There were several indications in the late 1800s that all was not right with classical physics. We have discussed the Michelson-Morley experiment and special relativity. For quantum mechanics, there were several indicators, which I mention briefly in a list and in more detail in lecture:

1. **Photoelectric effect**: The results made no sense if you think of light as a wave. You were forced to view the energy of light as a collection of particles—photons—each having energy \( (h \nu) \), where \( h \) = Planck constant = \( 6.63 \times 10^{-34} \) joule·second and \( \nu \) = frequency of light.

2. **Heat capacity** (\( = \frac{\text{energy in}}{\text{temperature change}} \)): Heat capacity for a given sample was expected to be independent of temperature. It is— for atoms. For molecules, it decreases with temperature. This was inexplicable for a long time.

3. **Spectra—light colors emitted—of a gas**: The frequencies are discrete, and no one understood the pattern of emitted frequencies until quantum mechanics was invented.

4. **Black body radiation**: A "black body" is a perfect absorber—if it absorbs all incident light of all frequencies. It is also a "maximal" emitter—it emits the most light per area, at a given temperature, that any object can emit. The spectrum of a black body object made no sense before quantum mechanics.
Let us start with blackbody radiation. This is a continuous spectrum of light. The total energy per area per time = \[ \text{power} = \frac{\text{energy}}{\text{area}} \]

where \( T = 5.67 \times 10^{-8} \text{ m}^2 \text{kg}^{-1} \text{s}^{-2} \text{ K}^{-4} \) and \( T \) in K. This is called the Stefan-Boltzmann law and was found experimentally well before it was explained.

Also, the spectrum looks like:

\[
\text{Power} \quad \frac{\text{area}}{\text{wavelength}}
\]

\[
\begin{align*}
\text{wavelength} & \quad \text{Power} \\
T = 6000 \text{ K} & \quad \text{Max} \\
T = 5000 \text{ K} & \quad \text{Mid} \\
T = 4000 \text{ K} & \quad \text{Min}
\end{align*}
\]

The wavelength corresponding to maximum radiance decreases as the temperature increases:

\[
\lambda_{\text{max}} = \text{constant} \times \frac{1}{T} = 2.898 \times 10^{-3} \text{ m} \cdot \text{K}
\]

Wien law - also found experimentally well before it was explained.

For almost 30 years the ideas used to explain blackbody radiation failed - catastrophically. Why? They started with light as a wave, a wave in a box (the sample):
wave number \( k = \frac{2\pi}{\lambda} \)
angular frequency \( \omega = 2\pi f \)
\( \frac{\lambda}{v} = \text{speed} = c = \frac{\omega}{k} \)

The wave is described by a wave function:
\( f(x, t) = A e^{i(kx-\omega t)} \)

\( A = \text{wave amplitude} \)
\( kx-\omega t = \text{phase} \)
\( \Rightarrow |f|^2 = |A|^2 = \text{constant} \)

To count how many distinct waves are in the box (sample), use periodic boundary conditions on the walls (edges of sample):
\( c k^2 = 1 \Rightarrow k_x = \frac{2\pi n_x}{L} \)

for a large sample:
\( dk_x = \frac{2\pi}{L} dn_x \)

The same result is obtained in the \( y \) - and \( z \) - directions
\( \Rightarrow \frac{dk_x dk_y dk_z}{V} = \left( \frac{2\pi}{L} \right)^3 \frac{1}{v} d^3k \)

\( \Rightarrow \) the density of states = \( d^3n = \left( \frac{c}{8\pi^2} \right) d^3k \)
\( = \frac{1}{8\pi^2} \frac{1}{v} d^3k \), \( V = \text{volume of box (sample)} \)

Inside the box, the radiation is isotropic and there are two polarization states:
\( \frac{d^3n}{V} = \frac{1}{(2\pi)^3} \cdot 2 \int k^2 dk d\psi = \frac{1}{112} k^2 dk = \frac{1}{112} \frac{w^2 dw}{c^3} \)

\( = \left( \frac{8\pi}{c^3} \right) \frac{w^2}{w} dw \)
If I use this to calculate the total energy emitted by the box (sample):

\[ dfU(f) = \frac{\text{average energy per state}}{\text{area}} \frac{d^3n}{V} \]

\[ \Rightarrow U(f)df = \left( \frac{8\pi}{c^2} \right) \left( \frac{\hbar}{2\pi} \right) f^2 df \]

in terms of wavelength:

\[ U(\lambda) d\lambda = \left( \frac{8\pi \hbar}{c^2} \right) d\lambda \]

So the intensity \( \frac{\text{energy}}{\text{area} \cdot \text{time}} \) from the black body:

\[ R = \left( \frac{\sigma}{4} \right) u \]

\[ \begin{align*}
\vec{u} & \rightarrow \vec{\hat{z}} \\
\text{BLACK BODY} & \\
\end{align*} \]

\[ \hat{k} \cdot \hat{z} = \hat{k} \cos \theta \]

\[ \int_{0}^{\pi/2} k \cos \theta \sin \theta d\theta = \frac{k}{2} \]

\[ \Rightarrow \text{This is the catastrophe. It was actually called the ultraviolet catastrophe because } R(f) \text{ at low frequencies works, but at high frequencies fails.} \]

Max Planck found the answer in 1904-05. He believed the phase space calculation was okay, but not the energy per frequency. Instead he took the energy of a frequency \( f \) was:
\[
E = hf \\
E = \text{Planck constant}
\]

He also assumed that the probability of occupying a state of frequency \( f \) is proportional to:

\[
e^{-\frac{hf}{kBT}} \quad n = \text{number of photons of frequency } f
\]

We will discuss this "Maxwell-Boltzmann distribution function" at the end of the course.

Using this, the probability of finding any \((1, 2, 3, \ldots)\) photons of frequency \( f \) is:

\[
\sum_{n=0}^{\infty} e^{-\frac{hf}{kBT}} = \frac{1}{1 - e^{-\frac{hf}{kBT}}}
\]

\[
\Rightarrow \text{the average energy, in stead of } (kBT) \text{, is:}
\]

\[
\langle E \rangle = \sum_{n=0}^{\infty} (nhf) e^{-\frac{hf}{kBT}} = \frac{hf}{e^{\frac{hf}{kBT}} - 1}
\]

This is now called Planck's formula.

**Notice:**

1. For low frequencies, \( \langle E \rangle \rightarrow kBT \)

2. \( R(f) = \left( \frac{c}{4} \right) \left( \frac{8\pi}{c^3} \right) \frac{hf^3}{e^{hf/kBT} - 1} \)

3. \( \int_{0}^{\infty} R(f) df = \left( \frac{2\pi}{c^2} \right) \int_{0}^{\infty} \frac{hf^3 df}{e^{hf/kBT} - 1} \)
Let \( x = \frac{hf}{k_B T} \) \( \Rightarrow \) \( f^3 df = \left( \frac{15k_B^4}{h^3} \right) \frac{3}{x^3} dx \)

\[ \Rightarrow \int_0^\infty R(f) df = \left( \frac{2\pi}{h} \right)^4 \int_0^\infty \frac{x^3 dx}{e^x - 1} = \left( \frac{2\pi^5 k_B^4}{h^3 c^2} \right)^4 \frac{\pi^4}{15} \]

Which predicts the (known) Stefan-Boltzmann law.

(4) For the Wien's law:

\[ R(\tau) d\tau = \frac{C_0 f^2 df}{e^{hf/k_B T} - 1} \]

\[ R(\lambda) d\lambda = (C_0 c^4) \frac{\frac{1}{\lambda^5} \frac{1}{e^{hc/\lambda k_B T} - 1}} \]

\[ \frac{dR}{d\lambda} = 0 \text{ when:} \]

\[ \frac{d}{d\lambda} \left[ \frac{1}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T} - 1}} \right] = 0 = \left[ \frac{-5}{\lambda^6} \frac{1}{e^{\frac{hc}{\lambda k_B T} - 1}} \right] + \left[ \frac{1}{\lambda^5} \frac{(\frac{hc}{\lambda k_B T}) e^{-\frac{hc}{\lambda k_B T}}}{\left( e^{\frac{hc}{\lambda k_B T} - 1} \right)^2} \right] \]

\[ \Rightarrow \lambda = \frac{1}{\beta} \frac{\beta e^{\frac{hc}{\lambda k_B T}}} {e^{\lambda k_B T} - 1} \] for \( \lambda = \lambda_{max} \)

\[ \Rightarrow 5 = \frac{1}{\lambda} \frac{\beta e^{\frac{hc}{\lambda k_B T}}}{e^{\frac{hc}{\lambda k_B T} - 1}} \] where \( \beta = \frac{hc}{k_B T} \)

Let \( x = \frac{\beta}{\lambda} \)

\[ \Rightarrow 5 (e^x - 1) = x e^x \]

\[ \Rightarrow x = 5 (1 - e^{-x}) \]

This is satisfied for \( x = 5 = \frac{hc}{k_B T} \cdot \frac{1}{\lambda_{max}} \)

\( (e^{-5} = 7 \times 10^{-3}\text{ small}) \)

\[ \Rightarrow \lambda_{max} T = \frac{hc}{5k_B} = 2.87 \times 10^{-3} \text{ very close to experimental result} \]