Lesson 9- Quantum Statistics

Quantum Statistics

So far, we have focused on the study of classical identical particles. However, as we have discussed, at low temperatures the fact that energy levels are discrete becomes important for the description of the macroscopic behavior of the system of particles.

According to the spin-statistics theorem we distinguish between two types of particles: bosons and fermions.

Bosons are elementary particles characterized by its integer value of spin. This means that the wave function of a group of N identical bosons with coordinates $\{x_1, \ldots, x_N\}$, $\psi(x_1, \ldots, x_N)$, is symmetric so that it remains the same if we exchange the coordinates of two of the particles $\psi(x_1, x_2 \ldots, x_N) = \psi(x_2, x_1, \ldots, x_N)$ (i.e. they are symmetric under permutation exchange).

As we will see later, bosons obey Bose–Einstein statistics, which means any number of them can occupy the same quantum state, i.e. can have the same energy.

Bosons play a crucial role in the fundamental forces of nature. There are many types of bosons, which are categorized based on the forces they mediate: photons (electromagnetic force), gluons (strong nuclear force that bands quarks together to form protons and neutrons), …

However, there are other particle-like objects in physics that also obey Bose-Einstein statistics. For instance, phonons are also considered boson-like particles which represent quantized vibrational modes of a crystal lattice in a solid, and they play a crucial role in understanding the thermal and mechanical properties of solids.

Quantum Statistics

Fermions, are a class of elementary particles that are characterized by their half-integer values of spin (intrinsic angular momentum). In contrast to bosons, the wave function of a group of N identical bosons with states $\{x_1, \ldots, x_N\}$, $\psi(x_1, \ldots, x_N)$, is anti-symmetric so that it changes signs if we exchange the states of two of the particles $\psi(x_1, x_2 \ldots, x_N) = -\psi(x_2, x_1, \ldots, x_N)$
Note that this implies that the amplitude of a wave function in which $x_1 = x_2$ has to be equal to zero to satisfy the antisymmetry condition
$\psi(x_1, x_1 \ldots, x_N) = -\psi(x_1, x_1, \ldots, x_N)$

This is the so called Pauli exclusion principle, which states that two fermions cannot occupy the same quantum state simultaneously. This principle is a fundamental aspect of the behavior of matter and is responsible for the stability and structure of atoms. As we will see later, fermions obey Fermi-Dirac statistics, which means that each quantum state ca be occupied by at most one particle.

In reality, fermions are not only restricted to half-integer spin ($s = \pm 1/2$), this is just the case for elementary particles (quarks, electrons, muons, tauons). There are also composite fermions (containing an odd number of fermions) such as protons or neutrons that are fermions (i.e. obey Fermi-Dirac statistics) and have half-odd spin (for instance, $s = 3/2$). Composite particles with an even number of elementary fermions have integer spin and are bosons.

Spin-statistics theorem

The theorem states that:

1. The wave function of a system of identical particles with integer spin has the same value when the positions of any pair of particles are swapped. Particles with wave functions symmetric under exchange are called bosons.

2. The wave function of a system of identical particles with half-integer spin changes sign when two particles are swapped. Particles with wave functions antisymmetric under exchange are called fermions.

In other words, the spin–statistics theorem states that integer-spin particles are bosons, while half-integer–spin particles are fermions.

Bose-Einstein statistics - non-interacting bosons

Let's assume we have a system of non-interacting bosons with $M+1$ non-degenerate energy levels $\epsilon_0 < \epsilon_1 < \ldots < \epsilon_M$. We have a reservoir of bosons with chemical potential μ that can occupy these energy levels.

Because these bosons are non-interacting, the occupation of one of the states is independent from the occupation of the other states, so that $\mathscr{Z} = \Pi_{i=0}^{M} z_i$, where z_i is the partition function of each level i.
Since in each level can have any number of particles $n_i = 0,1,\ldots,\infty$

$$z_i = \sum_{n_i=0}^{\infty} e^{-\beta(\epsilon_i-\mu)n_i} = \frac{1}{1-e^{-\beta(\epsilon_i-\mu)}}$$ which converges as long as $e^{-\beta(\epsilon_i-\mu)} < 1$ or $\mu < \epsilon_i$.

Note that because this has to be true for all ϵ_i, then $\mu < \epsilon_0$.

In equilibrium, the occupation number (i.e. expected number of particles) of each energy level is

$$\langle n_i \rangle = -\frac{1}{\beta}\frac{\partial \log \mathscr{Z}}{\partial \epsilon_i} = \frac{e^{-\beta(\epsilon_i-\mu)}}{1-e^{-\beta(\epsilon_i-\mu)}} = \frac{1}{e^{\beta(\epsilon_i-\mu)}-1}$$

which is known as Bose-Einstein distribution and describes the filling of energy level i by non-interacting bosons.

Bose-Einstein statistics - non-interacting bosons

In equilibrium, the occupation number (i.e. expected number of particles) of each energy level is

$$\langle n_i \rangle = -\frac{1}{\beta}\frac{\partial \log \mathcal{Z}}{\partial \epsilon_i} = \frac{e^{-\beta(\epsilon_i - \mu)}}{1 - e^{-\beta(\epsilon_i - \mu)}} = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1}$$

which is known as Bose-Einstein statistics.

For states with low occupancies, where $\langle n_i \rangle \ll 1$, $\langle n_i \rangle \approx e^{-\beta(\epsilon_i - \mu)}$, and the boson populations correspond to what we would guess naively from the Boltzmann distribution.

The condition for low occupancies is $\epsilon_i - \mu \gg k_B T$, which usually arises at high temperatures (where the particles are distributed among a larger number of states).

Fermi-Dirac statistics - non-interacting fermions

Let's assume we have a system of non-interacting fermions with $M+1$ non-degenerate energy levels $\epsilon_0 < \epsilon_1 < \ldots < \epsilon_M$. We have a reservoir of fermions with chemical potential μ that can occupy these energy levels.

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$z_i = 1 + e^{-\beta(\epsilon_i - \mu)}$, since in each level $N_i = 0,1$

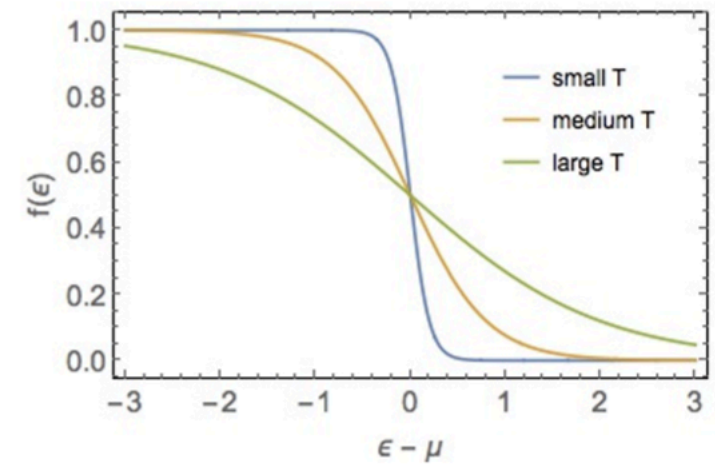
In equilibrium, the occupation number (i.e. expected number of particles) of each energy level is

$$\langle n_i \rangle = -\frac{1}{\beta}\frac{\partial \log \mathcal{Z}}{\partial \epsilon_i} = \frac{e^{-\beta(\epsilon_i - \mu)}}{1 + e^{-\beta(\epsilon_i - \mu)}} = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1}$$

which is known as Fermi-Dirac statistics

Fermi-Dirac statistics

$$\langle n_i \rangle = -\frac{1}{\beta}\frac{\partial \log \mathcal{Z}}{\partial \epsilon_i} = \frac{e^{-\beta(\epsilon_i-\mu)}}{1+e^{-\beta(\epsilon_i-\mu)}} = \frac{1}{e^{\beta(\epsilon_i-\mu)}+1} = f(\epsilon_i)$$



$f(\epsilon_i)$ is the Fermi-Dirac distribution that tells us what is the probability of finding a particle in energy level i.

Note that at high temperature, we expect that all energy levels are occupied and in particular those with high energies, therefore we expect that for those levels $e^{\beta(\epsilon_i-\mu)} \gg 1$, so that $f(\epsilon_i) \approx e^{-\beta(\epsilon_i-\mu)}$ as for classical particles.

Note that in this case, μ can be larger or smaller than any ϵ_i.

In fact in the limit $T \to 0, f(\epsilon)$ becomes a step function

if $\epsilon_i > \mu$: $\lim_{T\to 0} \langle n_i \rangle \to 0$

if $\epsilon_i < \mu$: $\lim_{T\to 0} \langle n_i \rangle \to 1$

if $\epsilon_i = \mu$: $\lim_{T\to 0} \langle n_i \rangle \to 1/2$

For finite temperatures, the behaviour is similar and only states with $\epsilon_i - \mu \approx k_B T$ are partially filled.

Note that, the value of μ sets a boundary between filled an unfilled (holes in the materials 'lingo') states, typically $\mu(T=0) = \epsilon_F$ is called the Fermi energy (but sometimes people use a temperature dependent Fermi energy and use $\epsilon_F = \mu(T)$).

Bose-Einstein and Fermi-Dirac statistics - degeneration

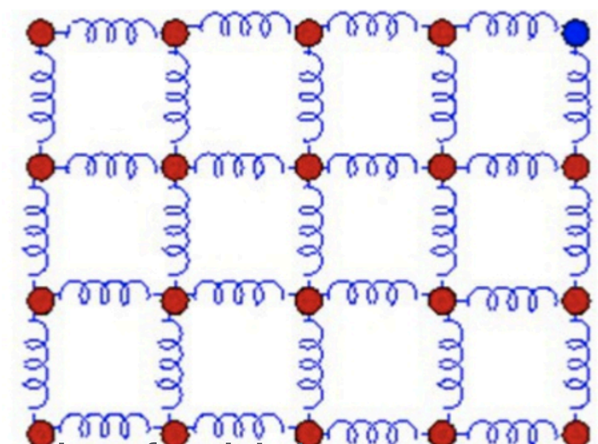
Note that if energy levels are degenerate, so that energy level ϵ_i has degeneration g_i, then the occupation numbers of each level are

$$\langle n_i \rangle_{\mathrm{BE}} = \frac{g_i}{e^{\beta(\epsilon_i - \mu)} - 1}$$

$$\langle n_i \rangle_{\mathrm{FD}} = \frac{g_i}{e^{\beta(\epsilon_i - \mu)} + 1}$$

Bose-Einstein statistics - non-interacting bosons
Application: the Debye model for vibrations in solids

A gas of non-interacting bosons provides a very accurate description for two types of bosons: photons and phonons. We will look in detail at the case of phonons and specifically to the Debye models of atom vibrations in solids to compute the heat capacity at low temperatures.



Debye model of solids : a **harmonic solid,** that is a (isotropic) lattice of nuclei connected by covalent bonds which act as springs.

The quanta of sound-wave excitations in solids are called phonons. The solid is made up of Natoms, each of which can move in 3 directions, so there are $3N$ springs (up to boundary conditions, which will not matter for N large). There will therefore be $3N$ normal modes of vibration.

Classical vibrations:

If $u(\vec{x}, t)$ is the displacement from equilibrium of the atom at position $\vec{x}$ at time t, it satisfies the wave equation $\partial_t^2 \vec{u}(\vec{x}, t) = c_s^2 \overrightarrow{\nabla}^2 \vec{u}(\vec{x}, t)$ (c_s: velocity of sound in the solid).

The solutions to these equations can be expressed in terms of the normal modes: $\vec{u}(\vec{x}, t) = \vec{u}_n \cos(\overrightarrow{k_n} \cdot \vec{x})\ \cos(\omega_n t)$

In a 3D volume of side L, $\vec{k}_n = \dfrac{\pi}{L}(n_x, n_y, n_z)$, $\omega_n = c_s |\vec{k}_n|$, and $\vec{u}_n$ carries the information about the polarization (longitudinal or 2 transversal).

Bose-Einstein statistics - non-interacting bosons
Applications - the Debye model for vibrations in solids

In quantum mechanics, the energy associated to the vibration of a harmonic oscillator with frequency ω_n is:

$$E_{\vec{n}} = \hbar\omega_n \left(m + \frac{1}{2} \right)$$

$\vec{n}$ is the mode (plane of vibrating atoms)
m is the level of excitation of such mode

The labels $\vec{n}$ for the normal modes are the states labeled i in the general discussion of Bose systems. The excitations m correspond to m phonons. The classical amplitude $\vec{u}_{\vec{n}}$ is proportional to the number of phonons in that mode (and therefore to the total energy associated to that mode), with $\vec{n}$ determining the wave-vector $\vec{k}$.

Ground state: no excitations, $E_0 = \sum_{\vec{n}} \frac{\hbar\omega_n}{2}$, we will set it to zero for convenience.

Our interest is to compute $\log \mathscr{Z} = \sum_i \log \frac{1}{1 - e^{-\beta(\epsilon_i - \mu)}}$

In this case:
$\mu = 0$ because phonons can be created and destructed with no cost in energy
$\epsilon_i = \epsilon_{\vec{n}} = \hbar\omega_n$ - energy associated to each phonon

$$\rightarrow \log \mathscr{Z} = 3 \sum_{\vec{n}} \log \frac{1}{1 - e^{-\beta\epsilon_{\vec{n}}}}$$ (factor 3 = 3 possible polarizations)

Bose-Einstein statistics - non-interacting bosons
Applications - the Debye model for vibrations in solids

For a large number N of atoms, the modes will be closely spaced and effectively continuous. If the integers $\vec{n}$ are very large, we can approximate the sum

$$3\sum_{\vec{n}} F(\vec{n}) \approx 3\int d\vec{n}\, F(\vec{n}) = 3\int_0^{n_x^{\max}} dn_x \int_0^{n_y^{\max}} dn_y \int_0^{n_z^{\max}} dn_z\, F(\vec{n}) = \frac{3}{8}\int_0^{n_D} dn\, 4\pi\, n^2 F(\vec{n})$$

where n_D is the maximum mode.

To get this result we use that $\int_0^{n_x^{\max}} dn_x = \frac{1}{2}\int_{-n_x^{\max}}^{n_x^{\max}} dn_x$ and then change to spherical coordinates and integrate out the angular degrees of freedom
$\int d\vec{n} = \int \sin\phi\, d\phi \int d\theta \int n^2 dn = 4\pi \int n^2 dn$ with $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$.

In the Debye model: we consider the dispersion relationship $\omega_n = c_s\,|\vec{k}_n| = c_s \frac{\pi}{L} n$

$$\frac{3}{8}\int_0^{n_D} dn\, 4\pi\, n^2 F(\vec{n}) = \frac{3}{8}\int_0^{\omega_D} d\omega 4\pi \frac{L^3}{\pi^3 c_s^3}\omega^2 F(\omega) = \int_0^{\omega_D} d\omega\, g(\omega) F(\omega)$$

with $g(\omega) = \dfrac{3V}{2\pi^2 c_s^3}\omega^2$ where ω_D is the mode of maximum frequency.

Bose-Einstein statistics - non-interacting bosons
Applications - the Debye model for vibrations in solids

From here knowing that the total umber of total modes is $3N$ we can get that:

$3N = \sum_{\text{phonons}+\text{polarizations}} 1 = 3\sum_{\vec{n}} 1$ so that $F(\vec{n}) = 1$ in the 'general' expression $\sum_{\vec{n}} F(\vec{n})$, using our expression for the integral over ω:

$$3N = \int_0^{\omega_D} d\omega\, g(\omega)\cdot 1 = \frac{V}{2\pi^2 c_s^3}\omega_D^3 \quad \text{so that} \quad g(\omega) = \frac{3V}{2\pi^2 c_s^3}\omega^2 = \frac{9N}{\omega_D^3}\omega^2$$

Heat capacity: To get the heat capacity, we need to compute the energy

$$\langle E\rangle = -\frac{\partial \log \mathcal{Z}}{\partial \beta} = \int_0^{\omega_D} d\omega\, g(\omega)\frac{\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} = \frac{9N\hbar}{\omega_D^3}\int_0^{\omega_D} d\omega\,\omega^3\frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

We cannot perform this integral, in general, but we can get the limits for high and low temperature.

For $T \gg \dfrac{\hbar\omega_D}{k_B}$, $\langle E\rangle \approx \dfrac{9N\hbar}{\omega_D^3}\displaystyle\int_0^{\omega_D} d\omega\,\omega^3\frac{1}{\beta\hbar\omega} = 3Nk_BT$

as expected from the equipartition theorem and $C_v = \left.\dfrac{\partial\langle E\rangle}{\partial T}\right|_V = 3Nk_B$

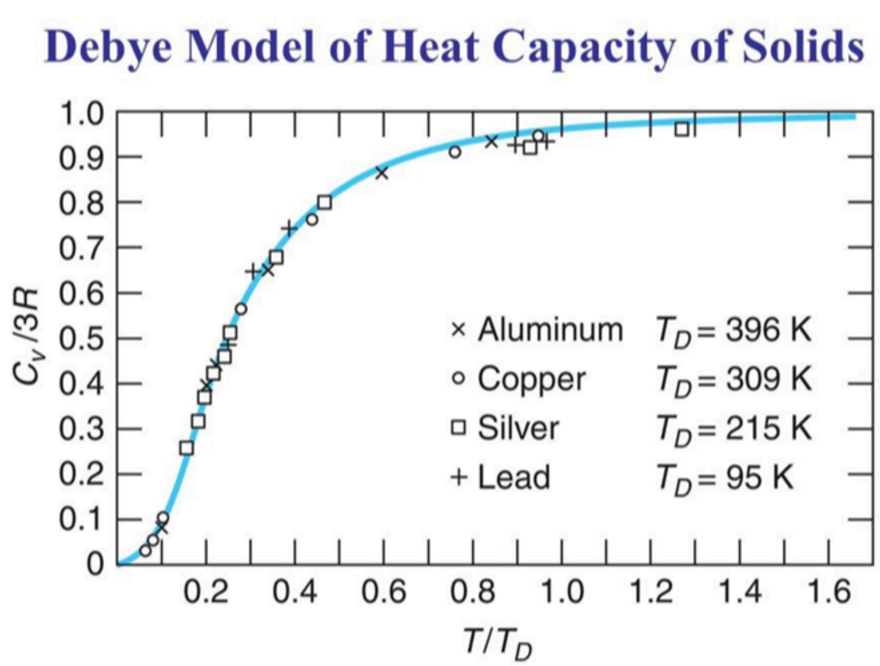
Bose-Einstein statistics - non-interacting bosons
Applications - the Debye model for vibrations in solids

For $T \to 0$, $\langle E \rangle \approx \dfrac{9N\hbar}{\omega_D^3} \displaystyle\int_0^{\omega_D} d\omega\, \omega^3\, e^{-\beta\hbar\omega} \propto \left(\dfrac{T}{T_D}\right)^4$

with $T_D = \dfrac{\hbar\omega_D}{k_B}$, the Debye temperature

So that at low temperatures $C_v \propto T^3$ (Which is the Debye expected behaviour of the heat capacity of solids at low temperatures)

This theory predicts remarkably well the observed behaviour of solids at low and high temperatures with a single parameter T_D (the temperature above which all phonons can be excited).



Bose-Einstein statistics - non-interacting bosons Applications

The idea of converting the sum over ‘states’ for an integral of the form: $\sum_{\epsilon_s} F(\epsilon_s) \approx \int d\epsilon\, g(\epsilon)F(\epsilon)$ is a good approximation when the number of ‘particles’ is large and the energy levels are close, where $g(\epsilon)$ is the density of sates with energy ϵ. Note that typically in this density of states we also have to include the number of possible states of a particle compatible with a certain energy (for instance, for spin 0 systems such as phonons there is only one state per energy or normal mode, for electrons (s=1/2) there are two possibilities as we will see later, in general, the number of states with same energy for particles with spin s is 2s+1).

Phonons: We have seen that $g(\omega) = \frac{9N}{\omega_D^3}\omega^2$ which given that $\epsilon_n = \hbar\omega_n$ and that $g(\omega)d\omega = g(\epsilon)\, d\epsilon$ yields that: $g(\epsilon) = \frac{9N}{\left(\hbar\omega_D\right)^3}\epsilon^2$.

Photons: For free photons (s=1) in a 3D box of volume V, we would obtain that $g(\epsilon) = \frac{3V\epsilon^2}{\left(\hbar\, c\right)^3 \pi^2}$.

Non-relativistic particles: For free non-relativistic particles with spin s and mass m in a box of volume V, we have that $g(\epsilon) = \frac{(2s+1)\, Vm^{3/2}\sqrt{\epsilon}}{\sqrt{2}\hbar^3\pi^2}$.

Fermi-Dirac statistics - non-interacting fermions
Applications: Free Electron gas

The possible single-particle states of the electrons in a free electron gas are the same as for a boson in a box. The allowed wave vectors are $\vec{k}_n = \frac{\pi}{L}(n_x, n_y, n_z)$

In the non-relativistic limit energies are determined by

$\epsilon_n = \frac{\hbar^2 \vec{k}^2}{2m_e}$ so that $n = \frac{L}{\pi}\sqrt{\frac{2m_e}{\hbar^2}}\sqrt{\epsilon}$ $\qquad dn = \frac{L}{2\pi}\sqrt{\frac{2m_e}{\hbar^2}}\frac{d\epsilon}{\sqrt{\epsilon}}$

For electrons ($s = 1/2$), so there are two spin states ($\uparrow$, $\downarrow$) per energy level, to compute $g(\epsilon)$ we do:

$$2\sum_{\vec{n}} \to 2 \times \frac{1}{8}\int dn\, 4\pi\, n^2 = \frac{V}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\int \sqrt{\epsilon}\, d\epsilon$$

so that $g(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\sqrt{\epsilon}.$

For $T \to 0$, the Fermi function becomes a step function $\langle n_\epsilon \rangle = 0{,}1$. The Fermi energy is the chemical potential al $T = 0$, so the number of states occupied at $T = 0$ is

$N = \int_0^\infty \langle n_\epsilon \rangle\, g(\epsilon)\, d\epsilon \to \frac{V}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\frac{2}{3}\epsilon_F^{3/2}$ (since levels are only occupied up to ϵ_F, that is $\langle n_\epsilon \rangle = 1$ if $\epsilon < \epsilon_F$ and 0 otherwise.)

Fermi-Dirac statistics - non-interacting fermions
Applications: Free Electron gas

So that $\epsilon_F = \dfrac{\hbar^2}{2m_e}\left(3\pi^3\dfrac{N}{V}\right)^{2/3}$ and we can express the density of states as a function of ϵ_F, $g(\epsilon) = \dfrac{3N}{2\epsilon_F^{3/2}}\sqrt{\epsilon}$.

We can then define the **Fermi temperature** $T_F = \epsilon_F / k_B$ above which energy states above $\epsilon \gtrsim \epsilon_F$ are populated. Typically $T \ll T_F$ so the probability of occupying these states is $\ll 1$.

The energy of the Fermi gas at zero temperature is then

$$E_0 = \int_0^{\epsilon_F} \epsilon\, g(\epsilon\,) d\epsilon = \frac{3N}{5\epsilon_F^{3/2}}\epsilon_F^{5/2} = \frac{3N}{5}\epsilon_F$$

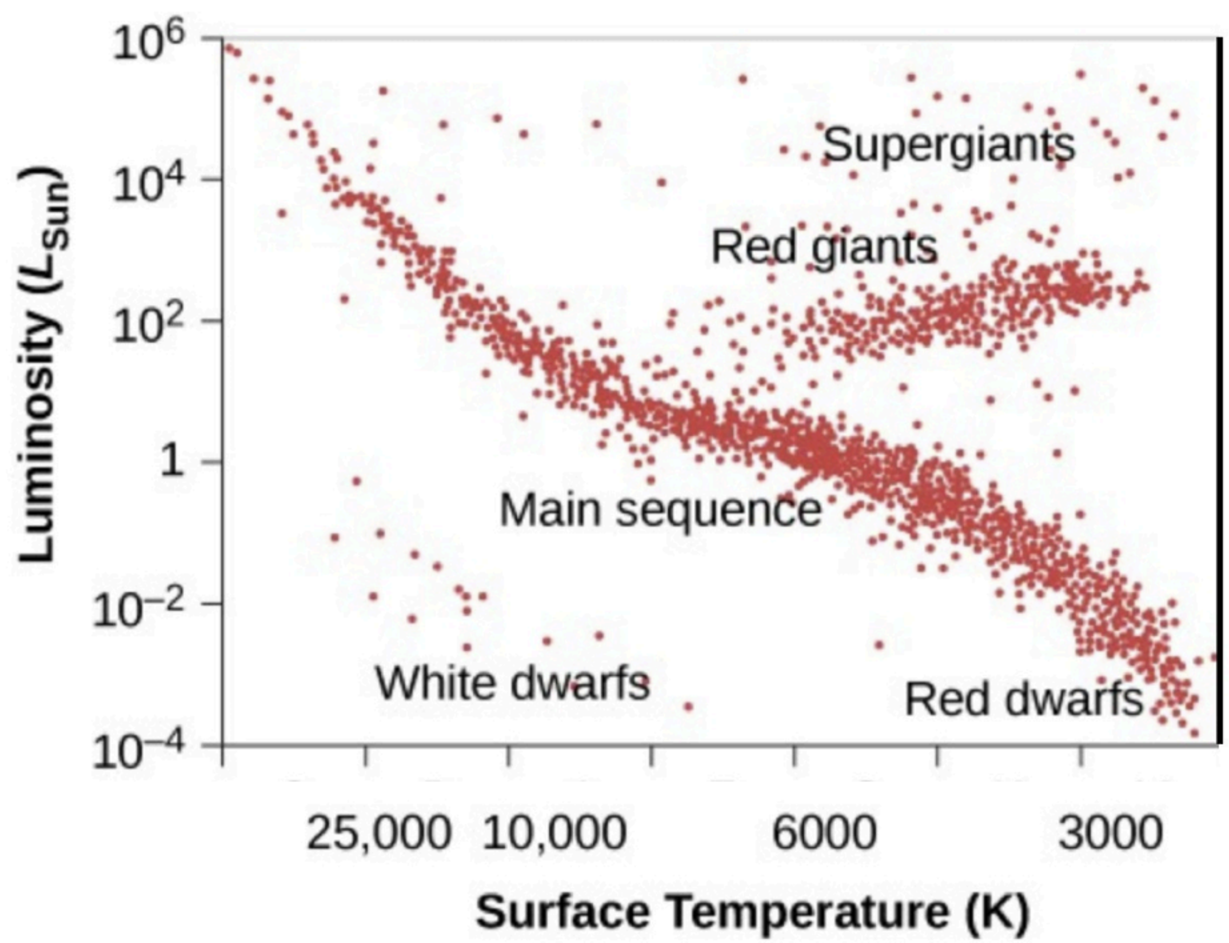
<u>Degeneracy pressure:</u> ideal gases and boson gases have $\lim\limits_{T\to 0} P \to 0$, however this is not the case for Fermi gases, for which as we approach the zero temperature limit, the pressure does not go to zero (i.e. there is a temperature independent term in the pressure).

Specifically since $P = -\left(\dfrac{\partial E}{\partial V}\right)_T = -\dfrac{3N}{5}\dfrac{\partial \epsilon_F}{\partial V} = \dfrac{3N}{5}\dfrac{2\epsilon_F}{3V} = \dfrac{2E_0}{3V}$

Fermi-Dirac statistics - non-interacting fermions
Applications: Stars

$$P = -\left(\frac{\partial E}{\partial V}\right)_T = -\frac{3N}{5}\frac{\partial \epsilon_F}{\partial V} = \frac{3N}{5}\frac{2\epsilon_F}{3V} = \frac{2E_0}{3V}$$

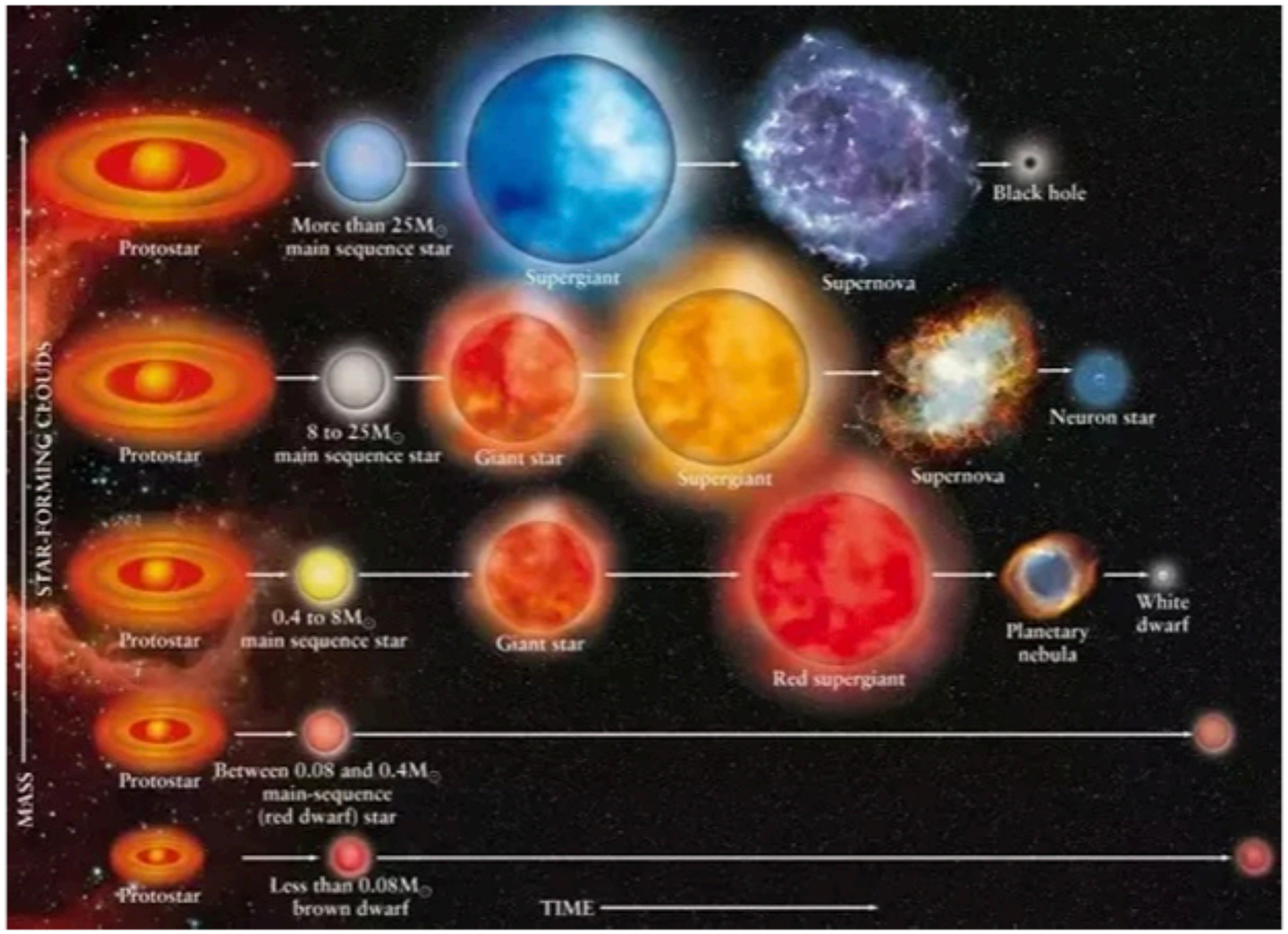
Degeneracy pressure is essential to understand the existence of some types of stars such as neutron stars and white dwarfs.



Hertzsprung-Russell star diagram: Luminosity (power emitted by photons in the star) vs Surface Temperature (Black Body Radiation)

Fermi-Dirac statistics - non-interacting fermions
Applications: Stars

Evolution of stars according to their mass:



White dwarfs are ‘hot stars’ that have no nuclear fusion activity (stars in the main sequence and above, do) and are composed of ions and free-electrons well below the degeneracy limit ($T \ll T_F$). The mass of their core is below the Chandrasekhar limit $1.4M_\odot$ ($\odot$ = sun), the force of gravity is compensated by degeneracy pressure. The existence of these stars can only be understood using statistical mechanics.