

# PHYS7721 Homework 5

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**Exercise 1.** Study the density matrix and the partition function of a system of free particles, using the *unsymmetrized* wavefunction (5.4.3) instead of the *symmetrized* wavefunction (5.5.7). Show that, following this procedure, one encounters neither the Gibbs' correction factor  $\frac{1}{N!}$  nor a spatial correlation among the particles.

**Solution.** In analogy with the process for (5.5.11),

$$\begin{aligned} \langle 1, \dots, N | e^{-\beta \hat{H}} | 1', \dots, N' \rangle &= \sum_K e^{-\beta \hbar^2 K^2 / 2m} [u_{k_1}(1) \dots u_{k_N}(N)] [u_{k_1} * (1') \dots u_{k_N} * (N')] \\ &= \prod_{j=1}^N \left( \sum_{k_j} e^{-\beta \hbar k_j^2 / 2m} [u_{k_j}(j) u_{k_j} * (j')] \right) \\ &= \left[ \frac{m}{2\pi\beta\hbar^2} \right]^{\frac{3N}{2}} e^{\frac{-m}{2\beta\hbar^2} [\eta_1^2 + \dots + \eta_N^2]} \end{aligned}$$

Now we consider the diagonal elements of the density matrix to get the partition function,

$$Q_N(V, T) = \text{Tr}(e^{-\beta \hat{H}}) = \int \left( \frac{m}{2\pi\beta\hbar^2} \right)^{\frac{3N}{2}} d^3N r = V^N \left( \frac{m}{2\pi\beta\hbar^2} \right)^{\frac{3N}{2}}$$

which has no spatial correlation or Gibbs' correction.  $\square$

**Exercise 2.** Show that in the first approximation the partition function of a system of  $N$  noninteracting, indistinguishable particles is given by

$$Q_N(V, T) = \frac{1}{N! \lambda^{3N}} Z_N(V, T),$$

where

$$Z_N(V, T) = \int e^{\beta \sum_{i < j} v_s(r_{ij})} d^3N r,$$

$v_s(r)$  being the statistical potential (5.5.28). Hence evaluate the *first order* correction to the equation of state of this system.

**Solution.** Apply

$$Q_N(V, T) = \text{Tr}(e^{-\beta \hat{H}}) = \frac{1}{N! \lambda^{3N}} Z_N(V, T)$$

For the  $0^{th}$  approx of  $Z_N$  we have  $\sum_P = 1$  so  $Z_N = V^N$ . In the first approx,

$$\sum_P = 1 \pm \sum_{i < j} e^{2\pi r_{ij}^2 / \lambda^2} \approx e^{-\beta \sum_{i < j} v_s(r_{ij})}$$

from  $\lambda$  is distance between particles. Now substitute and integrate,

$$Z_N(V, T) = V^N \pm \frac{N(N-1)}{2} V^{N-2} \frac{V \lambda^3}{2^{3/2}}$$

For  $N \gg 1$  and  $N\lambda^3 \ll V$ ,

$$Z_N \approx V^N \left(1 \pm \frac{N\lambda^3}{2^{5/2}V}\right)^N$$

So

$$\ln Q_N(V, T) \approx -N \ln N + N + N \left(\pm \frac{N\lambda^3}{2^{5/2}V}\right) + N \ln\left(\frac{V}{\lambda^3}\right)$$

giving

$$\frac{P}{kT} = \left(\frac{\partial \ln Q_N}{\partial V}\right)_{N,T} \approx \frac{N}{V} \mp \frac{N^2\lambda^3}{2^{5/2}V^2} = \frac{1}{v} \mp \frac{1}{2^{5/2}} \frac{\lambda^3}{v^2}$$

□

**Exercise 3.** Determine the values of the degeneracy discriminant ( $n\lambda^3$ ) for hydrogen, helium, and oxygen at NTP. Make an estimate of the respective temperature ranges where the magnitude of this quantity becomes comparable to unity and hence quantum effects become important.

**Solution.**  $\lambda$  is the deBroglie wavelength. We are considering  $T = 263K$ ,  $P = 100kPa$ . Consider the case of an ideal gas

$$n = \frac{P}{kT} = \frac{1 * 10^5}{263 * 1.38 * 10^{-23}} = 2.65 * 10^{25}$$

From the internet,

$$m_{hydrogen} = 1.67 * 10^{-27}kg, m_{helium} = 6.65 * 10^{-27}kg, m_{oxygen} = 2.66 * 10^{-26}kg$$

And we double for  $H_2$  and  $O_2$  because they are molecules. Plugging these in gives,

$$(n\lambda^3)_{He} = n \frac{h^3}{(2\pi mkT)^{\frac{3}{2}}} = 3.849 * 10^{-6}$$

$$(n\lambda^3)_{H_2} = 1.081 * 10^{-5}$$

$$(n\lambda^3)_{O_2} = 1.70 * 10^{-7}$$

We want

$$\frac{P}{kT} \frac{h^3}{(2\pi mkT)^{\frac{3}{2}}} = 1$$

Plugging in values for each gas (I just plugged the values into wolfram alpha and don't want to copy them all down),

$$H_2 \rightarrow 2.8K, He \rightarrow 1.87K, O_2 \rightarrow .54K$$

□