**"Enrico Fermi" Chair**
2021/2022

Lectures at Sapienza Università di Roma,
January-May 2022

A History of the Science of Light
From Galileo's telescope to the laser and the quantum information technologies

Serge Haroche,
Ecole Normale Supérieure and
Collège de France, Paris

Lecture 4. February 17th 2022

Lecture 4: The birth of Quantum Physics (1905-1925)

The ultraviolet catastrophe
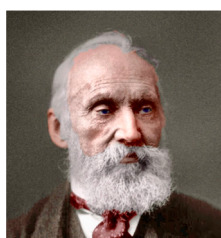
Lord Kelvin

Max Planck

Albert Einstein

Outline of lecture 4

Describe how interrogations about light phenomena which could not be explained by the principles of classical physics (Maxwell equations and thermodynamics) have led to the emergence of quantum concepts.

Follow the evolution of the quantum ideas between 1900 and 1924 from Planck's law to the eve of de Broglie hypothesis about matter waves.

Remind the central role played by Einstein in this story

This historical introduction to quanta will follow chronological order

Covered topics: The blackbody radiation puzzle and the introduction of the photon in physics, the photo-electric effect, the wave-particle duality, the heat capacity of solids, the Bohr-Sommerfeld atom, the discovery of stimulated emission, Bose statistics and the prediction of Bose-Einstein condensation, the Pauli exclusion principle and the Fermi Dirac statistics.

The two papers which started the quantum revolution

Zur Theorie des Gesetzes
der Energieverteilung im Normalspectrum;
von M. Planck.

(Vorgetragen in der Sitzung vom 14. December 1900.)

(Vgl. oben S. 235.)

Planck
(December 1900)

(On the theory of the energy distribution law of the normal spectrum)

6. Über einen
die Erzeugung und Verwandlung des Lichtes
betreffenden heuristischen Gesichtspunkt;
von A. Einstein.

Einstein
(March 1905)

(On a heuristic view point concerning the production and transformation of light)

The ultraviolet catastrophe and the birth of quanta (1900-1905)
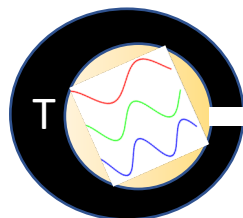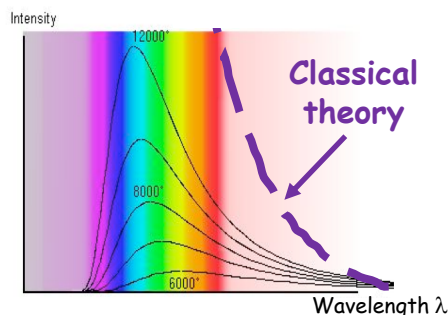
Measuring the spectral distribution of the light radiated by a « blackbody » furnace (important for industry)

A box with black walls (absorbing all the light) is pierced by a small hole. The em field inside the box is in equilibrium with the atoms of the walls at a fixed temperature T. Experimental spectrum of escaping light is universal and depends only on T. The intensity vs frequency (or wavelength) varies according to a bell-shaped curve with maximum at wavelength:

$$\lambda_{\max}(T) = \frac{C}{T} \quad with \quad C = 2.9 \times 10^{-3} m.K \quad \text{(Wien's law)}$$

Maximum shifts towards short wavelengths as T increases. Centered in the infrared at room temperature, it falls above 4000 K in the visible spectral window. *Classical theory unable to explain.*

Classical physics is unable to explain this universal spectrum and predicts absurd result: the uv catastrophe

In order to describe the spectrum, combine Maxwell's equations with the laws of thermodynamics. Maxwell says that the field expands over modes defined by their polarization and their k vector:

$$\vec{k} = \frac{2\pi\nu}{c}\vec{u}_{\theta,\varphi} \quad \vec{u}_{\theta,\varphi} : \text{unit vector along direction } \theta,\varphi$$

In a cubic box of side L and volume V=L³ , it is convenient to count the modes by introducing the cyclic boundary conditions:

$$k_x = n_x\frac{2\pi}{L}; k_y = n_y\frac{2\pi}{L}; k_z = n_z\frac{2\pi}{L} \quad n_x, n_y, n_z \text{ integers}$$

The number of modes with k comprised between k and k+dk or ν between ν and ν+dν is:

$$2 \times 4\pi k^2 dk\left(\frac{L}{2\pi}\right)^3 = \frac{V}{\pi^2}k^2 dk = \frac{8\pi V}{c^3}\nu^2 d\nu$$

Invoking the thermodynamical principle of equipartition of energy, Rayleigh and Jeans have assumed that at thermal equilibrium at temperature T, each mode is an oscillator which has on average the energy k_BT where k_B is the Boltzmann constant. They then find a spectral density of em energy in the box increasing as ν² and diverging at short wavelengths, yielding an infinite total field energy density:

$$I(\nu)d\nu = \frac{8\pi}{c^3}k_B T\nu^2 d\nu$$

There is good agreement with experiment for small ν, but for large ν there is a conflict between Maxwell and Boltzmann, as **there was one between Maxwell and Galileo!**

The second principle of thermodynamics: free energy

A system in contact with a reservoir at temperature T settles in equilibrium in the state which minimizes its free energy:
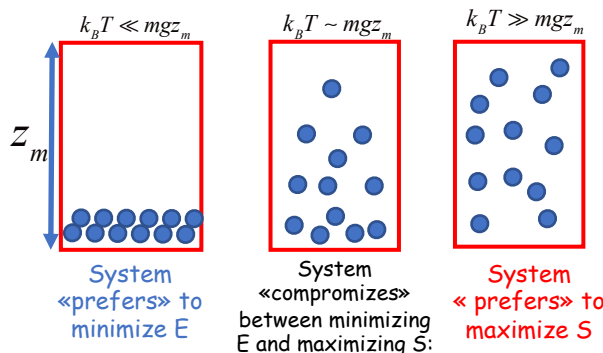
Free energy:
$$F = E - TS$$

Absolute temperature (K)

Energy (J)

Entropy (J/K)

Nature is at the same time "lazy" (a system at thermal equilibrium tends to decrease its energy) and "messy" (it tends to increase its disorder). The equilibrium between small E and large S depends on temperature.

Example of isotherm gas in a gravitational field

$k_B T \ll mgz_m$ $k_B T \sim mgz_m$ $k_B T \gg mgz_m$

z_m

System «prefers» to minimize E

System «compromizes» between minimizing E and maximizing S:

System «prefers» to maximize S

Compromise: exponential distribution of energy:

$$p(E) \sim e^{-E/k_B T} \quad \textit{Boltzmann law}$$

Entropy unit: $k_B = 1.38 \times 10^{-23} J / K$

The introduction of quanta freezes the high frequency modes

Considering that each field mode is an oscillator at thermal equilibrium and that its energy varies **continuously, Rayleigh and Jeans** got the oscillator energy probability distribution in each mode:

$$p(E) = \frac{1}{Z} e^{-E/k_B T}$$

with Z satisfying the normalization condition:

$$\int p(E) dE = 1 \rightarrow \quad Z = \int_0^\infty e^{-E/k_B T} dE = k_B T$$

A simple integration then yields the average energy in each mode:

$$\langle E \rangle = \int E p(E) dE = \frac{1}{k_B T} \int E e^{-E/k_B T} dE = k_B T$$

which is the result leading to the uv catastrophe. To avoid it, make the asumption that the energy of oscillators varies in discrete steps.

Divide instead the continuum of energies in small intervals proportional to ν:

$$\delta E_\nu = h\nu$$

where h is a small constant, with dimension of an action (Joule x second), with value to be fixed. The integral becomes a series:

$$E_\nu = \frac{1}{Z} \sum_n nh\nu\, e^{-nh\nu/k_B T} = \frac{k_B T}{Z} x \sum_n n e^{-nx}$$
$$(x = h\nu / k_B T)$$

and after straightforward steps:

$$Z = \sum_n e^{-nh\nu/k_B T} = \sum_n e^{-nx} = \frac{1}{1-e^{-x}}$$
$$\sum_n n e^{-nx} = -\frac{dZ}{dx} = \frac{e^{-x}}{\left(1-e^{-x}\right)^2}$$

$$\boxed{\langle E_\nu \rangle = k_B T \frac{x e^{-x}}{1-e^{-x}} = k_B T \frac{x}{e^x - 1}}$$

The discrete nature of the field energy scale freezes in ground state the high frequency modes of field

Low frequency modes

High frequency modes

$$\langle E_v \rangle = k_B T \frac{x}{e^x - 1} \; ; \; x = \frac{h\nu}{k_B T}$$

$k_B T$

$$h\nu < k_B T$$

$$\langle E \rangle \sim k_B T$$

Excited states are populated: equipartition of energy is satisfied

uv catastrophe avoided

$$h\nu > k_B T$$

$$\langle E \rangle \ll k_B T$$

It costs too much in energy to increase the entropy by populating excited states: field oscillators remain frozen in ground state

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Planck's law (1900)

M.Planck
(1858-1947)

$$\langle E_v \rangle = k_B T \frac{x}{e^x - 1} \qquad (x = h\nu / k_B T)$$

Equipartition of energy holds and R-J is a good approximation at long wavelength

For low frequencies $\nu \ll k_B T/h$: $\qquad x \ll 1 \rightarrow E_v = k_B T$

For high frequencies $\quad \nu \gg k_B T/h \qquad x \gg 1 \rightarrow E_v \rightarrow 0$

Modes are frozen in their ground states

The spectrum at temperature T is readily deduced:

$$I(\nu)d\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/k_B T} - 1} d\nu \qquad I(\lambda)d\lambda \sim \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda k_B T} - 1} d\lambda$$

These two equivalent expressions fit perfectly the experimental spectrum, when Planck gives to the free parameter h the value:

$$h = 6.626 \times 10^{-34} J \times s$$

The photon (1905)

For Einstein, the quanta were more than a trick to reconcile Maxwell with Boltzmann: the blackbody law shows that the em field is made of light quanta (which will be later called photons) propagating in empty space with light's velocity c. The energy and momentum of a plane wave photon of frequency ν are respectively:

$$E = h\nu \quad ; \quad p = \frac{h\nu}{c} = \frac{h}{\lambda}$$

We will see later that a photon of circularly polarized light also carries a unit of angular momentum S_{am} along its direction of propagation:

$$S_{am} = \pm\frac{h}{2\pi} = \pm\hbar$$

The energy of a red photon of frequency 4.10^{14} Hz (λ =0,75 microns) is:

$$E_{red} = 6.6\times10^{-34} \times 4\times10^{14} = 2.64\times10^{-19} J = 1,65 eV$$

(One eV=1.6 10^{-19}J is the energy acquired by an electron accelerated between points whose electric potential differ by one Volt)

A lamp with a light power of 100 watts emits 3.8×10^{20} photons per second!
Light quanta are very tiny but they have macroscopic effects: their existence resolves the mystery of the thermal radiation spectrum and explains many other phenomena

Field quantization explains the photoelectric effect (1905)
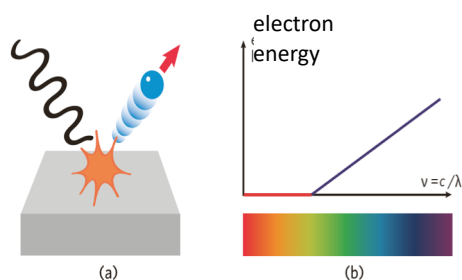
A light quantum is annihilated by ejecting an electron from metal, provided its energy hν exceeds the electron extraction threshold. The kinetic energy of the emitted electron must increase linearly with the light frequency above threshold (slope yields Planck's constant, verified experimentally by Millikan)

$$h\nu = W + E_{electron}$$

Intense red light (whose frequency is below threshold) does not extract any electron while a faint blue light whose frequency is above threshold does.

Einstein's Nobel Prize in 1921: the citation quotes the *photoelectric effect* with no mention of either Relativity or Quanta!

The photon introduces the **wave-particle dualism** in physics which will have tremendous consequences for our understanding of the world at the **microscopic** as well as **cosmological** levels

LIGHT IS A Wave!

Ambigram by Douglas Hofstadter
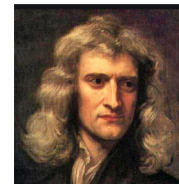

Reconciliation between Huygens and Newton?

Light behaves as a wave when it propagates and gives rise to interference, reflection and refraction effects. On the other hand, it behaves as a flow of particles when it interacts with atomic matter. How to describe this ambivalent behaviour in a consistant way?

Huygens

Einstein

Newton

Einstein extends quanta to matter by solving the puzzle of the heat capacity of solids (1911)

Empirical law: the heat capacity of a large class of solids is equal to $3k_B$ per atom (Dulong and Petit law, 19th century). Boltzmann explains it by assuming that each atom in a crystal is a small oscillator vibrating around its equilibrium position along the three directions of space. The equipartition of energy gives the energy $k_B T$ to each of these oscillators.

For some solids (for example carbon in the form of diamond), the heat capacity is at room temperature well below the $3k_B$ value (of the order of $0,8k_B$). Einstein assumed that the atomic oscillation vibrations are quantized like the modes of the em field and that for very rigid bodies like diamond, the vibration frequencies are so high that the corresponding vibration modes are frozen. By mererely applying Planck's law he finds:

$$\frac{dE_\nu}{dT} = \frac{d}{dT}\left[3k_B T \frac{x}{e^x - 1}\right] = 3k_B \frac{x^2 e^x}{\left(e^x - 1\right)^2} \qquad (x = h\nu / k_B T)$$

which tends towards $3k_B$ for $x \ll 1$ and decreases towards 0 when x increases

The vibration freezing starts for x of order 1. At room temperature T=300K, $x=1$ corresponds to $\nu = k_B T/h = 6.10^{12}$ Hz. The vibration frequency in diamond is 3.10^{13} Hz ($x = 5$), which explains its small heat capacity at room T. The Planck's law predicts that all elements obeying Dulong and Petit law have their heat capacity dropping below a certain temperature and tending towards zero as T approaches 0K. Einstein presented these results at the first Solvay meeting of 1911.

Solvay meeting of 1911 in Brussels
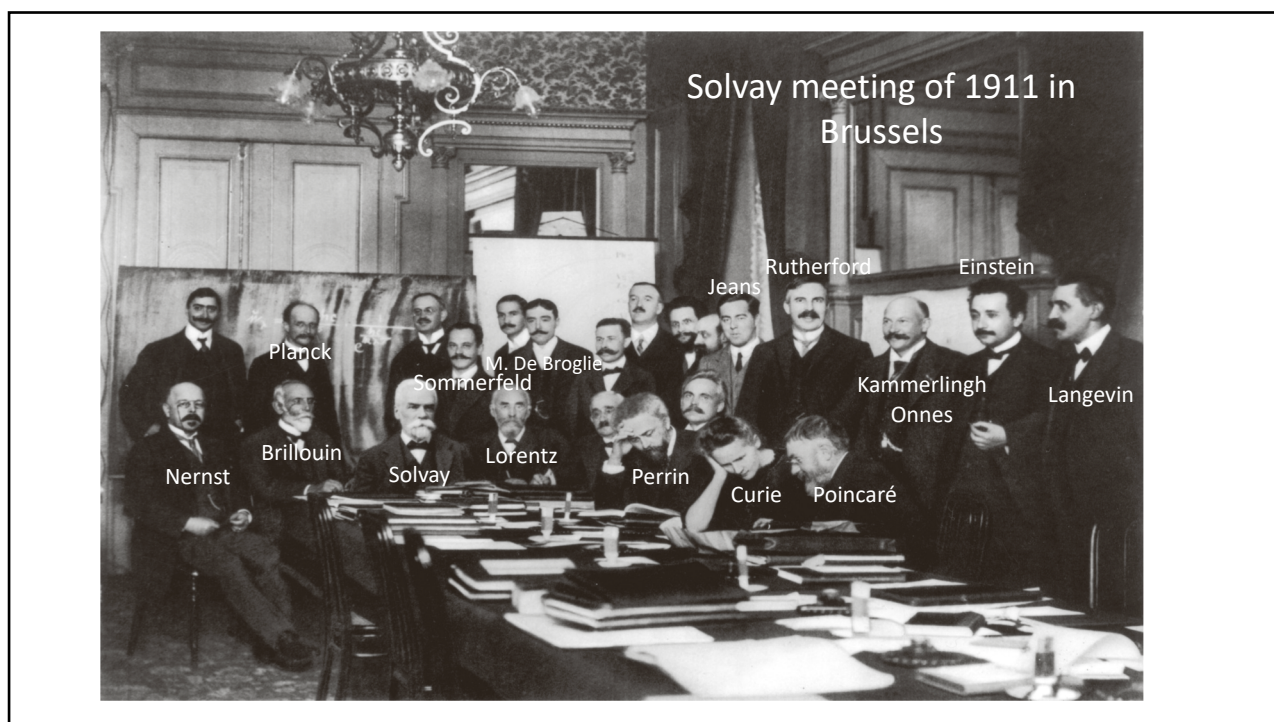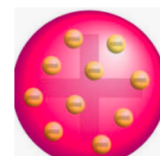
The birth of the quantum atom

J.J Thomson (1856-1940

E.Rutherford (1871-1937)

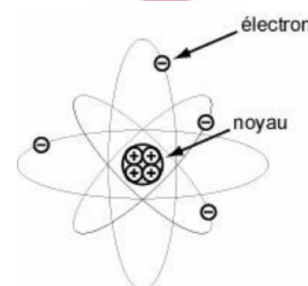J.Perrin (1871-1942)

1897-1904: Thomson discovers the electron in cathode rays and proposes an atom model with negative electrons immersed in a positively charged jelly (« plum-pudding » model)
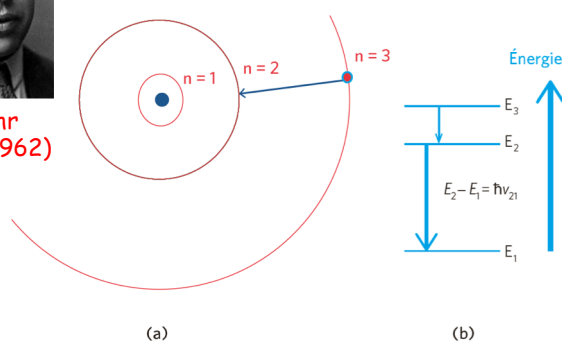
1909-1911: Rutherford bombards a thin gold foil with alpha particles and discovers that positively charged atomic nuclei concentrate nearly all the atomic mass: this suggests to Rutherford and Perrin that the atom is a microscopic planetary system, with light electrons orbiting the heavy nucleus like planets around the Sun.

électron

noyau

The Hydrogen Bohr atom (1913)

N.Bohr (1885-1962)

n = 1   n = 2   n = 3

Énergie

E_3

E_2

$E_2 - E_1 = \hbar v_{21}$

E_1

(a)   (b)

$$r_n = a_0 n^2 \qquad E_n = -\frac{R}{n^2}$$

Bohr radius

Rydberg constant

$$v_{nn'} = \frac{E_n - E_{n'}}{h}$$

The electron revolves on circular orbits whose energies and radii are quantized and labelled by the quantum number n. The electron can jump from one orbit to another by emitting or absorbing a photon, with conservation of energy of the atom+field system. These quantum jumps occur at random times whose probability can only be predicted. The ground state (n=1) is stable. This model gives accurately the observed spectrum of Hydrogen (series Lyman starting from n=1, Balmer from n=2 etc….)

Bohr's model

Bohr assumed that the angular momentum on the nth electron orbit is quantized:in units of h/2π= $\hbar$

Calling ω_n the angular velocity of the electron, r_n the radius of its orbit and m its mass, we have:

$$m\omega_n r_n^2 = n\hbar$$

Another relation between ω_n and r_n expresses the balance between the centrifugal force experienced by the electron and the electrostatic force attracting it to the nucleus:

$$m\omega_n^2 r_n = \frac{e^2}{r_n^2} \qquad (e^2 = q_e^2 / 4\pi\varepsilon_0)$$

From these two relations, Bohr gets: $\quad r_n = n^2 a_0 \quad with \quad a_0 = \frac{\hbar^2}{me^2}$

And the energy of the nth state: $E_n = -\frac{e^2}{2r_n} = -\frac{me^4}{2\hbar^2}\frac{1}{n^2} = -\frac{R_0}{n^2} \quad with \quad R_0 = \frac{me^4}{2\hbar^2}$

It is instructive to express these results in terms of the dimensionless fine structure constant α:

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137} \qquad E_n = -\alpha^2 \frac{mc^2}{2n^2} \quad ; \quad r_n = n^2 \frac{\hbar}{\alpha mc} \qquad v_n = \omega_n r_n = \alpha \frac{c}{n}$$

The small value of α indicates that the electron in Hydrogen is non-relativistic (its velocity is 137 n times smaller than c and its binding energy of the order of 10^{-4} to 10^{-5} times mc^2).

The Sommerfeld Hydrogen atom: elliptical orbits of principal quantum number n and angular momenta k=1,2,3…..n.

1916
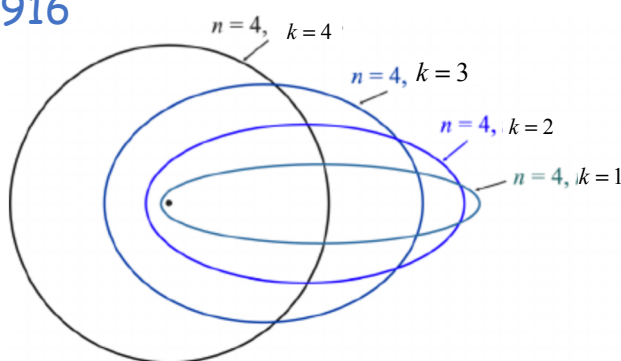
Sommerfeld elliptical orbits for the case n ¼ 4.

The orbits of same principal quantum number n and different angular momenta (k=1,2, …n) are degenerate when relativistic effects are neglected. When they are taken into account, the degeracy is lifted because the electron becomes heavier when it gets close to the nucleus on low angular momentum orbits. The model qualitatively explains the fine structure splitting of the spectral lines but is not quantitatively correct because it does not include another relativistic effect: the existence of the electron spin and its interaction with the motional magnetic field seen by the electron moving in the electrostatic field of the nucleus.

Einstein returns to Planck's law and discovers stimulated emission (1916)

Bohr's model allowed to describe both atoms and radiation with quantum concepts. Einstein decided to revisit Planck's law, analyzing the microscopic processes by which the atoms in the walls of the black box interact with light. Consider the following simple model: the walls contain subsets of two level atoms in thermal equlibrium at temperature T able to absorb or emit light at all frequencies and focus on the subset which interacts with a mode of frequency ν with a spectral density $I(\nu)$. Let us call $n_0(\nu)$ and $n_1(\nu)$ the number of atoms in the levels E_1 and E_0 such that $E_1-E_0=h\nu$ and let us express that these numbers remain stationnary at thermal equilibrium under the balanced effects of light absorption and emission.
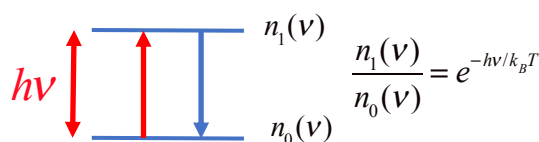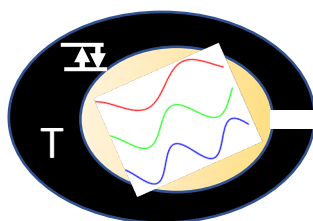
$$\frac{n_1(\nu)}{n_0(\nu)} = e^{-h\nu/k_B T}$$

The effect of light absorption and spontaneous emission on atoms thermal equilibrium: detailed balance

$$n_1(\nu)/n_0(\nu) = e^{-h\nu/k_B T}$$

Rate proportional to I(ν)

Absorption

$$\frac{dn_0}{dt} = -A(\nu)n_0 I(\nu) \quad ; \quad \frac{dn_1}{dt} = A(\nu)n_0 I(\nu)$$

Rate independent of I(ν)
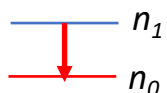
Spontaneous emission

$$\frac{dn_0}{dt} = B(\nu)n_1 \quad ; \quad \frac{dn_1}{dt} = -B(\nu)n_0$$

Assuming detailed balance between absorption and spontaneous emission yields:

$$\frac{dn_0}{dt} = -\frac{dn_1}{dt} = -A(\nu)n_0 I(\nu) + B(\nu)n_1 = 0 \implies I(\nu) = \frac{B(\nu)}{A(\nu)} \times \frac{n_1}{n_0} = \frac{B(\nu)}{A(\nu)} e^{-h\nu/k_B T}$$

This is Boltzmann's law, not Planck's: Einstein understood that a process is missing to understand the thermal equilibrium of radiation

Stimulated emission and detailed balance

$$\frac{dn_0}{dt} = A(v)n_1 I(v) \quad ; \quad \frac{dn_1}{dt} = -A(v)n_0 I(v)$$

A process symmetrical to absorption

The detailed balance then becomes:

$$\frac{dn_0}{dt} = -\frac{dn_1}{dt} = \underset{\text{absorption}}{-A(v)n_0 I(v)} + \underset{\text{Spontaneous emission}}{B(v)n_1} + \underset{\text{Stimulated emission}}{A(v)n_1 I(v)} = 0$$
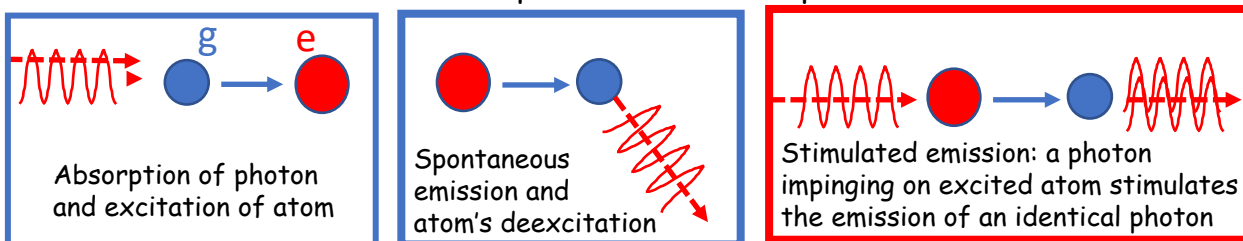
which allowed Einstein to recover the T dependence of Planck's law:

$$I(v) = \frac{B}{A}(v) \times \frac{n_1(v)}{n_0(v) - n_1(v)} = \frac{B}{A}(v) \times \frac{1}{e^{hv/k_B T} - 1}$$

We will justify in a later lecture the expression of the prefactor B(v)/A(v) which is independent of T. At this point, it is simply obtained by comparing the expression of I(v) with Planck's law.
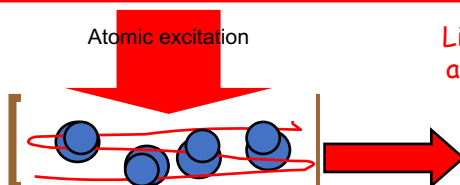
Stimulated emission announces the laser

The three atom-photon interaction processes

Absorption of photon and excitation of atom

Spontaneous emission and atom's deexcitation

Stimulated emission: a photon impinging on excited atom stimulates the emission of an identical photon

Stimulated emission is a light amplifying process. For amplification to overcome absorption, atoms should be out of thermal equilibrium with excited state more populated than ground state (population inversion: « negative temperature »)

First Laser in 1960 preceded by Maser in 1954

Atomic excitation

Light between mirrors amplified by excited atoms. The radiation noise increases to the point of self-oscillation and a fraction of light escapes through output mirror:

laser beam (photons "in step")

Stimulated emission manifests tendency of photons to accumulate in same mode

Laser light vs classical light
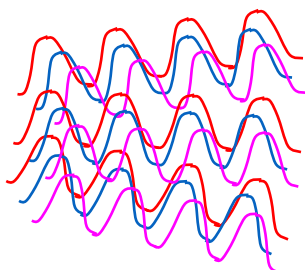
Classical light (sun, lamps): atoms emit spontaneously fields with randomphases and directions
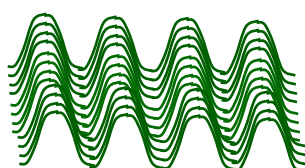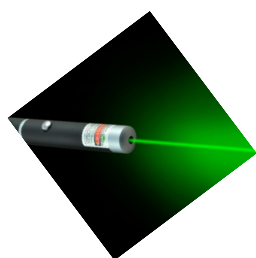
Laser light: atoms are stimulated to emit photons "in step" with same phase, frequency and direction:
"Tamed Light"

Bose recovers Planck's law by postulating the indistinguishability of photons (1923)

S.Bose
(1894-1974)

Bose computed the entropy of an ensemble of photons considered as a gas of indiscernable particles in a box, using a counting of configurations different from the one used by Boltzmann in his description of a classical ideal gas. Bose then recovered Planck's law, which vindicated his counting procedure for light quanta.

Bose sent his paper to Einstein who helped him publishing it. Einstein had the idea to extend Bose statistics to a material gas of identical atoms. The calculation revealed the possibility of a new quantum phase of matter: the Bose-Einstein condensate (BEC) which, like the laser, had to wait for many decades before beeing experimentally realized.

Stimulated emission and Bose statistics both reveal the tendency of photons to be gregarious, to accumulate in the same quantum state. This property extends to material particles called Bosons.

Bose-Einstein statistics and gregarious Bosons

Consider N=2 particles distributed in g=2 boxes. How many configurations possible?
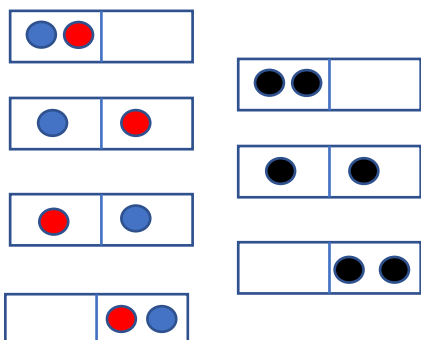
**Distinguishabe:
4 configurations**

**Undistinguishable:
3 configurations**

In the higest entropy (most disorded) state all configurations are equiprobable. The probability to find the 2 particles in the left box is 1/4 for classical particles and 1/3 for bosons.

The generalization to N > 2 is straightforward:

Probability to find N particles in box n°:1:

Numerable particles:	Bosons
$1/2^N$	$\dfrac{1}{N+1}$

After partitioning a gas of N particles in two equal volumes, it is $2^N/(N+1)$ more probable to find all of them in one side if their are undistinguishable bosons than (numerable) particles. For N=30, the probability enhancement is about 35,000,000 !

A reminder about the number of permutations of N objects

The number of (ordered) permutations of N objects is:

$$N! = 1 \times 2 \times 3 \times \cdots \times (N-1) \times N$$

There are N possibilities to chose the first object, then N-1 to chose the second and so on...

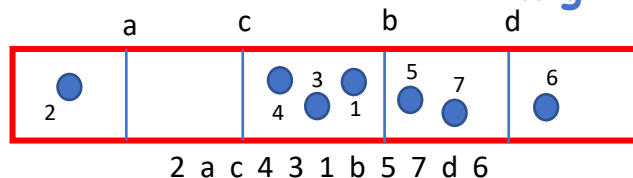The factorial of N noted N! increases exponentially with N. A good approximation of N! is given by Stirling formula:

$$N! \approx (N/e)^N \sqrt{2\pi N}$$

Or in logarithmic form:

$$Log(N!) \approx N Log(N) - N + \frac{1}{2} Log(2\pi N) + \cdots$$

Number of ways to distribute N undistinguishable particles in g boxes

a   c   b   d

2 a c 4 3 1 b 5 7 d 6

Suppose we display N distinguishable objects in g boxes created by g-1 distinguishable partitions a,b,c,d…. (in figure N=7 and g=5). The number of permutations of the objects + partitions is:

$$(N + g - 1)!$$

If the partitions are undistinguishable, the number of arrangements is divided by (g-1)! (here 24)

If the objects are also undistinguishable, the number of arrangements must again be divided by N!. Finally, the number of states available to N undistinguishable particules occupying g boxes is

$$\frac{(N + g - 1)!}{N!(g - 1)!}$$

(For N=7 and g=5 one finds 330 states).

Bose derivation of Planck's law

Photons energies are labelled by index i. The number of photons with this energy is N_i. There are g_i modes degenerate with the same energy. The average number of photons per mode is thus $n_i = N_i/g_i$.

The number of configurations of N_i identical photons distributed in g_i boxes is given by the simple counting argument of the previous slide:

$$W_i = \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!}$$

And the total number of configurations of the photon gas is:

$$W = \prod_i W_i = \prod_i \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!}$$

The entropy S = k_BLogW is approximated using Stirling formula for large integers:

$$Log(n!) \simeq nLogn - n$$

The entropy of the photon gas is:

$$S = k_B LogW = k_B \sum_i (N_i + g_i - 1)Log(N_i + g_i - 1)$$
$$- (N_i + g_i - 1) - N_i LogN_i + N_i$$
$$- (g_i - 1)Log(g_i - 1) + (g_i - 1)$$

and the variation of the entropy for small changes δN_i:

$$k_B \delta LogW = k_b \sum_i \delta N_i \left[Log(N_i + g_i - 1) - LogN_i \right]$$
$$= k_b \sum_i Log \frac{N_i + g_i}{N_i} \delta N_i$$

Bose derivation of Planck's law (continued)

To find the photon gas thermal equilibrium, Bose calculated the minimum of its free energy :

$$F = E - TS = \sum_i N_i \varepsilon_i - k_B T Log W$$

by solving the equation $\delta F = 0$ for small variations δN_i:

$$\delta F = \sum_i \delta N_i \left[\varepsilon_i - k_B T Log \frac{N_i + g_i}{N_i} \right] = 0$$

which yields:

$$N_i = \frac{g_i}{e^{\varepsilon_i / k_B T} - 1}$$

and finally replacing ε_i by $h\nu$ and g_i by the number $g(\nu)d\nu$ of modes per unit volume between frequencies ν and $\nu + d\nu$:

$$g(\nu)d\nu = \frac{8\pi \nu^2}{c^3} d\nu$$

Bose retrieved Planck's law for the thermal field spectral distribution:

$$I(\nu)d\nu = h\nu N_\nu g(\nu)d\nu$$

$$= \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{h\nu / k_B T} - 1}$$

This result validates Bose's method of configurations' counting.
He would not have found Planck's law by counting photons as distinguishable particles, like Boltzmann did for atoms

Einstein extends Bose statistic to a gas of identical atoms

Einstein considered an ideal gas of N identical (undistinguishable) atoms in a box of volume V, in thermal equilibrium at temperature T with the box walls.

The Bose calculation is valid, with a supplementary condition. While the total number of photons in thermal gas is free to vary, the total number N of atoms in the box is fixed, which adds a constraint to the minimization procedure of the gas free energy. Using the method of Lagrange multipliers, Einstein expressed the minimum of the free energy conditioned by the constraint by the equation:

$$\delta F - \mu \delta N = \sum_i \delta N_i \left[\varepsilon_i - k_B T Log \frac{N_i + g_i}{N_i} \right] - \mu \sum_i \delta N_i = 0$$

where the Lagrange multiplier μ, called the gas chemical potential, is a temperature dependent negative quantity with the dimension of an energy, determined by norma-lization. Solving this equation yields a result which coïncides with Bose's for $\mu = 0$:

$$N_i = \frac{g_i}{e^{(\varepsilon_i - \mu)/k_B T} - 1}$$

The particles obeying this statistics, whether they are massless particles like photons (with $\mu = 0$) or massive atoms (with $\mu < 0$) are called bosons.

The Bose-Einstein condensation

Introduce now the gas fugacity: $z = e^{\mu/k_B T}$

$$N_i = g_i \frac{z}{e^{\varepsilon_i/k_B T} - z}$$

z is defined by the normalization condition:

$$N = \sum_i N_i = \sum_i g_i \frac{z}{e^{\varepsilon_i/k_B T} - z}$$

Take the non-degenerate ground state as origin of energy and call N_0 its occupation number:

$$\varepsilon_0 = 0 \quad ; \quad g_0 = 1 \qquad \mu < 0$$

$$N_0 = \frac{z}{1-z} \qquad z = \frac{N_0}{N_0 + 1} < 1$$

As T decreases, z goes from 0 to 1 and N_0 increases. Let us separate N_0 from the occupation number of all the excited states:

$$N = N_0 + \sum_{i>0} g_i \frac{z}{e^{\varepsilon_i/k_B T} - z}$$

$N-N_0$ is an increasing vs z function, bounded by its value for z=1:

$$N - N_0 \le N_{max} = \sum_{i>0} g_i \frac{1}{e^{\varepsilon_i/k_B T} - 1}$$

For an ideal gas in a 3D volume V, N_{max} is a *finite number*. If for a fixed V and T the number N of atoms is increased above N_{max} the gas cannot accomodate the extra atoms in the excited states i > 0 whose population is saturated. All excess atoms have to go in the ground state whose population N_0 can increase to infinity as z approaches 1: the fraction of atoms in the ground state increases indefinitely.

Threshold Temperature of Bose Einstein Condensation

Instead of varying N at V,T fixed, consider to decrease T at N and V fixed. When N_{max}, which is a monotonous function of T, decreases and reaches N, the atoms start to leave the saturated gas phase and fall in the ground state: this is the phenomenon of **Bose-Einstein condensation.** The threshold temperature T_C satisfies the condition:

$$N = \sum_{i>0} g_i \frac{1}{e^{\varepsilon_i/k_B T_C} - 1}$$

The index i is replaced by the continuous momentum **p** of the atoms and the sum by an integral over p. The number of states with momentum comprised between p and p+dp is equal to the phase-space volume $4\pi p^2 V dp$ divided by the volume of an elementary cell h^3. Hence:

$$\sum_i g_i \quad \rightarrow \quad \frac{V}{h^3} \int 4\pi p^2 \, dp \quad ; \quad \varepsilon_i \rightarrow \frac{p^2}{2m}$$

To quantize the phase space in units of h^3 was an intuitive step for Einstein (note that the quantum of action has the dimension of a momentum x a distance). The justification of this quantization would become clear when de Broglie will introduce the concept of matter waves (lecture 5).

The relation between the gas density N/V and the threshold temperature T_c was obtained by solving the implicit equation:

$$N = \frac{V}{h^3} \int_0^\infty \frac{4\pi p^2 dp}{\exp(p^2/2mk_B T_C) - 1}$$

After a few mathematical steps, Einstein obtained:

$$N/V = 2.61 \times \left[\frac{mk_B T_c}{2\pi\hbar^2} \right]^{3/2}$$

The Bose Einstein condensation, predicted in 1924 by Einstein, had to wait for 71 years to be observed in 1995 in a gas of ultracold Rubidium atoms. In today's Bose Einstein Condensates, N is typically 10^5 to 10^6 and V of the order of a few μm^3. The threshold temperature is in the range of 10^{-7} K.

First Bose-Einstein Condensate experiment (Wieman and Cornell, 1995)

$\dfrac{N_0}{N}$

$0.5T_c$ T_c
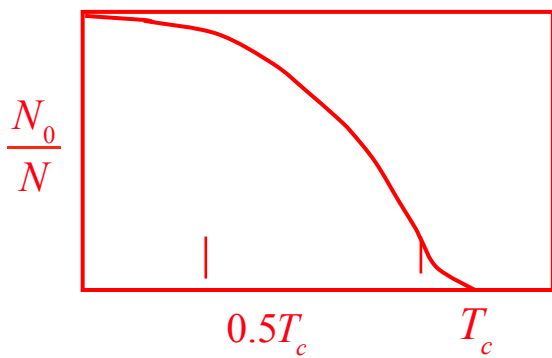
Fraction of condensed atoms vs temperature (theory)

$T > T_c$ $T = T_c$ $T < T_c$
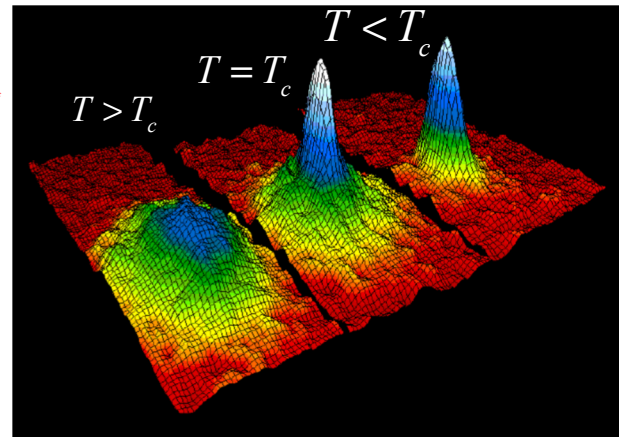
See in later lecture

Fermi-Dirac statistics and Fermions

In 1925, one year after the BEC paper, W.Pauli postulated that electrons obeyed to an exclusion principle which forbids more than one particle to occupy a given quantum state. This principle was generalized a few years later by Dirac and Fermi to the family of particles called Fermions. Instead of having -like bosons -a tendency to accumulate in the same state, fermions must be alone in a given quantum state. We will come back to the difference between bosons and fermions later. It is interesting to note that the caracteristics of Bosons and Fermions were guessed even before the wave nature of matter particles was firmly established. The distribution of fermions among energy states is obtained by a statistical argument similar to the one developed for bosons. Let us call N_i the number of particles with energy ε_i and g_i the degeneracy of this energy level. Counting the number of configurations of identical fermions obeying the exclusion principle we get (see demonstration on next slide):

$$W_i = \frac{g_i!}{N_i!(g_i - N_i)!} \qquad g_i \geq N_i$$

Calculating the Fermion distribution proceeds as for bosons, with an important sign change at the end:

$$S/k_B = Log\left(\prod_i W_i\right) = \sum_i \left(g_i Log\, g_i - N_i Log N_i - (g_i - N_i)Log(g_i - N_i)\right)$$

Minimize then the free energy with the constraint that N is conserved (introducing as for Bosons the chemical potential μ as a Lagrange multiplier):

$$\delta E_i - T\delta S_i = \left[\varepsilon_i - \mu + k_B T Log\left(\frac{N_i}{g_i - N_i}\right)\right]\delta N_i = 0 \implies \frac{N_i}{g_i - N_i} = e^{(\mu - \varepsilon_i)/k_B T} \to N_i = g_i \frac{1}{e^{(\varepsilon_i - \mu)/k_B T} + 1}$$

Number of ways to chose N boxes out of an ensemble of g boxes, placing no more than one particle per box
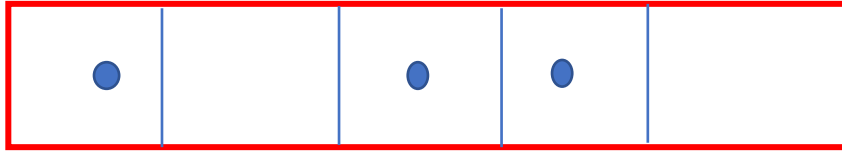
According to Fermi-Dirac statistics, the number of states available must be larger or equal to the number of particles for each energy state (in this figure, g=5 and N=3). Counting the number of configurations amounts to counting the number of ways to pick N boxes out of g. There are g ways to pick the first box, g-1 ways to pick the second,etc g-N+1 to pick the Nth one. This gives g!/(g-N)! choices. This procedure counts many times the same configuration since the order in which each box is chosen does not matter. We should thus divide by the number of permutations among the N chosen boxes and finally: W = g!/N!(g-N)!

In the example of the figure, W= 10

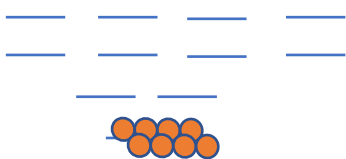## Ideal Boson and Fermion gases at T=0K (non interacting atoms)

Bosons

$$\frac{N_i}{g_i} = \frac{1}{e^{(\varepsilon_i - \mu)/k_B T} - 1} \quad \mu(T) < 0$$

$$N_0 \xrightarrow[T \to 0]{} N$$

$$N_{i>0} \xrightarrow[T \to 0]{} 0$$
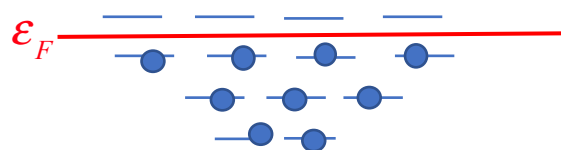
Ground state occupied by atoms. All states above are empty

Fermions

$$\frac{N_i}{g_i} = \frac{1}{e^{(\varepsilon_i - \mu)/k_B T} + 1} \quad \mu(T) > 0$$

$$\frac{N_i}{g_i} \xrightarrow[T \to 0]{} 1 \; for \; \varepsilon_i \leq \mu(0)$$

$$\frac{N_i}{g_i} \xrightarrow[T \to 0]{} 0 \; for \; \varepsilon_i > \mu(0)$$

All states occupied by one particle up to Fermi energy ε_F. All states above ε_F empty $\varepsilon_F = \mu(0)$

ε_F

High T limit of Bose-Einstein and Fermi-Dirac statistics

For $k_B T \gg |\mu - \varepsilon_i|$, the Bose-Einstein and Fermi Dirac distributions both tend toward the Boltzmann one:

$$N_i = \frac{g_i}{e^{(\varepsilon_i - \mu)/k_B T} \mp 1} = g_i \frac{e^{(\mu - \varepsilon_i)/k_B T}}{1 \mp e^{(\mu - \varepsilon_i)/k_B T}} \xrightarrow{k_B T \gg |\mu - \varepsilon_i|} \qquad N_i = g_i e^{(\mu - \varepsilon_i)/k_B T}$$

The indistinguishability of atoms is thus a quantum effect which becomes less and less pronounced when temperature increases. For a given system, there is a temperature range above which the statistical quantum effects are negligible and the classical numbering of particles becomes legitimate. This feature has become clear when the concept of de Broglie wavelength for material particles was introduced in the year following the Bose-Einstein calculation (see next lecture).

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Concluding remarks

During the first quarter of the 20th century (1900-1925) quanta have invaded physics, involving the description of light, of atomic oscillations in solids and of energy atomic spectra. With the concept of quanta has come the realization that the "indiscernability "of particles – photons or atoms - has very deep physical consequences. The notion of stimulated emission of light announced the laser and the prediction of Bose Einstein condensation pointed to the gregarious tendency of Bosons to gather in the same quantum states. On the other hand, the discovery of the exclusion principle for electrons started to shed light on important fermionic properties of matter.

In this early age of quanta, it became progressively clear that the discreteness of quantum phenomena manifests itself mostly at low temperatures.

Contrary to Relativity which was born from a simple principle, the quantum ideas emerged rather confusely from disparate observations of phenomena unexplained by classical physics.

The veil on quanta will be lifted in 1924-25 by the de Broglie hypothesis of matter waves, shortly followed by the discovery by Heisenberg and Schrödinger of two consistent and equivalent mathematical formalisms explaining under a unified picture all previous disparate observations and predicting new effects. We will start to describe the modern quantum theory in Lecture 5.

During this early period of development of the quanta, Einstein played an essential role. This is remarkable since he was during part of this time (from 1905 to 1916) heavily occupied by the development of the general theory of relativity.