**8.334:** Statistical Mechanics II    Problem Set # 2

## 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 $\sigma_r$ 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.*

$$m = \frac{1}{Z}\mathrm{Tr}\,\sigma e^{-\beta\sigma B_{eff}} = \tanh\beta B_{eff} \tag{3}$$

*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 $|T - T_c| \ll T_c$?*

Since $\tanh x < x$ for $x > 0$, for $\beta J \geq 1$ the only solution is $m = 0$. At $\beta J > 1$ there is a none-zero solution. The magnetization as a function of temperature is shown on Fig. 1.

Suppose $T$ is close to $T_c = J$. Then we expect magnetization to be small and can expand the RHS of the equation (3):

$$m = \frac{T_c}{T}m - \frac{1}{3}\left(\frac{T_c}{T}m\right)^3 + O(m^5) \tag{4}$$

and solve for $m$:

$$m \approx (3\tau)^{1/2}\,, \quad \tau \equiv (T_c - T)/T \tag{5}$$

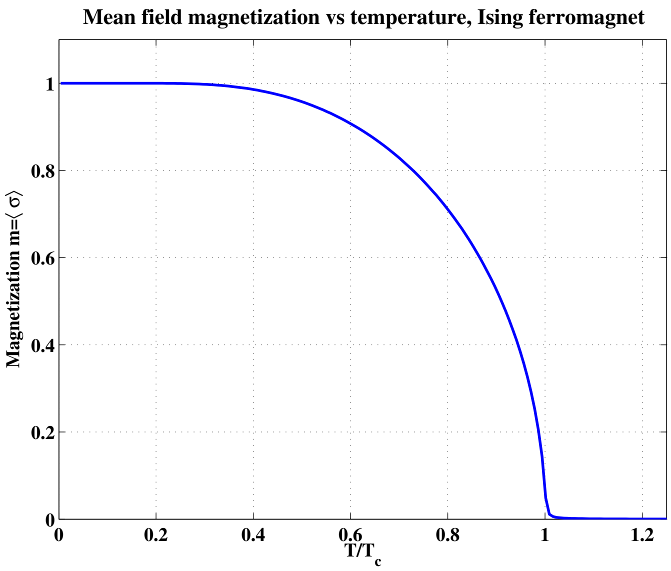
For small temperatures, $T \ll T_c$, i.e. large $\beta J$, $\tanh x \to 1 - 2e^{-2x} + O(e^{-4x})$ and we obtain

$$m(T) \approx 1 - 2e^{-2T_c/T} \tag{6}$$

*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 $C(T)$.*

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

Figure 1:




The expression for the free energy is given in Lecture 2:

$$F = \frac{1}{2}Jm^2 - T\ln(2\cosh\beta Jm) \tag{7}$$

For $T > T_c$ $F(T) = -T\ln 2$. Hence $S = \ln 2$ and $c = 0$. For $T < T_c$

$$F(T) = \frac{1}{2}Jm^2 + \frac{T}{2}\ln\left(1 - \tanh^2(\beta Jm)\right) - T\ln 2 = \frac{1}{2}Jm^2 + \frac{T}{2}\ln(1-m^2) - T\ln 2 \tag{8}$$

Expand this expression in m

$$F(T) = \frac{1}{2}(T_c - T)m^2 - \frac{T}{4}m^4 + O(m^6) - T\ln 2 \tag{9}$$

Near $T_c$ the first two terms are of the same order and the higher-order terms can be dropped:

$$F(T)_{T<T_c} = 3\frac{T_c}{2}\tau^2 - \frac{9T_c}{4}\tau^2 + O\left(\tau^3\right) - T\ln 2 \approx -\frac{3T_c}{4}\tau^2 - T\ln 2 \tag{10}$$

Therefore

$$S(T) = \ln 2 - \begin{cases} 3\tau/2\tau + O\left(\tau^2\right), & \tau > 0 \\ 0, & \tau < 0 \end{cases} \tag{11}$$

$$C(T) = \begin{cases} 3/2 + O\left(\tau\right), & \tau > 0 \\ 0, & \tau < 0 \end{cases} \tag{12}$$

**2. The Binary Alloy**

*In a model of a binary alloy, each site 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 ground 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?*

If the concentrations were not fixed, the system would have two ground states — all sites occupied by particles of type A or all sites occupied by particles of type B. For fixed densities the system will phase separate into A–rich and B–rich regions.

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

The energy per site is

$$E=\frac{1}{2}J_{AA}n_A^2+\frac{1}{2}J_{BB}n_B^2+J_{AB}n_An_B \tag{13}$$

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

The entropy is $S=\ln\Gamma$ where

$$\Gamma=\binom{M}{N_A}=\frac{N!}{N_A!N_B!}=e^{N\ln N-N_A\ln N_A-N_B\ln N_B} \tag{14}$$

(we used the Sterling formula, $n!=(2\pi n)^{1/2}(n/e)^n$). Therefore the entropy is

$$S=-n_A\ln n_A-n_B\ln n_B \tag{15}$$

*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 $T_c$.*

The free energy is $F=E-TS$. Introduce $x=n_A-n_B$ so that $n_{A,B}=(1\pm x)/2$. Then

$$E(x)=Const+\frac{1}{8}\left(J_{AA}+J_{BB}-2J_{AB}\right)x^2+\frac{1}{4}(J_{AA}-J_{BB})x \tag{16}$$

and

$$S(x)=-\frac{1}{2}\left((1+x)\ln\left(\frac{1+x}{2}\right)-(1-x)\ln\left(\frac{1+x}{2}\right)\right) \tag{17}$$

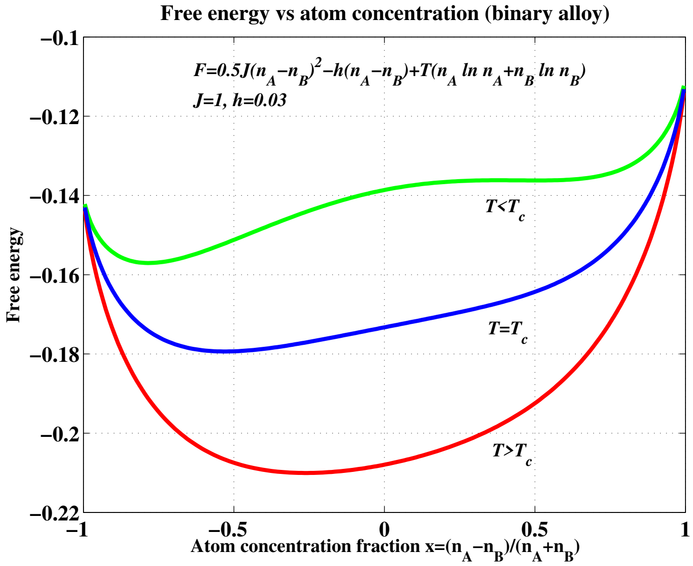
Now we compute $\partial^2F/\partial x^2$:

$$\frac{\partial^2F}{\partial x^2}=\frac{1}{4}\left(J_{AA}+J_{BB}-2J_{AB}\right)+T\frac{1}{1-x^2} \tag{18}$$

The first term is negative while the last term is positive . The lowest value of the second term, as a function of $x$, is $T/2$ (at $x=0$). Hence $\partial^2F/\partial x^2>0$ for $T>T_c=(2J_{AB}-J_{AA}-J_{BB})/4$ and becomes negative at $T<T_c$, first near $x=0$.

*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.*

Figure 2:




The free energy is plotted on Fig. 2

To find spinodal lines we solve $T < T_c$ $\partial^2 F/\partial x^2 = 0$:

$$\frac{1}{1-x^2} = \frac{T_c}{T} \tag{19}$$

which gives

$$x = \pm(1 - T/T_c)^{1/2} \tag{20}$$

Spinodal lines are plotted on Fig. 3

*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.*

If $F''(x) < 0$ the uniform state is unstable. The system separates into A–rich and B–rich phases with $x = x_A$ or $x = x_B$ given by common tangents (see Fig. 4). Volume fractions of the A,B rich phases are $(x_B - x)/(x_B - x_A)$ and $(x - x_A)/(x_B - x_A)$ respectively.

### 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 $M$.*

$$E = -\frac{1}{2}J(p_+ - p_-)^2 \tag{21}$$

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

Figure 3:

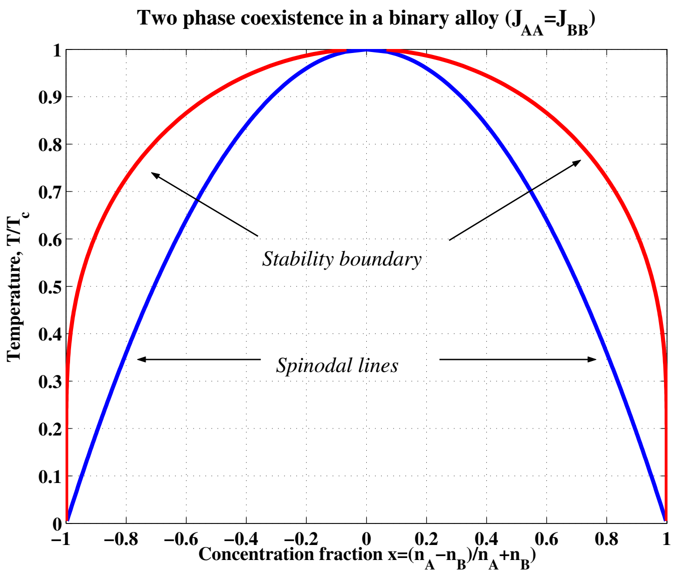
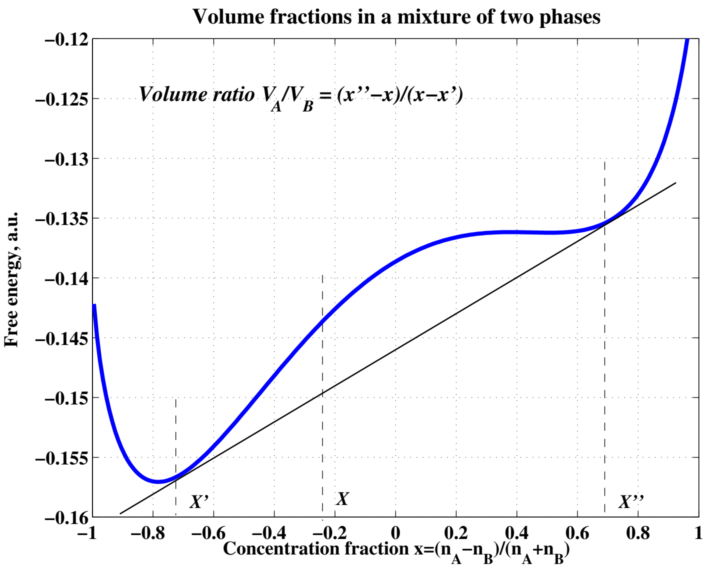



Figure 4:



where $p_\pm = (1 \pm m)/2$.

*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 $T_c$.*

$$S = -p_+ \ln p_+ - p_- \ln p_- \tag{22}$$

$$F = E - TS = -\frac{1}{2}Jm^2 + \frac{T}{2}\left[(1+m)\ln\frac{1+M}{2} + (1-m)\ln\frac{1-m}{2}\right] \tag{23}$$

$$\frac{\partial^2 F}{\partial m^2} = -J + \frac{T}{2}\left(\frac{1}{1+m} + \frac{1}{1-m}\right) = -J + \frac{T}{1-m^2} \tag{24}$$

Note that $\partial^2 F/\partial m^2$ becomes negative near $m = 0$ at $T < T_c$. (See the Fig. 2 in Problem 2).

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

Stable states correspond to energy minima $\partial F/\partial m = 0$. This gives

$$-Jm + \frac{T}{2}\ln\frac{1+m}{1-m} = 0 \tag{25}$$

or,

$$m = \tanh\left(\frac{J}{T}m\right) \tag{26}$$

the same equation for $m$ as in Problem 1.

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

Combining equations (23) and (25) we obtain:

$$F = -\frac{1}{2}Jm^2 + \frac{T}{2}\left[(1+m)\ln\frac{1+M}{2} + (1-m)\ln\frac{1-m}{2}\right] \tag{27}$$

$$= -\frac{1}{2}Jm^2 + \frac{T}{2}\left[\ln\left(\frac{1-m^2}{4} + m\ln\frac{1+m}{1-m}\right)\right] = \frac{1}{2}Jm^2 + \frac{T}{2}\ln\left[\frac{1-\tanh^2(Jm/T)}{4}\right] \tag{28}$$

$$= \frac{1}{2}Jm^2 - T\ln\left(2\cosh(J\beta m)\right) \tag{29}$$

**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?*

In the binary alloy problem we found a type I transition, while in the ferromagnet it is a type II transition. To see why this is consistent with the mapping, use the results of Problem 3:

$$F_{\text{Ising magnet}} = -\frac{1}{2}J\left(p_+ - p_-\right)^2 + T\left(p_+ \ln p_+ p_- \ln p_-\right); \tag{30}$$

$$F_{\text{Binary alloy}} = -\frac{1}{2}\left(2J_{AB} - J_{AA} - J_{BB}\right)\left(p_A - p_B\right)^2 + \left(J_{AA} - J_{BB}\right)\left(p_A - p_B\right) \tag{31}$$

$$+T\left(p_A \ln p_A + p_B \ln p_B\right) \tag{32}$$

Thus the binary alloy problem can be mapped to the magnet with $J = 2J_{AB} - J_{AA} - J_{BB}$ *in magnetic field* $h = -(J_{AA} - J_{BB})$. We observe that

- Finite magnetic field removes the $m \to -m$ symmetry of the magnet problem hence there is no type II transition
- Conserved particle number in the alloy problem translates into the fixed $M_{\text{total}}$ in the magnet problem, i.e. this is a microcanonical ensemble
- Cooling a magnet with fixed $M$ gives rise to phase separation into the regions $m$ up and $m$ down. In a finite external field this is a type I transition, just like in the alloy.

**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* $Q_{ij}$*,* $\mathrm{tr}\, Q = 0$*. 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.*

Consider the free energy of a liquid crystal expanded in $Q_{ij}$. In each order, we write all the invariant combinations

$$F(Q) = F_0 + AQ_{ij}Q_{ij} + B_1 \left(Q_{ij}Q_{ij}\right)^2 + B_2 Q_{ij}Q_{jp}Q_{pq}Q_{qi} + CQ_{ij}Q_{jp}Q_{pi} + \text{ gradient terms} \tag{33}$$

There are no other invariants, since $Q$ is traceless: $Q_{ii} = 0$. In the matrix form the free energy is

$$F = F_0 + A\mathrm{Tr}\, Q^2 + B_1 \left(\mathrm{Tr}\, Q^2\right)^2 + B_2 \mathrm{Tr}\, Q^4 + C\mathrm{Tr}\, Q^3 \; + \text{ gradient terms} \tag{34}$$

We found a cubic invariant allowed by the symmetry. This excludes type II transition in this system.