In Chapter 1, the birth of quantum mechanics is described. **Many consider Max Planck** the father of quantum mechanics. On December 14, 1900 he proposed that the energy of any system that exhibits a time dependence characterized by an oscillatory frequency ν is quantized in the following way

$$\varepsilon = nh\nu \qquad n = 0,1,2,3,...$$

where h is a universal constant called **Planck's constant** (h = 6.63 × 10^{-34} Js). Max Planck showed that this proposal was required to solve the **ultra-violet catastrophe**. In 1918, Max Planck received the Nobel Prize of Physics for this work.

It was clear at that time that classical physics was breaking down:

- Relativity: describes physics at high velocities (comparable to the speed of light).
- Quantum Mechanics: describes physics at small dimensions.

At low velocities and large dimensions, relativity and quantum mechanics approach classical physics.

Blackbody radiation contributed to the breakdown of classical physics. Blackbody radiation is the thermal radiation emitted by a body that absorbs all incident radiation. The thermal radiation emitted by any body has the following properties:

- The thermal radiation is independent of the material.
- The thermal radiation depends strongly on the temperature T.
- If the temperature T increases, the radiated energy and the frequency of the most intense radiation both increase.

The thermal radiation emitted by a blackbody is often specified in terms of the **spectral radiance $R_T(\nu)d\nu$** which is the energy emitted per unit time per unit area with a frequency between ν and $\nu + d\nu$. The total radiance R_T is obtained by integrating the spectral radiance over all frequencies:

$$R_T = \int_0^\infty R_T(\nu)\,d\nu$$

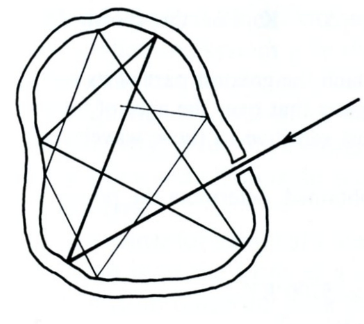
Experiments show that R_T is proportional to T^4. This relation is known as **Stephan's law**:

$$R_T = \sigma T^4$$

where σ = 5.67 × 10^{-8} W/(m^2K^4) is the Stefan-Boltzmann constant.

Now consider a **blackbody**. A blackbody is a body that absorbs all radiation that is incident on it. Since all incident radiation is absorbed, the emitted radiation depends only on the thermal emission properties of the body.

A good approximation of a blackbody is a cavity with a hole (see Figure on the right). The hole acts like a blackbody since:



- Radiation falling onto it from the outside will scatter in the cavity until being absorbed. All incident radiation is thus absorbed.
- The only radiation leaving the hole must be blackbody radiation (per definition) and we thus conclude that the cavity contains blackbody radiation that depends only on T and not on the material of the cavity.

In order to predict the properties of the radiation leaving the hole, we need to explore the properties of the radiation in the cavity. The energy of the thermal radiation with a frequency between ν and $\nu + d\nu$ per unit volume inside the cavity is equal to the product of the number of electromagnetic waves per unit volume with a frequency between ν and $\nu + d\nu$ and the average energy of each wave. **The classical and the quantum mechanical picture differ on the energy of each wave.**

Let us first consider the classical picture. For a one-dimensional cavity with conducting walls at $x = 0$ and $x = a$, we must require that the electric field of the electromagnetic (EM) wave at $x = 0$ and at $x = a$ must be zero at all times:

$$E(0,t) = E(a,t) = 0$$

This can only happen if the electric field is described by a standing wave:

$$E(x,t) = E_0 \sin\left(\frac{2\pi x}{\lambda}\right)\sin(2\pi\nu t)$$

With this definition of the electric field, the electric field at $x = 0$ is zero at all times. In order for the electric field to be zero at $x = a$ the following condition must be met:

$$\sin\left(\frac{2\pi a}{\lambda}\right) = 0 \quad \Rightarrow \quad \frac{2\pi a}{\lambda} = n\pi \quad \Rightarrow \quad \frac{2a}{\lambda} = n \text{ where } n = 1, 2, 3, 4, ...$$

Since the wavelength of the EM wave and its frequency are related ($\nu = c/\lambda$), the wavelength requirement of the standing wave can be expressed in terms of a frequency requirement:

$$\frac{2a}{\lambda} = \frac{2a}{c}\nu = n \text{ where } n = 1, 2, 3, 4, ...$$

This relation can be used to determine the number of states (or the number of distinct EM waves) with a frequency between ν_1 and ν_2:

$$n_2 - n_1 = \frac{2a}{c}(\nu_2 - \nu_1)$$

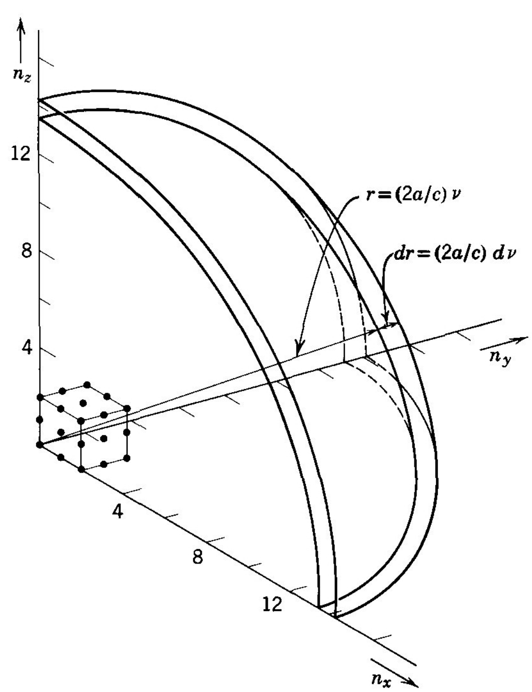
This relation is correct for one particular polarization of the EM wave. In a one-dimensional cavity there are two independent polarization directions and the number of states we need to consider is thus double the number of states calculated above. Thus:

$$n_2 - n_1 = \frac{4a}{c}(\nu_2 - \nu_1)$$

Over a small frequency interval, this equation can be rewritten as

$$N(\nu)d\nu = \frac{4a}{c}d\nu$$

How does this calculation change when we consider 3 dimensions? Any EM wave in three dimensions can be represented by a set of 3 n values and correspond to a point (n_x, n_y, n_z) in the coordinate system shown in the Figure. The frequency of the EM wave is related to the distance r of that point and the origin of the coordinate system:



$$\nu = \frac{cr}{2a}$$

The density of states in the coordinate system used in Figure is 1 state per unit volume. The number of waves with a frequency between ν and $\nu + d\nu$ is thus equal to the volume between 1/8th of a sphere of radius r and a sphere of radius $r + dr$:

$$\frac{1}{8}\left\{\frac{4}{3}\pi\left(r+dr\right)^3-\frac{4}{3}\pi r^3\right\}=\frac{1}{8}\left\{4\pi r^2 dr\right\}=\frac{1}{2}\pi\left(\frac{2a}{c}\nu\right)^2\left(\frac{2a}{c}d\nu\right)=4\pi\left(\frac{a}{c}\right)^3\nu^2 d\nu$$

Since each wave can have two polarizations, the number of states with a frequency between ν and $\nu + d\nu$ can now be determined and is equal to

$$N\left(\nu\right)d\nu=8\pi\left(\frac{a}{c}\right)^3\nu^2 d\nu=\frac{8\pi}{c^3}a^3\nu^2 d\nu=\frac{8\pi}{c^3}V\nu^2 d\nu$$

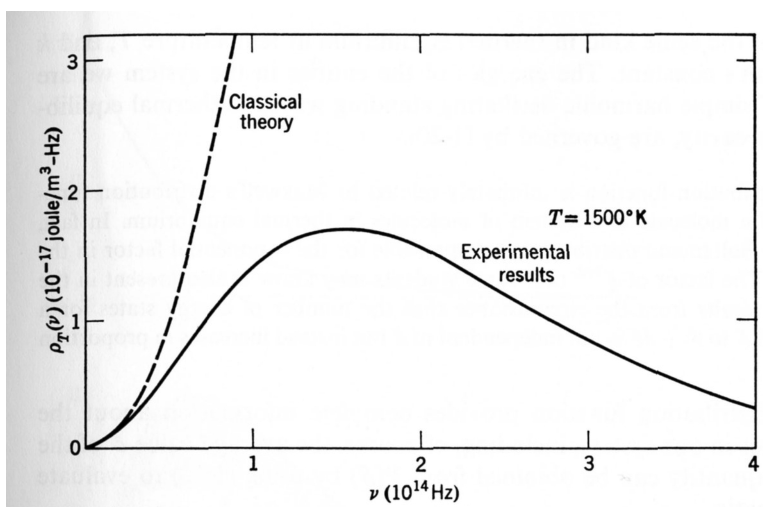
where V is the volume of the cavity.

In Physics 141 we showed that the average kinetic energy per degree of freedom is $kT/2$. The total energy of a system carrying out sinusoidal motion, such as a pendulum or and EM wave, is twice the average kinetic energy and it thus equal to kT. The energy density per unit volume of EM waves with frequencies between ν and $\nu + d\nu$ is thus equal to

$$\rho_T\left(\nu\right)d\nu=\frac{N\left(\nu\right)d\nu}{V}kT=\frac{8\pi\nu^2 kT}{c^3}d\nu$$

This relation is known as the **Rayleigh-Jeans formula for blackbody radiation**.

The classical theory thus predicts that the energy density is proportional to the square of the frequency. This prediction differs from the experimental results that show the energy density approaches 0 at high frequencies. This problem is known as **the ultraviolet catastrophe**.



In order to solve the ultraviolet catastrophe, Planck proposed that the assumption that the average total energy of an EM wave is kT, independent of frequency, couldn't be correct. He concluded that at high frequencies, the total energy of an EM wave must approach 0. The frequency independence of the average total energy of the EM wave is a consequence of the equipartition law of statistical mechanics. The equipartition law states that the probability to find a system with an energy between ε and $\varepsilon + d\varepsilon$ is equal to

$$P(\varepsilon)d\varepsilon = \frac{e^{-\varepsilon/kT}}{kT}$$

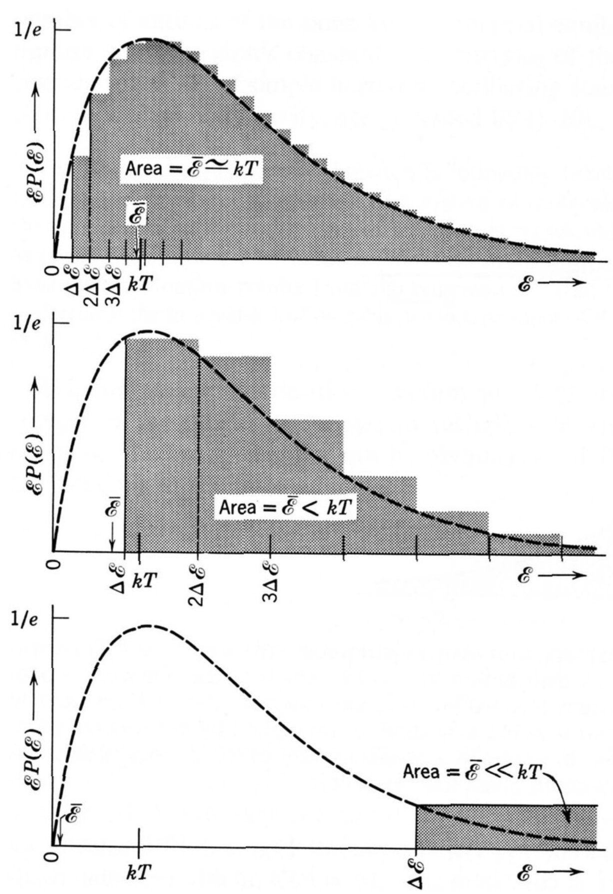
The corresponding average energy of the system is equal to

$$\bar{\varepsilon} = \frac{\int_0^\infty P(\varepsilon)\varepsilon d\varepsilon}{\int_0^\infty P(\varepsilon)d\varepsilon} = \frac{\int_0^\infty e^{-\varepsilon/kT}\varepsilon d\varepsilon}{\int_0^\infty e^{-\varepsilon/kT}\, d\varepsilon} = kT$$

Planck proposed that the energy of the EM wave is quantized, and that the energy can only take on values that are multiple of $h\nu$:

$$\varepsilon = nh\nu \qquad n = 0,1,2,3,...$$

When the energy is quantized, the integrals used to calculate the average energy of the EM wave are replaced by an infinite sum over n. For low frequencies, the average energy will still approach kT and in this frequency regime, the classical theory agrees with the experimental results. At higher frequencies, the area under $\varepsilon P(\varepsilon)$ decreases and the average energy of the EM wave thus decreases. Note: the sum over $P(\varepsilon)$ still must be equal to 1 since the probability distribution must be properly normalized. With this assumption, the average energy of the EM wave is found to be equal to



$$\bar{\varepsilon} = \frac{\sum_{n=0}^{\infty}(nh\nu)\left(\frac{e^{-nh\nu/kT}}{kT}\right)}{\sum_{n=0}^{\infty}\left(\frac{e^{-nh\nu/kT}}{kT}\right)} = h\nu\frac{\sum_{n=0}^{\infty}\left(ne^{-nh\nu/kT}\right)}{\sum_{n=0}^{\infty}\left(e^{-nh\nu/kT}\right)} = \frac{h\nu}{e^{h\nu/kT}-1}$$

The average energy thus has the required behavior:

- At low frequencies: $\bar{\varepsilon} \to \lim_{\nu \to 0}\left(\frac{h\nu}{e^{h\nu/kT}-1}\right) = \frac{h\nu}{\left(1+h\nu/kT\right)-1} = kT$
- At high frequencies: $\bar{\varepsilon} \to \lim_{\nu \to \infty}\left(\frac{h\nu}{e^{h\nu/kT}-1}\right) = 0$

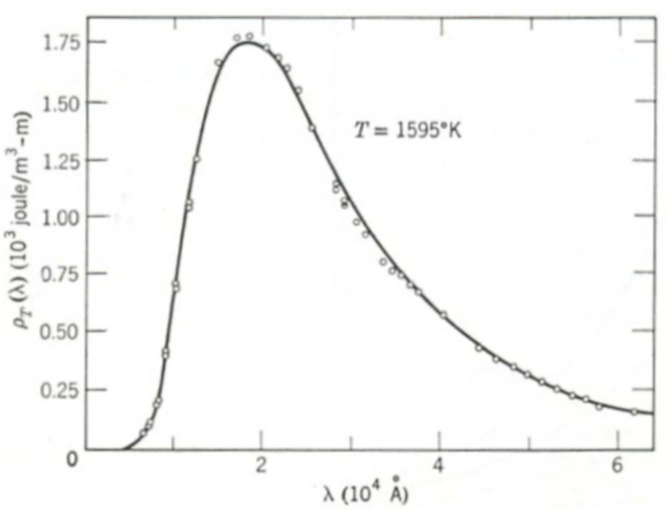
The energy density of EM waves is thus given by

$$\rho_T(\nu)d\nu = \frac{N(\nu)d\nu}{V}\bar{\varepsilon} = \frac{8\pi\nu^2}{c^3}\frac{h\nu}{e^{h\nu/kT}-1}d\nu = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/kT}-1}d\nu$$

Using the relation between wavelength and frequency ($\nu = c/\lambda$ and $d\nu = -(c/\lambda^2)d\lambda$) we can convert this relation to Planck's blackbody formula:

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

This relation describes the observed blackbody spectrum extremely well, as can be seen in the Figure on the right.



By integrating over all wavelengths we obtain Stephan's law and a relation between Stefan-Boltzmann constant and the Planck and Boltzmann constants. By differentiating the energy density with respect to the wavelength and with respect to the frequency, we can determine the wavelength and the frequency at which the energy density peaks.

We thus conclude that one can only understand blackbody radiation if the energy of an EM wave is quantized and equal to $nh\nu$ where n = 0, 1, 2, 3, ….. **The quantization of energy was introduced to explain continuous distributions.**