4.10 Problems for Chapter 4

4.1 The scaling expression for the reduced (magnetic) free energy is given in Section 4.1.9 by

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

(a) Show that the heat capacity is given by

$$C\sim\frac{\partial^2 f\left(t,B\right)}{\partial t^2}$$

and

(b) hence identify α as the heat capacity critical exponent (when $B=0$).

(a) The entropy is given by

$$S=-\left.\frac{\partial F}{\partial T}\right|_V$$

and the heat capacity is

$$C=\frac{\partial Q}{\partial T}=T\frac{\partial S}{\partial T}$$

so that

$$C=-T\frac{\partial^2 F}{\partial T^2}.$$

Now $f(T,B)$ is given from (Eq. (4.1.34)):

$$f=\frac{F_0-F}{kTV}$$

where F_0 is the Helmholtz free energy at the critical point.

F is then expressed

$$F=F_0-kTVf,$$

whose second derivative, in the vicinity of T_c is

$$\frac{\partial^2 F}{\partial T^2}=-kT_\mathrm{c}V\frac{\partial^2 F}{\partial T^2}.$$

(We don't differentiate the T factor as it varies smoothly in the vicinity of T_c; the singular behaviour is all in the f function.)

The heat capacity is then

$$C = kT_c^2 V \frac{\partial^2 f}{\partial T^2}.$$

And since $t = \frac{T}{T_c} - 1$, it follows that $\frac{\partial}{\partial T} = \frac{1}{T_c}\frac{\partial}{\partial t}$ so that

$$C = kV \frac{\partial^2 f(t, B)}{\partial t^2},$$

the required form.

(b) In the absence of a magnetic field the function Y is zero. Then

$$f = A\,|t|^{2-\alpha}$$

and differentiating twice, we find

$$\frac{\partial^2 f}{\partial t^2} = A|t|^{-\alpha}$$

so that

$$C = kVA|t|^{-\alpha}.$$

We thus identify α to be the heat capacity critical exponent.

4.2 Using the scaling expression for the reduced free energy in the previous question,

(a) show that the magnetization is given by

$$M \sim \frac{\partial f\,(t, B)}{\partial B}$$

and hence

(b) show that the order parameter exponent β is given by

$$\beta = 2 - \alpha - \Delta. \tag{4.10.1}$$

(c) Show that the magnetic susceptibility is given by

$$\chi \sim \frac{\partial^2 f\,(t, B)}{\partial B^2} \tag{4.10.2}$$

and hence

(d) show that the susceptibility exponent γ is given by

$$\gamma = -2 + \alpha + 2\Delta. \tag{4.10.3}$$

(a) The magnetization is given by

$$M = -\frac{\partial F}{\partial B}.$$

As in the previous question

$$F = F_0 - kTVf(t, B),$$

so upon differentiation

$$M = kTV\frac{\partial f}{\partial B}.$$

(b) Now

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

and differentiating this with respect to B gives

$$\frac{\partial f(t, B)}{\partial B} = A\left|t\right|^{2-\alpha-\Delta} D^2 Y'\left(D\frac{B}{\left|t\right|^{\Delta}}\right).$$

where Y' is the derivative of Y with respect to its argument, a smoothly varying function.

So the magnetization is

$$M = kTVA\left|t\right|^{2-\alpha-\Delta} D^2 Y'\left(D\frac{B}{\left|t\right|^{\Delta}}\right)$$

and the singular variation in the vicinity of the critical point is

$$M \sim \left|t\right|^{2-\alpha-\Delta}.$$

We identify the order parameter critical exponent β, from

$$M \sim \left|t\right|^{\beta}$$

to be

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

(c) The magnetic susceptibility is

$$\chi = \frac{\mu_0}{V}\frac{\partial M}{\partial B}.$$

But

$$M = kTV\frac{\partial f}{\partial B},$$

so the susceptibility is

$$\chi = \mu_0 kT\frac{\partial^2 f}{\partial B^2}$$

(d) We differentiate our previous

$$M = kTVA\,|t|^{2-\alpha-\Delta}\,D^2Y'\left(D\frac{B}{|t|^{\Delta}}\right)$$

to give

$$\frac{\partial M}{\partial B} = kTVA\,|t|^{2-\alpha-2\Delta}\,D^3Y''\left(D\frac{B}{|t|^{\Delta}}\right),$$

whose singular part is $|t|^{2-\alpha-2\Delta}$. We identify the susceptibility critical exponent γ, from

$$\chi \sim |t|^{-\gamma}$$

to be

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

4.3 For temperatures below T_B the heat capacity of a 3d Bose-Einstein gas is given by Eq. (2.6.37):

$$C_V = \frac{15}{4}Nk\frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})}\left(\frac{T}{T_\mathrm{B}}\right)^{3/2}$$

Express C_V as a function of $t = (T-T_\mathrm{B})/T_\mathrm{B}$ and hence show that the heat capacity critical exponent α (for $T < T_\mathrm{B}$) is -1.

From the definition of t we have $T = T_\mathrm{B}(1+t)$, so that

$$C_V = \frac{15}{4}Nk\frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})}(1+t)^{3/2}.$$

Close to the transition t is small so we may perform a binomial expansion:

$$C_V = \frac{15}{4} Nk \frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})} \left(1 + \frac{3}{2}t + \dots\right).$$

The singular part of C_V is then

$$C_V \sim \frac{45}{8} Nk \frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})} t.$$

From the definition of α, namely $C \sim |t|^{-\alpha}$ we then identify

$$\alpha = -1$$

as required.

4.4 The Bose-Einstein condensation, treated in Chapter 2, is an example of a non-interacting system which, nevertheless, exhibits a phase transition. Assume the ground state fraction is the order parameter of the transition.

(a) Obtain the order parameter critical exponent β for both the 3d free gas,

(b) and the 3d gas trapped in a harmonic potential.

(c) You should find these two critical exponents to be the same. Comment on this,

(d) and comment on the value of this critical exponent.

(a) For the 3d free Bose gas we found (Eq. (2.6.22))

$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_\mathrm{B}}\right)^{3/2}.$$

In terms of $t = \frac{T_\mathrm{B} - T}{T_\mathrm{B}}$ we have

$$\frac{N_0}{N} = 1 - (1 - t)^{3/2}.$$

Since t is small we perform a binomial expansion:

$$\begin{aligned} \frac{N_0}{N} &= 1 - (1 - \tfrac{3}{2}t + \dots) \\ &= \tfrac{3}{2}t \quad \text{to leading order.} \end{aligned}$$

The β critical exponent is defined, here, as $\frac{N_0}{N} \sim |t|^\beta$, so we conclude for the 3d free Bose gas, $\beta = 1$.

(b) For the 3d harmonically trapped Bose gas we found (Eq. (2.8.22))

$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_\mathrm{B}}\right)^3 .$$

In terms of $t = \frac{T_\mathrm{B}-T}{T_\mathrm{B}}$ we have

$$\frac{N_0}{N} = 1 - (1-t)^3.$$

Performing a binomial expansion gives, to leading order

$$\frac{N_0}{N} \sim 3t.$$

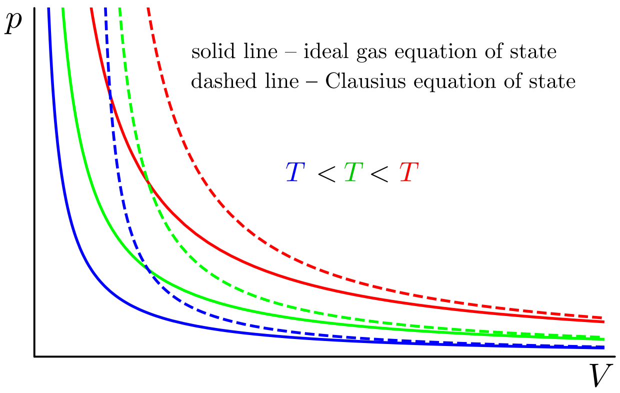
So again we conclude for the 3d free Bose gas, $\beta = 1$.

(c) These are the same, as required. Although this might seem surprising, given the different mathematical form for the order parameter, close to the transition point both systems have a linear dependence of order parameter on reduced temperature. We would understand this as both models belonging to the same universality class.

(d) The value of β is different from the ½ of the mean field model. Hardly surprising as the systems here are *exact* solutions of microscopic (having a hamiltonian description) models. [Some theorists claim the BEC transition should belong to the XY universality class, arguing that the order parameter should be the condensate wave function (a complex scalar). This would give $\beta \approx 0.35$, rather different from the exact calculation. So BEC is *not* in the XY universality class.]

4.5 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.

The dashed lines in the figure show isotherms for the Clausius equation of state. The solid lines show the corresponding isotherms for the ideal gas equation of state.



Isotherms for ideal gas and Clausius equation of state

The the Clausius isotherms are the same shape as the ideal gas ones, but displaced along the V axis by the excluded volume Nb.

The critical point is specified by $\partial p/\partial V = 0$ and $\partial^2 p/\partial V^2 = 0$. The ideal gas has no critical point. The Clausius equation is the same, but shifted, so that – also – has no critical point.

We might also observe that as the interaction is entirely repulsive, the gas cannot condense under its own pressure.

4.6 (a) Show that for a van der Waals fluid the critical parameters are given by $V_\mathrm{c} = 3Nb$, $p_\mathrm{c} = a/27b^2$, $kT_\mathrm{c} = 8a/27b$.

(b) Show that, for a van der Waals fluid the critical compressibility factor
$z_\mathrm{c} = p_\mathrm{c}V_\mathrm{c}/NkT_\mathrm{c}$ has the value $3/8 = 0.375$.

(a) The critical point is characterized by

$$\frac{\partial p}{\partial V} = 0, \qquad \frac{\partial^2 p}{\partial V^2} = 0.$$

We shall write the van der Waals equation of state as

$$p = \frac{NkT}{V - Nb} - a\frac{N^2}{V^2}.$$

The derivatives are

$$\begin{aligned} \frac{\partial p}{\partial V} &= -\frac{NkT}{(V - Nb)^2} + 2a\frac{N^2}{V^3} \\ \frac{\partial^2 p}{\partial V^2} &= 2\frac{NkT}{(V - Nb)^3} - 6a\frac{N^2}{V^4}. \end{aligned}$$

We set these to zero and solve the simultaneous equations for T and V, giving T_c and V_c:

$$kT_\mathrm{c} = \frac{8a}{27b}, \qquad V_\mathrm{c} = 3Nb$$

and these are substituted back into the equation of state to give p_c as

$$p_\mathrm{c} = \frac{a}{27b^2}.$$

(b) By substitution

$$z_\mathrm{c} = \frac{p_\mathrm{c}V_\mathrm{c}}{NkT_\mathrm{c}} = \frac{a}{27b^2} \times 3Nb \times \frac{1}{Nk}\frac{27b}{8a} = \frac{3}{8}$$

as required.

4.7 In Problem 3.20 the van der Waals parameters a and b were approximated in terms of the Lennard-Jones interaction potential parameters σ and ε:

$$a = \frac{16}{9}\pi\sigma^3\varepsilon$$
$$b = \frac{2}{3}\pi\sigma^3.$$

Use these expressions to estimate the van der Waals critical quantities in terms of the Lennard-Jones parameters.

By direct substitution of these expressions for a and b into

$$kT_\mathrm{c} = \frac{8a}{27b}, \quad V_\mathrm{c} = 3Nb, \quad p_\mathrm{c} = \frac{a}{27b^2}.$$

we obtain

$$kT_\mathrm{c} = \frac{64}{81}\varepsilon, \quad V_\mathrm{c} = 2\pi N\sigma^3, \quad p_\mathrm{c} = \frac{4\varepsilon}{27\pi\sigma^3}.$$

4.8 Show that for the Dieterici fluid the critical parameters are given by $V_\mathrm{c} = 2Nb$, $p_\mathrm{c} = a/4b^2e^2$, $kT_\mathrm{c} = a/4b$, and the critical compressibility factor has the value $z_\mathrm{c} = 2/e^2 = 0.271$.

The critical point is characterized by

$$\frac{\partial p}{\partial V} = 0, \qquad \frac{\partial^2 p}{\partial V^2} = 0.$$

We shall write the Dieterici equation of state as

$$p = \frac{NkT}{V - Nb} e^{-Na/kTV}.$$

The derivatives are

$$\frac{\partial p}{\partial V} = \frac{N(Na(V - Nb) - kTV^2)}{V^2(V - Nb)^2} e^{-Na/kTV}$$

$$\frac{\partial^2 p}{\partial V^2} = \frac{N\left(N^2a^2(V - Nb)^2 - 2NaVkT\left(N^2b^2 - 3NbV + 2V^2\right) + 2k^2T^2V^4\right)}{ktv^4(v - bn)^3} e^{-Na/kTV}.$$

We set these to zero and solve the simultaneous equations for T and V, giving T_c and V_c:

$$kT_\mathrm{c} = \frac{8a}{4b}, \qquad V_\mathrm{c} = 2Nb$$

and these are substituted back into the equation of state to give p_c as

$$p_\mathrm{c} = \frac{a}{4b^2e^2}.$$

By substitution

$$z_\mathrm{c} = \frac{p_\mathrm{c}V_\mathrm{c}}{NkT_\mathrm{c}} = \frac{a}{4b^2e^2} \times 2Nb \times \frac{1}{Nk}\frac{4b}{8a} = \frac{2}{e^2} \approx 0.271$$

as required.

4.9 Show that for the Berthelot fluid the critical parameters are given by $V_\mathrm{c} = 3Nb$, $p_\mathrm{c} = \sqrt{a/b^3}/6\sqrt{6}$, $kT_\mathrm{c} = (2/3)^{3/2}\sqrt{a/b}$, and the critical compressibility factor has the value $z_\mathrm{c} = 3/8 = 0.375$, just as for the van der Waals equation.

The critical point is characterized by

$$\frac{\partial p}{\partial V} = 0, \qquad \frac{\partial^2 p}{\partial V^2} = 0.$$

We shall write the Berthelot equation of state as

$$p = \frac{NkT}{V - Nb} - \frac{\alpha}{kT}\frac{N^2}{V^2}.$$

The derivatives are

$$\begin{aligned}\frac{\partial p}{\partial V} &= -\frac{NkT}{(V-Nb)^2}+\frac{2\alpha}{kT}\frac{N^2}{V^3}\\ \frac{\partial^2 p}{\partial V^2} &= 2\frac{NkT}{(V-Nb)^3}-6\alpha kT\frac{N^2}{V^4}.\end{aligned}$$

We set these to zero and solve the simultaneous equations for T and V, giving T_c and V_c:

$$kT_\mathrm{c}=\frac{2}{3}\sqrt{\frac{2}{3}}\sqrt{\frac{\alpha}{b}}, \qquad V_\mathrm{c}=3Nb$$

and these are substituted back into the equation of state to give p_c as

$$p_\mathrm{c}=\frac{1}{6\sqrt{6}}\sqrt{\frac{\alpha}{b^3}}.$$

By substitution

$$z_\mathrm{c}=\frac{p_\mathrm{c}V_\mathrm{c}}{NkT_\mathrm{c}}=\frac{1}{6\sqrt{6}}\sqrt{\frac{\alpha}{b^3}}\times 3Nb\times\frac{1}{Nk}\frac{2}{3}\sqrt{\frac{2}{3}}\sqrt{\frac{\alpha}{b}}=\frac{3}{8}$$

as required.

4.10 Show that for the Redlich-Kwong fluid the critical parameters are given by $V_\mathrm{c}=3.847Nb$, $p_\mathrm{c}=0.0299a^{2/3}/b^{5/3}$, $kT_\mathrm{c}=0.345(a/b)^{2/3}$, and the critical compressibility factor has the value $z_\mathrm{c}=1/3$.

The critical point is characterized by

$$\frac{\partial p}{\partial V}=0, \qquad \frac{\partial^2 p}{\partial V^2}=0.$$

We shall write the Redlich-kwong equation of state as

$$p=\frac{NkT}{V-Nb}-\frac{aN^2}{\sqrt{kT}\,V(V+Nb)}.$$

The derivatives are

$$\begin{aligned}\frac{\partial p}{\partial V} &= -\frac{NkT}{(V-Nb)^2}+\frac{aN(2V+Nb)}{\sqrt{kT}\,V^2(V+Nb)^2}\\ \frac{\partial^2 p}{\partial V^2} &= 2\frac{NkT}{(V-Nb)^3}-\frac{2N^2a(N^2b^2+3NbV+3V^2)}{\sqrt{kT}\,V^3(V+Nb^3)}.\end{aligned}$$

We must set these to zero and solve the simultaneous equations for T and V, giving T_{c} and V_{c}. This is quite complicated. You can use *Mathematica*, for example, to do the hard work for you.

$$\begin{aligned} kT_{\mathrm{c}} &= \frac{2^{4/9} \times 3^{2/3}}{\left(2+2^{1/3}+2^{2/3}\right)^{4/3}} \left(\frac{a}{b}\right)^{2/3} = 0.345 \left(\frac{a}{b}\right)^{2/3} \\ V_{\mathrm{c}} &= \left(1+2^{1/3}+2^{2/3}\right) Nb = 3.847 Nb. \end{aligned}$$

and these are substituted back into the equation of state to give p_{c} as

$$p_{\mathrm{c}} = \frac{2^{1/9}\left(4+4\times 2^{1/3}+3\times 2^{2/3}\right)}{3^{1/3}\left(2+2^{1/3}+2^{2/3}\right)^{7/3}\left(3+2\times 2^{1/3}+2\times 2^{2/3}\right)} \left(\frac{a^2}{b^5}\right)^{1/3} = 0.0299 \left(\frac{a^2}{b^5}\right)^{1/3}.$$

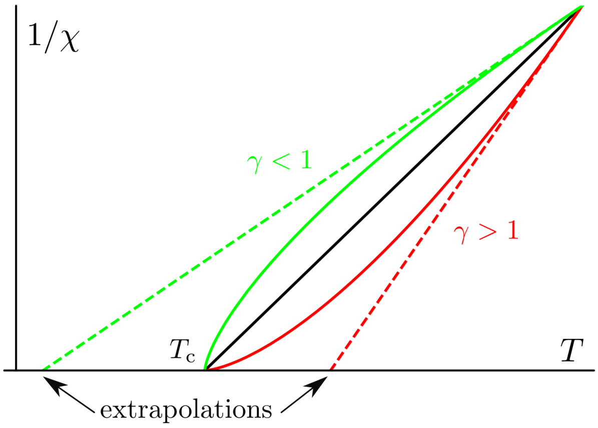
By substitution,

$$z_{\mathrm{c}} = \frac{p_{\mathrm{c}} V_{\mathrm{c}}}{NkT_{\mathrm{c}}} = \frac{1}{3}$$

exactly.

4.11 The discussion around Fig. 4.19 argued that the transition temperature of a ferromagnet could be estimated from measurements at high temperatures by plotting $1/\chi$ against temperature and extrapolating the line to the axis. While this is reliable for the mean field $\gamma = 1$ case, show that for the realistic case where $\gamma > 1$, the actual transition temperature will be lower than the mean field estimate. You should draw the Curie-Weiss line, as in Fig. 4.19, and note that it has slope of $\gamma = 1$. You should then show how low temperature deviations above and below $\gamma = 1$ alter the extrapolation to $1/\chi \to 0$.

When $\gamma > 1$ the inverse susceptibility will curve to the left as T reduces. This is the red line in the figure.



Extrapolated inverse susceptibility

So as $\chi^{-1} \to 0$ the actual temperature is *below* the mean field linear extrapolation.

4.12 Obtain an expression for the (Landau) Helmholtz free energy for the Weiss model in zero external magnetic field, in terms of the magnetization. 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

$$E = -\int B \, \mathrm{d}M.$$

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

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

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:

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

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

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

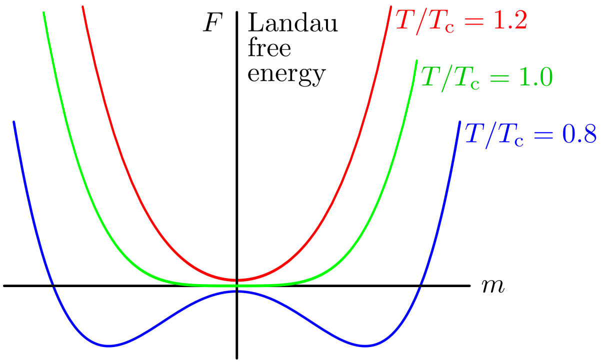
so that the entropy becomes

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

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.



Landau free energy.

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.

4.13 Show that $F = \frac{1}{2}Nk\left\{(T - T_\mathrm{c})\, m^2 + \frac{1}{6}T_\mathrm{c}m^4 + \ldots\right\}$ 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

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

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

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

By thus expanding and collecting terms we obtain

$$F = \frac{Nk}{2}\left\{-2T\ln 2 + (T - T_\mathrm{c})\, m^2 + \frac{T}{6}m^4 + \frac{T}{15}m^6 + \ldots\right\}.$$

In the vicinity of the critical point the first term may be approximated by $2T_\mathrm{c}\ln 2$; 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:

$$F = \frac{Nk}{2}\left\{(T - T_\mathrm{c})\, m^2 + \frac{T_\mathrm{c}}{6}m^4 + \ldots\right\}$$

as required.

4.14 Show that $\mathrm{d}^2F/\mathrm{d}\varphi^2 > 0$ below T_c at the two roots $\varphi = \pm\sqrt{-F_2/2F_4}$ in the Landau model. Show that $\mathrm{d}^2F/\mathrm{d}\varphi^2 < 0$ below T_c and $\mathrm{d}^2F/\mathrm{d}\varphi^2 > 0$ 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

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

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

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

so that

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

Now F_2 is negative for temperatures below the transition:

$$F_2=a\left(T-T_\mathrm{c}\right)$$

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

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

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

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

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

4.15 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

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

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:

$$F_2 = a\left(T - T_\mathrm{c}\right).$$

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

$$\varphi = \pm\sqrt{\frac{-F_4 + \sqrt{F_4^2 - 3a\left(T - T_\mathrm{c}\right)F_6}}{3F_6}}.$$

To find the order parameter critical exponent we must expand φ in powers of F_2 or $T - T_\mathrm{c}$

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

(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

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

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

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

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:

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

4.16 Show that the Landau free energy is consistent with the scaling free energy of Problem 4.1 above, with $\alpha = 0$. Comment on the value of Δ required. Start by considering the $B = 0$ case.

The scaling form for the free energy is

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

(a) First consider the $B = 0$ case; this is relatively straightforward. The expression for the Landau free energy is

$$F(\varphi) = F_2\varphi^2 + F_4\varphi^4.$$

The *equilibrium* free energy corresponds to the Landau free energy when φ takes its equilibrium value: the value for which $F(\varphi)$ is minimized. We saw this corresponds to

$$\varphi^2 = \frac{-F_2}{2F_4}.$$

So substitute this into $F(\varphi)$, gives

$$F_{\text{eq}} = -\frac{1}{4}\frac{F_2^2}{F_4}.$$

We use the standard temperature dependence of F_2, namely $a(T - T_{\text{c}})$. Then

$$F_{\text{eq}} = -\frac{1}{4}\frac{a^2(T - T_{\text{c}})^2}{F_4}.$$

The key point is that the temperature dependence of the free energy goes as $(T - T_{\text{c}})^2$, or $|t|^2$ which is precisely that proposed for the ($\alpha = 0$ and $B = 0$ case) scaling free energy, since $Y(0) = 1$.

(b) Now let's see if we can accommodate a non-zero B. This first approach uses power series in B. In (d) below we discuss how to proceed

without using a power series.
The Landau free energy is

$$F(\varphi) = B\varphi + F_2\varphi^2 + F_4\varphi^4.$$

The equilibrium φ is determined by minimizing $F(\varphi)$, but now we have a cubic equation for $F'(\varphi) = 0$ with consequent three roots. As $B \to 0$ the correct root will go to the previously-found $\varphi^2 = -F_2/2F_4$. The full expression for φ is complicated; let's consider an expansion in powers of B. We find

$$\varphi^2 = -\frac{F_2}{2F_4} + \frac{1}{\sqrt{-8F_2F_4}}B - \frac{1}{8F_2^2}B^2 + \dots$$

or

$$\varphi = \sqrt{\frac{-F_2}{2F_4}} + \frac{1}{4F_2}B - \frac{3\sqrt{-F_2F_4}}{16\sqrt{2}F_2^3}B^2 + \dots$$

We must substitute the equilibrium φ into the Landau free energy to obtain the equilibrium free energy:

$$F_{\text{eq}} = -\frac{F_2^2}{4F_4} + \frac{\sqrt{-F_2}}{\sqrt{2}\sqrt{F_4}}B + \frac{1}{8F_2}B^2 + \dots .$$

Of course, the leading term corresponds to the $B = 0$ case above.
It is convenient to factorise out this leading term:

$$F_{\text{eq}} = -\frac{F_2^2}{4F_4}\left\{1 + \frac{2\sqrt{2}\sqrt{F_4}}{-F_2^{3/2}}B - \frac{F_4}{2F_2^3}B^2 + \dots\right\}.$$

Then the curly bracket corresponds to the Y function in the scaling free energy.
Each term is a power of $\sqrt{F_4/F_2^3}B$. In other words, Y is a function of $\sqrt{F_4/F_2^3}B$. So putting in the temperature dependence of F_2, we conclude that Y is a function of $B/|t|^{3/2}$; This is the scaling form with $\Delta = 3/2$.

(c) We note that the scaling exponent Δ is related to the more common critical exponents through $\Delta = 2 - \alpha - \beta$. We were told to take $\alpha = 0$, the mean field value. We have concluded that consistency between the Landau and the scaling free energies requires $\Delta = 3/2$. And so we require $\beta = 1/2$: the mean field value.

The conclusion is that the Landau free energy is consistent with the scaling free energy with mean field critical exponents – as expected.

(d) The solution without a power series is difficult. You take the full expression for φ, the correct solution minimizing $F(\varphi)$,

$$\varphi = \frac{(-1)^{2/3}\left(\sqrt{81B^2F_4+24F_2^3}-9B\sqrt{F_4}\right)^{2/3}+2\sqrt[3]{-3}F_2}{2\;3^{2/3}\sqrt[3]{\sqrt{3F_4^3\left(27B^2F_4+8F_2^3\right)}-9BF_4^2}},$$

and substitute this into the Landau free energy. This is then divided by the $B = 0$ value to give the Y function, a very complicated formula involving B, F_2 and F_4. Then you need to observe that these variables always appear in the same particular combination $\sqrt{-F_4/F_2^3}B$. You could do this with the aid of *Mathematica*. The result is

$$\begin{aligned} Y(x) = \frac{1}{72}\Bigg(& 2\;3^{5/6}\sqrt{27x^2-8}\sqrt[3]{9x-\sqrt{81x^2-24}}+ \\ & +27x^2\left(27x-3\sqrt{81x^2-24}\right)^{2/3}+4\left(27x-3\sqrt{81x^2-24}\right)^{2/3}+ \\ & +9x\left(6\sqrt[3]{27x-3\sqrt{81x^2-24}}+\sqrt[6]{3}\sqrt{27x^2-8}\left(9x-\sqrt{81x^2-24}\right)^{2/3}\right)+ \\ & +48\Bigg) \end{aligned}$$

where $x = \sqrt{-F_4/F_2^3}B \propto B/|t|^{3/2}$.

4.17 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 polarization and x represents the strain. Minimize 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

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

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

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

4.18 The first-order ferroelectric has *two* spinodals, one above and one below the equilibrium transition temperature T_tr.

(a) At the spinodal the first and second derivatives of $F(\varphi)$ vanish. Explain this.

(b) Show that these correspond to $\varphi^\mathrm{sp} = \pm\sqrt{\frac{-F_4}{3F_6}}, F_2^\mathrm{sp} = \frac{F_4^2}{3F_6}$ and $\varphi^\mathrm{sp} = 0, F_2^\mathrm{sp} = 0$.

(c) The temperatures of these spinodals correspond to $T_\mathrm{sp}^\mathrm{u} = T_\mathrm{c} + \frac{1}{3a}\frac{F_4^2}{F_6}$ and $T_\mathrm{sp}^\mathrm{l} = T_\mathrm{c}$, where the u and l superscripts indicate the *upper* and the *lower* temperature spinodal. Derive these expressions and show their variation with F_4 by including them on a plot similar to Fig. 4.37.

(d) Now plot the order parameter as a function of temperature, as in Fig. 4.38, indicating the hysteretic jumps at T_sp^l and T_sp^u. Why are these called *hysteretic* jumps?

(a) The equilibrium state correspond to a *minimum* in $F(\varphi)$, so that $\mathrm{d}F/\mathrm{d}\varphi = 0$ and $\mathrm{d}^2F/\mathrm{d}\varphi^2 > 0$. At the spinodal the minimum broadens/flattens. This means that $\mathrm{d}^2F/\mathrm{d}\varphi^2 > 0$ gets smaller and smaller. Then as the minimum vanishes, the second derivative goes through zero.

(b) The Landau free energy is

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

so the first and second derivatives are

$$\begin{aligned}\frac{\mathrm{d}F}{\mathrm{d}\varphi} &= 2F_2\varphi + 4F_4\varphi^3 + 6F_6\varphi^5\\ \frac{\mathrm{d}^2F}{\mathrm{d}\varphi^2} &= 12F_4\varphi^2 + 30F_6\varphi^4\end{aligned}$$

and equating these to zero to solve for φ and F_2 gives

$$\varphi^{\mathrm{sp}} = \pm\sqrt{\frac{-F_4}{3F_6}}, \qquad F_2^{\mathrm{sp}} = \frac{F_4^2}{3F_6} \tag{i}$$

and

$$\varphi^{\mathrm{sp}} = 0, \qquad F_2^{\mathrm{sp}} = 0 \tag{ii}$$

as required.

(c) The key point here is that we give F_2 the "usual" temperature dependence, as in the second order case: $F_2 = a(T - T_{\mathrm{c}})$ and we take F_4 and F_6 to be temperature-independent, noting that $F_4 < 0$ and $F_6 > 0$ for the first order transition.

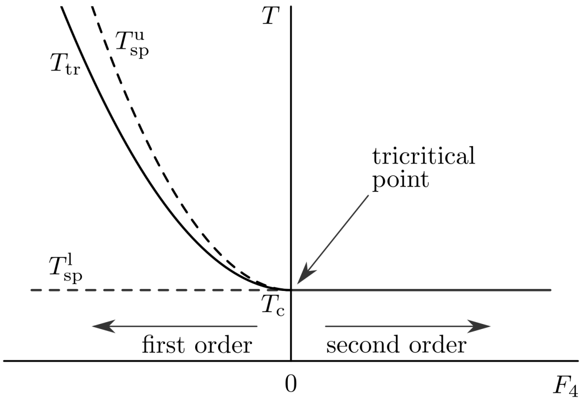
With the assumed temperature dependence for F_2 we have: from [i] above, $F_2^{\mathrm{sp}} = \frac{F_4^2}{3F_6} = a(T_{\mathrm{sp}} - T_{\mathrm{c}})$, giving the upper

$$T_{\mathrm{sp}}^{\mathrm{u}} = T_{\mathrm{c}} + \frac{1}{3a}\frac{F_4^2}{F_6},$$

while from [ii] above, $F_2^{\mathrm{sp}} = 0 = a(T_{\mathrm{sp}} - T_{\mathrm{c}})$, giving the lower

$$T_{\mathrm{sp}}^{\mathrm{l}} = T_{\mathrm{c}}.$$

The variation of these temperatures are shown in the figure below, together with the equilibrium transition temperature as in Fig. 4.37.

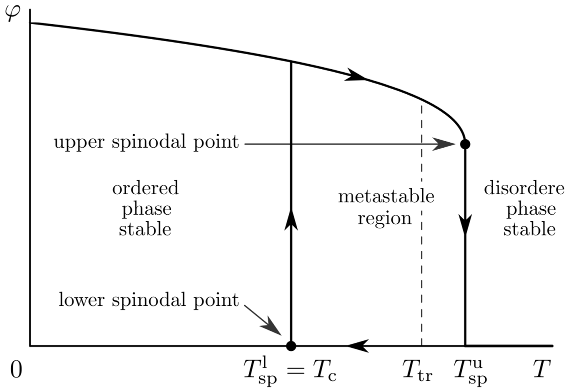


Variation of transition temperature and spinodal temperatures with F_4.

(d) The temperature dependence of the order parameter is given by Eq. (4.6.19):

$$\varphi^2 = \frac{|F_4|}{3F_6}\left\{1 + \sqrt{1 - \frac{3}{4}\frac{(T-T_{\mathrm{c}})}{(T_{\mathrm{tr}}-T_{\mathrm{c}})}}\right\}.$$

I have plotted $\varphi(T)$ in the figure below (for $T_{\mathrm{tr}} = \frac{3}{2}$). Compared with Fig. 4.38 in the text the curve is extended from T_{tr} to $T_{\mathrm{sp}}^{\mathrm{u}}$.



Order parameter in a first order transition showing hysteresis.

The equilibrium transition, the dashed line, occurs at T_{tr}. The transition happens here when where the fluctuations are sufficient to cause a rapid transition between the level minima in free energy at the transition point.

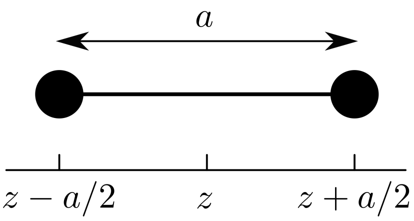
At the opposite extreme, where the fluctuations are negligible, the jump in φ will not occur until the spinodal point is reached.

- Upon cooling from a high temperature, the non-zero φ will not appear until T reaches the *lower* spinodal temperature $T_{\mathrm{sp}}^{\mathrm{l}}$.
- Upon warming from a low temperature, the finite φ will not appear until the T reaches the *upper* spinodal temperature $T_{\mathrm{sp}}^{\mathrm{u}}$.

In this case the temperature of the order parameter jump depends on the system *history*. Thus the designation *hysteretic*.

4.19 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 proportional to $a^2\varepsilon(\mathrm{d}x/\mathrm{d}z)^2$, where a is the spacing between atoms and ε is the energy parameter defined in Section 4.7.3. Determine the numerical coefficient.

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.



Bond joining two atoms.

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

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

$$x_{\mathrm{r}} = x + \frac{a}{2}\frac{\partial x}{\partial z} + \frac{1}{2}\left(\frac{a}{2}\right)^2\frac{\partial^2 x}{\partial z^2} + \dots .$$

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

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

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 $\bar{e}_{\mathrm{lr}}$ is a function of position z through the dependence of x upon position. Thus $\bar{e}_{\mathrm{lr}}$ 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

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

where

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

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

$$E = f(z) \left. \frac{\partial x}{\partial z} \right|_{z_1}^{z_2} - \int_{z_1}^{z_2} \frac{\partial f}{\partial z} \frac{\partial x}{\partial z} \, \mathrm{d}z.$$

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

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

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

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

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

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

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

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

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

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

$$F_{\mathrm{m}} = F_0 + Nk\left\{\frac{1}{2}\left(T - T_{\mathrm{c}}\right)\varphi^2 + \frac{1}{12}T_{\mathrm{c}}\varphi^4 + \frac{1}{30}T_{\mathrm{c}}\varphi^6 + \ldots\right\}$$

where $\varphi = 2x - 1$.

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

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

$$F_{\mathrm{m}}(x) = Nk\left\{2x(1-x)T_{\mathrm{c}} + T[x\ln x + (1-x)\ln(1-x)]\right\}.$$

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

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

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

This gives the expansion for the free energy as

$$F_\mathrm{m} = Nk\Big\{\tfrac{1}{2}T_\mathrm{c} + T\ln 2 + 2\left(T - T_\mathrm{c}\right)\left(x-\tfrac{1}{2}\right)^2 + \\ + \tfrac{4}{3}T\left(x-\tfrac{1}{2}\right)^4 + \tfrac{32}{15}T\left(x-\tfrac{1}{2}\right)^6 + \ldots\Big\}.$$

Except in the $T - T_\mathrm{c}$ 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

$$F_\mathrm{m} = Nk\Big\{\tfrac{1}{2}T_\mathrm{c} + T_\mathrm{c}\ln 2 + 2\left(T - T_\mathrm{c}\right)\left(x-\tfrac{1}{2}\right)^2 + \\ + \tfrac{4}{3}T_\mathrm{c}\left(x-\tfrac{1}{2}\right)^4 + \tfrac{32}{15}T_\mathrm{c}\left(x-\tfrac{1}{2}\right)^6 + \ldots\Big\}.$$

We now write the constant F_0, the value at the critical point, as

$$F_0 = Nk\left\{\frac{1}{2}T_\mathrm{c} + T_\mathrm{c}\ln 2\right\}$$

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

$$F_\mathrm{m} = F_0 + 2Nk\left\{\left(T - T_\mathrm{c}\right)\left(x-\tfrac{1}{2}\right)^2 + \tfrac{2}{3}T_\mathrm{c}\left(x-\tfrac{1}{2}\right)^4 + \tfrac{16}{15}T_\mathrm{c}\left(x-\tfrac{1}{2}\right)^6 + \ldots\right\}.$$

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.