Phys 971 Stat Mech: Homework 3

due 10/10/2013

1

Consider a liquid in equilibrium (both thermal and diffusive) with its vapor (treated as an ideal gas). For the liquid we will apply the following crude model. We treat the liquid as if the molecules still formed a gas of molecules moving independently, but with the following considerations. 1) each molecule is assumed to have a constant potential energy $-\epsilon$ due to its interaction with the rest of the molecules, and 2) each molecule is assumed free to move throughout a total volume $N_\ell v_0$, where v_0 is the average volume available per molecule in the liquid phase.

a) With these assumptions, write down the partition function for a liquid consisting of N_ℓ molecules.

b) Now set the chemical potential of the liquid equal to the chemical potential of the vapor phase and find an expression for the vapor pressure in terms of the temperature and other constants like v_0 and ϵ.

2

Pathria 4.5: Show that expression (4.3.20) for the entropy of a system in the grand canonical ensemble

$$S = k_B T \left(\frac{\partial q}{\partial T}\right)_{z,V} - N k_B \ln z + kq$$

can also be written as

$$S = k_B \left[\frac{\partial}{\partial T}(Tq)\right]_{\mu,V}.$$

Note: q is a function of z, T, and V while z is a function of T and μ. Also, $-k_B T q = \Phi$ where Φ is the grand potential from lecture.

3

Pathria 4.6: Define the isobaric partition function

$$Y_N(P,T) = \frac{1}{\lambda^3}\int_0^\infty Q_N(V,T) e^{-\beta PV} dV.$$

Show that in the thermodynamic limit the Gibbs free energy (4.7.1) is proportional to $\ln Y_N(P,T)$. Evaluate the isobaric partition function for a classical ideal gas and show that $PV = N k_B T$. [The factor of the cube of the thermal deBroglie wavelength, λ^3, serves to make the partition function dimensionless and does not contribute to the Gibbs free energy in the thermodynamic limit.]

4

Pathria 4.8: Determine the grand partition function of a gaseous system of "magnetic" atoms (with $J = 1/2$ and $g = 2$) which can have, in addition to the kinetic energy, a magnetic potential energy equal to $\mu_B H$ or $-\mu_B H$, depending on their orientation with respect to an applied magnetic field H. Derive an expression for the magnetization of the system, and calculate how much heat will be given off by the system when the magnetic field is reduced from H to zero at constant volume and constant temperature.