This problem is to find the rotational entropy, free energy and specific heat of a set of many non-interacting diatomic molecules. The molecules are each composed of two atoms and are treated as rigid rotors with moment of inertia I. Ignore translational and vibrational motion. Except in the last part (e) below, assume that the two atoms are distinguishable.

For each molecule the rotational kinetic energy can be expressed in spherical coordinates as

$$KE = \frac{1}{2} I \left[\dot{\theta}^2 + \sin^2\theta \, \dot{\phi}^2 \right]. \tag{1}$$

(a) Calculate the momenta p_θ and p_ϕ conjugate to the variables θ and ϕ, and show that the Hamiltonian H for the rotational motion can be expressed as

$$H = \frac{1}{2I} \left[p_\theta^2 + \frac{1}{\sin^2\theta} p_\phi^2 \right] \tag{2}$$

(b) In this part assume the rotation is described by classical physics. Give the basic definition of the classical partition function Z in terms of the quantities defined above, the temperature T, and any needed constants. Using this definition, find expressions for Z, the free energy F, the entropy S, and the rotational specific heat C per molecule as functions of T.

For the rest of the problem [parts (c), (d) and (e)] assume the rotation is described by quantum mechanics, where the rotational energies are given by

$$E_L = L(L+1)\frac{\hbar^2}{2I}. \tag{3}$$

(c) Write down the degeneracy of each state and give an expression for the quantum partition function. You may leave the expression as a sum.

(d) In the limit of low (but non-zero) temperature the rotational specific heat C per molecule can be approximated as a closed analytic expression. Find the explicit expression in terms of $\hbar$, I, and T.

(e) Suppose now that the two atoms in the molecule are indistinguishable, spinless Bose particles. What is the effect upon the rotational spectrum of the molecule? In this case, find the expression for the low temperature specific heat analogous to the result found in part (d).