In the last lecture, we had a first introduction of mean field theory using the van der Waals model for fluids. We now want to examine mean field theory in general and develop some basic tools for studying phase transitions in a variety of systems. Recall that mean field theory is a means by which to approximate the specific interactions between a given molecule and all the other molecules in the system. That is, instead of considering the detailed interactions of a molecule and its neighbours, we treat the neighbours as producing a mean field, like an “external field”, by which the molecule interacts. A common feature of mean-field theories is the identification of an order parameter. We will consider two approaches in dealing with these order parameters.

1. **Weiss molecular field approximation:**
   - approximate an interacting system by a non-interacting system in a self-consistent external field which is expressed in terms of the order parameter

2. **Bragg-Williams approximation**
   - express our approximate free energy in terms of an order parameter and minimize the free energy with respect to this order parameter.

### 12.1 Weiss molecular field approximation

In order to explore this method, we will use a simplified model, called the **Ising model**, for a magnetic system. We have actually studied this system in some detail in Stat Phys I; however, we did not include interactions between the spins. We consider $N$ magnetic atoms situated on a regular lattice which interact according to

\[
H = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i
\]  

(12.1)
where $J$ is a coupling constant (i.e. coupling between spins), $\langle ij \rangle$ implies that the sum is carried over nearest neighbour pairs of lattice sites, $h$ is proportional to the magnetic field but is in units of energy, and $\sigma_i = \pm 1$ denotes the spin of the atom.

The first term in 12.1 corresponds to the exchange interaction and the second term is the Zeeman interaction (interaction of atoms with external magnetic field).

Before getting into the details of the theory, let us consider the approximate behaviour of the system at different temperature limits:

At $T = 0$:
- ground state
- spins point in the same direction as the field in order to minimize the total energy (energy dominates)

At $T = \infty$:
- spins are randomly oriented and entropy dominates.

It is possible for these two states of the system to be separated by a phase transition for which, at some critical temperature, $T_c$, there is a sudden change in the system from the ordered to the disordered state.

How do we identify such a transition?

We will use an order parameter, which for the current model is just the magnetization,

$$ m = \langle \sigma \rangle \quad (12.2) $$

where $\sigma$ labels the spin orientation, as defined above.

Let us consider the $i$th spin. We will approximate our pair or exchange term as,

$$ H(\sigma_i) \approx -\sigma_i (qJ \langle \sigma \rangle + h) = \sigma_i (qJm + h) \quad (12.3) $$

That is, we consider the potential experienced by the $i$th spin in the mean-field of its neighbours, where we have replaced the fluctuating values of the exchange field with an effective average field.

For the moment, let us drop the external field component, so that $H(\sigma_i) = \sigma_i qJm$ and

$$ m = \langle \sigma_i \rangle = \frac{e^{\beta qJm} - e^{-\beta qJm}}{e^{\beta qJm} + e^{-\beta qJm}} $$

therefore,

$$ m = \tanh (\beta qJm) \quad (12.4) $$

Certainly one (trivial) solution for this equation is $m = 0$. To obtain other solutions, the above equation must be solved self-consistently, that is, substitute a guess for $m$ into the r.h.s. of the above equation and obtain a new value of $m$ from the l.h.s., which you then plug back into the r.h.s, etc. Alternatively, you could solve this “transcendental equation”
graphically: plot the l.h.s. (a line) and the r.h.s (the hyperbolic tan function), the value(s) of \( m \) where the two curves intersect represents the solution(s) to the above equation.

Before demonstrating this second procedure, let us first consider an expansion of \( \tanh(x) \), \( x = \beta q J m \) for small \( x \),

\[
\tanh(x) \approx x - \frac{1}{3} x^3
\]

Therefore, for \( m \neq 0 \), we have from 12.4

\[
m \approx \beta q J m - \frac{1}{3} (\beta q J m)^3
\]  

(12.5)

which requires that, \( \beta q J \geq 1 \) showing that the transition must occur at \( \beta_c q J = 1 \) or,

\[
T_c = \frac{q J}{k}
\]

(12.6)

where \( T_c \) denotes the transition temperature.

Note that near \( T_c \) we expect \( m \) to be small, therefore our above expansion is reasonable and we can solve for \( m \) as,

\[
m^2 = \frac{3 (\beta q J - 1)}{(\beta q J)^3}
\]

thus,

\[
m \approx \pm \sqrt{3 \left( \frac{T}{T_c} \right)^{3/2} \left( \frac{T_c}{T} - 1 \right)^{1/2}}
\]

(12.7)

which is the standard result characteristic of mean-field theory and demonstrates the general behaviour of a continuous phase transition.

**Graphical Analysis** With \( T_c = q J / k \), let \( y_1 = m \) and \( y_2 = \tanh \left( \frac{T_m}{T} \right) \) from Eq. 12.4. Note that the slope of \( y_1 \) is 1, whereas the slope of \( y_2 \) is,

\[
slope y_2 = \frac{d \tanh \left( \frac{T_m}{T} \right)}{dm} \bigg|_{m=0}
= \sec^2 \left( \frac{T_c m}{T} \right) \bigg|_{m=0} \frac{T_c}{T} = \frac{T_c}{T}
\]

Hence, for \( T > T_c \), the slope is less than one and, as discussed above, the only solution is \( m = 0 \). For \( T < T_c \), the slope is greater than 1 and we obtain 2 solutions. This may be seen graphically as follows,
In the figures above, we have included the effects of an external field $h$, which causes a shift in the curves. If we were then to plot the magnetization, $m$, as a function of $h$, we would obtain,

Therefore, we get a discontinuous jump in our value for $m$ as a function of $h$. The behaviour of the order parameter, for $T < T_c$, as shown above can be explained by looking at the free energy as a function of $m$ for different values of $h$.

Therefore, we get a discontinuous jump in our value for $m$ as a function of $h$. That is, for $h < 0$, now our new minimum occurs for $m < 0$, whereas it is greater than zero for $h > 0$. For $T > T_c$, the minimum value for the free energy changes continuously with a continuous change in $m$ \emph{i.e.}, $m$ for minimum $F$ is a continuous function of $h$.

In the above figure for $m$ vs $h$, we plotted a single isotherm. Let us consider other values of $T$, both for $T < T_c$ and $T > T_c$. 
From the above figure, it is clear that we obtain a similar pattern to that observed for the liquid gas problem. Namely, we observe first-order behaviour for values of $T < T_c$ and continuous (or 2$^{nd}$ order behaviour for values of $T > T_c$. we can summarize this graphically as follows,