**Problem 1: Two Identical Particles**

A system consists of two identical, non-interacting, spinless (no spin variables at all) particles. The system has only three single-particle states $\psi_1$, $\psi_2$, and $\psi_3$ with energies $\epsilon_1 = 0 < \epsilon_2 < \epsilon_3$ respectively.

a) List in a vertical column all the two-particle states available to the system, along with their energies, if the particles are Fermions. Use the occupation number notation $(n_1, n_2, n_3)$ to identify each state. Indicate which state is occupied at $T = 0$.

b) Repeat a) for the case of Bose particles.

c) Use the Canonical Ensemble to write the partition function for both Fermi and Bose cases.

d) Using only the leading two terms in the partition function, find the temperature dependence of the internal energy in each case. Contrast the behavior of the internal energy near $T = 0$ in the two cases.

**Problem 2: A Number of Two-State Particles**

Consider a collection of $N$ identical, non-interacting, spinless Bose particles. There are only two single-particle energy eigenstates: $\psi_0$ with energy $\epsilon = 0$ and $\psi_1$ with energy $\epsilon = \Delta$.

a) How would you index the possible $N$-body energy eigenstates in the occupation number representation? What are their energies? How many $N$-body states are there in all?

b) Find a closed form expression for the partition function $Z(N, T)$ using the Canonical Ensemble.

c) What is the probability $p(n)$ that $n$ particles will be found in the excited state $\psi_1$?

d) Find the partition function $Z_d(N, T)$ that would apply if the $N$ particles were distinguishable but possessed the same single particle states as above.
**Problem 3:** Identical Particle Effects in Rotational Raman Scattering

Begin by re-reading **Excited State Helium** in the Notes on our website. This reminds you that when anti-symmetry is required for a two-body wavefunction it can be carried by either the spin or the spatial part of the wavefunction. Next, read **Raman** on our website. That discussion shows how this concept is applied to the rotational motion of homonuclear diatomic molecules.

The chlorine atom exists stably as two different isotopes: $^{35\,17}\text{Cl}$ at 76% and $^{37\,17}\text{Cl}$ at 24%. In each case the nuclear spin is $3/2$.

a) For a gas composed only of diatomic molecules of the lighter isotope, $^{35\,17}\text{Cl} - ^{35\,17}\text{Cl}$, find the ratio of the intensities of the two series of alternating lines in the rotational Raman spectrum.

b) For rotational motion the Boltzmann factor decreases with angular momentum $L$ as \( \exp[-L(L+1)\Theta_R/T] \) and the degeneracy increases with angular momentum as $2L+1$. Near what value of $L$ does the Raman spectrum reach its peak?

c) The rotational temperature $\Theta_R$ of $\text{N}_2$ is 2.9 K. Does your result in b) agree with the nitrogen spectrum shown in the Raman notes? The rotational temperature for $\text{Cl}_2$ is about 0.35 K. Find the approximate number of lines in the spectrum out to the point where the scattered intensity reaches its maximum value.

d) Explain any qualitative changes that would occur if the chlorine experiment were to be done with a gas of molecules composed of only different isotopes: $^{35\,17}\text{Cl} - ^{37\,17}\text{Cl}$.

**Problem 4:** Langmuir Isotherm

a) How many ways can one place $N$ identical atoms on $M \geq N$ distinct sites, given that each site can hold no more than one atom?

b) Find the Canonical partition function $Z(T, N)$ if the atom has an energy $-\epsilon_0$ when it is on a site. Note that since each of the $N$ atoms in our system is always on some site, there is only one possible system energy with a massive degeneracy.

c) Find the Helmholtz Free Energy of the system, $F(T, N)$, and show that the chemical potential is given by

\[
\mu = -\epsilon_0 - k_B T \ln \left( \frac{M - N}{N} \right)
\]
Let \( f \equiv N/M \) be the probability that any given site is occupied. Assume the system we have been considering represents adsorption sites on the surface of some material in thermal equilibrium with a bulk 3-dimensional gas of \( N_{\text{gas}} \) atoms of the same type in a volume \( V \). The atoms, once adsorbed, are not free to move laterally: they have no kinetic energy. Find an expression for \( f \) in terms of the number density in the gas, \( n \equiv N_{\text{gas}}/V \), the thermal deBroglie wavelength \( \lambda(T) \), and the binding energy \( \epsilon_0 \). Show that \( f = 0 \) at all temperatures if Planck’s constant \( h \) were to be zero.

e) Express your result in d) in terms of the pressure \( P \) in the gas. This result is known as the Langmuir Isotherm. Make a sketch of \( f \) versus \( P \) at constant \( T \).

Problem 5: Information Theory Approach to Statistical Mechanics

Read section 15.1 in Blundell and Blundell on information and Shannon entropy. Note the difference between the information content of a given statement or message, and the average information content of similar material in some context, for example the material being sent across a communication channel. Electrical engineers are more often concerned with the latter than the former. Therefore the Shannon entropy \( S_I \) of a signal weights the information content of each item by the probability that the item occurs in the signal.

\[
S_I \equiv -k_B \sum_i P_i \ln P_i
\]

where \( \ln P_i \) is the information in a given item and \( P_i \) is the probability that the item will occur.

The information theory approach to statistical is based on two assumptions.

**Assumption 1** The physical thermodynamic entropy of a system has the same form as the Shannon entropy in information theory and can be written as

\[
S_I = -k_B \sum_{\text{states}} p_{\text{state}} \ln p_{\text{state}}
\]

where \( p_{\text{state}} \) is the probability that a microscopic state of the system occurs and the sum is over all the states of the system.

a) Show that this assumption gives the correct result for the Microcanonical Ensemble where

\[
p_{\text{state}} = \frac{1}{\Omega} \quad \text{and} \quad \Omega = \sum_{\text{states}} (1)
\]
b) Show that this assumption gives the correct result for the Canonical Ensemble where

\[ p_{\text{state}} = \frac{e^{-\beta E_{\text{state}}}}{Z} \]

\[ Z = \sum_{\text{states}} e^{-\beta E_{\text{state}}} \] and \[ F(T,V) = -k_B T \ln Z \]

Now we will show how to use the information theory approach to arrive at the microscopic probability densities. We will use the Grand Canonical Ensemble as our example. Once we understand this example, it would be straightforward to go back and derive the Micro-canonical and Canonical ensembles as well.

**Assumption 2** The equilibrium probabilities are found by maximizing \( S_I \) while taking into account certain constraints imposed on the system.

Since we are dealing with the Grand Canonical Ensemble, where the number of particles \( N \) can vary and is therefore an active variable in the probability density we seek, let \( p_{\text{state}} \) be replaced by \( p_{N,\nu} \) where the subscript \( \nu \) indicates all the other variables (these will be microscopic variables) that may come into the specification of the state of our system.

The constraints we impose on the system will be normalization, the average energy (which we will take to be the internal energy \( U \)) and the average number of particles, \( \bar{N} \). Then, according to Assumption 2, we must maximize

\[ S_I = -k_B \sum_{N,\nu} p_{N,\nu} \ln p_{N,\nu} \]

subject to the constraints

\[ \sum_{N,\nu} p_{N,\nu} = 1 \]

\[ \sum_{N,\nu} E_{N,\nu} p_{N,\nu} = U \]

\[ \sum_{N,\nu} N p_{N,\nu} = \bar{N} \]

c) Review the method of Lagrange multipliers in your favorite applied mathematics text or in Appendix C.13 of Blundell and Blundell. We have four functions of the many-variable set \( \{p_{N,\nu}\} \). We want to find the value of each of the \( p_{N,\nu} \) when \( S \) is maximized and the expressions for \( 1, U \) and \( \bar{N} \) are satisfied. The theory of Lagrange multipliers tells us this will occur when the partial derivative of the expression

\[ S_I + \lambda_1 (1) + \lambda_U U + \lambda_{\bar{N}} \bar{N} \]

with respect to each of the variables equals zero. Of course in this equation each of the three functions \( 1, U \) and \( \bar{N} \) must be represented by the sum of terms to which they are equal. That will give the variables we seek in terms of the \( \lambda \)s, which will have to
be determined by the nature of the system. Carry out this operation and show that
the dependance of \( p_{N,\nu} \) on the microscopic variables must have the form
\[
\ln p_{N,\nu} = \frac{\lambda_1}{k_B} - 1 + \left( \frac{\lambda_U}{k_B} \right) E_{N,\nu} + \left( \frac{\lambda_N}{k_B} \right) N
\]

\[d\] All that remains is to find expressions for the three \( \lambda \)s in terms of the thermodynamic
variables of the system. To do that multiply the expression you found above by \( k_B p_{N,\nu} \)
and sum over \( N \) and \( \nu \). Compare the result with the thermodynamic expression for
the grand potential \( \Phi \).
\[\Phi = U - TS - \mu \tilde{N}\]

You should end up with the desired result:
\[
p_{N,\nu} = \exp\left[ (N \mu - E_{N,\nu}) / k_B T \right] / Z
\]

**Problem 6: Maxwell Relations**

Express the following partial derivatives in terms of other partial derivatives that do not
involve the chemical potential \( \mu \).
\[
\left( \frac{\partial S}{\partial \mu} \right)_{V,N}
\]
\[
\left( \frac{\partial \mu}{\partial V} \right)_{T,N}
\]
\[
\left( \frac{\partial \mu}{\partial P} \right)_{T,N}
\]
\[
\left( \frac{\partial \mu}{\partial T} \right)_{P,N}
\]