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

\[ p = \frac{RT}{v-b} + \frac{a}{v^2}, \]

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

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

where we have invoked a Maxwell relation based on \( dF = -SdT - pdV \), we have

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

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

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

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

\[ dp = \frac{R}{v-b}dT - \left[ \frac{RT}{(v-b)^2} + \frac{2a}{v^3} \right] dv. \]
We then have
\[ \alpha_p(T, v) = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p = \frac{R(v-b)v^2}{RTv^3 + 2a(v-b)^2}. \]

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

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 \( s = N_{\lambda}S/N \) be the molar entropy. Then
\[
ds = \frac{1}{T} d\varepsilon + \frac{p}{T} dv \]
\[= \frac{1}{2} f R \frac{dT}{T} + \frac{R}{v-b} dv = R d \ln \left[ (v-b) T^{f/2} \right], \]
and therefore the adiabatic equation of state is
\[ (v-b) T^{f/2} = \text{constant}. \]

Thus, the result of a reversible adiabatic process must be
\[ T_2 = \left( \frac{v_1-b}{v_2-b} \right)^{2/f} T_1. \]
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 \( z = \exp(\mu/k_BT) \), and the temperature \( T \). You may choose to abbreviate \( \lambda_T = \sqrt{2\pi \hbar^2/mk_BT} \). 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 \( \varepsilon_f(k) = \hbar^2 k^2/2m \) and the boson dispersion is \( \varepsilon_B(k) = -\Delta + \hbar^2 k^2/4m \). 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,

$$n = g \int \frac{d^2k}{(2\pi)^2} \frac{1}{z^{-1} \exp(h^2k^2/2mk_B T) + 1} = g\lambda_T^{-2} \int_0^{\infty} \frac{dx}{x^{-1} \exp(x) + 1} = g\lambda_T^{-2} \ln(1 + z) .$$

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

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

Note that $n_B = -2 \ln \left(1 - z^2 e^{\Delta/k_B T}\right)$, 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,

$$n_f = 2 \ln \left(1 + e^{-\Delta/2k_B T}\right) , \quad n_B = \frac{3}{2}n .$$

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

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

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

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

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

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

\[ \rho_1(\hat{n}) = \frac{1}{4} (1 + 3x) \delta_{\hat{n}, \hat{x}} + \frac{1}{4} (1 - x) \delta_{\hat{n}, -\hat{x}} + \frac{1}{4} (1 - x) \delta_{\hat{n}, \hat{y}} + \frac{1}{4} (1 - x) \delta_{\hat{n}, -\hat{y}} , \]

where \( x \) is a variational parameter.

(a) What is the allowed range for \( x \)? Verify that the density matrix \( \rho_1 \) is appropriately normalized.

(b) Taking \( \rho_{\text{var}}(\{\hat{n}_i\}) = \prod_i \rho_1(\hat{n}_i) \), 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 \( \theta \equiv k_B T/J \).

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

\[ (1 + \varepsilon) \ln(1 + \varepsilon) = \varepsilon + \frac{1}{2} \varepsilon^2 - \frac{1}{6} \varepsilon^3 + \frac{1}{12} \varepsilon^4 - \frac{1}{20} \varepsilon^5 + \ldots . \]

(f) 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 \( x \in \left[ -\frac{1}{3}, 1 \right] \). Since the trace is \( \text{Tr} \rho_1 = \sum_{\hat{n}} \rho_1(\hat{n}) = 1 \), it is properly normalized.

(b) The Hamiltonian for this system is written

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

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 \(\left[\frac{1}{4}(1-x)\right]^2\), and one with probability \(\left[\frac{1}{4}(1+3x)\right]^2\). Thus, the total energy is

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

(c) The entropy per spin is given by

\[
s/k_B = -\text{Tr} \varrho \ln \varrho = -3 \times \frac{1}{4}(1-x) \ln \left[\frac{1}{4}(1-x)\right] - \frac{1}{4}(1+3x) \ln \left[\frac{1}{4}(1+3x)\right]
= \frac{3}{4}(1-x) \ln(1-x) + \frac{1}{4}(1+3x) \ln(1+3x) + \ln 4.
\]

The total entropy is \(N = Ns\). Note that in the disordered phase, where \(x = 0\), the entropy per spin is \(s = k_B \ln 4\).

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

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

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

(e) Using

\[
(1 + \varepsilon) \ln(1 + \varepsilon) = (1 + \varepsilon)(\varepsilon - \frac{1}{2} \varepsilon^2 + \frac{1}{3} \varepsilon^3 - \frac{1}{4} \varepsilon^4 + \ldots)
= \varepsilon + \frac{1}{2} \varepsilon^2 - \frac{1}{6} \varepsilon^3 + \frac{1}{12} \varepsilon^4 - \frac{1}{24} \varepsilon^5 + \ldots,
\]

we obtain

\[
f(x, \theta) = f_0 + \frac{3}{2} \left( \theta - \frac{1}{2} \right) x^2 - \theta x^3 + \frac{7}{4} \theta x^4 + O(x^5).
\]

Figure 1: \(x(\theta)\) for problem 3.
Writing \( f \equiv f_0 + \frac{1}{2}a x^2 - \frac{1}{2} b y x^3 + \frac{1}{4} b x^4 \), we have \( a = 3\theta - \frac{3}{2}, \) \( y = 3\theta, \) and \( b = 7\theta. \) The first order transition occurs for \( a = 2y^2/9b = \frac{2}{\theta}. \) Thus,
\[
3\theta_c - \frac{3}{2} = \frac{2}{\theta} \theta_c \quad \Rightarrow \quad \theta_c = \frac{21}{38}.
\]
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 \( x_c = 3a_c/y = \frac{2}{\theta}. \) 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.

(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
\[
dG = -SdT + Vdp + \mu dN.
\]
We then have the Maxwell relations
\[
\left( \frac{\partial S}{\partial p} \right)_{T, N} = - \left( \frac{\partial V}{\partial T} \right)_{p, N}, \quad \left( \frac{\partial S}{\partial N} \right)_{T, p} = - \left( \frac{\partial \mu}{\partial T} \right)_{p, N}, \quad \left( \frac{\partial V}{\partial N} \right)_{T, p} = \left( \frac{\partial \mu}{\partial p} \right)_{T, N}.
\]

b) For noninteracting spins, the only energy scale in the Hamiltonian is provided by \( H, \) hence the entropy is of the form \( S(T, H, N) = N s(H/T) \) 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
\[
T_2 = T_1 \frac{H_2}{H_1}.
\]
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 $T_c = 0$. 
