PHYS 301
Thermodynamics and Statistical Mechanics

Worksheet #7

Tuesday March 3 2026

Question 1.

Diatomic molecules: So far, we have focused our attention on monoatomic ideal gases with no internal degree of freedom. The partition function for one such gas particle is

$$Z_1 = \frac{V}{\lambda_Q^3}, \qquad \text{with} \qquad \lambda_Q \equiv \frac{h}{\sqrt{2\pi m k_B T}} \tag{1}$$

Most gases are, however, not monoatomic but instead composed of multiple atoms (e.g. N_2, O_2, CO, CO_2, etc.). This allows the gas to have *internal* degrees of freedom such as rotation and vibration. As these internal degrees of freedom are independent of the translational states captured in Z_1 above, the total partition is simply the product of the different partition functions

$$Z_1 \to Z_1 Z_{\text{int}} = \frac{V}{\lambda_Q^3} Z_{\text{int}}. \tag{2}$$

Here, let's focus on rotational degrees of freedom of diatomic gases (i.e. $Z_{\text{int}} = Z_{\text{rot}}$). In quantum mechanics, rotational energy levels are quantized according to

$$E_j = j(j+1)\epsilon, \qquad j = 0, 1, 2, \ldots \tag{3}$$

where ϵ is a constant capturing the energy associated with the rotation of molecule. Different gases have different value of ϵ. For each rotational level labeled by j, there are $2j+1$ degenerate states.

(a) Write down the partition function Z_{rot} for the rotational levels of a single diatomic molecule.

(b) By approximating the sum as an integral (which is valid when $k_B T \gg \epsilon$) and using the substitution $x = j(j+1)\beta\epsilon$, show that the partition function is approximately

$$Z_{\text{rot}} = \frac{k_B T}{\epsilon} \qquad (k_B T \gg \epsilon). \tag{4}$$

(c) The above result is value when the molecule is made of two distinguishable atoms (e.g. CO). How does the above result change when the diatomic molecule is made of two *identical* atoms (like N_2, O_2)? Think about how the molecule change under a 180° rotation.

(d) Write the total partition function for CO gas with N molecules in volume V and temperature T. Do the same for O_2 gas.

(e) Compute the Helmholtz Free energy $F = -k_B T \ln Z$ in each case, and use this to compute the chemical potential of CO and O_2.