Problem 1. Rotational Partition Functions

(a) Consider HCl gas, which is composed of Hydrogen of mass m_H and chlorine Cl

(i) Give a typical distance between the Hydrogen and the Chlorine atoms, r_0 (in meters). We will assume this distance is fixed.

(ii) Use classical considerations, to find the center of mass of the two atoms, and compute the moment of inertia of the two atoms around the center of mass exactly. Assume that the HCl is rotating in the xy plane. Show that

$$I = m_H r_0^2 \left(1 - \left(\frac{m_H}{m_{Cl}}\right) + \ldots\right) \tag{1}$$

up to terms further suppressed by terms of order $(m_H/m_{Cl})^2$. We will keep the leading term only $m_H r_0^2$ in what follows.

(iii) The rotational energy levels are

$$\epsilon_{\rm rot} = \left\langle \frac{L^2}{2I} \right\rangle = \frac{\ell(\ell+1)\hbar^2}{2I} = \ell(\ell+1)\Delta \tag{2}$$

where $\Delta = \hbar^2/2I$. Estimate Δ in eV and in GHz (i.e. $f = \Delta/h$). Estimate $\Delta/k_B T$ at room temperature, you should find that $\Delta/k_B T$ is around 12.

(b) (i) Show that for any system that C_V is directly determined by the variance in the energy

$$C_V = k_B \beta^2 \left(\langle E^2 \rangle - \langle E \rangle^2\right) \tag{3}$$

(ii) Show also that

$$C_V = k_B \beta^2 \frac{\partial^2}{\partial \beta^2} \log Z \tag{4}$$

(iii) Recall that the partition function of N molecules of H HCl consists of a translational partition function, and a rotational one:

$$Z_{\rm tot} \simeq \left(\frac{e Z_{\rm trans}}{N}\right)^N Z_{\rm rot}^N \tag{5}$$

(Where does the factor $(e/N)^N$ come from?). Show that

$$C_V = \frac{3}{2} N k_B + N k_B \left[\beta^2 \langle \epsilon_{\rm rot}^2 \rangle - \beta^2 \langle \epsilon_{\rm rot} \rangle^2\right] \tag{6}$$

where

$$\beta^2 \langle \epsilon_{\rm rot}^2 \rangle = \frac{1}{Z_{\rm rot}(\beta\Delta)} \sum_{\ell=0}^{\infty} (2\ell+1) \left(\ell(\ell+1)\beta\Delta\right)^2 e^{-\ell(\ell+1)\beta\Delta} \tag{7}$$

$$\beta \langle \epsilon_{\rm rot} \rangle^2 = \frac{1}{Z_{\rm rot}(\beta\Delta)} \sum_{\ell=0}^{\infty} (2\ell+1) \left(\ell(\ell+1)\beta\Delta\right) e^{-\ell(\ell+1)\beta\Delta} \tag{8}$$

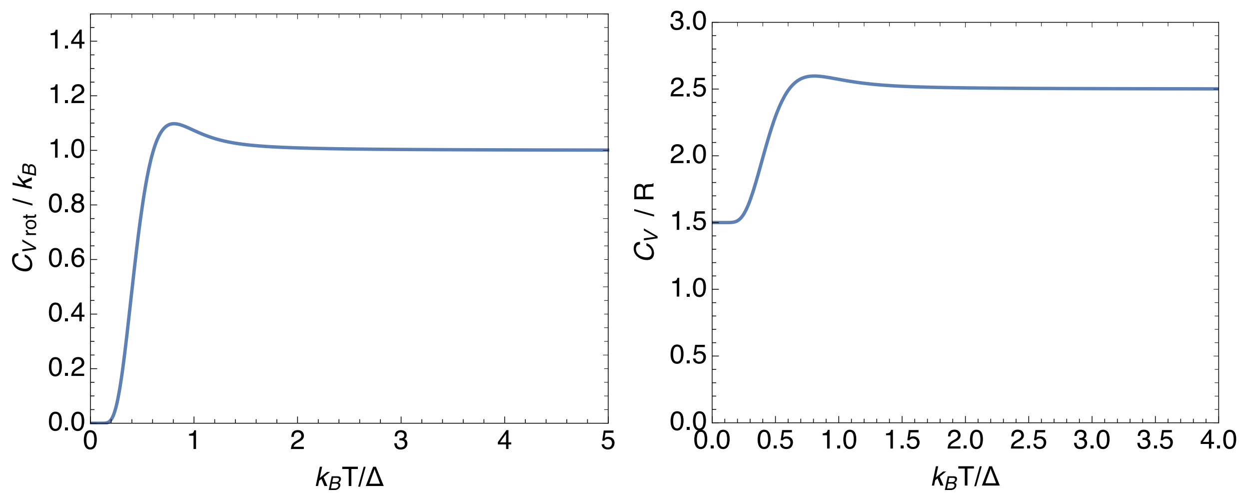

Figure 1: Left: the rotational contribution to the partition function (per particle), i.e. $\beta^2(\langle\epsilon_{\rm rot}^2\rangle - \langle\epsilon_{\rm rot}\rangle^2)$. Right: the full partition function for one mole.

(c) Write a program to sum from $\ell = 0$ up to 20 and to compute

$$\beta^2 \left\langle \epsilon_{\rm rot}^2 \right\rangle, \qquad \beta^2 \left\langle \epsilon_{\rm rot} \right\rangle^2 \qquad C_V/k_B \tag{9}$$

Make a graph of C_v/R vs. k_BT/Δ for one mole of substance. You should find something analogous to Figure. 1.

(d) For HCl, use your graph estimate the temperature (in Kelvin) where the classical approximation for the rotational partition function works at the 20% level.

Problem 2. Entropy of Paramagnets

Consider a paramagnet consisting of N independent spins, with $N_\uparrow$ spin up and $N_\downarrow$ spin down as discussed in class. A magnetic field B points in the z direction, and the spins want to align with the magnetic field. The energy levels of each spin are $\mp\mu_B B$, where the spin up states have lower energy $-\mu BB$, and the spin down states have an energy of $+\mu_B B$. So, the spin down states have a higher energy than the spin up states by an amount $\Delta = 2\mu_B B$. Since it is energetically favorable for the spin to be in the direction of B, it is the down spins that are excited. The mean number of excited atoms (spin down) is $n = N_\downarrow/N$. The total total energy of the systems is $E = -\mu_B B(N_\uparrow - N_\downarrow)$.

(a) Work problem 20.5 from Blundell.

(b) Show that the mean number of down spins $n = N_\downarrow/N$ is related to the temperature

$$\frac{1}{k_BT} = \ln\left(\frac{1-n}{n}\right) \tag{10}$$

(c) Determine the magnetization of the system M and sketch the magenetization versus B.

(d) Determine isothermal magnetic susceptibility $\chi_T(T, B)$. Show that for small fields $\chi_T \propto 1/T$.

Problem 3. (Optional) Paramagnets from the Microcanonial Ensemble

Now we will work through the problem in the micro-canonical ensemble. Recall that in the microcanonical ensemble we are supposed to directly count the number of configurations (states) with a given total energy E. This counting procedure determines the entropy, and from there all else can be determined.

(e) Describe the state of lowest possible energy (the ground state), and show that the energy of this state is $-\mu_B BN$. Let's define the *excitation* energy $\mathcal{E} = E - (-N\mu_B B)$, i.e. the energy *above* the ground state energy. Show that

$$\frac{\mathcal{E}}{N} = n\Delta \tag{11}$$

(f) Show that the total number of configurations with energy E is

$$\Omega(\mathcal{E}) = \frac{N!}{N_\uparrow! N_\downarrow!} \tag{12}$$

where $N_\uparrow = N - N_\downarrow$ and $\mathcal{E} = Nn\Delta$

(g) Show that the entropy as a function of energy is

$$S(\mathcal{E}) = Nk_B \left[(1-n)\log(1-n) - n\log n\right] \tag{13}$$

(h) Using Eq. (13) show that the temperature of the system with a given $\mathcal{E}$ is related to the mean number of down arrows

$$\frac{1}{k_B T} = \ln\left(\frac{1-n}{n}\right) \tag{14}$$

as deduced by the canonical approach.