Statistical Mechanics: Problems 6.1

1. **Problem:** A particle is confined to a 1-dimensional harmonic oscillator potential $V(x) = \frac{1}{2}Kx^2$. Evaluate the canonical partition function of the oscillator, and find the average of displacement squared, $\langle x^2\rangle$.
Solution: Energy of the Hamonic oscillator is given by

$$E = \frac{p^2}{2m} + \tfrac{1}{2}Kx^2$$

Partition function is written as

$$\begin{aligned}
Z =& \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp e^{-\beta E} \\
=& \int_{-\infty}^{\infty} e^{-\beta\frac{1}{2}Kx^2} dx \int_{-\infty}^{\infty} e^{-\frac{\beta p^2}{2m}} dp \\
=& \sqrt{\frac{2\pi}{\beta K}}\sqrt{\frac{2m\pi}{\beta}} \\
=& \frac{2\pi}{\beta}\sqrt{\frac{m}{K}}
\end{aligned}$$

Average of displacement squared,

$$\begin{aligned}
\langle x^2\rangle =& \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} x^2 \frac{e^{-\beta E}}{Z} dx dp \\
=& \frac{1}{Z}\int_{-\infty}^{\infty} x^2 e^{-\beta\frac{1}{2}Kx^2} dx \int_{-\infty}^{\infty} e^{-\frac{\beta p^2}{2m}} dp \\
=& \frac{1}{Z}\left(\frac{-2}{\beta}\right)\frac{\partial}{\partial K}\int_{-\infty}^{\infty} e^{-\beta\frac{1}{2}Kx^2} dx \int_{-\infty}^{\infty} e^{-\frac{\beta p^2}{2m}} dp \\
=& \left(\frac{-2}{\beta}\right)\frac{1}{Z}\frac{\partial}{\partial K} Z = \left(\frac{-2}{\beta}\right)\frac{\partial \log Z}{\partial K} \\
=& \frac{1}{\beta K}
\end{aligned}$$

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

$$\begin{aligned}
Z =& \sum_{l=0}^{1}(2l+1)\exp\left(\frac{-\beta\hbar^2 l(l+1)}{2I}\right) \\
=& 1 + 3\exp(-\beta\hbar^2/I) \qquad (1)
\end{aligned}$$

Average energy is given by

$$\begin{aligned}\langle E\rangle &= -\frac{\partial \log Z}{\partial \beta} \\ &= -\frac{\partial}{\partial \beta}\log(1+3\exp(-\beta\hbar^2/I)) \\ &= \frac{(3\hbar^2/I)\exp(-\beta\hbar^2/I)}{1+3\exp(-\beta\hbar^2/I)} \\ &= \frac{3\hbar^2/I}{\exp(\beta\hbar^2/I)+3} \end{aligned} \tag{2}$$

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.
Solution: 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

$$\langle E\rangle = -\frac{\partial \log Z}{\partial \beta} = \frac{\epsilon_1 e^{-\beta\epsilon_1} + \epsilon_2 e^{-\beta\epsilon_2}}{\left(e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}\right)} = \frac{\epsilon_1 + \epsilon_2 e^{-\beta\Delta}}{\left(1+e^{-\beta\Delta}\right)}$$

4. **Question:** 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 $\omega_x = \omega_y$.

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

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

The average energy can now be easily calculated

$$\langle E\rangle = -\frac{\partial \log Z}{\partial\beta} = \frac{\hbar\omega}{2}\coth(\beta\hbar\omega/2) \tag{3}$$

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.
Solution (b): The partition function can be written as

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

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.

5. **Question:** Consider a classical ideal gas in a box in three dimensions. Derive the Maxwell-Boltzmann distribution of velocity using canonical ensemble.

Solution: We know that the density function in canonical ensemble is given by

$$\rho(p,q) = \frac{e^{-E(p,q)/kT}}{\frac{1}{\Delta}\int dpdq e^{-E(p,q)/kT}} = \frac{e^{-E(p,q)/kT}}{Z}, \tag{4}$$

where the partition function is given by

$$Z = \frac{1}{\Delta}\int e^{-E(p,q)/kT} dpdq. \tag{5}$$

Here we have N gas atoms moving in 3-dimensions. Since the atoms are non-interacting, let us consider a single atoms in 3-dimensions. Energy of the atom is given by

$$E = \frac{p_{xi}^2}{2m} + \frac{p_{yi}^2}{2m} + \frac{p_{zi}^2}{2m} \tag{6}$$

The partition is function has already been calculated as

$$Z = \frac{1}{\hbar^{3N}}\int e^{-\beta E} dp_{xi}dp_{yi}dp_{zi}dx_i dy_i dz_i = \frac{1}{\hbar^3} V\left(\frac{2m\pi}{\beta}\right)^{3/2} \tag{7}$$

Probability of the atom to have a velocity $\vec{v}$, and hence momentum $\vec{p} = m\vec{v}$, is given by

$$\tilde{P}(\vec{p})d^3\vec{p} = \int dxdydx\rho(p,q)d^3\vec{p} = \frac{1}{Z}Vd^3\vec{p}e^{-\beta\vec{p}^2/2m}, \tag{8}$$

where $\tilde{P}(\vec{p})$ probability density for the atom to have a momentum $\vec{p}$, and the integral is only over space. We can write the above in terms of the absolute momentum p (irrespective of the direction), as

$$P(p)dp = p^2dp\int d\theta_p d\phi_p \tilde{P}(\vec{p}) = \frac{1}{Z}\frac{V}{\hbar^3}4\pi p^2dpe^{-\beta p^2/2m}, \tag{9}$$

where we have used spherical polar coordinates in momentum space, giving $\int d^3\vec{p} = \int p^2dpd\theta_p d\phi_p$. Substituting the expression for Z in the above, we get

$$P(p)dp = \left(\frac{\beta}{2m\pi}\right)^{3/2} 4\pi p^2dpe^{-\beta p^2/2m} \tag{10}$$

Probability of an atom to have an absolute velocity v (speed) can now be obtained by simply replacing p by mv in above equation, to get

$$P(v)dv = P(p)dp = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2e^{-mv^2/2kT}dv, \tag{11}$$

which is the required Maxwell-Boltzmann distribution of velocities.