Computational Nanoscience NSE C242 & Phys C203 Spring, 2008

Lecture 11: Phase Transitions via Monte Carlo : Ising February 26, 2008

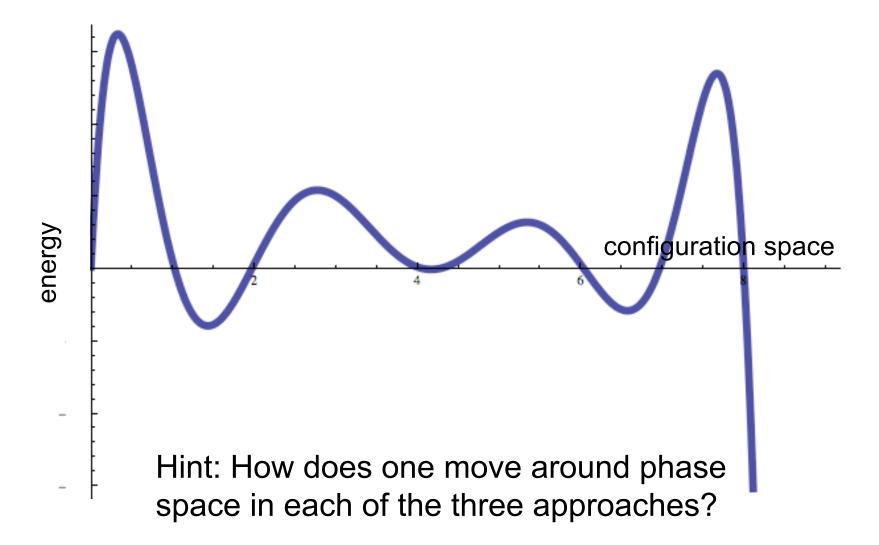
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But First: Kinetic Monte Carlo

- How many random numbers are generated for each iteration of a KMC algorithm?
- From what distributions are these random numbers generated?
- In a KMC simulation, what is our connection back to "time"?
- Outline the steps in a KMC algorithm
 - Which one is computationally rate limiting?
 - Which ones can give sources of error?

But First: Kinetic Monte Carlo

• Use the diagram below to compare and contrast MD, MC, and KMC.



Example: KMC of Chemical Vapor Deposition

- After C.C. Battaile and D. J. Srolovitz, Annu. Rev. Mater. Res. 2002, 32:297-319.
- CVD is a method for depositing films. In a CVD reactor, gaseous reactants are brought into contact with a solid surface which catalyzes a variety of reactions as the film grows.
- In addition to the reactions at the surface, there can be purely vapor phase reactions as well.
- The goal of KMC simulations of CVD growth is to predict film growth rates and film morphologies as a function of synthesis parameters
- In this case, H2 and CH4 are introduced into the reactor and the formation of diamond thin films is simulated
- For the reactions that are involved, the rates are given by

$$k_f = AT^N \exp\left(-\frac{E}{RT}\right)$$

Example: KMC of Chemical Vapor Deposition

\ <i>S</i>	ΔH	E	n	A	Reaction
5.3	-9.9	7.3	0	1.3×10^{14}	$1. H(s) + H(g) \leftrightarrow *(s) + H_2(g)$
-32.8	-96.9	0	0	1.0×10^{13}	2. $*(s) + H(g) \leftrightarrow H(s)$
7.9	-24.6	0	0	3.0×10^{13}	3. $CH_2(s) + H(g) \iff *(s) + CH_3(g)$
-42.0	-70.9	0	0	5.0×10^{12}	4. $*(s) + CH_3(g) \leftrightarrow CH_3(s)$
-1.9	-28.5	6.9	0	4.5×10^{11}	5. $(s) + C_2H_2(g) \leftrightarrow C_2H_2(s)$
6.6	-11.3	7.7	2	2.8×10^{14}	6. $CH_y(s) + H(g) \iff CH_{y-1}(s) + H_2(g)$
-34.1	-83.0	0	0	1.0×10^{13}	7. $CH_y(s) + H(g) \leftrightarrow CH_{y+1}(s)$
8.7	-8.9	5.0	2	9.0×10^{6}	8. $C_2H_y(s) + H(g) \iff C_2H_{y-1}(s) + H_2(g)$
-36.2	-47.7	0	0	2.0×10^{13}	9. $C_2H_y(s) + H(g) \iff C_2H_{y+1}(s)$
7.9	-24.6	0	0	3.0×10^{13}	$10. C_2H_y(s) + H(g) \iff CH_{y-2}(s) + CH_3(g)$
-42.0	-70.9	0	0	$5.0 imes 10^{12}$	11. $CH_y(s) + CH_3(g) \leftrightarrow C_2H_{y+3}(s)$
6.7	-6.2	7.3	0	$2.5 imes 10^{14}$	12. $H(d) + H(g) \leftrightarrow *(d) + H_2(g)$
-34.2	-100.6	0	0	1.0×10^{13}	$13.*(d) + H(g) \leftrightarrow H(d)$
8.0	-17.8	0	0	3.0×10^{13}	14. $CH_2(d) + H(g) \Leftrightarrow *(s) + CH_3(g)$
-42.2	-81.0	0	0	$5.0 imes 10^{12}$	$15.*(d) + CH_3(g) \leftrightarrow CH_3(d)$
0.4	4.9	0	0	1.0×10^{13}	16. $C_xH_y(d) \leftrightarrow *_2(s) + C_xH_y(s)$
		8.8	0	2.0×10^{13}	17. $*_2(s) + C_x H_y(s) \rightarrow C(s) + C_{x-1} H_y(s)$
		28.3	0	2.5×10^{9}	18. $C(s)H_2(s) + H(g) \rightarrow *_2(s) + CH_3(g)$
		0 8.8	0 0	1.0×10^{13} 2.0×10^{13}	

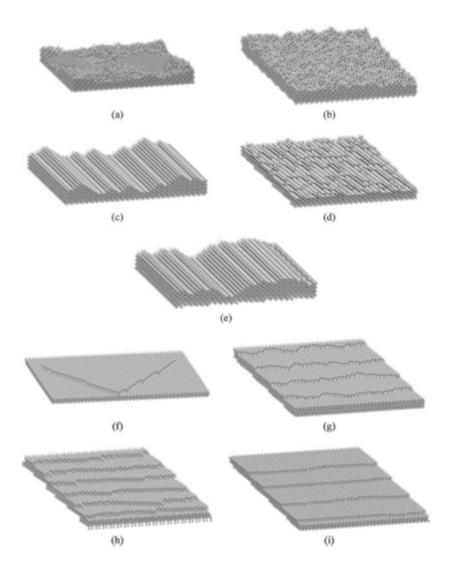
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TABLE 3 Chemistry for the deposition of diamond from a precursor of H2 and CH4a

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Example: KMC of Chemical Vapor Deposition

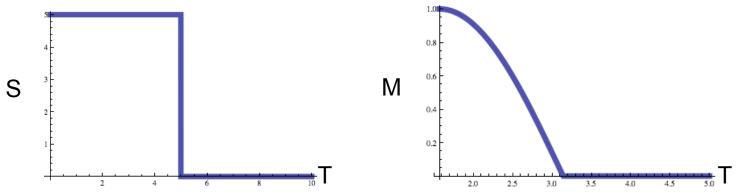


Resulting morphologies for growth temperatures of 1100K and pressures of 20 Torr (distributed amongst the various precursors), a variety of different substrate orientations.

The effects of the different surfaces are incorporated by choosing appropriate discrete sites ("onlattice KMC") at which atoms can be adsorbed on to the surface.

Phase Transitions

- For the purposes of this class, we will define a phase transition as an abrupt change in one or more physical properties of a system with a small change in a thermodynamic variable (such as temperature)
- Lots of examples: melting, sublimation, condensation, freezing, eutectic transition, spinodal decomposition, order-disorder transitions, ferroparamagnetic transition, superconducting transition
- We tend to classify phase transitions into two classes: first order and second order



- First order Involve a latent heat, associated with mixed-phase regimes. Discontinous change in some thermodynamic variables (such as entropy)
- Second-order "continuous" because the discontinuity is not in the firstderivatives of the potentials, but in the second.
- Actually, there is a 3rd class of phase transition, so-called "infinite order" continuous but break no symmetries. They are really interesting too -- but we will not discuss them here.

Phase Transitions

At least as far as classical phase transitions are concerned, they tend to be associated with **symmetry breaking**. Generally, during a phase transition, something goes from a disordered to a more ordered state. This is what we refer to as "spontaneous symmetry breaking." (It can go the other way as well).

For instance, as we transition from the liquid to the solid state, symmetries in the system are broken (the liquid state is more symmetric because all directions look the same, the solid state is less symmetric as all directions no longer look the same).

For these phase transitions, we associate something called an "order parameter". The order parameter is a way of measuring how ordered the state is.

For the melting transition, the order parameter is related to the (now familiar) pair-pair correlation function.

For the ferromagnetic-paramagnetic transition that we will study now, the order parameter is precisely the magnetization.

To explore this phase transition, we will use the Ising model. The Ising model is a natural extension of a Monte Carlo simulation.

Magnetic Systems: The Ising Model

The Ising model* was initially introduced to provide a *qualitative* description of one of the most interesting phenomena occurring in nature, namely *ferromagnetism*.

Successively, however, it became clear that its importance goes far beyond the realm of magnetism, for many reasons among which

- It is one of the very few models *exactly solvable* in some cases;
- It is perhaps the simplest model displaying a *phase transition*;
- Its simplicity renders it quite general: it is used in different areas of science (biology, sociology, economics etc.)

A thorough review of the enormous amount of work published in the last seventy years aimed at exploring the phase diagram of the Ising model would be out of our present scope.



* E. Ising, Z. Phys. 31, 253 (1925).

Magnetic Systems: The Ising Model

In the Ising model the complicated ionic and electronic structure of a magnetic material is represented by a cubic periodic lattice with a specific dimensionality (can be occasionally higher than three).

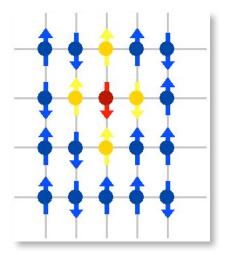
At each site of the lattice sits a variable to which we will refer as *spin*, mostly for conventional reasons.

It may be interpreted as representing a *domain* of the material in which the elementary *magnetic moments* of the atoms are aligned.

The spin variable associated with the **i**th site can only take on the two values which are conventionally represented pictorially with up/down arrows.

Ising Model

The figure below shows a two-dimensional Ising 5x5 lattice; circles are lattice sites, whereas arrows represent spins.



Each site has four nearest-neighboring sites (for example, in the figure, yellow sites are the nearest neighbors of the red site).

In one dimension there are only two nearest neighbors, whereas in two dimensions there are four, in three six, in **d** dimensions 2**d** (the number of nearest neighbors is often referred to as the *coordination number*.)

Ferromagnetic Ising Model

In the *Ferromagnetic Ising model*, the energy associated with a specific spin configuration is given by:

$$E({S_i}) = -J\sum_{(ij)} S_i S_j - H\sum_i S_i$$

where the sum runs over all pairs of nearest-neighboring sites **ij** (each such pair is also called a *bond*).

H is a possible external field, typically a magnetic field if one is studying the Ising model in the context of magnetism.

J (>0) is the characteristic energy scale of the system.

How would the expression for E change for anti-ferromagnets?

The Ising model *appears* very simple, and one of the goals of a large ongoing effort in theoretical physics during the last half century has been to obtain an *exact solution* for it.

We'll get back to that later. For now, let's explore the configurations using the expression for the energy using Monte Carlo methods.

$$E({S_i}) = -J\sum_{(ij)} S_i S_j - H\sum_i S_i$$

As usual, the goal is to evaluate thermodynamic averages in the ordinary way; for example, one of the important physical quantities is the *total magnetization* **M**, defined as

$$M(\{S_i\}) = \sum_i S_i$$

which, for a finite lattice, can take all integer values from -N to N.

The average magnetization <M> of the system at a temperature T=1/ β is

$$\langle \overline{M} \rangle = \frac{1}{Z} \sum_{\{S_i\}} M(\{S_i\}) \exp[-\beta E(\{S_i\})]$$

where **Z** is the partition function of the Ising model:

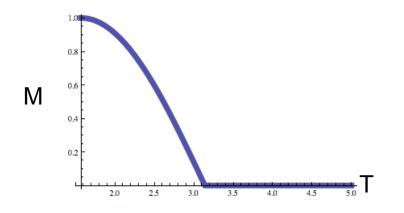
$$Z = \sum_{\{S_i\}} \exp\left[-\beta E\left(\{S_i\}\right)\right]$$
 (note, no integrals)

Ferromagnetic Ising Model

The form of this expression should look familiar -- it is in fact exactly the sort of thing for which Monte Carlo simulations are useful.

Our goal will be to determine how <M> varies for a system of spins as a function of temperature.

Of course, we already know what the answer is:



By but actually doing the computer experiment, not only will we explore the nature of the ferromagnetic-paramagnetic phase transition, but we will learn some things about simulating phase transitions along the way.

Ising Model

First, let's try to gain some intuitive understanding of this system.

$$E({S_i}) = -J\sum_{(ij)} S_i S_j - H\sum_i S_i$$

We will concern ourselves with the zero applied field case, so that

$$E(\{S_i\}) = -J\sum_{(ij)} S_i S_j$$

There are two lowest energy states ("ground states"), physically equivalent, namely the two ferromagnetic configurations with spins aligned, either all +1 or all -1.

However, there is more entropy associated with disordered states with mixed spins.

This interplay between energy minimization (dominant at lower temperatures) and entropy maximiation (dominant at high temperatures) is what gives us the rich behavior of the Ising system, and, ultimately, our phase transition.

Here's a thing Jeff liked that a guy at CalTech said on his website*

Energy Minimization

The interactions between the atomic-scale magnets (usually called "spins") is such that the lowest energy configuration with two spins has the two spin vectors pointing in the same direction. From the perspective of *energy alone*, the lowest energy state of a large chunk of matter would have *all* the little spin vectors aligned, giving huge total magnetic fields!

Entropy Maximization

The configuration in which *all* atomic magnets line up is **one very special** case out of an incomprehensibly large number of possible configurations. Unless there is a huge "energy cost" for an individual spin which is not lined up with its neighbors, the sheer number of possible unaligned configurations completely swamps the one unique "ground state", and a macroscopic-sized system shows no net magnetization. The randomness of the real configuration (and randomness is essentially what "entropy" measures) tends to wash out the large scale magnetism predicted by energy considerations alone.

* http://oscar.cacr.caltech.edu/Hrothgar/Ising/intro.html

Exact Solutions

An exact solution to the Ising model consists of the analytical evaluation of the partition function, from which all thermodynamic averages of interest can be obtained by differentiation^{*}.

It turns out that an exact solution exists for **d=1**, it is relatively simple to find. What may be surprising is that it exhibits no phase transition at any finite temperatures! That is, at any T>0, the system is disordered (entropy wins!).

It does exhibit a phase transition exactly at T=0. In this sense, its physics is somewhat peculiar and not really indicative of the behavior in higher dimensionality.

An exact solution also exists for **d=2**, and it is much more difficult to obtain**. In two dimensions the system shows a phase transition at finite temperature, to prove the important effect of the dimensionality on the physics of the model.

No exact solution is known for d>2, but the properties of the model are known with high accuracy, mostly owing to the large amount of numerical work based on Monte Carlo simulations.

*See, for instance, K. Huang Statistical Mechanics, J. Wiley (1987), p. 341 ff. **L. Onsager, *Phys. Rev.* **65**, 117 (1944); A. B. Zamalodchikov, *Int. J. of Mod. Phys. A* **4**, 4235 (1989).



Monte Carlo of Ising Model

In the next class, we are going to perform a 1D and 2D Monte Carlo study of the ferromagnetic Ising model for H=0 using the Metropolis algorithm with single-spin updates.

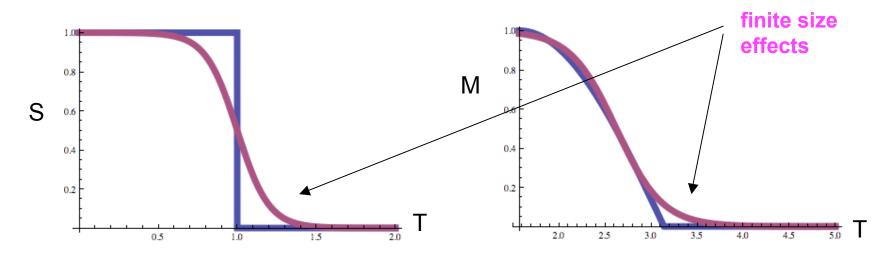
In the process, we will learn about two important things when it comes to simulating phase transitions. These are (1) finite size effects, and (2) the phenomenon of critical slowing down.

(1) Finite Size Effects

According to the analytical solution, the 1D Ising model does not exhibit a phase transition at any finite temperature T. The system is always disordered for T>0.

Your simulation, however, will indicate otherwise. How come?

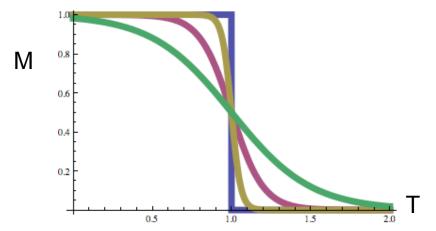
- This is a finite size effect. Entropy can really only "win" in the thermodynamic limit where the system size is infinite. When simulating any finite sized 1D Ising system, we will, in fact, observe a phase transition.
- As a rule, a true phase transition can only occur in infinite systems. By "true" phase transition, we mean one for which we see the standard behavior in the order parameter. In a finite system, the transition will be "smeared out".



(1) Finite Size Effects

These finite size effects make it challenging to determine the actual critical point (temperature, etc) where the phase transition occurs.

- We can sometimes get around this by using scaling analysis. That is, for critical phenomena, we can derive rules about how the transition smears out as a function of system size. (Renormalization Group, etc)
- If we conduct the simulation for a variety of system sizes, we obtain a variety of curves.

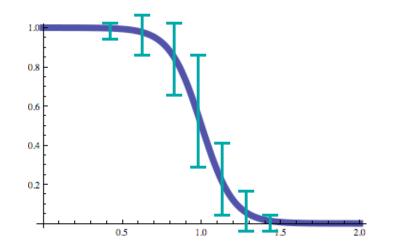


However, if we scale the variables (e.g. system size, magnetization and temperature) appropriately and superpose all the curves, they will fall on top of each other at the critical temperature.

(2) Critical Slowing Down

The second effect which we are going to look at is "Critical Slowing Down".

- Say we make a plot of <M> vs. T that we obtain by simulation for the Ising model.
- Like any good computational experimentalist, we include the error bars on our measurement of <M>. We would see something like this:



What is going on is that in the vicinity of a phase transition, the fluctuations in the system blow up. This is characteristic of all phase transitions. In infinite sized systems, the fluctuations themselves actually become infinite. Of course, they are limited by the size of the system in a finite size simulation.

Magnetic Susceptibility

Even though I said we will look only at the H=0 Ising model, it turns out that we can relate these fluctuations to the magnetic susceptibility of the system. The susceptibility is given by:

$$\chi = \lim(H \to 0) \frac{\partial \langle M \rangle}{\partial H}$$
 $M = \frac{1}{N} \sum_{i} S_{i}$

First of all, we can guess that the susceptibility diverges at $T=T_C$. (Why does it do this?)

One approach to study susceptibility would be to compute the behavior of the system at vanishingly small fields for all temperatures.

However, even in zero magnetic field one can obtain important information about the susceptibility by looking at thermal fluctuations of the relevant physical quantities.

For example,
$$\Delta e^2 = \langle e^2 \rangle - \langle e \rangle^2$$

 $\Delta m^2 = \langle m^2 \rangle - \langle m \rangle^2$

are the fluctuations of the energy per site **e** and the magnetization per site **m** at a given temperature.

Magnetic Susceptibility

The fluctuations in the absence of an external field can be related to the linear response of the system when the field is applied.

Roughly speaking, if in the absence of a field a system features large thermal fluctuations of the magnetization, this system will offer a greater magnetic response if a magnetic field is applied.

More precisely, it can be shown* that: $\chi = N\beta \left(\langle m^2 \rangle - \langle m \rangle^2 \right)$

The fluctuations in the absence of an external field can be related to the linear response of the system when the field is applied.

Note that the thermal averages in the above expression are computed in the absence of a magnetic field. This is a very general result, which permits to learn about the behavior of a system in the presence of an external probe by studying its behavior in the absence of such probe.

Near the critical temperature, the fluctuations (and hence the magnetic susceptibility) diverge.



In Class Simulation

We will play with some Ising Model simulations in 1D and 2D.

Bring your laptop!