

## Unit 4: Phase Transitions

Most of the models we have dealt with up to this point involved *non-interacting* particles, i.e. the ideal gas. This is mostly because models with interactions become extremely difficult to treat analytically! However, interactions between particles can be a crucial factor in determining the behavior of a system. In particular, they are important for understanding *phase transitions*. A phase transition is when the macroscopic behavior of a system changes in some singular way as a thermodynamic parameter is varied. The classical example is  $\text{H}_2\text{O}$ , which can exist in the forms of solid ice, flowing water, and vapor, each of which has quite different physical properties from the others. As one varies temperature and/or pressure, we can transition from one of these states to another. Clearly it is the interactions between the  $\text{H}_2\text{O}$  molecules that is important for such transitions. If the  $\text{H}_2\text{O}$  molecules were not interacting, then we could just compute the single-particle partition function  $Q_1$ , and then  $Q_N = Q_1^N/N!$  would give all the properties of the  $N$ -particle system, and everything would be continuous functions of  $T$ ,  $V$ , and  $N$  – and so no phase transitions!

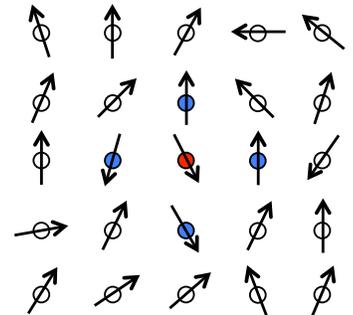
In this unit we will discuss phase transitions in the context of a class of simple models, that of interacting classical spins. One can think of these as a model for magnetic phase transitions, where each spin represents a local magnetic moment on an ion or atom. At high temperatures, most magnetic materials are paramagnetic (or diamagnetic) – the average magnetization of the system is zero *unless* there is an external applied magnetic field. But as one lowers  $T$  in some materials, there can be a ferromagnetic phase transition to a phase in which there can be a net magnetization even when the external magnetic field is zero. But such classical spin models also have wide application to other physical systems, such as the liquid-gas transition, ordering in binary alloys, and many others.

### Unit 4-1: Classical Spin Models

We consider a set of classical (i.e. *not* quantum) spins  $\mathbf{s}_i$  of unit magnitude,  $|\mathbf{s}_i| = 1$ , that are located on the sites  $i$  of a periodic  $d$ -dimensional lattice of sites. Each  $\mathbf{s}_i$  interacts only with its nearest neighbors  $\mathbf{s}_j$ , i.e. those spins that are physically closest to  $\mathbf{s}_i$ . We can write the Hamiltonian for this system as,

$$\mathcal{H} = -J \sum_{\langle ij \rangle} \mathbf{s}_i \cdot \mathbf{s}_j \quad (4.1.1)$$

where  $\langle ij \rangle$  denotes pairs of nearest neighbor spins. In the sketch to the right, the spin on the red site interacts only with the spins on the blue sites. When the coupling  $J > 0$ , the model is said to be *ferromagnetic* – nearest neighbor spins lower their energy by aligning in the same direction. If we have  $J < 0$ , the model is said to be *antiferromagnetic* – nearest neighbor spins lower their energy by aligning in opposite directions. We will be discussing ferromagnetic models.



One finds that the qualitative behavior of such models depends on two key parameters: (i) the dimensionality  $d$  of the space in which the spins sit ( $d = 1$  is a line,  $d = 2$  is a plane,  $d = 3$  is a volume, etc.), and (ii) the number of components  $n$  that the spin  $\mathbf{s}_i$  has.

Some well studied cases, corresponding to different values of  $n$ , are as follows. In all cases, the model with a given  $n$  can exist in any dimension of physical space, i.e. we can have any value for  $d$ .

#### Heisenberg Model ( $n = 3$ )

$\mathbf{s}_i$  is a spin pointing in any direction in three-dimensional space, so  $n = 3$  and  $\mathbf{s}_i = (s_x, s_y, s_z)$ .

#### XY Model ( $n = 2$ )

$\mathbf{s}_i$  is a spin pointing in any direction within a two-dimensional plane, so  $n = 2$  and  $\mathbf{s}_i = (s_x, s_y)$ . The model gets its name because, by convention, we take the plane in which the spins point to be the  $xy$ -plane.

### Ising Model ( $n = 1$ )

Here the spins are restricted to lie along only a single direction, and so they can only point parallel or antiparallel to that direction. By convention one usually calls the direction in which spins can point the  $\hat{\mathbf{z}}$ -direction. We have  $n = 1$  and  $s_i = \pm 1$ .

Some more unusual cases are:

### The Self-Avoiding Walk

Here we take the limit  $n \rightarrow 0$ . This model is often used to model polymers. What  $n \rightarrow 0$  has to do with self avoiding walks or polymers is a topic for another class!

### The Spherical Model

Here we take the limit  $n \rightarrow \infty$ . The spherical model is of interest because in many cases one can find an exact analytical solution.

Here we will focus on the *Ising* model (invented by Wilhelm Lenz in 1920 – Lenz gave it to his student Ernst Ising to solve. So sometimes it is good to be the student!).

## Ensembles

We can consider two different ensembles for our spin models. The first is the ...

### Fixed Magnetization Ensemble:

Here the total magnetization is  $M = \sum_{i=1}^N s_i$  and we work in an ensemble in which the value of  $M$  is fixed. The partition function is then,

$$\tilde{Z}(T, M) = \sum_{\{s_i\}} \delta\left(\sum_i s_i - M\right) e^{-\beta \mathcal{H}[s_i]} \quad (4.1.2)$$

where the sum is over all possible configurations of spins  $\{s_i\}$ , and the delta function restricts non-zero contributions to those configurations with a given value of  $M$ .

We can write  $M = \sum_i s_i = N^+ - N^-$ , where  $N^+$  is the number of spins that point up, and  $N^-$  is the number of spins that point down. The constant magnetization ensemble is thus similar to the canonical ensemble in the occupation number representation, where one sums over all sets of occupation numbers  $\{n_i\}$  but restricts the non-zero contributions to those configurations in which  $\sum_i n_i = N$  is fixed to a certain value. Thus  $M$  here is playing a role similar to the number of particles  $N$  in the canonical ensemble.

In this ensemble, the free energy is called the *Helmholtz free energy*  $F$ , and one has,

$$F(T, M) = -k_B T \ln \tilde{Z}(T, M) \quad \text{Helmholtz free energy} \quad (4.1.3)$$

The second ensemble is the ...

### Fixed Magnetic Field Ensemble:

To remove the constraint of fixed  $M$ , we can Legendre transform from  $M$  to a conjugate variable  $h$ . We will see that this  $h$  is just the external magnetic field. The free energy in this ensemble is called the *Gibbs free energy*  $G$ , and is obtained as the usual Legendre transform,

$$G(T, h) = F(T, M) - hM \quad \text{Gibbs free energy} \quad (4.1.4)$$

where

$$\left(\frac{\partial F}{\partial M}\right)_T = h \quad \Rightarrow \quad \left(\frac{\partial G}{\partial h}\right)_T = -M \quad (4.1.5)$$

With  $S = -\left(\frac{\partial F}{\partial T}\right)_M = -\left(\frac{\partial G}{\partial T}\right)_h$  the entropy, we have,

$$dF = -SdT + hdM \quad \text{and} \quad dG = -SdT - Mdh \quad (4.1.6)$$

To get the partition function  $Z$  for  $G$ , we take the Laplace transform of  $\tilde{Z}$ ,

$$Z(T, h) = \sum_M e^{\beta h M} \tilde{Z}(T, M) = \sum_M e^{\beta h M} \sum_{\{s_i\}} \delta\left(\sum_i s_i - M\right) e^{-\beta \mathcal{H}[s_i]} \quad (4.1.7)$$

If we switch the order of the sums around, we then get,

$$Z(T, h) = \sum_{\{s_i\}} \left[ \sum_M e^{\beta h M} \delta\left(\sum_i s_i - M\right) \right] e^{-\beta \mathcal{H}[s_i]} = \sum_{\{s_i\}} e^{\beta h \sum_i s_i} e^{-\beta \mathcal{H}[s_i]} = \sum_{\{s_i\}} e^{-\beta(\mathcal{H}[s_i] - h \sum_i s_i)} \quad (4.1.8)$$

Here the sum is now an unconstrained sum over all possible spin configurations  $\{s_i\}$ , with any value of  $M$ , and the term in the Boltzmann factor involving the conjugate variable  $h$  looks just like the interaction of the spins with a magnetic field  $h$ . The constant  $h$  ensemble is thus similar to the grand canonical ensemble in the occupation number representation, where one sums in an unconstrained way over all sets of occupation numbers  $\{n_i\}$ , and  $h$  is playing a role similar to the chemical potential.

One then has, for the Gibbs free energy,

$$G(T, h) = -k_B T \ln Z(T, h) \quad (4.1.9)$$

and one can show that  $G$  computed this way will agree with the  $G$  computed from the Legendre transform of  $F$ , in the thermodynamic limit where the number of spins  $N \rightarrow \infty$ . To check this we can compute,

$$\left(\frac{\partial G}{\partial h}\right)_T = -\frac{k_B T}{Z} \left(\frac{\partial Z}{\partial h}\right)_T = -\frac{k_B T}{Z} \sum_{\{s_i\}} \frac{\partial}{\partial h} \left( e^{-\beta(\mathcal{H} - h \sum_i s_i)} \right)_T \quad (4.1.10)$$

$$= -\frac{k_B T}{Z} \sum_{\{s_i\}} e^{-\beta(\mathcal{H} - h \sum_i s_i)} \left( \beta \sum_i s_i \right) = \frac{-\sum_{\{s_i\}} e^{-\beta(\mathcal{H} - h \sum_i s_i)} \left( \sum_i s_i \right)}{\sum_{\{s_i\}} e^{-\beta(\mathcal{H} - h \sum_i s_i)}} \quad (4.1.11)$$

$$= -\left\langle \sum_i s_i \right\rangle = -M \quad \text{so} \quad \left(\frac{\partial G}{\partial h}\right)_T = -M \quad \text{as required} \quad (4.1.12)$$

We can work in the fixed magnetization *or* fixed magnetic field ensemble, according to our convenience. Usually it is easiest to work with fixed magnetic field  $h$ . In this case we usually write,

$$\mathcal{H} = -J \sum_{\langle ij \rangle} s_i s_j - h \sum_i s_i \quad (4.1.13)$$

and include the magnetic field interaction within the definition of the Hamiltonian. With this definition of  $\mathcal{H}$ , we have for the partition function,

$$Z(T, h) = \sum_{\{s_i\}} e^{-\beta \mathcal{H}} \quad (4.1.14)$$

### Intensive Formulation

The above Helmholtz and Gibbs free energies are extensive quantities. It is useful to also define corresponding intensive quantities. For a system with  $N$  total spins, we can define the *magnetization density*, i.e. the magnetization per spin,

$$m = \frac{M}{N} = \frac{1}{N} \left\langle \sum_{i=1}^N s_i \right\rangle \quad (4.1.15)$$

we then have,

Helmholtz free energy density:

In the limit  $N \rightarrow \infty$ , we have  $F(T, M) = Nf(T, m)$ .

$$\frac{F}{N} \equiv f(T, m) \quad \text{depends on the magnetization density } m \quad (4.1.16)$$

$$df = -sdT + hdm \quad \text{where } s = \frac{S}{N} \text{ is the entropy per spin} \quad (4.1.17)$$

(don't confuse entropy per spin  $s$  with the spin  $s_i$ !)

Gibbs free energy density:

In the limit  $N \rightarrow \infty$ , we have  $G(T, h) = Ng(T, h)$ .

$$\frac{G}{N} \equiv g(T, h) \quad \text{depends on the magnetization field } h \quad (4.1.18)$$

$$dg = -sdT - mdh \quad (4.1.19)$$

We then have,

$$\left( \frac{\partial f}{\partial m} \right)_T = h \quad \text{and} \quad \left( \frac{\partial g}{\partial h} \right)_T = -m \quad (4.1.20)$$