Name and section: _____

$$U(S, V, N) = TS - pV + \mu N$$
$$S(U, V, N) = \frac{U}{T} + \frac{p}{T}V - \frac{\mu}{T}N$$
$$F(V, T, N) = U - TS$$
$$G(p, T, N) = U + pV - TS$$
$$H(S, p, N) = U + pV$$

1. Derive the Boltzmann law of probabilities $p_j^*$ by maximizing the entropy $S$ at constant $U = \langle E \rangle$ (this was done in class) and also by minimizing the free energy $F$ at constant $T$. These should give you the same optimized probability distributions. Starting with the following constraint equation should help:

$$dF = \sum_{j=1}^{t} \left[ E_j + k_B T \left( 1 + \ln p_j^* \right) + \alpha \right] dp_j^* = 0 \tag{1}$$

**Solution:** For eq. (1) to be true for any $dp_j^*$, the following must be true:

$$0 = E_j + k_B T \left( 1 + \ln p_j^* \right) + \alpha$$
$$p_j^* = e^{-\beta(E_j + \alpha) - 1}$$

Then we can use the normalization condition $\sum_j p_j^* = 1$, to remove the $\alpha$ dependence.

$$p_j^* = \frac{e^{-\beta\alpha - 1} e^{-\beta E_j}}{e^{-\beta\alpha - 1} \sum_j e^{-\beta E_j}}$$

$$\boxed{p_j^* = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}}$$

which is the familiar Boltzmann law as also derived in class by maximizing the entropy.

2. When calculating thermodynamic properties of molecules, why can we generally ignore the electronically excited states?

**Solution:** Electronically excited states are generally so high in energy relative to $k_B T$ that their occupancies are room temperature are so small as to be negligible. See lecture notes or question six on assignment 3 for examples.

3. Diatomic ideal gases at $T = 300\,\mathrm{K}$ have rotational partition functions of approximately $q = 200$. At what temperature would $q$ become small (say $q < 10$) so that the quantum effects become important?

> **Solution:**
>
> $$q_{\mathrm{rot}} = \frac{8\pi^2 I k_B T}{\sigma h^2} = 200$$
>
> $$\Downarrow$$
>
> $$q_{\mathrm{rot}} = \frac{2}{3}T$$
> $$10 = \frac{2}{3}T$$
> $$T = 15\,\mathrm{K}$$

4. Consider a protein of diameter $40\,\text{Å}$ trapped in the pore of a chromatography column. The pore is a cubic box with sides of length $100\,\text{Å}$. The protein mass is $10 \times 10^4\,\mathrm{g\,mol^{-1}}$. Assume the box is otherwise empty and $T = 300\,\mathrm{K}$.

   (a) Compute the translational partition function. Are quantum effects important?

   > **Solution:**
   >
   > $$q_{\mathrm{t}} = \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} V$$
   >
   > $$= \left(\frac{2\pi \left(10 \times 10^4\,\mathrm{g\,mol^{-1}}\right)\left(1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}\right)\left(300\,\mathrm{K}\right)}{\left(6.63 \times 10^{-34}\,\mathrm{J\,s}\right)^2}\right)^{\frac{3}{2}} \left(60\,\text{Å}\right)^3$$
   >
   > and after fixing the units,
   >
   > $$q_{\mathrm{t}} = 6.65 \times 10^{12}$$
   >
   > With such a large number of states, quantum effects should not be important.

   (b) If you deuterated all the hydrogens in the protein and increase the protein mass by 10%, does the free energy increase or decrease?

   > **Solution:** Increasing the mass will increase $q_{\mathrm{t}}$, increasing the entropy. Deuteration should have negligible effects on the electronic states and therefore the enthalpic contributions should not change. Therefore, the free energy will decrease and the protein will be more stable in the pore. (Heavier things are less likely to move.)

(c) By how much does the free energy change?

> **Solution:**
>
> $$\Delta F = -k_B T \ln \frac{Q_1}{Q_2}$$
> $$= -\frac{3}{2} N k_B T \ln 1.1$$
> $$\frac{\Delta F}{N} = 5.923 \times 10^{-22}\,\text{J}$$
> $$\frac{\Delta F}{n} = 85.3\,\text{cal mol}^{-1} = 0.0853\,\text{kcal mol}^{-1}$$
>
> This can obviously be converted to many different units, but this is not much energy. A typical hydrogen bond contributes $1\text{-}5\,\text{kcal mol}^{-1}$, so this mass difference is likely inconsequential compared to interactions between the protein and the column.

5. An electron moving through the lattice of a semiconductor has less inertia than when it is in a gas. Assume that the effective mass of the electron is only 10% of its actual mass at rest. Calculate the translational partition function of the electron at temperature $T = 273\,\text{K}$ in a semiconductor particle of a cubic shape with a side of

    (a) $1\,\text{mm}$

    > **Solution:**
    >
    > $$q_{\text{t}} = V \left( \frac{2\pi m}{\beta h^2} \right)^{3/2}$$
    >
    > where $m = 0.1\, m_{\text{e}}$
    >
    > $$q_{\text{t}} = 3.45 \times 10^{14}$$

    (b) $100\,\text{Å}$

    > **Solution:**
    >
    > $$q_{\text{t}} = 3.45 \times 10^{-7}$$

    (c) To which particle would the term 'quantum dot' (i.e., a system with quantum mechanical behavior) be applied and why?

    > **Solution:** In the smaller particle, the partition function is very small, meaning very few levels will be thermally accessible. Because of the relative level spacing for the

> small particle, quantum mechanical properties will play a very important role in this 'quantum dot'.

6. Heat capacity

   (a) When will the heat capacity of a two level system be maximized?

   > **Solution:** The heat capacity for a two level system is at a maximum when both sites are equally populated.

   (b) When will the constant-volume heat capacity $C_V = \left( \frac{\partial U}{\partial T} \right)_V$ of some molecule be maximized?

   > **Solution:** Heat capacity is maximized when in the middle of some sort of transition (electronic, vibrational, rotational, translational, etc.). This generally means heat capacities are maximized at phase transitions.

7. A gas is placed in an air-tight container. A piston decreases the volume by 10% in an adiabatic process, and the temperature is observed to increase by 10%. What is the constant volume heat capacity of the gas?

   > **Solution:** Assuming the gas behaves ideally ($C_V$ constant in this process and $pV = nRT$),
   > $$\begin{aligned} \mathrm{d}U &= \delta q + \delta w \\ &= \delta w \\ &= -p\,\mathrm{d}V \\ &= -\frac{Nk_B T}{V}\,\mathrm{d}V \\ \frac{1}{T}\frac{\partial U}{\partial T}\,\mathrm{d}T &= -\frac{Nk_B}{V}\,\mathrm{d}V \\ C_V \int_{T_0}^{1.1T_0} \frac{1}{T}\,\mathrm{d}T &= -Nk_B \int_{V_0}^{0.9V_0} \frac{1}{V}\,\mathrm{d}V \\ C_V \ln 1.1 &= -Nk_B \ln 0.9 \\ C_V &\approx 1.1 Nk_B \end{aligned}$$