QUANTITATIVE PROPERTIES

This unit deals with the properties of electromagnetic radiation and the electronic structure (that is the properties of the electrons) of atoms. This chapter describes at a very introductory level the fundamentals of quantum mechanics.

If a cavity is carved out of any material, and the walls of the cavity are kept at a uniform temperature T, then the cavity will fill with radiation. Assuming that the walls are thick enough so that no radiation can get through them, then the energy density (and also the entire spectrum of the radiation) is determined solely by the temperature T — the composition of the material is entirely irrelevant. The material is serving solely to keep the radiation at a uniform temperature. Radiation of this type is generally called either thermal radiation or black-body radiation.

The motivation for the name “black-body radiation” stems from the fact that a black body in empty space can be shown to emit radiation of exactly this intensity and spectrum. To see this, imagine a material inside the cavity which is genuinely black, in the sense that all light hitting it is absorbed. Since thermal equilibrium has been established, one concludes that the black body at temperature T must emit radiation which precisely matches the radiation which it is absorbing — otherwise it would either heat up or cool down, and that would violate the assumption of thermal equilibrium. Not only must the energy densities match, but the entire spectrum must match — otherwise one could imagine introducing a frequency selecting filter that would cause the black body to heat or cool. Note that the radiation emitted by the black body is not a reflection— we assumed that there was no reflection when we assumed that the body was black. Thus, the emitted radiation has to be attributed solely to thermal emission. Even if the black-body is removed from the cavity, it will continue to emit radiation of precisely this thermal spectrum.

First let us study how energy is distributed in the spectrum of a black body. The radiation emitted by a black body varies with its temperature. The intensity of radiation corresponding to different wavelengths is measured at different temperatures and plotted as shown in Fig. 6.1. From this study it is observed that

i) at a given temperature, the energy is not uniformly distributed in the radiation spectrum

ii) at a given temperature, the intensity of radiation is maximum at a particular wavelength λ_m.

iii) with increase in temperature, λ_m decreases.

iv) for all wavelengths, an increase in temperature causes an increase in the energy emission.

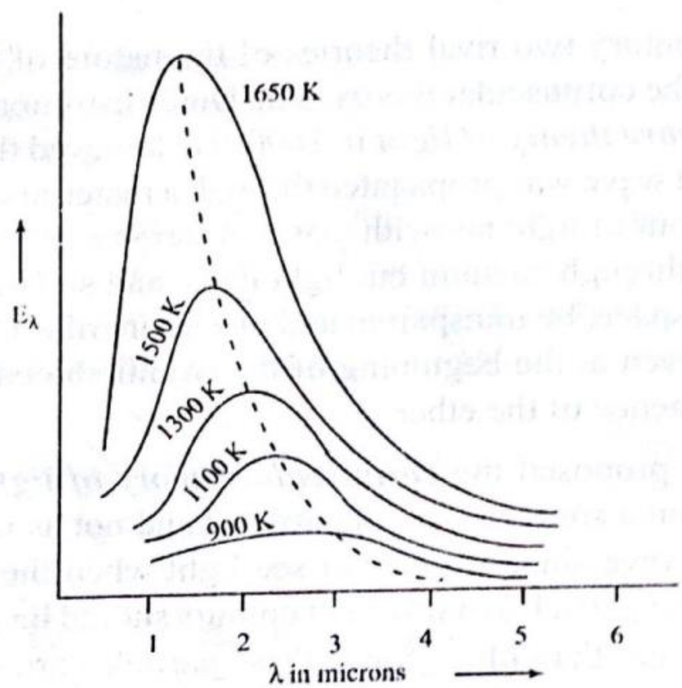

Fig. 6.1 Energy spectrum of a black body

6.2.1 Stefan-Boltzmann's law

The area under each energy spectrum curve of a black body represents the total energy emitted at that particular temperature. This area increases with increase in the temperature of the body. According to Stefan - Boltzmann law the area is directly proportional to the fourth power of the temperature of the body

$$\text{i.e.,} \quad E \propto T^4 \quad (6.$$

6.2.2 Wien's Displacement Law

From thermodynamical considerations, Wien showed that the product of the wave-length corresponding to maximum energy (λ_m) and absolute temperature is a constant. i.e.,

$$\lambda_m T = \text{constant} \tag{6.2}$$

This is called Wien's displacement law. Wien also showed that the maximum energy E_m is directly proportional to the fifth power of the absolute temperature.

$$E_m \propto T^5$$

$$\text{or} \quad E_m = \text{constant} \times T^5$$

Wien deduced the radiation law for the energy emitted at a given wavelength λ at a given temperature T

$$E_\lambda = C_1 \lambda^{-5} \exp(-C_2/\lambda T) \tag{6.3}$$

where C_1 and C_2 are constants. Eq. (6.3) represents the Wien's law of distribution of energy. Wien's law holds good only in the shorter wavelength region.

6.2.3 Rayleigh - Jean's law

According to Rayleigh, the energy distribution in the thermal spectrum is given by

$$E_\lambda = \frac{8\pi kT}{\lambda^4} \tag{6.4}$$

where k is the Boltzmann's constant.

The Reyleigh-Jean's law holds good in the region of longer wavelengths but not for shorter wavelengths.

6.2.4 Planck's quantum theory

In 1901 Planck derived a theoretical expression for the energy distribution on the basis of quantum theory of heat radiation. According to him, energy is emitted in the form of packets or quanta called ***photons***. Each photon has an energy $h\nu$ where h is the Planck's constant and ν is the frequency of radiation. According to this theory, the energy is not emitted continuously by the body but it is emitted in certain multiples of the fundamental frequency of the energy emitter (resonator). This means that the energy is emitted as quanta of energies $h\nu, 2h\nu, 3h\nu, \ldots$ etc.

For a system having a large number of similar components with different possible discrete energies. Boltzmann proposed the distribution law. Accordingly, if ε be a certain amount of energy, the number of units having energies $0, \varepsilon, 2\varepsilon, 3\varepsilon$, etc. are

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For a system having a large number of similar components with different possible discrete energies. Boltzmann proposed the distribution law. Accordingly, if ε be a certain amount of energy, the number of units having energies $0, \varepsilon, 2\varepsilon, 3\varepsilon$, etc. are in the ratio

$$1 : \exp\left(\frac{-\varepsilon}{kT}\right) : \exp\left(\frac{-2\varepsilon}{kT}\right) : \exp\left(\frac{-3\varepsilon}{kT}\right) : \ldots$$

where k is Boltzmann's constant and T, the absolute temperature. If N is the total number of members of the system, N_0 the members having zero energy, then those having energies $\varepsilon, 2\varepsilon, 3\varepsilon$ etc. will be $N_o x, N_o x^2, N_o x^3$ etc. where $x = \exp\left(\frac{\varepsilon}{kT}\right)$.

$$\text{i.e.} \quad N = N_o + N_o x + N_o x^2 + N_o x^3 + \ldots$$
$$= N_o[1 + x + x^2 + x^3 + \ldots]$$

This is an infinite geometrical progression.

$$\text{Therefore} \quad N = N_o(1-x)^{-1} = \frac{N_o}{(1-x)}$$

Now let us calculate the total energy of all the members

$$\begin{aligned} E &= (0 \times N_o) + (\varepsilon \times N_o x) + (2\varepsilon \times N_o x^2) + (3\varepsilon \times N_o x^3) + \ldots \\ &= N_o \varepsilon x(1 + 2x + 3x^2 + \ldots) \\ &= N_o \varepsilon x(1-x)^{-2} \\ &= \frac{N_o}{(1-x)} \cdot \frac{\varepsilon x}{(1-x)} \\ &= N \cdot \frac{\varepsilon}{(x^{-1}-1)} \end{aligned}$$

The average energy of each member

$$\begin{aligned} &= \frac{N\varepsilon}{(x^{-1}-1)} \times \frac{1}{N} = \frac{\varepsilon}{(x^{-1}-1)} \\ &= \frac{\varepsilon}{\left[\exp\left(\frac{\varepsilon}{kT}\right) - 1\right]} \end{aligned}$$

In the present study, members are nothing but photons of energies $h\nu, 2h\nu, 3h\nu$ e Hence average energy associated with each photon is given by

$$\frac{h\nu}{\left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]}$$

If we assume that all the photons are within the wavelength range λ and $\lambda + d\lambda$, th number of photons per unit volume (i.e. photon density) is given by

$$8\pi\lambda^{-4}d\lambda$$

Hence total energy of photon within the wavelength range λ and $\lambda + d\lambda$ is given by

$$dE = E_\lambda d\lambda = 8\pi\lambda^{-4} d\lambda \cdot \frac{h\nu}{\left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]}$$

$$\text{i.e.} \quad E_\lambda = \frac{8\pi h(c/\lambda)}{\lambda^4 \left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]}$$

$$= \frac{8\pi hc}{\lambda^5 \left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]} \qquad (6.5)$$

This represent ***Planck's law***.

(i) For shorter wavelengths

$$\exp\left(\frac{h\nu}{kT}\right) \geq 1$$

Eq. (6.5) reduces to

$$E_\lambda = 8\pi hc\lambda^{-5} \exp\left(-\frac{h\nu}{kT}\right)$$

$$= C_1\lambda^{-5} \exp\left(-C_2/\lambda T\right)$$

where $C_1 = 8\pi hc$ and $C_2 = \frac{hc}{k}$

This represents Wien's radiation law.

(ii) For longer wavelengths, $\frac{h\nu}{kT}$ is small.

$$\text{Hence} \quad \exp\left(\frac{h\nu}{kT}\right) = 1 + \frac{h\nu}{kT} \quad \text{(neglecting higher power)}$$

Hence Eq. (6.5) reduces to

$$E_\lambda = \frac{8\pi hc}{\lambda^5 \left[1 + \frac{h\nu}{kT} - 1\right]}$$

$$= \frac{8\pi hckT}{\lambda^5 h\nu}$$

$$\text{i.e.,} \quad E_\lambda = \frac{8\pi kT}{\lambda^4}$$

This represents Rayleigh-Jean's law