The Ultraviolet Catastrophe

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1 The Raleigh-Jeans Radiation Law

Consider a cube of length L where radiation is being reflected off the walls. Standing waves occur only if an integer number of half wavelengths fit into L. That is, $L = n\lambda/2$. Or

$$\lambda = \frac{2L}{m} \tag{1}$$

or

$$f = \frac{mc}{2L} \tag{2}$$

Switching to k-space, we obtain

$$k = \frac{2\pi}{\lambda} = \frac{2\pi f}{c} = \frac{m\pi}{L} \tag{3}$$

using Equation 2. If m_x, m_y, m_z are the integers for three orthogonal directions in k-space, then:

$$k^2 = \pi^2\left[\left(\frac{m_x}{L}\right)^2 + \left(\frac{m_y}{L}\right)^2 + \left(\frac{m_z}{L}\right)^2\right] \tag{4}$$

or

$$m_x^2 + m_y^2 + m_z^2 = \frac{4L^2f^2}{c^2} \tag{5}$$

Still in k-space, a spherical shell of radius R and outer radius $R + dr$ is given by

$$dV = 4\pi R^2\,dR\,. \tag{6}$$

If $R = \sqrt{m_x^2 + m_y^2 + m_z^2}$, then

$$R = \sqrt{\frac{4L^2f^2}{c^2}} = \frac{2Lf}{c}. \tag{7}$$

Differentiating,

$$dR = \frac{2L\,df}{c}. \tag{8}$$

Putting Equation 7 and Equation 8 back into Equation 6 gives

$$\begin{aligned} dV &= 4\pi\left(\frac{2Lf}{c}\right)^2\left(\frac{2L}{c}\right)df \qquad (9)\\ &= 32\pi\left(\frac{L^3f^2}{c^3}\right)df \qquad (10)\end{aligned}$$

However, we require m_x, m_y, m_z to be positive. Thus, we take only one octant of the spherical volume. So the number dN for the non-negative combinations of m_x, m_y, m_z in this volume is given by $dN = 1/8\, dV$. Therefore

$$dN = 4\pi f^2 \left(\frac{L}{c}\right)^3 df\,. \tag{11}$$

From thermodynamics, the average kinetic energy per degree of freedom is $1/2 k_B T$. For harmonic oscillators, the kinetic energy and potential energies are of same magnitude so the average energy is given by $\langle E \rangle = k_B T$. Thus,

$$\frac{dE}{df} = k_B T \frac{dN}{df} = 4\pi k_B T f^2 \left(\frac{L}{c}\right)^3 \tag{12}$$

and the average energy density u is given by

$$\frac{du}{df} = \frac{1}{L^3}\frac{dE}{df} = \frac{4\pi k_B T f^2}{c^3}. \tag{13}$$

However, we have only considered one polarisation of light, but there is another. So therefore we have

$$\frac{du}{df} = \frac{8\pi k_B T f^2}{c^3} \tag{14}$$

Or, in terms of wavelength:

$$\frac{du}{df} = u_f = \frac{8\pi}{\lambda^4} k_B T \tag{15}$$

Equation 15 is the Raleigh-Jeans law of radiation and it holds for small frequencies. However, it approaches a singularity at high frequencies and is not empirically supported as shown below.

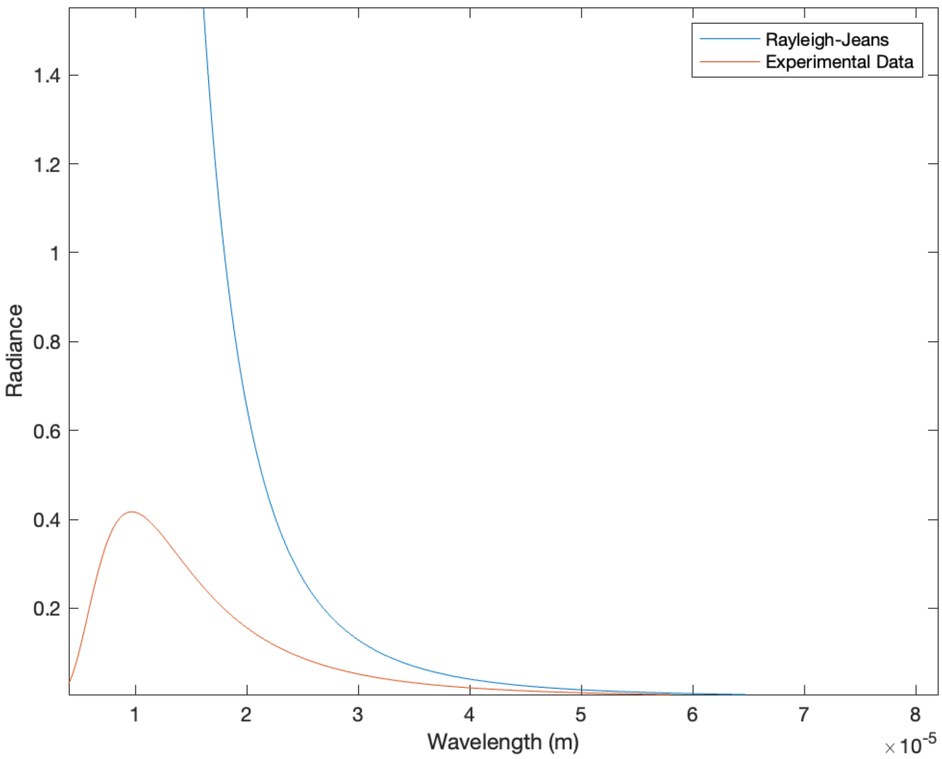

Figure 1: Rayleigh-Jeans prediction compared to experimental data

2 Planck's Radiation Law

Max Planck assumed that energy comes in discrete packets of energy in integer multiples of $\hbar\omega$. The crucial insight is that electromagnetic waves in a cavity can be described by quantum harmonic oscillators. The energy of the system is $E = (n + \frac{1}{2})\hbar\omega$ for $n = 0, 1, 2, ...,$, and so the Partition Function is

$$Z = \sum_{\alpha} e^{-\beta E_\alpha} = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega} = e^{-\frac{1}{2}\beta\hbar\omega} \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}. \tag{16}$$

The internal energy of this system is given by

$$U = -\frac{d \ln Z}{d\beta} = \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right) \tag{17}$$

The density of states of electromagnetic waves as a function of wave vector k is given by

$$g(k)\, dk = \frac{4\pi k^2\, dk}{(2\pi/L)^3} \times 2, \tag{18}$$

where the cavity is a cube of length L and the factor of 2 corresponds to two possible polarisations of the electromagnetic waves. Thus

$$g(k)\, dk = \frac{V k^2\, dk}{\pi^2} \tag{19}$$

and the density of states $g(\omega)$, now written as a function of frequency is

$$g(\omega) = g(k)\frac{dk}{d\omega} = \frac{g(k)}{c}, \tag{20}$$

and so

$$g(\omega)\, d\omega = \frac{V\omega^2\, d\omega}{\pi^2 c^3} \tag{21}$$

Now we can derive the internal energy for the photon gas by using the expression of U for a single quantum harmonic oscillator in Equation 17 to give

$$U = \int_0^\infty g(\omega)\hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right) d\omega\,. \tag{22}$$

There is a problem since the first time diverges in the integral

$$\int_0^\infty g(\omega)\frac{1}{2}\hbar\omega\, d\omega \to \infty. \tag{23}$$

However, we can redefine our zero point of energy as $\frac{1}{2}\hbar\omega$ so that this infinity is conveniently swept underneath the rug. We are left with

$$U = \int_0^\infty g(\omega)\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\, d\omega = \frac{V\hbar}{\pi^2 c^3}\int_0^\infty \frac{\omega^3\, d\omega}{e^{\beta\hbar\omega} - 1}. \tag{24}$$

Using the integral relation

$$\int_0^\infty \frac{x^3\, dx}{e^x - 1} = \zeta(4)\Gamma(4) = \frac{\pi^4}{15} \tag{25}$$

to obtain

$$U = \left(\frac{V\pi^2 k_B^4}{15 c^3 \hbar^3}\right) T^4 \tag{26}$$

Now using $P = \frac{1}{4}uc = \frac{1}{4}\frac{U}{V}c$, we find that

$$P = \frac{\pi^2 k_B^4}{60c^2\hbar^3} T^4 = \sigma T^4 \tag{27}$$

where the Stefan-Boltzmann constant σ is

$$\sigma = \frac{\pi^2 k_B^4}{60c^2\hbar^3} = 5.67 \times 10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}} \tag{28}$$

Equation 24 can be rewritten as

$$u = \frac{U}{V} = \int u_\omega \, d\omega \tag{29}$$

where u_ω is a different form of the spectral energy density as a function of angular frequency. It thus takes the form

$$u_\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \tag{30}$$

This spectral density is known as the blackbody distribution. It's also expressed in terms of wavelength λ by the change of variables to get

$$u_\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{\beta hc/\lambda} - 1}. \tag{31}$$

This is in remarkable agreement with experimental data and we can see that for temperature of a human body (310.15 K), the maximum radiance occurs at $\sim 10^{-5}$m. This is the infrared region of the electromagnetic spectrum, which is why infrared cameras are effective at spotting humans by detecting infrared radiation coming from our body.

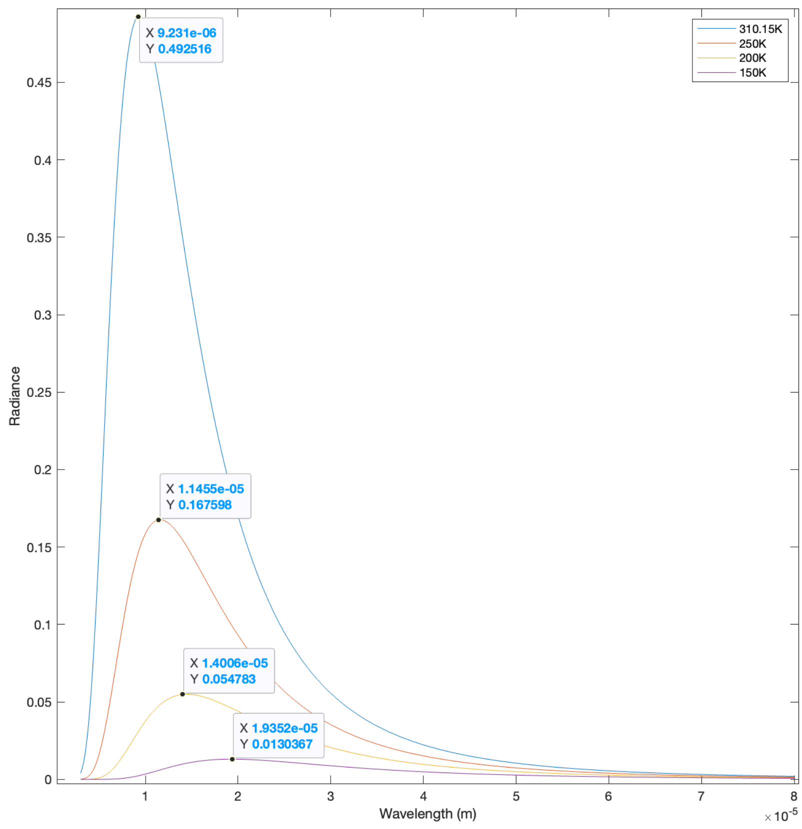

Figure 2: Planck's Law of blackbody radiation plotted for a range of temperatures

Note that at long wavelengths (low frequencies), when $\beta hc/\lambda << 1$, the exponential term can be written as

$$e^{\beta hc/\lambda} \approx 1 + \frac{\beta hc}{\lambda}, \tag{32}$$

using the Taylor Expansion. Thus, Equation 31 becomes

$$u_\lambda = \frac{8\pi hc}{\lambda^5}\frac{\lambda}{\beta hc} = \frac{8\pi}{\lambda^4}k_B T \tag{33}$$

in the limit of long wavelengths. This is identical to Rayleigh-Jeans Law in Equation 15.