

Problem Set 5
Solutions - McQuarrie Problems
3.20 MIT
Dr. Anton Van Der Ven
Fall 2003

Problem 3-4

We have to derive the thermodynamic properties of an ideal monatomic gas from the following:

$$\Theta = e^{q\lambda}$$

$$\lambda = e^{\beta\mu} \text{ and } q = \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} V$$

Θ is the partition function for the grand canonical ensemble, where T, V, μ are fixed. The characteristic potential for the grand canonical ensemble is the "grand canonical potential".

$$\phi = E - TS - \mu N = -pV$$

(since $E = TS - pV + \mu N$)

$$d\phi = -SdT - pdV - Nd\mu$$

The thermodynamic properties for the grand canonical ensemble are:

$$S = - \left(\frac{\partial \phi}{\partial T} \right)_{N, V}$$

$$p = - \left(\frac{\partial \phi}{\partial V} \right)_{T, \mu}$$

$$N = - \left(\frac{\partial \phi}{\partial \mu} \right)_{T, V}$$

The grand canonical potential is related to Θ according to

$$\phi = -kT \ln \Theta \quad (\text{see table 3-1})$$

but $\Theta = e^{q\lambda}$ so,

$$\phi = -kT \cdot q\lambda = -kT \cdot \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} V \cdot e^{\beta\mu} = - (kT)^{\frac{5}{2}} \left(\frac{2\pi m}{h^2} \right)^{\frac{3}{2}} V \cdot \exp \left(\frac{\mu}{kT} \right)$$

Starting with N ,

$$N = - \left(\frac{\partial \phi}{\partial \mu} \right)_{T, V} = \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} V \cdot \exp \left(\frac{\mu}{kT} \right) \quad (3-8-11)$$

and p

$$p = - \left(\frac{\partial \phi}{\partial V} \right)_{T, \mu} = kT \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \exp \left(\frac{\mu}{kT} \right)$$

Putting those together we can get the ideal gas equation of state, namely

$$p = \frac{N}{V} kT$$

Now S ,

$$S = - \left(\frac{\partial \phi}{\partial T} \right)_{N, V} = \frac{5}{2} k \cdot (kT)^{\frac{3}{2}} \left(\frac{2\pi m}{h^2} \right)^{\frac{3}{2}} V e^{\beta\mu} + (kT)^{\frac{3}{2}} \left(\frac{2\pi m}{h^2} \right)^{\frac{3}{2}} V \left(\frac{-\mu}{kT^2} \right) e^{\beta\mu}$$

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