

The Ultraviolet Catastrophe

The radiation rate is proportional to this energy density for frequency interval from ν to $\nu + d\nu$. The formula due to Rayleigh-Jeans predicts, as the frequency ν increases towards the ultraviolet end of the spectrum, the energy density should increase as ν^2 . In the limit of infinitely high frequencies, $u(\nu)d\nu$ therefore should also go to infinity. In reality, the energy density (and radiation rate) falls to 0 as $\nu \rightarrow \infty$ shown in figure 4. This discrepancy became known as the *ultraviolet catastrophe* of classical physics. Thus, classical physics was failed to explain the blackbody spectrum.

Figure 6

The figure 6 shows a comparison of the Rayleigh-Jeans formula for the spectrum of the radiation from a blackbody at 1500K with the observed spectrum. The discrepancy is known as the ultraviolet catastrophe because it increases with increasing frequency. This failure of classical physics led Planck to discover that radiation is emitted in *quanta* whose energy is $h\nu$.

Quantum Explanation: Planck's Law

Planck's Quantum Postulates

In 1900 the German physicist Max Planck announced that by making a somewhat peculiar modification in the classical calculation he could derive a correct formula that agreed with the experimental data at all frequencies. Planck found that he could derive a correct formula by modifying the calculation of the average energy per standing wave in the cavity.

Postulate I: Planck postulates that the energy of an oscillator is *discrete*, i.e., it can have only certain values ϵ_n . He stated that, *a system undergoing S. H. M. with frequency ν can only have and therefore can only emit energies given by $\epsilon_n = nh\nu$, where $n = 1, 2, 3, \dots$ and h is a constant*, which is now known as Planck's constant. The value of h , which resulted in a good fit between the experimental data and formula found by Planck, is 6.63×10^{-34} Joule-sec.

Postulate II: We know that the energy of a harmonic oscillator (such as an oscillating spring) is

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proportional to the square of the amplitude of the motion. In a classical treatment, this amplitude may vary continuously from zero to infinity. In contrast, Planck postulated that atomic oscillator can have only *discrete* energy values. By Planck's, because an oscillator can take only certain values for the energy, when they lose that energy (when it drops from one energy state to the next lower one) they lose it in multiples of $h\nu$. These discrete bundle of energy $h\nu$ are called **quanta** (singular, *quantum*) from the Latin for “how much.” This is now known as **Planck radiation law**.

Planck Radiation Law

As the procedure adopted by Rayleigh and Jeans did not yield a formula consistent with experimental data, Planck abandoned the hypothesis of continuous emission of radiation by oscillator, and assumed that they emit energy only when the energy absorbed is a certain minimum quantity ϵ or some integral multiple of ϵ . Thus radiation of energy ϵ can be obtained from oscillator having the energy content $\epsilon, 2\epsilon, 3\epsilon, \dots, n\epsilon, \dots$, where n is any integer. Let us now find the average energy per oscillator (and so per standing wave) in the cavity.

This can be done by classical methods, using Maxwell-Boltzmann formula according to which the probability that an oscillator will possess the energy ϵ_n is proportional to $\exp(-\epsilon_n/kT)$ at the temperature T . Now let $N_0, N_1, N_2, \dots, N_n, \dots$ be the number of oscillator having the energy, $0, \epsilon, 2\epsilon, 3\epsilon, \dots, n\epsilon, \dots$ etc. Then, we have

$$N_n = N_0 \exp(-n\epsilon/kT) \quad (9)$$

The total number of oscillators, N , is given by

$$\begin{aligned} N &= N_0 + N_1 + N_2 + \dots + N_n + \dots \\ N &= N_0(1 + e^{-\epsilon/kT} + e^{-2\epsilon/kT} + \dots + e^{-n\epsilon/kT} + \dots) \\ N &= N_0(1 - e^{-\epsilon/kT})^{-1} \end{aligned} \quad (10)$$

and similarly the total energy of the oscillator is

$$\begin{aligned} E &= \epsilon N_1 + 2\epsilon N_2 + 3\epsilon N_3 + \dots + n\epsilon N_n + \dots \\ E &= \epsilon N_0(e^{-\epsilon/kT} + 2e^{-2\epsilon/kT} + 3e^{-3\epsilon/kT} + \dots + ne^{-n\epsilon/kT} + \dots) \\ E &= \epsilon N_0 e^{-\epsilon/kT} (1 + 2e^{-\epsilon/kT} + 3e^{-2\epsilon/kT} + \dots + ne^{-(n-1)\epsilon/kT} + \dots) \\ E &= \epsilon N_0 e^{-\epsilon/kT} (1 - e^{-\epsilon/kT})^{-2} \end{aligned} \quad (11)$$

Hence the average energy per oscillator (and so per standing wave) in the cavity is

$$\begin{aligned} \bar{\epsilon} &= \frac{E}{N} = \frac{\epsilon e^{-\epsilon/kT}}{(1 - e^{-\epsilon/kT})} = \frac{\epsilon}{e^{\epsilon/kT} - 1} \\ \text{or } \bar{\epsilon} &= \frac{h\nu}{e^{h\nu/kT} - 1} \end{aligned} \quad (12)$$

instead of the energy equipartition average of kT which Rayleigh and Jeans used. Thus, the energy $u(\nu)d\nu$ per unit volume in the cavity in frequency interval between ν to $\nu + d\nu$, i.e., spectral energy density of blackbody is, therefore

$$u(\nu)d\nu = \bar{\epsilon} G(\nu)d\nu = \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1} \quad (13)$$

which agrees with the experimental findings. This is now known as **Planck radiation formula** (in terms of

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frequency). Here we write $\epsilon = h\nu$ where the h is called the Planck's constant.

Since, $\nu = c/\lambda$, hence

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

As an increase in frequency corresponds to a decrease in wavelength, so

$$u(\lambda)d\lambda = -u(\nu)d\nu$$

therefore
$$u(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda kT} - 1} \quad (14)$$

This is known as **Planck radiation formula** (in terms of wavelength). This gives the energy density for wavelength in the spectrum of blackbody. This law has been verified by numerous experiments (including the experiments of Lummer and Pringsheim).

Complete Fit with the Experiments

At high frequencies, $h\nu \gg kT$ and $e^{h\nu/kT} \rightarrow \infty$, which means that $u(\nu)d\nu \rightarrow 0$ as observed in reality. So now the Planck's formula is perfectly in agreement with experimental results obtain by Lummer and Pringsheim for the spectrum of blackbody, at high frequencies and now no more *ultraviolet catastrophe*.

Wien's Law: Special Case of Planck's Radiation Formula

When frequency is large (and hence wavelength is small), then $e^{hc/\lambda kT}$ would be so large that we may neglect the 1 present in the denominator of eq. 14 and is written as

$$u(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5} e^{-hc/\lambda kT} d\lambda$$

Substituting, $c_1 = 8\pi hc$ and $c_2 = hc/k$, we get

$$u(\lambda)d\lambda = \frac{c_1}{\lambda^5} e^{-c_2/\lambda T} d\lambda$$

It is Wien's law holding at high frequencies (short wavelengths) only.

Rayleigh-Jeans Law: Special Case of Planck's Radiation Formula

At low frequencies, $h\nu \ll kT$ and $h\nu/kT \ll 1$. In general,

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

If x is small, $e^x \approx 1 + x$, and so for $h\nu/kT \ll 1$ we have

$$\frac{1}{e^{h\nu/kT} - 1} \approx \frac{1}{1 + \frac{h\nu}{kT} - 1} \approx \frac{kT}{h\nu}$$

Thus at low frequencies Planck's formula becomes

$$u(\nu)d\nu \approx \frac{8\pi h}{c^3} \nu^3 \left(\frac{kT}{h\nu} \right) d\nu \approx \frac{8\pi kT}{c^3} \nu^2 d\nu$$

which is the **Rayleigh-Jeans formula** deduce from Planck's law, which is already in agreement with experimental results at low frequencies.

Planck's formula is clearly on the right track, in fact, it has turned out to be completely correct.