

Problem 1. Ideal gas in one and two dimensions

- Use methods of partition functions to find the free energy, energy, pressure, and entropy in one and two dimensions. Compare your result to the 3D case. Express your result for the entropy in terms of the thermal de Broglie wavelength.

Problem 2. Estimates of Entropy

The Sackur-Tetrode equation which determines the entropy of an ideal mono-atomic gas:

$$S = Nk_B \left[\log \left(\frac{v_N}{\lambda_{\text{th}}^3} \right) + \frac{5}{2} \right] \quad (1)$$

where $v_N = V/N$ and λ_{th} is the thermal de Broglie wavelength. You should not have to look up numbers here.

- (a) Take an ideal gas of Helium at Standard Temperature Pressure (STP) – the volume per particle is $v_N = V/N$, and the interparticle spacing is ℓ_0 , with $\ell_0 = v_N^{1/3}$. Determine the inter particle spacing in nm.
- (b) Take an ideal gas of Helium at Standard Temperature Pressure (STP). Determine the thermal de Broglie wavelength in nm.
- (c) Sackur-Tetrode equation says

$$S = Nk_B \left[\log \left(\frac{v_N}{\lambda_{\text{th}}^3} \right) + \frac{5}{2} \right] \quad (2)$$

Thus, up to a logarithm (which is never very large), the entropy is of order Nk_B . This gives a simple way to estimate entropy of any substance. It is of order the number of particles (times k_B). Determine $S/(Nk_B)$ for Helium gas at STP.

Problem 3. Degeneracy

Often there may be more than one quantum mechanical state with the same energy level E_ℓ – this is known as degeneracy. A very common source of degeneracy is the quantum mechanical spin. If a particle has spin $\frac{1}{2}$, then it can be in two quantum mechanical spin states, spin up and spin down. If the energy is independent of the spin, then there will be two quantum mechanical states with the same energy level E_ℓ (one with spin up and one with spin down), and the degeneracy of the energy level is two, $g_\ell = 2$. In the partition function we sum over *states*, which is clearly related to the sum over energy levels as follows:

$$\sum_{\text{states}} e^{-E_s/kT} = \sum_{\text{energy-levels}, E_\ell} g_\ell e^{-E_\ell/kT} \quad (3)$$

where g_ℓ is the degeneracy of the ℓ -th energy level.

- (a) Do problem Blundell, 21.4

Problem 4. 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

$$I = m_H r_0^2 \left(1 - \left(\frac{m_H}{m_{Cl}} \right) + \dots \right) \quad (4)$$

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

$$\epsilon_{\text{rot}} = \left\langle \frac{L^2}{2I} \right\rangle = \frac{\ell(\ell+1)\hbar^2}{2I} = \ell(\ell+1)\Delta \quad (5)$$

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

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

$$C_V = k_B \beta^2 (\langle E^2 \rangle - \langle E \rangle^2) \quad (6)$$

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

$$Z_{\text{tot}} \simeq \left(\frac{e Z_{\text{trans}}}{N} \right)^N Z_{\text{rot}}^N \quad (7)$$

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

$$C_V = \frac{3}{2} N k_B + N k_B [\beta^2 \langle \epsilon_{\text{rot}}^2 \rangle - \beta^2 \langle \epsilon_{\text{rot}} \rangle^2] \quad (8)$$

where

$$\beta^2 \langle \epsilon_{\text{rot}}^2 \rangle = \frac{1}{Z_{\text{rot}}(\beta\Delta)} \sum_{\ell=0}^{\infty} (2\ell+1) (\ell(\ell+1)\beta\Delta)^2 e^{-\ell(\ell+1)\beta\Delta} \quad (9)$$

$$\beta \langle \epsilon_{\text{rot}} \rangle = \frac{1}{Z_{\text{rot}}(\beta\Delta)} \sum_{\ell=0}^{\infty} (2\ell+1) (\ell(\ell+1)\beta\Delta) e^{-\ell(\ell+1)\beta\Delta} \quad (10)$$

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

$$\beta^2 \langle \epsilon_{\text{rot}}^2 \rangle, \quad \beta^2 \langle \epsilon_{\text{rot}} \rangle^2, \quad C_V/k_B \quad (11)$$

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

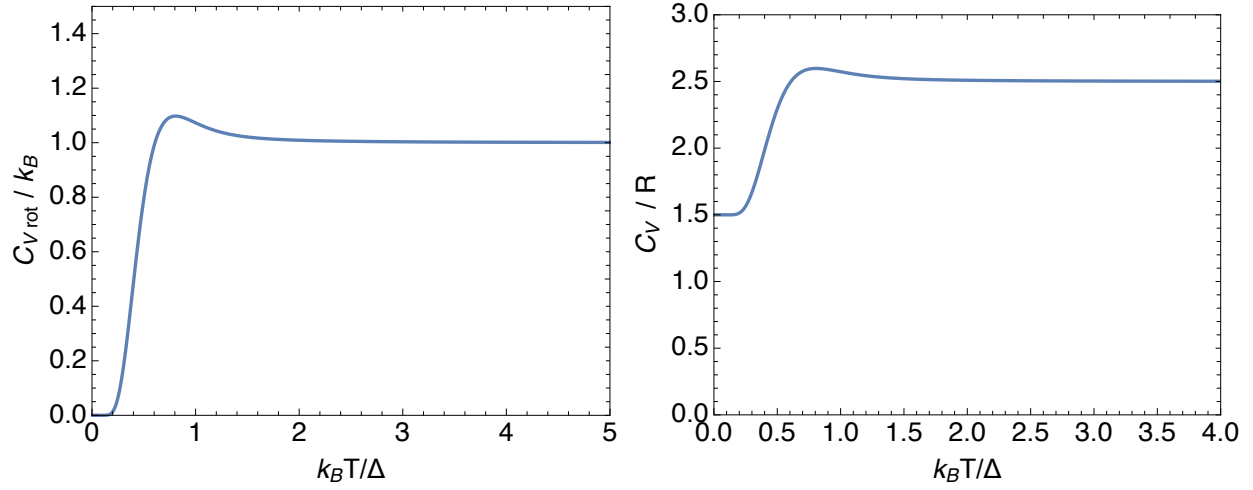


Figure 1: Left: the rotational contribution to the partition function (per particle), i.e. $\beta^2(\langle \epsilon_{\text{rot}}^2 \rangle - \langle \epsilon_{\text{rot}} \rangle^2)$. Right: the full partition function for one mole.

- (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.