

**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:

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

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

$\Theta$  is the partition function for the grand canonical ensemble, where  $T, V, \mu$  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  $\Theta$  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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