Thermodynamics: Classical to Statistical
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Lecture 16
Introduction to Molecular Partition Function

The probability in canonical ensemble,

$$p_j\,(N, V, T) = \sum_j e^{-\beta E_j(N,V)} \text{ where } \beta = \frac{1}{k_B T}$$

$$E_j(N,V) = \epsilon_{1j} + \epsilon_{2j} + \ldots\ldots\ldots\ldots + \epsilon_{Nj}$$

Where ϵ_{1j} = energy of the particle '1' in the j-th state

ϵ_{2j} = energy of the particle '2' in the j-th state and so on

Now, if we substitute the value of E_j into p_j or if substitute directly the value of E_j into the canonical partition function Q,

$$Q\,(N, V, T) = \sum_j e^{-\beta E_j(N,V)}$$

$$\Rightarrow \quad Q\,(N, V, T) = \sum_j e^{-\beta(\epsilon_{1j}+\epsilon_{2j}+\cdots+\epsilon_{Nj})}$$

$$\Rightarrow \quad Q\,(N, V, T) = \sum_j e^{-\beta\epsilon_{1j}} \sum_j e^{-\beta\epsilon_{2j}} \ldots\ldots\ldots\ldots \sum_j e^{-\beta\epsilon_{Nj}}$$

Now, if all the particles are the same, then it is not necessary to level them, so we can omit 1, 2, 3 those terms. We can write

$$Q\,(N, V, T) = \sum_j e^{-\beta\epsilon_j} \sum_j e^{-\beta\epsilon_j} \ldots\ldots\ldots\ldots \sum_j e^{-\beta\epsilon_j} \text{ [N number of terms]}$$

$$Q\,(N, V, T) = \left(\sum_j e^{-\beta\epsilon_{j(V)}} \right)^N$$

$$Q\,(N, V, T) = q^N$$

Where q is molecular partition function

$$q = \left(\sum_j e^{-\beta\epsilon_{j(V)}} \right)$$

for distinguishable particles $Q\,(N, V, T) = \frac{q^N}{N!}$

So, we reduces the N body problem into N number of single body problems.

So next we will discuss more about molecular partition function. Suppose we have total N number of distinguishable particles, out of these capital N number of distinguishable particles, out of N number of particles, n_1 number of particles are present in energy state $^{\epsilon}1$. similarly, n_2 number of particles are present in energy state $^{\epsilon}2$ and so on. We can write

$$\sum_i n_i = N = \text{constant} \ldots\ldots\ldots\ldots..(1)$$

$$\sum_i n_i \in_i = E = \text{constant} \ldots\ldots\ldots\ldots(2)$$

We are distributing capital N number of particles in different energy state. So a general configuration can be achieved in W different ways. So we can write

$$W(n_1, n_2, \ldots..) = \frac{N!}{n_1!\, n_2!} \ldots\ldots\ldots\ldots..(3)$$

Suppose for simplicity, we have 3 distinguishable particles, rather we can consider 3 balls red, we say red is R, blue, we denote blue as B and we have yellow ball and we define yellow by Y and we have 3 baskets. In first case we have all 3 balls in basket 1, we consider 3 basket as b1, b2 and b3.

Now

Case I. suppose we consider that all 3 baskets are present in basket 1.

b1	b2	b3
R B Y		

So, $$W = \frac{3}{3! \times 0! \times 0!} = 1$$

Case II. Two balls are present in b1 and 1 ball is present in basket b2. Let us see how many ways we can put.

b1	b2	b3
R B	Y	

b1	b2	b3
R Y	B	

b1	b2	b3
BY	R	

So $$W = \frac{3}{2! \times 1! \times 0!} = 3$$

Case III. Each basket contains one ball.

b1	b2	b3
R	B	Y

b1	b2	b3
B	Y	R

b1	b2	b3
Y	B	R

b1	b2	b3
B	R	Y

b1	b2	b3
Y	R	B

b1	b2	b3
R	Y	B

So, $$W = \frac{3}{1! \times 1! \times 1!} = 6$$

So, higher the weight W, higher will be the probability of the system to be found in the particular configuration, but equations 1 and 2 must be satisfied.

So $$W = \frac{N!}{n_1!\, n_2!}$$

$$\ln W = \ln N! - \ln n_1! - \ln n_2! \ldots\ldots\ldots\ldots\ldots$$

by using Stirling approximation that is $\ln x! = x \ln x - x$, we get

$$\ln W = N \ln N - N - \sum_i (n_i \ln n_i - n_i)$$

$$\ln W = N \ln N - N - \sum_i n_i \ln n_i - \sum_i n_i$$

$$\ln W = N \ln N - N - \sum_i n_i \ln n_i - N$$

$$\ln W = N \ln N - \sum_i n_i \ln n_i$$

so in order to get the configuration for which W has its maximum we need to do differentiation

$$d\ln W = d(N \ln N) - \sum_i n_i \ln dn_i$$

$$d\ln W = \sum_i \left(\frac{\partial \ln w}{\partial n_i}\right) dn_i$$

Again, $$\sum_i n_i = N = \text{constant}$$

So, $\sum_i dn_i = 0$

Similarly, $\sum_i n_i \in_i = E =$ constant

$\Rightarrow \sum_i \in_i dn_i = 0$

$$\mathrm{dln}\ W = \sum_i \left(\frac{\partial \ln w}{\partial n_i}\right) + \alpha - \beta \in_i \int dn_i$$

where α and – β are Lagrange's multipliers.

Since, $dn_i \neq 0$

$$\sum_i \left(\frac{\partial \ln w}{\partial n_i}\right) + \alpha - \beta \in_i \neq 0$$

This is true for every 'i' value

$$\Rightarrow -\ln n_i + 1 + \alpha - \beta \in_i = 0$$

1 can be neglected in comparison to n_i

$$\Rightarrow -\ln n_i + \alpha - \beta \in_i = 0$$

$$\Rightarrow n_i = e^{\alpha} e^{-\beta \epsilon_i}$$

Now $\sum_i n_i = N$

$$\Rightarrow \sum_i e^{\alpha} e^{-\beta \epsilon_i} = N$$

$$\Rightarrow e^{\alpha} = \frac{N}{\sum_i^N e^{-\beta \epsilon_i}}$$

$$n_i = \frac{N e^{-\beta \epsilon_i}}{\sum_i e^{-\beta \epsilon_i}}$$ [here 'i' is state]

$$\Rightarrow \frac{n_i}{N} = p_i = \frac{e^{-\beta \epsilon_i}}{\sum_i e^{-\beta \epsilon_i}}$$ ⇒ This is Boltzman distribution law

If we consider degeneracy we get,

$$\frac{n_i}{N} = \frac{g_i e^{-\beta\epsilon_i}}{\sum_i g_i e^{-\beta\epsilon_i}}$$ [where gi is the degeneracy of ith state]

$$Q\ (N, V, T) = \sum_j e^{-\beta E_j(N,V)}$$

$$\Rightarrow \quad Q\ (N, V, T) = q^N$$ for distinguishable particles

$$q = \sum_j e^{-\beta\epsilon_i\ (V)}$$

To calculate partition function of N number of particles or capital Q we need to calculate q because we decompose the N body problem into N number of single body problems. Once we get the capital Q we can calculate different thermodynamic quantities.

So our goal at this moment is to calculate q or molecular partition function. So for this we consider the simplest system one can think of that is ideal mono atomic gas.

So next we discuss ideal mono atomic gas. A mono atomic gas has translational, electronic and nuclear degrees of freedom. The translational Hamiltonian is separable from the electronic and nuclear degrees of freedom and electronic and nuclear Hamiltonians are separable to a very good approximation. So, we can write

$$q\ (V, T) = q_{trans}\ q_{elec}\ q_{nucl}$$

while q_{trans} is the translational partition function, q_{elec} is electronic partition function and q_{nucl} is nuclear partition function.

So once we calculate q trans, q electronic and q nuclear we can calculate q for ideal mono atomic gas. In order to calculate the translational partition function, we consider particle in 3 dimensional box of edge length ‘a’. So the expression for energy in particle in 3 dimensional box is

$$\epsilon_{n_{x,}n_{y,}n_z} = \left(\frac{n_x^2+n_y^2+n_z^2}{8ma^2}\right)h^2$$

$$q_{\mathrm{trans}} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-\beta \epsilon_{n_x n_y n_z}}$$

Now, if we substitute the values of epsilon n_x, n_y, n_z, here we get

$$q_{\mathrm{trans}} = \sum_{n_x=1}^{\infty} e^{-\frac{\beta n_x^2 h^2}{8ma^2}} \sum_{n_y=1}^{\infty} e^{-\frac{\beta n_y^2 h^2}{8ma^2}} \sum_{n_z=1}^{\infty} e^{-\frac{\beta n_z^2 h^2}{8ma^2}}$$

$$q_{\mathrm{trans}} = \left(\sum_{n=1}^{\infty} e^{-\frac{\beta n^2 h^2}{8ma^2}}\right)^3$$

The power 3 represents the dimensionality of the box

Now for or at room temperature the successive terms in the summation differ so little from each other that the terms vary essentially continuously and the summation can be replaced by integral or integration.

$$q_{\mathrm{trans}}(V,T) = \left(\int_0^{\infty} e^{-\frac{\beta n^2 h^2}{8ma^2}} dn\right)^3$$

$$q_{\mathrm{trans}}(V,T) = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V$$

Where V = volume of the box = a^3

Suppose $\Lambda = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2}$

$$q_{\mathrm{trans}} = \frac{V}{\Lambda^3}$$

This is the expression for translational partition function.

Unit of Λ

$$\Lambda = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2}$$

So Λ has dimension of length.