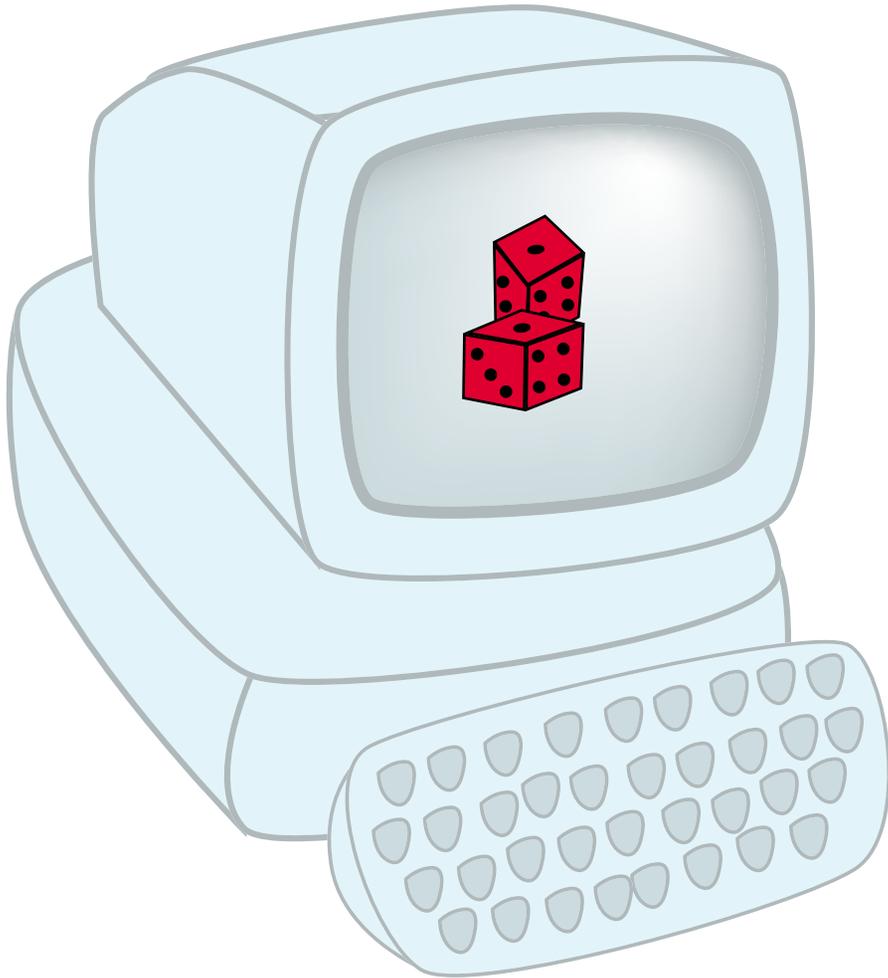


3.320: Lecture 17 (4/7/05)



Monte Carlo Simulation,
and some Statistical
Mechanics to entertain ...

Figure by MIT OCW.

Thurs , 31 Mar	Molec ular Dynamics III .
Tues, 5 Apr	La b 4 : Molec ular Dyna mics.
Thurs , 7 Apr	MonteCar lo simu lat ions: Applica ti on to latt ice m odels, sam pling error s, meta sta bilit y.
Tues, 12 Apr	Coar se gr a ining: Allo y th eor y.
Thurs , 14 Apr	Alloy The ory II , fr ee en erg y int egrat ion . Show diff erent ways of integr ation (la mb da , te mper ature , field, part icle, pote ntia ls).
Tues, 19 Apr	Pa tr io ts Day: MIT Va cat ion
Thurs , 21 Apr	Ca se St udies Na not ube s and High Pressu re
Tues, 26 Apr	La b 5 : MonteCar lo (off line)
Thurs , 28 Apr	Hyperd ynami cs and Ca se St udies
Tues, 3 May	Gree n Kubo
Thurs , 5 May	Modeling in ind us try (Chr is Wolvert on fr om Ford Motor Company)
Tues, 10 May	Ca se St udies III
Thurs , 12 May	Conc lusions (G C)

Time or (Phase) Space

In MD system is followed in time

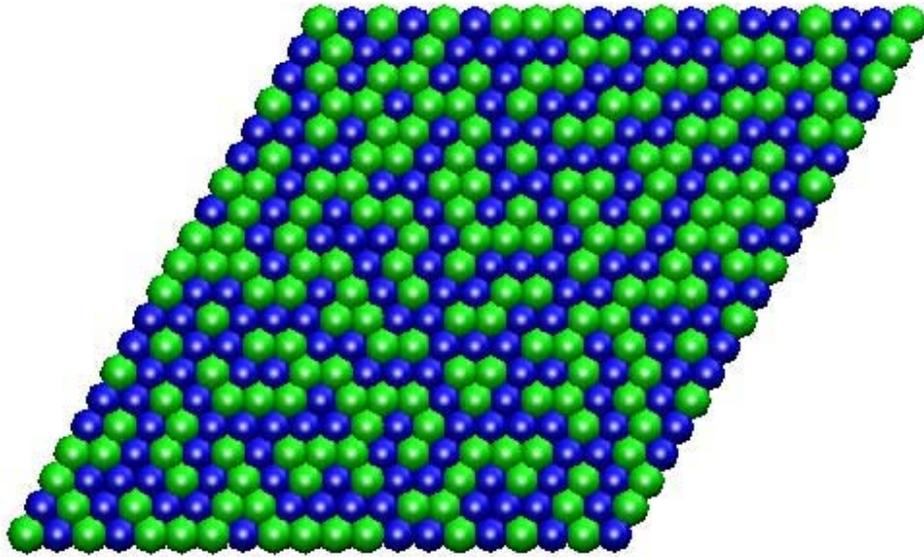
$$U = \frac{1}{t} \int_0^t E(\tau) d\tau$$
$$V = \frac{1}{t} \int_0^t V(\tau) d\tau$$

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



Estimate Diffusion constant required to get significant number of atom exchanges

$$\frac{\partial}{\partial t} \langle r^2(t) \rangle = 2dD$$

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

-> **Diffusion required**

Assume random walk

$$\frac{\partial Na^2}{\partial t} = 2dD$$

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

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

What does this mean for the activation barrier ?

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

Assume ν is vibrational frequency $\approx 10^{13}$ Hz

To get Γ of 10^{10} Hz:

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

$$T = 300 \text{ K} \quad 6.9kT = 180 \text{ meV}$$

$$T = 1000 \text{ K} \quad 6.9kT = 590 \text{ meV}$$

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

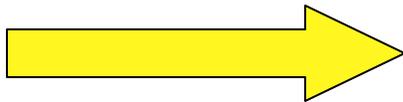
$$E_a < 6.9kT$$

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

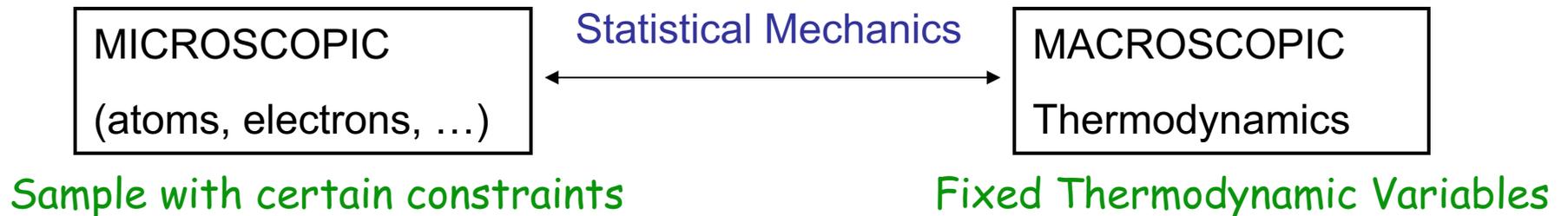
- How to go from microscopic description to macroscopic behavior/variables ?*
- How do macroscopic constraints/environments relate to simulation approach ?*

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



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

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

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), ...

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

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)*

$E(T,V,\mu)$ -> 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

$$P_v = \frac{\exp(-\beta H_v)}{\sum_{v \in \mathcal{E}} \exp(-\beta H_v)}$$

$$Q = \sum_{v \in \mathcal{E}} \exp(-\beta H_v)$$

Hamiltonian is relevant Legendre transform of the entropy

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

$$P_v = \frac{\exp(-\beta E_v)}{\sum_{v \in \mathcal{E}} \exp(-\beta E_v)}$$

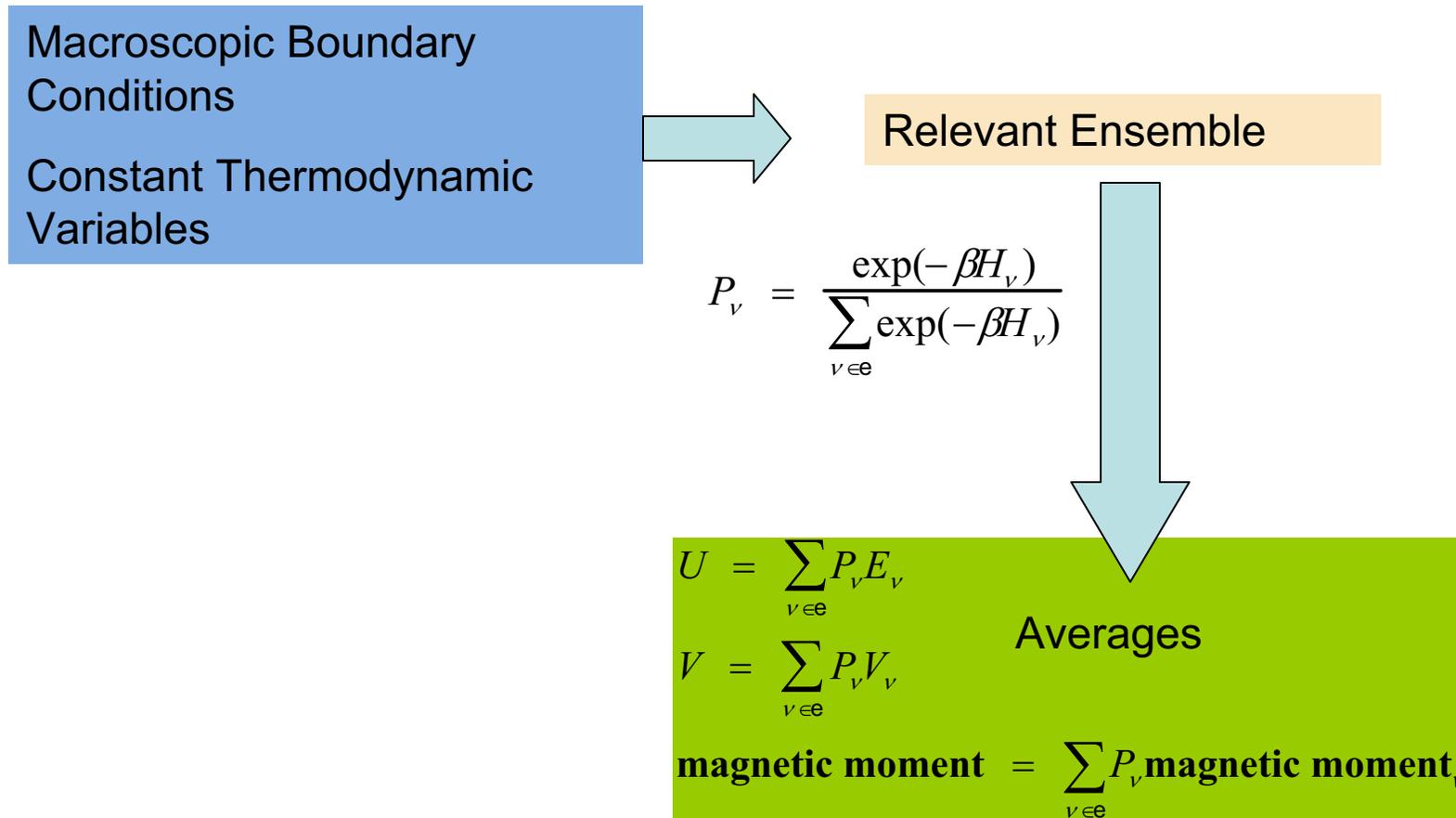
Example: Fixed N, V, T : $-F/T = S - \langle E \rangle / T$

Example: Fixed μ, V, T : $-F/T = S - \langle E \rangle / T + \mu / T$

$$P_v = \frac{\exp(-\beta(E_v - \mu N))}{\sum_{v \in \mathcal{E}} \exp(-\beta(E_v - \mu N))}$$

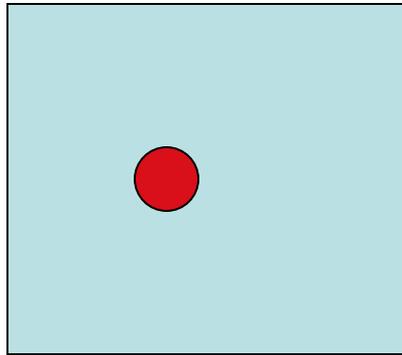
Summary: In case you can't see the trees anymore

...



Can get averages without need for dynamics !

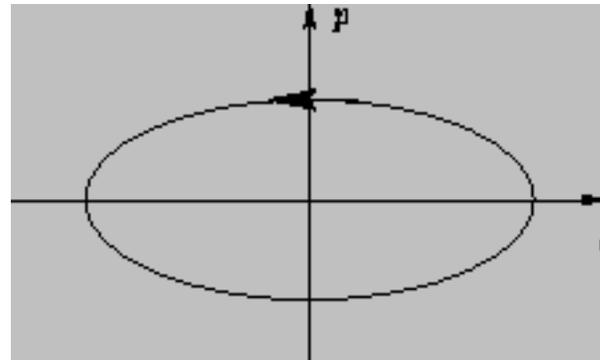
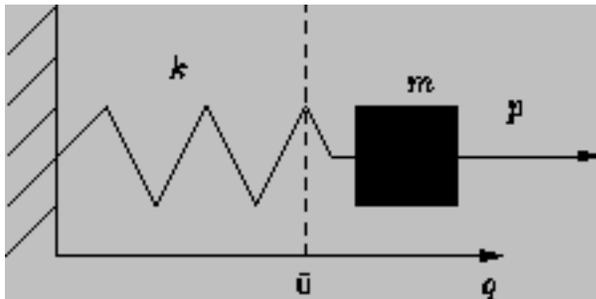
The catch: Ergodicity and time scales



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 \rightarrow 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.

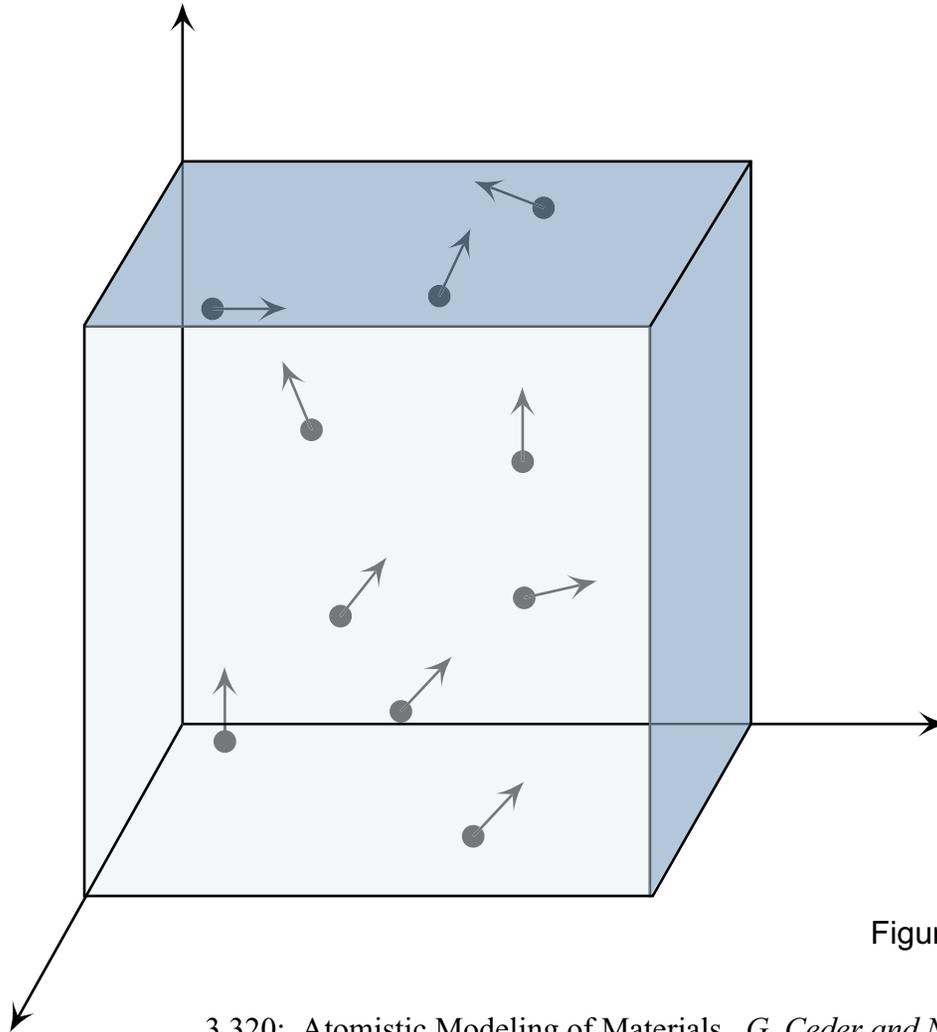
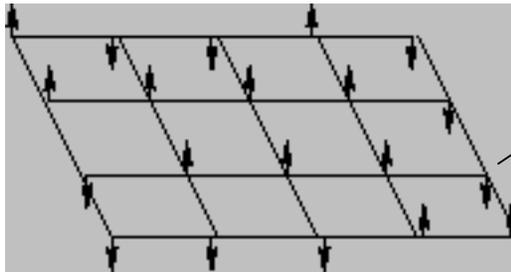


Figure by MIT OCW.

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 $\sigma_i = +1$ or -1

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

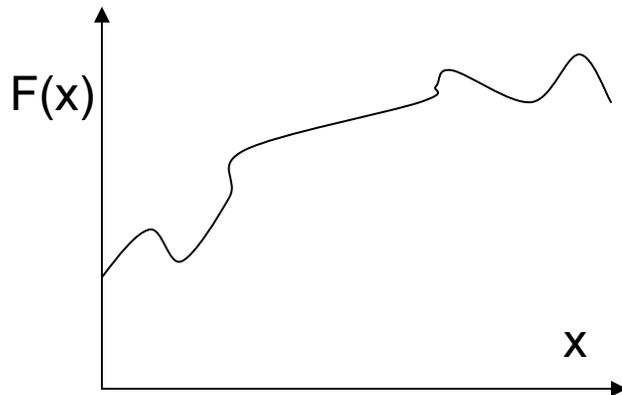
When $J > 0$, ferromagnetic behavior; when $J < 0$ Anti-ferro

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

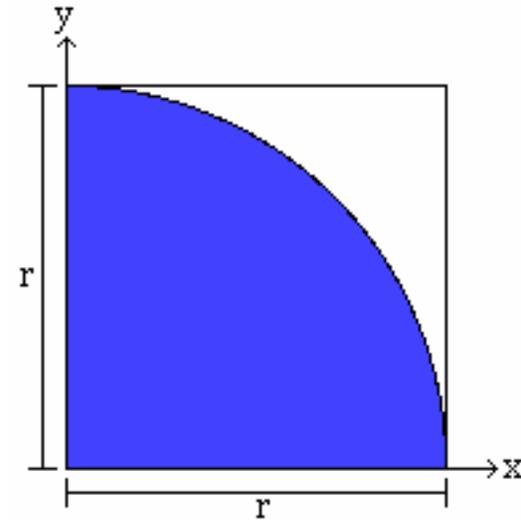
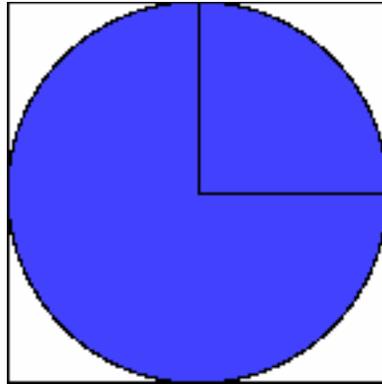
The Monte Carlo Method: Do you take it *simple* or *important* ?

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)).



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:

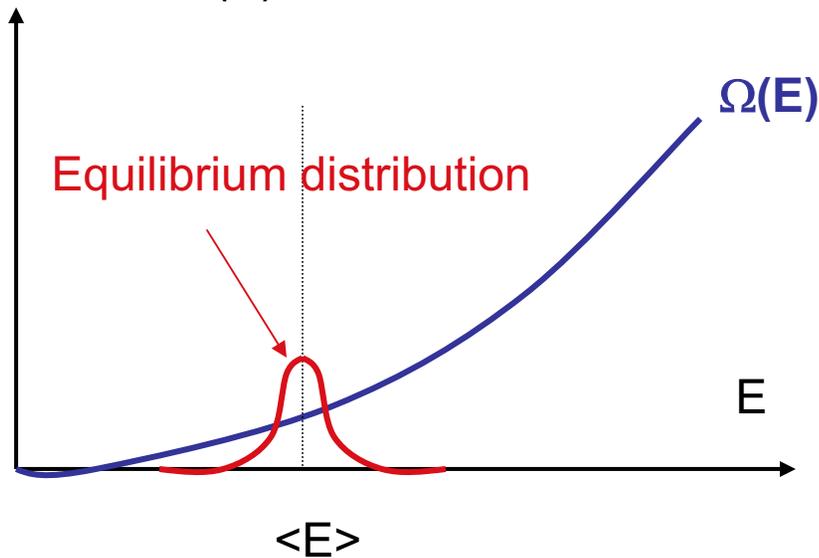
$$\langle A \rangle = \sum_{\nu=1}^M P_{\nu} A_{\nu}$$
$$P_{\nu} = \frac{\exp(-\beta H_{\nu})}{\sum_{\nu=1}^M \exp(-\beta H_{\nu})}$$

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.

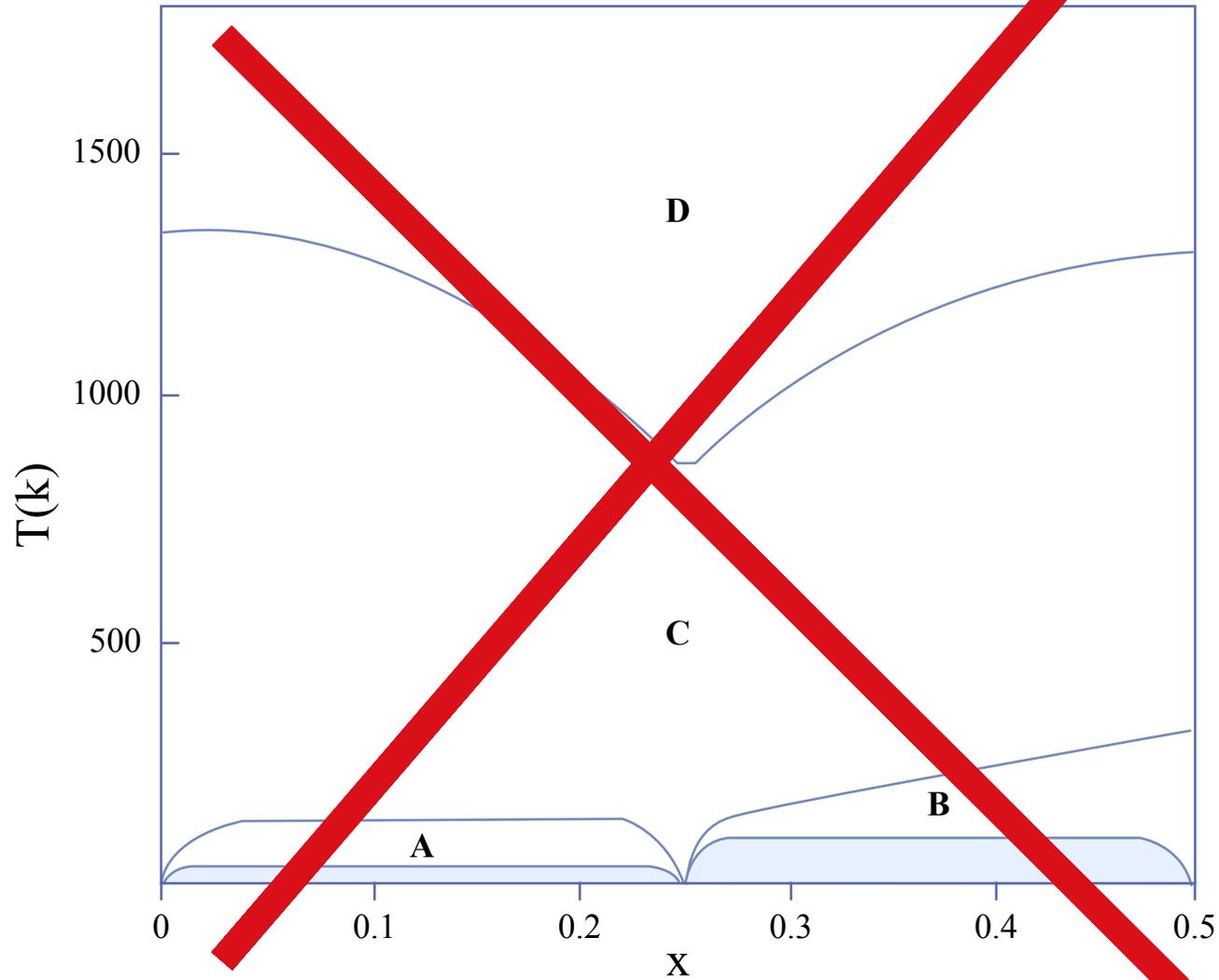


Figure by MIT OCW.

Simple sampling for cartographers

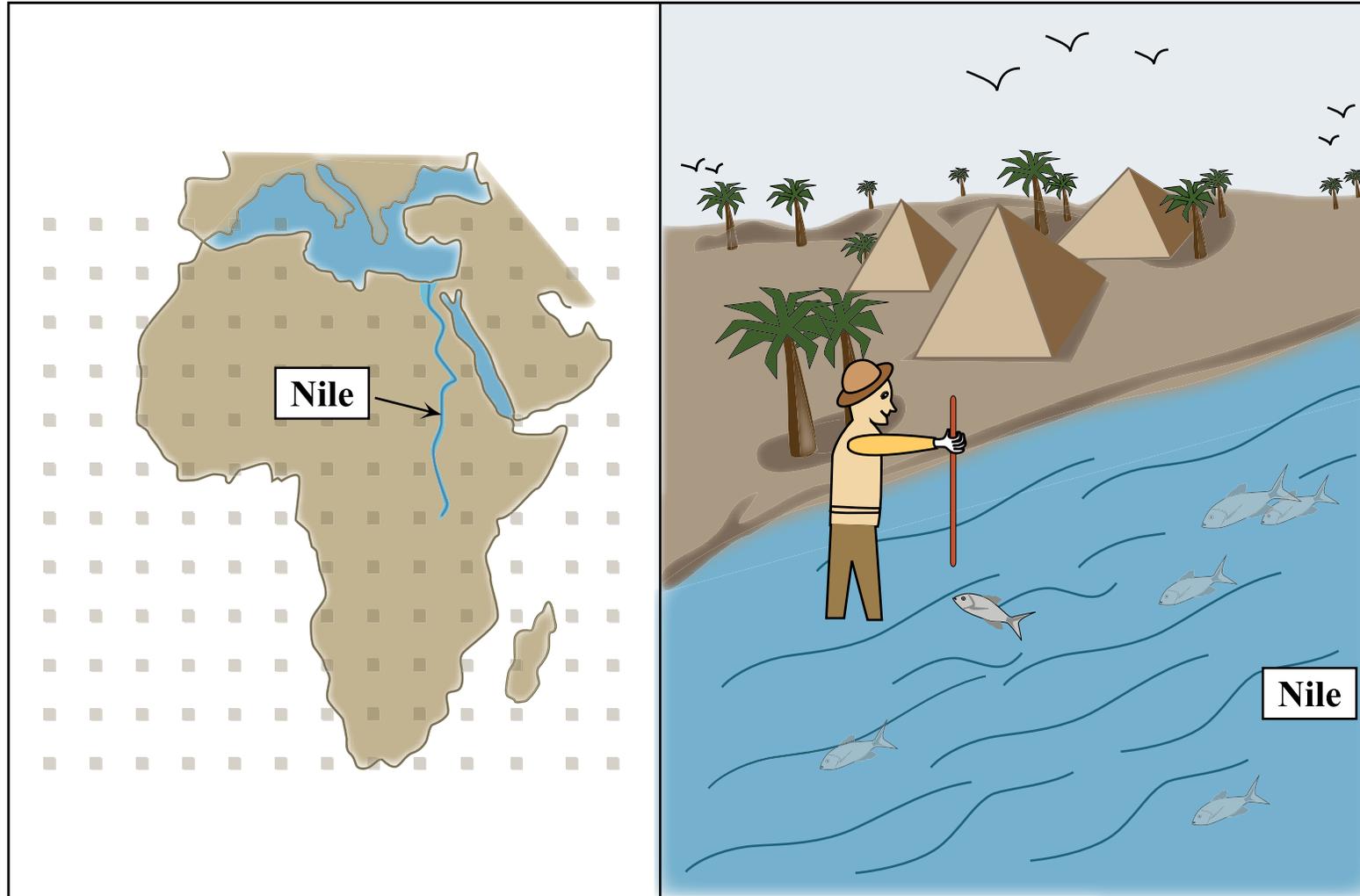


Figure by MIT OCW.

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

Conditions for generating proper probability distribution

Equal a-priori probabilities: $W_{i \rightarrow j}^0 = W_{j \rightarrow i}^0$

Detailed Balance: $P_i W_{i \rightarrow j} = P_j W_{j \rightarrow i}$

When $W_{i \rightarrow j}^0$ and $P_{i \rightarrow j}$ 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:

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

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

$$P_{i \rightarrow j} = 1 \quad \text{when } E_j < E_i$$

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

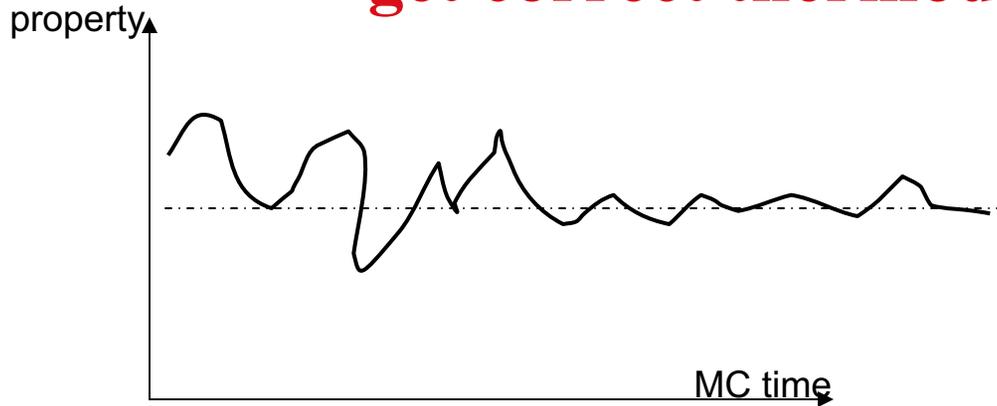
Downhill moves always accepted, uphill moves with some “thermal-like” probability

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 $\Delta E < 0$ \rightarrow accept perturbation
If $\Delta E > 0$ \rightarrow 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.

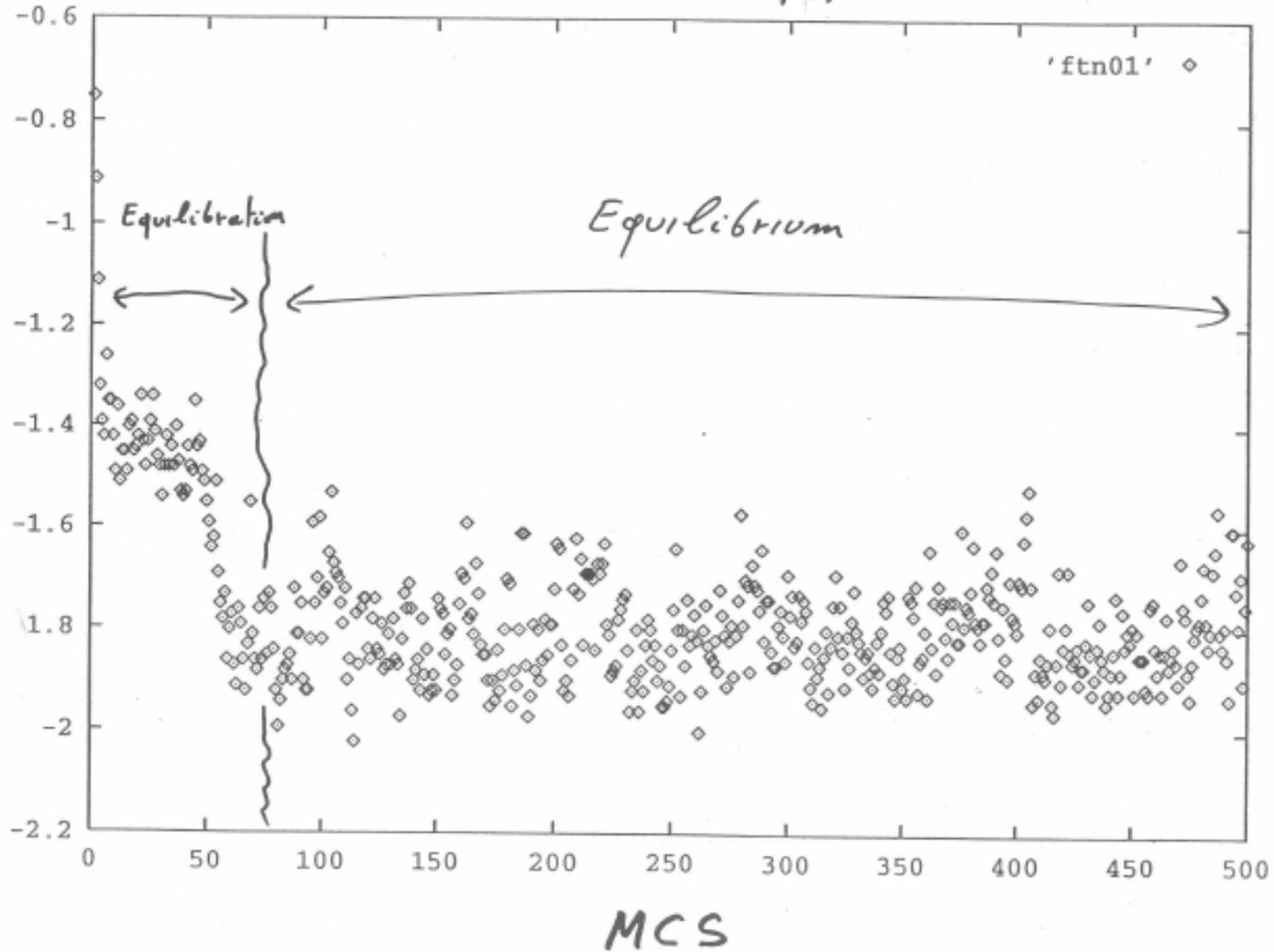
Example 1: The Ising Model

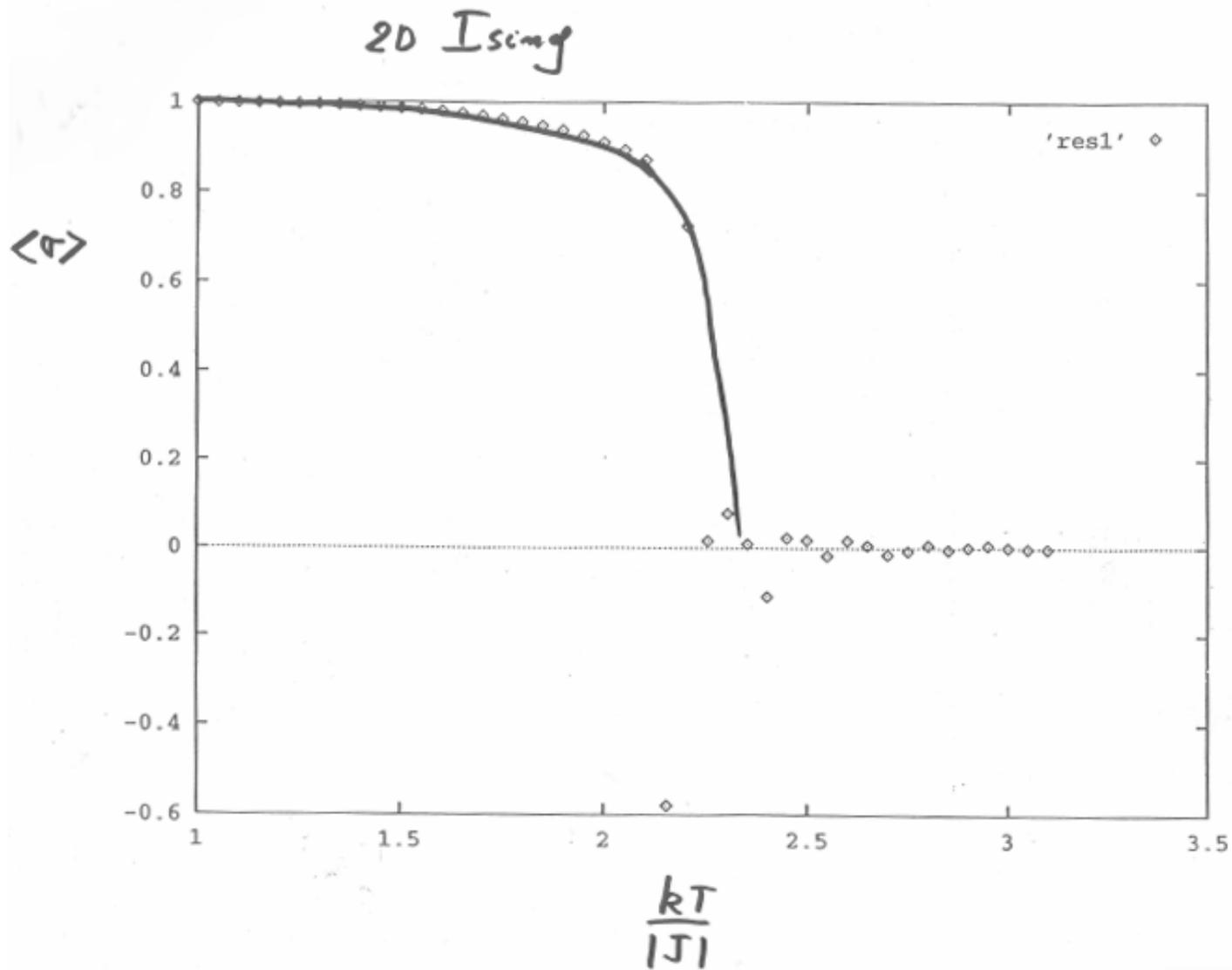
Which perturbation ? Pick spin and flip over

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 $\Delta E < 0$ \rightarrow accept perturbation
If $\Delta E > 0$ \rightarrow accept perturbation, accept
perturbation with probability $\exp\left[\frac{-\Delta E}{kT}\right]$
5. Go back to 2

Trajectory for the Energy

2D - Ising $\frac{kT}{|J|} = 2$





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

$$C = \frac{1}{N} \left(\frac{\partial U}{\partial T} \right) = \frac{1}{N} \frac{\langle E^2 \rangle - \langle E \rangle^2}{kT^2} \longrightarrow \text{Can be obtained from energy distribution}$$

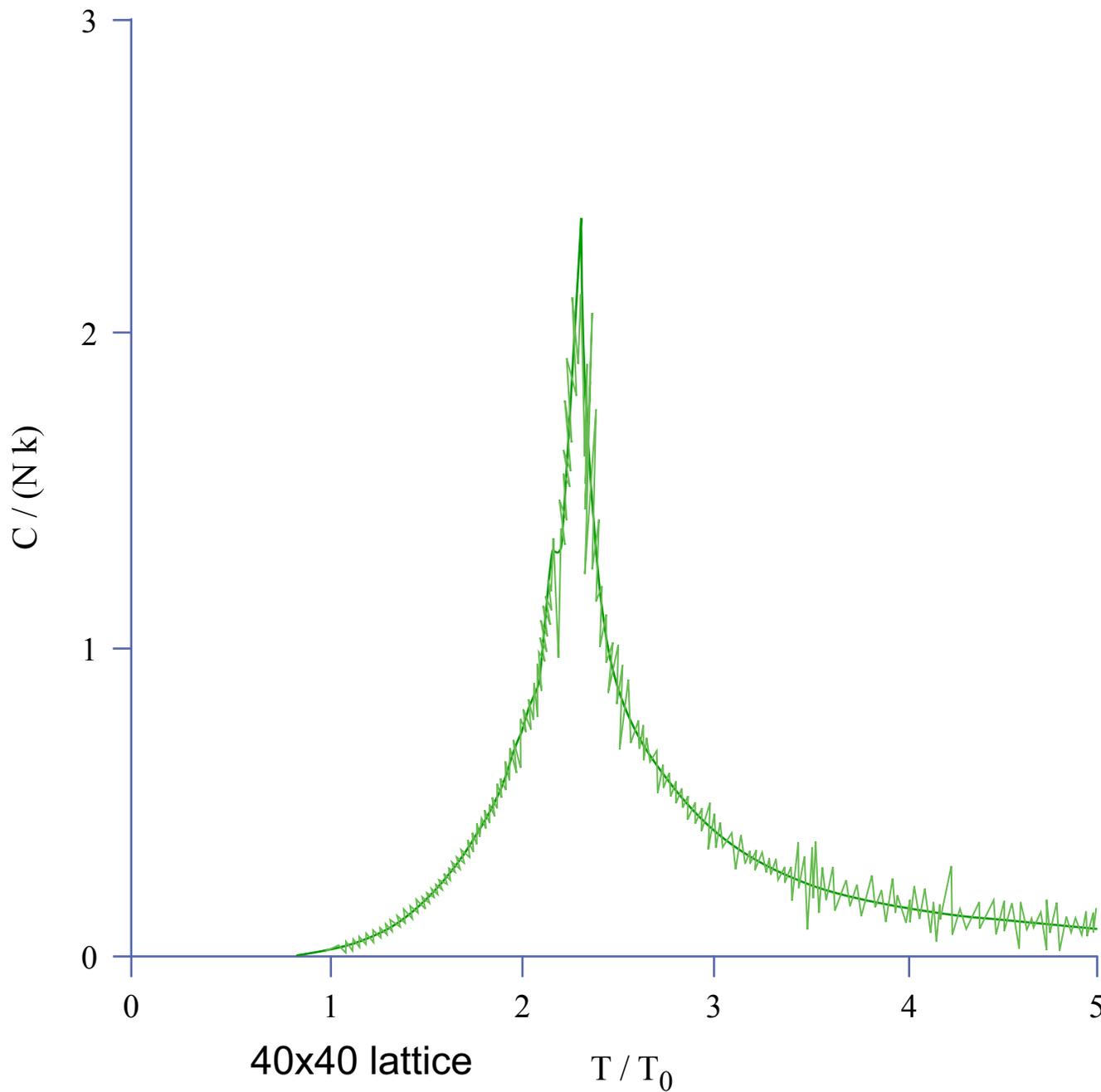


Figure by MIT OCW.

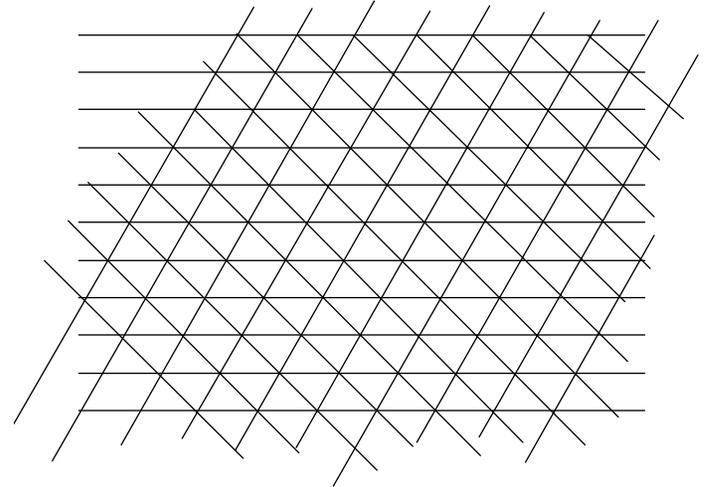
If you want to see and play with an Ising model, go to:
<http://bartok.ucsc.edu/peter/java/ising/ising.html>

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

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

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

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

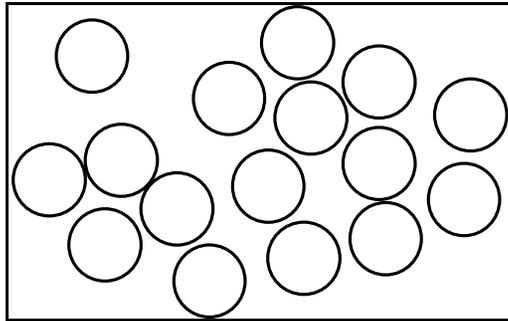
Transfer to spin notation

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

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

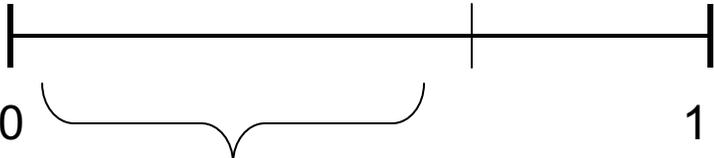
- 1) randomly pick an atom
- 2) displace by some random amount between two limits
- 3) compute $\Delta E = E_{\text{new}} - E_{\text{old}}$
- 4) if $\Delta E < 0$ accept perturbation
if $\Delta E > 0$ accept perturbation with probability

$$P_i \propto \exp\left(-\frac{\Delta E}{k_B T}\right)$$

Random numbers

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

Needed to implement probability


$$P[\text{rand}(0,1) < \exp(-\beta\Delta E)] = \exp(-\beta\Delta E)$$

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"