Origins of Quantum Theory

Blackbody — that absorb all the light (radiation) incident on it. $\epsilon(\lambda) = 1 \ \forall \lambda$

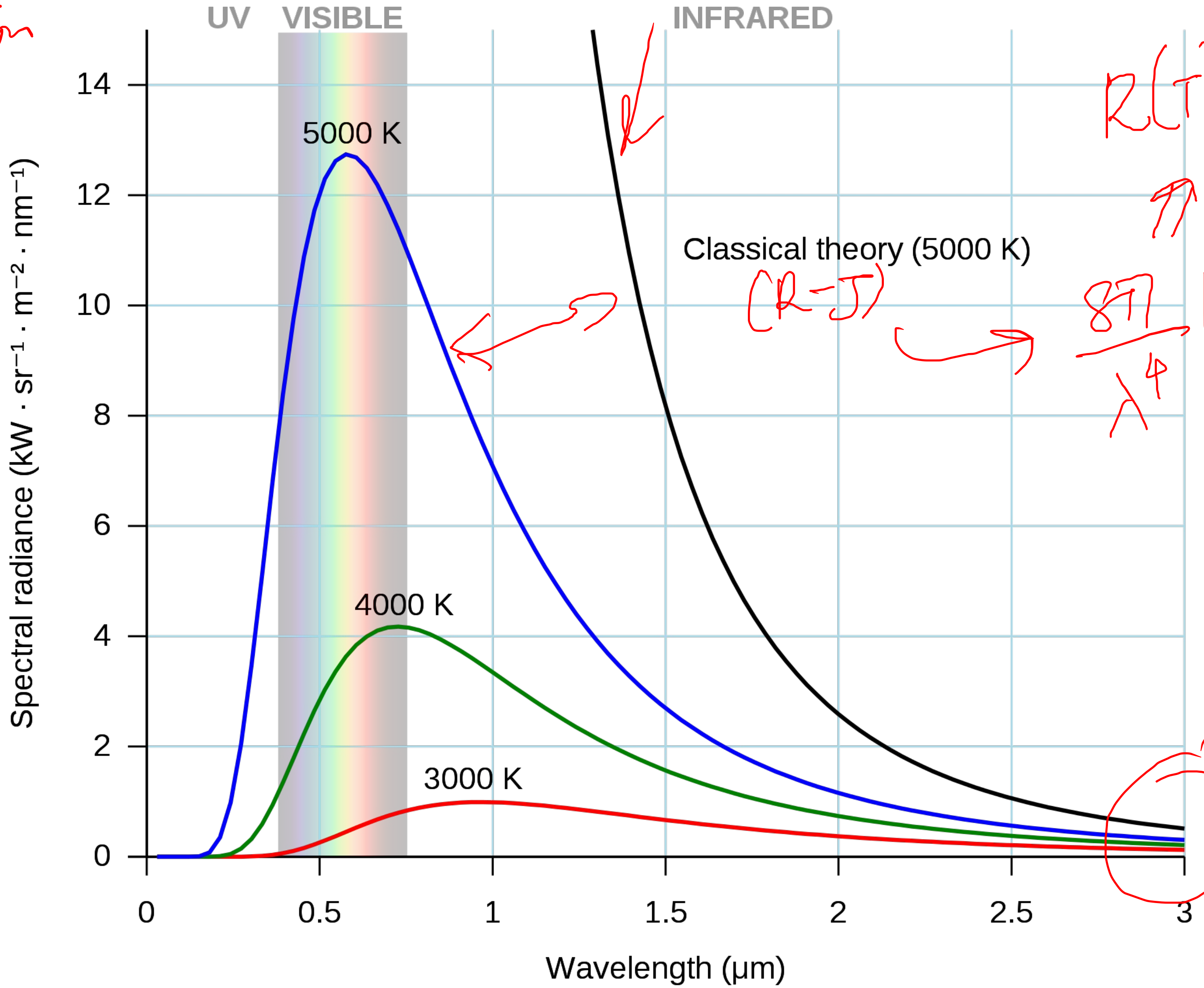
speed of light $\rightarrow c$ $\qquad \boxed{c = \nu\lambda}$ — (1)

Hot bodies will emit e.m. radiation characteristic of mainly the temperature of the body.

Emissive power or spectral emittance:

$R(\lambda, T)\, d\lambda \rightarrow$ amount of energy per unit time per unit area of body emitted in a wavelength range λ to $\lambda + d\lambda$

Thermal Radiation



$R(T) \to \infty$??!!

$\frac{8\pi}{\lambda^4} k_B T$

good agreement

Stefan-Boltzmann Law

(1879, 1884)

$$R^{BB}(T) = \sigma T^4 \quad \text{--- } (2)$$

$5.67 \times 10^{-8}\ W m^{-2} K^{-4}$
Stefan's constant.

$$R^{BB}(T) = \int_0^\infty d\lambda\, R^{BB}(\lambda, T) \quad \text{--- } (3)$$

Wein's displacement Law

$$\lambda_{max} T = b \quad \text{--- } (4)$$

$$b = 2.898 \times 10^{-3}\ m\,K$$

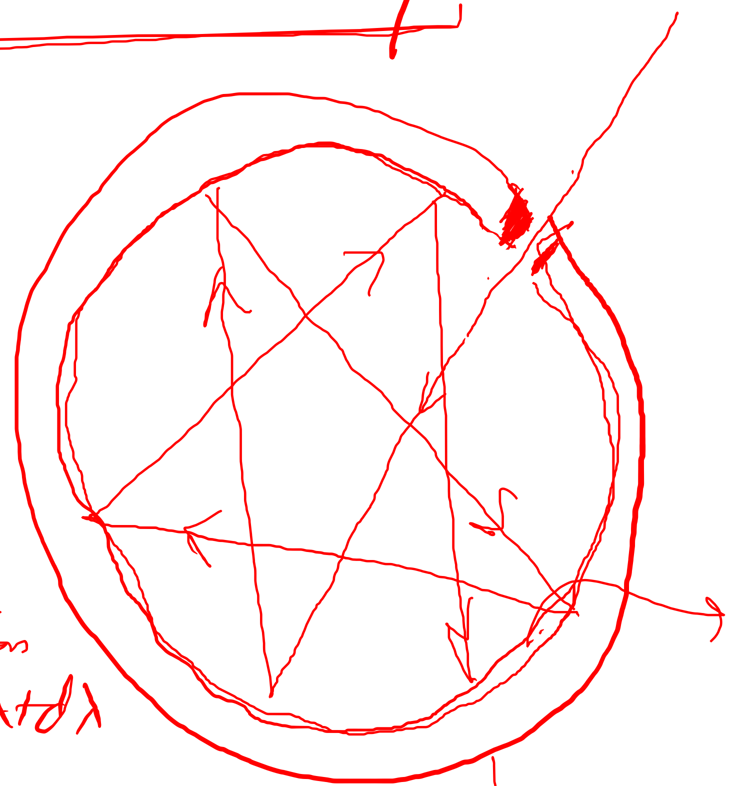
Blackbody as a cavity

Wein's law :

$$\rho(\lambda, T) = \lambda^{-5} f(\lambda T) \quad \text{— (5)}$$

spectral (energy) density

= energy per unit volume in the cavity from radiation with wavelength between λ & $\lambda + d\lambda$



$$\rho(\lambda, T) = \frac{4}{c} R(\lambda, T) \quad \text{— (6)}$$

energy inside

emitted power

Kirchoff showed that the flux of radiation

→ in the cavity is the same in all directions.

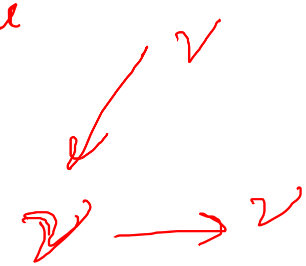
→ The energy density (ρ) is uniform inside the cavity

⇒ The same radiation that is trapped inside escapes through the cavity and is also the spectral density of a B.B. at that T.

A microscopic theory: Raleigh & Jeans

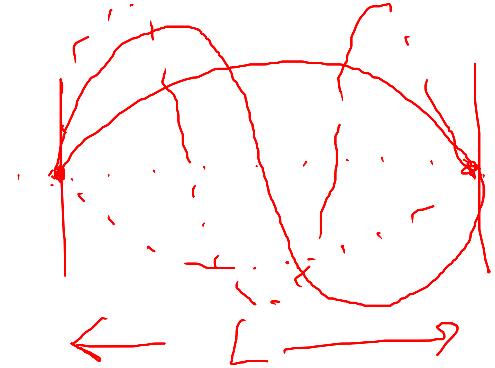
→ Assumed that cavity walls were made up of atomic dipoles which absorbed the incident radiation to get excited, i.e. started oscillating harmonically.

⇒ dipole oscillations ⇒ re-emit light at the same frequency of oscillation.



→ The dipoles could be excited by any arbitrary energy.

The emitted radiation is sustained in the cavity only if the wavelength is compatible with dimensions of the cavity:



1) How many modes exist for a given wavelength $(\lambda$ to $\lambda + d\lambda)$ per unit vol. of the cavity? $\longrightarrow n(\lambda)\,d\lambda$

$\lambda = 2L$

$\lambda = L$

$\lambda = \frac{2}{3}L$

$\vdots$

modes of oscillation

2) Average energy per mode for a wavelength $\lambda \longrightarrow \overline{E}(T)$

$$\rho(\lambda, T) = n(\lambda)\,\overline{E}(T) \quad \text{— (7)}$$

$$n(\lambda) = 8\pi/\lambda^4 \quad \text{—} \; (8)$$

$\bar{\varepsilon} \rightarrow$ from classical equipartition theorem

prob. for a mode to have energy ε

$$\propto \exp(-\varepsilon/k_B T)$$

$k_B \rightarrow$ Boltzmann constant

For every vibrational degree of freedom we get $k_B T$ as the average energy.

$$\therefore \boxed{\rho^{R-J}(\lambda, T) = \frac{8\pi}{\lambda^4} k_B T = \frac{1}{\lambda^5}} \underbrace{(8\pi k_B \lambda T)}_{f(\lambda T)}$$

$\hookrightarrow (9)$

At short wavelengths $\Rightarrow R(\lambda) \to \infty$

& $\therefore R \to \infty$ violating the S-B law.

This is called the UV catastrophe.

And basically brought an end to dominance of classical notions of light matter interaction.

Planck's distribution Law:

What if the atomic dipoles could only exchange energy in fixed quanta ε_0?

$$\bar{\varepsilon} = \frac{\sum_{n=0}^{\infty} (n\varepsilon_0)\exp\left(-(n\varepsilon_0)/k_B T\right)}{\sum_{n=0}^{\infty} \exp\left(-(n\varepsilon_0)/k_B T\right)} \quad \text{— } 10$$

$$= \frac{\varepsilon_0}{\exp\left(\varepsilon_0/k_B T\right) - 1} \quad \text{— } 11$$

$$\rho^{Planck}(\lambda, T) = \frac{8\pi}{\lambda^4} \times \frac{\varepsilon_0}{\exp(\beta\varepsilon_0) - 1} \qquad \beta = 1/k_BT$$

$$= \frac{1}{\lambda^5} \times \frac{8\pi\varepsilon_0\lambda}{(\exp(\beta\varepsilon_0) - 1)} \quad \text{—} \; (12)$$

$$\hookrightarrow = \frac{1}{\lambda^5} f(\lambda T)$$

Then, $\varepsilon_0 = B/\lambda$

$$= hc/\lambda \quad \text{—} \; (13)$$

$h \rightarrow$ Planck's constant

$$= h\nu$$

$$\boxed{\rho^{Planck}(\lambda, T) = \left(\frac{1}{\lambda^5}\right) \times \frac{8\pi hc}{\exp\left(\frac{hc}{k_BT\lambda}\right) - 1}} \quad \text{—} \; (14)$$

when $\lambda \to \infty$, i.e. $\frac{hc}{k_B T \lambda} \to 0$ then the R-J result is recovered.

whereas for $\lambda \to 0$, $\rho \to 0$ avoiding the UV catastrophe!!

Planck's suggestion was unprecedented.

$$\lambda_{max} T = \frac{hc}{4.965 k_B} = b \quad — (15)$$

$$P_{tot}(T) = a T^4 \text{ where } a = \frac{8\pi^5}{15} \frac{k_B^4}{h^3 c^3} \quad — (16)$$

can relate to σ

$$h = 6.55 \times 10^{-34} \text{ Js}$$
$$k_B = 1.346 \times 10^{-23} \text{ JK}^{-1}$$

December 1900

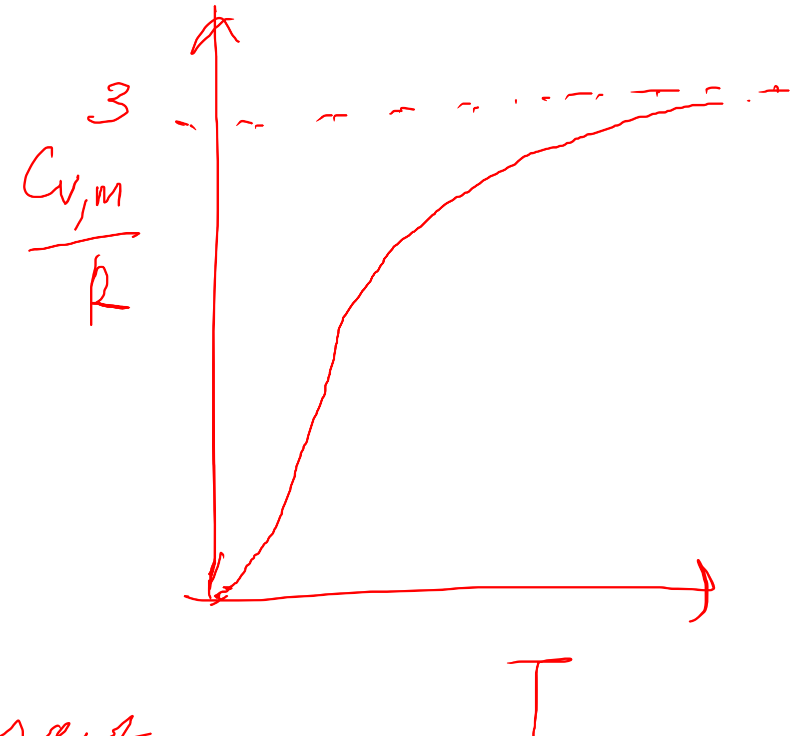
$\Downarrow$

$$h = 6.626 \times 10^{-34} \text{ JS}$$
$$k_B = 1.38066 \times 10^{-23} \text{ JK}^{-1}$$

This idea of quantisation of energy was later used by others to explain other mysteries plaguing classical physics.

(1819)

3 vib. d.o.f per atom in a crystal $\Rightarrow$ 3RT. energy/mol $\Rightarrow C_{V,m} = 3R$



Einstein ~1907 said what if Planck's idea could be applied here to say that the oscillators themselves are quantized.

$$C_{V,m}(T) = 3R\, f_E(T) \qquad f_E(T) = \left[\frac{\Theta_E}{T}\cdot\frac{e^{\Theta_E/2T}}{1-e^{\Theta_E/T}}\right]^2$$

$$\Theta_E = h\nu/k_B$$