PHYS 522: Statistical Mechanics

Homework #3

Prakash Gautam

Nov 20, 2018

1. **(Pathria and Beale 6.1)** Show that the entropy of an ideal gas in thermal equilibrium is given by the formula

$$S = k\sum_{\varepsilon}\left[\langle n_\varepsilon + 1\rangle \ln\langle n_\varepsilon + 1\rangle - \langle n_\varepsilon\rangle \ln\langle n_\varepsilon\rangle\right]$$

in the case of bosons and by the formula

$$S = k\sum_{\varepsilon}\left[-\langle 1 - n_\varepsilon\rangle \ln\langle 1 - n_\varepsilon\rangle - \langle n_\varepsilon\rangle \ln\langle n_\varepsilon\rangle\right]$$

in the case of fermions. Verify that these results are consistent with the general formula

$$S = -k\sum_{\varepsilon}\left\{\sum_{n} p_\varepsilon(n)\ln p_\varepsilon(n)\right\},$$

where $p_\varepsilon(n)$ is the probability that there are exactly n particles in the energy stare ε.
Solution:
The general form of entropy of of the system is given by

$$S = K\sum_{i}\left[n_i^*\ln\left(\frac{g_i}{n_i^*}\right) + \left(n_i^* - \frac{g_i}{a}\right)\ln\left(1 - a\frac{n_i s^*}{g_i}\right)\right]$$

where, n_i^* is the set confirming to most probable distribution among the cells. With the degeneracy factor $g_i = 1$, we get $\frac{n_i}{g_i} = n_i^*$ Also the average n_ε is given by

$$\langle n_\varepsilon\rangle = z\left(\frac{\partial q}{\partial z}\right)_{V,T} = \frac{1}{z^{-1}e^{-\beta\epsilon} + a} = n_i^*$$

Substituting $n_i^* = \langle n_\varepsilon\rangle$ we get

$$S = k\sum_{\varepsilon}\left[-\langle n_\varepsilon\rangle \ln\langle n_\varepsilon\rangle + \left(\langle n_\varepsilon\rangle - \frac{1}{a}\right) ln\left(1 - a\langle n_\varepsilon\rangle\right)\right]$$

Now for bosons $a = -1$, we get

$$S = k\sum_{\varepsilon}\left[-\langle n_\varepsilon\rangle \ln\langle n_\varepsilon\rangle + \left(\langle n_\varepsilon\rangle + 1\right) ln\left(1 + \langle n_\varepsilon\rangle\right)\right]$$

Which is the required expression for the bosons. Now for fermions we substitute $a = 1$ and obtain To show that the general expression

$$S = -k\sum_{\varepsilon}\left\{\sum_{n} p_\varepsilon(n)\ln p_\varepsilon(n)\right\},$$

works for the entropy we first notice that the expression can be modified rewritten as

$$S = -k\sum_{\varepsilon}\langle \ln p_\varepsilon(n)\rangle$$

Also for bosons the probability of having exactly n particle in the state with energy ε is given by

$$p_\varepsilon(n) = \frac{\langle n_\varepsilon \rangle^n}{(\langle n_\varepsilon \rangle + 1)^{n+1}} \tag{1}$$

$$\ln p_\varepsilon(n) = n \ln \langle n_\varepsilon \rangle - (1+n) ln\left(\langle n_\varepsilon \rangle + 1\right) \tag{2}$$

Now substituting this to the general expression of entropy the inner summ over all n becomes

$$\begin{aligned} S &= -k \sum_\varepsilon \langle n \ln \langle n_\varepsilon \rangle - (1+n) ln\left(\langle n_\varepsilon \rangle + 1\right) \rangle \\ &= -k \sum_\varepsilon \langle n_\varepsilon \rangle \ln \langle n_\varepsilon \rangle - (1+\langle n_\varepsilon \rangle) ln\left(\langle n_\varepsilon \rangle + 1\right) \\ &= k \sum_\varepsilon \left[- \langle n_\varepsilon \rangle \ln \langle n_\varepsilon \rangle + \left(\langle n_\varepsilon \rangle + 1\right) ln\left(1 + \langle n_\varepsilon \rangle\right) \right] \end{aligned}$$

which shows that the general expression is true for bosons.
Substituting $a = 1$ for fermions we get

$$S = k \sum_\varepsilon \left[- \langle n_\varepsilon \rangle \ln \langle n_\varepsilon \rangle + \left(\langle n_\varepsilon \rangle - 1\right) ln\left(1 - \langle n_\varepsilon \rangle\right) \right]$$

Which is the required expression for the fermions entropy.
The probability of faving exactly $n = \{0, 1\}$ particles in the cell for fermoins is given by

$$p_\varepsilon(n) = \begin{cases} 1 - \langle n_\varepsilon \rangle & \text{if } n = 0 \\ \langle n_\varepsilon \rangle & \text{if } n = 1 \end{cases}$$

This gives only two terms in the inner sum of the general expression so

$$S = -k \sum_\varepsilon \left[\langle n_\varepsilon \rangle ln \langle n_\varepsilon \rangle + (1 - \langle n_\varepsilon \rangle \ln(1 - \langle n_\varepsilon \rangle)) \right]$$

Which shows that the general expression holds for fermions too. □

2. **(Pathria and Beale 6.2)** Derive for all three statistics, the relevant expressions for the quantity

$$\langle n_\varepsilon^2 \rangle - \langle n_\varepsilon \rangle^2 = kT \left(\frac{\partial \langle n_\varepsilon \rangle}{\partial \mu} \right)_T$$

Compare with the previous results that we showed in class,

$$\langle n^2 \rangle - \langle n \rangle^2 = kT \left(\frac{\partial \langle n \rangle}{\partial \mu} \right)_T$$

for a system embedded in a grand canonical ensemble.
Solution:
This problem is the find the first and second moments of n_ε and their difference. Once we know the probability mass function (pmf) of the variable finding moment quite generally is

$$\langle f(x) \rangle = \sum_x f(x) p(x)$$

where $p(x)$ is the pmf. Now for the bosons, (3) can be slightly rewritten as

$$p_\varepsilon(n) = \frac{\langle n_\varepsilon \rangle^n}{(\langle n_\varepsilon \rangle + 1)^{n+1}} = \frac{1}{\langle n_\varepsilon \rangle + 1} \frac{\langle n_\varepsilon \rangle^n}{(\langle n_\varepsilon \rangle + 1)^n} = \left(1 - \frac{\langle n_\varepsilon \rangle}{1 + \langle n_\varepsilon \rangle}\right) \left(\frac{\langle n_\varepsilon \rangle}{\langle n_\varepsilon \rangle + 1}\right)^n \tag{3}$$

With substitution $\frac{\langle n_\varepsilon \rangle}{1 + \langle n_\varepsilon \rangle} = t$ we get

$$p(n) = (1-t) t^n$$

Now the first moment of this pmf is

$$\langle n \rangle = \sum_{n=0}^{\infty} n(1-t)t^n = (1-t)\frac{t}{(1-t)^2} = \frac{t}{1-t} \qquad \because \frac{1}{(1-t)^2} = \sum_{n=0}^{\infty} nt^{n-1}$$

Similarly the second moment is

$$\left\langle n^2 \right\rangle = \sum_{n=0}^{\infty} n^2(1-t)t^n = (1-t)\frac{t(1+t)}{(1-t)^3} = \frac{t(1+t)}{(1-t)^2} \qquad \because$$

Thus the variance is

$$\left\langle n_\varepsilon^2 \right\rangle - \langle n_\varepsilon \rangle^2 = \frac{t(1+t)}{(1-t)^2} - \frac{t^2}{(1-t)^2} = \frac{t}{(1-t)^2}$$

Now substuting back the value of t we get

$$\left\langle n_\varepsilon^2 \right\rangle - \langle n_\varepsilon \rangle^2 = \langle n_\varepsilon \rangle + \langle n_\varepsilon \rangle^2$$

For the Fermions we get

$$\left\langle n_\varepsilon^2 \right\rangle = \sum_{n=0}^{1} n^2 p_(n) = p_(1) = \langle n_\varepsilon \rangle$$

This implies tht the variance is

$$\left\langle n_\varepsilon^2 \right\rangle - \langle n_\varepsilon \rangle^2 = \langle n_\varepsilon \rangle - \langle n_\varepsilon \rangle^2$$

For Boltzmann particle the pmf is a poisson distribution

$$p_\varepsilon(n) = \frac{\langle n_\varepsilon \rangle^n e^{-\langle n_\varepsilon \rangle}}{n!}$$

For poisson distribution is it can be easily shown that the mean and variance is just the parameter $\langle n_\varepsilon \rangle$ Thus we have

$$\left\langle n_\varepsilon^2 \right\rangle - \langle n_\varepsilon \rangle^2 = \langle n_\varepsilon \rangle$$

Looking at each of these three variances we see that it is of the general from

$$\left\langle n_\varepsilon^2 \right\rangle - \langle n_\varepsilon \rangle^2 = \langle n_\varepsilon \rangle - a\langle n_\varepsilon \rangle^2$$

Also the expectation value $\langle n_\varepsilon \rangle$ is given by

$$\langle n_\varepsilon \rangle = \frac{1}{z^{-1}e^{\beta\varepsilon} + a}$$

Differentiating this with respect to μ at constant temperature we get

$$\left[\frac{\partial \langle n_\varepsilon \rangle}{\partial \mu}\right]_T = \frac{\langle n_\varepsilon \rangle^2}{kT}\left[\frac{1}{\langle n_\varepsilon \rangle} - a\right]$$

Rearranging we get

$$KT\left[\frac{\partial \langle n_\varepsilon \rangle}{\partial \mu}\right]_T = -\langle n_\varepsilon \rangle - a\langle n_\varepsilon \rangle^2$$

Now the comparision of this expression for all the statistics leads to

$$\left\langle n_\varepsilon^2 \right\rangle - \langle n_\varepsilon \rangle^2 = KT\left[\frac{\partial \langle n_\varepsilon \rangle}{\partial \mu}\right]_T$$

This expression is true in general for all statistics. □

3. **(K. Huang 8.6)** What is the equilibrium ratio of ortho- to para-hydrogen at a temperature of 300 K? What is this ratio in the limit of high temperature? Assume that the distance between the protons in the molecule is 0.74 Angstrom.
Solution:
The equilibrium ratio is given by

$$\frac{N_{\text{ortho}}}{N_{\text{para}}} = 3\frac{\sum_{n=odd}(2n+1)e^{-\beta\hbar^2/2Il(l+1)}}{\sum_{n=even}(2n+1)e^{-\beta\hbar^2/2Il(l+1)}}$$

Evaluating this sum explicitly with series method we get For large values of n the ratio go to one because for large n the two quantities in Numerator and denomenator are essentially the same. So we get

$$\frac{N_{\text{ortho}}}{N_{\text{para}}} = 3$$

This gives the equilibrium ratio of ortho and para hydrogen in the temperature required. □

4. Consider the thermal properties of conducting electrons in a metal and treat electrons as non-interacting particles, when particle density is high. Assuming each Cu atom donates an electron to the conducting electron gas, calculate the chemical potential, or the Fermi energy, of copper, for which the mass density is $\frac{9g}{cm^3}$. Express your answer in Kelvin.
Solution:
The fermi energy is given by

$$E_f = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{\frac{2}{3}}$$

For Cu the density of atoms is

$$n = 8.5 \times 10^{28} m^{-3}$$

Thus we get the fermi energy equal to

$$E_f = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{\frac{2}{3}} = \frac{(6.6\times10^{-34})^2}{8\times9.1\times10^{-31}}\left(\frac{3}{\pi}8.5\times10^{28}\right)^{-\frac{2}{3}} = 1.1\times10^{-18} = 6.7eV$$

In kelvin this is equivalent to $6.7eV = 6.4 \times 10^4 K$ □