Planck's Derivation of the Energy Density of Blackbody Radiation

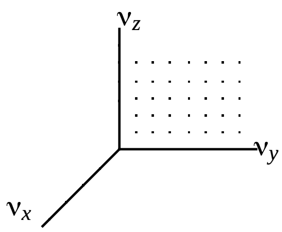
To calculate the number of modes of oscillation of electromagnetic radiation possible in a cavity, consider a one-dimensional box of side L. In equilibrium only standing waves are possible, and these will have nodes at the ends $x = 0, L$.

$$\frac{L}{\lambda} = \frac{n_x}{2} \qquad n_x = 1, 2, \ldots$$

and since $\lambda\nu = c$ = speed of propagation for all wave motion,

$$\nu = n_x \frac{c}{2L}$$

There will be two modes for each trio of integers (one for each dimension) n_x, n_y, n_z because there are two independent polarizations possible. To find the number of modes with frequency between ν and $\nu + d\nu$, look at an array of points:



Each cube has side $\frac{c}{2L}$.

There is one point per cube of volume $\left(\frac{c}{2L}\right)^3$, and only positive integers, n_x, n_y, n_z are acceptable. Thus the number of triplets of positive integers is equivalent to the volume of one octant of the space divided by the volume $\left(\frac{c}{2L}\right)^3$:

$$\begin{array}{c}\text{no. modes of oscillation}\\ \text{between } \nu \text{ and } \nu + d\nu\end{array} = \frac{2 \times \frac{1}{8} \times 4\pi\nu^2\, d\nu}{\left(\frac{c}{2L}\right)^3} = \frac{8\pi V}{c^3}\nu^2 d\nu$$

The factor $4\pi\nu^2\, d\nu$ is the volume of a thin spherical shell; L^3 has been replaced by V, the volume of the cavity. It is convenient to express this *density of states* in terms of other variables:

$$g(\nu)\, d\nu = \frac{8\pi V}{c^3}\nu^2 d\nu \qquad\qquad g(\lambda)\, d\lambda = \frac{8\pi V}{\lambda^4} d\lambda$$

$$g(\varepsilon)\, d\varepsilon = \frac{8\pi V}{(hc)^3}\varepsilon^2 d\varepsilon \qquad\qquad g(p)\, dp = \frac{8\pi V}{h^3} p^2 dp$$

$$\varepsilon = h\nu = pc$$

The expressions involving frequency ν, energy ε, and wavelength λ are classical physics. If we assume that each mode of oscillation represents a harmonic oscillator, with $\frac{1}{2}kT$ each potential and kinetic energy on the average (in accordance with the equipartition theorem), we get the *Rayleigh-Jeans law*:

$$\frac{\text{Energy}}{\text{Volume}} \equiv u_\nu d\nu = \frac{8\pi}{c^3} kT\nu^2 d\nu \quad \text{or} \quad \frac{\text{Energy}}{\text{Volume}} \equiv u_\lambda d\lambda = \frac{8\pi\, kT}{\lambda^4} d\lambda$$

The divergence of this relation at high frequency or low wavelength was known as the *ultraviolet catastrophe*. Planck's new idea was to assume that the possible energies of the oscillators were quantized, *i.e.*, that oscillators of frequency ν could only have energy

$$\varepsilon_n = nh\nu \qquad n = 0, 1, 2, \ldots$$

where h was a new constant he introduced. Now known as *Planck's constant*, it was determined by fitting the theoretical curve to the experimental data. The average energy per oscillator was calculated from the Maxwell-Boltzmann distribution:

$$\bar{\varepsilon} = \frac{\sum_n \varepsilon_n\, e^{-\varepsilon_n/kT}}{\sum_n e^{-\varepsilon_n/kT}}$$

The denominator is called the *partition function*, and is often represented by Z. It is easily evaluated by summing the geometric series:

$$Z = \sum_{n=0}^{\infty} e^{-\varepsilon_n/kT} = \sum_{n=0}^{\infty} e^{-nx} = \frac{1}{1 - e^{-x}} \quad \text{where } x = \frac{h\nu}{kT}$$

The numerator can then be found from the denominator:

$$\sum_{n=0}^{\infty} n\,h\nu e^{-nx} = h\nu\left(-\frac{dZ}{dx}\right) = \frac{h\nu e^{-x}}{\left(1 - e^{-x}\right)^2}$$

and the average energy per oscillator is seen to be

$$\bar{\varepsilon} = \frac{h\nu}{e^{x} - 1} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

Thus the energy per unit volume of the radiation in the cavity is

$$u_\nu(T)\,d\nu = \frac{8\pi}{c^3}\frac{h\nu^3}{e^{h\nu/kT} - 1}\,d\nu \qquad \text{or} \qquad u_\lambda(T)\,d\lambda = \frac{8\pi hc}{\lambda^5}\frac{1}{e^{hc/\lambda kT} - 1}\,d\lambda$$

The total energy per unit volume (energy density) is the integral over all frequencies or wavelengths:

$$u(T) = \frac{8\pi h}{c^3}\int_0^\infty \frac{\nu^3}{e^{h\nu/kT} - 1}\,d\nu = \frac{8\pi\left(kT\right)^4}{(hc)^3}\int_0^\infty \frac{x^3}{e^{x} - 1}\,dx$$

The integral is obviously a pure number. It happens to be $\pi^4/15$. Thus the energy density in a black body is

$$u(T) = \frac{8\pi^5\left(kT\right)^4}{15(hc)^3} \equiv aT^4$$

This may be thought of as one form of the Stefan-Boltzmann law. [Josef Stefan in 1879 showed experimentally that the flux from a cavity in thermal equilibrium is proportional to the fourth power of the absolute temperature, and Ludwig Boltzmann in 1884 derived this fourth power relation from thermodynamic theory. Until Planck's work, there was no theoretical method of determining the constants of proportionality.]

The *flux* radiated from the surface of a black body is related to the energy density:

$$F_\nu = \frac{c}{4}u_\nu = \frac{2\pi}{c^2}\frac{h\nu^3}{e^{h\nu/kT} - 1} \qquad \text{or} \qquad F_\lambda = \frac{c}{4}u_\lambda = \frac{2\pi hc^2}{\lambda^5}\frac{1}{e^{hc/\lambda kT} - 1}$$

where $F_\nu\,d\nu = \text{flux} = \dfrac{\text{energy}}{\text{area time}}$ with frequency between ν and $\nu + d\nu$.

The total flux, obtained by integrating over all frequencies, is

$$F = \frac{c}{4}u = \frac{ac}{4}T^4 \equiv \sigma T^4$$

This is the usual form of the Stefan-Boltzmann law. The constant

$$\sigma = 5.670 \times 10^{-8}\,\frac{\text{W}}{\text{m}^2\,\text{K}^4} = 5.670\times\ 10^{-5}\,\frac{\text{erg}}{\text{cm}^2\ \text{s}\ \text{K}^4} = \textbf{Stefan-Boltzmann constant}.$$

It is of interest to look at the limits of the Planck distribution.
At low frequency or large wavelength,

$$u_\nu(T) \rightarrow \frac{8\pi\nu^2 kT}{c^3} \qquad \text{and} \qquad u_\lambda(T) \rightarrow \frac{8\pi kT}{\lambda^4} = \text{Rayleigh-Jeans law.}$$

Note that Planck's constant drops out. This is one example of the correspondence principle; as h becomes negligible compared to other quantities in the quantum mechanical law, the result approaches the classical law. At high frequency or small wavelength,

$$u_\nu(T) \rightarrow \frac{8\pi h\nu^3}{c^3}e^{-h\nu/kT} \qquad \text{and} \qquad u_\lambda(T) \rightarrow \frac{8\pi hc}{\lambda^5}e^{-hc/\lambda kT}$$

The frequency or wavelength of maximum flux can be found by setting the derivative with respect to ν or λ equal to zero:

$$0 = \frac{d}{d\nu}F_\nu = \frac{2\pi h}{c^2}\frac{1}{e^{h\nu/kT}-1}\left[3\nu^2 - \frac{\nu^3(h/kT)e^{h\nu/kT}}{e^{h\nu/kT}-1}\right]$$

which simplifies to $\left[3 = \frac{xe^x}{e^x-1}\right]$ with $x = \frac{h\nu}{kT}$

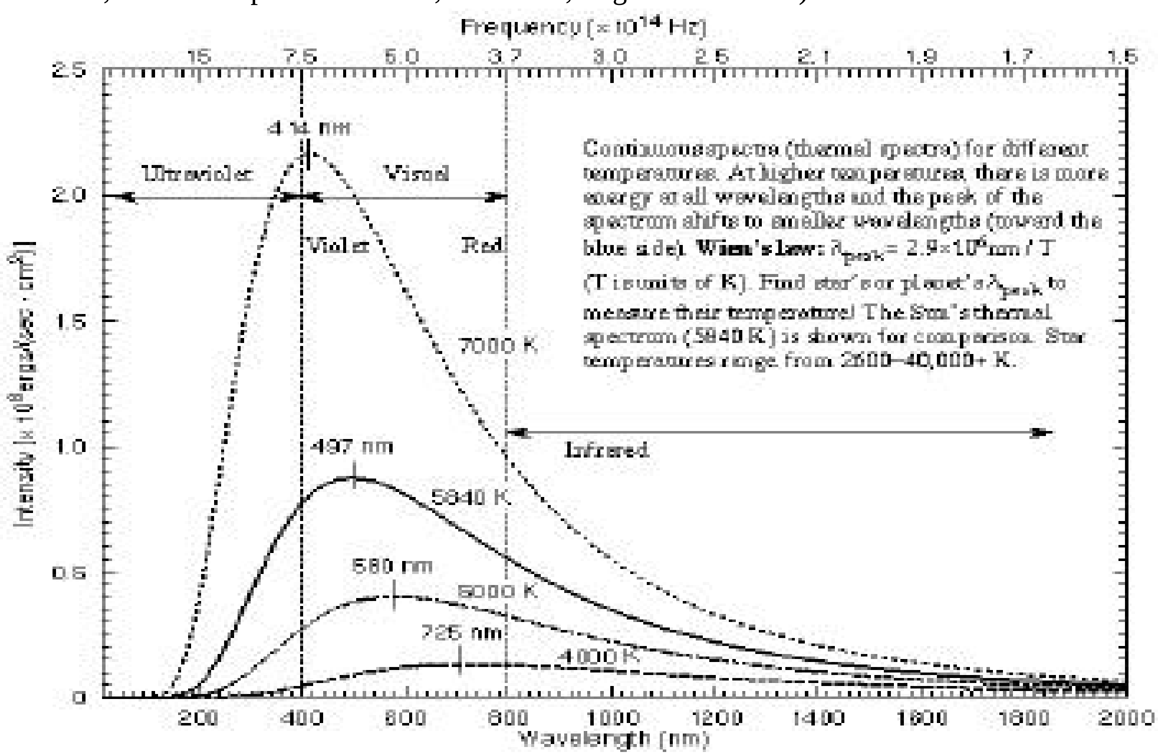
The transcendental equation may be solved graphically [graph $y = x$ and $y = 3(1 - e^{-x})$ and find the nonzero point of intersection] or numerically. The result is $x = 2.821$ meaning that flux as a function of frequency is a maximum at $\nu_{max} = 2.821\ kT/h$. Maximization of F_λ is similar:

$$0 = \frac{d}{d\lambda}F_\lambda \qquad \frac{ye^y}{e^y-1} = 5 \quad \text{with} \quad y = \frac{hc}{\lambda kT} \qquad \text{which yields } y = 4.965.$$

Flux as a function of wavelength is a maximum at

$$\lambda_{max} = \frac{hc}{4.965kT} = \frac{2.90\ \text{mm K}}{T}.$$

At room temperature T 290 K, and thermal radiation is a maximum at λ 0.01 mm = 10 μm, in the infrared. Fortunately, our eyes are not sensitive to this wavelength. The maximum intensity of the sun's radiation is at λ 500 nm, implying that the sun's *surface temperature* is T 5800 K. The variation of intensity with wavelength of the sun [and other stars] is not exactly that of a black body, but it is rather close. The universal microwave background radiation, peaked at λ 1mm, fits the Planck curve for a black body of $T = 2.728$ K to great precision. (The deviation, of order 6 parts in 10^6 is, of course, of great interest.)



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