Thermodynamic properties of electromagnetic radiation $\Rightarrow$ Ideal gas of photons.

At any temperature above 0K, all matter emits EM radiation. This represents a conversion of body's thermal energy into EM energy.

Analogy to phonons / vibrations in a solid.

Waves with a range of modes $\Rightarrow$ Each mode defined by a frequency or wave-vector or wavelength.

Energy within each mode is quantized in packets of $h\nu$. Equivalently, we can consider a quasiparticle (known as photon) as a carrier of a quantum of EM energy $h\nu$.

Thus we can represent the energy within each mode in terms of an occupation number of photons of that given frequency. (i.e $E = \sum_\nu E_\nu = \sum_\nu n_\nu h\nu \Rightarrow \{n_\nu\}$ set of occupation numbers

Photons are massless / chargeless. They do not interact with each other. Hence, EM radiation can be treated as an ideal gas of photons. They also have a spin of 1. They are bosons.

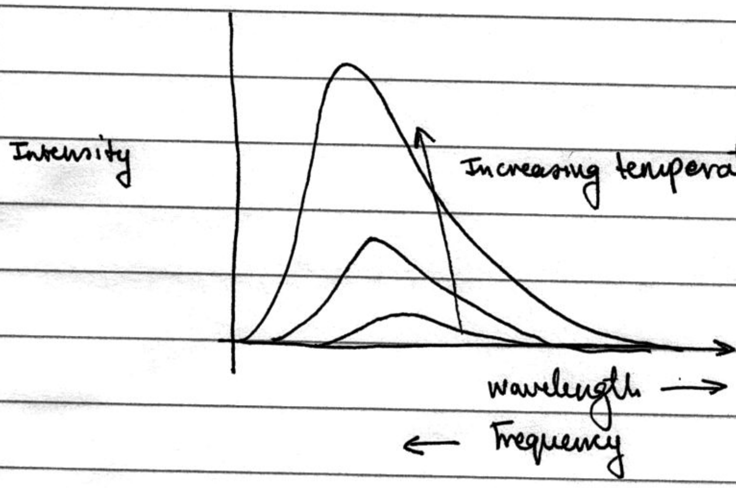
How can a gas of photons achieve thermal equilibrium if they do not "talk" to each other. $\Rightarrow$ no "collisions" between photons.

Consider photons in a cavity. Place an ideal black-body within such a cavity. This ideal body is able to absorb and emit perfectly all allowed modes of radiation. This process of absorption and emission can establish thermodynamic equilibrium between photons. Photons of one type $\rightarrow$ frequency can exchange energy to photons of another type (frequency). Former are annihilated and latter are created.

Blackbody is like a processor that takes energy of all photons in cavity & repartitions it. The partitioning depends on temperature of the radiation which at equilibrium is same as temperature of black body. The partitioning ⇒ gives spectral (mode) distribution of energy

Photons are virtual particles ⇒ carriers of EM energy hence the number of photons is not conserved. We can have as many as needed to take up all the available energy.

Now distribution of energy across different modes depends on the temperature of the ideal gas ⇒ which is the same as the temperature of the black-body (thermal equilibrium).



Expt shows ⇒ As temperature increases, the contribution to total energy from higher frequency modes increases. There is a frequency at which this contribution peaks ⇒ represents color emitted by the black body.

In analogy to phonons, the allowed modes of EM radiation in a cavity of volume V can be analyzed. The number of modes with frequency between ν and $\nu + d\nu$ is given by

$$g(\nu)\,d\nu = \frac{8\pi V \nu^2 d\nu}{c^3}$$

c → velocity of light

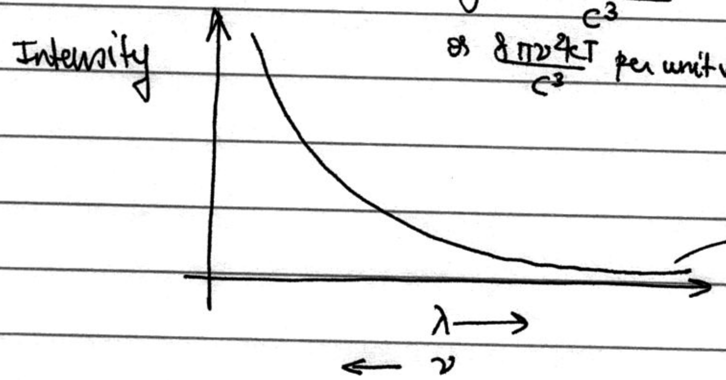
Instead of 3 modes (1 long + 2 trans) EM radiation has only 2 modes (2 trans) at each ν or k. These correspond to two polarizations or spin states of +1 & −1

As per classical equipartition each mode (oscillator) has an energy kT. So, higher frequency modes by virtue of their higher density would contribute more energy (contribution goes as ν^2).

$\longrightarrow$ precisely as $\frac{8\pi V \nu^2 kT}{c^3}$

or $\frac{8\pi \nu^2 kT}{c^3}$ per unit volume

known as Rayleigh-Jeans' law.



classical treatment $\Rightarrow$ If this were the case, the energy would diverge as one moved to higher frequencies.

Since there is no bound on frequency as in case of phonons in a solid, this would suggest an infinite energy content within the cavity $\Rightarrow$ known as the ultraviolet catastrophe.

The trend given by this classical treatment is in agreement with experiment at low frequencies but completely invalid at high frequencies

As we know, energy of each mode is quantized (in packets of $h\nu$). As the frequency increases it gets "harder and harder" to energize the mode at given temperature since the energy packet needed for a higher frequency mode is much large and the thermal bath may find it hard to provide such a big packet.

Planck encoded this effect & reproduced the expt trend by accounting for energy quantization.

Thus for each mode (of given frequency ν) energy E_ν is quantized as $E_\nu = nh\nu$ where $n = 0, 1, 2, \ldots$

Thus total energy $E = \sum_\nu E_\nu = \sum_\nu n_\nu \varepsilon_\nu = \sum_\nu n_\nu h\nu$

Thus, we can think of this as a system with allowed energy levels 1, 2, ... with energy $\varepsilon_1, \varepsilon_2, \ldots$ (or $h\nu_1, h\nu_2, \ldots$) and occupation number $n_1, n_2, \ldots$

The occupation number is for photons $\Rightarrow$ i.e. the number of photons in a given energy level. (i.e. of a given frequency)
Each value of E can be achieved by a set of occupation numbers $\{n_\nu\}$
Thus two quantizations needed $\rightarrow$ allowed modes or energy levels.
For each allowed mode $\Rightarrow$ discrete # of particles occupying that energy level. i.e. even fields are quantized, not just matter.

The allowed modes in the cavity are already known, so is their density as a function of frequency.

Now the partifition function for this ideal system of photons is given as (canonical ensemble)

$$Q = \sum_E e^{-\beta E} = \sum_{\{n_\nu\}} e^{-\beta \sum_\nu E_\nu}$$

$\hookrightarrow$ sum over all possible energies or sets of occupation numbers.

Note Q is a function of T and V

T: through β

V: through allowed modes within cavity

$$Q = \sum_{\{n_\nu\}} e^{-\beta \sum_\nu \varepsilon_\nu n_\nu}$$

sum over all possible sets of $\{n_\nu\}$ without any restriction $\because$ total number of photons (virtual or quasi-particles) does not need to be conserved. We can have as many to account for or accommodate the total energy. Q does not depend on any N as in case of real particles.

$$\therefore Q = \sum_{\{n_\nu\}} \prod_\nu e^{-\beta \varepsilon_\nu n_\nu}$$

$$Q = \prod_\nu \underbrace{\sum_{n_\nu = 0,1,2\ldots} e^{-\beta \varepsilon_\nu n_\nu}}_{1 + e^{-\beta\varepsilon_\nu} + (e^{-\beta\varepsilon_\nu})^2 + \ldots}$$

A geometric series where $e^{-\beta\varepsilon_\nu} < 1$

$$Q = \prod_\nu \left(\frac{1}{1 - e^{-\beta\varepsilon_\nu}}\right)$$

$$\ln Q = -\sum_\nu \ln(1 - e^{-\beta\varepsilon_\nu}).$$

Average occupation number $\bar{n}_\nu$ of any level is given as

$$\bar{n}_\nu = \sum n_\nu P_\nu = \frac{\sum_{\text{all } E\text{'s}} n_\nu e^{-\beta E}}{\sum_{\text{all } E\text{'s}} e^{-\beta E}} = \frac{\sum_{\{n_\nu\}} n_\nu e^{-\beta \sum n_\nu \varepsilon_\nu}}{Q}$$

$$= \frac{\sum_{\{n_\nu\}} n_\nu \prod_\nu e^{-\beta n_\nu \varepsilon_\nu}}{Q} = \frac{1}{Q}\left(\frac{\partial Q}{\partial(-\beta\varepsilon_\nu)}\right)_{\text{all other } n\text{'s constant}}$$

$$= \frac{-1}{\beta}\frac{\partial \ln Q}{\partial \varepsilon_\nu}$$

$\because \beta$ is constant at thermodynamic equi^{m}

$$\therefore \bar{n}_\nu = +\frac{1}{\beta} \frac{\partial \sum_\nu \ln\left(1-e^{-\beta\varepsilon_\nu}\right)}{\partial \varepsilon_\nu}$$

$$\bar{n}_\nu = \frac{1}{\beta} \frac{1}{1-e^{-\beta\varepsilon_\nu}} \cdot -e^{-\beta\varepsilon_\nu}(-\beta)$$

all other terms except for ε_ν constant hence zero upon differentiation.

$$\therefore \bar{n}_\nu = \frac{e^{-\beta\varepsilon_\nu}}{1-e^{-\beta\varepsilon_\nu}} = \frac{1}{e^{\beta\varepsilon_\nu}-1}$$

This is same as Bose-Einstein distribution except that $\mu = 0$ here. Photons can be created or annhilated as required to satisfy total energy available. Hence one can ~~or~~ have an equilibrium exchange of photons like:

$$aP \rightleftharpoons bP \quad \text{where } a \neq b$$

i.e a # of photons transform to b # of photons.
We know for such equilibrium

$$a\mu_p = b\mu_p \quad \therefore \mu_p = 0$$

Thus chemical potential of the photon gas is zero. No energy cost associated with removing or adding a photon as required to take up available energy.

$$\therefore \text{Average energy } \bar{E} = \sum_\nu n_\nu h\nu$$

$$\bar{E} = \sum_\nu \left(\frac{h\nu}{e^{h\nu/kT}-1}\right)$$

The summation can be converted to an integral over all frequencies, taking into account the density of modes $g(\nu)$

no upper bound $\therefore \quad \bar{E} = \int_{\nu=0}^{\infty} \frac{h\nu}{e^{h\nu/kT}-1} \cdot g(\nu)\, d\nu$

$$\bar{E} = \int_{\nu=0}^{\infty} \frac{h\nu}{e^{h\nu/kT}-1} \cdot \frac{8\pi V \nu^2}{c^3} \cdot d\nu$$

$$\bar{E} = \int_0^{\infty} \frac{8\pi V h}{c^3}\left(\frac{\nu^3}{e^{h\nu/kT}-1}\right) d\nu$$

The energy per unit volume is then

$$\frac{E}{V} = \int_0^{\infty} \rho(\nu, T)\, d\nu$$

where $\rho(\nu,T) = \frac{8\pi V h}{V c^3} \frac{\nu^3}{e^{h\nu/kT}-1}$

$$\rho(\nu,T) = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{h\nu/kT}-1}$$

energy density as a function of frequency and temperature.

At low frequency limit, i.e. $h\nu \ll kT$ $\therefore$ Using Taylor's series

$$\rho(\nu,T) = \frac{8\pi h}{c^3} \frac{\nu^3}{1+\frac{h\nu}{kT}-1} = \frac{8\pi k T \nu^2}{c^3}$$ Rayleigh-Jeans law

matches classical result.
but deviates at high frequencies and reproduces experimental observation.

$$E = \int_0^\infty \frac{8\pi V h}{c^3} \left(\frac{h\nu}{kT}\right)^3 \frac{1}{e^{h\nu/kT}-1} \cdot d\left(\frac{h\nu}{kT}\right) \cdot \left(\frac{kT}{h}\right)^4$$

$$= \frac{8\pi V h}{c^3} \left(\frac{kT}{h}\right)^4 \underbrace{\int_0^\infty \frac{x^3}{e^x-1} \cdot dx}_{\frac{\pi^4}{15}}$$

$$E = \frac{8\pi^5 V (kT)^4}{15(hc)^3}$$

Thus the total energy of radiation is proportional to T^4, as was ~~described~~ observed (from Stefan-Boltzmann law).

$$c_v = 4 \times \frac{8\pi^5 Vk}{15} \left(\frac{kT}{hc}\right)^3 = \frac{32\pi^5 Vk}{15} \left(\frac{kT}{hc}\right)^3$$

Thus temperature dependence ($c_v \propto T^3$) same as that of a crystal at low temperatures.