Discussion 11

Name and section: ________________________________________

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

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:

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

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

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?

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?

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

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

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 $T = 273\,\mathrm{K}$ in a semiconductor particle of a cubic shape with a side of

   (a) 1 mm

   (b) 100 Å

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

6. Heat capacity

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

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

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?