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.) (cf $h = 6.6262 \times 10^{-27}$ erg-sec — modern value)

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 $\Delta E = n\hbar\omega$

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

$$E_{1\,\text{quantum}}(\omega) = \hbar\omega$$

("Light-quantum hypothesis")

Thus electron energy will be

$$E_{max} = \hbar\omega - P$$ "workfunction" of the metal

Brilliantly confirmed by Millikan (then at U. Chicago) In 1915, he finds $h = 6.57 \times 10^{-27}$ erg-sec

Why was this radical? Because Einstein was tampering with the greatest success of 19th century physics — Maxwell's e+m theory, which established that light is an electro-magnetic wave. It was one thing to suggest new phenomena in the interaction of radiation with matter (Planck); quite another to suggest that the (Maxwell) theory of free e+m field is wrong.

<u>No one</u> accepted this hypothesis

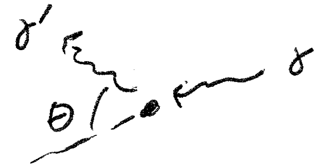
Planck (1913), in letter nominating Einstein for Prussian Academy of Sciences:

"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 semicorpuscular 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



$E = \hbar\omega \quad \vec{p} = \hbar\vec{k} \Longrightarrow$

(Idea of 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 photon enabled deBroglie to propose same for electron the next year.)

The modern derivation of Planck 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 concepts of classical statistical mechanics (equipartition theorem), he derived

$$u_\omega = \frac{\omega^2}{\pi^2 c^3} \tau$$

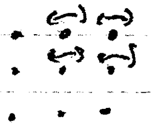
(the $\hbar \to 0$ limit of Planck's formula) Also derived by Rayleigh and Jeans in 1905, and known as the "Rayleigh-Jeans Law". Einstein recognized that this law must fail at high frequency (or $U/V = \int d\omega\, u_\omega = \infty$), as indeed it does according to Planck's law. Something radically new had entered physics, something beyond classical concepts (Jeans thought it arose 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 ω



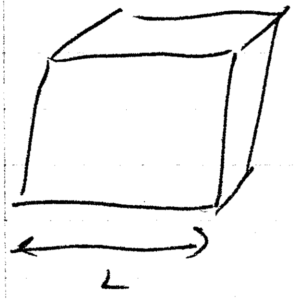
For a large crystal, we may think of the modes as traveling (sound) waves with various wavelengths (and polarizations). It is a good approximation to take dispersion relation

(Assume isotropic)
$$\omega^2 = v^2 \vec{k}^2$$ (no dispersion)

— where v is speed of sound

(Not exactly right at very short wavelength, but good enough)

— this is just like light (em radiation)



If the crystal is in a finite box (side L), we'll have discrete values for $\vec{k}$

$$\vec{k} = \frac{\pi}{L}\vec{n}$$

- Unlike light — there are 3 polarizations for each value of $\vec{k}$ (Longitudinal, too) (assume isotropy, and same v for all 3 pol.)
- Also unlike light — wavelength of light can be arbitrarily short. Not so for vibrations of crystal --- wavelengths less than interparticle spacing have no meaning.

Another way to say this — a system of N masses (in 3 dimensions) has 3N degrees of freedom, and so there are 3N normal modes (a finite number that scales with the crystal volume). To estimate maximum value of $\vec{k}$:

$$\sum_n \to \underset{\uparrow}{3}\left(\frac{L}{\pi}\right)^3 \frac{1}{8}\int^{K_{max}} 4\pi K^2 dK$$

(3 polarizations) $= \frac{3}{2}\frac{L^3}{\pi^2}\frac{1}{3}K_{max}^3 = 3N$

or $\boxed{K_{max}^3 = 6\pi^2 \frac{N}{V}}$ called K_D (for debye)

This makes sense

$$\lambda_{min}^3 = \left(\frac{2\pi}{K_{max}}\right)^3 = \frac{8\pi^3}{6\pi^2}\frac{V}{N} = \frac{4}{3}\pi\frac{V}{N} = \frac{4}{3}\pi a^3$$

(λ_{min}^3 is actually volume of a sphere of radius a)
But why?

$\lambda_{min} \sim$ spacing a (since $N = a^3 \frac{V}{a^3}$)

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

$$\epsilon_\omega = n\hbar\omega$$

Sound is carried by quanta (analogous to photons) called phonons

A crystal at temperature τ will vibrate. Let us calculate the energy stored in the vibrations. This is almost exactly the same as calculating em energy in a cavity. But with ~~one~~ two important differences — the wavelength cutoff (and the longitudinal polarization)

So

$$U/V = \frac{3}{2\pi^2}\int_0^{K_D} dK\, K^2 \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1}$$

($\frac{3}{2}$ × Planck)

And dispersion relation $\omega = v K \Rightarrow$

$$U/V = \frac{3}{2\pi^2}\hbar v\left(\frac{\tau}{\hbar v}\right)^4 \int_0^{x_D} dx\, \frac{x^3}{e^x - 1}$$

$$x = \frac{\hbar v K}{\tau} \quad \text{and} \quad x_D = \frac{\hbar v}{\tau} K_D \equiv \theta/\tau$$

(Define $\theta = \hbar v K_D$ = Debye temperature)

$$\theta^3 = (\hbar v)^3\, 6\pi^2 \frac{N}{V} \Rightarrow V = 6\pi^2(\hbar v)^3 \frac{N}{\theta^3}$$

$$\Rightarrow \boxed{U = 9N\, \tau^4/\theta^3 \underbrace{\int_0^{x_D} dx\, \frac{x^3}{e^x - 1}}_{f(\theta/\tau)}}$$

Let's consider the limiting case of large and small τ:

(i) Low Temperature $x_D = \theta/\tau \gg 1$
Make an exponentially small error by extending integral to $x = \infty$

$$I = \pi^4/15$$

$$\Rightarrow \boxed{U = \frac{3\pi^4}{5} N\, \tau^4/\theta^3}$$

same τ^4 behavior as for B.B. radiation At low τ - the wavelength cutoff is unimportant, because high ω modes are unoccupied anyway

This formula works very well for solids at low temperature — the <u>Debye T^3 law</u>

Typical values are $\theta \sim 200° - 600°K$

Note: called T^3 law because

$$\boxed{C_V = \left(\frac{\partial U}{\partial \tau}\right)_V = \frac{12\pi^4}{5} N \left(\tau/\theta\right)^3}$$ – what one actually measures.

So $\tau/k \lesssim 100°K$ (liquid N_2) is typically low enough.

(ii) High Temperature $x_D = \theta/\tau \ll 1$

then $$\int_0^{x_D} dx \frac{x^3}{e^x - 1} \sim \int_0^{x_D} dx\, x^2 = \frac{1}{3} x_D^3$$

$$\boxed{U = 3N\tau}$$ – this is just the "Rayleigh - Jeans Law"

for *phonons*, integrated up to cutoff. It is a *classical* result (no $\hbar$) $\rightsquigarrow$ i.e. equipartition: energy τ in each oscillator

the high-τ limit $\boxed{C_V = 3N}$

is known as *Law of Dulong and Petit*, discovered (experimentally) in 1819.

And derived by Boltzmann, in 1876, by using *classical* statistical mechanics (equipartition)

It was Einstein (1906) who first understood that this result is $T \to \infty$ limit, and that 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 "monochromatic phonons" – all with the same ω – instead of a frequency spectrum)