

**PHYSICS 210A : STATISTICAL PHYSICS  
FINAL EXAM SOLUTIONS**

(1) Consider the analog of the van der Waals equation of state for a gas of diatomic particles with *repulsive* long-ranged interactions,

$$p = \frac{RT}{v-b} + \frac{a}{v^2} \quad ,$$

where  $v$  is the molar volume.

- (a) Does this system have a critical point? If not, give your reasons. If so, find  $(T_c, p_c, v_c)$ .
- (b) Find the molar energy  $\varepsilon(T, v)$ .
- (c) Find the coefficient of volume expansion  $\alpha_p = v^{-1}(\partial v / \partial T)_p$  as a function of  $v$  and  $T$ .
- (d) Find the adiabatic equation of state in terms of  $v$  and  $T$ . If at temperature  $T_1$  a volume  $v_1 = 3b$  of particles undergoes reversible adiabatic expansion to a volume  $v_2 = 5b$ , what is the final temperature  $T_2$ ?

**Solution :**

(a) Since

$$\left( \frac{\partial p}{\partial v} \right)_T = -\frac{RT}{(v-b)^2} - \frac{2a}{v^3}$$

is negative definite, for any  $T$ , there is no critical behavior in this model.

(b) We have

$$\left( \frac{\partial \varepsilon}{\partial v} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - p = T \left( \frac{\partial p}{\partial T} \right)_v - p \quad ,$$

where we have invoked a Maxwell relation based on  $dF = -SdT - pdV$ , we have

$$\left( \frac{\partial \varepsilon}{\partial v} \right)_T = -\frac{a}{v^2} \quad ,$$

whence  $\varepsilon(T, v) = \omega(T) + \frac{a}{v}$ . In the  $v \rightarrow \infty$  limit, we recover the diatomic ideal gas, hence  $\omega(T) = \frac{5}{2}RT$  and

$$\varepsilon(T, v) = \frac{5}{2}RT + \frac{a}{v} \quad .$$

(c) To find  $\alpha_p$ , set  $dp = 0$ , where

$$dp = \frac{R}{v-b} dT - \left[ \frac{RT}{(v-b)^2} + \frac{2a}{v^3} \right] dv \quad .$$

We then have

$$\alpha_p(T, v) = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p = \frac{R(v-b)v^2}{RTv^3 + 2a(v-b)^2} \quad .$$

Note that we recover the ideal gas value  $\alpha_p = T^{-1}$  in the  $v \rightarrow \infty$  limit. We may also evaluate the isothermal compressibility,

$$\kappa_T(T, v) = -\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T = \frac{(v-b)^2 v^2}{RTv^3 + 2a(v-b)^2} \quad .$$

In the limit  $v \rightarrow \infty$ , we have  $\kappa_T = v/RT$ . Since  $pv = RT$  in this limit,  $\kappa_T(T, v \rightarrow \infty) = 1/p$ , which is the ideal gas result.

(d) Let  $s = N_A S/N$  be the molar entropy. Then

$$\begin{aligned} ds &= \frac{1}{T} d\varepsilon + \frac{p}{T} dv \\ &= \frac{1}{2} f R \frac{dT}{T} + \frac{R}{v-b} dv = R d \ln [(v-b) T^{f/2}] \quad , \end{aligned}$$

and therefore the adiabatic equation of state is

$$(v-b) T^{f/2} = \text{constant} \quad .$$

Thus, the result of a reversible adiabatic process must be

$$T_2 = \left( \frac{v_1 - b}{v_2 - b} \right)^{2/f} T_1 \quad .$$

For  $v_1 = 3b$  and  $v_2 = 5b$ , find  $T_2 = 2^{-2/5} T_1$ .

(2) Consider a two-dimensional gas of ideal nonrelativistic fermions of spin- $\frac{1}{2}$  and mass  $m$ .

- (a) Find the relationship between the number density  $n$ , the fugacity  $z = \exp(\mu/k_B T)$ , and the temperature  $T$ . You may choose to abbreviate  $\lambda_T = \sqrt{2\pi\hbar^2/mk_B T}$ . Assume the internal degeneracy (e.g., due to spin) is  $g$ .
- (b) A two-dimensional area  $A$  is initially populated with nonrelativistic fermions of mass  $m$ , spin- $\frac{1}{2}$ , and average number density  $n = N/A$  at temperature  $T$ . The fermions are noninteracting with the exception that opposite spin fermions can pair up to form spin-0 bosons of mass  $2m$  and binding energy  $\Delta$ . In other words, the fermion dispersion is  $\varepsilon_f(\mathbf{k}) = \hbar^2 \mathbf{k}^2 / 2m$  and the boson dispersion is  $\varepsilon_B(\mathbf{k}) = -\Delta + \hbar^2 \mathbf{k}^2 / 4m$ . Assuming the reaction  $f_\uparrow + f_\downarrow \rightleftharpoons B$  has achieved equilibrium, find the relationship between the initial number density  $n$ , fugacity  $z$ , and temperature  $T$ . *Hint: The total mass density of the system  $\rho_{\text{tot}} = mn$  is conserved. Use this to first find the relation between the equilibrium densities  $n_f$ ,  $n_B$ , and  $n$ .*
- (c) Assuming the conditions in (b), in the limit  $n\lambda_T^2 \gg 1$  at fixed  $T$ , what are the fermion and boson densities  $n_f$  and  $n_B$ , to leading order?

- (d) Now suppose the initial particles are spin-0 bosons of mass  $m$ , which undergo the reaction  $2b \rightleftharpoons B$ , where  $B$  is a boson of mass  $2m$ . The initial density is again  $n$ . What is the relation between  $n$ ,  $T$ , and  $z$ ? What are  $n_b$  and  $n_B$  to leading order when  $n\lambda_T^2 \gg 1$ ?

**Solution :**

- (a) For nonrelativistic fermions of mass  $m$  and internal degeneracy  $g$  in equilibrium,

$$\begin{aligned} n &= g \int \frac{d^2k}{(2\pi)^2} \frac{1}{z^{-1} \exp(\hbar^2 \mathbf{k}^2 / 2mk_B T) + 1} \\ &= g\lambda_T^{-2} \int_0^\infty dx \frac{1}{z^{-1} \exp(x) + 1} = g\lambda_T^{-2} \ln(1+z) \quad . \end{aligned}$$

Thus,  $n\lambda_T^2 = g \ln(1+z)$ . The corresponding result for bosons is  $n\lambda_T^2 = -g \ln(1-z)$ .

- (b) Let  $z$  be the fugacity of the fermions and  $z_B$  be the fugacity of the bosons. Clearly  $\mu_B = 2\mu$ , i.e.  $z_B = z^2$ . Due to the reactions,  $n_f$  and  $n_B$  are not separately conserved, but  $n = n_f + 2n_B$  is conserved, hence

$$n\lambda_T^2 = 2 \ln(1+z) - 4 \ln(1 - z^2 e^{\Delta/k_B T}) \quad .$$

Note that  $n_B = -2 \ln(1 - z^2 e^{\Delta/k_B T})$  with the prefactor of 2 arising from  $m_B = 2m$ .

- (c) When  $n\lambda_T^2 \gg 1$ , we must have  $z^2 e^{\Delta/k_B T} = 1^-$ , i.e.  $z = e^{-\Delta/2k_B T}$ , and therefore, to leading order,

$$n_f = 2 \ln(1 + e^{-\Delta/2k_B T}) \quad , \quad n_B = \frac{1}{2}n \quad .$$

*I.e.* almost all the fermions pair up into bound boson states.

- (d) If the initial particles are spin-0 bosons, then

$$n\lambda_T^2 = -\ln(1-z) - 4 \ln(1 - z^2 e^{\Delta/k_B T}) \quad .$$

When  $n\lambda_T^2 \gg 1$ , again we have  $z = e^{-\Delta/2k_B T}$ , and

$$n_b = -\ln(1 - e^{-\Delta/2k_B T}) \quad , \quad n_B = \frac{1}{2}n \quad .$$

**(3)** On each site  $i$  of a (two-dimensional square) lattice exists a unit vector  $\hat{n}_i$  which can point in any of four directions:  $\{\pm\hat{x}, \pm\hat{y}\}$ . These vectors interact between neighboring sites. Of the  $4^2 = 16$  configurations, two have energy  $-J$  and the remaining 14 have energy zero. The nonzero energy configurations for horizontal and for vertical links are shown here:

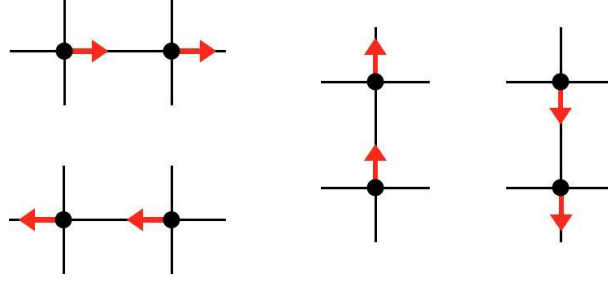


Figure 1: For both horizontal and vertical links, there are only two configurations with energy  $E_{ij} = -J$ , depicted here.

Consider a variational density matrix approach to this problem, based on the single site density matrix

$$\varrho_1(\hat{n}) = \frac{1}{4}(1 + 3x)\delta_{\hat{n}, \hat{x}} + \frac{1}{4}(1 - x)\delta_{\hat{n}, -\hat{x}} + \frac{1}{4}(1 - x)\delta_{\hat{n}, \hat{y}} + \frac{1}{4}(1 + x)\delta_{\hat{n}, -\hat{y}} \quad ,$$

where  $x$  is a variational parameter.

- What is the allowed range for  $x$ ? Verify that the density matrix  $\varrho_1$  is appropriately normalized.
- Taking  $\varrho_{\text{var}}(\{\hat{n}_i\}) = \prod_i \varrho_1(\hat{n}_i)$ , find the average energy  $E$ . (Please denote the total number of lattice sites by  $N$ .)
- Find the entropy  $S$ .
- Find the dimensionless free energy per site  $f \equiv F/NJ$  in terms of the variational parameter  $x$  and the dimensionless temperature  $\theta \equiv k_B T/J$ .
- Find the Landau expansion of  $f(x, \theta)$  to fourth order in  $x$ . *Hint:*

$$(1 + \varepsilon) \ln(1 + \varepsilon) = \varepsilon + \frac{1}{2}\varepsilon^2 - \frac{1}{6}\varepsilon^3 + \frac{1}{12}\varepsilon^4 - \frac{1}{20}\varepsilon^5 + \dots \quad .$$

- Based on the fourth order Landau expansion of the free energy, sketch the equilibrium curve of  $x$  versus  $\theta$  and identify the location(s) any and all phase transitions, as well as their order(s).

**Solution :**

(a) The density matrix is non-negative definite, which entails  $x \in [-\frac{1}{3}, 1]$ . Since the trace is  $\text{Tr} \varrho_1 = \sum_{\hat{n}} \varrho_1(\hat{n}) = 1$ , it is properly normalized.

(b) The Hamiltonian for this system is written

$$\hat{H} = -J \sum_{\langle ij \rangle \in \mathcal{X}} (\delta_{\hat{n}_i, \hat{x}} \delta_{\hat{n}_j, \hat{x}} + \delta_{\hat{n}_i, -\hat{x}} \delta_{\hat{n}_j, -\hat{x}}) - J \sum_{\langle ij \rangle \in \mathcal{Y}} (\delta_{\hat{n}_i, \hat{y}} \delta_{\hat{n}_j, \hat{y}} + \delta_{\hat{n}_i, -\hat{y}} \delta_{\hat{n}_j, -\hat{y}}) \quad ,$$

where  $\mathcal{X}$  is the set of  $\hat{x}$ -directed links and  $\mathcal{Y}$  is the set of  $\hat{y}$ -directed links. We can associate to each site  $i$  the two links to its north ( $\hat{y}$ ) and to its east ( $\hat{x}$ ). There are then four nonzero energy configurations to account for, each with energy  $-J$ , as depicted in the above figure. From our variational density matrix, three of these configurations occur with probability  $[\frac{1}{4}(1-x)]^2$ , and one with probability  $[\frac{1}{4}(1+3x)]^2$ . Thus, the total energy is

$$E = \text{Tr}(\varrho_{\text{var}} \hat{H}) = -3NJ \times \frac{1}{16}(1-x)^2 - NJ \times \frac{1}{16}(1+3x)^2 = -\frac{1}{4}NJ(1+3x^2) \quad .$$

(c) The entropy per spin is given by

$$\begin{aligned} s/k_{\text{B}} &= -\text{Tr} \varrho_1 \ln \varrho_1 = -3 \times \frac{1}{4}(1-x) \ln \left[ \frac{1}{4}(1-x) \right] - \frac{1}{4}(1+3x) \ln \left[ \frac{1}{4}(1+3x) \right] \\ &= -\frac{3}{4}(1-x) \ln(1-x) - \frac{1}{4}(1+3x) \ln(1+3x) + \ln 4 \quad . \end{aligned}$$

The total entropy is  $N = Ns$ . Note that in the disordered phase, where  $x = 0$ , the entropy per spin is  $s = k_{\text{B}} \ln 4$ .

(d) The dimensionless free energy per site  $f = F/NJ$  is then

$$f(x, \theta) = f_0 - \frac{3}{4}x^2 + \frac{3}{4}\theta(1-x) \ln(1-x) + \frac{1}{4}\theta(1+3x) \ln(1+3x) \quad ,$$

with  $f_0 = -\frac{1}{4} - \theta \ln 4$ . The condition  $\partial f / \partial x = 0$  yields the self-consistent mean-field equation,

$$x = \frac{1}{2} \ln \left( \frac{1+3x}{1-x} \right) \quad .$$

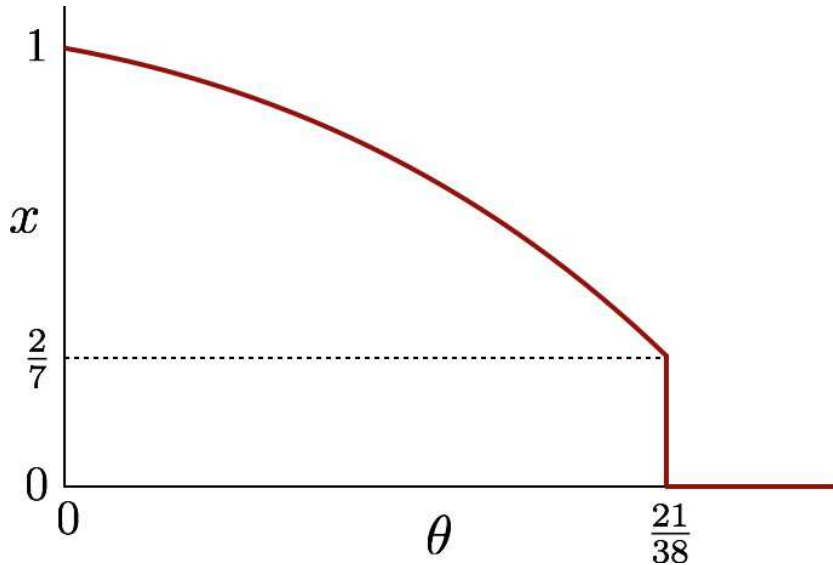


Figure 2:  $x(\theta)$  for problem 3.

(e) Using

$$\begin{aligned}(1 + \varepsilon) \ln(1 + \varepsilon) &= (1 + \varepsilon) \left( \varepsilon - \frac{1}{2}\varepsilon^2 + \frac{1}{3}\varepsilon^3 - \frac{1}{4}\varepsilon^4 + \dots \right) \\ &= \varepsilon + \frac{1}{2}\varepsilon^2 - \frac{1}{6}\varepsilon^3 + \frac{1}{12}\varepsilon^4 - \frac{1}{20}\varepsilon^5 + \dots \quad ,\end{aligned}$$

we obtain

$$f(x, \theta) = f_0 + \frac{3}{2}(\theta - \frac{1}{2})x^2 - \theta x^3 + \frac{7}{4}\theta x^4 + \mathcal{O}(x^5) \quad .$$

(f) Writing  $f \equiv f_0 + \frac{1}{2}ax^2 - \frac{1}{3}yx^3 + \frac{1}{4}bx^4$ , we have  $a = 3\theta - \frac{3}{2}$ ,  $y = 3\theta$ , and  $b = 7\theta$ . The first order transition occurs for  $a = 2y^2/9b = \frac{2}{7}\theta$ . Thus,

$$3\theta_c - \frac{3}{2} = \frac{2}{7}\theta_c \quad \Rightarrow \quad \theta_c = \frac{21}{38} \quad .$$

Note that  $\theta_c > \frac{1}{2}$ , *i.e.* the first order transition preempts what would have been a second order transition at  $\theta = \frac{1}{2}$  ( $a = 0$ ). The value of  $x(\theta_c^-)$  is  $x_c = 3a_c/y = \frac{2}{7}$ . Please note that this value of  $\theta_c$  pertains *only* to the truncated fourth order Landau expansion of the free energy. In general, one must find the nontrivial (*i.e.*  $x \neq 0$ ) solution of the simultaneous equations  $f(x, \theta) = f_0$  and  $\partial f/\partial x = 0$  for the two unknowns  $\theta$  and  $x$  to obtain the critical values  $(\theta_c, x_c)$  at the first order transition. In fact, it is easy to check that the solution is  $\theta_c = \frac{2}{3 \ln 3} \approx 0.6068$  and  $x_c = \frac{2}{3}$ .

(4) Provide brief but accurate answers to each of the following:

- (a) For a single-component system, the Gibbs free energy  $G$  is a function of what state variables? Write its differential and all the Maxwell equations resulting from consideration of the mixed second derivatives of  $G$ .
- (b) A system of noninteracting spins is cooled in a uniform magnetic field  $H_1$  to a temperature  $T_1$ . The external field is then adiabatically lowered to a value  $H_2 < H_1$ . What is the final value of the temperature,  $T_2$ ?
- (c) For a two-level system with energy eigenvalues  $\varepsilon_1 < \varepsilon_2$ , the heat capacity vanishes in both the  $T \rightarrow 0$  and  $T \rightarrow \infty$  limits. Explain physically why this is so. What will happen in the case of a three-level system?
- (d) Sketch the phase diagram of the  $d = 2$  Ising model in the  $(T, H)$  plane. Identify the critical point and the location of all first order transitions. Then make a corresponding sketch for the  $d = 1$  Ising model.

**Solution :**

(a) The Gibbs free energy  $G = E - TS + pV$  is a double Legendre transformation of the energy  $E$ . Thus  $G = G(T, p, N)$ , with

$$dG = -S dT + V dp + \mu dN \quad .$$

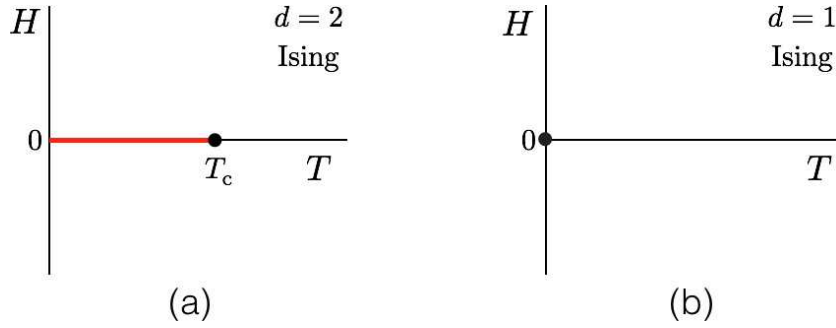


Figure 3: Sketches for problem 4 solutions. (a) Phase diagram of the two-dimensional Ising model. The red line is a line of first order transitions. The black dot is the critical point  $(T_c, H_c)$  with  $H_c = 0$ . (b) Phase diagram for the one-dimensional Ising model. The critical temperature has collapsed to  $T_c = 0$ . There is a first order transition as a function of  $H$  at  $H_c = 0$  and fixed temperature  $T = 0$ .

We then have the Maxwell relations

$$\left(\frac{\partial S}{\partial p}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{p,N} \quad , \quad \left(\frac{\partial S}{\partial N}\right)_{T,p} = -\left(\frac{\partial \mu}{\partial T}\right)_{p,N} \quad , \quad \left(\frac{\partial V}{\partial N}\right)_{T,p} = \left(\frac{\partial \mu}{\partial p}\right)_{T,N} .$$

b) For noninteracting spins, the only energy scale in the Hamiltonian is provided by  $H$ , hence the entropy is of the form  $S(T, H, N) = Ns(H/T)$  and therefore if  $dS = 0$ , assuming as always  $dN = 0$  for spins, we have that  $H/T$  is constant. Therefore  $H_1/T_1 = H_2/T_2$  and

$$T_2 = T_1 \cdot \frac{H_2}{H_1} \quad .$$

(c) The occupation probabilities are  $P_n = e^{-\beta \epsilon_n} / (e^{-\beta \epsilon_1} + e^{-\beta \epsilon_2})$ . At low temperatures,  $P_1 \approx 1$  and  $P_2 \approx 0$ , hence  $E = P_1 \epsilon_1 + P_2 \epsilon_2 \approx \epsilon_1$ . This pertains so long as  $k_B T \ll \epsilon_2 - \epsilon_1$ , in which case  $C = \partial E / \partial T \approx 0$ . In the opposite limit  $k_B T \gg \epsilon_2 - \epsilon_1$ , both  $P_1 \approx P_2 \approx \frac{1}{2}$ , and  $E \approx \frac{1}{2}(\epsilon_1 + \epsilon_2)$ . Again, changing  $T$  has very little effect, and  $C \approx 0$ . The same considerations apply for any system comprised of a finite number of energy levels.

(d) See Fig. 3. In  $d = 2$  dimensions, there is a critical point at  $(T_c, H_c)$ , with  $T_c > 0$  and where, by symmetry,  $H_c = 0$ . For  $T < T_c$ , there is a line of first order transitions at  $H = 0$ . In  $d = 1$  dimension, the critical temperature collapses to  $T_c = 0$ .