Quantum Theory

Black Body Radiation – The Birth of a New Era

Thermal Radiation – Black Body Radiation

The radiation emitted by a body as a result of its temperature is called *thermal radiation.* All bodies emit such radiation to their surroundings and absorb such radiation from them. If a body is at first hotter than its surroundings, it will cool off because its rate of emitting energy exceeds its rate of absorbing energy. When thermal equilibrium is reached the rates of emission and absorption are equal. The spectrum of energy distribution of radiation emitted by a hot body is continuous over a wide range of frequencies with a maximum at certain frequency depending on temperature.

At ordinary temperatures most bodies are visible to us not by their emitted light but by the light they reflect. If no light shines on them we cannot see them. At very high temperatures, however, bodies are self-luminous. We can see them glow in a darkened room; but even at temperatures as high as several thousand degrees Kelvin well over 90% of the emitted thermal radiation is invisible to us, being in the infrared part of the electromagnetic spectrum. Therefore, self-luminous bodies are quite hot.

Generally speaking, the detailed form of the spectrum of the thermal radiation emitted by a hot body depends somewhat upon the composition of the body. However, experiment shows that there is one class of hot bodies that emits thermal spectra of a universal character . These are called *blackbodies,* that is, bodies that have surfaces which absorb all the thermal radiation incident upon them. Spectral energy distribution is independent of shape and size of the material of black body.

Prelude to A Beginning of a New Era

In 1859 Gustav Kirchoff proved using second law of thermodynamics the following result:

if radiation and material bodies are in equilibrium at a common (absolute) temperature *T*, the former being reflected, scattered, absorbed and emitted by the. latter, then the energy density of the radiation per unit frequency interval ρ(ν) is a *universal* function of frequency and temperature, independent of the particular material bodies present.

ρ(ν)dν =Energy radiated per unit volume in the frequency range ν and ν+d ν at temperature T

= (universal function of ν and T) x dν

Twenty years later, in 1879, the experimentalist Josef Stefan measured the total energy density of thermal radiation by 'summing' over all frequencies, and stated in the form of empirical equation that it was proportional to T^4: Soon after, in 1884, Ludwig Boltzmann was able to give a thermodynamic proof of this result, using Maxwell's result that the pressure of radiation is one third of its energy density.

Total energy density of the cavity at temperature T,

$$u(T)= \int_0^\infty u_\nu(T)d\nu = \int_0^\infty \rho_\nu(T)d\nu = \sigma' T^4$$

Thermodynamic Proof of Stefan-Boltzmann Law

Total energy U(T)= ρ (T)V= u(T) V

Thus, $\left(\frac{\partial U}{\partial V}\right)_T$ = u(T) , where V= volume of cavity

Now, $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

Again according to Maxwell radiation pressure

PV= $\frac{1}{3}U(T)$

i.e. P = $\frac{1}{3}u(T)$

u(T) $= T\left(\frac{\partial P}{\partial T}\right)_V - \frac{1}{3}u(T)$

i.e., $\left(\frac{\partial P}{\partial T}\right)_V = \frac{4}{3T}u(T) = \frac{1}{3}\left(\frac{\partial u(T)}{\partial T}\right)_V$

or, ln u(T)=lnT^4 + I.C

Thus, u(T) = $\sigma' T^4$

Wien's law

From the 1860's onwards many guesses were made for the form of the function $\rho_v(T)$. In 1893 Wilhelm Wien showed with thermodynamical argument that $\rho_v(T)$ must have functional form $\nu^3 f(\nu/T)$. He proved that

$$\rho_\nu(T)=\alpha\,\nu^3\exp(-\beta\nu/T)$$

Wien's law fails in the lower frequency region. Radiation spectrum deviates from its experimental values of the spectrum in lower frequency range.

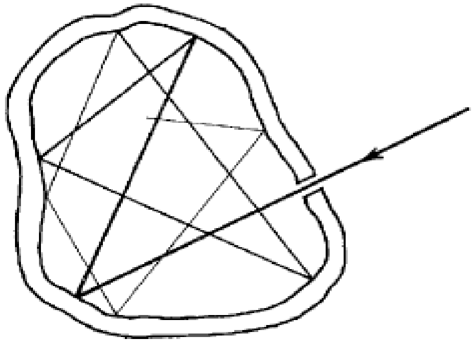
Wien's displacement law

With increasing temperature the maximum of the spectral energy distribution, $\rho_v(T)$, shifts towards higher frequency

$\nu_{max} \propto T$ or $\lambda_{max} T$ = constant=b =2.9x 10^{-3} m.K

Black Body Used in the Laboratory

A cavity in a body connected by a small hole to the outside. Radiation incident on the hole is absorbed completely on the walls of the cavity after successive reflections by these walls . On heating the walls of the cavity to a certain temperature walls emits thermal radiation filling the cavity and the small fraction of the radiation emitted by the hole has the same spectrum as that of the black-body radiation at the same temperature.



The spectrum emitted by the hole in the cavity is specified in terms of the emittance or radiancy, $R_\nu(T)$, **energy emitted per unit time from a unit area of the surface per unit width of the frequency interval at temperature T.** It is more useful, however, to specify the spectrum of radiation inside the cavity, called *cavity radiation*, in terms of an *energy density* , which is defined as the energy contained in a unit volume of the cavity at temperature *T* in the frequency interval ν to $\nu + d\nu$. It is evident that these quantities are proportional to one another; that is

$$R_\nu(T) \propto \rho_\nu(T)$$

Stefan- Boltzmann Rule

The integral of the spectral radiancy $R_\nu(T)$ over all ν is the total energy emitted per unit time per unit area from a blackbody at temperature *T*. It is called the *radiancy* R(T).

$$R(T) = \int_0^\infty R_\nu(T)d\nu = \sigma T^4$$

$\sigma = 5.67\times10^{-8}\ J.m^{-2}.sec^{-1}.K^{-4}$

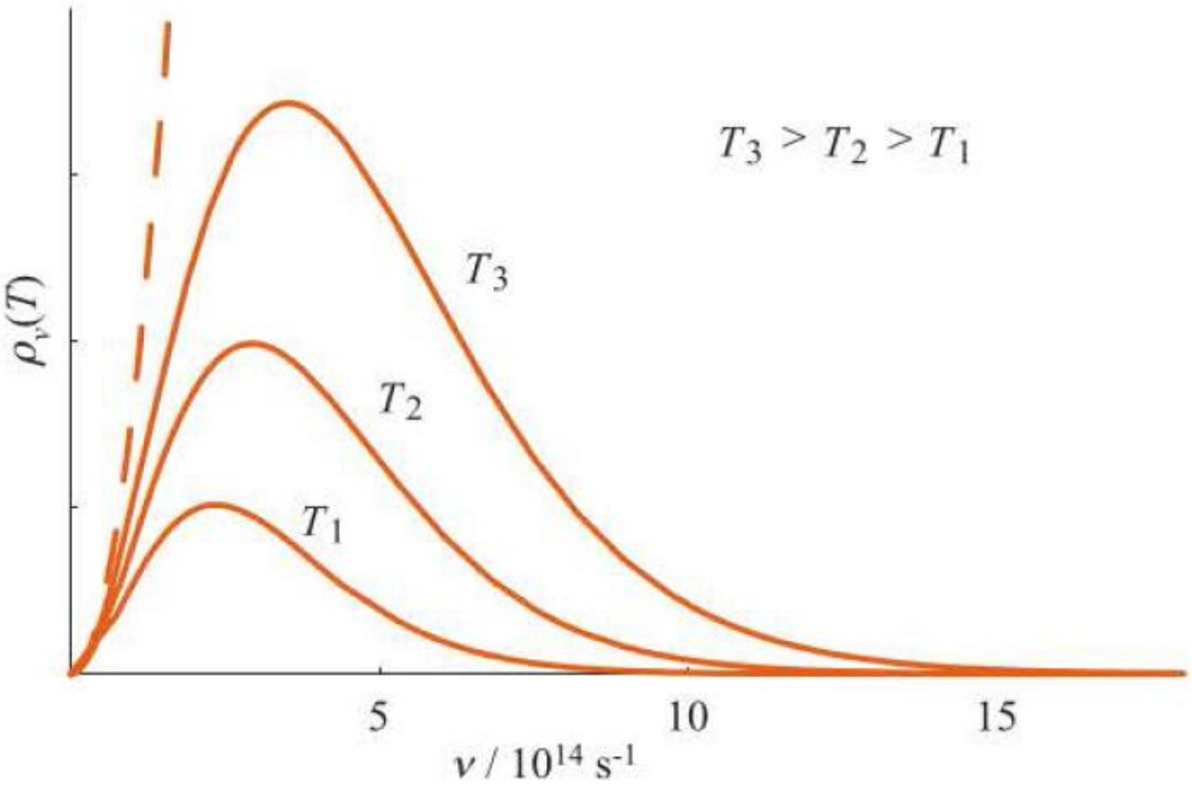
Total energy density of the cavity at temperature T,

$U(T) = \int_0^\infty u_\nu(T)d\nu = \int_0^\infty \rho_\nu(T)d\nu = \sigma' T^4$

$\sigma' = 4\ \sigma/c = 7.57\times10^{-16}\ J.m^{-3}.K^{-4}$

σ or σ′ are called Stefan-Boltzmann constant.

Black Body Radiation



Spectral distribution of the energy density of blackbody radiation as a function of frequency for several temperatures. The intensity is given in arbitrary units. The dashed line is the prediction of classical physics. As the temperature increases, the maximum shifts to higher frequencies and the total radiated energy (the area under each curve) increases sharply.

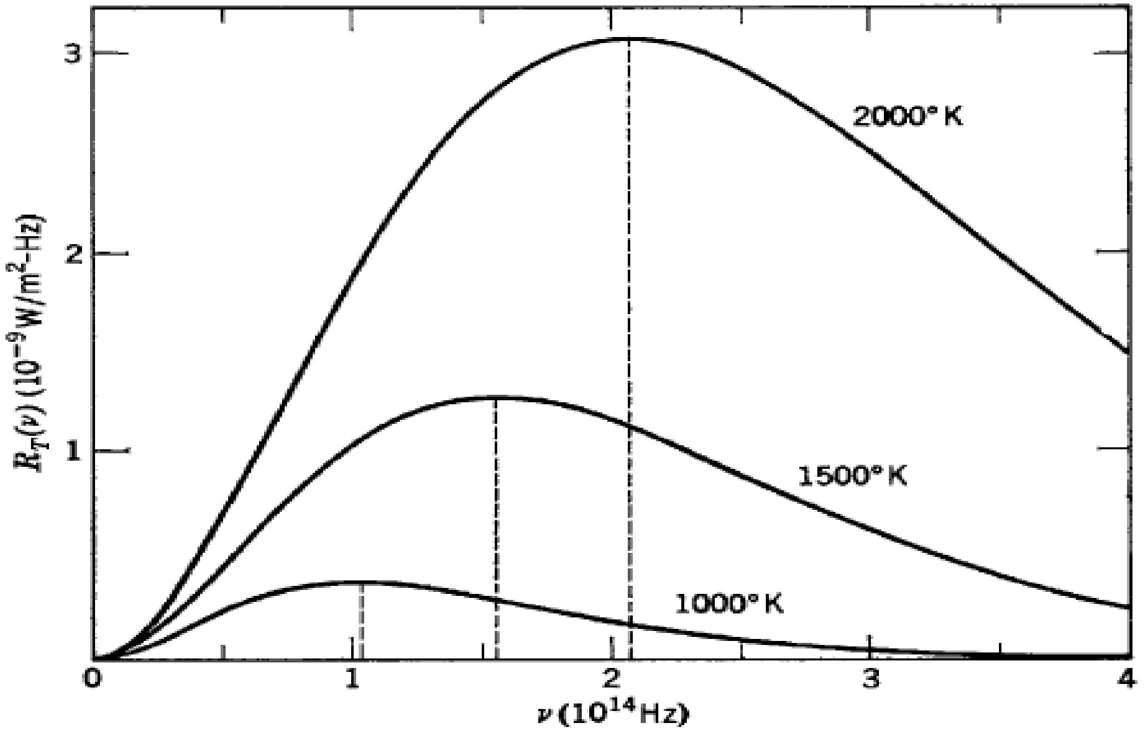


Figure 1-1 The spectral radiancy of a blackbody radiator as a function of the frequency of radiation, shown for temperatures of the radiator of 1000°K, 1500°K, and 2000°K. Note that the frequency at which the maximum radiancy occurs (dashed line) increases linearly with increasing temperature, and that the total power emitted per square meter of the radiator (area under curve) increases very rapidly with temperature.

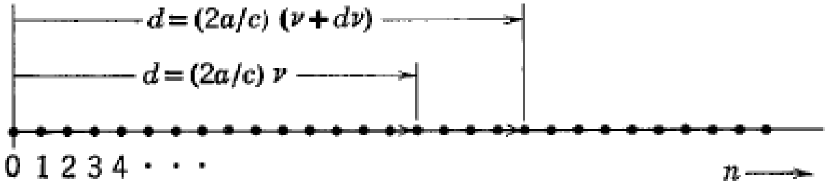
Theoretical determination of $\rho_v(T)$

When the cavity with metallic walls heated uniformly to temperature *T*, the walls emit electromagnetic radiation over a wide range of frequencies. We know that this happens, basically, because of the accelerated motions of the electrons in the metallic walls that arise from thermal agitation. Radiation inside the cavity must be in the form of standing waves with their nodes at the walls. Standing waves correspond to various modes of oscillation or degrees of freedom.

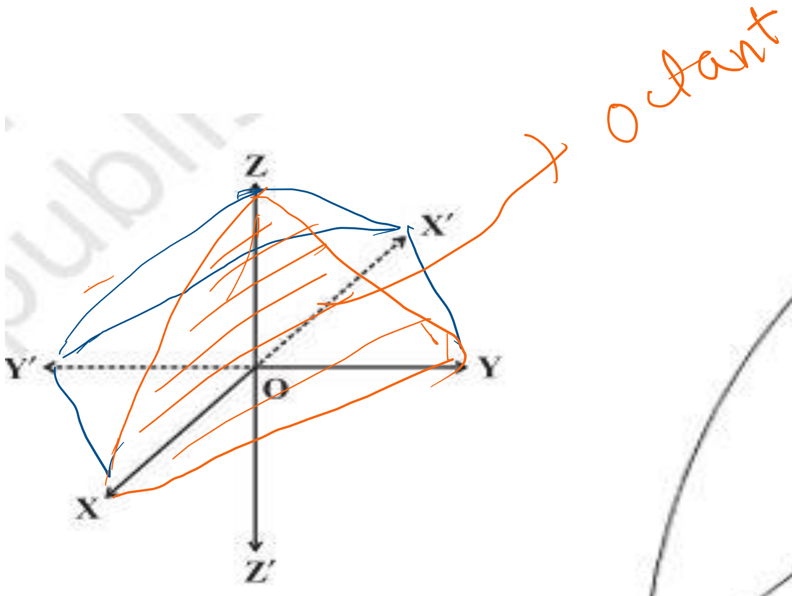
$\rho_v(T)$ = (number of standing waves in the frequency interval x average energy of the waves)/ (volume of cavity)

Considering the cavity to be a cubical cell with sides of length L, the integral number of half of the wavelengths of the allowed waves fit into length L.

Thus, $L = n\lambda/2$ Now, $\nu = c/\lambda = cn/(2L)$ or $2L/\lambda = n$



The allowed values of the index *n*, which determines the allowed values of the frequency, in a one-dimensional cavity of length *L*.



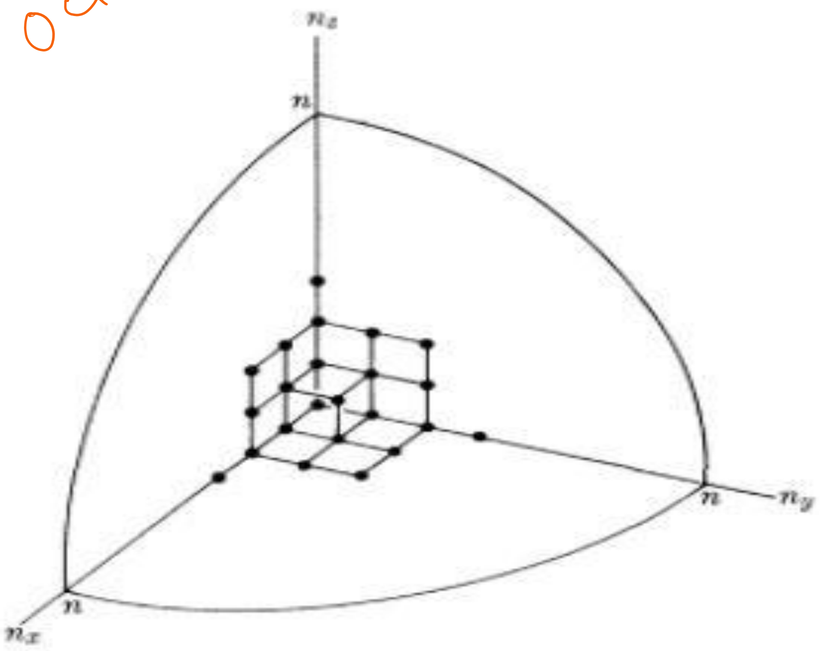


FIG. 1–2. Lattice points representing combinations of integers n_x, n_y, n_z.

Now we shall enumerate the number of allowed frequencies in a given frequency interval by constructing a uniform cubic lattice in one octant of a rectangular coordinate system in such a way that the three coordinates of each point of the lattice are equal to a possible set of the three integers n_x, n_y and n_z . By construction, each lattice point corresponds to an allowed frequency. Furthermore, $N(\nu)d\nu$, the number of allowed frequencies between ν and $\nu + d\nu$, is equal to $N(n)$ dn the number of lattice points of the spherical shell of thicknes dn between two concentric spheres of radii n and n+dn.

$$n^2 = n_x^2 + n_y^2 + n_z^2$$

Thus, $\frac{2L}{\lambda} = n = \sqrt{n_x^2 + n_y^2 + n_z^2}$ (2)

Where n_x, n_y, n_z, can take any possible integer values

This equation gives the values of the possible wavelengths of the electromagnetic radiation contained in the cavity. We will continue the discussion in terms of the allowed frequencies instead of the allowed wavelengths.

$$\nu = \frac{c}{\lambda} = \frac{c}{2L}\sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{cn}{2L} \quad (3)$$

Calculation of number of degrees of freedom in the frequency range ν and ν+dν

The required number of lattice points between n and n+dn in one octant = N(n)dn

$N(n)dn = 1/8(4\pi\, n^2 dn) = ½(\pi\, n^2\, dn)$

$4\pi\, n^2 dn$ = volume of the spherical shell of thickness dn

Thus, N(ν)d ν, the number of allowed waves in the frequency range ν and ν+dν is twice the number of N(n)dn, since there are two modes of oscillation or degrees of freedom corresponding to two directions of polarization

$N(\nu)d\nu = 2 \times \frac{\pi}{2} \times \left(\frac{4L^2\upsilon^2}{c^2}\right) \times \left(\frac{2L}{c}\right) d\nu$, since $n = \frac{2L\nu}{c}$

$= \frac{8\pi\nu^2}{c^3}\ d\nu\ V$

Rayleigh –Jeans Law

Rayleigh-Jeans law resulted from application of classical equipartition theorem

$$\rho_\nu(T)d\nu = \frac{8\pi k_B T}{c^3}\nu^2 d\nu$$

where $\rho_\nu(T)d\nu$ is the radiant energy density between the frequencies ν and $\nu + d\nu$ and has units of joules per cubic meter ($J \cdot m^{-3}$). In Equation 1.1, T is the kelvin temperature, and c is the speed of light. The quantity k_B is called the *Boltzmann constant* and is equal to the ideal gas constant R divided by the Avogadro constant (formerly called Avogadro's

UltraViolet catastrophe

$$\int_{-\infty}^{\infty} \rho_\nu(T)d\nu = \infty$$

Thus, Rayleigh-Jean law fails in the higher frequency region,

Planck’s Law of Black Body Radiation

Planck introduced a revolutionary idea. He assumed that the electronic oscillators cannot have any value of energy . They are allowed to have only discrete values of energy and exchange energy with their surrounding in discrete unit of energy ε so that the available energy states are E= 0, ε, 2ε, 3ε, …… etc.

According to Planck’s assumption the average energy of each oscillator is

$$\langle E\rangle=\frac{\sum n\varepsilon e^{-n\varepsilon/KT}}{\sum e^{-n\varepsilon/KT}}=\frac{\sum n\varepsilon x^{n}}{\sum x^{n}}=\frac{\varepsilon x/(1-x)^{2}}{1/(1-x)}=\frac{\varepsilon x}{1-x}$$

$$\frac{1}{(1-x)^{2}}= 1 + 2x +3x^{2}$$

$$\frac{1}{(1-x)} = 1 +x + x^{2}$$

Planck's Law of Black Body Radiation

Thus,

$\langle E \rangle = \frac{\varepsilon x}{1-x} = \frac{\varepsilon}{e^{\varepsilon/kT} - 1}$ where x= $e^{-\varepsilon/kT}$

Comparing with Wien's Law, Planck interpolated that ε= hν

Thus , $\rho_\nu(T)d\nu = \frac{8\pi h\nu^3}{c^3\left(e^{h\nu/kT} - 1\right)}$

This equation is in agreement with the experiment

EXAMPLE 1–2

Planck's distribution of blackbody radiation gives the energy density between ν and $\nu + d\nu$. Integrate the Planck distribution over all frequencies and compare the result to Equation 1.6.

SOLUTION: The integral of Equation 1.2 over all frequencies is

$$E_V = \int_0^\infty \rho(\nu, T)\, d\nu = \frac{8\pi h}{c^3} \int_0^\infty \frac{\nu^3 d\nu}{e^{h\nu/k_B T} - 1} \tag{1.7}$$

If we use the fact that

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$$

then we obtain

$$\begin{aligned} E_V &= \frac{8\pi h}{c^3} \left(\frac{k_B T}{h}\right)^4 \int_0^\infty \frac{x^3 dx}{e^x - 1} \\ &= \frac{8\pi^5 k_B^4 T^4}{15 h^3 c^3} \end{aligned} \tag{1.8}$$