I. INTRODUCTION AND HISTORICAL PERSPECTIVE

A. Failures of Classical Physics

At the end of the 19th century, physics was described via two main approaches. Matter was described by Newton's laws while radiation (waves) obeyed Maxwell's equations. These two approaches were connected by the Lorentz Force law. $[\vec{F} = q(\vec{E} + \vec{v} \times \vec{B})]$

While there were many impressive results, there existed some "minor" problems. On balance there was a satisfactory picture given the existing experimental evidence.

Near the beginning of the 20th century it was found that there needed to be radical changes in physical theories (resulting in relativity and quantum mechanics). We examine below some of the experimental facts which could not be explained by the existing theory.

1. Black-body Radiation

It is observed that "hot" bodies radiate. A black-body is defined as one that absorbs all incident radiation. This can be achieved in practice by a small hole in a cavity; anything going in bounces around and cannot get out. If you heat such a cavity up, what comes out is called "black-body radiation."

As an example consider a cubical metal box. The energy flux (A) associated with radiation of frequency ν and an enclosure at a temperature T is proportional to the product of the energy density u and the velocity c,

$$A \propto [u(\nu, T)d\nu] \cdot c,$$

where $d\nu$ is a small frequency interval of the detector. From geometrical arguments we find $A = \frac{1}{4}u(\nu, t)cd\nu$. This allow us to turn our attention from the flux of radiation to the energy density within the cavity.

From Kirchhoff's work (1860) one expects $u(\nu, T)$ is independent of the shape and character of the black body. It is important to determine the dependence of u on ν and T.

We use classical electricity and magnetism. First look at the wave equation for an electromagnetic (EM) field

$$\Box\,\vec{\epsilon} \equiv (\frac{1}{c^2}\frac{\partial}{\partial t^2} - \nabla^2)\vec{\epsilon} = 0.$$

If we make a Fourier decomposition of the EM field then we obtain

$$\vec{\epsilon} = \sum_{\kappa} \vec{e}(\vec{\kappa}, t)e^{i\vec{\kappa}\cdot\vec{x}}\ , \quad \ddot{e} + (\kappa^2 c^2)e = 0$$

Assuming each mode is linearly independent results in the identification of a simple harmonic oscillator for each mode with $\omega = \kappa c$.

Using standing wave boundary conditions (like a vibrating string) implies $\vec{\epsilon}$ must vanish on the boundary. So $\vec{\epsilon}$ must have an integral number of halfwavelengths ($\frac{n\lambda}{2}$) in the cavity. Thus we have

$$\frac{n_i\lambda_i}{2} = L, \qquad i = 1, 2, 3 \text{ (spatial component)}, \qquad n_i > 0 \text{ (mode number)}$$

If we define

$$k_i = \frac{2\pi}{\lambda_i} = (\frac{\pi}{L})n_i$$

then

$$\vec{k}^2 = (\frac{\pi}{L})^2(n_1^2 + n_2^2 + n_3^2).$$

Note only certain values of $\vec{k}^2$ are allowed. Now we calculate the number of modes between ν and $\nu + d\nu$ (divided by the volume). In the limit as $L \to \infty$, the modes are very closely spaced so we treat the n_i as continuous variables. Thus the total number of modes allowed (with wave number $\leq |k|$) is given by

$$N = 2(\frac{1}{8})(\frac{4\pi}{3}n^3) = 2(\frac{1}{8})(\frac{4\pi}{3})(\frac{L^3}{\pi^3})k^3$$

or

$$\frac{N}{V} = 2(\frac{1}{8})(\frac{4\pi}{3})\frac{k^3}{\pi^3}$$

which implies

$$\frac{dN}{V} = 2(\frac{1}{8\pi^3})(\frac{4\pi}{3})3k^2dk = 2(\frac{1}{8\pi^3})4\pi k^2dk.$$

Using $k = 2\pi\nu/c$

$$\frac{dN}{V} = \frac{1}{\pi^2}(\frac{2\pi}{c})^3\nu^2 d\nu = \frac{8\pi\nu^2}{c^3}d\nu.$$

Now from the equipartition theorem the mean kinetic energy in each mode is $\frac{1}{2}k_BT$ and from the virial theorem (for an oscillator) the average kinetic energy equals the average potential energy. Thus the average energy associated with each mode is k_BT.

$$\langle E\rangle = k_BT$$

Thus we obtain the Rayleigh-Jeans (1900) law

$$\frac{dE}{V} = \frac{dN}{V}k_BT = (\frac{8\pi\nu^2}{c^3})k_BTd\nu$$

But this result, while agreeing with experiment at low frequency, yields an infinite total energy density at fixed T (ultraviolet catastrophe).

Planck resolved the difficulty by suggesting that

$$\langle E\rangle = \frac{h\nu}{e^{h\nu/k_BT}-1} \rightarrow \begin{cases} k_BT & k_BT >> h\nu \quad (\text{low } \nu) \\ h\nu e^{-h\nu/k_Bt} & k_BT << h\nu \quad (\text{high } \nu) \end{cases}$$

Thus at high frequency there is a damping factor. A method of motivating this result is to assume that oscillators in the surface only emit energy in discrete amounts (quanta) $\epsilon_o = h\nu$ (for each frequency). Now if we calculate the average energy in each mode (using the Boltzmann weight factor)

$$\begin{aligned}\langle E\rangle =& \frac{\sum_{n=0}^{\infty} nh\nu e^{-nh\nu/k_BT}}{\sum_{n=0}^{\infty}\exp(-nh\nu/k_BT)} \\ =& -\frac{\partial}{\partial(1/k_BT)}\ln\left[\sum_{n=0}^{\infty}\exp(-nh\nu/k_BT)\right] = \frac{\partial\ln(1-e^{-h\nu/k_BT})}{\partial(1/k_BT)} \\ =& \frac{h\nu}{(e^{h\nu/k_BT}-1)}.\end{aligned}$$

Thus the cutoff at large frequency also removes the divergence resulting in a finite total energy. Note the failure of the *classical* principle of the equipartition of energy.

2. Photoelectric effect

One observes that when monochromatic light is incident on a metal that the maximum kinetic energy of emitted electrons is related to the frequency of the light and work function ϕ_{wf} of the metal via

$$KE|_{max} = h\nu - \phi_{wf}$$

Consider the classical description for harmonically bound electrons where the spring is driven by the incident light electromagnetic wave

$$m\ddot{x} = -Kx + e\epsilon_0 \cos\omega t.$$

If $\omega_0^2 \equiv K/m$, the solution to the equation above is given by

$$x = \frac{e\epsilon_0}{m}\frac{\cos\omega t}{\omega_0^2 - \omega^2}.$$

The average energy of the electron in one period is

$$\langle E_e \rangle = \langle \frac{1}{2}Kx^2 + \frac{1}{2}m\dot{x}^2 \rangle = \frac{\pi e^2}{m}(\frac{\epsilon_0^2}{4\pi})\left[\frac{\omega^2 + \omega_0^2}{(\omega^2 - \omega_0^2)^2}\right].$$

Thus for a given frequency, the energy given to the electron depends on ϵ_0, the intensity of the beam. In addition there is no frequency threshold effect. The classical prediction **incorrectly** predicts that an intense enough beam should always eject an electron.

Einstein (1904) extended Planck's ideas regarding the oscillators in the cavity walls to the light *photons*. He assumed that electromagnetic waves consist of photons with energy $h\nu$ and that photons must transfer their energy in discrete bundles (this explains the threshold effect). Since the intensity is only proportional to the number of photons, and not the energy $h\nu$ of each photon, a higher intensity results in more electrons being emitted but with the same maximum kinetic energy.

3. Specific Heat of Solids

A classical solid may be modeled as consisting of three-dimensional simple harmonic oscillators (oscillating about a mean position). Then we may use equipartition of energy and the virial theorem to obtain

$$\langle E_T \rangle = 3N \langle E_{osc} \rangle = 3N k_B T$$

The specific heat $C_V = dE/dT = 3Nk_B = 3R = 5.96 cal/(mole\ ^0K)$
The experimental result is

Einstein (1907) again used the quantum idea and assuming that the energy of oscillators of frequency ν_0 can only occur in quanta of $\epsilon_0 = h\nu_0$ obtained

$$E = 3N \left[\frac{h\nu_0}{e^{h\nu_0/k_BT} - 1} \right] \Rightarrow C_V = \frac{dE}{dT} = 3Nk_B \left[\frac{x^2 e^x}{(e^x - 1)^2} \right]$$

where $x \equiv h\nu_0/k_BT$. Thus we find $C_V \underset{T\to 0}{\longrightarrow} 3Nk_B x^2 e^{-x} \to 0$ but this is too fast compared to experiment ($\sim T^3$).

To obtain agreement with experiment one needs to allow for a frequency distribution (as with the blackbody radiation) associated with the crystal normal modes (Debye, 1912).

A simple model (like the blackbody) yields for the frequency distribution

$$g(\nu) \propto \frac{\nu^2}{c_s^2} \quad (c_s \equiv \text{speed of sound})$$

Then

$$E = \int_0^{\nu_{max}} g(\nu) \left[\frac{h\nu}{e^{h\nu/k_BT} - 1} \right] d\nu$$

where for normalization

$$3N = \int_0^{\nu_{max}} g(\nu) d\nu.$$

There is a maximum frequency since the crystal lattice is discrete. Now one obtains

$$C_V \to \begin{cases} 3Nk_B & \text{as } T \to \infty \\ \frac{12\pi^4}{5} Nk_B (\frac{k_BT}{h\nu_{max}})^3 & \text{as } T \to 0. \end{cases}$$

Which is in agreement with experiment.

4. Atomic Spectra

An obvious contradiction to classical physics occurs in atomic spectra. For example Maxwell's equations yield

$$\frac{emitted\ E}{Time} = \frac{2e^2a^2}{3c^3}.$$

Thus there should be

a) instability

b) continuous radiation pattern

c) broadened spectrum from increased pressure on gas.

Experimentally one has stable atoms, discrete spectra and a pressure-induced shifted spectrum.

Bohr hypotheses (1913)

a) Atoms exist in non-radiating stationary states determined by $mvr = n\hbar$

b) Atoms can make discrete transitions with appearance of photon of frequency $\omega = (E - E')/\hbar$

These rules worked but they were *ad-hoc*.