

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

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

(a) Show that the heat capacity is given by

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

and

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

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

$$\beta = 2 - \alpha - \Delta. \quad (4.10.1)$$

(c) Show that the magnetic susceptibility is given by

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

and hence

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

$$\gamma = -2 + \alpha + 2\Delta. \quad (4.10.3)$$

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

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

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

- 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.
- Obtain the order parameter critical exponent β for both the 3d free gas,
 - and the 3d gas trapped in a harmonic potential.
 - You should find these two critical exponents to be the same. Comment on this,
 - and comment on the value of this critical exponent.
- 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.
- 4.6 (a) Show that for a van der Waals fluid the critical parameters are given by $V_c = 3Nb$, $p_c = a/27b^2$, $kT_c = 8a/27b$.
- (b) Show that, for a van der Waals fluid the critical compressibility factor $z_c = p_c V_c / NkT_c$ has the value $3/8 = 0.375$.
- 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.

- 4.8 Show that for the Dieterici fluid the critical parameters are given by $V_c = 2Nb$, $p_c = a/4b^2 e^2$, $kT_c = a/4b$, and the critical compressibility factor has the value $z_c = 2/e^2 = 0.271$.
- 4.9 Show that for the Berthelot fluid the critical parameters are given by $V_c = 3Nb$, $p_c = \sqrt{a/b^3}/6\sqrt{6}$, $kT_c = (2/3)^{3/2} \sqrt{a/b}$, and the critical compressibility factor has the value $z_c = 3/8 = 0.375$, just as for the van der Waals equation.

- 4.10 Show that for the Redlich-Kwong fluid the critical parameters are given by $V_c = 3.847Nb$, $p_c = 0.0299a^{2/3}/b^{5/3}$, $kT_c = 0.345(a/b)^{2/3}$, and the critical compressibility factor has the value $z_c = 1/3$.
- 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 $1/\chi \rightarrow 0$.
- 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 $T < T_c$.
- 4.13 Show that $F = \frac{1}{2}Nk \left\{ (T - T_c) m^2 + \frac{1}{6}T_c m^4 + \dots \right\}$ for the Weiss model ferromagnet in the limit of small m . Explain the appearance of T_c in the m^4 term.
- 4.14 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?
- 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.
- 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.
- 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?

- 4.18 The first-order ferroelectric has *two* spinodals, one above and one below the equilibrium transition temperature T_{tr} .
- At the spinodal the first and second derivatives of $F(\varphi)$ vanish. Explain this.
 - Show that these correspond to $\varphi^{\text{sp}} = \pm \sqrt{\frac{-F_4}{3F_6}}$, $F_2^{\text{sp}} = \frac{F_4^2}{3F_6}$ and $\varphi^{\text{sp}} = 0$, $F_2^{\text{sp}} = 0$.
 - The temperatures of these spinodals correspond to $T_{\text{sp}}^{\text{u}} = T_c + \frac{1}{3a} \frac{F_4^2}{F_6}$ and $T_{\text{sp}}^{\text{l}} = T_c$, 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.
 - 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?

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 $a^2 \varepsilon (dx/dz)^2$, where a is the spacing between atoms and ε is the energy parameter defined in Section 4.7.3. Determine the numerical coefficient.

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

$$F_{\text{m}} = F_0 + Nk \left\{ \frac{1}{2} (T - T_c) \varphi^2 + \frac{1}{12} T_c \varphi^4 + \frac{1}{30} T_c \varphi^6 + \dots \right\}$$

where $\varphi = 2x - 1$.

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