PHYSICS 846

Home Work Assignment # 6 2/24/2009

Due: **Tues., Mar. 3, 2009**.

1. Using the definition of the Gibbs free energy $G = U - TS + pV$, it was shown in class that $G(p, T, N) = N\mu(p, T)$. Equating these two expressions we obtain the result: $U = TS - pV + \mu N$.

Here we wish to prove this important result in a different way. The first law of thermodynamics $dU = TdS - pdV + \mu dN$ shows us that U is a function of S, V and N. Since U is an extensive function of three extensive variables, argue that $\lambda U = U(\lambda S, \lambda V, \lambda N)$ for any choice of λ. Use this to show that $U = TS - pV + \mu N$.

2. In HW # 5 you showed that the grand canonical partition function, or Gibbs sum, for the classical, ideal gas is $\mathcal{Z}(\mu, T, V) = \exp\left(yV/\lambda_T^3\right)$, where where $y = \exp(\beta\mu)$ is the *fugacity* and λ_T the thermal deBroglie wavelength.

Starting with $\mathcal{Z}$ determine the following quantities: **(a)** the density $n(\mu, T)$ and hence find $\mu(n, T)$; **(b)** the internal energy $U(\mu, T, V)$; **(c)** the entropy $S(\mu, T, V)$; and **(d)** the equation of state $p(\mu, T, V)$. **(e)** Rewrite your answers for U, S and p as functions of (N, T, V) to recover familiar results.

The grand canonical ensemble is an unnecessarily hard way to solve the classical ideal gas; the canonical ensemble is definitely much simpler. Nevertheless this problem shows you how to compute compute thermodynamic observables as functions of (μ, T, V) and then switch to (N, T, V). As we shall see later, the grand canonical ensemble is the simplest way to build in the effects of quantum statistics.

3. A classical ideal gas of atoms of mass m is placed in a centrifuge, which is a cylinder of radius R rotating along its axis with angular velocity ω_0. Assuming that the gas is at thermal equilibrium at temperature T find the density profile $n(r)$ given that the density on the axis is $n(0)$.

First, a subtle conceptual point: to discuss the statistical mechanics of a system with moving walls, one cannot work in the lab frame because the constraints are time dependent and can do work on the system. For the problem at hand we thus have to work in the non-inertial frame rotating at angular velocity ω_0.

Let the Hamiltonian in the lab frame be denoted by $\mathcal{H}$. The Hamiltonian $\mathcal{H}_R$ in the rotating frame is then given by

$$\mathcal{H}_R = \mathcal{H} - \vec{\omega}_0 \cdot \vec{L} \quad \text{where} \quad \vec{L} = \sum_{i=1}^{N} \vec{r}_i \times \vec{p}_i.$$

Here $\vec{L}$ is the total angular momentum of the N-particle system. You can simply assume this result; if you want to see a derivation, look at Landau and Lifshitz, "Mechanics" (3rd edition) Sec. 39, p. 126 - 129.

Next breakup the system into several suitable subsystems and find the condition for diffusive equilibrium between these subsystems. Hence determine the density profile $n(r)$.

4. This problem derives the Saha ionization equation used in astrophysics. The results are of great interest in diverse branches of science: the result analogous to (a) is central to the study of chemical reactions, and the result (c) is very useful in semiconductor physics. See, e.g., Prob. 12, Chap. 7 on p. 208 of Kardar on excitonic dissociation in semiconductors.

Consider the ionization of atomic hydrogen: $H \rightleftharpoons e^- + p^+$.
(a) Show that, at constant temperature and pressure, the change in Gibbs free energy can be written as $dG = \sum_j \mu_j dN_j$ where j labels the three species involved: e, p and H. From this determine the constraint on the three chemical potentials at equilibrium.
(b) Next, use the classical ideal gas result for the chemical potential for each species, taking care to place the ground state energy of the composite particle H to be at $-E_b$ with that of the constituents e and p taken to be zero. Here E_b is the (positive) energy required to ionize the Hydrogen atom. Thus show that the equilibrium concentrations of the three species satisfies the equation

$$\frac{n_e n_p}{n_H} = \lambda_{T,e}^{-3} \exp(-E_b/k_B T).$$

Here $\lambda_{T,e}$ is the thermal deBroglie wavelength for the electrons.
(c) If all the electrons and protons come from ionized hydrogen show that

$$n_e = \sqrt{n_H} \lambda_{T,e}^{-3/2} \exp(-E_b/2k_B T).$$

Note two interesting features of this result: (i) the exponential factor is not quite the "Boltzmann factor" since it involves $E_b/2$ and not E_b, and (ii) the electron concentration is proportional to the square root of the Hydrogen concentration.