PHYS 3014: Statistical Mechanics

Lecture Notes
Part 18

Photon Gas : Black Body Radiation

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Single Particle density of states of photons

In K-space, the density of states i.e the number of states having wave vector in the range K and K+dK is

$$g(K)\,dK = V\frac{K^2 dK}{2\pi^2}$$, V is the volume of enclosure.

The energy of a photon of frequency ν is

$$\epsilon = h\nu$$
$$= \frac{hc}{\lambda}$$
$$= \hbar K c$$, K = wave vector, c = velocity of light

For electromagnetic wave of angular frequency $\omega = 2\pi\nu$, we have $\omega = cK$.

Therefore, the density of states of photons having energy in the range ϵ and $\epsilon + d\epsilon$ is

$$g(\epsilon)\, d\epsilon = 2 \cdot \frac{V \cdot \left(\frac{\epsilon}{\hbar c}\right)^2 \left(\frac{d\epsilon}{\hbar c}\right)}{2\pi^2}$$

, the electromagnetic wave has two state of polarization.

or: $$g(\epsilon) d\epsilon = V \frac{\epsilon^2 d\epsilon}{\pi^2 \hbar^3 c^3}$$

in terms of ω,

no. of photon states in which photon has angular frequency in the range ω and $\omega + d\omega$ is

$$g(\omega) d\omega = V \frac{\hbar^2 \omega^2 \hbar d\omega}{\pi^2 \hbar^3 c^3}$$

$$= V \frac{\omega^2 d\omega}{\pi^2 c^3}$$

$\therefore$ No. of states per unit volume will be $\frac{\omega^2 d\omega}{\pi^2 c^3}$.

Black-body Radiation (Photon Gas)

Photons have unit spin so are bosons. The electromagnetic radiation can be considered as consisting of non-interacting photons each of energy $h\nu$ where ν is the frequency of electromagnetic radiation. The electromagnetic radiation in an enclosure is called as black body radiation. If there is radiation in an enclosure at temperature T, equilibrium is established and maintained by the interactions of the photons with the atoms of the wall of the enclosure. Since the atoms emit and absorb photons, the total no. of photons in the enclosure is not conserved.

The Helmholtz free energy F must be minimum at constant T and V in the thermodynamic equilibrium.

i.e $dF = -Pdv + \mu dN - sdT = 0$

but dN is not zero for photon gas in enclosure.

$\therefore \quad dF = 0$

$\Rightarrow \quad \mu dN = 0$

$\Rightarrow \quad \mu = 0$

So chemical potential of photon vanishes.

Photon Statistics

In context of black body radiation, inside an enclosure the number of photons is not conserved because photons are continuously absorbed or emitted by the atoms of the wall of enclosure. So we can use either canonical or grand canonical ensemble.

Consider canonical ensemble and a photon gas in equilibrium at temperature T. The total energy of the system of photon gas in state s is

$$E_s = n_1\epsilon_1 + n_2\epsilon_2 + n_3\epsilon_3 + \cdots$$

where n_i is the number of photons with energy ϵ_i. For photons, each n_i can take values $0, 1, 2, 3, \cdots$.
The canonical partition function

$$Z(T,V) = \sum_{s} e^{-\beta E_s}$$

$$= \sum_{n_1, n_2, n_3 \cdots}^{\infty} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + n_3\epsilon_3 + \cdots)}$$

$$= \left(\sum_{n_1=0}^{\infty} e^{-\beta n_1\epsilon_1}\right)\left(\sum_{n_2=0}^{\infty} e^{-\beta n_2\epsilon_2}\right)\left(\sum_{n_3=0}^{\infty} e^{-\beta n_3\epsilon_3}\right)\cdots$$

$$= \prod_{i} \sum_{n_i=0}^{\infty} e^{-\beta n_i\epsilon_i}$$

$$\therefore \quad Z(T,V) = \left(\frac{1}{1-e^{-\beta\epsilon_1}}\right)\left(\frac{1}{1-e^{-\beta\epsilon_2}}\right)\left(\frac{1}{1-e^{-\beta\epsilon_3}}\right) - - - -$$

$$\therefore \quad Z(T,V) = \prod_i \frac{1}{1-e^{-\beta\epsilon_i}}$$

$$\therefore \quad \ln Z(T,V) = -\sum_i \ln\left(1-e^{-\beta\epsilon_i}\right)$$

$\therefore$ mean number of photons $\bar{n}_k$ in an energy state ϵ_k is

$$\bar{n}_k = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \epsilon_k}$$

Differentiation w.r.t. one term involving ϵ_k

$$= \frac{e^{-\beta\epsilon_k}}{1-e^{-\beta\epsilon_k}}$$

$$\therefore \quad \boxed{\bar{n}_k = \frac{1}{e^{\beta\epsilon_k}-1}}$$

It is called the Planck distribution.

This distribution can also be obtained as follows.

$\exp\{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + n_3\epsilon_3 + \cdots)\}$ is the relative probability of finding the photon gas in a state where n_1 photons are in state with ϵ_1, n_2 are in state with ϵ_2 etc. Therefore, the mean number of particles in state i is

$$\bar{n}_i = \frac{\sum\limits_{n_1, n_2, n_3 \cdots}^{\infty} n_i \exp\{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)\}}{\sum\limits_{n_1, n_2, n_3 \cdots}^{\infty} \exp\{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)\}}$$

$$= \frac{\sum\limits_{n_i} n_i \exp(-\beta n_i \epsilon_i) \sum\limits_{n_1, n_2, n_3 \cdots}^{(i)} \exp\{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)\}}{\sum\limits_{n_i} \exp(-\beta n_i \epsilon_i) \sum\limits_{n_1, n_2, n_3 \cdots}^{(i)} \exp\{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)\}}$$

where summation $\Sigma^{(i)}$ does not contain particular state i. n_i can take values $0, 1, 2, 3, \ldots$

$\therefore$ mean number of photons in state with ϵ_i

$$\bar{n}_i = \frac{\sum_{n_i} n_i \exp(-\beta n_i \epsilon_i)}{\sum_{n_i} \exp(-\beta n_i \epsilon_i)}$$

$$= \frac{-\frac{1}{\beta}\frac{\partial}{\partial \epsilon_i}\left\{\sum_{n_i} \exp(-\beta n_i \epsilon_i)\right\}}{\sum_{n_i} \exp(-\beta n_i \epsilon_i)}$$

$$= -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_i}\left[\ln\left\{\sum_{n_i} \exp(-\beta n_i \epsilon_i)\right\}\right]$$

$$= -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_i}\left[\ln\left(\frac{1}{1-e^{-\beta \epsilon_i}}\right)\right]$$

$$= \frac{1}{\beta}\frac{\partial}{\partial \epsilon_i}\left\{\ln\left(1-e^{-\beta \epsilon_i}\right)\right\}$$

$$\therefore \quad \bar{n}_i = \frac{e^{-\beta \epsilon_i}}{1 - e^{-\beta \epsilon_i}}$$

or,
$$\boxed{\bar{n}_i = \frac{1}{e^{\beta \epsilon_i} - 1}}$$

This can also be obtained with grand canonical ensemble.

The grand partition function for a single level ϵ_i where n_i particles are distributed and n_i can take values $0, 1, 2, 3, \ldots$ etc. is

$$Z_i = \mathcal{Z}_a = \sum_{n_i} \exp[n_i \beta(\mu - \epsilon_i)]$$

For photons, $\mu = 0$

$$\therefore \quad Z = \sum_{n_i} \exp(-\beta n_i \epsilon_i)$$

$\therefore$ average or mean number of particles distributed in levels with energy ϵ_i

$$\bar{n}_i = \frac{\sum_{n_i} n_i \exp(-\beta n_i \epsilon_i)}{\sum_{n_i} \exp(-\beta n_i \epsilon_i)}$$

$$= \frac{-\frac{1}{\beta}\frac{\partial}{\partial \epsilon_i}\left\{\sum_{n_i} \exp(-\beta n_i \epsilon_i)\right\}}{\sum_{n_i} \exp(-\beta n_i \epsilon_i)}$$

$$= -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_i}\left[\ln\left\{\sum_{n_i} \exp(-\beta n_i \epsilon_i)\right\}\right]$$

$$= -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_i}\left[\ln \frac{1}{1-e^{-\beta\epsilon_i}}\right] = \frac{1}{\beta}\frac{\partial}{\partial \epsilon_i} \ln(1-e^{-\beta\epsilon_i})$$

$$\therefore \quad \bar{n}_i = \frac{e^{-\beta\epsilon_i}}{1-e^{-\beta\epsilon_i}}$$

or, $$\boxed{\bar{n}_i = \frac{1}{e^{\beta\epsilon_i}-1}}$$ Planck distribution

Planck's law of black body radiation

Planck's derivation

Consider a black body enclosure in which radiation is filled at temperature T. The volume of enclosure is V. The system can be considered as consisting of an assembly of harmonic oscillators with quantized energies $n\hbar\omega$ where $n = 0, 1, 2, 3, \cdots$ and ω is the frequency of an oscillator. The oscillators are distinguishable from one another and obey M-B statistics.

The average value of energy of a Planck oscillator of frequency ω is

$$\bar{\epsilon}_n = \frac{\sum_n \epsilon_n e^{-\beta\epsilon_n}}{\sum_n e^{-\beta\epsilon_n}}$$

$$= -\frac{\frac{\partial}{\partial \beta}\left(\sum_n e^{-\beta \epsilon_n}\right)}{\sum_n e^{-\beta \epsilon_n}}$$

$$= -\frac{\partial}{\partial \beta} \ln\left[\sum_n e^{-\beta \epsilon_n}\right]$$

$$= -\frac{\partial}{\partial \beta} \ln\left[1 + e^{-\beta \hbar \omega} + e^{-2\beta \hbar \omega} + e^{-3\beta \hbar \omega} + \cdots\right]$$

$$= -\frac{\partial}{\partial \beta} \ln \cdot \left(\frac{1}{1 - e^{-\hbar \omega \beta}}\right)$$

$$= \frac{\partial}{\partial \beta} \ln\left(1 - e^{-\hbar \omega \beta}\right)$$

$$= \frac{1}{1 - e^{-\hbar \omega \beta}} \left(-e^{-\hbar \omega \beta}\right) \cdot (-\hbar \omega)$$

$$\bar{\epsilon}_n = \frac{\hbar \omega}{e^{\hbar \omega \beta} - 1}$$

The no. of modes of oscillation per unit volume in the frequency range ω and $\omega + d\omega$ is $\frac{\omega^2 d\omega}{\pi^2 c^3}$.

Therefore, energy density associated with the frequency range ω and $\omega + d\omega$ is

$$u(\omega)d\omega = \frac{\hbar\omega}{e^{\frac{\hbar\omega}{KT}} - 1} \cdot \frac{\omega^2 d\omega}{\pi^2 c^3}$$

$$\boxed{u(\omega)d\omega = \frac{\hbar\omega^3 d\omega}{\pi^2 c^3 \left[e^{\frac{\hbar\omega}{KT}} - 1\right]}}$$ Planck's radiation formula

It represents the distribution of energy over the black body spectrum.

Bose derivation

Bose considered the system as consisting of a gas of identical and indistinguishable particles called as photons. The energy of a photon corresponding to the frequency ω of mode of vibration is $\hbar\omega$.

Photons are distributed over different energy levels in the system.

For finding the probability of an energy level ϵ_i ($= \hbar\omega_i$) to be occupied by n_i photons at a time, Boltzmannian statistics of the energy levels was used.

The mean value of n_i and ϵ_i is

$$\bar{n}_i = \frac{\sum_{n_i} n_i e^{-n_i \hbar\omega_i/kT}}{\sum_{n_i} e^{-n_i \hbar\omega_i/kT}}$$

$$= \frac{1}{e^{\hbar\omega_i/kT} - 1}$$

and $$\bar{\epsilon}_i = \hbar\omega_i \bar{n}_i = \frac{\hbar\omega_i}{e^{\frac{\hbar\omega_i}{kT}} - 1}$$

The no. of photon states per unit volume lying in the frequency range ω and $\omega + d\omega$.

$$g(\omega)\, d\omega / V = 2 \cdot \frac{1}{h^3} \left\{ 4\pi p^2 dp \right\}$$

$$= \frac{2}{h^3} \cdot 4\pi \left(\frac{\hbar\omega}{c}\right)^2 \left(\frac{\hbar d\omega}{c}\right)$$

$$= \frac{\omega^2 d\omega}{\pi^2 c^2}$$

photon states with momentum lying between $\frac{\hbar\omega}{c}$ and $\frac{\hbar(\omega + d\omega)}{c}$.

* volume of phase space $\int d^3q\, d^3p = V 4\pi p^2 dp$
* phase space is divided into elementary cells of volume h^3.
* 2 is two state of polarization for each mode.

∴ the energy density associated with the frequency in the range ω and $\omega + d\omega$ is

$$\boxed{u(\omega)\, d\omega = \frac{\hbar\omega^3 d\omega}{\pi^2 c^3 \left[e^{\frac{\hbar\omega}{kT}} - 1\right]}}$$

Planck's radiation formula.

Einstein's derivation

Einstein considered the statistics of both photons and energy levels. Photons are indistinguishable and distributed in the various energy levels. Since the number of photons in the volume of enclosure is not conserved i.e is indefinite. So the constraint of fixed N is removed for deriving statistics. It means that Lagrange multiplier α does not come in the statistics.

The mean number of photons $\bar{n}_i$ in the energy state ϵ_i is

$$\bar{n}_i = \frac{1}{e^{\epsilon_i/kT} - 1}$$

The total no. of modes lying in frequency range ω and $\omega + d\omega$ per unit volume is $\frac{\omega^2 d\omega}{\pi^2 c^3}$.
Therefore, the energy density associated with the frequency range ω and $\omega + d\omega$ is

$$u(\omega)\,d\omega = \frac{\hbar \omega^3 d\omega}{\pi^2 c^3 \left[e^{\frac{\hbar\omega}{kT}} - 1\right]}$$

Thermodynamic functions of photon gas

The grand partition function of photon gas is $\mathcal{Z}(V, T)$

$$\therefore \quad \frac{PV}{KT} = -\sum_{\epsilon} \ln\left(1 - e^{-\epsilon/KT}\right)$$

Summation can be replaced by integration

$$\sum_{\epsilon} \longrightarrow \int_0^{\infty} g(\epsilon)\, d\epsilon$$

where $\quad g(\epsilon)\, d\epsilon = \dfrac{8\pi V \epsilon^2}{h^3 c^3}\, d\epsilon$

$$\therefore \quad \ln \mathcal{Z}(V, T) = \frac{PV}{KT} = -\int_0^{\infty} \frac{8\pi V \epsilon^2\, d\epsilon}{h^2 c^3} \ln\left(1 - e^{-\epsilon/KT}\right)$$

After integration by parts,

$$\frac{PV}{KT} = \frac{8\pi V}{3h^3 c^3} \cdot \frac{1}{KT} \int_0^{\infty} \frac{\epsilon^3\, d\epsilon}{e^{\epsilon/KT} - 1}$$

or, $PV = \frac{8\pi V}{3h^3c^3}(KT)^4 \int_0^\infty \frac{x^3 dx}{e^x - 1}$ $\qquad \because x = \frac{\epsilon}{KT}$

$= \frac{8\pi V}{3h^3c^3}(KT)^4 \cdot \frac{\pi^4}{15}$

$= \frac{8\pi^5 V}{45h^3c^3}(KT)^4 = \frac{U}{3}$

Since total energy U is

$U = V\int_0^\infty u(\omega)d\omega = V\int_0^\infty \frac{(KT)^4}{\pi^2\hbar^3c^3} \cdot \frac{x^3 dx}{e^x - 1}$ $\qquad \because x = \frac{\hbar\omega}{KT}$

$= \frac{8\pi^5 V}{15h^3c^3}(KT)^4$

$\therefore$ pressure of radiation is equal to one third of its energy density.

Helmholtz free energy

$F = U - TS$

we know that $G = \mu N = U - TS + PV$

$\Rightarrow \quad U - TS = -PV \quad \because$ for photons $\mu = 0$

$\therefore \quad F = -PV$

$= -\frac{1}{3} U$

Entropy $\quad S = \frac{U - F}{T} = \frac{4}{3}\frac{U}{T}$

$S \propto V T^4 / T \Rightarrow S \propto V T^3$

$\therefore$ specific heat

$$C_V = \left(\frac{dQ}{dT}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = 3S$$

For reversible adiabatic change of a radiation, $dQ = 0 \Rightarrow$ entropy remains constant

$\Rightarrow \quad V T^3 = $ Constant

$\because \quad P \propto T^4$

$\therefore \quad PV^{4/3} = \text{Constant}$

But for photon gas, value of $\frac{C_p}{C_V} = \gamma = \text{infinite}$

The equilibrium number of photons in the enclosure

$$N = \int_0^\infty N(\omega)\, d\omega = \frac{V}{\pi^2 c^3} \int_0^\infty \frac{\omega^2 d\omega}{e^{\frac{\hbar\omega}{KT}} - 1}$$

$$= \frac{V}{\pi^2 c^3} \left(\frac{KT}{\hbar}\right)^3 \int_0^\infty \frac{x^2 dx}{e^x - 1}$$

$$= \left(\frac{KT}{\hbar c}\right)^3 V \cdot \frac{2}{\pi^2} \times 1.202$$

$$= 0.2438 \left(\frac{KT}{\hbar c}\right)^3 V$$

$$\Rightarrow \quad N \propto VT^3$$

References:

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- Elementary Statistical Physics by C. Kittel
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Thank You

For any questions/doubts/suggestions and submission of assignments

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