8.334: Statistical Mechanics II   Problem Set # 2   Due: **2/19/03**

Phase transitions, the mean field approach, Landau theory

1. Ising ferromagnet

In an Ising model of a ferromagnet the spin degrees of freedom are discrete, $\sigma_r = \pm 1$, and the Hamiltonian of spin interaction is[1]

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

Here $J(r-r') > 0$ is spin exchange interaction.

For spin interaction of large radius, the effect of spin interaction can be analyzed using the mean field approach. For that, the interaction of a spin σ_r with all other spins is replaced by interaction with an effective field

$$\mathcal{H}(\sigma_r) = -\sigma_r B_r\,, \quad B_r \equiv -\delta\mathcal{H}/\delta\sigma_r = \sum_{r'} J(r-r')\,\langle\sigma_{r'}\rangle\,, \tag{2}$$

with $\langle\sigma_{r'}\rangle$ the statistical average values of the spins. For the interaction of large radius, replacing spins by their average values in the sum over r' can be justified by the central limit theorem.

a) Find spin magnetization $m = \langle\sigma_r\rangle$ for the problem (2) and, using the relation between B_r and $\langle\sigma_{r'}\rangle$, obtain an equation for the magnetization.

b) Show that there is a temperature T_c, called Curie temperature, below which this equation has a nonzero solution. Sketch $m(T)$. How does it behave at $T \ll T_c$ and $|T - T_c| \ll T_c$?

c) Near $T = T_c$, find the free energy F, entropy S and specific heat C above and below T_c. Sketch the temperature dependence $S(T)$ and $C(T)$.

2. The Binary Alloy

In a model of a binary alloy, each cite of the lattice can be occupied by a particle of type A or one of type B. The interactions between the different types of particles are given by $J_{AA}(r-r')$, $J_{BB}(r-r')$ and $J_{AB}(r-r')$. Consider an alloy consisting of N_A particles of type A, and N_B particles of type B. Assume attractive an interaction energy J_{AA}, $J_{BB} < 0$ between like neighbors $A-A$ and $B-B$, but a repulsive energy $J_{AB} > 0$ for an $A-B$ pair. In a generic alloy, $J_{AA} \neq J_{BB}$.

a) What is the gound state of the system at zero temperature, the particle densities $n_A = N_A/(N_A+N_B)$ and $n_B = N_B/(N_A+N_B)$ being fixed?

b) At finite tmperature, estimate the total interaction energy assuming that the atoms are randomly distributed among lattice cites, i.e. each cite occupied independently with probabilities $p_A = n_A$, $p_B = n_B$.

c) Estimate the mixing entropy of the alloy within the same approximation. Assume $N_{A,B} \gg 1$.

d) Using the above, obtain a free energy function $F(x)$, where $x = (n_A - n_B)$. Show that the requirement of convexity of $F(x)$ breaks down below a critical temperature T_c.

[1] This model describes a situation when due to a spin-orbital crystal field spins are aligned with some particular crystal axis.

e) Sketch $F(x)$ for $T > T_c$, $T = T_c$ and $T < T_c$. For $T < T_c$ there is a range of compositions $x_1 < x < x_2$ where $F(x)$ is not convex and thus the composition is locally unstable. Plot the so-called *spinodal lines*[2] $x_{1,2}(T)$ in the (T, x) plane.

f) Describe what happens with an alloy cooled from higher to lower temperature, depending on the composition. In the (T, x) plane sketch the phase separation boundary, dividing the (T, x) plane into the stability regions of the A rich and B rich phases and the unstable region.

3. Ising ferromagnet, a different approach

Let us solve Problem 1 by using the method of Problem 2. To map the spin problem (1) on the binary alloy problem, consider a microcanonical ensemble with fixed total magnetization $M = \sum_r \sigma_r$. In this case, out of total N spins, $N_+ = (N + M)/2$ is up and $N_- = (N - M)/2$ is down.

a) Assuming the occupation of different sites to be statistically independent, and using the occupation probabilities $p_\pm = (N \pm M)/2N$, find the energy of spin interaction as a function of M.

b) Find the entropy and the free energy as a function of M. Sketch $F(M)$ at different temperatures. Show that $F(M)$ does not satisfy the convexity requirement at $T < T_c$. Find the critical temperature T_c.

c) Below T_c find the values of M for which the uniform state is stable.

d) Evaluate the free energy and compare the result with that of Problem 1.

4. Symmetry and transition type

Consider an Ising ferromagnet (1) with the nearest neighbor interaction: $J(r - r') \neq 0$ only when $|r - r'| = 1$. Map this problem onto the binary alloy problem. Now, note that the ferromagnetic ordering emerges via a second order phase transition, whereas the ordering transition in a generic binary alloy is first order. Can you interpret/explain this by a symmetry argument in the Landau theory spirit?

5. Liquid crystal ordering transition

In some liquid crystals, the order parameter is the local electric quadrupole moment, which can be represented by a symmetric traceless tensor Q_{ij}, tr $Q = 0$. The specific form of the tensor Q_{ij} depends on the ordering type. For instance, in nematic liquid crystals discussed in class, the relation between Q_{ij} and nematic director vector $\mathbf{n}$ is $Q_{ij} = Q(T)(n_i n_j - \frac{1}{3}\delta_{ij})$.

Consider a spatially uniform state (no gradients!). Near the phase transition from liquid into liquid crystal, consider the Landau free energy $F(Q)$ as power series in Q. What are the various lower order terms that are allowed, by rotational symmetry, to appear in the free energy? Show that this suggests that the transition into the ordered phase should be the first order for this system.

[2] The spinodal line indicates onset of metastability and hysteresis effects.