Thermodynamic properties of electromagnetic radiation ⇒ 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.

Waves with a range of modes ⇒ 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. That is $E = \sum E_\nu = \sum n_\nu h\nu \Rightarrow \{n_\nu\}$ 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? Two 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 can exchange energy to photons of another type (frequency). Former are annihilated and latter are created.
Black body 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 blackbody. The partitioning => gives spectral distribution of energy.

Photons are virtual particles => carries 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 blackbody (thermal equilibrium).

\[ I(\nu) \sim \frac{2\pi^2\hbar^2}{3\mu_0 c^4} \nu^5 \exp(-\frac{\hbar \nu}{kT}) \]

\[ I(\lambda) \sim \frac{2\pi^2\hbar c}{3\mu_0 kT} \lambda^{-5}\exp(-\frac{\hbar c}{kT\lambda}) \]

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 \( \nu \) and \( \nu + \Delta \nu \) is given by:

\[ g(\nu) d\nu = \frac{\Delta \nu}{c^3} \]

Instead of 3 modes (long + 2 trans) EM radiation has only 2 modes (2-trans) at each \( \nu \) & \( k \). These correspond to two polarizations or spin states of \( \psi \).
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 $\nu^2$). Precisely as $8\pi\nu^2 kT \frac{c}{a}$, known as Rayleigh-Jeans law.

The trend given by this classical treatment is in agreement with experiment at low frequencies but completely invalid at high 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, known as the ultra-violet catastrophe.

As we know, energy of each mode is quantized. 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 effect by accounting for energy quantization.
Thus for each mode (of given frequency $\nu$) energy $E_\nu$ is quantized as $E_\nu = n\hbar\nu$ where $n = 0, 1, 2, \ldots$

Thus total energy $E = \sum E_\nu = n\hbar\nu = \frac{\hbar}{\beta} \sum n_\nu E_\nu$

Thus, we can think of this as a system with allowed energy levels $\hbar\nu, 2\hbar\nu, \ldots$ with energy $E_\nu, E_2, \ldots$ (or $n\hbar\nu, 2n\hbar\nu, \ldots$) and occupation numbers $n_\nu, n_2, \ldots$.

The occupation number $n_\nu$ is for photons $\nu$ 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 $\mapsto$ allowed modes or energy levels.

For each allowed mode $\mapsto$ 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 partition function for this system of photons is given as (canonical ensemble)

$$Q = \sum_{E_\nu} e^{-\beta E_\nu} = \frac{\hbar}{\beta} \sum_{E_\nu} e^{-\beta E_\nu}$$

Note $Q$ is a function of $T$ and $V$ through allowed modes within cavity.
\[ Q = \sum_{n=0}^{\infty} e^{-\beta E_n n^p} \]

sum over all possible sets of \( n_p \)s without any restriction.

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.

\[ Q = \prod_{n=0}^{\infty} e^{-\beta E_n n_p} \]

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A geometric series where \( e^{-\beta E_n} < 1 \)

\[ \ln Q = -\sum_{n=0}^{\infty} \ln(1-e^{-\beta E_n}) \]

Average occupation number \( \bar{n}_p \) of any level is given as

\[ \bar{n}_p = \sum_{n=0}^{\infty} n_p P_n = \sum n_p e^{-\beta E} = \sum_{n=0}^{\infty} n_p e^{-\beta E} \cdot e^{-\beta E} \]

\[ \bar{n}_p = \frac{\sum_{n=0}^{\infty} n_p e^{-\beta E} \cdot e^{-\beta E}}{Q} \]

\[ = \frac{\sum_{n=0}^{\infty} n_p \beta e^{-\beta E} \cdot e^{-\beta E}}{Q} = \frac{1}{Q} \frac{\partial Q}{\partial (-\beta E)} \]

\[ \beta \text{ is constant} \]

\[ \beta e^{-\beta E} \text{ at thermodynamic equilibrium} \]
\[ \bar{n}_\nu = + \frac{1}{\beta} \ln \left( 1 - e^{-\beta E_\nu} \right) \]

\[ \bar{n}_\nu = \frac{1}{\beta} \frac{1 - e^{-\beta E_\nu}}{1 - e^{-\beta E_\nu}} (\beta) \] all other terms except for \( E_\nu \) constant hence zero upon differentiation.

\[ \bar{n}_\nu = \frac{e^{-\beta E_\nu}}{1 - e^{-\beta E_\nu}} = \frac{1}{e^{\beta E_\nu} - 1} \]

This is same as Bose-Einstein distribution except that \( \mu = 0 \) here. Photons can be created or annihilated as required to satisfy total energy available. Hence one cannot have an equilibrium exchange of photons like:

\[ a\nu \leftrightarrow b\nu \text{ where } a \neq b \]

i.e. @ photons transform to @ photons.

We know for such equilibrium

\[ a\mu = b\mu \quad \therefore \mu = 0 \]

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.

\[ \therefore \text{Average energy } \bar{E} = \sum \bar{n}_\nu \hbar \nu \]

\[ \bar{E} = \frac{\Xi}{\sum e^{\hbar \nu / kT} - 1} \]
The summation can be converted to an integral over all frequencies, taking into account the density of modes $g(v)$:

$$E = \int_{v=0}^{\infty} \frac{h v}{e^{h v/kT} - 1} g(v) dv$$

$$E = \int_{v=0}^{\infty} \frac{h v^2}{e^{h v/kT} - 1} \frac{8\pi V v^2}{c^3} dv$$

$$E = \int_{v=0}^{\infty} \frac{8\pi V h}{c^3} \left( \frac{v^3}{e^{h v/kT} - 1} \right) dv$$

The energy per unit volume is then:

$$E = \frac{1}{V} \int_{v=0}^{\infty} p(v, T) dv$$

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

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

energy density as a function of frequency and temperature.

At low frequency limit, i.e. $h v < kT$. Using Taylor's series

$$p(v, T) = \frac{8\pi h}{c^3} \frac{v^3}{1 + \frac{h v}{kT} - 1} = \frac{8\pi kT}{c^3} \frac{v^2}{kT}$$

Planckian law

matches classical results but deviates at high frequencies and reproduces experimental observation.
\begin{align*}
E &= \int_0^\infty \frac{8\pi V h}{c^3} \frac{(b_2^2)^3}{kT} \frac{1}{e^{h\nu/kT} - 1} \cdot \frac{d(h\nu)}{kT} \cdot \left(\frac{kT}{h}\right)^4 \\
&= \frac{8\pi V h}{c^3} \frac{(kT)^4}{h} \int_0^\infty \frac{x^3}{\sqrt{e^x - 1}} \cdot dx \\
&= \frac{\pi^4}{15}
\end{align*}

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

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

\[ C_v = 4 \cdot \frac{8\pi^5 V k}{15} \frac{(kT)^3}{hc} = \frac{32\pi^5 V k}{15} \frac{(kT)^3}{hc} \]

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