Spring 2002 #13 (p 1 of 2)

Consider an ideal monoatomic gas in which each atom has two internal energy states, one an energy Δ above the other. There are N atoms in a volume V at temperature T.

Find

(a) chemical potential

As usual start with the partition function. Let ϵ be the energy of the lower state. Then $\epsilon + \Delta$ is the energy of the other state.
So, the partition function of one atom is

$$Z_1 = \sum_r e^{-\beta \epsilon_r} = e^{-\beta\epsilon} + e^{-\beta(\epsilon+\Delta)}$$

since this is a monatomic ideal gas, we know the energy is

$$\epsilon = \frac{3}{2} KT$$

The partition function for N indistinguishable atoms is

$$Z = \frac{1}{N!}(Z_1)^N = \frac{1}{N!}\left[e^{-\beta\epsilon} + e^{-\beta(\epsilon+\Delta)}\right]^N$$

$$\Rightarrow \ln Z = -\ln N! + N\ln\left[e^{-\beta\epsilon} + e^{-\beta(\epsilon+\Delta)}\right]$$

since $N \gg 1$ use Stirling's formula

$$\cong -N\ln N + N + N\ln\left[e^{-\beta\epsilon}\left(1 + e^{-\beta\Delta}\right)\right]$$

$$\therefore \ln Z \cong -N\ln N + N - N\beta\epsilon + N\ln\left[1 + e^{-\beta\Delta}\right]$$

Then, the free energy is

$$F = -KT\ln Z$$

$$= KTN\ln N - KTN + N\epsilon - KTN\ln\left[1 + e^{-\beta\Delta}\right]$$

Now, we know that the chemical potential is

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = KT\ln N + KT - KT + \epsilon - KT\ln\left[1 + e^{-\beta\Delta}\right]$$

$$\Rightarrow \boxed{\mu = kT\left[\ln N + \frac{3}{2} - \ln\left(1+e^{-\beta\Delta}\right)\right]} \quad , \quad \epsilon = \frac{3}{2}kT$$

(b) Free energy

see part (e)

$$\boxed{F = -kTN\left[-\ln N + 1 - \frac{3}{2} + \ln\left(1+e^{-\beta\Delta}\right)\right]}$$

(c) entropy

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = -kN\ln N + kN + kN\ln\left(1+e^{-\beta\Delta}\right) + kTN\,\frac{\frac{\Delta}{kT^2}e^{-\Delta/kT}}{1+e^{-\beta\Delta}}$$

$$\Rightarrow \boxed{S = kN\left[-\ln N + 1 + \ln\left(1+e^{-\beta\Delta}\right) + \frac{\Delta}{kT}\,\frac{1}{1+e^{\beta\Delta}}\right]}$$

(d) pressure

$$\boxed{p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = 0}$$

(e) heat capacity at constant pressure

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = T\Bigg[\underbrace{\frac{\frac{\Delta}{kT^2}e^{-\beta\Delta}}{1+e^{-\beta\Delta}} - \frac{\Delta}{kT^2}\,\frac{1}{1+e^{\beta\Delta}}}_{=0} + \frac{\Delta}{kT}\,\frac{\frac{\Delta}{kT^2}e^{\beta\Delta}}{\left(1+e^{\beta\Delta}\right)^2}\Bigg]$$

$$\therefore \boxed{C_p = \left(\frac{\Delta}{kT}\right)^2 \frac{e^{\beta\Delta}}{\left(1+e^{\beta\Delta}\right)^2}}$$