



# Partition Function of a Classical Gas

(Post-Graduate Level)

Course Code: MPHYCC-8

By

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### Partition Function:

The partition function is an important quantity in statistical mechanics, which describe and explain the statistical properties of a system in thermodynamic equilibrium.

For a canonical ensemble that is classical and discrete, the canonical partition function is defined as

$$Z = \sum_i e^{-\beta \epsilon_i} \dots\dots\dots(1)$$

Where,

$\epsilon_i$  = Total energy of the system in the  $i^{th}$  microstate

$$\beta = \frac{1}{k_\beta T}$$

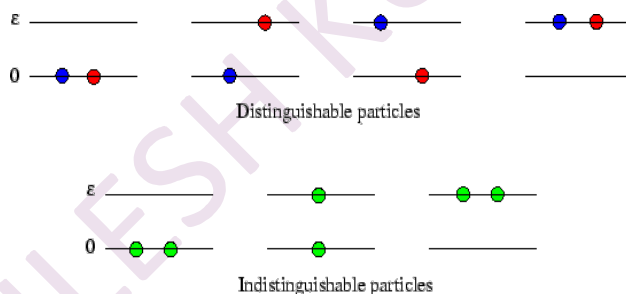
$k_\beta$  = Boltzmann Constant

The exponential factor  $e^{-\beta \epsilon_i}$  known as the Boltzmann factor

## Partition Function of N number of Particles.

Considering the simplest case of two particles distributed in two energy levels 0 and  $\epsilon$ . If the particles are distinguishable, there are four states, two of which have energy  $\epsilon$ , and the partition function of two-particles is given as:

$$Z_2 = e^0 + 2e^{-\beta\epsilon} + e^{-2\beta\epsilon} \quad \dots\dots\dots(2)$$



If the particles are *indistinguishable*, however there are only three possible states. The distribution of distinguishable and indistinguishable particles is shown in the above figure. The partition function of indistinguishable two particles is given as:

$$Z_2 = e^0 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} \quad \dots\dots\dots(3)$$

Partition function for two distinguishable and indistinguishable particles is given by equation (2) and (3) respectively.

If we use  $(Z_1)^2$ , we over-count the number of state of the distribution of particles in different energy levels. In general there is no simple expression for the N-particle partition function for indistinguishable particles.

However we observe that  $(Z_1)^N$  over-counts the states in which all N particles are in different energy levels by exactly  $N!$ . So if there are many accessible energy levels, the probability of any two particles being in the same energy level is small, and almost all states will have all the particles in different levels. Hence a good approximation for finding the partition function of N particles is:

$$Z_N = \frac{1}{N!} (Z_1)^N \quad \dots\dots\dots(4)$$

## Partition Function of a Classical Gas

Classical gases are kept at high temperature so that there is very low interaction between the gas molecules/atoms. The separation between the gas molecules/atoms should be sufficiently large so that the De-Broglie wavelength of the gas molecules/atoms does not overlap on each other.

Consider a monatomic ideal gas consisting of  $N$  identical atoms of mass  $m$  each having translational degrees of freedom  $f = 3$  and obeying the ideal gas law,

$$PV = nk_{\beta}T \dots\dots\dots(5)$$

Classical gases obey the Maxwell-Boltzmann law and classical statistics.

The ideal gas is composed of noninteracting atoms. A monatomic gas can be considered to consist of point masses, which have linear kinetic energy but no rotational kinetic energy, no vibrational energy and no internal excitations.

Thus the total energy of an N particle ideal monatomic gas is

$$E = \sum_{i=1}^N \frac{\vec{P}_i \cdot \vec{P}_i}{2m} \dots\dots\dots(6)$$

Partition function of N identical atoms is given by equation (4) as

$$Z_N = \frac{1}{N!} (Z_1)^N$$

Now we need to write the partition function of a single particle having only translational kinetic energy.

Using equation (1)

$$Z_{TR} = \sum e^{-\beta \frac{p^2}{2m}} \quad (\text{For non-degenerate state})$$

(Degeneracy factor may be included for degenerate states.)

Elementary volume of the phase space

$$\int dV = \iiint dx dy dz \iiint dp_x dp_y dp_z = \iint d^3 r d^3 p = V(4\pi) \int p^2 dp$$

$$= h^3 = \text{Phase space volume of a single quantum state}$$

(According to Heisenberg uncertainty principle  $\Delta x \Delta p \approx h$ )

Now,

Partition function for a single quantum state of a classical gas is therefore given as

$$\begin{aligned}
 Z_{TR} &= \iint \frac{d^3r d^3p}{h^3} e^{-\beta \cdot \frac{p^2}{2m}} \\
 &= \frac{4\pi V}{h^3} \int p^2 e^{-\beta \frac{p^2}{2m}} dp \\
 &= - \frac{2\pi V}{h^3} \frac{d}{d\alpha} \int_{-\infty}^{+\infty} e^{-\alpha p^2} dp \quad \text{where, } \alpha = \frac{\beta}{2m} \\
 &= - \frac{2\pi V}{h^3} \frac{d}{d\alpha} \sqrt{\frac{\pi}{\alpha}} \\
 &= V \left( \frac{2\pi m k T}{h^2} \right)^{3/2} \\
 Z_{TR} &= \frac{V}{h^3} (2\pi m k T)^{3/2} \dots\dots\dots(7)
 \end{aligned}$$

Equation (7) represents the partition function of a single quantum state classical gas.

For continuous energy distribution

$$Z = \int_0^{\infty} g(E).e^{-\beta E} dE \quad \dots\dots\dots(8)$$

Where,  $g(E) =$  Density of states (DOS)

$$g(E) = \frac{2\pi V}{h^3} (2m)^{3/2} .E^{1/2} \quad \dots\dots\dots(9)$$

$$Z = \int_0^{\infty} \frac{2\pi V}{h^3} (2m)^{3/2} .e^{-\beta E} dE$$

$$Z = \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^{\infty} E^{1/2} .e^{-\beta E} dE \quad \dots\dots\dots(10)$$

$$\int_0^{\infty} x^n .e^{-ax^m} = \frac{1}{m} \frac{\Gamma\left(\frac{n+1}{m}\right)}{\left(\frac{n+1}{m}\right)} \quad \text{for } n = \frac{1}{2} \quad m = 1 \quad \text{and } a = \beta$$

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$$Z = \frac{2\pi V}{h^3} (2m)^{\frac{3}{2}} \frac{\sqrt{\frac{3}{2}}}{\beta^{3/2}}$$

$$Z = \frac{2\pi V}{h^3} (2m)^{\frac{3}{2}} \cdot \frac{\frac{1}{2} \sqrt{\pi}}{\left(\frac{1}{k_{\beta} T}\right)^{\frac{3}{2}}}$$

$$Z = \frac{2\pi V}{h^3} (2m)^{\frac{3}{2}} \frac{1}{2} \sqrt{\pi} (k_{\beta} T)^{3/2}$$

$$Z = \frac{V}{h^3} (2\pi m k T)^{\frac{3}{2}}$$

The above expression of the partition function of a classical gas of continuous energy distribution is same as given in equation (7).