Statistical Mechanics Assignment 3

Due: January 30, 11:00 a.m.

Marks: 26

1. How many rotational and vibrational modes would each of the following molecules have? What is the symmetry number for each of these molecules? [3 marks each]

   (a) methane

   (b) H–C≡C–C≡C–H

   (c) BF_3

2. We will often be interested in $\ln Q$ rather than Q itself. Consider a sample of 1 mol of neon held in a 10 L container at 200 K. What is the value of $\ln Q$, considering only the translational degrees of freedom? [5 marks]

   Bonus: In the above problem, you probably treated neon as if it had a single kind of atom whose mass could be calculated from the mean molar mass. However, there are three isotopes of neon:

Isotope	Mass/amu	Percentage
^{20}Ne	19.992 440 175 9	90.48
^{21}Ne	20.993 846 74	0.27
^{22}Ne	21.991 385 51	9.25

   What is the value of the canonical partition function for a mole of neon with this composition? Does it make a big difference whether we account for the isotopic mixture or not?

3. For $^{12}C^{16}O$, $\tilde{\nu} = 2170.21\,\mathrm{cm}^{-1}$ and $B = 1.9313\,\mathrm{cm}^{-1}$. The rotational and vibrational state of this molecule is described by the quantum numbers (v, J).

   (a) In the gas phase, diatomic molecules don't undergo pure vibrational transitions. Rather, we see transitions which involve changes in both the vibrational and rotational quantum numbers. Here is one possible transition: $(0, 0) \rightarrow (1, 1)$. What is the wavelength of this transition? In what region of the electromagnetic spectrum would this transition be seen? [5 marks]

   (b) Suppose that we want to describe the statistical mechanics of this molecule at temperatures between 100 and 500 K. Can we use the integrated form of the rotational partition function? [2 marks]

   (c) Suppose that we want to see how the probability of occupying the $J = 8$ level depends on temperature. Write down an equation for this probability. Plot this probability as a function of temperature over the range 100 to 500 K. What do you observe? [5 marks]