Statistical Mechanics: Problems 9.1

1. **Problem:** Consider a collection of N noninteracting spins ($s = 1$), in a magnetic field B, such that the Hamiltonian is given by $\hat{S}_z B$. Using canonical ensemble, find the average magnetization of the gas.
   Solution: Suppose the magnetic field is in the z-direction. The Hamiltonian em for one spin is given by $\hat{H} = -g_S\mu_B\vec{B}\cdot\vec{S}/\hbar = -g_S\mu_B B\hat{S}_z/\hbar$. The energy eigenvalues are given by $\hat{H}|m\rangle = E_m|m\rangle$, where $E_m = -g_S\mu_B Bm$, $m = -1, 0, +1$. Energy of N spins can then be written as

$$E_{m1,m2...mN} = -g_S\mu_B B(m_1 + m_2 + m_3... + m_N)$$

where $m_1, m_2...$ can take values $-1, 0, +1$ each. Summing over microstates would amount to summing over these values. The canonical partition function can then be written as

$$\begin{aligned} Z &= \sum_{m_1=-1}^{+1}\sum_{m_2=-1}^{+1}\cdots\sum_{m_N=-1}^{+1} \exp\left(\beta g_S\mu_B B(m_1 + m_2 + m_3... + m_N)\right) \\ &= \sum_{m_1=-1}^{+1}\sum_{m_2=-1}^{+1}\cdots\sum_{m_N=-1}^{+1}\prod_{i=1}^{N} e^{\beta g_S\mu_B B m_i} \\ &= \prod_{i=1}^{N}\sum_{m_i=-1}^{+1} e^{\beta g_S\mu_B B m_i} \\ &= \left[1 + 2\cosh(\beta g_S\mu_B B)\right]^N \qquad (1) \end{aligned}$$

Magnetization in any microstate is given just by the sum of the magnetic moments of all spins, $M(m_1, m_2...m_N) = -g_S\mu_B(m_1 + m_2 + m_3... + m_N)$. Average magnetization can be calculated by taking the ensemble average of this quantity:

$$\langle M\rangle = \frac{1}{Z}\sum_{m_1=-1}^{+1}\cdots\sum_{m_N=-1}^{+1} M(m_1, m_2...m_N)e^{-\beta BM(m_1,m_2...m_N)}$$

The partition function can also be written in terms of magnetization as

$$Z = \sum_{m_1=-1}^{+1}\cdots\sum_{m_N=-1}^{+1} e^{-\beta BM(m_1,m_2...m_N)}$$

It should be noticed that the sum in the above equation can also be obtained by taking a derivative of Z with respect to B, and multiplying with $-1/\beta$:

$$\begin{aligned} \langle M\rangle &= \frac{1}{Z}\left(-\frac{1}{\beta}\right)\frac{\partial}{\partial B}\sum_{m_1=-1}^{+1}\cdots\sum_{m_N=-1}^{+1} e^{-\beta BM(m_1,m_2...m_N)} \\ &= -\frac{1}{\beta}\frac{\partial \log Z}{\partial B} \qquad (2) \end{aligned}$$

Plugging the expression for Z from (1) in the above equation, we get

$$\langle M\rangle = -\frac{2Ng_S\mu_B\sinh(\beta g_S\mu_B B)}{1 + 2\cosh(\beta g_S\mu_B B)} \qquad (3)$$

2. **Problem:** Let there be quantum mechanical rotator with a Hamiltonian $\hat{H} = \frac{\hat{L}^2}{2I}$. Assuming that the rotator can take only two angular momentum values $l = 0$ and $l = 1$, calculate the average energy in canonical ensemble.
Solution: Eigenvalues of the Hamiltonian can be obtained by using the simultaneous eigenstates of $\hat{L}^2$ and $\hat{L}_z$, which are denoted by $|lm\rangle$. These states are also eigenstates of $\hat{H}$,
$$\hat{H}|lm\rangle = \frac{\hbar^2 l(l+1)}{2I}|lm\rangle$$
There are $2l+1$ values of m corresponding to each value of l. Eigenvalues do not depend on m, and hence energy-levels are $(2l+1)$-fold degenerate. The partition function can thus be written as
$$\begin{aligned} Z =& \sum_{l=0}^{1}(2l+1)\exp\left(\frac{-\beta\hbar^2 l(l+1)}{2I}\right) \\ =& 1 + 3\exp(-\beta\hbar^2/I) \end{aligned} \tag{4}$$
Average energy is given by
$$\begin{aligned} \langle E\rangle =& -\frac{\partial \log Z}{\partial\beta} \\ =& -\frac{\partial}{\partial\beta}\log(1+3\exp(-\beta\hbar^2/I)) \\ =& \frac{(3\hbar^2/I)\exp(-\beta\hbar^2/I)}{1+3\exp(-\beta\hbar^2/I)} \\ =& \frac{3\hbar^2/I}{\exp(\beta\hbar^2/I)+3} \end{aligned} \tag{5}$$

3. **Problem:** An ideal gas of N spinless atoms occupies a volume V at temperature T. Each atom has only two energy levels separated by an energy Δ. Find the chemical potential, free energy, average energy.
Let the two energy levels have energy ϵ_1 and ϵ_2, with $\epsilon_2 - \epsilon_1 = \Delta$. For one particle, the partition function can be written as $Z = e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}$. The atoms being, non-interacting, one can write the partition function for N particles as
$$Z = \left(e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}\right)^N$$
Helmholtz free energy is given by
$$F = -kT\log Z = -NkT\log\left(e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}\right)$$
The chemical potential is given by
$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\log\left(e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}\right)$$
Average energy is given by
$$\langle E\rangle = -\frac{\partial \log Z}{\partial\beta} = \frac{\epsilon_1 e^{-\beta\epsilon_1} + \epsilon_2 e^{-\beta\epsilon_2}}{(e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2})} = \frac{\epsilon_1 + \epsilon_2 e^{-\beta\Delta}}{(1+e^{-\beta\Delta})}$$

4. **Problem:** A simple harmonic one-dimensional oscillator has energy levels $E_n = (n + 1/2)\hbar\omega$, where ω is the characteristic oscillator (angular) frequency and $n = 0, 1, 2, \ldots$
   (a) Suppose the oscillator is in thermal contact with a heat reservoir kT at temperature T. Find the mean energy of the oscillator as a function of the temperature T, for the cases $\frac{kT}{\hbar\omega} \ll 1$ and $\frac{kT}{\hbar\omega} \gg 1$
   (b) For a two-dimensional oscillator, $n = n_x + n_y$, where $E_{n_x} = (n_x + 1/2)\hbar\omega_x$ and $E_{n_y} = (n_y + 1/2)\hbar\omega_y$, $n_x = 0, 1, 2, \ldots$ and $n_y = 0, 1, 2, \ldots$, what is the partition function for this case for any value of temperature? Reduce it to the degenerate case $\omega_x = \omega_y$.

   Answer (a): The partition function can be written as

$$Z = \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega} = e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega}$$
$$= e^{-\beta\hbar\omega/2} \frac{1}{1 - e^{-\beta\hbar\omega}} = \frac{1}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}} = \frac{1}{2\sinh(\beta\hbar\omega/2)}$$

The average energy can now be easily calculated

$$\langle E \rangle = -\frac{\partial \log Z}{\partial \beta} = \frac{\hbar\omega}{2} \coth(\beta\hbar\omega/2) \tag{6}$$

For $\beta\hbar\omega \ll 1$, which is the high-temperature limit, $\coth(\beta\hbar\omega/2) \approx 2/\beta\hbar\omega$. The average energy takes the form $\langle E \rangle \approx kT$. For $\beta\hbar\omega \gg 1$, which is the very-low-temperature limit, $\coth(\beta\hbar\omega/2) \approx 1$. The average energy takes the form $\langle E \rangle \approx \frac{\hbar\omega}{2}$, which is precisely the zero-point energy of the oscillator.

Answer (b): The partition function can be written as

$$Z = \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} e^{-\beta(n_x+1/2)\hbar\omega_x - \beta(n_y+1/2)\hbar\omega_y}$$
$$= \sum_{n_x=0}^{\infty} e^{-\beta(n_x+1/2)\hbar\omega_x} \sum_{n_y=0}^{\infty} e^{-\beta(n_y+1/2)\hbar\omega_y}$$
$$= \frac{1}{4\sinh(\beta\hbar\omega_x/2)\sinh(\beta\hbar\omega_y/2)}$$

When $\omega_x = \omega_y = \omega$, the above relation reduces to

$$Z = \frac{1}{4\sinh^2(\beta\hbar\omega/2)}$$

This is exactly the same as the partition function of two independent, similar, one-dimensional harmonic oscillators.