Thermo and intro to Stat Mech 2019

Homework assignment 2

Reading assignment: Chapter 4 and 20.1 in B&B.

Problem 1:

Consider a solid made of molecules that have two accessible energy levels that differ in energy by $\Delta\epsilon$. The lower level is threefold degenerate and the upper one is twofold degenerate. Take the zero of the energy axis to be the lower energy level. Assume the molecules are not interacting with each other but are coupled to a heat bath and can be considered to be a canonical ensemble.

(a) Find the partition function, Z, for a molecule.

(b) Calculate the population of the two energy levels as a function of temperature and discuss the two limits as the temperature approaches zero and infinity (explain the meaning of your results).

(c) Calculate the average energy of the system as a function of temperature and discuss the two limits as the temperature approaches zero and infinity (explain the meaning of your results).

(d) Calculate the heat capacity as a function of temperature. Find the high and low temperature limits. Why are the high and low temperature results for this system so different from the classical results where the heat capacity is a constant independent of temperature?

(e) Assume that the system has been prepared in such a way that the population of the higher energy level is three times larger than the population of the lower energy state. While it do not really apply in this case, use the expression for the Boltzmann distribution to define an effective temperature for the system. Note and discuss the sign of the value you obtain.

(f) The zero of energy us arbitrary, just as the reference point for the measure of the height of a mountain (which is usually taken to be sea level). Repeat the calculation in (b) and (c) choosing the zero of energy to be the higher energy level. To what extend do the results change?

Problem 2:

At sea level, the composition of dry air is 78% nitrogen, 21% oxygen, 0.9% argon and 0.03% carbon dioxide. Estimate how the ratio of carbon dioxide to nitrogen content changes with altitude assuming the temperature is constant at $290K$. What do you predict the ratio to be on top of Mt. Everest? (To simplify the calculations, you can use the result discussed in the problem solving session that the density of N_2 molecules has dropped to

1/e at a heigt of 8.5 km with respect to the density at sea level).

Problem 3:

The rate constant for atomic rearrangements (such as diffusion of atoms in and on the surface of solids and chemical reactions) can typically be written as

$$k = \nu e^{-E_{act}/k_B T}$$

where E_{act} is the activation energy, ν is the so-called pre-exponential factor and k_B the Boltzmann constant. A typical value for ν is 10^{12} sec^{-1}. Assume the activation energy is 0.5 eV.

(a) Calculate the value of $k_B T$ at room temperature and express it in electron volts, eV.

(b) Calculate the rate constant at temperature of 150 K, 300 K and 600 K.

(c) The average time between rearrangement events (diffusion hops or chemical reactions) is the inverse of the rate constant, $\tau = 1/k$. Evaluate τ for temperature of 150 K, 300 K and 600 K. Note the enormous variation with the temperature.