CML 100: 2017-2018
Thermo Tutorial 1

1. **Einstein's model of heat capacity:** An atomic crystal = N atoms situated at lattice sites. Each atom vibrates as a 3D harmonic oscillator with frequency ν. This is the only allowed frequency. These can therefore be treated as N independent harmonic oscillators. Show that this model leads to the partition function,

$$Q = e^{-\beta U_0}\left(\frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}\right)^{3N}$$

U_0 is the sublimation energy at 0 K or consider it as the zero-energy where all N atoms are separated infinitely. Show that,

$$\overline{C_V} = 3R\left(\frac{h\nu}{k_B T}\right)^2 \frac{e^{-h\nu/k_B T}}{(1-e^{-h\nu/k_B T})^2}$$

Show that it obeys the Dulong-Petit Law at high T.

2. For the partition function,

$$Q(N,V,\beta) = \frac{1}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{3N/2}(V-Nb)^N e^{\beta a N^2/V}$$

calculate the equation of state. Briefly explain how the terms arise in the partition function. Calculate the heat capacity of this gas.

3. Consider a system of three noninteracting identical particles, each of which has states with energies $\varepsilon_1, \varepsilon_2$ and ε_3. How many terms are there in the unrestricted evaluation of Q(3,V,T)? Enumerate the total energies in the summation

$$Q(N,V,T) = \sum_{i,j,k\ldots} e^{-\beta\left(\varepsilon_i\ +\varepsilon_j\ +\varepsilon_k\ +\cdots\right)}$$

How many terms occur in $Q(3,V,T)$ when (a) fermion restriction is taken into account (one fermion per energy), (b) bosons are filled up (any number per energy).

4. For CO, $\Theta_{rot} = 2.77$ K, $\Theta_{vib} = 3103$ K. Estimate the population of the first 20 levels (use a spreadsheet) and plot f_J as a function of J. For f_v $vs.$ v plot use only the first four levels. T=300 K.
5. Three normal modes of vibration of CO2 have $\Theta_{vib} = 3360, 954, 1890$. The second mode is doubly degenerate (any guesses as to which mode?). Calculate the contribution of each normal mode to the total heat capacity due to vibration. T=300 K.
6. Show that the equation $W(a_1, a_2 \ldots) = \mathcal{A}!/\prod_j a_j!$ for two states, 1 and 2 results in a maximum when $a_1 = a_2$. Extend this result to three states. (Hint: Use Stirling's approximation $\ln N! = N\ln N - N$)

7. In the lecture we saw: $dU = TdS - PdV$. $\therefore U = U(S,V)$ and we can write

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

Further, it does not matter whether we change the entropy first or volume first – the order is immaterial as internal energy is a state function. This gives one of the Maxwell relation,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

Likewise, show that $H(S,P)$, $A(V,T)$ and $G(T,P)$ are the other state functions. Derive the similar relations for them too.

8. Derive the relations: $(i) C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$; $(ii) C_p - C_V = \frac{\alpha^2 TV}{\beta}$; $(iii) \mu_{JT} = -\left(\frac{V}{C_p}\right)(\beta C_V \mu_J - \beta p + 1)$; $(iv) \left(\frac{\partial H}{\partial V}\right)_S = \frac{-\gamma}{\beta}$; $(v) \left(\frac{\partial V}{\partial T}\right)_p = \frac{(C_P - C_V)\beta}{T\alpha}$

(A few useful things here $\gamma = C_P/C_V, \alpha = \frac{1}{V}(\partial V/\partial T)_P, \beta = -\frac{1}{V}(\partial V/\partial P)_T, \mu_{JT} = (\partial T/\partial P)_H$

9. It is possible to cool liquid water below its freezing point of 273.15 K without the formation of ice if proper care is taken to prevent nucleation. A kilogram of sub-cooled liquid water at 263.15 K is contained in a well-insulated vessel. Nucleation is induced by the introduction of a speck of dust, and a spontaneous crystallization process ensues. Find the _nal state of the water and calculate the total entropy change for the process. (Heat of fusion is $334\ \mathrm{Jg^{-1}}$, $\mathrm{C_p(l)} = 4.185\ \mathrm{Jg^{-1}K^{-1}}$; $\mathrm{C_p(s)} = 2.092\ \mathrm{Jg^{-1}K^{-1}}$)

10. Calculate the maximum work and the maximum non-expansion work that can be obtained from the freezing of supercooled water at -5 °C and 1.0 atm. The densities of water and ice are 0.999 and 0.917 g $\mathrm{cm^{-3}}$, respectively at -5 °C. (for this you need to read a bit about ΔA and ΔG. Atkins or McQuarrie both have this concept of maximum work and maximum non-expansion work)