

# Physics 3410 Homework #10

4 problems

Due by April 20

▷ 1.

Fun with standard deviations. We showed in class that  $\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$ . Now

(a) Show that, for a system in equilibrium with a reservoir at temperature  $T$ , the average value of  $E^2$  is

$$\langle E^2 \rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}$$

(b) The standard deviation of the energy (that is, the size of its fluctuations around the average) is defined as

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2$$

Prove that the standard deviation is related to the heat capacity  $C = \frac{\partial \langle E \rangle}{\partial T}$  by the formula

$$\sigma_E = kT \sqrt{C/k}$$

▷ 2.

Starting from the partition function for the ideal gas that we derived in class, by way of the Helmholtz free energy, derive

(a) The ideal gas law

(b) The Sackur-Tetrode equation

▷ 3.

Write the partition function of an ideal gas of carbon monoxide. Treat the vibrations in the bond between the atoms as a harmonic oscillator (see last week's homework), and assume that the temperature is high enough so that all modes are active.

▷ 4.

Consider a system (like a bonding site on a molecule) which is surrounded by a reservoir of particles having a chemical potential of  $\mu = -0.3 \text{ eV}$  and temperature  $T = 300 \text{ K}$ . The system can be empty, or can contain one or two particles. if the system is empty, its energy is  $0 \text{ eV}$ . If it holds one particle, the system has energy  $-0.4 \text{ eV}$ , and if it holds two particles, it has energy  $-0.5 \text{ eV}$ .

(a) Find the Gibbs factor for each of the three possible states

(b) Find the grand partition function  $\mathcal{Z}$

(c) What is the probability that the system is empty?

(d) What is the average occupancy  $\bar{n}$  of the system? That is, on average how many particles does it contain?

