

## The Planck law of Black body radiation

The **Stefan-Boltzmann law** predicts that the radiant energy  $I$  emitted per second per unit area of a hot body is proportional to the fourth power of the absolute temperature of the body. Unless a body is radioactive, radiant heat is re-radiated energy that it has previously absorbed. A **Black-body** is the most extreme case. This means all radiant energy incident upon the body is absorbed (and in time re-radiated). The **emissivity** is unity for a Black body, and between 0 and 1 for real-world objects. Paint, ice, water all have emissivities over 0.9, but aluminium foil, copper and silver are less than 0.05.

Radiation power per square metre  $\rightarrow$   $I = \epsilon \sigma T^4$  Absolute temperature /K

↑  
Emmissivity

$$\sigma = 5.67 \times 10^{-8} \text{ Wm}^{-2} \text{ K}^{-4}$$

Stefan-Boltzmann constant

For a Black body at  $20^\circ\text{C} = 293\text{K}$ ,  $I = 418 \text{ Wm}^{-2}$

It is interesting to compare this to the maximum solar energy incident upon the Earth, which is on average about  $1,361 \text{ Wm}^{-2}$

The *spectrum* of radiative emissions from a Black body has a characteristic curve. This is the **Planck law**, named after Max Planck, who proposed the curve in 1899. To derive the curve we must combine classical ideas relating to the energy density of waves in a box (Rayleigh 1900) with *quantum* concepts, initially developed by Planck, Einstein and many others between 1900 and 1910.

$$I = \int_0^\infty B(\lambda, T) d\lambda = \sigma T^4$$

$$\sigma = \frac{2\pi^5 k_B^4}{15c^2 h^3}$$

$$B(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}$$

← This formula for irradiance is the Planck law

$$k_B = 1.381 \times 10^{-23} \text{ m}^2 \text{ kgs}^{-2} \text{ K}^{-1}$$
 Boltzmann's constant  

$$h = 6.626 \times 10^{-34} \text{ m}^2 \text{ kgs}^{-1}$$
 Planck's constant  

$$c = 2.998 \times 10^8 \text{ ms}^{-1}$$
 Speed of light

$$c = f\lambda \Rightarrow f = \frac{c}{\lambda}$$

$$\therefore df = -\frac{c}{\lambda^2} d\lambda$$

We can write an alternative expression for the Planck law in terms of radiation frequency. The derivation of the Planck law is slightly simpler in this form.

A **summary** of the results (derived on the next page) are as follows:

$$I = \sigma T^4 = \frac{1}{4} uc$$
 ← Radiant energy flux upon the walls of a black cavity containing energy per unit volume  $u$  (from Kinetic theory).  

$$u = \int_0^\infty \phi(f) df$$
 ← Energy density (energy per unit volume)  

$$\phi(f) = \frac{8\pi f^2}{c^3} \frac{hf}{e^{\frac{hf}{k_B T}} - 1}$$
 Energy density within frequency range  $f \rightarrow f + df$

$$\eta = \frac{8\pi f^2}{c^3}$$

is the 'density of states' i.e. number of photons per unit volume that can be activated within frequency range  $f \rightarrow f + df$

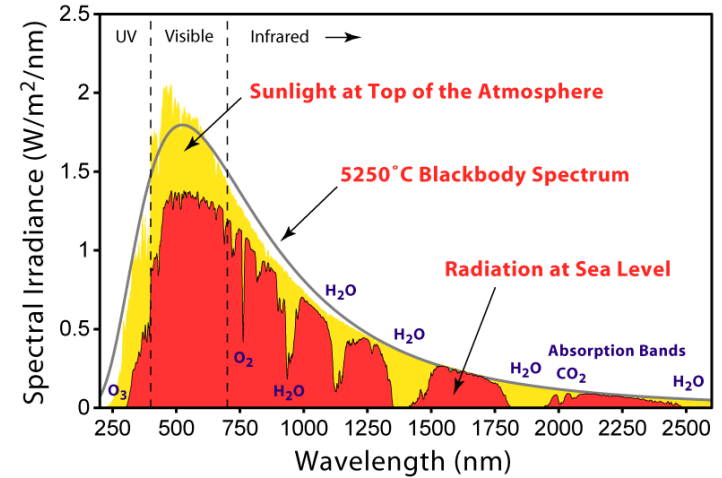
$$\bar{E} = \frac{hf}{e^{\frac{hf}{k_B T}} - 1}$$

is the average energy of a photon of frequency  $f$  ← We will use Einstein's 'geometric sum of quantized photons' plus ideas of **Boltzmann statistics** to derive this bit



**Max Planck**  
1858 – 1947  
Nobel Prize 1918

We will use Rayleigh's 'waves in a box' concept to derive this part



The measured solar irradiance (i.e. power received on Earth per square metre within a wavelength interval  $\lambda \rightarrow \lambda + d\lambda$  i.e.  $B(\lambda)$  vs  $\lambda$ )

Note the measured spectrum differs from the Planck law due to the absorption of sunlight at particular frequencies by the atmosphere. The frequencies correspond to excitations of molecules. According to Quantum theory, these will be at *discrete*, rather than continuous, frequencies.

So:  $\phi(f) = \eta \bar{E}$   $u = \int_0^\infty \eta(f) \bar{E}(f) df$

### Rayleigh's derivation of the density of states for a cavity containing radiation

$$\eta = \frac{8\pi f^2}{c^3}$$

For electromagnetic waves in a *cubical* box of side  $L$ , the amplitude (of the electric field) must be *zero* at the boundaries of the box. A sensible model is therefore to consider the waves to be *sinusoidal* of the form

$$\psi = \psi_0 \sin(kx) \quad \text{where allowed wavenumbers are subject to the condition } kL = n\pi$$

$$\text{i.e. } L = \frac{1}{2}n\lambda \quad \text{where } n \text{ is an integer}$$

This condition must be met for x,y,z dimensions of the cavity, so the overall wavenumber (i.e. the magnitude of the overall *wavevector*  $\mathbf{k}$ ) must obey the condition

$$k^2 = k_x^2 + k_y^2 + k_z^2 = \frac{\pi^2}{L^2}(l^2 + m^2 + n^2) \quad \text{where } l, m, n \text{ are all positive integers}$$

$$\text{Define an integer } p \text{ such that } p^2 = l^2 + m^2 + n^2 \therefore p = \frac{kL}{\pi}$$

Since this expression defines the radius of a sphere in  $l, m, n$  space, the number  $N$  of possible values, given  $p$ , is simply an eighth of the volume of the sphere, x 2. It is an eighth because  $l, m, n$  are all positive integers, and therefore we can only use one octant of the sphere when this is true. The x 2 factor is because we can have *two polarizations* for any electromagnetic wave in the cubical cavity, for a given wavevector characterized by coordinate  $(l, m, n)$ .

$$N(p) = 2 \times \frac{1}{8} \frac{4}{3} \pi p^3$$

$$\therefore N(k) = 2 \times \frac{1}{8} \frac{4}{3} \pi \frac{k^3 L^3}{\pi^3} = \frac{1}{3} \frac{k^3 L^3}{\pi^2}$$

$$\text{Converting to frequency: } \omega = ck = 2\pi f \therefore k = \frac{2\pi f}{c}$$

$$\therefore N(f) = \frac{1}{3} \frac{\left(\frac{2\pi f}{c}\right)^3 L^3}{\pi^2} = \frac{8\pi f^3 L^3}{3c^3}$$

The *density of states* that can be activated within frequency range  $f \rightarrow f + df$  is therefore

$$\eta df = \frac{dN}{L^3} df \Rightarrow \eta = \frac{8\pi f^2}{c^3} \quad \text{as required.}$$

This method is applicable in general if we can subdivide a Black Body into small cubes. We run into problems of course when the cube dimensions are *not* a large number of radiation wavelengths. However, for most practical *macroscopic* structures, this assumption will be correct.

### Einstein's derivation of the average photon energy in a black body cavity

$$\bar{E} = \frac{hf}{e^{\frac{hf}{k_B T}} - 1}$$

Planck idea for *quantizing* the energy of photons / electromagnetic waves

$$E = nhf \quad \text{where } n \text{ is an integer}$$

**Boltzmann distribution** for the probability of a photon having energy  $E$ , given the average (absolute) temperature of photons to be  $T$

$$p(E) = p_0 e^{-\frac{E}{k_B T}} \quad k_B = 1.381 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1} \quad \text{Boltzmann's constant}$$

$$\text{Now since the sum of all possible probabilities must be unity: } 1 = \sum_{n=0}^{\infty} p_0 e^{-\frac{nhf}{k_B T}} \Rightarrow p_0 = \frac{1}{\sum_{n=0}^{\infty} \left( e^{-\frac{hf}{k_B T}} \right)^n}$$

The average oscillator energy is given by:

$$\bar{E} = \sum_{n=0}^{\infty} E p(E) = p_0 \sum_{n=0}^{\infty} nhf e^{-\frac{nhf}{k_B T}} = hf \frac{\sum_{n=0}^{\infty} n \left( e^{-\frac{hf}{k_B T}} \right)^n}{\sum_{n=0}^{\infty} \left( e^{-\frac{hf}{k_B T}} \right)^n} = hf \frac{\sum_{n=0}^{\infty} nx^n}{\sum_{n=0}^{\infty} x^n} \quad x = e^{-\frac{hf}{k_B T}}$$

Now consider an infinite geometric progression

$$\sum_{n=0}^{\infty} x^n = 1 + x + x^2 + x^3 + \dots = \frac{1}{1-x} \quad |x| < 1 \quad x = e^{-\frac{hf}{k_B T}} \therefore |x| < 1 \quad \text{since } f \geq 0$$

$$\frac{d}{dx} \left( \frac{1}{1-x} \right) = \frac{1}{(1-x)^2}$$

$$\frac{d}{dx} \sum_{n=0}^{\infty} x^n = \sum_{n=0}^{\infty} nx^{n-1} = \frac{1}{x} \sum_{n=0}^{\infty} nx^n$$

$$\therefore \sum_{n=0}^{\infty} nx^n = \frac{x}{(1-x)^2}$$

$$\text{Hence: } \bar{E} = hf \frac{\sum_{n=0}^{\infty} nx^n}{\sum_{n=0}^{\infty} x^n} = hf \frac{x}{(1-x)^2} \times (1-x) = \frac{hfx}{1-x}$$

$$\bar{E} = \frac{hfe^{-\frac{hf}{k_B T}}}{1 - e^{-\frac{hf}{k_B T}}} = \frac{hf}{e^{\frac{hf}{k_B T}} - 1}$$

$$k = 2\pi / \lambda \therefore kL = n\pi \Rightarrow 2\pi L / \lambda = n\pi \Rightarrow L = \frac{1}{2}n\lambda$$

## Final assembly of the Planck law of Black Body radiation

So far we have shown:

$$I = \frac{1}{4}uc$$

Re-radiated power per unit area of Black Body  $I$  in terms of energy density  $u$

$$u = \int_0^\infty \phi(f)df$$

Energy density within frequency range  $f \rightarrow f + df$

$$\phi(f) = \eta \bar{E}$$

'Density of states' i.e. number of photons per unit volume that can be activated within frequency range  $f \rightarrow f + df$

$$\eta = \frac{8\pi f^2}{c^3}$$

Average energy of a photon of frequency  $f$

$$\bar{E} = \frac{hf}{e^{\frac{hf}{k_B T}} - 1}$$

Combining these results:

$$I = \frac{1}{4}c \int_0^\infty \frac{8\pi f^2}{c^3} \frac{hf}{e^{\frac{hf}{k_B T}} - 1} df$$

$$I = \frac{2\pi h}{c^2} \int_0^\infty \frac{f^3}{e^{\frac{hf}{k_B T}} - 1} df$$

$$I = \frac{2\pi h}{c^2} \int_{\lambda=\infty}^0 \left(\frac{c}{\lambda}\right)^3 \left(-\frac{c}{\lambda^2} d\lambda\right)$$

Note the change of limits!  $c = f\lambda \Rightarrow f = \frac{c}{\lambda}$

$$I = \int_0^\infty \frac{2\pi hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1} d\lambda$$

$\therefore df = -\frac{c}{\lambda^2} d\lambda$

$$I = \int_0^\infty B(\lambda) d\lambda$$

Define irradiance  $B$

$$B(\lambda) = \frac{2\pi hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}$$

This is the **Planck radiation law**  
In terms of frequency we can write this as:

$$B(f) = \frac{2\pi hf^3}{c^2} \frac{1}{e^{\frac{hf}{k_B T}} - 1}$$

To prove the **Stefan-Boltzmann law** we must evaluate  $I = \int_0^\infty B(\lambda) d\lambda$  → Evaluated numerically for measured data

Let:  $x = \frac{hc}{\lambda k_B T} \therefore \frac{dx}{d\lambda} = -\frac{hc}{\lambda^2 k_B T} \Rightarrow d\lambda = -\frac{\lambda^2 k_B T}{hc} dx$

$$\frac{1}{\lambda} = \frac{k_B T}{hc} x$$

$$\therefore I = 2\pi hc^2 \int_{x=\infty}^0 \frac{1}{\lambda^5} \frac{1}{e^x - 1} \left(-\frac{\lambda^2 k_B T}{hc} dx\right)$$

$$I = 2\pi ck_B T \int_0^\infty \frac{1}{\lambda^3} \frac{1}{e^x - 1} dx$$

Note the change of limits!

$$I = 2\pi ck_B T \int_0^\infty \left(\frac{k_B T}{hc}\right)^3 \frac{x^3}{e^x - 1} dx$$

$$I = \frac{2\pi k_B^4 T^4}{h^3 c^2} \int_0^\infty \frac{x^3}{e^x - 1} dx$$

Standard integral

$$I = \frac{2\pi k_B^4 T^4}{h^3 c^2} \times \frac{\pi^4}{15}$$

$$I = \sigma T^4$$

$$\sigma = \frac{2\pi^5 k_B^4}{15h^3 c^2}$$

$k_B = 1.381 \times 10^{-23} \text{ m}^2 \text{ kgs}^{-2} \text{ K}^{-1}$  Boltzmann's constant  
 $h = 6.626 \times 10^{-34} \text{ m}^2 \text{ kgs}^{-1}$  Planck's constant  
 $c = 2.998 \times 10^8 \text{ ms}^{-1}$  Speed of light  
 $\sigma = 5.67 \times 10^{-8} \text{ Wm}^{-2} \text{ K}^{-4}$  Stefan-Boltzmann constant

To find the wavelength at the *peak* of the Planck radiation law, solve  $\frac{dB}{d\lambda} = 0$

$$\frac{d}{d\lambda} \left( \frac{\lambda^{-5}}{e^{\frac{hc}{\lambda k_B T}} - 1} \right) = 0 \Rightarrow \frac{-5\lambda^{-6} \left( e^{\frac{hc}{\lambda k_B T}} - 1 \right) - \lambda^{-5} e^{\frac{hc}{\lambda k_B T}} \left( -\frac{hc}{\lambda^2 k_B T} \right)}{\left( e^{\frac{hc}{\lambda k_B T}} - 1 \right)^2} = 0$$

$$-5\lambda^{-6} \left( e^{\frac{hc}{\lambda k_B T}} - 1 \right) + \lambda^{-7} \frac{hc}{k_B T} e^{\frac{hc}{\lambda k_B T}} = 0 \Rightarrow -5 \left( e^{\frac{hc}{\lambda k_B T}} - 1 \right) + \frac{hc}{\lambda k_B T} e^{\frac{hc}{\lambda k_B T}} = 0$$

$$-5(e^x - 1) + xe^x = 0 \Rightarrow x = 5(1 - e^{-x}) \quad x = \frac{hc}{\lambda k_B T}$$

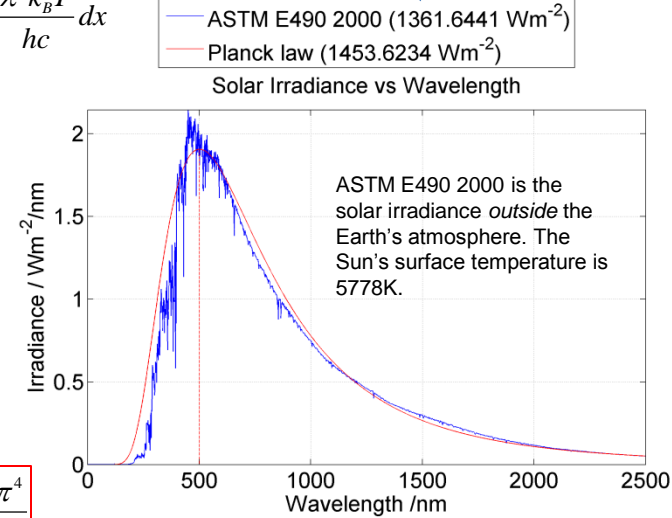
$$x_1 = 1$$

$$x_{n+1} = 5(1 - e^{-x_n})$$

$$x_\infty = 4.9651$$

Iterative method

$$\therefore \lambda_{\max} = \frac{hc}{4.9651 k_B T}$$



Red	620-750nm
Yellow	570-590nm
Green	495-570nm
Blue	450-495nm

## Einstein's model of the molar heat capacity of a solid

The formula for the average energy of a photon in the 'Black Body cube' was used by Einstein to suggest a formula for the molar heat capacity of solids. Although this is only an approximate model, it is significantly better than the **Dulong & Petit Law**, which predicts a molar heat capacity of  $3R$ . Whereas this is fine for gaseous molecules (and possibly liquids) with three-degrees of movement (i.e. no rotation or vibration is significant), this *does not* fit experimental data for solids. As a solid cools to absolute zero, it clearly must have reduced capacity since almost nothing is vibrating. So a constant heat capacity *must* be wrong for cold solids.

Let us assume the solid vibrates at a fixed\* 'Einstein frequency'  $f_E$

$$\bar{E} = \frac{hf_E}{e^{\frac{hf_E}{k_B T}} - 1} \quad \text{from the 'Black body analysis'}$$

Each mole of solid contains *Avogadro's number* of atoms

$$N_A = \frac{R}{k_B} \quad R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

is the molar gas constant

If we assume three degrees of translational motion for the atoms in a solid lattice, the total internal energy per mole is:

$$U = 3N_A \bar{E}$$

The molar heat capacity is therefore:

$$C = \frac{dU}{dT}$$

$$C = \frac{d}{dT} \left( \frac{3Rhf_E}{k_B} \frac{1}{e^{\frac{hf_E}{k_B T}} - 1} \right)$$

$$C = \frac{3Rhf_E}{k_B} (-1) \frac{1}{\left( e^{\frac{hf_E}{k_B T}} - 1 \right)^2} e^{\frac{hf_E}{k_B T}} \left( -\frac{hf_E}{k_B T^2} \right)$$

$$C = 3R \left( \frac{hf_E}{k_B T} \right)^2 \frac{e^{\frac{hf_E}{k_B T}}}{\left( e^{\frac{hf_E}{k_B T}} - 1 \right)^2}$$

Element	Debye temperature /K	Einstein frequency / $10^{13}\text{Hz}$
Gold (Au)	170	0.2855
Copper (Cu)	343.5	0.5769
Titanium (Ti)	420	0.7054
Aluminium (Al)	428	0.7188
Iron (Fe)	470	0.7893
Silicon (Si)	645	1.0832
Carbon (C)	2,230	3.7451

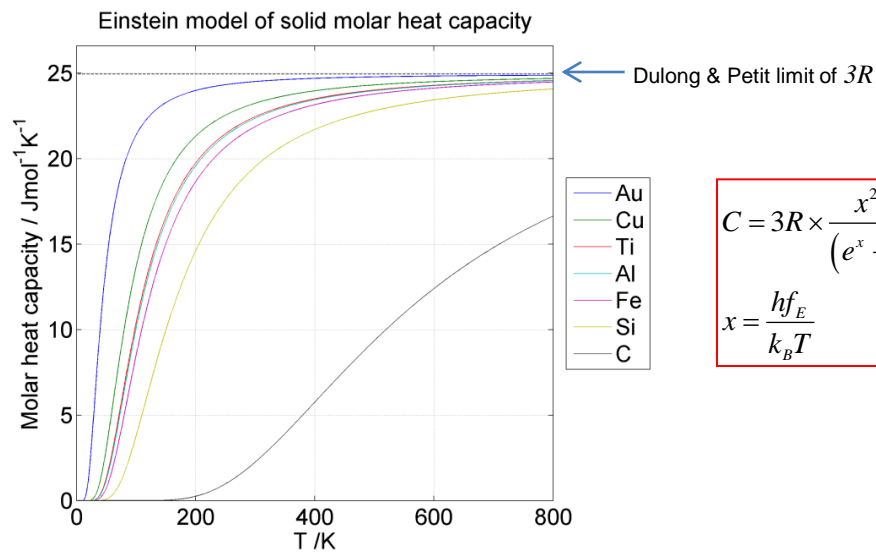
The heat capacity in the Debye model is characterized by a *Debye temperature*. A corresponding *Einstein temperature* can be determined using the relation:

$$T_E = T_D \sqrt[3]{\frac{\pi}{6}}$$

Since the Einstein model regards the solid vibrating at a fixed frequency:

$$hf_E = k_B T_E$$

$$\therefore f_E = \frac{k_B T_E}{h}$$



$$C = 3R \times \frac{x^2 e^x}{(e^x - 1)^2}$$

$$x = \frac{hf_E}{k_B T}$$

It is clear from the graphs above that the molar heat capacities at 'high temperature' tend towards the Dulong & Petit value of  $3R$ . However, 'high temperature' depends on the element, and essentially means 'much greater than the Einstein temperature.' For the elements other than Gold, this means one predicts quite a significant deviation from  $3R$  around room temperature (e.g. 295K).

\*The more accurate **Debye model** assumes a *spectrum* of frequencies, rather than just one