PHYSICS 210A : STATISTICAL PHYSICS
FINAL EXAM SOLUTIONS

(1) Consider the analog of the van der Waals equation of state for a gas if 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 $dF = -S\,dT - p\,dV$, 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 $v \to \infty$ limit, we recover the diatomic ideal gas, hence $\omega(T) = \frac{5}{2}RT$ and

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

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

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

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

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 Δ. In other words, the fermion dispersion is $\varepsilon_f(\boldsymbol{k}) = \hbar^2\boldsymbol{k}^2/2m$ and the boson dispersion is $\varepsilon_B(\boldsymbol{k}) = -\Delta + \hbar^2\boldsymbol{k}^2/4m$. 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* $\rho_{tot} = mn$ *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 $2\text{b} \rightleftharpoons \text{B}$, 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,

$$n = \mathsf{g}\int \frac{d^2k}{(2\pi)^2}\, \frac{1}{z^{-1}\exp(\hbar^2\boldsymbol{k}^2/2mk_\text{B}T)+1}$$
$$= \mathsf{g}\lambda_T^{-2}\int_0^\infty dx\, \frac{1}{z^{-1}\exp(x)+1} = \mathsf{g}\lambda_T^{-2}\ln(1+z) \quad .$$

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

(b) Let z be the fugacity of the fermions and z_B be the fugacity of the bosons. Clearly $\mu_\text{B} = 2\mu$, *i.e.* $z_\text{B} = z^2$. Due to the reactions, n_f and n_B are not separately conserved, but $n = n_\text{f} + 2n_\text{B}$ is conserved, hence

$$n\lambda_T^2 = 2\ln(1+z) - 4\ln\left(1 - z^2 e^{\Delta/k_\text{B}T}\right) \quad .$$

Note that $n_\text{B} = -2\ln\left(1 - z^2 e^{\Delta/k_\text{B}T}\right)$ with the prefactor of 2 arising from $m_\text{B} = 2m$.

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

$$n_\text{f} = 2\ln\left(1 + e^{-\Delta/2k_\text{B}T}\right) \quad , \quad n_\text{B} = \tfrac{1}{2}n \quad .$$

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

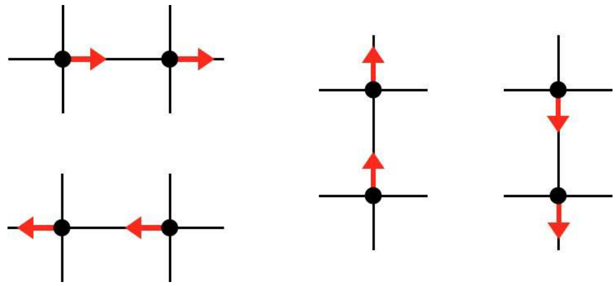
(d) If the initial particles are spin-0 bosons, then

$$n\lambda_T^2 = -\ln(1-z) - 4\ln\left(1 - z^2 e^{\Delta/k_\text{B}T}\right) \quad .$$

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

$$n_\text{b} = -\ln\left(1 - e^{-\Delta/2k_\text{B}T}\right) \quad , \quad n_\text{B} = \tfrac{1}{2}n \quad .$$

(3) On each site i of a (two-dimensional square) lattice exists a unit vector $\hat{\boldsymbol{n}}_i$ which can point in any of four directions: $\{\pm\hat{\boldsymbol{x}}, \pm\hat{\boldsymbol{y}}\}$. 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:



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

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

where x is a variational parameter.

(a) What is the allowed range for x? Verify that the density matrix ϱ_1 is appropriately normalized.

(b) Taking $\varrho_{\text{var}}(\{\hat{\boldsymbol{n}}_i\}) = \prod_i \varrho_1(\hat{\boldsymbol{n}}_i)$, find the average energy E. (Please denote the total number of lattice sites by N.)

(c) Find the entropy S.

(d) Find the dimensionless free energy per site $f \equiv F/NJ$ in terms of the variational parameter x and the dimensionless temperature $\theta \equiv k_{\text{B}}T/J$.

(e) Find the Landau expansion of $f(x,\theta)$ to fourth order in x. *Hint:*

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

(f) *Based on the fourth order Landau expansion of the free energy*, sketch the equilibrium curve of x *versus* θ 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 $x \in \big[-\frac{1}{3}\,,\,1\big]$. Since the trace is $\text{Tr}\,\varrho_1 = \sum_{\hat{n}} \varrho_1(\hat{\boldsymbol{n}}) = 1$, it is properly normalized.

(b) The Hamiltonian for this system is written

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

where $\mathcal{X}$ is the set of $\hat{\boldsymbol{x}}$-directed links and $\mathcal{Y}$ is the set of $\hat{\boldsymbol{y}}$-directed links. We can associate to each site i the two links to its north ($\hat{\boldsymbol{y}}$) and to its east ($\hat{\boldsymbol{x}}$). 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 $\left[\frac{1}{4}(1-x)\right]^2$, and one with probability $\left[\frac{1}{4}(1+3x)\right]^2$. Thus, the total energy is

$$E = \mathsf{Tr}\,\big(\varrho_{\rm var}\,\hat{H}\big) = -3NJ \times \tfrac{1}{16}(1-x)^2 - NJ \times \tfrac{1}{16}(1+3x)^2 = -\tfrac{1}{4}NJ\,(1+3x^2) \quad .$$

(c) The entropy per spin is given by

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

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

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

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

with $f_0 = -\frac{1}{4} - \theta\ln 4$.

(e) Using

$$\begin{aligned} (1+\varepsilon)\ln(1+\varepsilon) &= (1+\varepsilon)\big(\varepsilon - \tfrac{1}{2}\varepsilon^2 + \tfrac{1}{3}\varepsilon^3 - \tfrac{1}{4}\varepsilon^4 + \ldots\big) \\ &= \varepsilon + \tfrac{1}{2}\varepsilon^2 - \tfrac{1}{6}\varepsilon^3 + \tfrac{1}{12}\varepsilon^4 - \tfrac{1}{20}\varepsilon^5 + \ldots \quad , \end{aligned}$$

we obtain

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

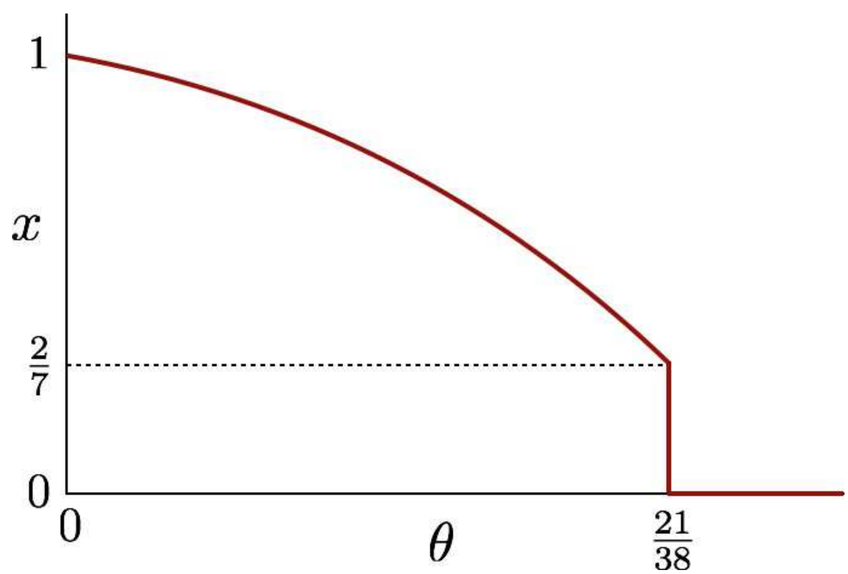


Figure 1: $x(\theta)$ for problem 3.

(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,

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

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 θ_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 θ and x to obtain the critical values (θ_c, x_c) at the first order transition.

(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 $T \to 0$ and $T \to \infty$ 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

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

We then have the Maxwell relations

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

b) For noninteracting spins, the only energy scale in the Hamiltonian is provided by H, hence the entropy is of the form $S(T, H, N) = N s(H/T)$ 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

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

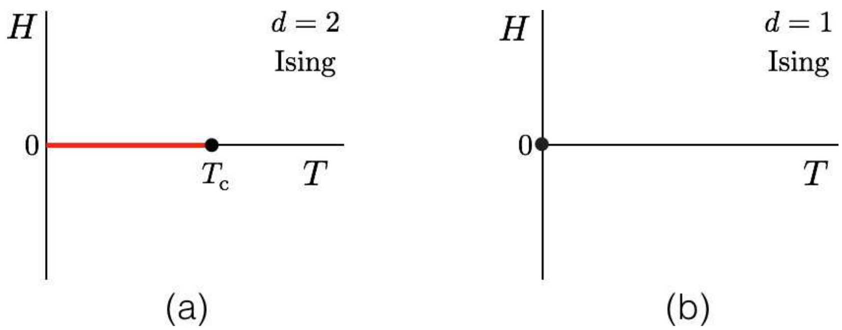


Figure 2: Sketches for problem 4 solutions. (a) Phase diagram of the two-dimensional Ising model. The red line is a line of first order transitions. The black dot is the critical point (T_c, H_c) with $H_c = 0$. (b) Phase diagram for the one-dimensional Ising model. The critical temperature has collapsed to $T_c = 0$. There is a first order transition as a function of H at $H_c = 0$ and fixed temperature $T = 0$.

(c) The occupation probabilities are $P_n = e^{-\beta\varepsilon_n}/(e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2})$. At low temperatures, $P_1 \approx 1$ and $P_2 \approx 0$, hence $E = P_1\,\varepsilon_1 + P_2\,\varepsilon_2 \approx \varepsilon_1$. This pertains so long as $k_B T \ll \varepsilon_2 - \varepsilon_1$, in which case $C = \partial E/\partial T \approx 0$. In the opposite limit $k_B T \gg \varepsilon_2 - \varepsilon_1$, both $P_1 \approx P_2 \approx \frac{1}{2}$, and $E \approx \frac{1}{2}(\varepsilon_1 + \varepsilon_2)$. 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. 2. 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 $T_c = 0$.