Foundation of Quantum Chemistry

Sem –III, Physical Chemistry Honours

Paper – CEMACOR05T

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Lecture 2

Recapitulation

Black-body spectrum

Stefan-Boltzmann Law

Power per unit area radiated by black-body $R = \sigma T^4$

Found empirically by Joseph Stefan (1879); later calculated by Boltzmann
$\sigma = 5.6705 \times 10^{-8}$ W.m^{-2}.K^{-4}.

Wien's displacement Law

$$\lambda_m T = \text{constant} = 2.898 \times 10^{-3} \text{ m.K, or } \lambda_m \propto T^{-1}$$

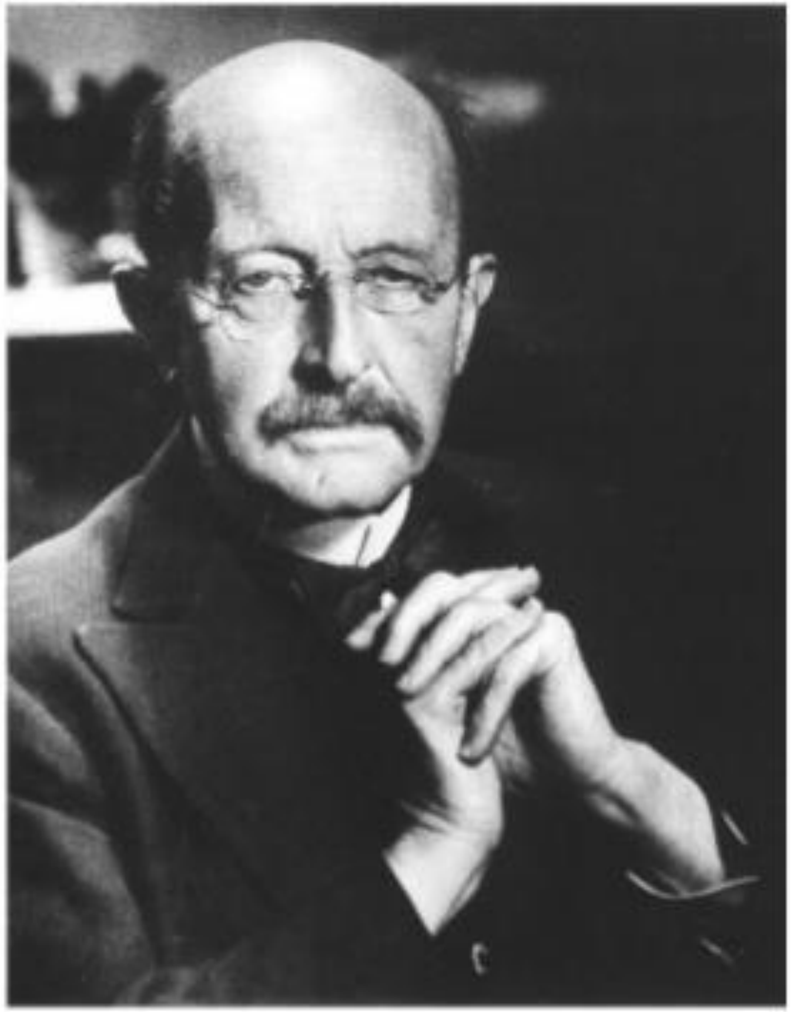
Rayleigh-Jeans equation

Define spectral energy distribution such that $u(\lambda)d\lambda$ is the fraction of energy per unit volume in the cavity with wavelengths in the range λ to $\lambda + d\lambda$.

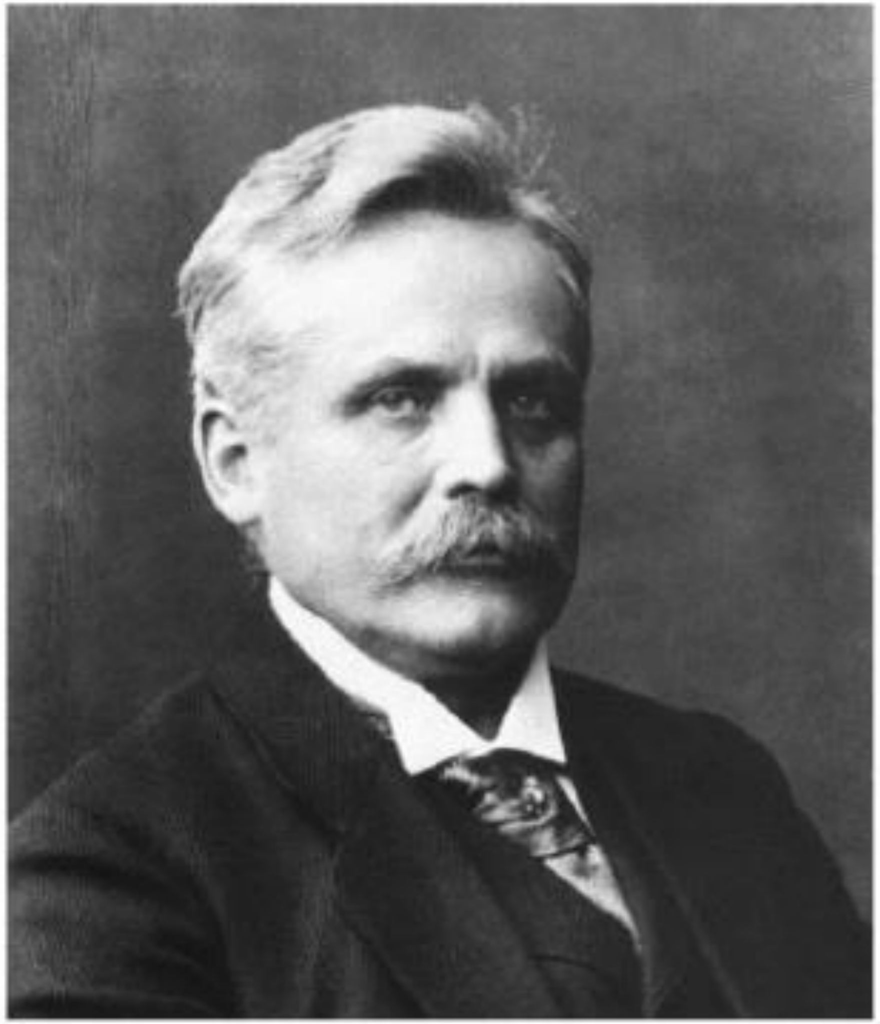
$u(\lambda)d\lambda$ = (# modes in cavity in range $d\lambda$) × (average energy of modes)

Density of modes: $n(\lambda) = \dfrac{8\pi}{\lambda^4}$; Average mode energy $\bar{U}_1 = k_B T$

$$u(\lambda) = n(\lambda)\bar{U}_1 = n(\lambda) k_B T = \frac{8\pi k_B T}{\lambda^4}$$



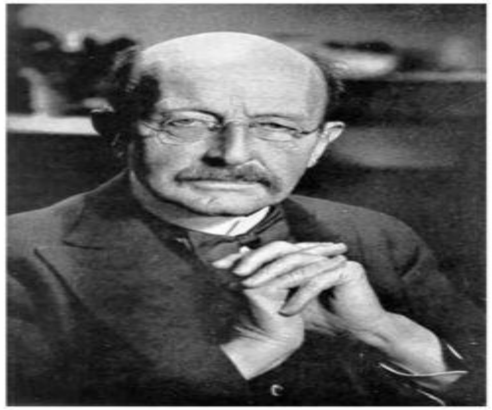
Planck 1900: *...the whole procedure was an* ***act of despair*** *because a theoretical interpretation had to be found at any price, no matter how high that might be...*



Wilhelm Wien (1864-1928).

Max Planck (1858-1947)

- Founder of quantum theory 1900
- Introduced "Planck's constant" *h* to make sense of "black-body radiation"
- $h = 6.626068 \times 10^{-34}$ m^2 kg / s
- $\hbar = h/2\pi$
- Early champion of Einstein
- Father figure in German science



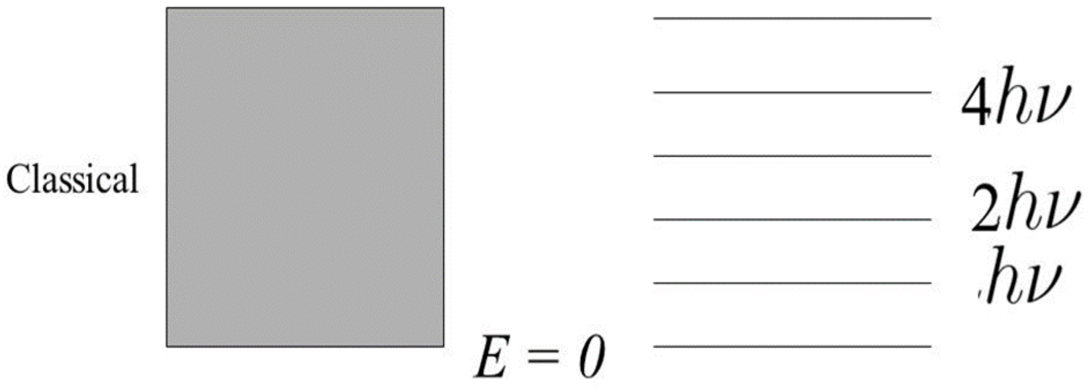
- Planck won the Nobel Prize in Physics in 1918

The recognition that energy changes in discreet quanta at the atomic level marked the beginning of quantum mechanics.

Planck's postulate

Any physical entity with one degree of freedom and whose ``co-ordinate" is oscillating sinusoidally with frequency ν can possess only total energies E as integral multiple of $h\nu$

$$E = nh\nu \qquad h = \textit{Planck's constant}$$



PLANCK RADIATION LAW: How a photon gas behaves

In 1900 the German physicist Max Planck used "lucky guesswork" (as he later called it) to come up with a formula for the spectral energy density of blackbody radiation:

Planck radiation formula

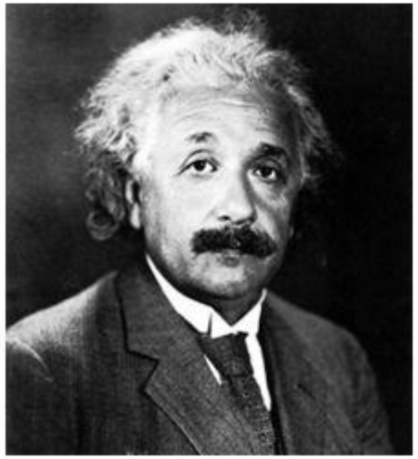
$$u(\nu)d\nu = \frac{8\pi}{c^3}\frac{h\nu^3}{e^{h\nu/k_BT}-1}d\nu$$

Here h is a constant whose value is

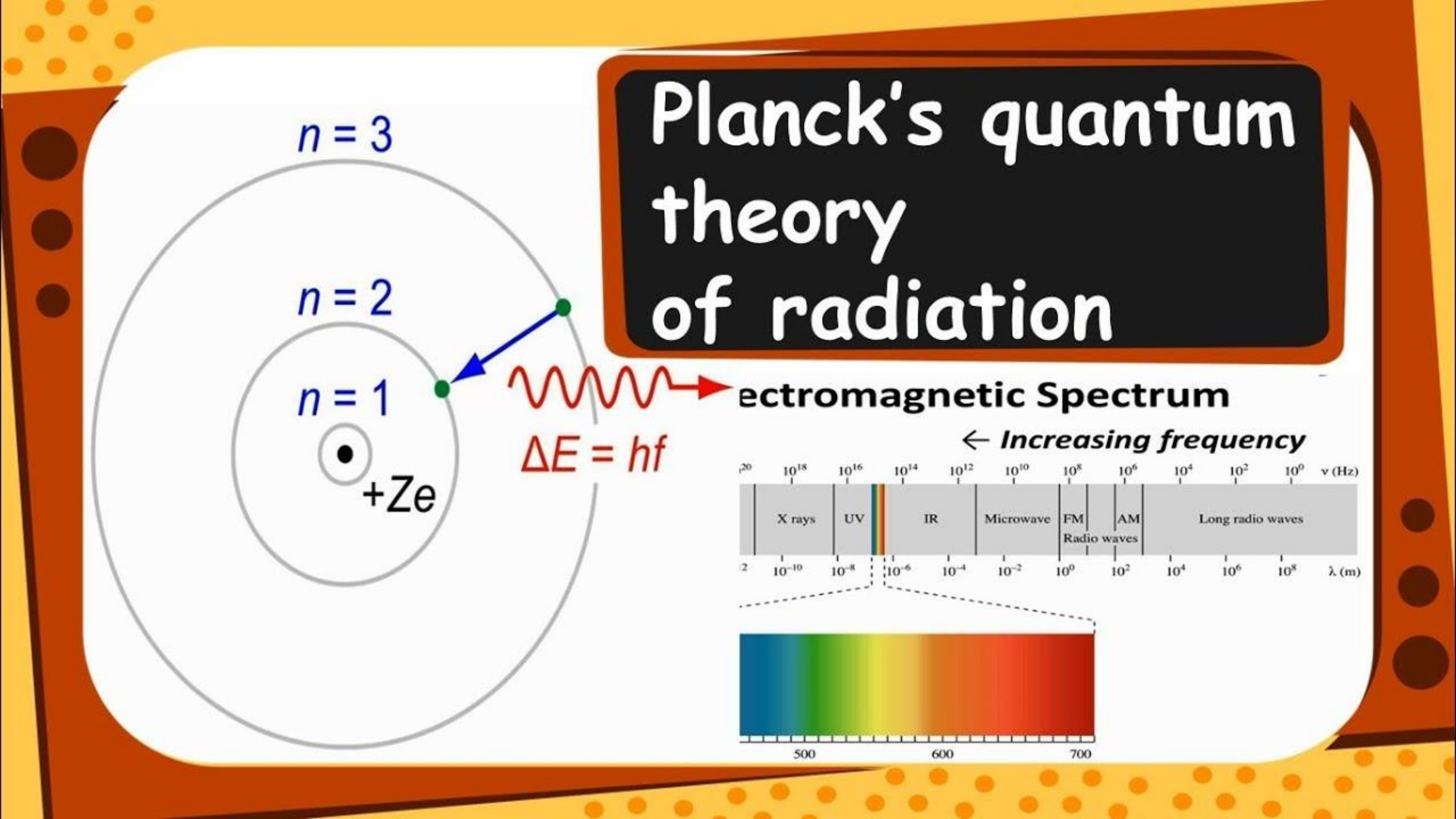
Planck's constant $h = 6.626 \times 10^{-34}\ J.s$

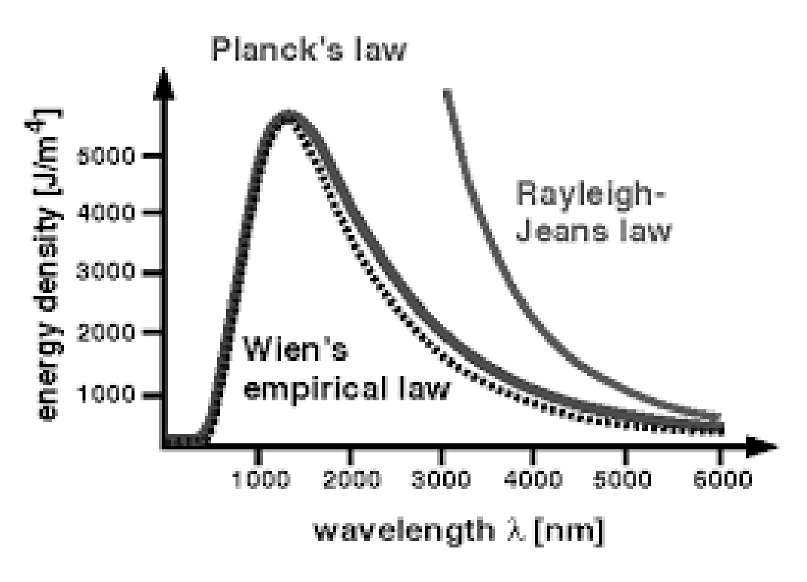
- Max Planck, a German physicist developed an equation the explained the whole curve but only if he hypothesized that the energy of the atoms was NOT continuous but occurred in multiples of a small quantity of energy.

- Planck was reluctant to pursue this reasoning since it contradicted the classical physics known at the time.
- Albert Einstein only a few years later proved Planck was correct in his thinking: energy does indeed come in little packets.



- A packet of energy is known as a QUANTUM of energy


Planck's quantum theory of radiation
n = 3
n = 2
n = 1
+Ze
ΔE = hf
ectromagnetic Spectrum
← Increasing frequency
10^18 10^16 10^14 10^12 10^10 10^8 10^6 10^4 10^2 10^0 ν (Hz)
X rays
UV
IR
Microwave
FM
AM
Radio waves
Long radio waves
10^-10 10^-8 10^-6 10^-4 10^-2 10^0 10^2 10^4 10^6 10^8 λ (m)
500
600
700



Planck's law (quantization of light energy)

In fact, no classical physical law could have accounted for measured blackbody spectra

Max Planck, and others, had no way of knowing whether the calculation of the number of modes in the cavity, or the average energy per mode (*i.e.* kinetic theory), was the problem. It turned out to be the latter.

Planck found an empirical formula that fit the data, and then made appropriate changes to the classical calculation so as to obtain the desired result, which was non-classical.

The problem is clearly connected with $u(\lambda) \rightarrow \infty$, as $\lambda \rightarrow 0$

The problem boils down to the fact that there is no connection between the energy and the frequency of an oscillator in classical physics, *i.e.* there exists a continuum of energy states that are available for a harmonic oscillator of any given frequency. Classically, one can think of such an oscillator as performing larger and larger amplitude oscillations as its energy increases.

Planck Distribution Law –Deduce (Question)

➢Planck considered the black body radiations to consist of linear oscillators of molecular dimensions and that the energy of a linear oscillator can assume only the discrete values

0,hv,2hv,3hv....nhv

If N_0, N_1, N_2...are the number of oscillators per unit volume of the hologram possessing energies 0, hv, 2hv.... respectively, then the total number of oscillators N per unit volume will be

$$N = N_0 + N_1 + N_2 + \ldots$$

But the number of oscillators, N_r having energy E_r is given by (Maxwell's formula)

$$N_r = N_0\, e^{-h\nu/kT}$$

Putting these values in eqn.. we get

$$N = N_0 + N_0\, e^{-h\nu/kT} + N_0\, e^{-2h\nu/kT} + \ldots N_0\, e^{-nh\nu/kT}$$

$$= N_0(1 + e^{-h\nu/kT} + e^{-2h\nu/kT} \ldots + e^{-nh\nu/kT})$$

$$= \frac{NO}{1 - e^{-h\nu/kT}} \quad [\because (1-e^{-x})^{-1} = 1 + e^{-x} + e^{-2x} + \ldots]$$

x= hν/kT

Total energy of oscillators :

The total energy of oscillators having energy $nh\nu$ is

$$E_n = nh\nu N_n$$

Hence the total energy of all oscillators in the blackbody

$$E = \Sigma E_n = \Sigma nh\nu N_n$$

$$\begin{aligned}
E &= N_1 \cdot h\nu + N_2 \cdot 2h\nu + N_3 \cdot 3h\nu + ... \\
&= h\nu(N_1 + 2N_2 + 3N_3 + ...) \\
&= h\nu(N_0 e^{h\nu/kT} + 2N_0 e^{2h\nu/kT} + 3N_0 e^{-3h\nu/kT} + ...) \\
&= N_0 h\nu(e^{-h\nu/kT} + 2e^{-2h\nu/kT} + 3e^{-3h\nu/kT} + ...) \\
&= N_0 h\nu e^{-h\nu/kT}(1 + 2e^{-h\nu/kT} + 3e^{-2h\nu/kT} + ...) \\
&= N_0 h\nu e^{-h\nu/kT}(1 + 2x + 3x^2 + ...) \quad (where\, x = e^{-h\nu/kT}) \\
&= N_0 h\nu e^{-h\nu/kT}(1 - x)^{-2} \\
&= \frac{N_0 h\nu e^{-h\nu/kT}}{(1-x)^2} = N_0 h\nu \frac{e^{-h\nu/kT}}{(1-e^{-h\nu/kT})^2}
\end{aligned}$$

$\Rightarrow$ average energy of oscillator is

$$\langle E \rangle = \frac{\texttt{total energy of oscillator}}{\texttt{total number of oscillator}}$$

or

$$\langle E \rangle = \frac{\Sigma n h\nu N_n}{\Sigma N_n}$$

Total no, of oscillators

$$= \frac{NO}{1-e^{-h\nu/kT}} \qquad [\because (1-e^{-x})^{-1} = 1 + e^{-x} + e^{-2x} + \ldots]$$

$$E = \frac{E}{N} = N_0 h\nu \frac{e^{-h\nu/kT}}{(1-e^{-h\nu/kT})^2} \times \frac{1-e^{-h\nu/kT}}{No}$$

$$= \frac{h\nu e^{-h\nu/kT}}{1-e^{-h\nu/kT}} = \frac{h\nu}{e^{-h\nu/kT}-1}$$

Complete Distribution Law

According to Planck energy density between range λ to $\lambda + d\lambda$ is

$$u_\lambda d\lambda = N_\lambda d\lambda \langle E \rangle$$

Planck used the calculation made by Rayleigh Jeans for number of oscillations. Hence

$$N_\lambda d\lambda = \frac{8\pi}{\lambda^4} d\lambda$$

thus

$$u_\lambda d\lambda = \frac{8\pi hc d\lambda}{\lambda^5 exp(\frac{hc}{\lambda kT}) - 1} \quad (21)$$

In terms of frequency

$$U_\nu d\nu = \frac{8\pi h\nu^3 d\nu}{c^3 exp(\frac{h\nu}{kT}) - 1} \quad (22)$$

The above equation is called Planck,s distribution law.

Explanation in small λ range

$$E_\lambda d\lambda = A\lambda^{-5}e^{-a/\lambda T}d\lambda$$

Wien's Distribution Law

for $\frac{hc}{kT} \gg \lambda$

$$exp(\frac{hc}{kT}) \gg 1$$

using this in Planck's distribution law

$$u_\lambda d\lambda = \frac{8\pi hc}{\lambda^5}\frac{1}{e^{hc/\lambda kT}}d\lambda$$

$$= \frac{8\pi hc}{\lambda^5}e^{-hc/\lambda kT}d\lambda$$

This equation is similar to Wien's distribution law which is correct for small wavelengths. We have already discussed how can it explain the small λ region of blackbody radiation.

Explanation in large wavelength region

$$U_\lambda d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda$$

Rayleigh Jeans Law

if $\frac{hc}{kT} \ll \lambda$ then

$$exp(\frac{hc}{kT}) \approx 1 + \frac{hc}{\lambda}$$

Using this in Planck's law we get

$$u_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{1 + hc/\lambda kT - 1} d\lambda$$

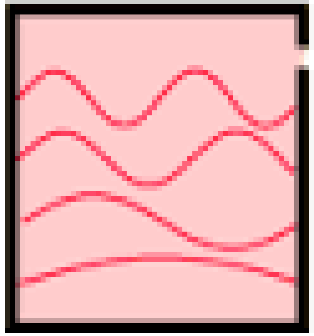
or

$$u_\lambda d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda$$

Which is Rayleigh Jeans distribution law. It can explain all the properties of black-body radiation at large wavelengths.

Modifications by Planck

Radiation modes in
a hot cavity provide
a test of quantum theory



	#Modes per unit frequency per unit volume	Probability of occupying modes	Average energy per mode
CLASSICAL	$\frac{8\pi\nu^2}{c^3}$	Equal for all modes	kT
QUANTUM	$\frac{8\pi\nu^2}{c^3}$	Quantized modes: require $h\nu$ energy to excite upper modes, less probable	$\frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$

Planck's Concept

- The average energy per "mode" or "quantum" is the energy of the quantum times the probability that it will be occupied

$$\langle E \rangle = \frac{h\upsilon}{e^{h\upsilon/kT} - 1}$$