PHYS 522: Statistical Mechanics

Homework #2

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1. We mentioned in class that in calculating the matrix of $e^{-\beta\mathcal{H}}$, $\langle 1,2,3,N|e^{-\beta\mathcal{H}}|1,2,3,N\rangle$, permutation goth the particle coordinates in the first wave function and energy states in the second yields a result which is N! of the result for a fixed set of $\{k,\}$ states that is, without permuting the energy states. Do it explicitly of two particle and two state case starting with $u_a(1)u_b(2)$.
   Solution:
   The general matrix element for N particle n state system from Pathria eq (5.5.12) is

$$\langle 1,\ldots,N|e^{-\beta\mathcal{H}}|1',\ldots,N'\rangle = \frac{1}{N!}\sum_k e^{-\frac{\beta\hbar^2k^2}{2m}}\left[\sum_p \delta_p\left\{u_{k_1}(p_1)\ldots u_{kn}\right\}\right]\ldots\left[\sum_p \delta_p\left\{u^*_{k_1}(p_1)\ldots u^*_{kn}\right\}\right]$$

For two particle and two sate we get

$$\langle 1,2|e^{-\beta\mathcal{H}}|1',2'\rangle = \frac{1}{2!}\sum_k e^{-\frac{\beta\hbar^2k^2}{2m}}\left[u_a(1)u_b(2)\pm u_a(2)u_b(1)\right]\left[u^*_a(1)u^*_b(2)\pm u^*_a(2)u^*_b(1)\right]$$

Multiplying the wavefunctions we get

$$\langle 1,2|e^{-\beta\mathcal{H}}|1',2'\rangle = \frac{1}{2!}\sum_k e^{-\frac{\beta\hbar^2k^2}{2m}}\left[u_a(1)u_b(2)u^*_a(1)u^*_b(2)\pm u_a(1)u_b(2)u^*_a(1)u^*_b(2)\right.$$
$$\left.+u_a(1)u_b(2)u^*_a(1)u^*_b(2)\pm u_a(1)u_b(2)u^*_a(1)u^*_b(2)\right.$$

For the case of fixed $\{k_i\}$, i.e., if only the particles are permuted

$$\langle 1,2|e^{-\beta\mathcal{H}}|1',2'\rangle = \frac{1}{2!}\sum_k e^{-\frac{\beta\hbar^2k^2}{2m}}\left[u_a(1)u_b(2)u^*_a(1)u^*_b(2)\pm u_a(1)u_b(2)u^*_a(1)u^*_b(2)\right]$$

But since the density operator is hermition, the matrix elements are equal to the complex conjugate of itself with the coordinate exchanged

$$\langle 1,2|e^{-\beta\mathcal{H}}|1',2'\rangle = \langle 1,2|e^{-\beta\mathcal{H}}|2',1'\rangle^*$$

This would essentially mean

$$u_a(1)u^*_a(1')u_b(2)u^*_b(2') = u_a(2)u^*_a(2')u_b(1)u^*_b(1')$$
$$u_a(2)u^*_a(1')u_b(1)u^*_b(2') = u_a(1)u^*_a(2')u_b(1)u^*_b(2')$$

Using this in the sum we get

$$\langle 1,2|e^{-\beta\mathcal{H}}|1',2'\rangle = \frac{1}{2!}\sum_k e^{-\frac{\beta\hbar^2k^2}{2m}}\left[u_a(1)u_b(2)\pm u_a(2)u_b(1)\right]\left[u^*_a(1)u^*_b(2)\pm u^*_a(2)u^*_b(1)\right]$$
$$= \sum_k e^{-\frac{\beta\hbar^2k^2}{2m}}\left[u_a(1)u_b(2)u^*_a(1)u^*_b(2)\pm u_a(1)u_b(2)u^*_a(1)u^*_b(2)\right]$$

Here the last expression is exactly twice the expression for fixed $\{k_i\}$case. Where 2 is equal to the factorial of itself $2! = 2$ thus the rusult is $N!$ times the expression for fixed $\{k_i\}$ case. □

2. Study the density matrix and the partition function of a system of free particles, using un symmetrized wave function instead of symmetried wave function. Show that, following the text procedure, on encounters neighter th Gibbs' correction factor $\frac{1}{N!}$ nor a spatial correlation among the particles.
Solution:
If we used unsymmetrized wave function rather than symmetrized wave function we get

$$
\begin{aligned}
\langle 1,2,\ldots,N|e^{-\beta\mathcal{H}}|1,2,\ldots,N\rangle &= \sum_k e^{-\beta\frac{\hbar^2k^2}{2m}}(u_{k_1}(1)\ldots u_{k_n}(N))(u^*_{k_1}(1')\ldots u^*_{k_N}(N')) \\
&= \sum_{k_1,\ldots k_N} e^{\beta\hbar^2\frac{k_1^2+\ldots+k_N^2}{2m}}(u_{k_1}(1)\ldots u_{k_n}(N))(u^*_{k_1}(1')\ldots u^*_{k_N}(N'))
\end{aligned}
$$

The summation in the exponential can now be changed into product of the exponential and the expression becomes

$$
= \prod_{i=1}^{N}\left[e^{-\beta\hbar^2/2m}\left\{u_{k_i}(i)u^*_{k_j}(j')\right\}\right]
$$

Since the states are dense we can change the summation over k_i by the integration

$$
\langle 1,2,\ldots,N|e^{-\beta\mathcal{H}}|1,2,\ldots,N\rangle = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{\frac{3N}{2}}\exp\left(-\frac{m}{2\beta\hbar^2}\left(|r_1-r_2'|^2+\ldots|r_N-r_N'|^2\right)\right)
$$

From this expression its easy to calculate the diagonal elements, because for diagonal elements we have $r_i = r_i'$. This makes the exponential identically equal to zero and we get the matrix element

$$
\langle 1,2,\ldots,N|e^{-\beta\mathcal{H}}|1,2,\ldots,N\rangle = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{\frac{3N}{2}}
$$

Using the wavelength parameter

$$
\lambda = \sqrt{\frac{m}{2\pi\beta\hbar^2}}
$$

we get the Matrix element as

$$
\langle 1,2,\ldots,N|e^{-\beta\mathcal{H}}|1,2,\ldots,N\rangle = \left(\frac{1}{\lambda}\right)^{3N}
$$

Now the cannonical partition function is just the trace of this expression

$$
Q_N(T,V) = \mathrm{Tr}(e^{-\beta\mathcal{H}}) = \int\left(\frac{1}{\lambda}\right)^{3N} d^{3N}r = \left(\frac{V}{\lambda^3}\right)^N
$$

This expression has neigher the gibbs correction factor $\frac{1}{N!}$ nor the spatial correction factor. □

3. Determine the values of the degeneracy discriminant $n\lambda^3$ for hydrogen, helium and oxygen at NTP. Make an estimate of the respectivey temperature ranges where the magnitues of this quantity becomes coparamble to unity and hence quantum effects become important.
Solution:
The quantity $n\lambda^3$ can be written in terms of temperature and boltzman constant as

$$
n\lambda^3 = \frac{nh^3}{(2\pi mkT)^{3/2}} = \frac{N}{V}\frac{h^3}{(2\pi mkT)^{3/2}} = \frac{h^3P}{(2\pi m)^{3/2}(kT)^{5/2}} \tag{1}
$$

For standard temperature and pressure

$$
T = 293K and P = 1.01\times10^5
$$

Using the mass of Hiydrogen, Helium and Oxygen we get

$$H_2 : n\lambda^3 = \frac{6.63 \times 10^{-34} 1.01 \times 10^5}{2\pi(1.67 \times 10^{-27})^{3/2}(1.38 \times 10^{-23} \times 293)^{5/2}} = 2.86 \times 10^{-5}$$
$$He_2 : n\lambda^3 = \frac{6.63 \times 10^{-34} 1.01 \times 10^5}{2\pi(6.64 \times 10^{-27})^{3/2}(1.38 \times 10^{-23} \times 293)^{5/2}} = 3.61 \times 10^{-6}$$
$$O_2 : n\lambda^3 = \frac{6.63 \times 10^{-34} 1.01 \times 10^5}{2\pi(25.6 \times 10^{-27})^{3/2}(1.38 \times 10^{-23} \times 293)^{5/2}} = 4.78 \times 10^{-7}$$

INverting the relation (1) and setting $n\lambda^3 \simeq 1$ we get

$$T = \frac{1}{K}\left(\frac{h^6 P^2}{(2\pi m)^3}\right)^{1/5}$$

So for the different masses of H2, He2 and O2 we get

$$H_2 : T = 4.46K$$
$$He_2 : T = 1.95K$$
$$O_2 : T = 0.868K$$

This give the temperature in which the discriminant is close to 1. □

4. A system consists of three particles, each of which has three possible quantum states, which energy 0 , $2E$, or $5E$ respectively. Write out the complete expression of the cannonical partition function Q for this system:
   (a) if the articles obey Maxwells-Boltzman statistics.
   Solution:
   The single particle cannonical parition function for

$$Q_1(V,T) = \sum_n e^{-\beta E_n} = 1 + e^{-2\beta} + e^{-5\beta}$$

The cannonical partition function for N distinguishable particles is obtained by $Q_N(V,T) = \frac{1}{N!}\left[Q_1(V,T)\right]^N$ So for three particles we get

$$Q_3(V,T) = \frac{1}{3!}\left[1 + e^{-2\beta} + e^{-5\beta}\right]^3$$

The free energy of the system is

$$F = kT \ln Q = kT \ln\left(\frac{1}{6}\left[1 + e^{-2\beta E} + e^{-5\beta E}\right]^3\right) = -kT \ln 6 + 3kT \ln\left(1 + e^{-2\beta E} + e^{-5\beta E}\right)$$

The entropy is given by

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V}$$
$$= \frac{Tk\left(\frac{6Ee^{-\frac{2E}{Tk}}}{T^2 k} + \frac{15Ee^{-\frac{5E}{Tk}}}{T^2 k}\right)}{1 + e^{-\frac{2E}{Tk}} + e^{-\frac{5E}{Tk}}} + k \ln\left(\frac{\left(1 + e^{-\frac{2E}{Tk}} + e^{-\frac{5E}{Tk}}\right)^3}{6}\right)$$

This gives the expression for the entropy of the particles. □

   (b) if they obey Bose-Einstein statistics,
   Solution:
   For bose einstein case, the particle sare counted indistinguishable. So each of the three particle can belong to following energy state So the total partition function of the system becomes

n0,n1,n2	5,0,2	5,5,2	5,5,0	5,2,2	0,2,2	5,0,0	0,2,0	5,5,5	2,2,2	0,0,0
Total Energy	7E	12E	10E	9E	4E	5E	2E	15 E	6E	0

$$Q_N(T,V) = 1 + e^{-2E\beta} + e^{-4E\beta} + e^{-5E\beta} + e^{-6E\beta} + e^{-7E\beta} + e^{-9E\beta} + e^{-10E\beta} + e^{-12E\beta} + e^{-15E\beta}$$

Similarly the free energy is given by $F = kT \ln Q_N(V,T)$ and the entropy is given by $S = -\frac{\partial F}{\partial T}$ This gives the expression for the entropy of the particles. □

(c) if they obey Fermi-Dirac statistics,
Solution:
For the particle satisfying Fermi-Dirac statistics no two particles can occupy the same energy levels so each has to sit on its own energy leven which gives the partition function

$$Q_N(V,T) = \left[1 + e^{-2\beta E} + e^{-5\beta E}\right]$$

The free energy of the system is

$$F = Tk \log\left(1 + e^{-\frac{2E}{Tk}} + e^{-\frac{5E}{Tk}}\right)$$

So the entropy becomes

$$S = -\frac{\partial F}{\partial T} = -\frac{E\left(2e^{3E\beta} + 5\right)}{T\left(e^{5E\beta} + e^{3E\beta} + 1\right)} - k\log\left(1 + e^{-2E\beta} + e^{-5E\beta}\right)$$

This gives the entropy of particles for Fermi-Dirac statistics. □