

Kinetic Theory:

Maxwell's speed distribution, Mean free path, Elementary treatment of transport phenomena, Viscous flow and Thermal conduction in gases. Real gases, Andrew's curves, Equation of state, Virial coefficients, van der Waals equation, Critical constants.

Phase transition, Coexistence of phases, Triple point.

Joule-Thomson effect, Thermodynamic analysis, Inversion temperature, Liquefaction of gases. Properties of liquid helium, Introduction to superfluidity and superconductivity.

Radiation:

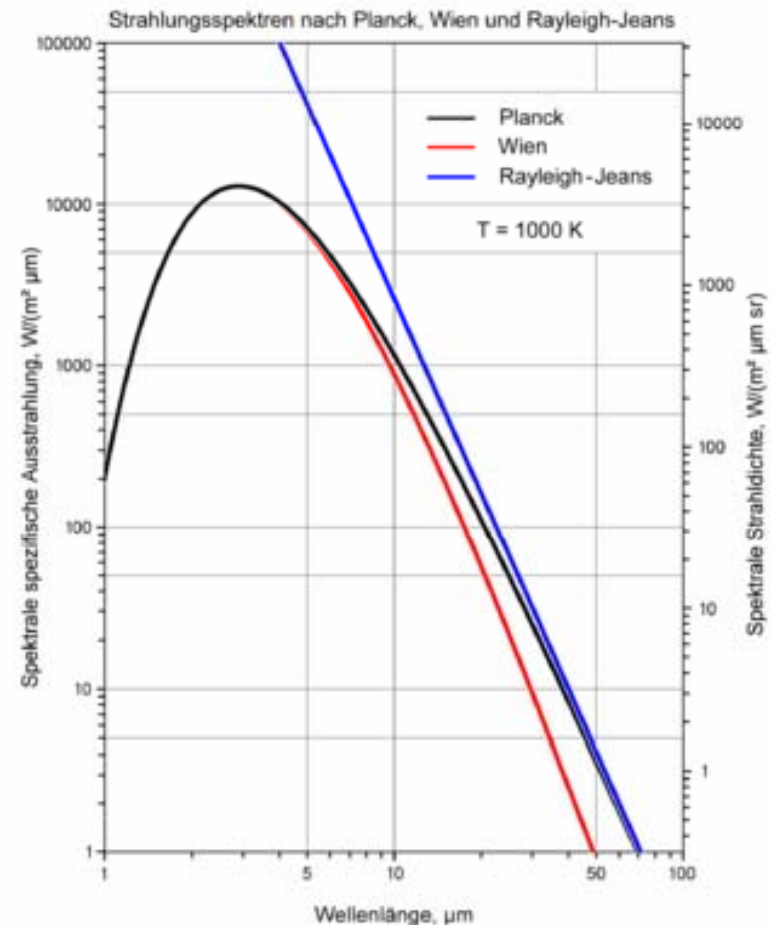
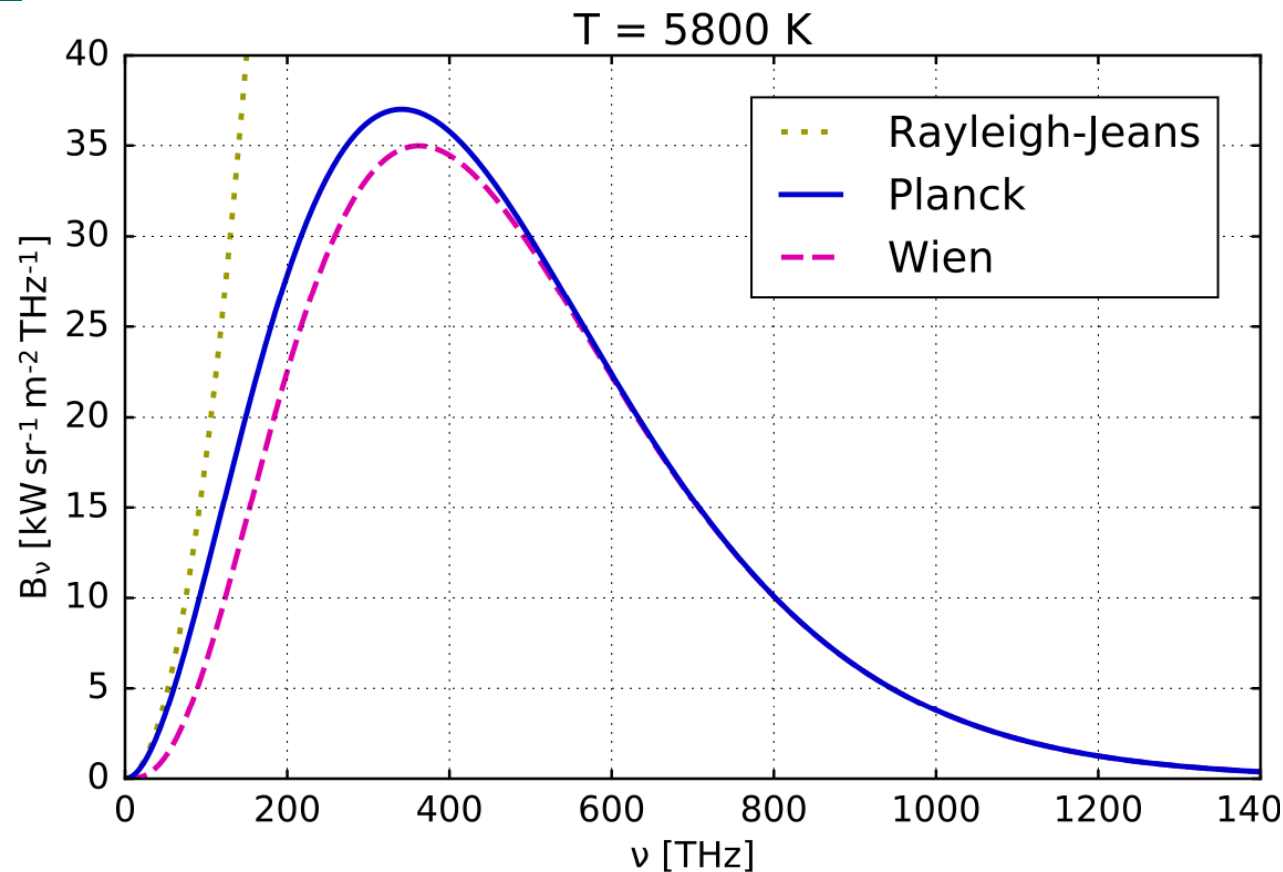
The blackbody spectrum, Wien's displacement law, Rayleigh-Jean's law, Planck's quantum theory of radiation.

**Reference Books:**

1. Heat and Thermodynamics: K.W. Zeemansky.
2. Thermal Physics: B.K. Agarwal.
3. Heat and Thermodynamics: Brij Lal and N. Subramanyam.
4. Heat and Thermodynamics: Dayal, Verma and Pandey.
5. A Treatise on Heat: M.N. Saha and B.N. Srivastava.

Wien's Displacement law

To obtain a form for $F(\lambda T)$ Wien in 1896 introduced some special arbitrary assumptions regarding the nature of radiation. He assumed that the radiation inside the enclosure is produced by some kind of resonators of molecular dimensions and that the frequency of the waves emitted by the resonators is proportional to their kinetic energies. That is



$$\frac{1}{2}mv^2 = av = \frac{ac}{\lambda} \quad (1)$$

where a is a constant and ν is the frequency of the radiation emitted. He further assumed that the energy (or speed) distribution of the resonators obeys the law of Maxwell and Boltzmann. That is, the number of resonators with energies between av and $a(\nu + d\nu)$ is given by

$$\begin{aligned} N_\nu &= f(\nu) \exp\left(-\frac{mv^2}{2kT}\right) \\ &= \phi(\nu) \exp\left(-\frac{av}{kT}\right) \end{aligned} \quad (2)$$

If the energy density is taken to be proportional to N_ν , we get

$$\Psi_\nu d\nu = A\phi(\nu) \exp\left(-\frac{av}{kT}\right) d\nu \quad (3)$$

where A is a constant. Since $\nu = c/\lambda$, we get

$$d\nu = -(c/\lambda^2) d\lambda \quad (4)$$

$$\Psi_\lambda d\lambda = A\phi(\lambda) \exp\left(-\frac{ac}{k\lambda T}\right) d\lambda \quad (5)$$

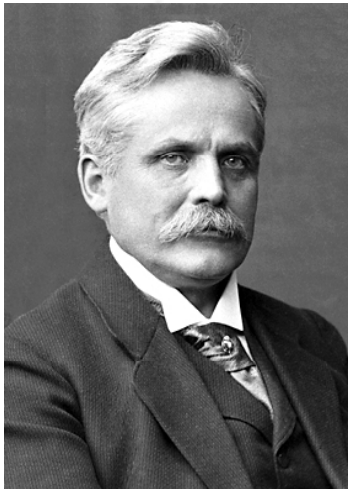
Comparison with Wien's law (Eqn. 12 of Section 6.17) gives

$$\phi'(\lambda) = \frac{1}{\lambda^5} \quad (6)$$

$$F(\lambda T) = \text{constant} \times \exp\left(-\frac{b}{\lambda T}\right),$$

$$b = ac/k \quad (7)$$

$$\Psi_\lambda d\lambda = \frac{\text{const.}}{\lambda^5} \exp\left(-\frac{b}{\lambda T}\right) \quad (\text{Wien formula}) \quad (8)$$



The *Wien formula* (8) with two underdetermined constants fits the experimental data in the short *wavelength region* but shows disagreement in the long wavelength region.



Rayleigh-Jean's law



John William Rayleigh (12 November 1842 – 30 June 1919), was a **British scientist** who made extensive contributions to both theoretical and experimental physics. He spent all of his academic career at the University of Cambridge. He received the **1904 Nobel Prize** in Physics for his discovery of argon gas.

Sir James Hopwood Jeans FRS (11 September 1877 – 16 September 1946) was an English physicist, astronomer and mathematician. President of the 25th session of the Indian Science Congress in 1938.

On the basis of the law of equipartition of energy we have shown that for a vibrator (or oscillator) the average energy for each vibrational degree of freedom is kT ($\frac{1}{2} kT$ for the kinetic energy plus $\frac{1}{2} kT$ for the potential energy). Lord Rayleigh (1900) and Jeans (1905) suggested that the energy equipartition law can be applied to the radiation problem.

The radiation within an enclosure can be considered to consist of stationary waves of various frequencies. In the one-dimensional case of vibrating string (Fig. 6.25), the wavelength λ of a standing wave is such that

$$l = n \frac{\lambda}{2}, \quad n = 1, 2, 3, \dots, \infty \quad (1)$$

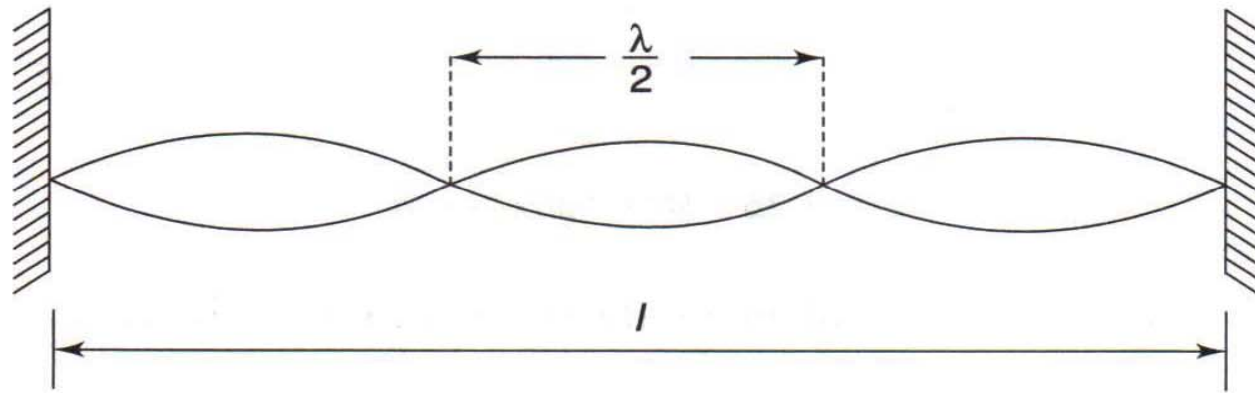


Fig. 6.25 *Vibrating string*

Thus, the ‘allowed’ wavelengths are

$$\lambda = \frac{2l}{n}, \quad n = 1, 2, 3, \dots, \infty \quad (2)$$

In the three-dimensional case we can calculate the allowed modes of vibrations by considering stationary waves in a hollow cube of side l , with the walls of the cube as nodal planes. For one direction then

$$l = n_x \lambda/2$$

If the vibrations propagate making an α with the direction, we have to replace l by the projection of cube-edge on the direction of propagation. That is

$$l \cos \alpha = n_x \lambda/2 \quad (3)$$

In general, if the angles made with the three edges forming the three axes in space are α, β, γ , then

$$l \cos \alpha = n_x \frac{\lambda}{2}, l \cos \beta = n_y \frac{\lambda}{2}, l \cos \gamma = n_z \frac{\lambda}{2} \quad (4)$$

where n_x, n_y , and n_z are positive integers.

Consider a vector \vec{l} forming the angles α, β, γ with the three axes, Fig. 6.26. Its three components have the lengths

$$l_x = l \cos \alpha, l_y = l \cos \beta, l_z = l \cos \gamma$$

Since $l^2 = l_x^2 + l_y^2 + l_z^2$, the direction cosines must obey the relation

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1 \quad (5)$$

From Eqns. (4) and (5), we get

$$n_x^2 + n_y^2 + n_z^2 = \left(\frac{2l}{\lambda}\right)^2 \quad (6)$$

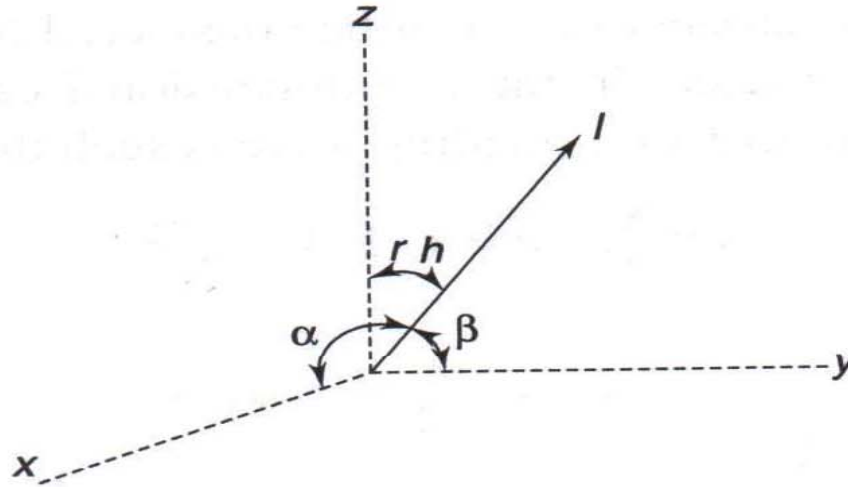


Fig. 6.26 Direction cosines

Thus, allowed modes of vibration are those for which (6) holds for every set of three positive integers n_x, n_y, n_z .

If we put $2l/\lambda = n$, Eqn. (6) becomes $n_x^2 + n_y^2 + n_z^2 = n^2$. Then n is the radius of a sphere in (n_x, n_y, n_z) space. The number of allowed modes can be evaluated by making a three-dimensional plot of n_x, n_y , and n_z (Fig. 6.27) and counting the number of points, for which these numbers are integral, which lies within the positive octant of a sphere of radius n . For sufficiently large values of n , each point will correspond to one unit cube (each point is shared by adjacent cubes) in this octant. Therefore, the volume of the octant gives the required number of modes of vibration g as

$$g = \frac{1}{8} \left(\frac{4}{3} \pi n^3 \right) = \frac{1}{8} \frac{4}{3} \pi \left(\frac{2l}{\lambda} \right)^3$$

$$= \frac{4\pi l^3}{3\lambda^3} \quad (7)$$

The number of modes, or of degrees of freedom, between λ and $\lambda + d\lambda$ is obtained by differentiating Eqn. (7). Thus

$$dg = \frac{4\pi V}{\lambda^4} d\lambda \quad (8)$$

where $V = l^3$ and both dg and $d\lambda$ are taken as positive quantities for simplicity. This number should be multiplied by 2 because transverse electromagnetic waves have two possible polarizations for each mode. Thus, the number of degrees of freedom of the waves is

$$dg = \frac{8\pi V}{\lambda^4} d\lambda = \frac{8\pi V}{c^3} \nu^2 d\nu \quad (9)$$

The law of equipartition of energy allows us to associate an energy kT with each degree of freedom. Therefore, the total energy inside the box within the wavelength range λ and $\lambda + d\lambda$ is

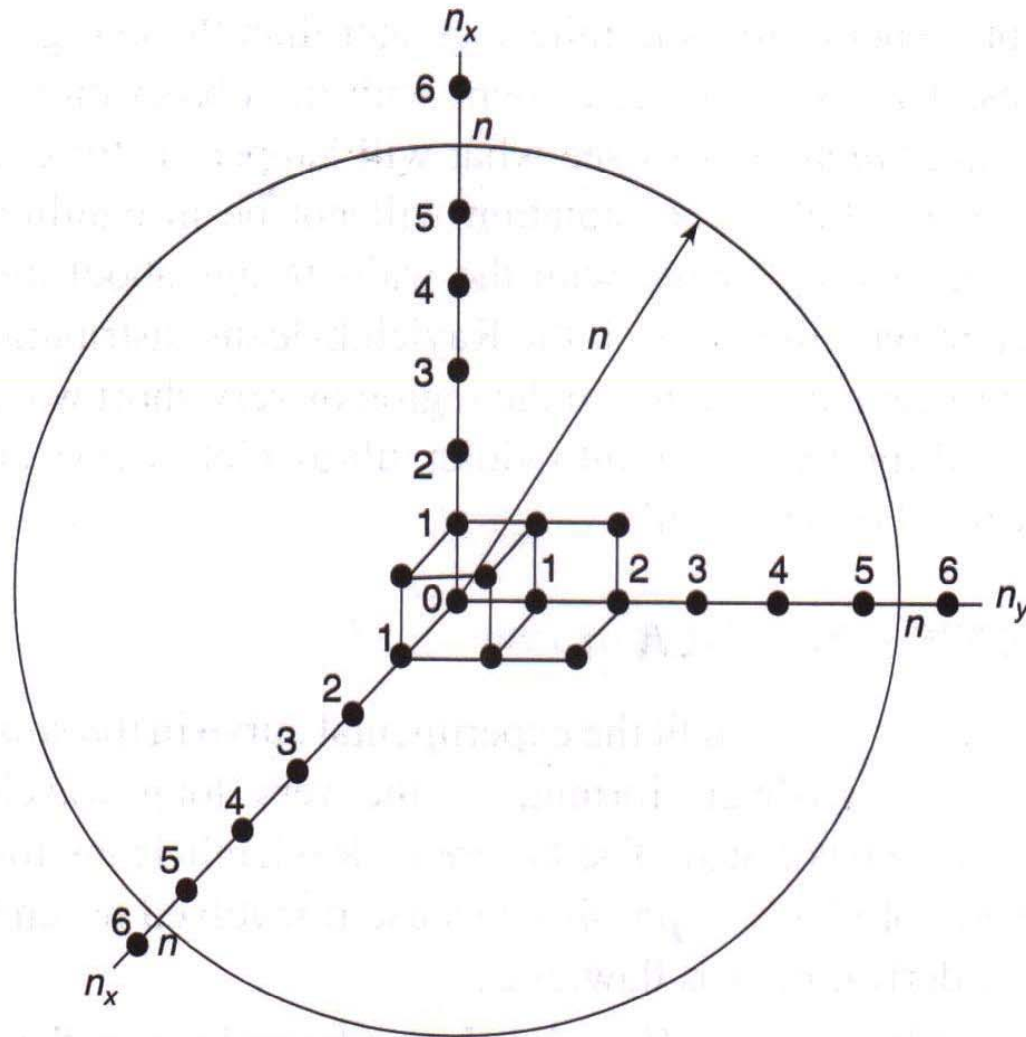


Fig. 6.27 Points in the (n_x, n_y, n_z) space

$$V \Psi_\lambda d\lambda = dg kT = \left(\frac{8\pi V}{\lambda^4} d\lambda \right) kT$$

or

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

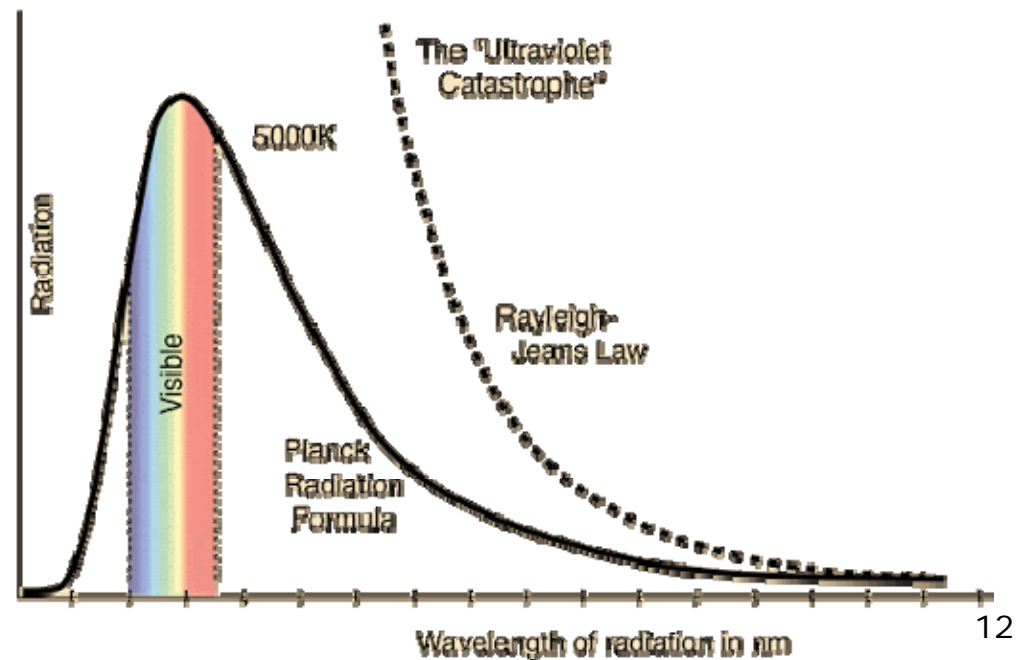
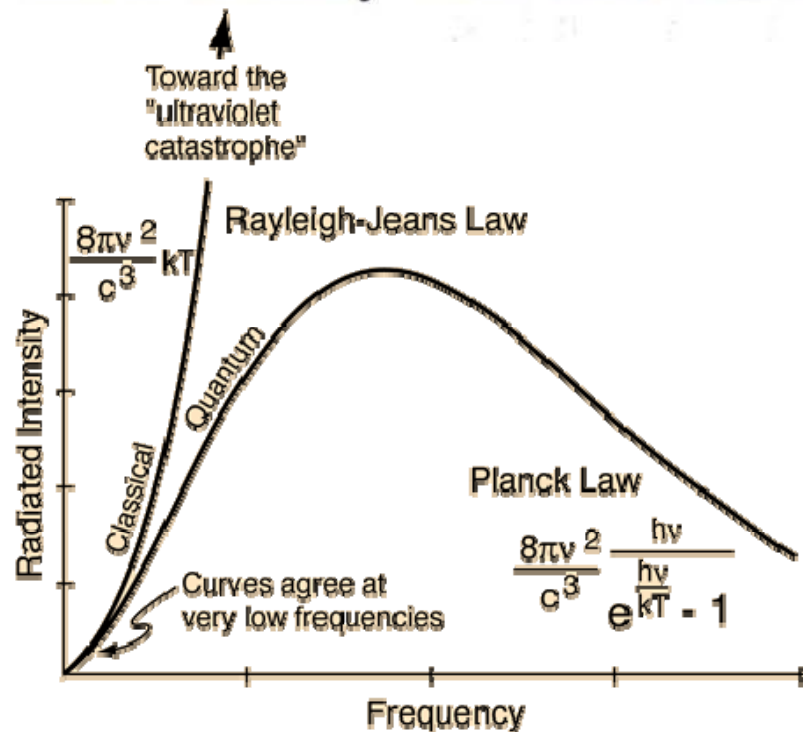
$$\Psi_{\lambda} d\lambda = \frac{8\pi k}{\lambda^5} \lambda T d\lambda \quad (\text{Rayleigh-Jeans law}) \quad (10)$$

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

This is the *Rayleigh-Jeans law*, which results from the application of the classical equipartition law. In this case $F(\lambda T) = \lambda T$. This law agrees with observations at *long wavelengths* but fails miserably at short wavelengths or high frequencies. For example, as $\lambda \rightarrow 0$, $\Psi_{\lambda} \rightarrow \infty$, when we know (Fig. 6.11) that actually as $\lambda \rightarrow 0$, $\Psi_{\lambda} \rightarrow 0$.

The total energy is given by $\int_0^{\infty} \Psi_{\nu} d\nu$. With Ψ_{ν} given by the Rayleigh-Jeans law, this integral gives infinite value (*diverges*) because Ψ_{ν} increases with ν . It means that the energy density of blackbody radiation, when in equilibrium

with the walls of a enclosure, is infinitely greater than the energy density in the walls themselves. This is not in agreement with the observations and is called the *ultraviolet catastrophe*. Let us see what will happen if, for example, we fill an enclosure with red light. The radiation will not be in equilibrium with the enclosure. As exchange of energy with the walls brings about the equilibrium, the energy distribution will approach the Rayleigh-Jeans distribution; that is, the energy will tend to get concentrated in the region of very short wavelengths. This implies that the red light will turn into violet, ultraviolet, X-rays and γ -rays, etc. This is contrary to all observations.



Planck's quantum theory of radiation



MAX PLANCK

**Max Karl Ernst Ludwing Planck
FRS**

23 April 1858- 4 October 1947

A German theoretical Physicist

Originated Quantum Theory

Nobel Prize 1918

Planck's Quantum Theory

The amount of energy associated with quantum of radiation is directly proportional to the frequency (ν) of radiation i.e.

$$E \propto \nu$$

$$E = h\nu$$

Where, h = Planck's Constant = 6.626×10^{-34} J.s

The Wien formula was found to fit the experimental curve in the small wavelength region and the Rayleigh-Jeans formula in the very long wavelength region. Otherwise, both formulas failed. The failure of Rayleigh-Jeans formula showed a serious limitation of classical physics because it involved no underdetermined constants and the derivation was flawless.

The essential failure of the Rayleigh-Jeans formula was that it led to the ultraviolet catastrophe. The total energy density $\Psi = \int_{\infty}^0 \Psi_{\lambda} d\lambda = \int_0^{\infty} \Psi_{\nu} d\nu$ diverges (becomes infinite) as $\lambda \rightarrow 0$ or $\nu \rightarrow \infty$, contrary to observations. The only way to avoid this is to discourage the radiation oscillators from exchanging energy with the enclosure walls as λ becomes small or ν becomes large. This is easily achieved by assuming with Max Planck (1900) that the radiation oscillators exchange energy with their surroundings not continuously (as in classical physics) but in *discrete* units

$$\epsilon_n = n h \nu \quad (1)$$

$$\epsilon_n = n h \nu \quad (1)$$

where h is *Planck's constant* (6.6×10^{-27} erg sec.) and n is an integer. The available states are only those for which energy is $0, h\nu, 2h\nu, \dots$, etc. Now when ν is large, the available states are widely separated in energy and the radiation oscillator can reach it only by the absorption of very high energy quanta in one step, a very rare occurrence. Thus, no contribution to the integral $\Psi = \int_0^{\infty} \Psi_\nu d\nu$ is obtained for $\nu \rightarrow \infty$ and the ultraviolet divergence or catastrophe is avoided.

Consider a collection of N oscillators having a characteristic vibration frequency ν . By Planck's assumption these can absorb energy only in increments of $h\nu$. If N_0 is the number of oscillators in the lowest energy state, the number N_n , in a state whose energy is ϵ_n , is given by the Boltzmann distribution law

$$N_n = N_0 \exp(-\epsilon_n/kT), \epsilon_n = n h \nu \quad (2)$$

The total number N of the oscillators is the sum of all N_n s from $n = 0$ to $n = \infty$,

$$\begin{aligned} N &= N_0 + N_1 + N_2 + N_3 + \dots \\ &= N_0 + N_0 \exp(-hv/kT) + N_0 \exp(-2hv/kT) + \dots \\ &= N_0 \sum_{n=0}^{\infty} \exp(-nhv/kT) \end{aligned} \quad (3)$$

The total energy is the sum of $N_n \epsilon_n$,

$$U = N_0 \sum_{n=0}^{\infty} nhv \exp(-nhv/kT) \quad (4)$$

Therefore, on the Planck's hypothesis, the average energy $\bar{\epsilon}$ of an oscillator is

$$\begin{aligned} \bar{\epsilon} &= \frac{U}{N} = \frac{hv \sum n \exp(-nhv/kT)}{\sum \exp(-nhv/kT)} \\ &= hv \frac{\sum ny^n}{\sum y^n}, \quad \left(x = \frac{hv}{kT}, y = e^{-x} \right) \\ &= hv \frac{y(1 + 2y + 3y^2 + \dots)}{1 + y + y^2 + \dots} \\ &= hv \frac{y/(1-y)^2}{1/(1-y)} = hv \frac{y}{1-y} \\ &= \frac{hv}{1/y - 1} \\ &= \frac{hv}{\exp(hv/kT) - 1} \end{aligned} \quad (5)$$

We can now combine Planck's expression for the average energy of an oscillator with the Rayleigh-Jeans analysis of the electromagnetic radiation where the various modes of vibration were treated as oscillators. There were $8\pi d\lambda/\lambda^4$ modes of vibration or degrees of freedom per unit volume in the wavelength region λ to $\lambda + d\lambda$. The Rayleigh-Jeans formula was obtained by multiplying this by kT according to the classical energy equipartition law, which applies only when the modes of oscillation are continuously distributed as to energy. In the *quantum theory of Planck* we multiply this number not by kT but by $\bar{\epsilon}$ as given by (5). Thus

$$\begin{aligned}\Psi_{\lambda} d\lambda &= 8\pi \frac{d\lambda}{\lambda^4} \cdot \frac{hv}{\exp(hv/kT) - 1} \\ &= \frac{8\pi ch}{\lambda^5} \cdot \frac{d\lambda}{\exp(ch/\lambda kT) - 1} \quad (\text{Planck's formula}) \quad (6)\end{aligned}$$

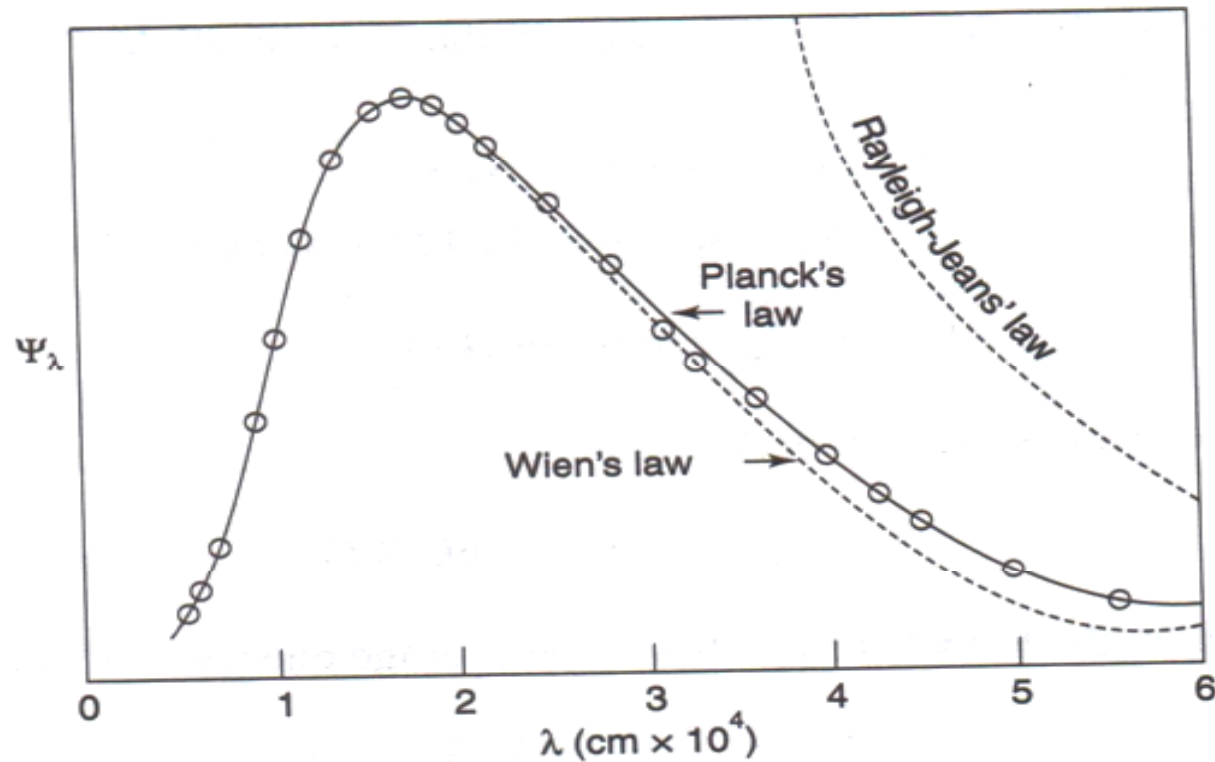


Fig. 6.28 Comparison of the three radiation laws with experiment at 1600°K. The ordinate represents Ψ_λ or $e_\lambda^{(b)}$ on an arbitrary scale

This is the famous *Planck radiation law*. It is in complete agreement with the experiments of Rubens and Kurlbaum in the entire wavelength range, Fig. 6.28. Clearly,

$$e_\lambda^{(b)} = \frac{c}{4} \Psi_\lambda = \frac{F(\lambda T)}{\lambda^5},$$

$$F(\lambda T) = \frac{2\pi ch}{\exp(ch/\lambda kT) - 1} \quad (7)$$

To fit the experimental data, we need

$$h = 6.61 \times 10^{-27} \text{ erg sec}$$

If the values of constants c , h and k are inserted, Eqn. (6) is

$$\Psi_{\lambda} = \frac{4.98 \times 10^{-15}}{\lambda^5} \cdot \frac{1}{\exp(-1.435/\lambda T) - 1} \frac{\text{ergs}}{\text{cm}^3} \quad (8)$$

where λ is in centimeters and T in degrees Celsius.

The Planck formula reduces to Wien's formula for shorter wavelengths,

$$\exp(ch/\lambda kT) \gg 1 \quad \text{for } \lambda T \ll 1$$

$$\Psi_{\lambda}^{(\text{Planck})} \xrightarrow{\lambda T \ll 1} \frac{8\pi ch}{\lambda^5} \exp(-ch/\lambda kT)$$

and to the Rayleigh-Jeans formula for longer wavelengths,

$$\exp(ch/\lambda kT) = 1 + \frac{ch}{\lambda kT} + \frac{c^2 h^2}{2\lambda^2 k^2 T^2} + \dots$$

$$= 1 + \frac{ch}{\lambda kT} \quad \text{for } \lambda T \gg 1$$

$$\Psi_{\lambda}^{(\text{Planck})} \xrightarrow{\lambda T \gg 1} \frac{8\pi ch}{\lambda^5} \cdot \frac{\lambda kT}{ch} = \frac{8\pi kT}{\lambda^4}$$



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