Planck had announced result on Oct 19, 1900, and found $h = 6.55 \times 10^{-27}$ erg-sec (radiation law since has been beautifully confirmed by better data.)

but Planck did much more than fit the curve. He announced a derivation of the radiation law on Dec 14, 1900. In what he described as "an act of desperation," he hypothesized that radiation could be emitted and absorbed by the cavity only in quantized form $\Delta E = nh\nu$.

That a new era in physics had begun was not yet appreciated.

**Photoelectric effect** ("second coming of $h"\))

Lenard 1902 finds electron energy independent of light intensity.

Einstein 1905: an explanation

He radically extends Planck's idea, by proposing that quantization applies not just to interaction of radiation with the cavity, but to radiation itself. Light consists of quanta with

$$E_{\text{quantum}}(\nu) = h\nu$$

("light-quantum hypothesis")
Thus electron energy will be

\[ E_{\text{max}} = k\nu \quad \text{"work function" of the metal} \]

Brilliantly confirmed by Millikan (then at U. Chicago) in 1915, he finds \( k = 6.57 \times 10^{-7} \text{ erg-sec} \)

Why was this valued? Because Einstein was tempering with the greatest success of 19th century physics — Maxwell's electromagnetism, which established that light is an electromagnetic wave. It was one King to suggest new phenomena in the interaction of radiation with matter (Planck); quite another to suggest that the (Maxwell) theory of free electromagnetic field is wrong.

No one accepted this hypothesis.

Planck (1913), in letter nominating Einstein for Prussian Academy of Sciences:

"That he may sometimes have missed the target with his speculations, as, for example, in his hypothesis of light-quanta, cannot really be held against him, for it is not possible to introduce really new ideas even in the most exact sciences without sometimes taking a risk."
Millikan (1915), in his paper on the experiments
Einstein's photoelectric equation —— appears in every case to predict exactly the observed results —— Yet the semi-corpuscular theory by which Einstein arrived at his equation seems at present to be wholly untenable.

The tide was eventually turned by the Compton effect—electron-photon scattering explained by relativistic kinematics

\[ E = mc^2 \quad \vec{p} = \hbar \vec{k} \]

(earlier photon momentum introduced by Einstein in 1916)

\[ \Delta \lambda = \frac{h}{mc} (1 - \cos \theta) \]

This was 1923. (The acceptance of wave-particle duality for photons enabled de Broglie to propose same for electron the next year.)

The modern derivation of Planck's radiation law (counting photons) due to Bose and Einstein (1924).

It was Einstein, in 1905 paper on photoelectric effect, who first clearly stated that Planck's radiation law created a crisis for classical physics. Applying concept of classical statistical mechanics (equivalent to Fermi), he derived
\[ n \omega = \frac{\omega^2}{\pi^2 c^2} \]

(The \( t \to 0 \) limit of Planck's formula)

also derived by Rayleigh and Jeans in 1905, and known as the "Rayleigh-Jeans Law".

Einstein recognized that this law must fail at high frequency

\[ \frac{V}{U} = \sum n \omega = \infty \]

as indeed it does according to Planck's law. Something radically new had entered physics, something beyond classical concepts (Jeans thought to arise because high-frequency modes are not in equilibrium).

Debye Theory of Phonons

(sound quanta)

Uses similar mathematics to derivation of Planck's law but applies it to a rather different physical context.

Consider vibrations of a crystal about equilibrium position. For small vibrations, restoring forces are harmonic, like a system of masses and springs (coupled oscillators) can be expanded in terms of normal modes, which behave like independent uncoupled oscillators—each with characteristic \( \omega \).

For a large crystal, we may think of the modes as traveling (sound)
waves with various wavelengths (and polarizations). It is a good approximation to take dispersion relation
\[ \omega^2 = \mathbf{v}^2 \cdot \mathbf{k}^2 \] (no dispersion)
where \( \mathbf{v} \) is speed of sound
(Not exactly right at very short wavelength, but good enough)
This is just like light (or radiation)

If the crystal is in a finite box (size \( L \)), we'll have discrete values for \( \mathbf{k} \)
\[ \mathbf{k} = \frac{n}{L} \mathbf{\hat{e}} \]

- Unlike light — there are 3 polarizations for each value of \( n \) (longitudinal, too)
  (assume isotropic, same \( \mathbf{v} \) inside 3 pol.)
- Also unlike light — wavelength of light can be arbitrarily short. Not so for vibrations of crystal — wavelength less than interparticle spacing have no meaning.
  Another way to say this — a system of \( N \) moles (in 3 dimensions) has \( 3N \) degrees of freedom, and so there are \( 3N \) normal modes (a finite number and scale with the crystal volume). To estimate maximum volume \( V \),
\[ \Sigma_n \rightarrow 3 \left( \frac{L}{\pi} \right)^3 \frac{1}{8} \int \frac{k \omega}{4\pi} k^2 \, dk \]

\[ (3 \text{ polarizations}) = \frac{3}{2} \frac{L^3}{\pi^2} \frac{L}{3} k_{\text{max}}^3 = 3N \]

\[ k_{\text{max}} = \frac{6\pi^2 N}{V} \]

\[ \text{called } k_D \]

\[ (\text{in Debye}) \]

This makes sense

\[ \lambda_{\text{min}} = \left( \frac{2\pi}{k_{\text{max}}} \right)^3 = \frac{8\pi^3}{6\pi^2 N} = \frac{4\pi}{3} \frac{V}{N} = \frac{A^3}{3} \]

\[ \lambda_{\text{min}} = \text{smallest } a \]

\[ \text{since } N = a^3 \frac{V}{\lambda^3} \]

\[ \text{volume of a sphere of radius } a \]

\[ \text{but why?} \]

Now – in quantum theory, energies of all the oscillators are quantized

\[ E_n = n \hbar \omega \]

Sound is carried by \underline{quanta} \underline{~(analogous to photons)} \underline{~called phonons~}

A crystal at \underline{temperature} \underline{~will vibrate.} Let us calculate the energy stored in the vibrations. This is almost exactly the same as calculating \underline{~energy in a cavity.} But with one important difference – the \underline{~wavelength} \underline{~cutoff} (and \underline{~longitudinal} polarization)

\[ \left( \underline{3} \times \text{Planck} \right) \]

\[ \frac{1}{V} = \frac{3}{2\pi^2} \int_0^{k_B} \frac{k^2 \omega}{e^{\hbar k \omega/T} - 1} \]
And dispersion relation \( \omega = \kappa \mathbf{K} \Rightarrow \)
\[
\frac{\omega}{\nu} = \frac{3}{2\pi^2} \nu \left( \frac{7}{\kappa \nu} \right)^4 \int_0^\infty dx \frac{x^3}{e^x - 1}
\]

\( X = \frac{\nu \kappa \mathbf{K}}{\Theta} \) and \( X_0 = \frac{\kappa \nu}{\Theta} K_0 \equiv \frac{\Theta}{2} \)

(Define \( \Theta = \nu \kappa K_0 = \) Debye Temperature)

\[
\Theta^3 = (\kappa \nu)^3 \frac{6\pi^2 N}{V} \Rightarrow V = \frac{6\pi^2 (\kappa \nu)^3 N}{\Theta^3}
\]

\[
\Rightarrow U = 9 N \frac{\kappa^4}{\Theta^3} \int_0^{X_0} dx \frac{x^3}{e^x - 1} \rightarrow f(\Theta/2)
\]

Let's consider the limiting cases of large and small \( \Theta \):

(i) Low Temperature \( X_0 = \Theta/2 \gg 1 \)

Make an exponentially small error by extending integral to \( X = \infty \)

\[
I = \pi^4/15
\]

\[
\Rightarrow \sqrt{U} = \frac{3\pi^4}{5} \frac{N \kappa^4}{\Theta^3}
\]

At low \( \Theta \) - the wavelength \( \mathbf{K} \) gets unimportant, because high \( \kappa \) modes are unoccupied anyway.

This formula works very well for solid at low temperature - the Debye \( \mathbf{K}^3 \) law.

Typical values are \( \Theta \sim 200-500 \text{ K} \).
Note: called $T^3$ law because 
\[
C_v = \left( \frac{3N}{s^3} \right) V = \frac{12\pi^4}{5} N \left( \frac{3\Theta}{k} \right)^3
\]
- what one actually measures.

So \( \frac{\Theta}{k} \leq 100^\circ K \) (liquid \( N_2 \)) is typically low enough.

(ii) High temperature \( x_D = \Theta/k \ll 1 \)

Then \( \int_0^{x_D} dx \frac{x^3}{e^x - 1} \sim \int_0^{x_D} dx x^2 = \frac{1}{3} x_D^3 \)

\[
U = 3NT \quad \text{this is just the Rayleigh - Jeans Law}
\]

For phonons, integrated up to cutoff. It is a classical result (no \( \hbar \)) i.e. equilibrium energy in coherent oscillators is known as Law 1) Dulong and Petit, discovered (experimentally) in 1819.

And derived by Boltzman, in 1876, by using classical statistical mechanics (equi-partition).

It was Einstein (1906) who first understood that this result is \( T \to \infty \) limit, and in quantum theory one should have \( C_v \to 0 \) as \( T \to 0 \) (first hint of 3rd law of thermodynamics).

Debye derived \( T^3 \) law in 1912, one of the great early experimental triumphs of quantum theory. (Einstein had assumed "incommensurate phonons" - all with the same \( \Theta - \) instead of a frequency spectrum.)