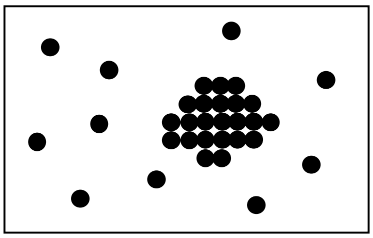
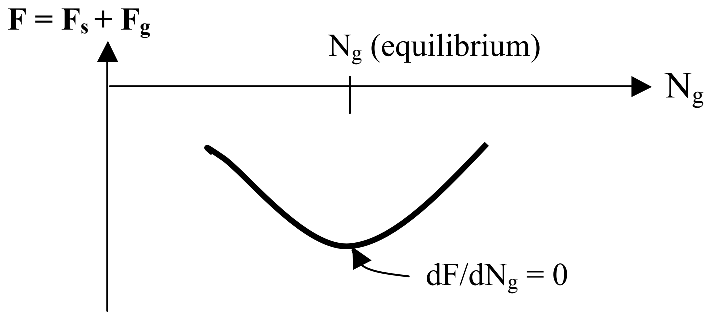
Solution

Physics 213 **Problem 4** **Week 7**

Equilibrium between phases

Consider the equilibrium between a simple solid and its gas phase. In equilibrium at temperature T, an average of N_s atoms are in the solid and N_g are in the gas. We will compute the vapor pressure in equilibrium with the solid, with a little approximation. Here's the picture:





The equilibrium condition $dF/dN_g = 0$ is equivalent to equalizing the chemical potentials of the solid and gas:

$$\boxed{\mu_s = \mu_g}$$ *Equilibrium condition between phases*

Pretend that the solid is a perfect crystal with every atom held in place (only one microstate), so the entropy of the solid is zero. Also assume that the kinetic energy of the solid is zero. The binding energy of each atom in the solid is Δ, so its free energy is simply $F_s = U_s - TS_s = -N_s\Delta$.

a) Write out the chemical potentials for the solid and gas in terms of Δ, T, and number densities n and n_Q. (We need n_Q here because we're comparing state counts in the gas and in the solid.)

$\mu_s = -\Delta$

$\mu_g = kT \ln(n/n_Q)$

b) With the equilibrium condition, find the vapor pressure, p in terms of T, Δ, and n_Q.

$\mu_s = \mu_g \Rightarrow n = n_Q e^{-\Delta/kT}$, so $p = nkT = n_Q kT e^{-\Delta/kT}$

c) Evaluate the vapor pressure (in atm) at T = 600K for atoms with an atomic weight of 28 that form a solid with binding energy Δ = 4.63 eV. Interpret this.

The quantum density of the gas is $n_Q = 10^{30}\text{m}^{-3} \times (28)^{3/2} \times (600/300)^{3/2} = 4.2\times10^{32}\text{m}^{-3}$.

$p = (4.2\times10^{32}\text{m}^{-3})(1.38\times10^{-23})(600\text{K})e^{-4.63/k600} = 4.6\times10^{-27}$ Pa $= 4.6\times10^{-32}$ atm

The fact that this is so low means that at atmospheric pressure, silicon will never evaporate.