Homework #12

MSAE-E4201 Spring 2017

Due April 25 before 5:30 pm in course mailbox

1. (20 points) A material consist of N non-interacting atoms that can be in the neutral state A, singly ionized state A^+ (which takes energy ε_1 to form) and doubly ionized state A^{++} (which takes energy ε_2 to form). Using grand canonical ensemble methods, find the number of each type and the average atom charge if the chemical potential of electrons is μ.

2. (20 points) A hemoglobin molecule has four heme sites, each which can bind oxygen.
(a) Model a hemoglobin molecule as one heme site to which one O_2 molecule can bind, with an energy -0.65 eV compared to 0 eV for the unbound state. Assume now and later that O_2 in the blood has a chemical potential of -0.6 eV at body temperature (310 K). Use the Gibbs factors to find the fraction of such sites occupied by O_2.

(b) Now model hemoglobin as having two heme sites, each that can be bound by one O_2 molecule. Each occupied site has energy -0.65 eV. By considering the hemoglobin molecule as one unit, find the fraction of such sites occupied by O_2. Compare your answer to that in (a) and explain any differences.

(c) Now model hemoglobin as having two heme sites, each that can again be bound by one O_2 molecule. The overall energy when only one site is occupied is -0.65 eV and when both states are occupied it is -1.45 eV. Again, by considering the hemoglobin molecule as one unit, find the fraction of such sites occupied by O_2. Compare your answer to those in (a) and (b) and explain any differences. Does this model suggest that probability a heme site is occupied increases, decreases or remains the same when other heme sites are occupied?

3. (20 points) (a) For a grand canonical ensemble partition function $\mathcal{Z}$, show that the average number of particles $\langle N\rangle = - \partial \ln \mathcal{Z}/\partial\gamma$, with $\gamma = - \beta\mu$.

(b) Show that the square of the standard deviation in particle number (the variance), σ_N^2, is $k_BT\, \partial\langle N\rangle/\partial\mu|_{V,T}$, and so using $\partial\mu/\partial\langle N\rangle|_{V,T} = - (V^2/\langle N\rangle^2)\, \partial P/\partial V|_{\langle N\rangle,T}$, that the fractional fluctuation in number (or density for constant volume) is $\sigma_N/\langle N\rangle = (k_BT\kappa/V)^{1/2}$ where κ is the compressibility. This means that energy fluctuations are related to the specific heat and number/density/pressure fluctuations to the compressibility. (The first part of (b) is analogous to the derivation of energy fluctuations in the canonical ensemble; it would be better to use the improved derivation of this on page 20 in the third installment of the notes and not the original, longer Callen version presented in class.)

4. (15 points) Derive the Fermi-Dirac and then the Bose-Einstein distribution functions directly using the grand canonical ensemble approach, using the Gibbs factors.

5. (25 points) Use the Sommerfield expansion method to find the total energy and heat capacity of electrons in a metal above T = 0 K.