

Lecture 25

The description of the interaction of EM radiation with matter based on Maxwell's equations and the classical laws of motion gives an excellent account (quantitatively) of all the phenomena in optics such as reflection, diffraction, refraction, change in polarization etc. However it fails fundamentally to describe certain features in which intrinsic statistical properties of matter are probed. The first two major problems with this description to be discovered (and solved) were:

1. Black body radiation
2. The photo-electric effect.

As it turned out, in order to solve these problems one should modify the picture of EM radiation as made from classical waves. In this picture the amplitude of the waves can take arbitrary values. This, as we will see, leads to unphysical predictions that are in conflict with experiments. Instead, the EM field can be thought of as a collection of elementary waves with

a fixed elementary amplitude. By superimposing few such basic excitations one can have a wave with larger amplitude, but this will always be an integer multiple of the elementary one. These basic excitations are called Photons and in many ways they behave like particles.

(more precisely fixed elementary energy)

To appreciate the problem of black body radiation one must first have an understanding of statistical mechanics - We don't have time to do that. Instead I will just state the facts that we need to know.

Statistical mechanics is primarily concerned with systems that are in Equilibrium. I will not attempt to give the precise definition of thermal equilibrium but will just tell you that a way to bring a system to equilibrium is to bring it into good contact with a very large "infinite" environment of temperature T . After long enough time the properties of the system under investigation will settle into their equilibrium time independent values and its temperature will be the same as that of the environment.

A basic result of statistical mechanics is that the probability to find a system in a state whose energy is E_s is proportional

in thermal equilibrium
with temperature T

$$P(E_s, T) \propto e^{-\beta E_s} \quad ; \quad \beta = \frac{1}{k_B T}$$

k_B is a fundamental constant called Boltzmann's constant

$$k_B = 1.38 \cdot 10^{-16} \frac{\text{ergs}}{\text{deg}}$$

The state of a classical system is specified by giving the values of its coordinates $\{q\}$ and momenta $\{p\}$.

The thermal average of some physical function $f(q, p)$ is given by

$$\langle f \rangle = \frac{\sum_s f(q_s, p_s) e^{-\beta E(q_s, p_s)}}{\sum_s e^{-\beta E(q_s, p_s)}}$$

The sum is over all possible states of the system.

For example let's look at a particle moving in one dimension under the influence of a potential $V(x)$.

The state of the particle is given by its coordinate x and momentum p . The energy of the state is $\frac{p^2}{2m} + V(x) = E(x, p)$.

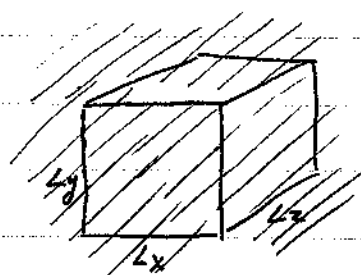
The average energy of such a particle in thermal equilibrium at temperature T is then

$$\langle E \rangle = \frac{\int dx dp E(x, p) e^{-\beta E(x, p)}}{\int dx dp e^{-\beta E(x, p)}} \quad \beta = \frac{1}{k_B T}$$

Let us apply these notions to the EM field. What do we mean by saying the EM field is in thermal equilibrium at temperature T ?

We may think of a hole carved in an infinite piece of material which is at temperature T .

If the EM field in the hole is in "good contact" with the surrounding material it will also be in thermal equilibrium with the same temperature.



By good contact we mean that the EM radiation that is incident on the walls is completely absorbed by them and in turn the matter that absorbed the radiation and was excited by it, re-emits radiation into the free-space cavity.

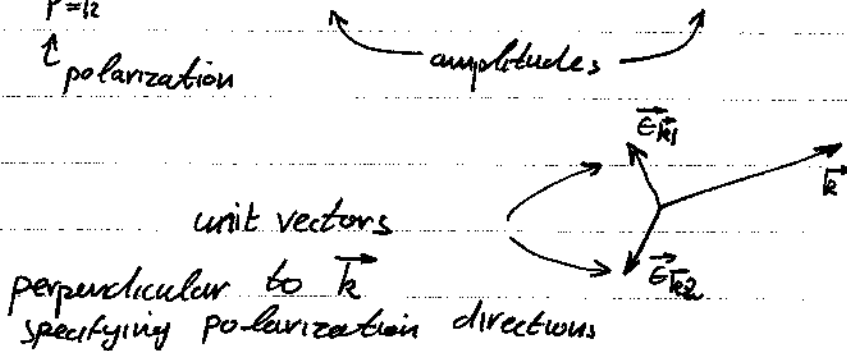
How do we specify the state of the EM field in the cavity?

As we saw, the EM field in empty space can be described as superposition of EM waves. Each wave is characterized by its:

1. Wavevector \vec{k} : giving the direction of propagation of the wave and its frequency through $\omega = ck$.
2. Polarization
3. Amplitude

For example, we can expand a general configuration of the EM field in terms of plane waves:

$$\vec{E}(\vec{r}, t) = \sum_{\vec{k}} \sum_{P=1,2} \vec{E}_{\vec{k}, P} \cdot \left[A_{\vec{k}, P} \cos(\vec{k}\vec{r} - \omega t) + B_{\vec{k}, P} \sin(\vec{k}\vec{r} - \omega t) \right]$$



and a similar expression for $\vec{B}(\vec{r}, t)$.

The energy of such configuration is:

$$E = \int d^3r \frac{1}{8\pi} (E^2 + B^2) = \frac{V}{16\pi} \sum_{\vec{k}} \sum_p (A_{\vec{k},p}^2 + B_{\vec{k},p}^2) \quad \begin{array}{l} V = L_x L_y L_z \\ \text{is the volume} \\ \text{of the cavity} \end{array}$$

The average energy of the EM field in the cavity is then:

$$\langle E \rangle = \frac{\prod_{\vec{k}} \prod_{p=1,2} \int dA_{\vec{k},p} dB_{\vec{k},p} E e^{-\beta E}}{\prod_{\vec{k}} \prod_{p=1,2} \int dA_{\vec{k},p} dB_{\vec{k},p} e^{-\beta E}}$$

$$= -\frac{2}{\partial\beta} \ln \left[\prod_{\vec{k}} \prod_{p=1,2} \int dA_{\vec{k},p} dB_{\vec{k},p} e^{-\beta E} \right]$$

$$= -\frac{2}{\partial\beta} \ln \left[\prod_{\vec{k}} \prod_{p=1,2} \int_{-\infty}^{\infty} dA_{\vec{k},p} dB_{\vec{k},p} e^{-\frac{\beta V}{16\pi} (A_{\vec{k},p}^2 + B_{\vec{k},p}^2)} \right]$$

$$= -\frac{2}{\partial\beta} \ln \left[\prod_{\vec{k}} \prod_{p=1,2} \frac{16\pi^2}{\beta V} \right] \quad \text{Use } \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

$$= -\frac{2}{\partial\beta} \sum_{\vec{k}} \sum_{p=1,2} \ln \frac{16\pi^2}{\beta V} = \sum_{\vec{k}} \sum_{p=1,2} \frac{1}{\beta}$$

$\Rightarrow \frac{1}{\beta} = k_B T$ is the average energy per mode in the EM field.

Let's impose periodic boundary conditions on the EM field in the cavity. The allowed values of \vec{k} are then quantized according to:

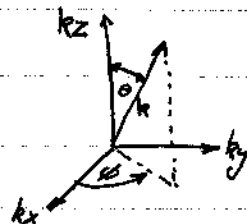
$$k_x = \frac{2\pi}{L_x} n_x \quad ; \quad k_y = \frac{2\pi}{L_y} n_y \quad ; \quad k_z = \frac{2\pi}{L_z} n_z \quad n_x, n_y, n_z: \text{integers}$$

Defining $\Delta k_x = \frac{2\pi}{L_x}$, $\Delta k_y = \frac{2\pi}{L_y}$, $\Delta k_z = \frac{2\pi}{L_z}$ we can transform the sum over \vec{k} to an integral:

$$\sum_{\vec{k}} = \sum_{k_x k_y k_z} = \frac{1}{\Delta k_x \Delta k_y \Delta k_z} \sum_{k_x k_y k_z} \Delta k_x \Delta k_y \Delta k_z$$

$$\xrightarrow{\Delta k \rightarrow 0} \frac{V}{(2\pi)^3} \int_{-\infty}^{\infty} dk_x dk_y dk_z$$

Going to spherical coordinates



$$d^3k = k^2 \sin\theta \, d\phi \, d\theta \, dk$$

$$k = |\vec{k}|$$

$$= \frac{V}{(2\pi)^3} \int_{\phi=0}^{2\pi} d\phi \int_{\theta=0}^{\pi} d\theta \int_0^{\infty} dk \, k^2 \sin\theta$$

Since our integrand is independent on the direction of k (i.e. ϕ and θ) we can integrate over ϕ and θ $\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta = 4\pi$ to obtain

$$\langle E \rangle = \frac{V}{(2\pi)^3} \cdot 4\pi \cdot 2 \int_0^{\infty} dk \cdot k^2 \cdot \frac{1}{\beta} = \int_0^{\infty} dk \frac{V}{\pi^2} k_B T k^2$$

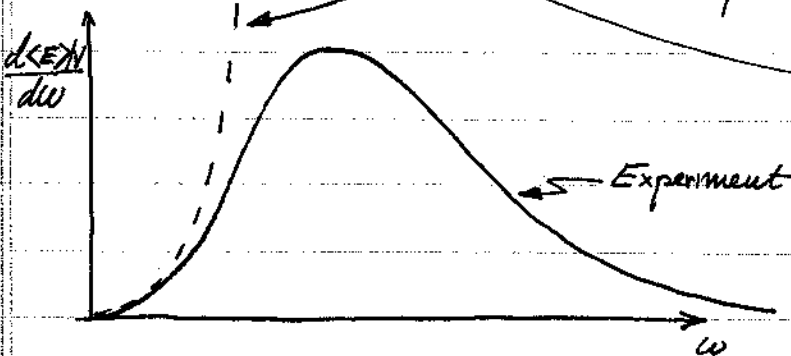
sum over polarizations

$$= \int_0^{\infty} dk \frac{d\langle E \rangle}{dk} \quad ; \quad \frac{d\langle E \rangle}{dk} = \frac{V}{\pi^2} k_B T k^2$$

This can also be expressed in terms of frequency $\frac{\omega}{c} = k$

$$\Rightarrow dk = \frac{d\omega}{c} \quad ; \quad k^2 = \frac{\omega^2}{c^2}$$

$$\Rightarrow \frac{d\langle E \rangle}{d\omega} V = \frac{1}{\pi^2} \frac{k_B T}{c^3} \omega^2 \quad ; \quad \text{Spectral Density: average energy per unit volume and unit frequency}$$



This is known historically as the Rayleigh-Jeans law

This classical result disagrees with the experimental observations especially as $\omega \rightarrow \infty$. It coincides with experiments as $\omega \rightarrow 0$.

Moreover, this result leads to a divergent result in the energy in the EM field:

$$\langle E \rangle = \int_0^{\infty} d\omega \frac{1}{\pi^2} \frac{k_B T}{c^3} \omega^2 \rightarrow \infty$$

This is known as the "ultraviolet catastrophe" - there is an infinite amount of energy coming from the high frequencies.

Any box held at nonzero temperature would be producing an infinite amount of energy.

This fundamental failure of the combination of statistical mechanics and Maxwell theory of EM radiation forced physicists to develop the quantum theory of light.