Dylan Sheehan's Solutions to the 3rd Pset written in $\LaTeX$

1. The average value of any measurable quantity, A, is given by:

$$<A> = \frac{1}{Q}\sum_{j=1}^{max} g_j A_j \exp\left(-\frac{E_j}{k_B T}\right)$$

   We then derived :

$$\text{Where } Q = \sum_{j=1}^{max} g_j \exp\left(\frac{E_j}{k_B T}\right)$$

   For the average energy
   a. Use this function to relate $<E^2>$ to $\ln Q$ in terms of temperature derivatives.

$$<E^2> = \frac{1}{Q}\sum_{j=1}^{max} g_j E_j^2 e^{-E_j/k_B T}$$

$$<E> = \frac{1}{Q}\sum_{j=1}^{max} g_j E_j e^{-E_j/k_B T} = k_B T^2 \frac{\partial \ln Q}{\partial T}$$

$$\frac{d}{dT} e^{-E_j/k_B T} = \frac{E_j}{k_B T^2} e^{-E_j/k_B T}$$

$$\frac{d}{dT} \ln Q = \frac{1}{Q}\frac{dQ}{dT}$$

Try : $\frac{\partial^2 \ln Q}{\partial T^2}$

$$\frac{d^2}{dT^2}\ln Q = \frac{d}{dT}\left(\frac{d}{dT}\ln Q\right) = \frac{d}{dT}\left(\frac{1}{Q}\frac{dQ}{dT}\right)$$

$$\left(\frac{d}{dT}\frac{1}{Q}\right)\left(\frac{dQ}{dT}\right) + \frac{1}{Q}\frac{d^2Q}{dT^2}$$

$$\frac{1}{Q^2}\left(\frac{dQ}{dT}\right)\left(\frac{dQ}{dT}\right) + \frac{1}{Q}\frac{d^2Q}{dT^2}$$

$$-\left[\frac{1}{Q}\frac{dQ}{dT}\right]^2 + \frac{1}{Q}\frac{d^2Q}{dT^2}$$

$<E> = k_B T^2 \frac{1}{Q}\frac{\partial Q}{\partial T}$

$$\frac{d^2 \ln Q}{dT^2} = -\left(\frac{<E>}{k_B T^2}\right)^2 + \frac{1}{Q}\frac{d^2Q}{dT^2}$$

Now to solve for the right side term :

$$\frac{1}{Q}\frac{d^2}{dT^2} = \frac{1}{Q}\frac{d}{dT}\frac{dQ}{dT} = \frac{1}{Q}\frac{d}{dT}\left(\sum_j g_j \frac{d}{dT} e^{-E_j/k_B T}\right)$$

Solving :

$$\frac{1}{Q}\frac{d}{dT}\left(\sum g_j \frac{d}{dT} e^{E_j/k_BT}\right)$$

Solving the right most derivative is elementary, using a simple derivative property.

$$\frac{d}{dT} e^{E_J/k_BT} = \frac{E_j}{k_BT^2} e^{-E_j/k_BT}$$

This now leaves us in the form :

$$\frac{1}{Q}\frac{d^2Q}{dT^2} = \frac{1}{Q}\frac{d}{dT}\sum_{j=1}\left(g_j \frac{E_j}{k_BT^2} e^{-E_j/k_BT}\right)$$

We can now multiply to get rid of the $\frac{1}{Q}$ term.

$$\frac{d^2Q}{dT^2} = \frac{d}{dT}\sum_{j=1}\left(g_j \frac{E_j}{k_BT^2} e^{-E_j/k_BT}\right)$$

We can pull everything in the series out of the derivative that does not have a T component due to them not being impacted by a derivative term.

$$\frac{d^2Q}{dT^2} = \left(\sum_j g_j \frac{E_j}{k_B}\right)\frac{d}{dT}\left(\frac{e^{-E_j/k_BT}}{T^2}\right)$$

The right side can be solved with the chain rule

$$\frac{d}{dT}\left(e^{-E_j/k_BT}\cdot\frac{1}{T^2}\right)$$

$$-\frac{2e^{E_j/k_BT}}{T^3} + \frac{Ee^{-E_j/k_BT}}{k_BT^4}$$

The sum can then be distributed across these.

$$\frac{d^2Q}{dT^2} = -\frac{2}{k_BT^3}\sum e^{-E_j/k_BT} g_jE_j + \frac{1}{k_b^2T^4}\sum g_je^{-E_j/k_BT}E_j^2$$

$$\text{To solve for } \frac{1}{Q}\frac{\partial Q}{\partial T}$$

$$\frac{1}{Q}\frac{d^2Q}{dT^2} = -\frac{2}{k_BT^3}\cancelto{<E>}{\sum e^{-E_j/k_BT} g_jE_j} + \frac{1}{k_b^2T^4}\cancelto{<E^2>}{\sum g_je^{-E_j/k_BT}E_j^2}$$

We have finally found an $<E^2>$ term. Now everything is just about algebraic manipulation and moving stuff around.
So we can now pull back the original formula :

$$\frac{d^2\ln Q}{dT^2} = -\left(\frac{1}{k_BT^2<E>}\right)^2 - \frac{2}{k_BT^3}<E> + \frac{1}{k_B^2T^4}<E^2>$$

$$<E^2> = k_B^2T^4\left[\left\{\frac{d^2\ln Q}{dT^2}\right\} + \left\{\frac{1}{k_BT^2}<E>\right\}^2 + \frac{2}{k_BT^3}<E>\right]$$

Distributing :

$$\boxed{<E^2> = k_B^2 T^4 \left(\frac{d^2 \ln Q}{dT^2}\right) + <E>^2 + 2k_B T<E>}$$

b. Use your expression and the common formula for $<E>$ to determine an equation for the uncertainty in energy, $\Delta E = \sqrt{<E^2> - <E>^2}$.
This is just simple substitution :

$$\Delta E = \sqrt{k_B^2 T^4 \left(\frac{d^2 \ln Q}{dT^2}\right) + \cancel{<E>^2} + 2k_B T<E> - \cancel{<E>^2}}$$

$$\boxed{\Delta E = \sqrt{k_B^2 T^4 \left(\frac{d^2 \ln Q}{dT^2} + 2k_B T<E>\right)}}$$

2. The pressure of a gas can be defined in terms of the partition function by the expression :

$$P = -\left(\frac{\partial <\epsilon>}{\partial V}\right) = \sum_j \frac{g_j e^{-\epsilon_j/k_B T}}{q}\left(\frac{\partial \epsilon_j}{\partial V}\right) = k_B T\left(\frac{\partial \ln q}{\partial V}\right)$$

Determine the general formula for the "rotational pressure" of a diatomic gas using :

$$\epsilon_j = j(j+1)\frac{\hbar^2}{2\mu R^2}, j = 0, 1, 2, 3 \ldots$$

Where the degeneracy for this is $g_j = (2j+1)$ Recall that the volume of a sphere is : $V = \frac{4}{3}\pi R^3$

$$q = \sum (2j+1) e^{-j(j+1)\hbar^2/2\mu l^2 k_B T}$$

We have to make two substitutions for both q_j and ϵ_j
q_j substitution

$$\sum_{j=0}^{\infty} \frac{(2j+1)e^{-\epsilon_j/k_B T}}{q}\left(\frac{\partial \epsilon_j}{\partial V}\right)$$

ϵ_j substitution

$$\sum_{j=0}^{\infty} \frac{(2j+1)}{q} e^{-(j(j+1)\hbar^2/2\mu R^2 k_B T)}\left(\frac{\partial}{\partial V}\left(\frac{-j(j+1)\hbar^2}{2\mu R^2}\right)\right)$$

The R value is a distance, based on the hint we can assume this is therefor a radius of a sphere. Since we are integrating with respect to volume we have to equate radius to the volume of a sphere with the help of the hint.

$$V = \frac{4}{3}\pi R^3$$

$$R = \left(\frac{3V}{4\pi}\right)^{1/3}$$

$$R^2 = \left(\frac{3V}{4\pi}\right)^{2/3}$$

So we can rewrite the derivative :

$$\frac{\partial}{\partial V}\left(-\frac{j(j+1)\hbar^2}{2\mu R^2}\right) = \frac{\partial}{\partial V}\left(-\frac{j(j+1)\hbar^2}{2\mu(\frac{3V}{4\pi})^{2/3}}\right)$$

We can actually simplify this greatly because we are only deriving with respect to volume. So we can take out all constants.

$$-\left(\frac{4\pi}{3}\right)^{2/3}\left(\frac{j(j+1)\hbar^2}{2\mu}\right)\frac{\partial}{\partial V}V^{-2/3}$$

This is a much easier derivative and the entire term simplifies to :

$$\frac{2}{3}\left(\frac{4\pi}{3}\right)^{2/3}\left(\frac{j(j+1)\hbar^2}{2\mu}\right)V^{-5/3}$$

Now putting this solved derivative back into the original sum we are left with :

$$\frac{2}{3}\left(\frac{4\pi}{3}\right)^{2/3}V^{-5/3}\underbrace{\sum_{j=0}^{\infty}\frac{(2j+1)}{q}e^{-(j(j+1)\hbar^2/2\mu R^2 k_B T)}}_{<E>}\left(\frac{j(j+1)\hbar^2}{2\mu}\right)$$

So now we can write a simplified solution :

$$\boxed{\frac{2}{3}\left(\frac{4\pi}{3}\right)^{2/3}V^{-5/3}<E>\left(\frac{j(j+1)\hbar^2}{2\mu}\right)}$$

3. Consider an an-harmonic oscillator with quantized energy:
Where α is the an-harmonicity factor. The probability for being in a given state is given by the usual formula:

$$P_v = \frac{\exp\left(\frac{\epsilon_v}{k_B T}\right)}{Q} = \frac{\exp\left(\frac{\epsilon_v}{k_B T}\right)}{\sum_v \exp\left(\frac{\epsilon_v}{k_B T}\right)}$$

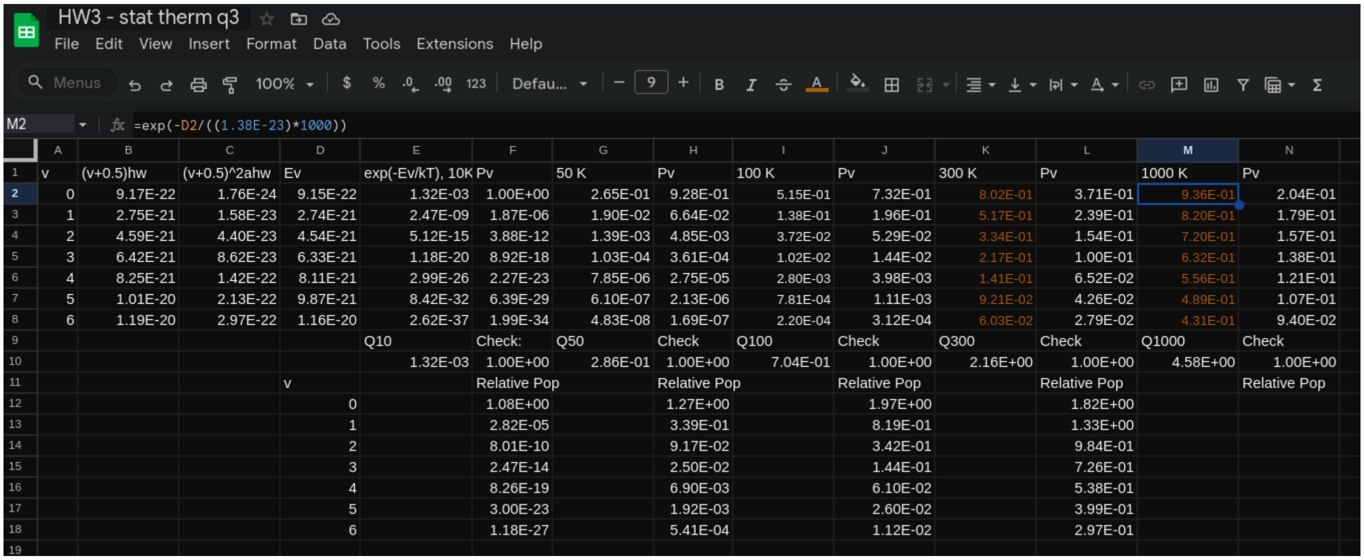
The values for ω and $\alpha\omega$ for the K_2 molecule are $92.3cm^{-1}$ and $0.354cm^{-1}$, respectively.
a.) Can you find a function that describes the partition function, q, using the techniques we employed in class?
We have to do some algebraic manipulation here :

$$Q = \frac{\exp\left(\frac{\epsilon_v}{k_B T}\right)}{P_v} = \frac{\frac{\exp\left(\frac{\epsilon_v}{k_B T}\right)}{\exp\left(\frac{\epsilon_v}{k_B T}\right)}}{\sum_v \exp\left(\frac{\epsilon_v}{k_B T}\right)}$$

$$\boxed{Q = \sum_v \exp\left(\frac{\epsilon_v}{k_B T}\right)}$$

Using a program to find the numerical value of the partition function ,q, defined using the $SUMMATION$ (i.e not your function from part a) at the following temperatures :
$T = 10\,\mathrm{K}, 50\,\mathrm{K}, 100\,\mathrm{K}, 300\,\mathrm{K},\ \text{and}\ , 1000\,\mathrm{K}$. Use these results to find :
b.) The probabilities for being in the first 6 vibrational levels (i.e $0 \le v \le 5$) at each temperature.
c.) The relative populations of the adjacent levels (i.e $\frac{prob_v}{prob_{v+1}}$) Do you notice a trend?
There is a clear trend that as temperature increases there is a significantly higher chance of finding

an oscilator in the higher energy vibrational energy levels. This is quite intuitive. TThis result is pretty funny because it shows that for the first few energy increases, the proprotion of oscillators in the 2nd lowest energy state will at first increase, then it will decrease as more molecules enter the higher energy levels.



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M2   =exp(-D2/((1.38E-23)*1000))
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	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	v	(v+0.5)hw	(v+0.5)^2ahw	Ev	exp(-Ev/kT), 10K	Pv	50 K	Pv	100 K	Pv	300 K	Pv	1000 K	Pv
2	0	9.17E-22	1.76E-24	9.15E-22	1.32E-03	1.00E+00	2.65E-01	9.28E-01	5.15E-01	7.32E-01	8.02E-01	3.71E-01	9.36E-01	2.04E-01
3	1	2.75E-21	1.58E-23	2.74E-21	2.47E-09	1.87E-06	1.90E-02	6.64E-02	1.38E-01	1.96E-01	5.17E-01	2.39E-01	8.20E-01	1.79E-01
4	2	4.59E-21	4.40E-23	4.54E-21	5.12E-15	3.88E-12	1.39E-03	4.85E-03	3.72E-02	5.29E-02	3.34E-01	1.54E-01	7.20E-01	1.57E-01
5	3	6.42E-21	8.62E-23	6.33E-21	1.18E-20	8.92E-18	1.03E-04	3.61E-04	1.02E-02	1.44E-02	2.17E-01	1.00E-01	6.32E-01	1.38E-01
6	4	8.25E-21	1.42E-22	8.11E-21	2.99E-26	2.27E-23	7.85E-06	2.75E-05	2.80E-03	3.98E-03	1.41E-01	6.52E-02	5.56E-01	1.21E-01
7	5	1.01E-20	2.13E-22	9.87E-21	8.42E-32	6.39E-29	6.10E-07	2.13E-06	7.81E-04	1.11E-03	9.21E-02	4.26E-02	4.89E-01	1.07E-01
8	6	1.19E-20	2.97E-22	1.16E-20	2.62E-37	1.99E-34	4.83E-08	1.69E-07	2.20E-04	3.12E-04	6.03E-02	2.79E-02	4.31E-01	9.40E-02
9					Q10	Check:	Q50	Check	Q100	Check	Q300	Check	Q1000	Check
10					1.32E-03	1.00E+00	2.86E-01	1.00E+00	7.04E-01	1.00E+00	2.16E+00	1.00E+00	4.58E+00	1.00E+00
11				v		Relative Pop		Relative Pop		Relative Pop		Relative Pop		Relative Pop
12				0		1.08E+00		1.27E+00		1.97E+00		1.82E+00		
13				1		2.82E-05		3.39E-01		8.19E-01		1.33E+00		
14				2		8.01E-10		9.17E-02		3.42E-01		9.84E-01		
15				3		2.47E-14		2.50E-02		1.44E-01		7.26E-01		
16				4		8.26E-19		6.90E-03		6.10E-02		5.38E-01		
17				5		3.00E-23		1.92E-03		2.60E-02		3.99E-01		
18				6		1.18E-27		5.41E-04		1.12E-02		2.97E-01		
19														