1 Lecture 2. Phase transitions, the mean field approach

1.1 Phase transition types

The degree of ordering in every system is negotiated between interactions that enforce order and thermal motion acting to enhance disorder. As a result of the competition between the tendencies to minimize energy and to maximize entropy, many systems can form two (or more) different macroscopic phases, depending on parameters, such as temperature, pressure, etc. The phases are in equilibrium at certain temperature and pressure values, usually forming a *transition line.* Because of different thermodynamic properties of the phases, away from the transition line one of them is lower in energy than the other one.

For the phases coexisting in thermodynamic equilibrium, certain conditions must be satisfied. Thermodynamic variables such as pressure, chemical potential, etc., have to be equal. However, for distinct phases the quantities such as entropy and density are typically not equal, — they experience a jump at the transition line (thus a finite latent heat and volume change). Such *discontinuous transitions* are known as phase transitions of first order, or type I transitions.

The canonical example is a liquid–gas transition. Remind of the phase diagram, coexistence line, Clausius-Clapeyron equation for the slope of this line, the van der Waals equation of state, and describe the critical point at which the phase transition line terminates.

The characteristic feature here, from the symmetry point of view that we are developing, is that the two phases are not different in symmetry in any way. Indeed, the liquid and gas states differ only by density, but have the same order (rather, disorder!) characteristics. Many other examples of this nature exist. In fact, most of the phase transitions, especially in material science, metallurgy, chemistry, etc. are of type I.

Briefly mention binary alloys, a solid state version of the liquid–gas transition. A lattice gas problem: two kinds of atoms occupying sites of the same lattice at random. Due to atom interaction, ordering takes place at low temperature. Depending on the interaction details, the ordering can be different. If, for example, like atoms attract each other, while unlike atoms repel each other, the system phase separates in the phases rich in atoms of one particular sort. For more detail see PS2, Problem #2.

Besides the transitions in which system state and properties experience a jump, there is a totally different kind of phase transitions, known as transitions of second order, or type II. In such transitions, as first pointed out by Landau, there is an abrupt symmetry change, while the state of a system may evolve continuously through the transition. The symmetry change may occur, e.g. via a small displacement of atoms in a crystal lattice (breaking lattice periodicity), ordering of spins in a magnet (breaking the time reversal symmetry), Bose condensate formation (breaking the gauge invariance), etc. More generally, the second order transitions are related with some kind spontaneous symmetry breaking, that takes place below certain temperature.

Let us illustrate the difference in symmetry change between the type I and II transitions by an example. Consider a binary alloy with cubic lattice structure, in which like atoms repel, while unlike atoms attract. When the density of the two atoms is equal, there are two ground states at $T = 0$, with atoms of each type occupying one of the two sublattices of the cubic lattice:

$$\begin{array}{cccc} a & b & a & b \\ b & a & b & a \\ a & b & a & b \\ b & a & b & a \end{array} \quad \text{or} \quad \begin{array}{cccc} b & a & b & a \\ a & b & a & b \\ b & a & b & a \\ a & b & a & b \end{array} \tag{1}$$

These states have lower symmetry than the disordered state at high temperature, since they are not invariant under translation by lattice period. Such a translation maps one of the two states onto the other one, and reverse. This means that there is an abrupt symmetry change when an ordering like this takes place. Note that the overall density of atoms, however, does not change. This is in contrast with the above example of a type I transition, the phase separation in a binary alloy, where the low temperature phases have the same symmetry as the high temperature phase, while there is a density jump at the transition.

Although the quantities like entropy, density, etc. are continuous at the transition (hence the name "type II"), the abrupt symmetry change leads to a number of very striking physical phenomena, most notably, divergences and singularities in physical quantities of a power law form, strong fluctuations and slow relaxation, the appearance of soft modes. The physics of these transitions is conceptually extremely rich, and many areas of physics besides statistical mechanics, have benefited from the theory of second order phase transitions. Which is an excuse for us to spend a fair fraction of the course studying the properties of such transitions.

2 Mean field theory

There is a very simple and useful method that starts with a microscopic model and enables to estimate the temperature at which the transition occurs, and to relate the quantities below and above the transition. It is highly popular because of broad applicability and relatively high accuracy, not to mention simplicity.

Let us illustrate it for the Ising ferromagnet model

$$\mathcal{H} = -\frac{1}{2}\sum_{r\neq r'} J(r-r')\sigma_r\sigma_{r'} \tag{2}$$

with $\sigma_r = \pm 1$. The exchange interaction $J(r-r') > 0$, in principle, can be arbitrary. However, the approximation to be made can be justified rigorously only for exchange interaction of large radius, such as

$$J(r-r') = \begin{cases} U, & |r-r'| < R; \\ 0, & |r-r'| > R, \end{cases} \quad \text{with} \quad R \gg 1 \tag{3}$$

The partition function of the system in magnetic field H is

$$Z = \mathrm{tr}\ \exp\left(\frac{1}{2}\beta \sum_{r\neq r'} J(r-r')\sigma_r\sigma_{r'} + \sum_r \sigma_r \beta H\right) \tag{4}$$

where tr stands for a sum over all spin variables $\sigma_r = \pm$.

Without the couplings $J(r-r')$ one would have independent spins, each polarized by magnetic field as

$$(\sigma_r) = \frac{\sum_{\sigma_r=\pm} \sigma_r e^{\sigma_r\beta H}}{\sum_{\sigma_r=\pm} e^{\sigma_r\beta H}} = \tanh(\beta H) \tag{5}$$

But with the couplings the problem becomes more complicated. :–(

The central idea of the mean field approach is to approximate the interacting problem (4) by a simpler interacting partition function. Usually this is the point when insight enters the analysis. In this case, since the interaction radius is large, each spin experiences an average field of many spins, and thus we can replace spin–spin interaction by an interaction of each spin with an average magnetization of spins around it. :–) There are many ways to do it, some of which are illustrated in the homework (PS#2). One particularly nice way is to rewrite the product $\sigma_r\sigma_{r'}$ in the partition function (4) as

$$\sigma_r\sigma_{r'} = (M + (\sigma_r - M))(M + (\sigma_{r'} - M)) \tag{6}$$

where $M = (\sigma_r)$. Expanding this to first order in the deviations $\delta\sigma_r = \sigma_r - M$,

$$M^2 + M((\sigma_r - M) + M(\sigma_{r'} - M) + O(\delta\sigma_r^2), \tag{7}$$

we approximate the exponent in (4) by

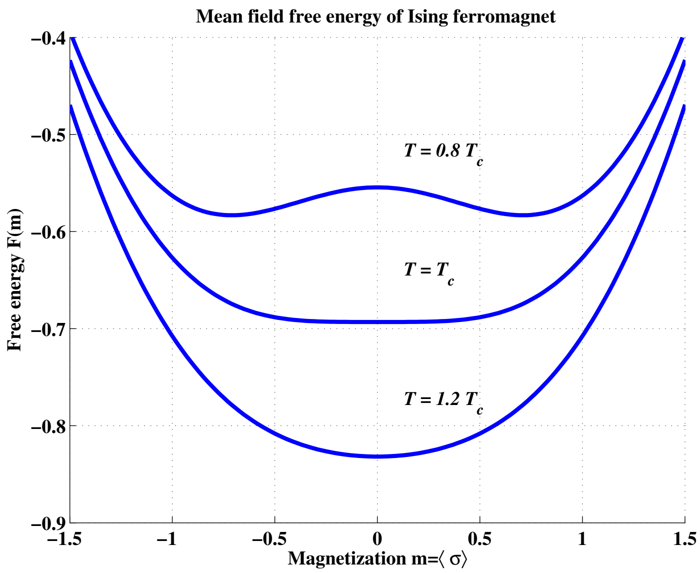
$$\frac{1}{2}\beta \sum_{r\neq r'} J(r-r')(M(\sigma_r + \sigma_{r'}) - M^2) + \beta H \sum_r \sigma_r = -\frac{1}{2}N\beta J M^2 + \beta(JM + H)\sum_r \sigma_r \tag{8}$$

where $J = \sum_{r'\neq r} J(r-r')$, and N is the total number of sites. The terms ignored in making this approximation correspond to correlations of the spins. This may be too drastic and even questionable when interactions are nearest neighbor. For interactions of large radius, due to a large number of interacting spins and the central limit theorem, the replacement of a sum of fluctuating spin variables by its average value is a reasonable approximation.

This yields an answer for Z,

$$Z = e^{-\frac{1}{2}N\beta J M^2} \left[2\cosh(\beta(JM + H))\right]^N , \tag{9}$$

Figure 1:



and for the free energy per site

$$F(M) = -T \ln Z/N = \frac{1}{2} J M^2 - \beta^{-1} \ln\left[2\cosh(\beta(JM + H))\right] \tag{10}$$

with irrelevant constant subtracted.

We have not yet specified M. The value M is determined by minimizing $F(M)$, since the most probable value corresponds to the lowest free energy. Evaluating the derivative dF/dM and setting it to zero, obtain

$$M = \tanh(\beta(JM + H)) \tag{11}$$

Interpretation: the field polarizing each spin is enhanced by JM due to a feedback from other polarized spins. The corresponding contribution, JM, is called *the molecular field.* In the theory of magnetism it was introduced by Weiss.

There are, in general, several different solutions to Eq.(11). To decide which of them should be chosen, it is instructive to consider the system in the absence of external field. For $H = 0$ and small M, the free energy Taylor expansion is

$$F(M) = \frac{1}{2} J(1 - \beta J) M^2 + O(M^4) \tag{12}$$

Depending on the sign of the M^2 term, there are two situations. For large $T > J$, there is single minimum of $F(M)$ at $M = 0$. At low $T < J$, the point $M = 0$ is a local maximum, with two degenerate minima $M = \pm M_0$. The system has to choose one of them and then the $\sigma_r \to -\sigma_r$ symmetry is spontaneously broken. The value $T_c = J$ is the mean field theory result for the critical temperature.

At finite H, the function $F(M)$ is asymmetric, the two minima are not degenerate. In this case, there is no symmetry loss, or bifurcation, upon lowering temperature. The spins are polarized along H even at high temperature and this polarization gradually increases as T goes below T_c. An interpretation of the difference from $H = 0$, from symmetry point of view, is that the Hamiltonian in the presence of a finite H does not possess the $\sigma_r \to -\sigma_r$ symmetry. Hence no symmetry breaking occurs.

Another example is provided by the Heisenberg model

$$\mathcal{H} = -\frac{1}{2} \sum_{r \neq r'} J(r - r')\, \mathbf{S}_r \cdot\, \mathbf{S}_{r'} \tag{13}$$

with $\mathbf{S}_r$ unit classical vectors. The partition function of the system in magnetic field $\mathbf{H}$ has the form

$$Z = \mathrm{tr}\ \exp\left(\frac{1}{2}\beta \sum_{r \neq r'} J(r - r')\mathbf{S}_r \cdot \mathbf{S}_{r'} + \sum_r \beta \mathbf{S}_r \cdot \mathbf{H}\right) \tag{14}$$

where tr stands for an integral over the configuration space (N independent integrals over unit sphere $|\mathbf{S}_r| = 1$ for N spins).

Introducing the mean polarization $\mathbf{M} = \langle \mathbf{S}_r \rangle$ and repeating the above steps (6), (7), (8), we have

$$F(\mathbf{M}) = \frac{1}{2} J\mathbf{M}^2 - \beta^{-1} \ln\left[\int \exp(\beta(J\mathbf{M} + \mathbf{H}) \cdot \mathbf{S}) d\mathbf{S}\right] \tag{15}$$

with the integral taken over the sphere $|\mathbf{S}| = 1$. The integral over $d\mathbf{S}$ is

$$2\pi \int_{-1}^{1} e^{\beta(JM+H)x} dx = 4\pi \frac{\sinh(\beta(JM + H))}{\beta(JM + H)} \tag{16}$$

Minimizing $F(\mathbf{M})$, obtain an equation for magnetization:

$$M = \coth(\beta(JM + H)) - 1/(\beta(JM + H)) \tag{17}$$

Despite looking very different from the above result (11) for the Ising model, this equation has the same qualitative properties. The equation for critical temperature $T_c = \frac{1}{3}J$ is obtained by setting $H = 0$ and expanding the right hand side of Eq.(17) in powers of M.

Comment 1: The mean field estimate for T_c is almost always an overestimate. This is because thermal fluctuations, partly ignored in the derivation, reduce the molecular field.

Comment 2: The large radius of interaction condition, required for the mean field approach to be accurate, is often replaced within a nearest neighbor interaction model by a requirement of a large number of neighboring spins. Since in a d-dimensional cubic lattice the number of nearest neighbors of each site is $2d$, this is equivalent to taking the limit of a high space dimension.

3 Summarize

- **Type I phase transitions** are discontinuous, accompanied by jumps in physical quantities, such as density or entropy, latent heat and volume change. The symmetry is typically not changed in such transitions.

- **Type II phase transitions** are very different. In such transitions, physical quantities vary continuously, while symmetry changes abruptly. The phase transformation in a type II transition is described by spontaneous symmetry breaking.

- **Mean field theory:** a very successful approximation technique that captures correctly all qualitative features of the type I and II transitions. It gives numerically accurate results for the phase transitions in systems with large interaction radius or large number of interacting neighbors.