PChem Pset #2

1a. $Q = \frac{1}{N!}\left(\frac{V}{\Lambda^3(T)}\right)^N$

$4^?$

$\ln Q = \ln\left(\frac{1}{N!}\left(\frac{V}{\Lambda^3(T)}\right)^N\right)$

$= \ln\left(\frac{1}{N!}\right) + N\left(\ln V - \ln \Lambda^3(T)\right)$

$= \ln\left(\frac{1}{N!}\right) + N\left(\ln V - \ln\left(\left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{3}{2}}\right)\right)$

$\ln Q = \ln\left(\frac{1}{N!}\right) + N\underbrace{\left(\ln V - \frac{3}{2}\left(2\ln(h)\right.\right.}_{0 \text{ bc no } T \text{ dependance}}\left.\left. - \ln(2\pi m k_B T)\right)\right)$

b. $\frac{3N}{2}\ln(2\pi m k_B T)$

↓ chain rule

$\frac{3N}{\cancel{2}} \cdot \frac{\cancel{2\pi m k_B}}{\cancel{2\pi m k_B}\, T}$

$\frac{\partial \ln Q}{\partial T} = \frac{3N}{2T}$

c. $\frac{\partial \ln Q}{\partial V} = \frac{N}{V}$ * $N\ln V$ was the only term w/ V dependance

d. $P = k_B T\left(\frac{\partial \ln Q}{\partial V}\right) = \frac{k_B T N}{V}$ ✓

$U = k_B T^2\left(\frac{\partial \ln Q}{\partial T}\right) = k_B T^2\left(\frac{3N}{2T}\right) = \frac{3}{2} N k_B T$ ✓

$\frac{-1}{T^2}$

1, Pt.2, a $\quad T^{\frac{3}{2}} \exp\left(\frac{-\Delta}{k_B T}\right)$

product rule

$T^{\frac{3}{2}} \cdot \frac{\Delta}{k_B T^2} \exp\left(\frac{-\Delta}{k_B T}\right) + \frac{3}{2} T^{\frac{1}{2}} \exp\left(\frac{-\Delta}{k_B T}\right)$

chain rule

$\frac{\Delta}{k_B T^{\frac{1}{2}}} \exp\left(\frac{-\Delta}{k_B T}\right) + \frac{3}{2} T^{\frac{1}{2}} \exp\left(\frac{-\Delta}{k_B T}\right)$

$\frac{df}{dT} = \exp\left(\frac{-\Delta}{k_B T}\right)\left(\frac{\Delta}{k_B T^{\frac{1}{2}}} + \frac{3}{2} T^{\frac{1}{2}}\right)$

1, Pt.2, ii $\quad \frac{d}{dT} \ln f(T) = \frac{f'(T)}{f(T)}$

$= \frac{\exp\left(\frac{-\Delta}{k_B T}\right)\left(\frac{\Delta}{k_B T^{\frac{1}{2}}} + \frac{3}{2} T^{\frac{1}{2}}\right)}{T^{\frac{3}{2}} \exp\left(\frac{-\Delta}{k_B T}\right)}$

$= \frac{\frac{\Delta}{k_B T^{\frac{1}{2}}} + \frac{3}{2} T^{\frac{1}{2}}}{T^{\frac{3}{2}}}$

$= \frac{\Delta}{k_B T^{\frac{1}{2}}} \cdot T^{-\frac{3}{2}} + \frac{3}{2} T^{\frac{1}{2}} \cdot T^{-\frac{3}{2}}$

$= \frac{\Delta}{k_B T^2} + \frac{3}{2T}$

2a i. $E_f = \frac{3}{2} N k_B T_f$

$E_i = \frac{3}{2} N k_B T_i$

$\Delta E_{sys} = E_f - E_i = \frac{3}{2} N k_B T_f - \frac{3}{2} N k_B T_i$

$\Delta E_{sy} = \frac{3}{2} N_{sys} k_B (T_{f_{sys}} - T_{i_{sys}})$

ii. $\Delta E_{sys} = -\Delta E_{env}$

$\frac{3}{2} N_{sys} k_B \Delta T_{sys} = -\frac{3}{2} N_{env} k_B \Delta T_{env}$

$-\frac{N_{sys}}{N_{env}} \Delta T_{sys} = \Delta T_{env}$

2b. $\frac{N_{sys}}{N_{env}} \Delta T_{sys} \geq 0.1$

$\frac{N_{sys}}{N_{env}} \geq \frac{0.1}{\Delta T_{sys}}$

$\frac{N_{env}}{N_{sys}} \geq \frac{\Delta T_{sys}}{0.1}$

For $\Delta T_{sys} = 100K$

$\frac{N_{env}}{N_{sys}} \geq \frac{100}{0.1} = 1000$

$$P = \frac{g_i \cdot Q_i^{-5}}{Q_{total}}$$

2c. Based on the results from 2b, if the environment has 1000x # particles as the system, the environment will experience 1000x less of a temperature change. As the environment becomes even larger, it will experience even less of a temperature change. Therefore, boiling pasta in a large volume of water will lead to $\approx$ constant temperature because $N_{water} >> N_{pasta}$

3a. $Q = 5$ * Plots at the end of PDF

$P_m = 1$

The number of thermally accessible microstates does not depend on temperature

b. $Q = 3 + 2e^{-\Delta/k_B T}$

At low T, only the three lower energy states w/ energy $E = 0$ are accessible. As temperature increases, the two higher energy states become more accessible, reaching a max probability at 0.37 at 1000K, => # of thermally accessible microstates increases w/ T

3c. $Q = 2 + \exp(-\beta\Delta_1) + \exp(-\beta(\Delta_1+\Delta_2)) + \exp(\beta(\Delta_1+\Delta_2+\Delta_3))$

At low T, only the lowest-energy states are the only accessible state. The probability of the lowest-energy states quickly drops off as T increases and the other three microstates become accessable. The microstates become accessible in the order of E_2, E_3, E_4. At all T, E_1 is the most probable state =>.

4a. $\ln Q = \ln(\frac{1}{N!}) + N(\ln(V-Nb) - \frac{3}{2}(2\ln(h) - \ln(2\pi m k_B T))) + \frac{N^2 a}{V k_B T}$

$$\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = \frac{3N \cdot 2\pi m k_B}{2\pi m k_B T} - \frac{N^2 a}{V k_B T^2}$$

$$= \frac{3N}{2T} - \frac{N^2 a}{V k_B T^2}$$

$$\Rightarrow U = \frac{3}{2} N k_B T - \frac{N^2 a}{V}$$

b. $\left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} N k_B$

c. $P = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{T,N}$

$$N \ln(V - nb) + \frac{N^2 a}{V k_B T}$$

$$\left(\frac{\partial \ln Q}{\partial V} \right)_{T,N} = \frac{N}{V - nb} - \frac{N^2 a}{V^2 k_B T}$$

$$P = \frac{k_B T N}{V - nb} - \frac{\cancel{k_B T} N^2 a}{V^2 \cancel{k_B T}}$$

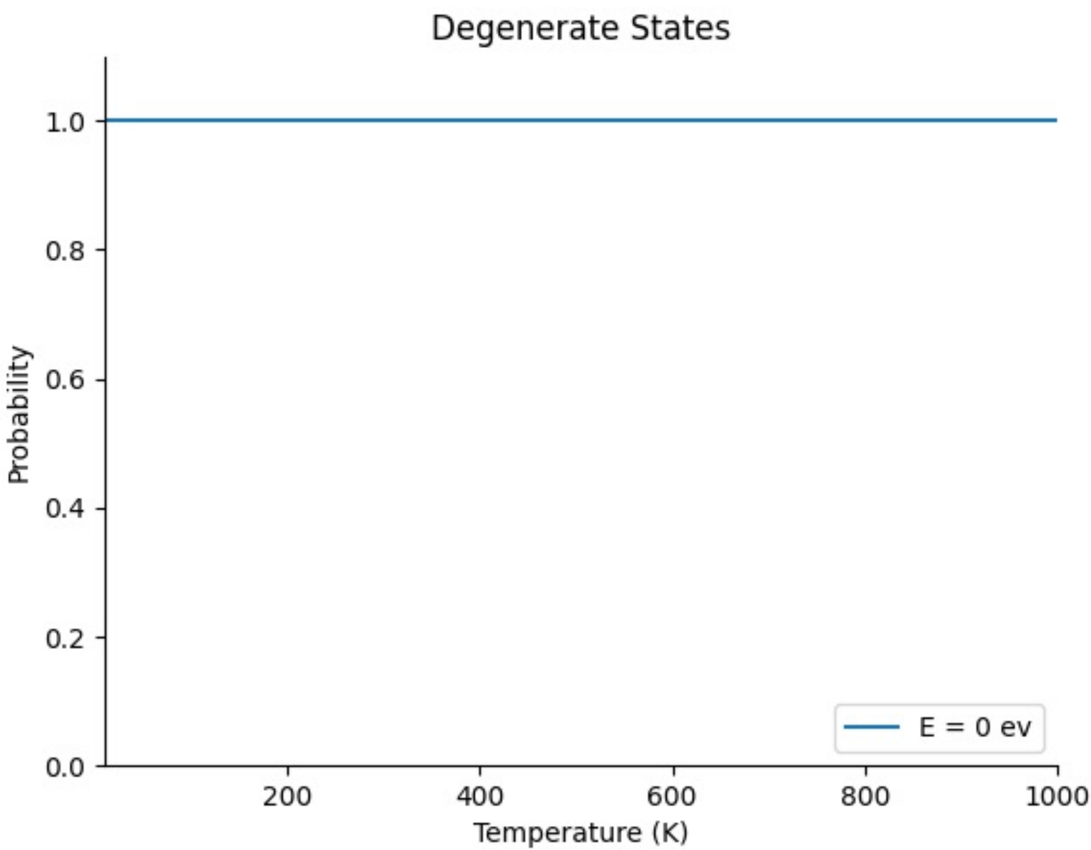
$$P = \frac{N k_B T}{V - Nb} - \frac{N^2 a}{V^2}$$

5a. Done in python, screenshots appended to this pdf file

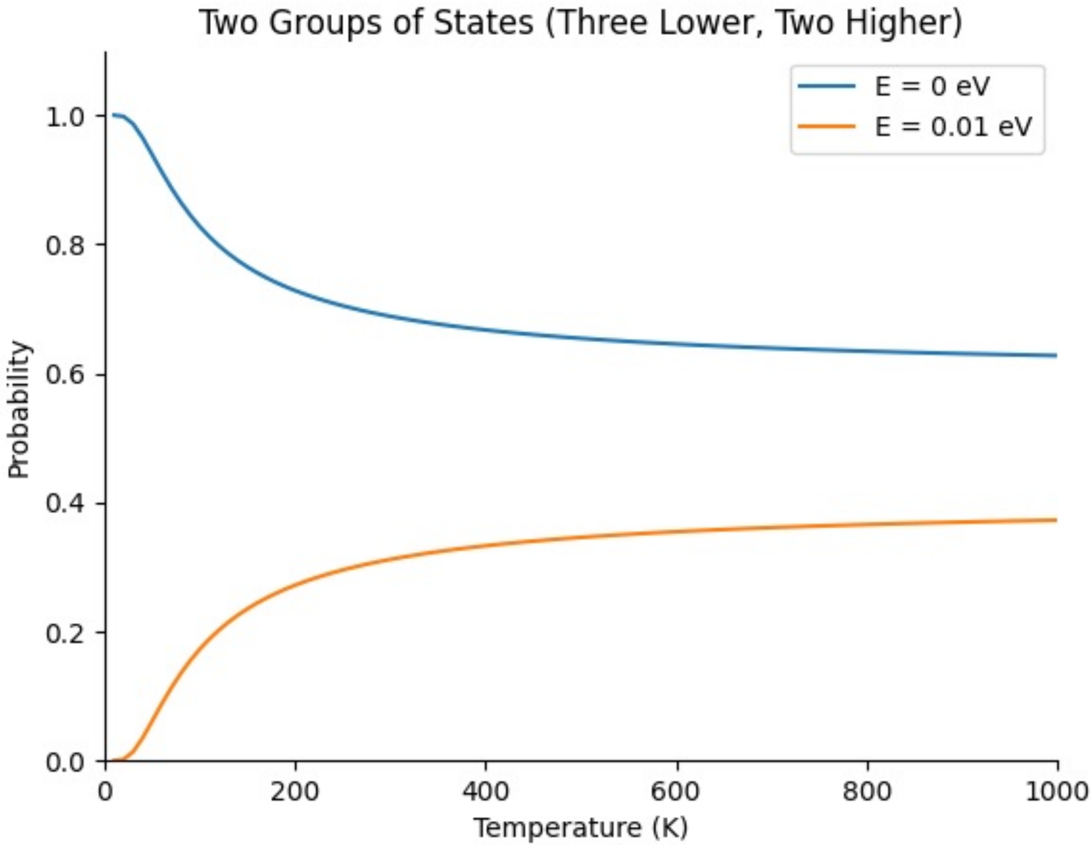
b. i. At $T = 300K$, $P = 1$ bar, the $\frac{\lambda}{d}$ % are all 1.5 % or lower, meaning the interparticle distance is much larger than the de Broglie λ, suggesting that quantum effects are not significant.

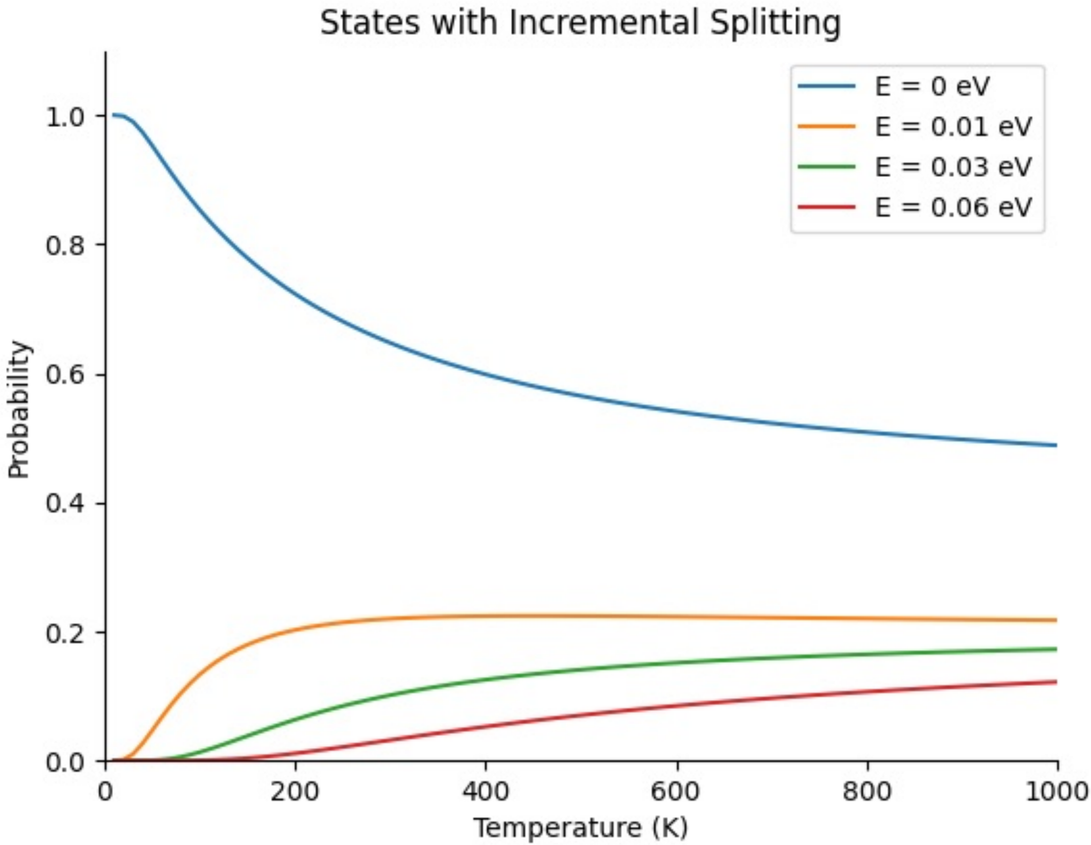
At $T = 300K$, $P = 100$ bar, the $\frac{\lambda}{d}$ % is larger than at $P = 1$ bar for all elements. However, the interparticle distances are still much larger than the de Broglie wavelength, suggesting that quantum effects are not significant.

At $T = 3K$, $P = 100$ bar, the minimum $\frac{\lambda}{d}$ % is 54% and the maximum is 317%, which means the de Broglie wavelength is comparable to the average interparticle distance if not much larger, suggesting that quantum effects are significant.



Degenerate States
Probability
1.0
0.8
0.6
0.4
0.2
0.0
200
400
600
800
1000
Temperature (K)
E = 0 ev


Two Groups of States (Three Lower, Two Higher)
E = 0 eV
E = 0.01 eV
Probability
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
Temperature (K)


States with Incremental Splitting
E = 0 eV
E = 0.01 eV
E = 0.03 eV
E = 0.06 eV
Probability
0.0
0.2
0.4
0.6
0.8
1.0
0
200
400
600
800
1000
Temperature (K)