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C14T (Statistical Mechanics) , Topic :- Entropy of Photon Gas

❖ Entropy of photon gas :

The most probable BE-distribution is given by

$$N_i = \frac{g_i}{e^{\alpha + \beta \epsilon_i} - 1} = \frac{g_i}{e^{\beta \epsilon_i} - 1} \quad (\alpha = 0 \text{ for photon})$$

Maximum entropy S_{\max} is given

$$\begin{aligned} S_{\max} &= k \sum [(g_i + N_i) \ln(N_i + g_i) - g_i \ln g_i - N_i \ln N_i] \\ &= k \sum [(g_i) \ln \left(1 + \frac{N_i}{g_i}\right) + N_i \ln \left(1 + \frac{g_i}{N_i}\right)] \\ &= k \sum [g_i \ln \left(1 + \frac{1}{e^{\beta \epsilon_i} - 1}\right) + N_i \ln(e^{\beta \epsilon_i})] \\ &= k \sum N_i \beta \epsilon_i + k \sum g_i \ln \frac{e^{\beta \epsilon_i}}{e^{\beta \epsilon_i} - 1} \\ &= T^{-1} \sum N_i E_i + k \sum g_i \ln \frac{e^{\beta \epsilon_i}}{1 - e^{-\beta \epsilon_i}} \\ &= \frac{8\pi^5 k^4}{15c^3 h^3} VT^3 - k \int_0^\infty \frac{8\pi v_i^3 dv_i}{c^3} \ln(1 - e^{\frac{hv_i}{kT}}) V \\ &= \frac{8\pi^5 k^4}{15c^3 h^3} VT^3 - \frac{8\pi V}{c^3} \int_0^\infty v_i^2 \ln((1 - e^{\frac{hv_i}{kT}}) dv_i \quad \dots\dots\dots(1) \end{aligned}$$

The integral of the second term of R.H.S can be evaluated by parts . The result is $-\frac{1}{45} k^3 T^3 \pi^4 / h^3$.

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Identical with the expression for entropy of equilibrium radiation in an enclosure of volume V , obtained classically where $A = \frac{8\pi^5 k^4}{15c^3 h^3}$.

❖ **Phase volume and eigenstates :**

The relation between the number of unit cells and the number of eigenstates would help to understand the correlation between classical and quantum statistics.

Volume element in phase space for a system with f degrees of freedom is

$$dq_1 dq_2 \dots \dots dq_f dp_1 dp_2 \dots \dots dp_f$$

$$\text{Total phase volume} = \int_{-\infty}^{\infty} dq_1 dq_2 \dots \dots dq_f dp_1 dp_2 \dots \dots dp_f$$

Now, the dimensions of $pq = [M^1 L^2 T^{-1}]$, so that for a system having D.O.F = f , the dimension of volume in phase space = $[M^1 L^2 T^{-1}]^f$. Planck's constant h has also the dimension $[M^1 L^2 T^{-1}]$. So, we may reasonably identify the volume

$$dq_1 dq_2 \dots \dots dq_f dp_1 dp_2 \dots \dots dp_f = h^f$$

No. of eigenstates for a system is then

$$g = \frac{1}{h^f} \int_{-\infty}^{\infty} dq_1 dq_2 \dots \dots dq_f dp_1 dp_2 \dots \dots dp_f$$

$$g = \frac{\text{Total phase volume}}{h^f}$$

❖ **Number of eigenstates in an energy range : Density of States**

Quantum mechanically, the energy eigen values i.e., quantized energies of a particle of mass m in a three - dimensional potential box of edges l_x, l_y and l_z are given by

$$E = \frac{h^2}{2m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) \dots \dots \dots (2)$$

Where n_x, n_y and n_z are integers, and h is Planck's constant.

The allowed momentum components p_x, p_y and p_z are (since $p^2 = 2mE$)

$$p_x = \frac{hn_x}{l_x}; p_y = \frac{hn_y}{l_y}; p_z = \frac{hn_z}{l_z} \dots\dots\dots (3)$$

For a microscopic volume, l_x 's are large. So, the above allowed momentum components are closely spaced. For a small change dp_x in p_x , there will therefore be many allowed states for different n_x 's. The number Δn_x of the integers n_x for which p_x lies between p_x and $p_x + dp_x$ is from eqn.(3)

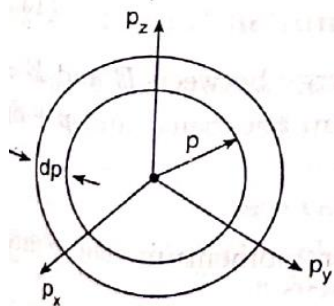
$$\begin{aligned} \Delta n_x &= \frac{l_x}{h} dp_x \\ \Delta n_y &= \frac{l_y}{h} dp_y \dots\dots\dots (4) \\ \Delta n_z &= \frac{l_z}{h} dp_z \end{aligned}$$

The number of states for which the momentum components (a) p_x and $p_x + dp_x$, (b) p_y and $p_y + dp_y$, and (c) p_z and $p_z + dp_z$, that is, $g(p)dp$ is given by the product

$$\begin{aligned} \Delta n_x \Delta n_y \Delta n_z &= \frac{l_x l_y l_z}{h^3} dp_x dp_y dp_z \\ &= \frac{V}{h^3} dp_x dp_y dp_z \dots\dots\dots (5) \end{aligned}$$

Where $l_x l_y l_z$ is the volume V of the potential.

Now, $dp_x dp_y dp_z$ represents a volume element in momentum space and is thus the volume enclosed between two concentric spheres of radii p and $p+dp$. This is simply $4\pi p^2 dp$ (Fig.1).



$$g(p)dp = \frac{V}{h^3} 4\pi p^2 dp \quad \dots\dots\dots (6)$$

This equation indicates that the number of quantum states for the particle is obtained by dividing the phase space into cells each of volume h^3 , where h is the Planck's constant.

Switching over from the momentum p to the energy E via the relation $p^2 = 2mE$ and $dp = \frac{mdE}{\sqrt{2mE}}$

We have

$$g(E)dE = \frac{V}{h^3} \frac{4\pi(2mE)mdE}{\sqrt{2mE}} = \frac{4\pi mV}{h^3} (2mE)^{\frac{1}{2}}dE \quad \dots\dots\dots(7)$$

Which is the number of eigenstates in energy range E and $E + dE$.

The function $g(E)$ gives the number of quantum states per unit energy range at the given energy E and is known as the density of (quantum) states.

- Since an electron has two independent directions of spin orientation, equation (7) will be modified as

$$g(E)dE = \frac{8\pi mV}{h^3} (2mE)^{\frac{1}{2}}dE \quad \text{for electron particles}$$