

PH4211 Statistical Mechanics

Problem Sheet 4 — Answers

1 Obtain an expression for the Helmholtz free energy for the Weiss model in zero external magnetic field, in terms of the magnetisation. Plot $F(M)$ for $T > T_c$, $T = T_c$ and $T < T_c$.

The Helmholtz free energy is defined as

$$F = E - TS .$$

The internal energy is given by

$$E = -\int B.dM .$$

The magnetic field, in the Weiss model, is the sum of the applied field and the local (mean) field

$$B = B_0 + b .$$

We shall write the local field in terms of the critical temperature:

$$b = \frac{Nk}{M_0^2} T_c M .$$

Integrating up the internal energy we obtain

$$E = -B_0 M - \frac{NkT_c}{2} \left(\frac{M}{M_0} \right)^2 .$$

For the present we will consider the case where there is no external applied field. Then $B_0 = 0$, and in terms of the reduced magnetisation $m = M/M_0$ (the order parameter) the internal energy is

$$E = -\frac{NkT_c}{2} m^2 .$$

Now we turn to the entropy. This is most easily obtained from the definition

$$S = -Nk \sum_j p_j \ln p_j$$

where p_j are the probabilities of the single-particle states. It is simplest to treat spin one half, which is appropriate for electrons. Then there are two states to sum over:

$$S = -Nk [p_\uparrow \ln p_\uparrow + p_\downarrow \ln p_\downarrow] .$$

Now these probabilities are simply expressed in terms of m , the fractional magnetisation

$$p_\uparrow = \frac{1+m}{2} \quad \text{and} \quad p_\downarrow = \frac{1-m}{2}$$

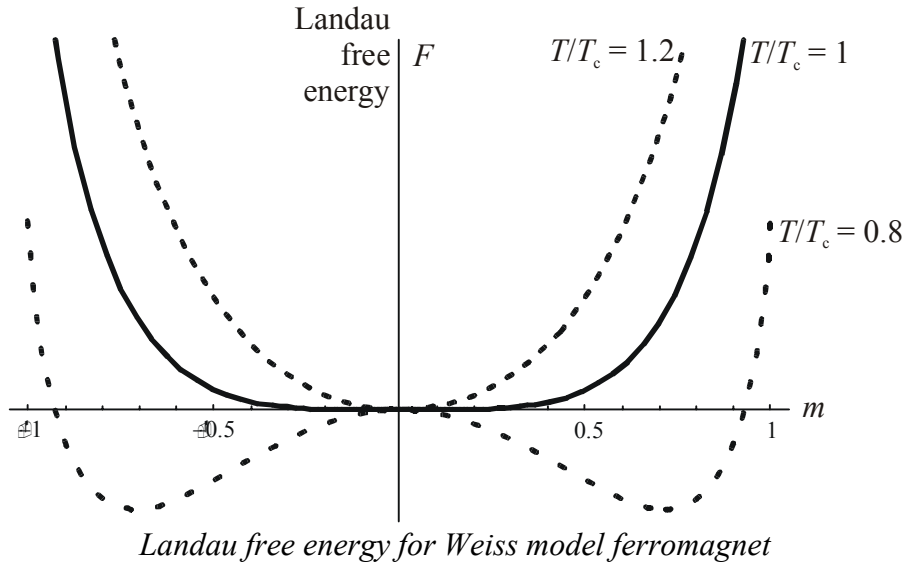
so that the entropy becomes

$$S = \frac{Nk}{2} [2 \ln 2 - (1+m) \ln(1+m) - (1-m) \ln(1-m)] .$$

We now assemble the free energy $F = E - TS$, to obtain

$$F = -\frac{Nk}{2} \left\{ T_c m^2 + T \left[2 \ln 2 - (1+m) \ln(1+m) - (1-m) \ln(1-m) \right] \right\}.$$

This is plotted for temperatures less than, equal to and greater than the critical temperature.



The occurrence of the ferromagnetic phase transition can be seen quite clearly from this figure. For temperatures above T_c we see there is a single minimum in the Landau free energy at $m = 0$, while for temperatures below T_c there are two minima either side of the origin. The symmetry changes precisely at T_c . There the free energy has flattened, meaning that m may make excursions around $m = 0$ with negligible cost of free energy – hence the large fluctuations at the critical point.

2 Show that $F = \frac{Nk}{2} \left\{ (T - T_c) m^2 + \frac{T_c}{6} m^4 + \dots \right\}$ for the Weiss model ferromagnet in the limit of small m . Explain the appearance of T_c in the m^4 term.

The free energy is given by

$$F = -\frac{Nk}{2} \left\{ T_c m^2 + T \left[2 \ln 2 - (1+m) \ln(1+m) - (1-m) \ln(1-m) \right] \right\}.$$

In order to expand this in powers of m we must expand the logarithms:

$$\log(1 \pm m) = \pm m - \frac{m^2}{2} \pm \frac{m^3}{3} - \frac{m^4}{4} \pm \dots$$

By expanding and collecting terms we obtain

$$F = \frac{Nk}{2} \left\{ -2T \ln 2 + (T - T_c) m^2 + \frac{T}{6} m^4 + \frac{T}{15} m^6 + \dots \right\}.$$

In the vicinity of the critical point the first term may be approximated by $2T_c \ln 2$; this is a constant and so it may be ignored. By a similar argument the T in the m^4 and the m^6 term should be replaced by T_c as T is restricted to the vicinity of the critical point. Then we have the expression for the free energy:

$$F = \frac{Nk}{2} \left\{ (T - T_c) m^2 + \frac{T_c}{6} m^4 + \dots \right\}$$

as required.

3 Show that $d^2F/d\varphi^2 > 0$ below T_c at the two roots $\varphi = \pm\sqrt{-F_2/2F_4}$ in the Landau model. Show that $d^2F/d\varphi^2 < 0$ below T_c and $d^2F/d\varphi^2 > 0$ above T_c at the single root $\varphi = 0$. What is the physical meaning of this?

The Landau free energy is

$$F = F_2\varphi^2 + F_4\varphi^4$$

so that its second derivative is

$$\frac{d^2F}{d\varphi^2} = 2F_2 + 12F_4\varphi^2.$$

For the two roots $\varphi = \pm\sqrt{-F_2/2F_4}$ below the transition

$$\varphi^2 = -F_2/2F_4$$

so that

$$\begin{aligned} \frac{d^2F}{d\varphi^2} &= 2F_2 + 12F_4 \frac{F_2}{2F_4} \\ &= -4F_2. \end{aligned}$$

Now F_2 is negative for temperatures below the transition:

$$F_2 = a(T - T_c),$$

so we see that below the transition the second derivative of F is positive for the two roots $\varphi = \pm\sqrt{-F_2/2F_4}$.

But at the root $\varphi = 0$ then

$$\frac{d^2F}{d\varphi^2} = 2F_2.$$

And since F_2 is negative then the second derivative is negative for the root at $\varphi = 0$.

From this we conclude that below the critical temperature the roots $\varphi = \pm\sqrt{-F_2/2F_4}$ are *minima* while the root at $\varphi = 0$ is a *maximum*.

Above the critical temperature there is the single root at $\varphi = 0$. Then

$$\frac{d^2F}{d\varphi^2} = 2F_2$$

but now F_2 is positive. So above the critical point the single root at $\varphi = 0$ is a *minimum*.

4 In the Landau theory of second order transitions calculate the behaviour of the order parameter below the critical point, $\varphi(T)$, when the *sixth* order term in the free

energy expansion is not discarded. What influence does this term have on the critical exponent β ? Comment on this.

The sixth order expression for the free energy is

$$F = F_2\varphi^2 + F_4\varphi^4 + F_6\varphi^6.$$

The equilibrium state is determined by minimising F : differentiate and set equal to zero

$$\frac{dF}{d\varphi} = 2F_2\varphi + 4F_4\varphi^3 + 6F_6\varphi^5 = 0.$$

One root of this equation is $\varphi = 0$. The other roots are roots of the equation

$$F_2 + 2F_4\varphi^2 + 3F_6\varphi^4 = 0.$$

And these roots are

$$\varphi^2 = \frac{-F_4 \pm \sqrt{F_4^2 - 3F_2F_6}}{3F_6},$$

but we must take the positive square root since φ^2 must be positive – note that F_2 is negative. Then the values of φ at the roots are

$$\varphi = \pm \sqrt{\frac{-F_4 + \sqrt{F_4^2 - 3F_2F_6}}{3F_6}}.$$

The singular behaviour arises from the temperature dependence of F_2 , which goes through zero at the critical point:

$$F_2 = a(T - T_c).$$

Then the (singular part of the) temperature variation of the order parameter is given by

$$\varphi = \pm \sqrt{\frac{-F_4 + \sqrt{F_4^2 - 3a(T - T_c)F_6}}{3F_6}}.$$

To find the order parameter critical exponent we must expand φ in powers of F_2 or $T - T_c$:

$$\varphi = \sqrt{-\frac{F_2}{2F_4}} + \frac{3F_6}{8} \sqrt{-\frac{F_2^3}{2F_4^5}} + \frac{63F_6}{128} \sqrt{-\frac{F_2^5}{2F_4^9}} + \dots$$

(This expansion may be obtained using a symbolic algebra system such as *Mathematica* or *Maple*, or it may be evaluated by hand as indicated below.) The temperature dependence of the order parameter is then given by

$$\varphi = \sqrt{-\frac{a(T - T_c)}{2F_4}} + \frac{3F_6}{8} \sqrt{-\frac{a^3(T - T_c)^3}{2F_4^5}} + \frac{63F_6}{128} \sqrt{-\frac{a^5(T - T_c)^5}{2F_4^9}} + \dots$$

The first term gives the leading order singularity. We see that it gives the order parameter critical exponent as $\beta = 1/2$. Observe that this leading order term is independent of F_6 ; indeed the series is seen to be an expansion in powers of F_6 . So the critical exponent is unaffected by the inclusion of the F_6 term.

▮ In order to perform the power series expansion of φ by hand we write the inner square root as

$$\begin{aligned}
\sqrt{F_4^2 - 3F_2F_6} &= F_4 \left(1 - \frac{3F_2F_6}{F_4^2} \right)^{1/2} \\
&= F_4 \left(1 - \frac{3F_2F_6}{2F_4^2} - \frac{9F_2^2F_6^2}{8F_4^4} + \dots \right) \\
&= F_4 - \frac{3F_2F_6}{2F_4} - \frac{9F_2^2F_6^2}{8F_4^3} + \dots
\end{aligned}$$

The expression for φ is then

$$\begin{aligned}
\varphi &= \pm \sqrt{-\frac{F_2}{2F_4} - \frac{3F_2^2F_6}{8F_4^3} - \frac{9F_2^3F_6^2}{16F_4^5} - \dots} \\
&= \pm \sqrt{-\frac{F_2}{2F_4}} \sqrt{1 + \frac{3F_2F_6}{4F_4^2} + \dots}
\end{aligned}$$

In the case that F_6 is zero we have the familiar expression

$$\begin{aligned}
\varphi &= \pm \sqrt{-\frac{F_2}{2F_4}} \\
&= \pm \sqrt{\frac{\alpha(T - T_c)}{2F_4}}
\end{aligned}$$

so we obtain the critical exponent $\beta = 1/2$.

Now incorporating the higher order terms, we have

$$\varphi = \pm \sqrt{-\frac{F_2}{2F_4}} \sqrt{1 + \frac{3F_2F_6}{4F_4^2} + \dots},$$

and since F_2 is small we can expand the second square root:

$$\varphi = \pm \sqrt{-\frac{F_2}{2F_4}} \left(1 + \frac{3F_2F_6}{8F_4^2} + \dots \right)$$

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5 A ferroelectric has a free energy of the form

$$F = \alpha(T - T_c)P^2 + bP^4 + cP^6 + DxP^2 + Ex^2$$

where P is the electric polarisation and x represents the strain. Minimise the system with respect to x . Under what circumstances is there a first order phase transition for this system?

The equilibrium value of the strain is x is found by minimising F with respect to variations in x :

$$\frac{\partial F}{\partial x} = DP^2 + 2Ex = 0,$$

the solution of which is

$$x = -\frac{DP^2}{2E}.$$

Then

$$DxP^2 = -\frac{D^2P^4}{2E}, \quad Ex^2 = \frac{D^2P^4}{4E}$$

and at the equilibrium strain the Landau free energy is

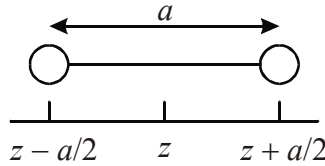
$$F = \alpha(T - T_c)P^2 + \left(b - \frac{D^2}{4E}\right)P^4 + cP^6.$$

There will be a first order transition when the coefficient of P^4 becomes negative, that is when

$$\frac{D^2}{4E} > b.$$

6 Consider a one-dimensional binary alloy where the concentration of A atoms varies slowly in space: $x = x(z)$. Show that the spatial variation of x results in an additional term in the free energy per bond of $a^2\varepsilon(dx/dz)^2$, where a is the spacing between atoms and ε is the energy parameter defined in Section 4.7.3.

When the system is inhomogeneous then the concentration of A atoms varies in space. In this case the calculation of the bond energy is a little more complicated. The direction from the left atom to the right atom is chosen to be along the z axis and the 'position' of the bond is taken as its mid point.



The concentration is a function of position. It is assumed to vary smoothly so that a Taylor expansion is appropriate.

$$x_l = x - \frac{a}{2} \frac{\partial x}{\partial z} + \frac{1}{2} \left(\frac{a}{2}\right)^2 \frac{\partial^2 x}{\partial z^2} - \dots$$

$$x_r = x + \frac{a}{2} \frac{\partial x}{\partial z} + \frac{1}{2} \left(\frac{a}{2}\right)^2 \frac{\partial^2 x}{\partial z^2} + \dots$$

where l and r stand for left and right. The expression for \bar{e}_r is then given by

$$\bar{e}_r = \bar{e}_0 + \frac{a^2}{2} \varepsilon \left(\frac{\partial x}{\partial z}\right)^2 + \frac{a^2}{8} (\varepsilon_{aa} - \varepsilon_{bb} + 2\varepsilon(1-2x)) \frac{\partial^2 x}{\partial z^2} - \frac{a^4}{8} \varepsilon \left(\frac{\partial^2 x}{\partial z^2}\right)^2 + \dots$$

where \bar{e}_0 is the energy per bond in the homogeneous case.

It is a fundamental assumption that the concentration x varies slowly with position; in other words, the spatial derivatives are small. The terms in a^2 are second order in smallness; these contain the leading order contributions from the spatial variation in x . The term in a^4 is fourth order in smallness; this may be ignored. Both terms in a^2 must be considered as these are of the same order. However it is possible to transform

the term in $\partial^2 x / \partial z^2$ through integration by parts, to a term in $(\partial x / \partial z)^2$ plus a surface term that may be ignored.

The key point is that the expression for \bar{e}_r is a function of position z through the dependence of x upon position. Thus \bar{e}_r is an energy *density* and the total energy is found by integrating over the system, and since we are considering variations in the z direction, this means integrating over z . The contribution to the total energy from the $\partial^2 x / \partial z^2$ term is then

$$E = \int_{z_1}^{z_2} f(z) \frac{\partial^2 x}{\partial z^2} dz$$

where

$$f(z) = \frac{a^2}{8} (\varepsilon_{aa} - \varepsilon_{bb} + 2\varepsilon(1 - 2x(z)))$$

and z_1 and z_2 are the extremities. Now the expression for E is integrated by parts to give

$$E = f(z) \frac{\partial x}{\partial z} \Big|_{z_1}^{z_2} - \int_{z_1}^{z_2} \frac{\partial f}{\partial z} \frac{\partial x}{\partial z} dz .$$

The first term is the surface term. This will be zero if we chose the extremities to be away from any spatial variation in concentration. In the second term the first derivative may be re-expressed using the chain rule for differentiation

$$\frac{\partial f}{\partial z} = \frac{\partial f}{\partial x} \frac{\partial x}{\partial z}$$

and then E is given by

$$E = - \int_{z_1}^{z_2} \frac{\partial f}{\partial x} \left(\frac{\partial x}{\partial z} \right)^2 dz .$$

The integrand is the energy density. We see it has been transformed into a term in $(\partial x / \partial z)^2$. Then since

$$\frac{\partial f}{\partial x} = - \frac{a^2}{2} \varepsilon$$

it follows that

$$E = \frac{a^2 \varepsilon}{2} \int_{z_1}^{z_2} \left(\frac{\partial x}{\partial z} \right)^2 dz ,$$

corresponding to an energy density of

$$\frac{a^2 \varepsilon}{2} \left(\frac{\partial x}{\partial z} \right)^2 .$$

We add this to the original term in $(\partial x / \partial z)^2$ to give the result

$$\bar{e}_r = \bar{e}_0 + a^2 \varepsilon \left(\frac{\partial x}{\partial z} \right)^2 .$$

We now relax the restriction that the variation in concentration is in the z direction. Then the derivative $\partial x/\partial z$ becomes the gradient of x and the second derivative becomes the Laplacian, thus

$$\bar{e}_r = \bar{e}_0 + a^2 \varepsilon (\nabla x)^2.$$

This gives the additional free energy per bond when there is a spatial variation in the concentration.

7 Show that in the vicinity of the critical point the free energy of the binary alloy may be written as

$$F_m = F_0 + 2Nk \left\{ (T - T_c) \left(x - \frac{1}{2}\right)^2 + \frac{2}{3} T_c \left(x - \frac{1}{2}\right)^4 + \frac{16}{15} T_c \left(x - \frac{1}{2}\right)^6 + \dots \right\}$$

Discuss the Landau truncation of this expression; in particular, explain at what term the series may/should be terminated.

We shall write the free energy (of mixing) for the binary alloy as

$$F_m(x) = Nk \left\{ 2x(1-x)T_c + T [x \ln x + (1-x) \ln(1-x)] \right\}.$$

This is rather like the expression for the magnet treated in Problem 2. Now we must expand the logarithms about the point $x = 1/2$.

$$\log x = -\log 2 + 2\left(x - \frac{1}{2}\right) - 2\left(x - \frac{1}{2}\right)^2 + \dots$$

$$\log(1-x) = -\log 2 - 2\left(x - \frac{1}{2}\right) - 2\left(x - \frac{1}{2}\right)^2 + \dots$$

This gives the expansion for the free energy as

$$F_m = Nk \left\{ \frac{1}{2} T_c + T \ln 2 + 2(T - T_c) \left(x - \frac{1}{2}\right)^2 + \frac{4}{3} T \left(x - \frac{1}{2}\right)^4 + \frac{32}{15} T \left(x - \frac{1}{2}\right)^6 + \dots \right\}$$

Except in the $T - T_c$ term, we may replace T by the constant T_c as we are considering the behaviour only in the vicinity of the critical point. Then

$$F_m = Nk \left\{ \frac{1}{2} T_c + T_c \ln 2 + 2(T - T_c) \left(x - \frac{1}{2}\right)^2 + \frac{4}{3} T_c \left(x - \frac{1}{2}\right)^4 + \frac{32}{15} T_c \left(x - \frac{1}{2}\right)^6 + \dots \right\}.$$

We now identify the constant F_0 as

$$F_0 = Nk \left\{ \frac{1}{2} T_c + T_c \ln 2 \right\}$$

and this enables us to write the free energy in the vicinity of the critical point as

$$F_m = F_0 + 2Nk \left\{ (T - T_c) \left(x - \frac{1}{2}\right)^2 + \frac{2}{3} T_c \left(x - \frac{1}{2}\right)^4 + \frac{16}{15} T_c \left(x - \frac{1}{2}\right)^6 + \dots \right\}.$$

Observe that the coefficient of the fourth order term is positive. This means that the transition is second order (for the critical concentration) and the series may be truncated at this term. That is, because the coefficient of the fourth order term is positive, we do not need any higher order terms.

8 Plot some isotherms of the Clausius equation of state $p(V - Nb) = NkT$. How do they differ from those of an ideal gas? Does this equation of state exhibit a critical point? Explain your reasoning.

9 The scaling expression for the reduced free energy is given in Section 4.1.9 by

$$f(T, B) = A|t|^{2-\alpha} Y\left(D \frac{B}{|t|^\Delta}\right).$$

Show that the heat capacity is given by

$$C \sim \frac{d^2 f(t, B)}{dt^2}$$

and hence identify α as the heat capacity critical exponent.

10 Using the scaling expression for the reduced free energy in the previous section, show that the magnetisation is given by

$$M \sim \frac{df(t, B)}{dB}$$

and hence show that the order parameter exponent β is given by

$$\beta = 2 - \alpha - \Delta.$$

Show that the magnetic susceptibility is given by

$$\chi \sim \frac{d^2 f(t, B)}{dB^2}$$

and hence show that the susceptibility exponent γ is given by

$$\gamma = 2 - \alpha - 2\Delta.$$

11 Show that the Landau free energy has the scaling form of Problem 4.9 above, with $\alpha = 0$.