1. Consider a system of two noninteracting particles. Each particle may occupy one of two energy levels, $E_0 = 0$ and $E_1 = \varepsilon$.

   (a) Assume the particles are *distinguishable*. Determine the number of available configurations, then using direct enumeration, write down the partition function.

   $2 \times 2 = 4$ configurations

$$Q = \sum_i e^{-\beta E_i}$$
$$= e^{-\beta(0+0)} + e^{-\beta(0+\varepsilon)} + e^{-\beta(\varepsilon+0)} + e^{-\beta(\varepsilon+\varepsilon)}$$
$$= \boxed{1 + 2e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}}$$

   (b) Now assume the particles are *indistinguishable*. Determine the number of available configurations, then using direct enumeration, write down the partition function.

   2 particles, 1 bar, $\binom{3}{1} = 3$ configurations

$$Q = \sum_i e^{-\beta E_i}$$
$$= e^{-\beta \cdot 0} + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}$$
$$= \boxed{1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}}$$

2. A bare proton in a magnetic field B_z has energy $E_{\pm\frac{1}{2}} = \mp\frac{1}{2}\hbar\gamma B_z$, where γ is the gyromagnetic ratio. Show that the partition function can be written as $Q(\beta, B_z) = 2\cosh\left(\frac{\beta\hbar\gamma B_z}{2}\right)$, where $\cosh(x) = \frac{e^x + e^{-x}}{2}$

$$Q(\beta, B_z) = \sum_i e^{-\beta E_i}$$
$$= e^{-\beta(-\frac{1}{2}\hbar\gamma B_z)} + e^{-\beta(+\frac{1}{2}\hbar\gamma B_z)}$$
$$= e^{\frac{\beta\hbar\gamma B_z}{2}} + e^{-\frac{\beta\hbar\gamma B_z}{2}}$$
$$= 2 \cdot \frac{e^{\frac{\beta\hbar\gamma B_z}{2}} + e^{-\frac{\beta\hbar\gamma B_z}{2}}}{2}$$
$$= \boxed{2\ \cosh\left(\frac{\beta\hbar\gamma B_z}{2}\right)}$$

3. Consider a system at temperature $T = 298$ K with three energy states $E = 0, 100, 500\ \frac{\text{J}}{\text{mol}}$. Using the Boltzmann distribution:

(a) Evaluate the partition function Q

$$k_B T = (1.3806 \times 10^{-23}\ \text{J K}^{-1})(298\ \text{K}) = 4.11 \times 10^{-21}\ \text{J}$$

These units don't line up, we have energy in $\frac{\text{J}}{\text{mol}}$ so we need to convert $k_B T$ (remember exponentials are unitless) to $\frac{\text{J}}{\text{mol}}$ using N_A

$$k_B T \cdot N_A = (4.11 \times 10^{-21}\ \text{J})(6.022 \times 10^{23}\ \text{mol}^{-1}) = 2477\ \frac{\text{J}}{\text{mol}}$$

$$\begin{aligned} Q &= \sum_i e^{-E_i/(k_B T)} \\ &= 1 + e^{-100/2477} + e^{-500/2477} \\ &= 1 + 0.9604 + 0.8171 \\ &= 2.7775 \end{aligned}$$

A range of answers (±10%) would be accepted due to rounding

(b) What is the probability of occupying the highest energy level at 298 K?

The probability of a state is given by

$$P_i = \frac{e^{-E_i/(k_B T)}}{Q} \rightarrow P_{500} = \frac{e^{-500/2477}}{2.7775}$$

$$P_{500} = \boxed{0.294}$$

(c) What is the average energy at 298 K?

The average energy is given by:

$$\langle E \rangle = \sum_i E_i P_i$$

Evaluating the probabilities:

$$P_0 = \frac{e^{-0/2477}}{2.7775} = 0.360 \qquad P_{100} = \frac{e^{-100/2477}}{2.7775} = 0.346 \qquad P_{500} = 0.294$$

Substituting in the energies we get:

$$\begin{aligned} \langle E \rangle &= (0\ \frac{\text{J}}{\text{mol}})(0.360) + (100\ \frac{\text{J}}{\text{mol}})(0.346) + (500\ \frac{\text{J}}{\text{mol}})(0.294) \\ &= 181.6\ \frac{\text{J}}{\text{mol}} \end{aligned}$$

Homework Problem 3

1. A system has four energy levels given by:

$$\tilde{E}_0 = 0 \qquad \tilde{E}_1 = 25 \text{ cm}^{-1} \qquad \tilde{E}_2 = 50 \text{ cm}^{-1} \qquad \tilde{E}_3 = 100 \text{ cm}^{-1}$$

   Calculate the probability of being in an excited state at 300K. Use $k_B = 0.695 \frac{\text{cm}^{-1}}{\text{K}}$