The classical view predicts that all oscillators, regardless of their natural freq., have the same average energy.

\[ I(\omega) = \frac{1}{\pi^2 c^2} \frac{W}{\omega} \]

The classical view predicts, then,

\[ I(\omega) = \frac{1}{\pi^2 c^2} \frac{W}{\omega} = \frac{2}{\pi^2 c^2} \frac{K T}{\omega} \]
But,

Classical prediction

Experiment

Good agreement at low frequencies
Serious discrepancies at high frequencies

"ULTRAVIOLET CATASROPHIE"

Thus, something must be wrong in expression (3)

\[ I(w) = \frac{w^2}{\pi^2 c^2} W \]
CLASSICAL VIEW

$\omega = \omega_0$

$E$ oscillator of natural frequency $\omega_0$

Since the value of the amplitude $A$ can be tuned to any value (in a continuous range), the values of the energy imparted to the oscillator would be also in a continuous range

$E \ (0 \ to \ \infty)$

QUANTUM VIEW

1900, Max Planck

He suggested that the oscillator above can take up energies only $\hbar \omega_0$ at a time. The energies possible for the oscillator would be $\hbar \omega_0, 2\hbar \omega_0, 3\hbar \omega_0, \ldots$
Planck did not question the classical procedures or reasoning that led to

$$I(\omega) = \frac{\omega^2}{\pi^2 c^2} \frac{W}{\text{average energy of the oscillator}}$$

He questioned the classical way to calculate $W$. 


Since the oscillator is interchanging energy with its surrounding (a box at temperature $T$ containing radiation) it will have, at equilibrium, an average energy $\mathcal{W}$. How to calculate $\mathcal{W}$?
How to arrive to the quantized $\Delta E = \hbar \omega_0$ hypothesis?

Consider a large number of oscillators, whose natural frequencies $\omega_0$ range from 0 to $\infty$ (in a continuum.)

For each value of $\omega_0$ (between 0 and $\infty$) there are many many oscillators.

Planck postulated that a given oscillator of natural frequency $\omega$ (notice we have dropped the sub-index "0", just to simplify the notation) can take up energies in the form of lumps.

oscillator energy $= \epsilon, 2\epsilon, 3\epsilon, \ldots$

How does $\epsilon$ relate to $\omega$? This is not specified yet.
Following Planck's hypothesis, the average energy $W$ would have to be calculated according to

$$W^{\text{Planck}} = \langle E \rangle = \frac{\sum_{n=0}^{\infty} (n\epsilon) P(n\epsilon)}{\sum_{n=0}^{\infty} P(n\epsilon)}$$

A discrete sum (rather than an integral as in the classical case).

The form of $P$ still being of the same form:

$$P(n\epsilon) \propto e^{-\frac{n\epsilon}{kT}}$$

How could Planck's hypothesis lead to an agreement of $U(w)$ with the experimental results?

For low $W$, when adding all those vertical segments we expect that the resulting $W^{\text{Planck}}$ to be very close to the classical value $W$ (Remember, the latter is close to the experimental value).
So, Planck's hypothesis would do well at low $\hbar$.

For larger $\hbar$

When adding those vertical bars, the resulting $W_{\text{Planck}}$ would be much smaller than the classical value $W$.

In fact, the larger $\hbar$, the larger step $\epsilon$ to be chosen, the smaller $W_{\text{Planck}}$.

And, indeed, the experimental results indicate that $W$ should decrease at large $\hbar$. Thus $W_{\text{Planck}}$ would reproduce better the experimental results.

How to choose the step $\epsilon$?

$\epsilon$ should be chosen to increase with $\hbar$, but in what form?
The simplest choice is to assume a linear relationship

\[ \varepsilon(w) = \theta(w) \]

where \( \theta \) is a constant of proportionality to be conveniently chosen to fit the experimental results.

Thus

\[
W_{\text{Planck}} = \frac{\sum_{n=0}^{\infty} (n+1)w \left[ e^{-\frac{n+1}{kT}} \right]}{\sum_{n=0}^{\infty} e^{-\frac{n}{kT}}} = W_{\text{Planck}}(w)
\]

\( \text{Average energy of the electron magnetic mode of freq. } w \)

- Let \( \alpha = \frac{\theta}{kT} \), \( A = \sum_{n=0}^{\infty} e^{-\alpha w} \), \( \frac{\partial A}{\partial \alpha} = \sum_{n=0}^{\infty} (-nw)e^{-\alpha w} \)

\[
W = \frac{1}{A} \sum_{n=0}^{\infty} (n+1)w \left[ e^{-\alpha w} \right]
\]

\[
= \frac{1}{A} (-\alpha) \frac{\partial A}{\partial \alpha} = -\alpha \frac{1}{A} \ln A
\]

- Let \( x = e^{-\alpha w} \), then

\[ A = 1 + x + x^2 + \ldots \text{ which is equal to } \frac{1}{1-x} \]
\[ A = \frac{1}{1 - e^{-\alpha \omega}} \quad i \frac{d}{dx} \ln A = (1 - e^{-\alpha \omega}) \frac{\omega e^{-\alpha \omega}}{(1 - e^{-\alpha \omega})^2} \]

\[ W = (-\alpha)(-1) \frac{\omega e^{-\alpha \omega}}{(1 - e^{-\alpha \omega})} = \frac{\alpha \omega}{e^{\alpha \omega} - 1} \]

\[ W_{\text{Planck}}(\omega) = \frac{\frac{k}{e^{\frac{k}{h} \omega} - 1}}{e^{\frac{k}{h} \omega}} \quad (\text{This time, } W \text{ depends on } \omega) \]

and

\[ I(\omega) = \frac{1}{\pi^2 c^2} \omega^2 W = \frac{k}{\pi^2 c^2} \frac{\omega^3}{e^{\frac{k}{h} \omega} - 1} \]
\[ I(w) = \# \omega^2 \bar{W} \]

average energy of the oscillator

using Planck's hypothesis

\[ \bar{W} = \frac{\hbar \omega}{e^{\frac{\hbar \omega}{kT}} - 1} \]
Einstein's Laws of Radiation

Planck figured out that the spectral energy density required for equilibrium was

\[ I(\omega) \, d\omega = \frac{k \omega^3}{\pi^2 c^2} \cdot \frac{1}{e^{\hbar \omega / kT} - 1} \, d\omega \]

For Planck: the matter was quantized

(the oscillator can take energy only in discrete amounts)

- light, once radiated, spreads out like a wave.

For Einstein - radiant energy is quantized as well.
Calculation of the electromagnetic energy density $U$ inside the cavity.

First, let's count the number of electromagnetic modes inside a cavity.

$$E(x) = E_0 \sin\left(\frac{2\pi}{\lambda} x\right) \sin(\omega t)$$

where $\lambda \frac{\omega}{2\pi} = c$

The value of $\omega$ specifies the electromagnetic mode.

Many modes can exist inside the cavity (a cube of side "a"). But, not all values of $\omega$ are allowed.

The requirement that $E=0$ at $x=a$ implies

$$\frac{2\pi}{\lambda} a = n \times \pi$$

$$\Rightarrow$$

$$\frac{1}{c} \frac{\omega}{2\pi} = \frac{n}{2a} \quad \text{or} \quad \omega = 2\pi \frac{n}{2a}$$

$n=1, 2, 3, ...$

Modes allowed in the cavity.
In a given interval $\Delta w$, how many modes there exist?

Answer: $\frac{1}{2\pi} \frac{2a}{c} \Delta w$ (one dimensional "cube")

In a three dimensional cube

$$\left[ \frac{1}{2\pi} \frac{2a}{c} \right]^3 \times \left[ \frac{4\pi}{8} w^2 \Delta w \right] = \text{Number of modes allowed (in a cube cavity of side "a") that have a frequency between } w \text{ and } w + \Delta w$$

$$= \frac{V}{2\pi^2 c^3} w^2 \Delta w$$, where $V = a^3$

Since for each mode, 2 polarizations are possible,

$$= \frac{V}{\pi^2 c^3} w^2 \Delta w$$
Thus, we find that
\[
\frac{\omega^2}{n^2 c^3} \Delta \omega = N(\omega) \Delta \omega
\]

**WHAT IS THE ENERGY STORED IN EACH MODE?**

Since the perfectly reflecting walls are kept at temperature \( T \), we can picture a given mode interchanging energy with the walls. That is, sometimes the mode will have small amplitudes, other times large amplitudes, etc. But it will have an average amplitude, and, hence, an average energy. Let's call it \( W \).

\( W \) could depend on \( T \) and the frequency \( \omega \) of the mode.
Accordingly, the energy density \( \left( \frac{J}{m^3} \right) \) in the cavity, contributed by the modes whose angular frequency lie between \( w \) and \( w + \Delta w \)

\[
N(w) \Delta w = \frac{w^2}{\pi^2 c^3} \Delta w = U(w) \Delta w
\]

\[
U(w) = \frac{w^2}{\pi^2 c^3} \frac{W}{w} \quad \text{(4)}
\]

average energy of the mode of frequency \( w \)

Notice the similarity between expressions (3) and (4)
Relationship between $U$ and $I$

Take a look to the "cylinder" of length $l$ and cross section area $A$:

$$\Delta U = \text{total energy} = U \cdot l \cdot A$$
inside the cylinder

$\Delta U$ will cross a section $A$ in $\Delta t = \frac{l}{c}$ seconds

$$\text{Traveling energy per unit time} = \frac{\Delta U}{\Delta t} = UAc$$

So

$$I = \frac{\text{traveling energy per unit area \times per unit time}}{\text{per unit area \times per unit time}} = UC$$
How to calculate the average energy of a mode of frequency ω?

To answer this question, we should realize the analogy between these two problems:

i) a charged oscillator of natural frequency ω, in equilibrium with radiation in a box at temperature T (as studied in the previous sections)

and

ii) an electromagnetic mode ω in thermal equilibrium inside a box at temperature T.

For the first case, Planck derived a formula to calculate the average energy of the oscillator.

For the second case Einstein extended Planck's ideas about quantized energies of an oscillator to the electromagnetic radiation. Yes, the energy of the radiation would be also quantized.

Einstein used; then, Planck's formula
to calculate the average energy of a electromagnetic mode

\[ \mathcal{W}(\omega) = \frac{k \omega}{e^{\frac{k \omega}{k T}} - 1} = \mathcal{W}_{\text{Einstein}} \]

average energy of a mode of frequency \( \omega \)

[that is, it does make no difference whether we have an atom (or oscillator) of natural frequency \( \omega \), or an electromagnetic mode of frequency \( \omega \).]

\[ \mathcal{U}(\omega) = \frac{\omega^2}{\pi^2 \epsilon^3} \frac{k \omega}{e^{\frac{k \omega}{k T}} - 1} \]
to calculate the average energy of a electromagnetic mode

$$W(w) = \frac{kW}{e^{\frac{1}{kT}w} - 1} = W_{\text{Einstein}}$$

average energy of a mode of frequency $w$

[That is, it does make no difference whether we have an atom (or oscillating) of natural frequency $w$, or an electromagnetic mode of frequency $w$.]

$$U(w) = \frac{w^2}{\pi^2 c^3} \frac{kW}{e^{\frac{1}{kT}w} - 1}$$

$$I(w) = \frac{kW^3}{\pi^2 c^2} \frac{1}{e^{\frac{1}{kT}w} - 1}$$

Einstein used this result to obtain new information about radiation-matter interaction.
**Light-Matter Interaction**

Einstein's coefficients

Consider a large number of atoms having a quantized energy levels $E_m$ and $E_n$.

When the incident light has the right frequency $\hbar \nu = E_m - E_n$, three processes can occur:

**ABSORPTION**

An atom absorbs a photon thus making a transition from state $n$ to state $m$.

The probability of this transition would depend on:

- the intensity of the light $I(\nu)$
- the nature of the states $m$ and $n$
let's assume the probability of this transition $P_{nm}$ is proportional to $I(w)$ per second: $P_{nm} = B_{nm}I(w)$ Absorption

**Emission**

Einstein suggested there should be two types of emission processes:

**Spontaneous emission**

Even when there is no light present, there is a certain probability $A_{mn}$ per second that the atom will transit from the excited state $m$ to the lower state $n$.

We further assume that $A_{mn}$ is the same whether light is present or not.

**Stimulated emission**

The emission probability is further influenced by the presence of light.
Einstein assumed this probability per second to be proportional to \( I(w) \)

\[
\text{stimulated emission} = B_{mn} I(w)
\]

\[
\text{probability} \sim \text{const of proportionality}
\]

Accordingly, the total emission probability would be

\[
P_{mn} = A_{mn} + B_{mn} I(w)
\]

Equilibrium conditions

At temperature \( T \), \( N_m \) atoms will be in the state \( n \), and \( N_m \) in the state \( m \).

\[
R_{n \rightarrow m} = N_n B_{nm} I(w)
\]

Rate at which atoms transit from \( n \) to \( m \)

\[
R_{m \rightarrow n} = N_m (A_{mn} + B_{mn} I(w))
\]
At equilibrium, these two rates should be equal (so the number of atoms in each energy level remains constant.)

\[ N_n B_{nm} I(w) = N_m (A_{mn} + B_{mn} I(w)) \]

\[ \Rightarrow \]

\[ I(w) = \frac{A_{mn}}{N_m B_{nm} - B_{mn}} \]

Since \( N_n \propto e^{-\frac{1}{kT}E_n} \)
\( N_m \propto e^{-\frac{1}{kT}E_m} \)

\[ \Rightarrow \]

\[ \frac{N_n}{N_m} = e^{\frac{1}{kT}(E_mE_m - E_nE_n)} = e^{\frac{\hbar\omega}{kT}} \]

But the frequency \( \omega \) that we are considering above is the one matching \( \hbar \omega = E_m - E_n \).

Thus,

\[ \frac{N_n}{N_m} = e^{\frac{\hbar\omega}{kT}} \]

\[ I(w) = \frac{A_{mn}}{B_{nm} e^{\frac{\hbar\omega}{kT}} - B_{mn}} \]
But Planck's formula tells us what $I(\omega)$ we should have under equilibrium conditions:

$$I(\omega) = \frac{\hbar \omega^3}{\pi^2 c^2} \frac{1}{e^{\frac{\hbar \omega}{kT}} - 1}$$

This implies,

$$B_{mn} = B_{nm}$$

Induced emission and absorption probabilities are equal.

And

$$A_{mn} = \frac{\hbar \omega^3}{\pi^2 c^2} B_{nm}$$

The cubic dependence $A_{mn}$ on $\omega$ accounts for the principal difficulty in achieving laser action at x-ray frequencies.

At these high frequencies spontaneous emission occurs so rapidly that a sustained stimulated...
emission is difficulty to achieve. At lower frequencies (visible) this difficulty is, fortunately, no great.

**Stimulated Emission (LASER)**

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- Stimulated absorption
- Spontaneous emission
- Stimulated emission

1. in phase!
The most striking feature in the stimulated emission process is that the photon resulting from the transition is in phase with the incident photon that provokes the transition.

Stimulated emission is a constructive interference process.

**Can we have a sustained stimulated emission process?**

Two factors play against,

1) At equilibrium, there are only a few atoms in the excited state.

2) Out of the few excited atoms, the spontaneous emission process lowers even more the number of atoms available for stimulated emission.
We can not avoid the spontaneous emission. So, scientists had to figure out how to revert the condition $N_m < N_n$, which implies to consider situations out of equilibrium then. One strategy is shown in the figure below: OPTICAL PUMPING

Pump light

metastable state
(atom tends to stay long in this state)

No pumping Moderate pumping Intense pumping
For perfectly parallel mirrors, the horizontally collimated beam intensity is reinforced through a) many back and forth reflections, b) the accompanying stimulated emission they produced. The latter occurs provided the population inversion is maintained.
Let's consider the variation in intensity of a collimated beam (photons of energy $h\omega$) advancing in a medium containing atoms that have energy levels $E_m$ and $E_n$ such that $E_n - E_m = h\omega$

\[ N_n \quad \text{atoms} \]
\[ N_m \]

\[ U(z) = \frac{I(z)}{c} \]

$U$: energy per unit volume
\[ \frac{U}{h\omega} = \text{photons per unit volume} = \eta \]

# of photons in that volume = $\frac{U(z)}{h\omega} A \Delta z = \eta(z) A \Delta z$
\[ N_n = N_n^e A \Delta z \]
\[ N_m = N_m^e A \Delta z \]

We assume there is a constant and uniform density of excited states \( N_n^e \), \( N_m^e \) (which will change, but only after the beam has passed).

\[
\frac{N_m B_{mn} I(x)}{\text{Probability per second an atom will be absorbed}} = \# \text{ of photons lost per second by the collimated beam.}
\]

\[
N_n B_{nm} I(x) = \# \text{ of photons gained per second by the collimated beam.}
\]

\[
(N_n - N_m) B_{nm} I(x) = \frac{\Delta N(z)}{\Delta t} \quad \text{(Net gain of photon in the collimated beam)}
\]

The net gain of photons can also be expressed in terms of the net flux traversing the volume \( A \Delta z \):

\[
\frac{\Delta n}{\Delta t} = \frac{I(z + \Delta z) - I(z) A}{k \Delta z} A
\]
\[
\Delta n = \frac{A}{\hbar w} \left[ I(z+\Delta z) - I(z) \right]
\]

\[
= \frac{A}{\hbar w} \frac{\Delta I}{\Delta z} \Delta z
\]

Equating (1) and (2)

\[
(N_n - N_m) B_{nm} I(x) = \frac{dI}{dx} \frac{1}{\hbar w} A \Delta z
\]

\[
\Rightarrow \frac{dI}{dx} = \hbar w (N_n - N_m) B_{nm} I(x)
\]

If the gas of atoms is in equilibrium, \(N_n \approx N_m\), so \(\frac{dI}{dx}\) decreases.

\[
\frac{dI}{dz} = - (N_n - N_m) B_{nm} \hbar w \alpha I(z)
\]

\[
I(z) = I(0) e^{-\alpha z} \quad \alpha = (N_m - N_n) B_{nm} \hbar w
\]

Absorption coefficient
If, however, we created a condition where

\[ N_m^0 > N_n^0 \quad \text{m \quad \ldots \ldots} \]

\[ N_n^0 \quad \text{\ldots} \]

the \( \alpha \) would become negative, and the intensity \( I \) would grow with distance

\[ I(z) = I(0) e^{\beta z} \]

\[ \beta = (N_n^0 - N_m^0) \]

called "small-signal gain coefficient"