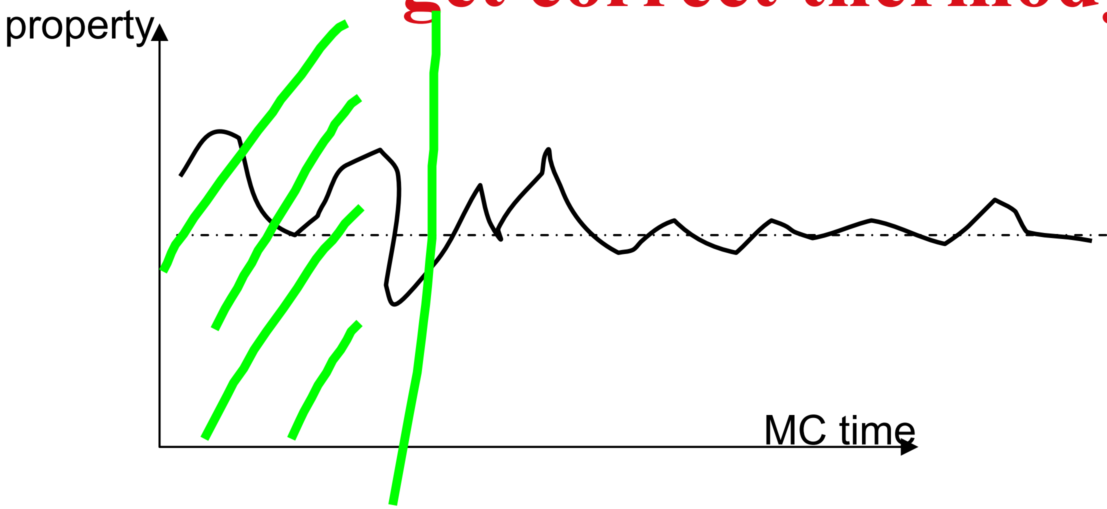
1. Start with some configuration
2. Choose perturbation of the system
3. Compute energy for that perturbation

4. If $\Delta E < 0$ –> accept perturbation

   If $\Delta E > 0$ –> accept perturbation, accept perturbation with probability $\exp\left[\frac{-\Delta E}{kT}\right]$
5. Choose next perturbation

Property will be average over these states

Monte Carlo "trajectory' can be averaged over to get correct thermodynamic averages



Note: trajectory is not a dynamical trajectory, only an efficient way to sample phase space.

Example 1: The Ising Model

Which perturbation ? Pick spin and flip over

1. Start with some spin configuration

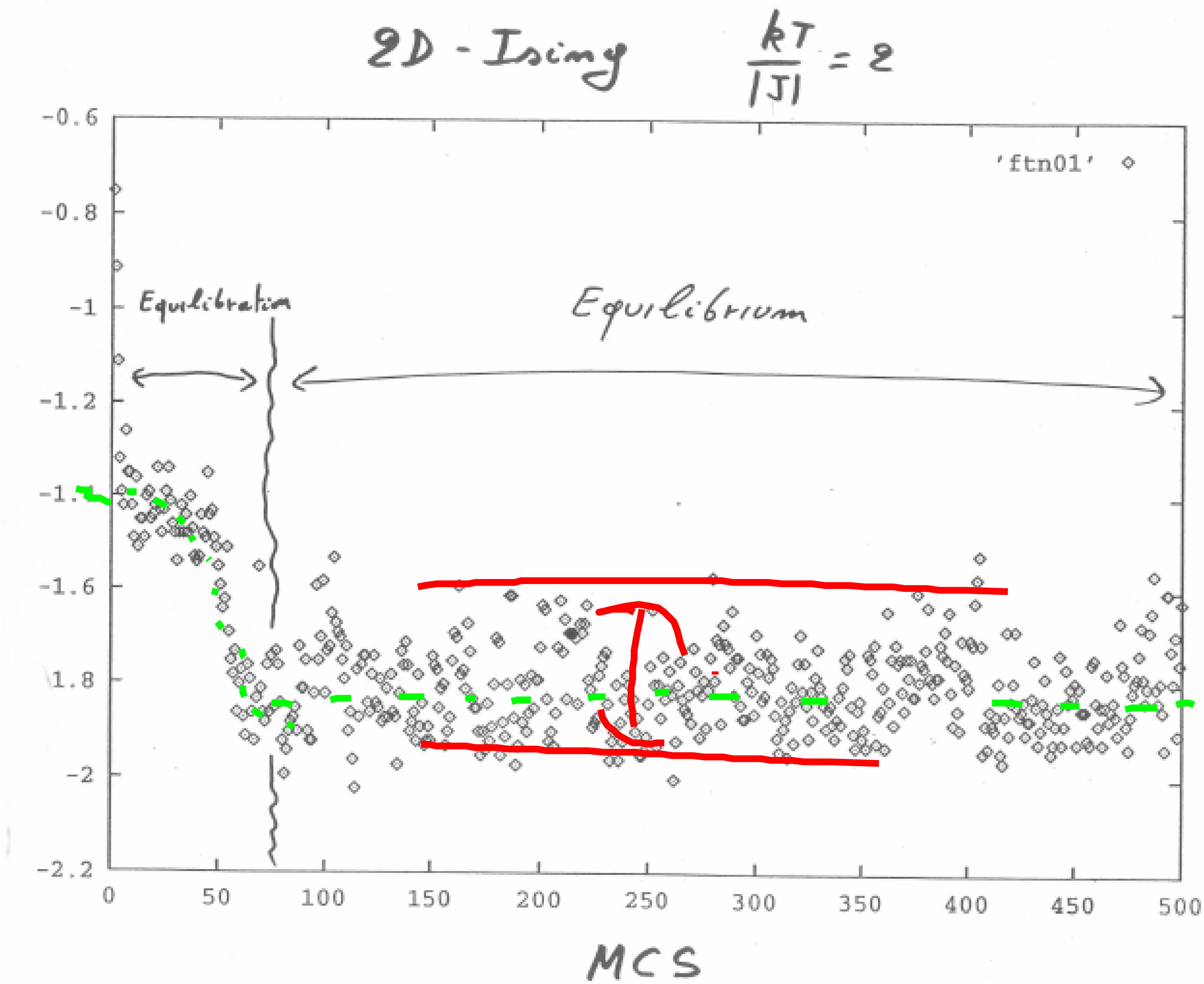
2. Randomly pick a site and consider flipping the spin over on that site

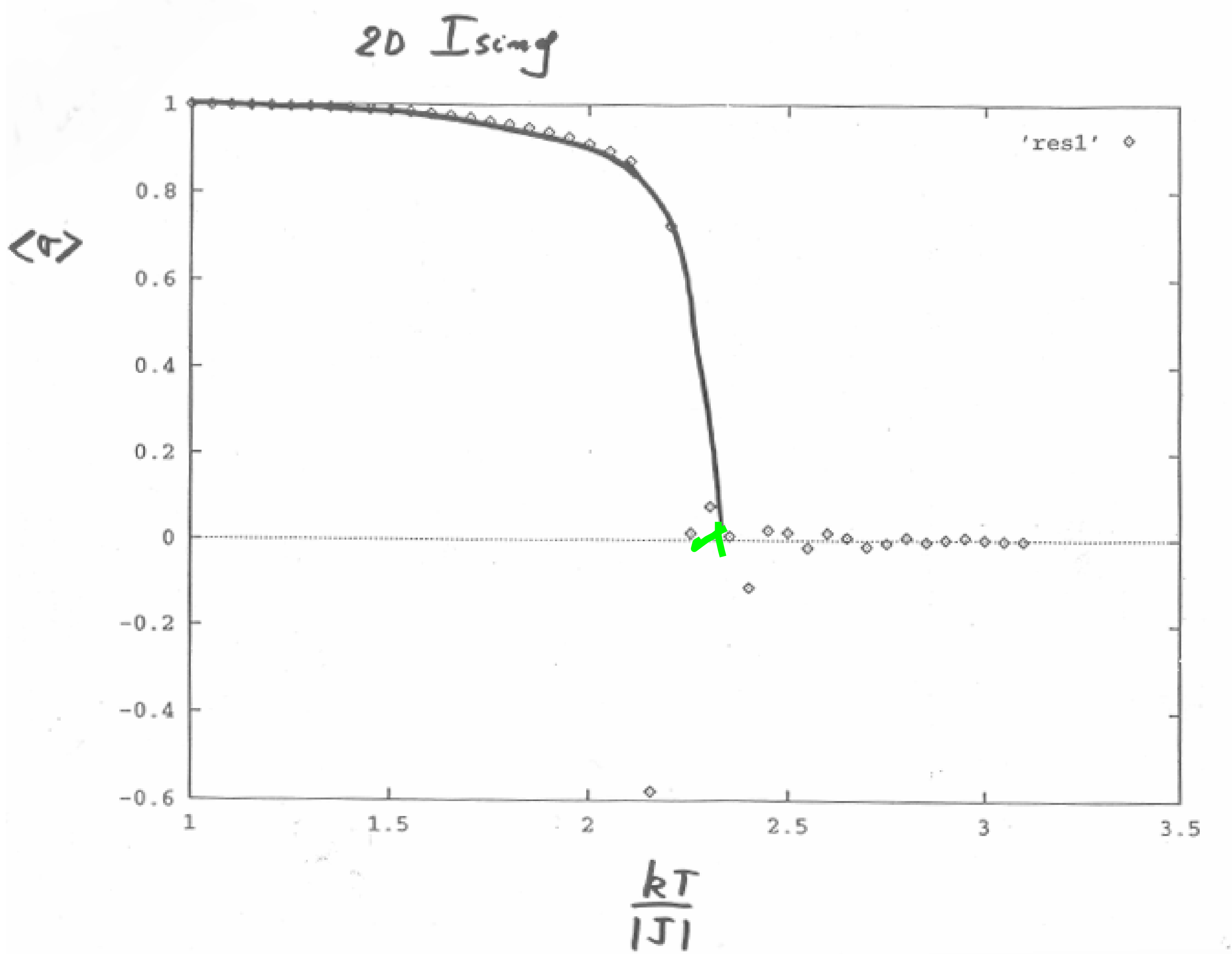
3. Compute energy for that perturbation

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

Trajectory for the Energy





2D Ising
<σ>
'res1'
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
1
1.5
2
2.5
3
3.5
kT / |J|

Detecting phase transitions

Look at physical properties (just like for a real system !)

- Energy discontinuity indicates first order transition
- Concentration discontinuity (when working at constant chemical potential indicates first order transition.
- Heat capacity: is infinite at first order transition (but is difficult to spot)

  has log-like infinite singularity for second order transitions

$$C = \frac{1}{N}\left(\frac{\partial U}{\partial T}\right) = \frac{1}{N}\frac{\langle E^2\rangle - \langle E\rangle^2}{kT^2} \longrightarrow$$

Can be obtained from energy distribution

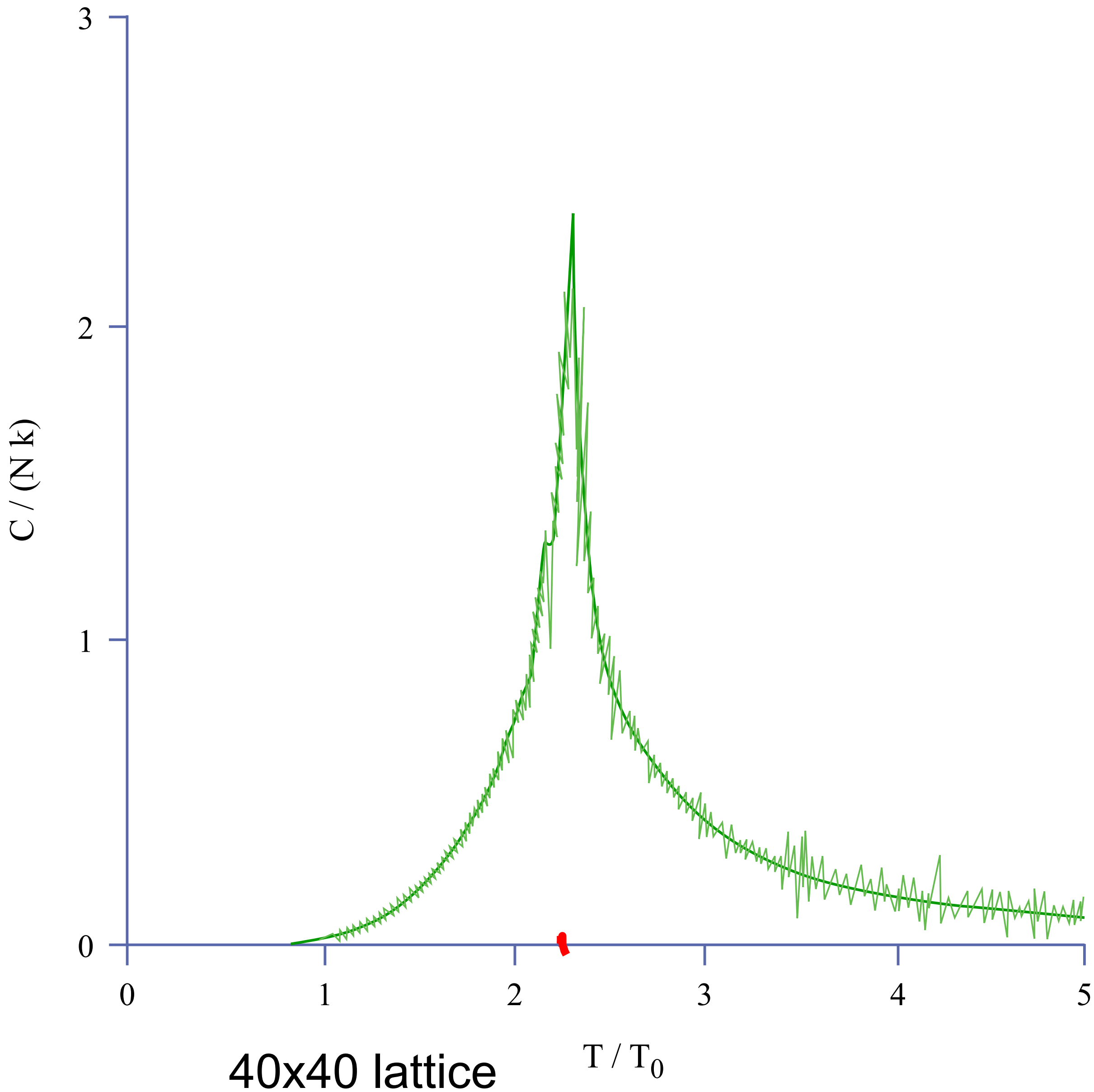


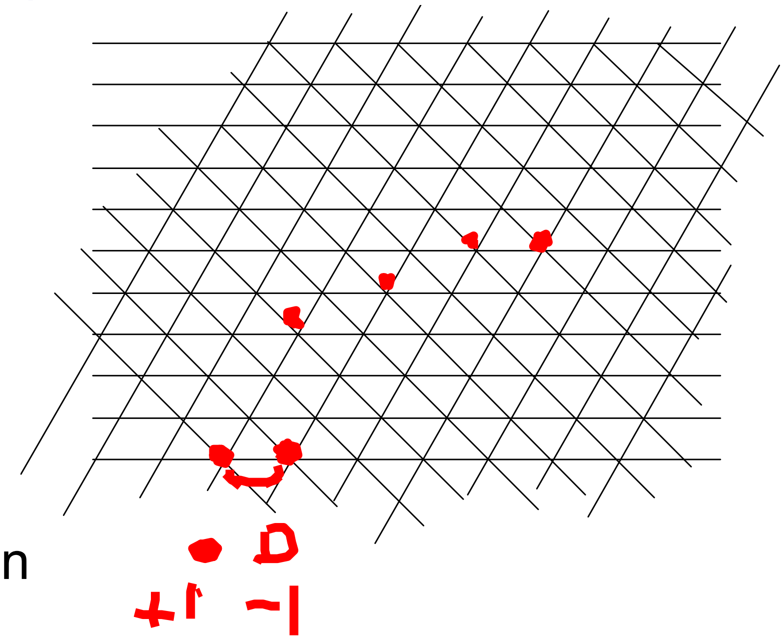
Figure by MIT OCW.

40x40 lattice

If you want to see and play with an Ising model, go to:
http://bartok.ucsc.edu/peter/java/ising/ising.html

Relevance of Ising model for other fields

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



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

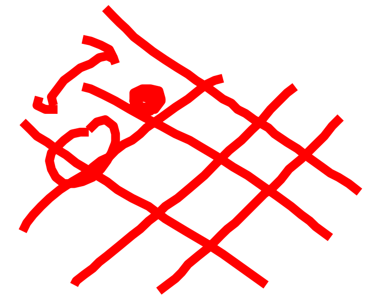
p_i = 1 when site is occupied, =0 when not

Spin can indicate whether a site is occupied by an A or B atom -> model for binary solid mixtures

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

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

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

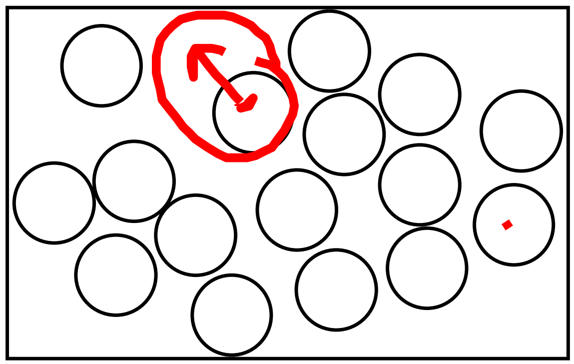
Transfer to spin notation

$$\sigma_i = 2p_i^A - 1 \quad or \quad p_i^A = \frac{(1+\sigma_i)}{2} \; ; \; p_i^B = \frac{(1-\sigma_i)}{2}$$

Lattice model for mixing and lattice model for surface adsorption become equal to Ising-like spin model

One can do Monte Carlo on any Hamiltonian

e.g. liquid



Which perturbations to pick ?

Anything consistent with the degrees of freedom of the system

Δx $\quad -a/2 \quad +a/2$

Δy

Δz

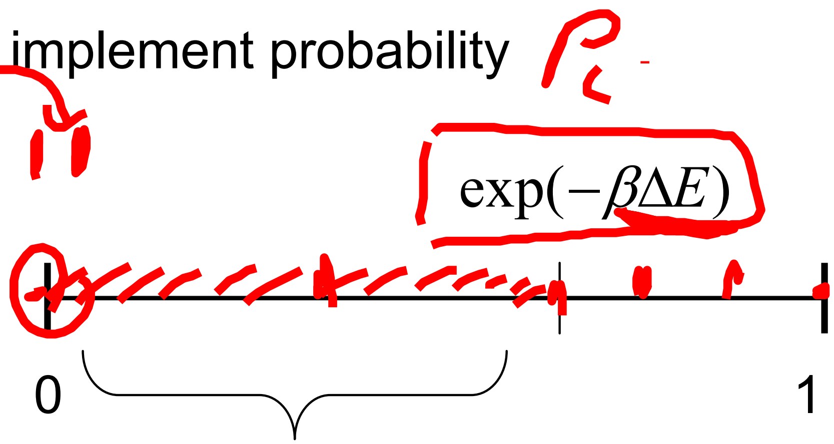
1) randomly pick an atom
2) displace by some random amount between two limits
3) compute $\Delta E = E_{new} - E_{old}$
4) if $\Delta E < 0$ accept perturbation

if $\Delta E > 0$ accept perturbation with probability $P_i \propto \exp\left(-\frac{\Delta E}{k_B T}\right)$

Random numbers

Needed or random picking of perturbations (e.g. which spin to flip or how much to displace an atom in the liquid)

Needed to implement probability



$$P\left[rand(0,1) < \exp(-\beta\Delta E)\right] = \exp(-\beta\Delta E)$$

Quite difficult to get truly random numbers

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"