You are GIVEN that the law of mass action states that the equilibrium concentrations of a chemical reaction \( \sum_i \nu_i A_i = 0 \) (where the \( A_i \) are the chemical species and the \( \nu_i \) are integers which characterize the reaction) satisfy
\[
\prod_j \left( \frac{n_j}{c_j} \right)^{\nu_j} = 1,
\]
where
\[
c_j = n_{Qj} Z_j \text{(int)},
\]
in which \( Z_j \text{(int)} \) is the “internal partition function”, and
\[
n_{Qj} = \left( \frac{m_j k_B T}{2 \pi \hbar^2} \right)^{3/2},
\]
is the quantum concentration for species \( j \).

1. [15 points]
   Consider an atom which has two energy levels: a ground state with degeneracy \( g_1 \) and an excited state of degeneracy \( g_2 \) at an energy \( \Delta \) above the ground state.
   (a) Determine the partition function.
   (b) Hence determine the free energy and average energy, and show that the specific heat (heat capacity) is given by
   \[
   C = \frac{g_1 g_2 \Delta^2 e^{-\beta \Delta}}{k_B T^2 (g_1 + g_2 e^{-\beta \Delta})^2},
   \]
   where \( \beta = 1/(k_B T) \).

2. [15 points]
   Consider bosons hopping on and off a site. If there is one boson on the site the energy is \( \epsilon \). If there is more than one boson, then the energy is not just \( n\epsilon \) because different bosons repel. Hence we write the total energy of \( n \) bosons as
   \[
   E_n = n\epsilon + U n(n - 1),
   \]
   where \( U (> 0) \) is a parameter describing the repulsion. The system is in diffusive contact with a reservoir, so the number of bosons is not fixed but the mean number is controlled by the chemical potential.
   (a) Write down an expression for the mean number of bosons \( \langle n \rangle \). Your answer will involve infinite series which you are not required to evaluate.
   (b) Evaluate explicitly \( \langle n \rangle \) for the case \( U = 0 \).
   (c) Show that for \( U \to \infty \)
   \[
   \langle n \rangle = \frac{1}{\exp[\beta (\epsilon - \mu)] + 1}.
   \]
   \text{Hint: In the limit of } U \to \infty \text{ what are the allowed values of } n?
3. [25 points]  
Consider an ideal gas of \( N \) Fermions with mass \( m \) and spin-\( S \), i.e. there are \( 2S + 1 \) spin states. You are given that the density of states is

\[
\rho(\epsilon) = V \frac{2S + 1}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2}.
\]

(No need to derive this.)

(a) Determine the Fermi energy \( \epsilon_F \).

(b) Show that the energy at \( T = 0 \) is given by

\[
U = \frac{3}{10} \left( \frac{6\pi^2}{2S + 1} \right)^{2/3} \left( \frac{\hbar^2}{m} \right) \frac{N^{5/3}}{V^{2/3}}.
\]

(c) Determine the pressure at \( T = 0 \) from \( P = -(\partial U/\partial V)_{N,T} \).

(d) A sliding piston separates two compartments of a container. Compartment 1 contains spin-\( 1/2 \) particles and compartment 2 contains spin-\( 3/2 \) particles. All the particles have the same mass, and the temperature is \( T = 0 \). Find the relative density of the two gases in equilibrium.

Note:
- Express your answer as a fraction to a power. You are not required to evaluate it numerically.
- Classically, the pressure of an ideal gas is independent of spin and so the densities would be equal. Hence, a ratio of densities different from one is a quantum effect.

4. [20 points]  
Consider the chemical reaction

\[
A + A \leftrightarrow B.
\]

When the two atoms \( A \) combine to form the molecule \( B \) there is a gain in energy (binding energy) of magnitude \( \Delta E \).

Using the law of mass action, defined at the beginning of the exam, show that the condition for the densities of the atoms \( A \) to equal the density of the molecules \( B \) is

\[
\frac{n_A}{n_{QA}} = \frac{1}{2^{3/2}} e^{-\beta \Delta E}.
\]

(Exam continues on next page.)
5. [25 points]
Consider a spin-1 Ising model in which $S_i$, the spin on site $i$, takes values 1, 0 and $-1$. In the absence of interactions between spins the $S_i = \pm 1$ states have an energy $\Delta$ higher than the $S_i = 0$ state (see figure below). (This represents an “anisotropy” due to the neighboring non-magnetic ions in the crystal). If one applies a magnetic field $B$, the $S_i = \pm 1$ states split and the energies become
\[
S_i = 1, \quad E = \Delta - B,
S_i = 0, \quad E = 0,
S_i = -1, \quad E = \Delta + B,
\]
see the figure:

\[
\begin{align*}
S = -1 & \quad \Delta + B \\
S = 0 & \quad \Delta \\
S = 1 & \quad \Delta - B
\end{align*}
\]

(a) Calculate $m \equiv \langle S_i \rangle$ of a single spin in the presence of a field.

(b) Now suppose that different spins on the lattice interact through an additional energy
\[
-J \sum_{(i,j)} S_i S_j,
\]
where the sum is over all nearest-neighbor pairs (counted once). In the mean field approximation the neighbors give rise to a mean field $B^{MF}$. What is $B^{MF}$? (Assume that each spin interacts with $z$ neighbors).

(c) Substitute your result for $B = B^{MF}$ from 5b into the equation you got for $m$ in 5a to obtain a self-consistent expression for $m$.

(d) Assuming that the transition is continuous (second order) show that the transition temperature $T_c$ is given by the self-consistent equation
\[
k_B T_c = \frac{2e^{-\Delta/k_B T_c}}{1 + 2e^{-\Delta/k_B T_c}} z J.
\]

(e) For the limit $\Delta \to 0$ show that
\[
k_B T_c = \frac{2}{3} z J.
\]

[Note: This model has been studied in the literature, and is called the Blume-Capel model. As $\Delta$ increases from zero, the mean field approximation to $T_c$ decreases from $(2/3)zJ$. It turns out that if $\Delta$ is large enough that the transition temperature decreases below $(1/3)zJ$ (i.e. half the $\Delta = 0$ value) the transition becomes discontinuous (first order). This can be deduced from the self-consistent expression for $m$ that you obtained in part 5c, but you are not required to show it here. When the transition is first order, the transition temperature is no longer given by Eq. (1).]