Structure of matter and thermodynamics

1. | Structure of the matter

Kinetic theory of gases

Definition 1. A gas is constituted by large amount of particles moving at higher velocities and satisfying Newton's laws. Hence, we may consider the following assumptions:

- We can underestimate the gravity acting on the particles.
- The collisions between particles and between a particle and a wall of the container (perfectly rigid and with infinite mass) are completely elastic.
- The particles are point-particles.
- There is no interaction between particles (a part from the momentum of a collision).
- There is no preferred position and direction for the particles.

Proposition 2 (Molecular pressure). Consider a container of volume V that contains N molecules, each of mass m, of a gas. Then, the pressure P of the gas is:

$$P = \frac{N}{V} m \langle {v_x}^2 \rangle$$

where $\langle {v_x}^2 \rangle$ is the mean of the squares of the x-components of the velocities of all particles.

Proposition 3 (Molecular kinetic energy). Consider a gas at a temperature T. The average kinetic energy of a particle associated with x-axis movement of it is:

$$\langle K_x \rangle = \frac{1}{2} k_B T$$

where k_B is the Boltzmann constant. Since, by one of the initial hypothesis, $\langle {v_x}^2 \rangle = \langle {v_y}^2 \rangle = \langle {v_z}^2 \rangle$, then $\langle v^2 \rangle = 3\langle {v_x}^2 \rangle$ and therefore the mean kinetic energy $\langle K \rangle$ of a molecule is:

$$\langle K \rangle = \frac{3}{2} k_B T$$

Proposition 4 (Molecular velocities). Consider a gas of molar mass M constituted by molecules of mass m at a temperature T. Then, the *mean-square speed* of the particles is:

$$\langle v^2 \rangle = \frac{3k_B T}{m} = \frac{3RT}{M}$$

The *root-mean-square speed* is defined as $v_{\text{rms}} = \sqrt{\langle v^2 \rangle}$

Proposition 5 (Boltzmann distribution). Consider a system at a temperature T in thermodynamic equilibrium. Then, the probability $P(E)$ to find a particle with energy E is proportional to *Boltzmann factor*. That is:

$$P(E) \propto \mathrm{e}^{-\frac{E}{k_B T}}$$

[1] In liquids and solids we have $C_p \approx C_V =: C$.

Proposition 6 (Maxwell-Boltzmann distribution). The number of molecules (from a total of N) of mass m in a gas moving at velocities between v and $v + \mathrm{d}v$ and at a temperature T is:

$$\mathrm{d}N = N f(v)\, \mathrm{d}v$$

where $f(v)$ is:

$$f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} v^2 \mathrm{e}^{-\frac{mv^2}{2k_B T}}$$

Proposition 7 (Distribution of molecular velocities). Consider a gas constituted of molecules of mass m moving at a velocity v at a temperature T. If $v_{\max}$, $\langle v \rangle$ and v_{rms} are the maximum speed, mean speed and root-mean-square speed respectively, then:

$$\frac{\mathrm{d}f(v)}{\mathrm{d}v} = 0 \implies v_{\max} = \sqrt{\frac{2k_B T}{m}}$$

$$\langle v \rangle = \int_0^\infty v f(v)\, \mathrm{d}v = \sqrt{\frac{8k_B T}{\pi m}}$$

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\int_0^\infty v^2 f(v)\, \mathrm{d}v} = \sqrt{\frac{3k_B T}{m}}$$

Specific heat and equipartition theorem

Definition 8. When we heat up a substance, we transfer energy to it resulting in an increase of its internal energy U. The amount of heat Q necessary to increase the temperature of a substance is proportional to the variation of the temperature and its mass m. That is:

$$Q = C\Delta T = cm\Delta T$$

Definition 9. *Heat capacity* C is defined as the amount of heat to be supplied to an object to increase its temperature by one degree.

Definition 10. *Specific heat* c is defined as the heat capacity per unit of mass:

$$c = \frac{C}{m}$$

where m is the mass of the object to heat.

Definition 11. *Molar heat capacity* c_{m} is defined as the heat capacity per unit of mole:

$$c_{\text{m}} = \frac{C}{n} = \frac{mc}{n} = \frac{M}{n}$$

where n is the number of moles of the object to heat, m its mass and M its molar mass.

Definition 12. The *adiabatic index* γ is defined as:

$$\gamma = \frac{C_P}{C_V}$$

where C_P is the heat capacity at constant pressure and C_V is the heat capacity at constant volume[1].

Definition 13 (Internal energy). The internal energy U of an ideal gas constituted of monoatomic particles is:

$$U = N\langle K_{\text{trans}}\rangle = \frac{3}{2}nRT$$

where N is the number of particles in the gas on it; n, the number of moles, and T, its the temperature.

Proposition 14 (Mayer's relation). Consider a substance constituted by n moles of an ideal gas. Then:

$$C_P = C_V + nR$$

Proposition 15 (Heat capacities in gases). Consider a substance constituted by n moles of an ideal gas. Since $C_V = \frac{\mathrm{d}U}{\mathrm{d}T}$, we have:

$$C_V = \frac{3}{2}nR \qquad C_P = \frac{5}{2}nR$$

Therefore, $\gamma = \frac{5}{3}$.

Theorem 16 (Equipartition theorem). Consider a substance at a temperature T in thermodynamic equilibrium. Then, the energy behave equally in each quadratic degree of freedom associated at each component of the kinetic or potential energy. Thus, there exists an average energy of $\frac{1}{2}k_BT$ per molecule or an average energy of $\frac{1}{2}RT$ per mole associated with each degree of freedom[2].

Corollary 17 (Equipartition theorem on diatomic molecules). Consider a diatomic molecule of mass m rotating around x and y axis. Then, its energy will be of the form:

$$E = \frac{1}{2}m\left({v_x}^2 + {v_y}^2 + {v_z}^2\right) + \frac{1}{2}I_x{\omega_x}^2 + \frac{1}{2}I_y{\omega_y}^2$$

Since we have 5 quadratic degrees of freedom, the total energy E will be $E = \frac{5}{2}k_BT$. If a gas in constituted by N diatomic molecules, then:

$$U = NE = \frac{5}{2}Nk_BT = \frac{5}{2}nN_Ak_BT = \frac{5}{2}nRT$$

where N_A is the Avogadro constant and n is the number of moles of the gas. Therefore, we will have $C_V = \frac{5}{2}nR$, $C_P = \frac{7}{2}nR$ and $\gamma = \frac{7}{5}$.

Corollary 18 (Dulong-Petit law). Consider a solid and suppose its atoms are connected with springs with effective constant k_{eff}. Then:

$$E = \frac{1}{2}m\left({v_x}^2 + {v_y}^2 + {v_z}^2\right) + \frac{1}{2}k_{\text{eff}}\left(x^2 + y^2 + z^2\right)$$

Since we have 6 quadratic degrees of freedom, the total energy E will be $E = \frac{6}{2}k_BT$. If a gas in constituted by N atoms, then:

$$U = NE = \frac{6}{2}Nk_BT = 3nN_Ak_BT = 3nRT$$

where n is the number of moles of the solid. Therefore, we will have $C = 3nR$.

Black-body radiation

Definition 19 (Thermal radiation). *Thermal radiation* is the electromagnetic radiation emitted by a body as a consequence of its temperature. All bodies emit this radiation and absorb the one emitted by its surroundings. In thermal equilibrium the emission and absorption are equal.

Proposition 20 (Black body). A *black body* is an object that absorbs all electromagnetic radiation incident on it.

Proposition 21 (Stefan-Boltzmann law). The energy radiated by a black body at a temperature T per unit of area and time (called *radiance*) is:

$$I = \sigma T^4$$

where σ is the Stefan-Boltzmann constant.

Proposition 22 (Wien's displacement law). The radiance does not distribute uniformly along all wavelengths (*spectral radiance* $I(\lambda)$). The maximum of this function is taken when

$$\lambda_{\max} =: \frac{b}{T}$$

where b is the *Wien's displacement constant* and T is the temperature of the body.

Proposition 23 (Rayleigh-Jeans law). *Rayleigh-Jeans law* is an approximation to the spectral radiance of electromagnetic radiation of a black body at a given temperature T as a function of the wavelength through classical arguments:

$$I(\lambda) = \frac{2\pi ck_BT}{\lambda^4}$$ [3]

[2] The equipartition theorem fails when temperatures are very high or very low due to the discretization of the energy postulated by quantum physics.

[3] The Rayleigh-Jeans law agrees with experimental results at large wavelengths (low frequencies) but strongly disagrees at short wavelengths (high frequencies). This inconsistency between observations and the predictions of classical physics is commonly known as the *ultraviolet catastrophe*.

[4] Note that from here we can deduced Stefan-Boltzmann and Wien's displacement laws as follows:

$$I = \int_0^\infty I(\lambda)\mathrm{d}\lambda = \frac{2\pi^5{k_B}^4}{15c^2h^3}T^4 =: \sigma T^4 \qquad \frac{\mathrm{d}I(\lambda)}{\mathrm{d}\lambda} = 0 \implies \lambda = \frac{hc}{4.965}\cdot\frac{1}{T} =: \frac{b}{T}$$

Proposition 24 (Planck's law). To solve the ultraviolet catastrophe, Planck deduced the following formula for the spectral radiance:

$$I(\lambda) = \frac{2\pi hc^2}{\lambda^5 \left(\mathrm{e}^{\frac{hc}{\lambda k_B T}} - 1\right)}^{4}$$

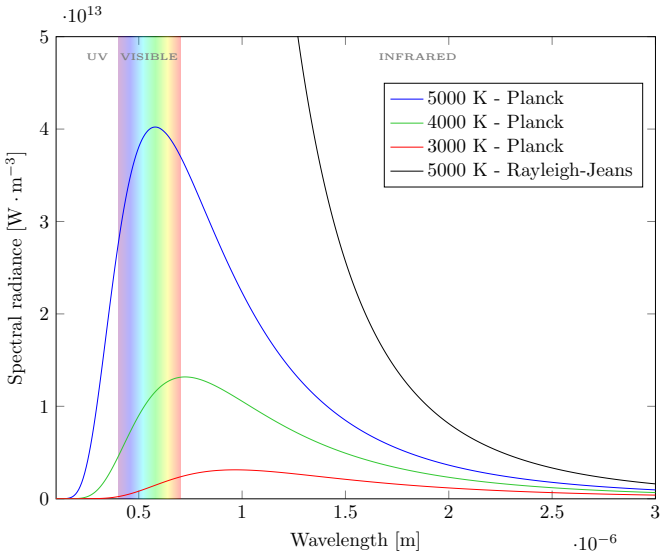


Figure 1: Graphical illustration of the ultraviolet catastrophe

Photoelectric effect

Definition 25 (Photoelectric effect). The *photoelectric effect* consists in the emission of electrons when electromagnetic radiation hits a material. Electrons emitted in this manner are called *photoelectrons*. Moreover we have the following properties:

- Photoelectric effect only occurs when the incident light is of frequency greater than or equal to a *threshold frequency* ν_0.
- Kinetic energy of the electrons increase proportionally to the frequency of the incident light.
- Increasing the intensity of the incident light does not increase the energy of photoelectrons, but the number of photoelectrons.

Proposition 26 (Stopping potential). Let ϕ be the energy required to remove an electron from the surface of a material. If we hit this surface with photons of frequency ν, then:

$$\frac{1}{2} m_e {v_{\max}}^2 = h\nu - \phi$$

Moreover, if we connect a potential difference V contrary to the movement of the electrons, then:

$$eV = h\nu - \phi$$

The electrons with lower energy than $\phi = h\nu_0$ won't have enough energy to remove an electron of the material.

Proposition 27 (Planck-Einstein relation). Relating the energy E of a photon of frequency ν and wavelength λ we have:

$$E = h\nu = \frac{hc}{\lambda}$$

Proposition 28 (De Broglie relation). The momentum p of photons of energy E and wavelength λ is:

$$p = \frac{E}{c} = \frac{h}{\lambda}$$

Light

Definition 29 (Light). We can think the light as a particle or as a wave. In particular, when it propagates, it behave like an electromagnetic wave and travels at a velocity

$$c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}}$$

where ε_0 is the vacuum permittivity and μ_0 vacuum permeability. Moreover the oscillating directions of the electric and magnetic field are perpendicular to each other and to the direction of propagation.

Definition 30 (Compton scattering). The *compton scattering* occurs when a photon of wavelength λ_1 collides with an electron and as a consequence the collision produces another photon of wavelength $\lambda_2 > \lambda_1$ (with less energy than the pervious one) deflected an angle θ from the original trajectory of the photon. Moreover, we have:

$$\lambda_2 - \lambda_1 = \frac{h}{m_e c}(1 - \cos\theta)^{5}$$

where m_e is the mass of the electron.

Matter wave

Proposition 31 (Bohr's complementary principle). There are experiments in which bodies behave like particles and other ones in which they behave like waves.

Definition 32 (Wavelenth of a particle). Consider a particle of mass m, kinetic energy K and momentum p. Then its wavelength is:

$$\lambda = \frac{h}{p} = \frac{hc}{2mc^2 K}$$

As a consequence, all elementary particles propagate like waves an exchange energy like particles.

Proposition 33 (Heisenberg's uncertainty principle). Let ΔY be the uncertainty of the magnitude Y of a particle. Then, for all particles we have:

$$\Delta x \Delta p \geq \frac{\hbar}{2} \qquad \Delta E \Delta t \geq \frac{\hbar}{2}$$

[5] This is deduced taking into account the conservation of energy and momentum.

Wave function

Definition 34 (Schrödinger equation). Given that we cannot know the position and velocity of a particle with unlimited precision, a particle of mass m is described with a *wave function* $\Psi(x,t)$[6] which is a solution to *Schrödinger equation*:

$$\frac{-\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+U(x,t)\Psi(x,t)=\mathrm{i}\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

where $U(x,t)$ is the potential energy that the particle is subject to. More generally, the Schrödinger equation in three dimensions is:

$$\frac{-\hbar^2}{2m}\Delta\Psi(\mathbf{r},t)+U(\mathbf{r},t)\Psi(\mathbf{r},t)=\mathrm{i}\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t}$$

where $\mathbf{r}=x\mathbf{i}+y\mathbf{j}+z\mathbf{k}$.

Proposition 35 (Properties of Schrödinger equation). Consider a particle whose wave function is $\Psi(x,t)$. Then:

- The probability to find the particle between x and $x+\mathrm{d}x$ is:
$$|\Psi(x,t)|^2\,\mathrm{d}x$$
- *Probability density*:
$$P(x,t)=|\Psi(x,t)|^2=\Psi(x,t)\Psi^*(x,t)$$
- *Normalization condition*:
$$\int_{-\infty}^{\infty}|\Psi(x,t)|^2\,\mathrm{d}x=1$$
- *Expectation value* of x:
$$\langle x\rangle=\int_{-\infty}^{\infty}x\Psi(x,t)\Psi^*(x,t)\,\mathrm{d}x=1$$

Here $\Psi^*(x,t)$ denotes the complex conjugate of $\Psi(x,t)$.

Definition 36 (Time-independent Schrödinger equation). Consider a stationary solution of the Schrödinger equation of the form:

$$\Psi(x,t)=\Phi(x)\mathrm{e}^{\frac{-\mathrm{i}Et}{\hbar}}$$

Then, if the potential energy $U(x,t)$ to which the particle is subject does not depend on time, that is $U(x,t)=U(x)$, we get the *time-independent Schrödinger equation*:

$$\frac{-\hbar^2}{2m}\frac{\mathrm{d}^2\Phi(x)}{\mathrm{d}x^2}+U(x)\Phi(x)=E\Phi(x)\tag{1}$$

Proposition 37 (Particle in a box-1D). Consider a particle of mass m confined in a 1-dimensional box of length L. We can think that it is subjected to a potential

$$U(x)=\begin{cases}\infty & \text{if } x\le 0\\ 0 & \text{if } 0<x<L\\ \infty & \text{if } x\ge L\end{cases}$$

Since the particle cannot leave the region $(0,L)$, we have that $\Phi(x)=0$ for $x\le 0$ and $x\ge L$. Therefore, by Eq. (1):

$$\frac{-\hbar^2}{2m}\frac{\mathrm{d}^2\Phi(x,t)}{\mathrm{d}x^2}=E\Phi(x)\qquad\text{for } 0\le x\le L$$

If we define $k^2=\frac{2mE}{\hbar^2}$, we have

$$\frac{\mathrm{d}^2\Phi(x,t)}{\mathrm{d}x^2}+k^2\Phi(x)=0\qquad\text{for } 0\le x\le L$$

which is the equation of a simple harmonic oscillator with solution $\Phi(x)=A\sin(kx)+B\cos(kx)$. Taking into account boundary conditions, we have that:

$$\Phi(x)=\Phi_n(x)=\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$$

where the number $n\in\mathbb{N}$ is called *quantum number*. In particular, $k=k_n=\frac{n\pi}{L}$ and therefore:

$$E_n=\frac{\hbar^2k_n^2}{2m}=n^2\left(\frac{h^2}{8mL^2}\right)=n^2E_1$$

And we observe that the energy is discretized in different levels.

Proposition 38 (Particle in a box-3D). If the particle of mass m is now confined to a three-dimensional box of edges a, b and c, we get:

$$\Phi_{n_xn_yn_z}(\mathbf{r})=\sqrt{\frac{8}{abc}}\sin\left(\frac{n_x\pi}{a}x\right)\sin\left(\frac{n_y\pi}{b}x\right)\sin\left(\frac{n_z\pi}{c}x\right)$$

where n_x, n_y and n_z are independent quantum numbers[7]. Moreover:

$$E_{n_xn_yn_z}={n_x}^2\left(\frac{h^2}{8ma^2}\right)+{n_y}^2\left(\frac{h^2}{8mb^2}\right)+{n_z}^2\left(\frac{h^2}{8mc^2}\right)$$

Definition 39. An energy level is *degenerate* if it corresponds to two or more different measurable states of a quantum system. For example, if a particle is contained in a cube, then:

$$E_{112}=E_{121}=E_{211}=6E_1$$

where E_1 is the ground-state energy of the particle contained in a 1-dimensional box.

Proposition 40 (Bohr's correspondence principle). In the limit of very large quantum numbers, the classical calculation and the quantum calculation must yield the same results.

[6] It is important that the function $\Psi(x,t)$ must be continuous.

[7] This is obtained from the fact that the solutions $\Phi n_xn_yn_z(\mathbf{r})$ of the Schrödinger equation in three dimensions are of the form: $\Phi n_xn_yn_z(\mathbf{r})=\Phi_{n_x}(x)\Phi_{n_y}(y)\Phi_{n_z}(z)$

Atoms

Definition 41 (Bohr model). The Bohr model[8] of an atom can be sum up with three postulates:

1. The electrons can move only in certain non-radiating circular orbits called stationary states.

2. If E_i and E_f are the initial and final energies of the atom, the frequency of the emitted radiation during a transition is given by

$$\nu = \frac{E_i - E_f}{h}$$

3. The angular momentum is quantized:

$$m_e v_n r_n = n\hbar \qquad n \in \mathbb{N}$$

where v_n and r_n are the speed of the electron and the radius of the orbit respectively in the state n.

Proposition 42 (Radii of Bohr orbits). The radius r_n of the n-th Bohr orbit of a monoelectronic atom with atomic number Z is:

$$r_n = n^2 \frac{\hbar^2}{m_e k Z e^2} =: n^2 \frac{a_0}{Z}$$

where k is the Coulomb constant. $a_0 = 0.0529$ nm is called *first Bohr radius*.

Proposition 43 (Energy levels). The total energy E_n of the n-th orbit of a monoelectronic atom with atomic number Z is is:

$$E_n = -Z^2 \frac{E_0}{n^2} \tag{2}$$

where $E_0 = \frac{m_e k^2 e^4}{2\hbar^2} = 13.6$ eV.

Proposition 44 (Rydberg-Ritz law). An electron that goes from an energy level n_i to a lower one $n_f < n_i$ emits a photon whose wavelength is:

$$\frac{1}{\lambda} = \frac{k^2 m_e e^4}{4\pi c \hbar^3} Z^2 \left(\frac{1}{{n_f}^2} - \frac{1}{{n_i}^2} \right) =: R_H Z^2 \left(\frac{1}{{n_f}^2} - \frac{1}{{n_i}^2} \right)$$

where R_H is the *Rydberg constant*.

Quantum theory of atoms

Definition 45 (Quantum numbers in spherical coordinates). Consider an atom with a single electron. Then, the potential energy for the electron depends only on the radial component and so we can make a change of variable to spherical coordinates (r, θ, ϕ)[9]. Hence, the independent quantum numbers n_x, n_y and n_z obtained from Cartesian coordinates will become the quantum numbers n (associated with r), ℓ (associated with θ) and m_ℓ[10] (associated with ϕ), which in this case, are not independent. More precisely we have:

- *Principal quantum number*: $n = 1, 2, 3, \ldots$

  The energy, as seen in Eq. (2), is given by:

$$E_n = -Z^2 \frac{13.6 \text{ eV}}{n^2}$$

- *Orbital quantum number*: $\ell = 0, 1, 2, \ldots, n-1$

  Moreover the magnitude $\|\mathbf{L}\|$ of the orbital angular momentum $\mathbf{L}$ is related to the orbital quantum number ℓ by:

$$\|\mathbf{L}\| = \sqrt{\ell(\ell+1)}\hbar$$

- *Magnetic quantum number*: $m_\ell = 0, \pm 1, \pm 2, \ldots, \pm \ell$

  Moreover the z component L_z of the orbital angular momentum $\mathbf{L}$ is given by the quantum condition

$$L_z = m_\ell \hbar$$

Therefore are n^2 degenerate states for the energy E_n. In terms of wave function we can write

$$\Psi_{n\ell m_\ell}(\mathbf{r}) = R_{n\ell}(\mathbf{r}) Y_{\ell m_\ell}(\mathbf{r})$$

Definition 46 (Spin). An electron has a *intrinsic orbital angular momentum* or simply *spin* $\mathbf{S}$ such that:

$$\|\mathbf{S}\| = \sqrt{s(s+1)}\hbar \qquad S_z = s\hbar$$

where $s = \pm\frac{1}{2}$ is another quantum number to be considered in the wave function and it is called *spin quantum number*. This fact result in $2n^2$ possible states for the energy E_n of an electron.

n	ℓ	Type of orbital	m_ℓ
1	0	s	0
2	0	s	0
2	1	p	-1, 0, 1
3	0	s	0
3	1	p	-1, 0, 1
3	2	d	-2, -1, 0, 1, 2
4	0	s	0
4	1	p	-1, 0, 1
4	2	d	-2, -1, 0, 1, 2
4	3	f	-3, -2, -1, 0, 1, 2, 3
5	0	s	0
5	1	p	-1, 0, 1
5	2	d	-2, -1, 0, 1, 2
5	3	f	-3, -2, -1, 0, 1, 2, 3
5	4	g	-4, -3, -2, -1, 0, 1, 2, 3, 4

Table 1: Atomic orbitals in terms of quantum numbers n, ℓ and m_ℓ. Moreover for each configuration we have two possible values for the spin: $-\frac{1}{2}$ and $\frac{1}{2}$.

[8] Bohr model only works for monoelectronic atoms, that is, atoms with only one electron.
[9] Here ϕ denotes the azimuthal angle.
[10] Sometimes for simplicity the subindex ℓ is omitted.

Polyelectronic atoms

Proposition 47 (Schrödinger equation). Consider an atom with N electrons. The Schrödinger equation becomes:

$$\left\{ \frac{-\hbar}{2\mu} \sum_{i=1}^{N} {\nabla_i}^2 - \sum_{i=1}^{N} \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \sum_{\substack{i,j=1 \\ i>j}}^{N} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \right\} \cdot \Phi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

where $\mu = \dfrac{m_{\text{nuc}} m_e}{m_{\text{nuc}} + m_e}$ is the reduced mass of the electron (m_e) and the nucleus (m_{nuc}), $\mathbf{r}_i = x_i\mathbf{i} + y_i\mathbf{j} + z_i\mathbf{k}$ and ${\nabla_i}^2 = \dfrac{\partial^2}{\partial x_i^2} + \dfrac{\partial^2}{\partial y_i^2} + \dfrac{\partial^2}{\partial z_i^2}$. This equation cannot be solved exactly but we can find approximations to it if we suppose:

- We neglect the interactions between electrons.
- We consider that the particles are identic and we cannot distinguish them.

Definition 48 (Fermions). A *fermion* is a particle that follows Fermi-Dirac statistics and has half integer spin.

Definition 49 (Boson). A *boson* is a particle that follows Bose-Einstein statistics and has integer spin.

Proposition 50 (Pauli exclusion principle). Two or more identical fermions cannot occupy simultaneously the same quantum state.

Proposition 51 (Symmetry of the wave function). Consider two non-interacting identical particles. The probability density of the two particles with wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ must be identical to that with wave function $\Psi(\mathbf{r}_2, \mathbf{r}_1)$. Therefore,

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\Psi(\mathbf{r}_2, \mathbf{r}_1)|^2$$

and hence Ψ has to be necessary symmetric ($\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_2, \mathbf{r}_1)$) or antisymmetric ($\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1)$). Moreover we have:

1. Φ is symmetric if and only if the particles are bosons.
2. Φ is antisymmetric if and only if the particles are fermions.

Nuclear physics

Definition 52 (Atom). An atom X formed by Z protons and N neutrons is denoted as ${}^{\text{A}}_{\text{Z}}\text{X}$ where $A := Z + N$[11]. The number Z is called *atomic number* and the number A, *mass number*.

Definition 53. Two nuclides are

- *isotopes* if they have the same Z but different N and A.
- *isobars* if they have the same N but different Z and A.
- *isotones* if they have the same A but different Z and N.
- *isomers* if they have the same Z, N and A. They differ in the grouping structure.

Proposition 54 (Radii of nucleus). The stable nucleus has approximately constant density and therefore the nuclear radius R can be approximated by the following formula:

$$R = R_0 A^{1/3}$$

where $R_0 \approx 1.2$ fm.

Proposition 55 (Nucleus mass). The mass of a nucleus $M_{\text{nuc}}(Z, A)$ of atomic number Z and mass number A satisfies:

$$M_{\text{nuc}}(Z, A)c^2 = Zm_{\text{p}}c^2 + (A - Z)m_{\text{n}}c^2 - E_{\text{b}}(Z, A)$$

where $E_{\text{b}}(Z, A)$ is the *binding energy*, that is, the energy required to break up the nucleus into Z protons and $A-Z$ neutrons. If we take into account the mass of the electrons on the atomic mass $M_{\text{at}}(Z, A)$ we get:

$$M_{\text{at}}(Z, A)c^2 = M_{\text{nuc}}(Z, A)c^2 + Zm_e c^2 - E_e(Ze) \approx \approx ZM_{\text{at}}({}^1_1\text{H})c^2 + (A - Z)m_{\text{n}}c^2 - E_{\text{b}}(Z, A)$$

where $E_e(Ze)$ is the *electron binding energy* and $E_e(Ze) \ll E_{\text{b}}(Z, A)$ so it can be neglected, and $M_{\text{at}}({}^1_1\text{H})$ is the mass of hydrogen atom ${}^1_1\text{H}$. From this, we can define the *mass defect* Δm:

$$\Delta m = M_{\text{at}}(Z, A) - A$$

where $M_{\text{at}}(Z, A)$ is expressed in u[12].

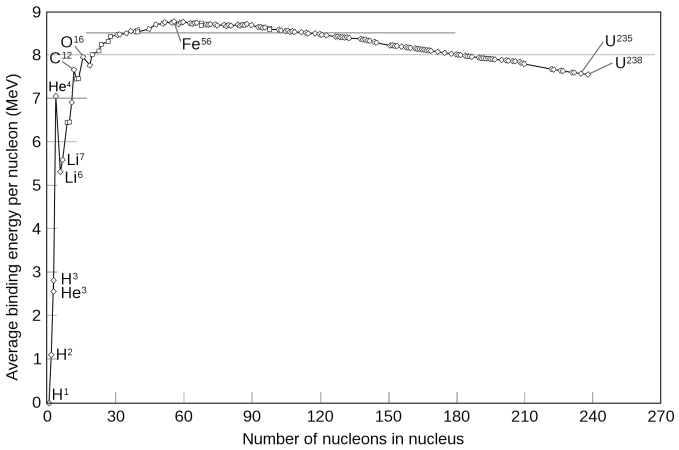


Figure 2: Binding energy curve

Proposition 56 (Semi-empirical mass formula). For a nucleus of atomic number Z and mass number A, we have:

$$E_{\text{b}}(Z, A) = c_1 A - c_2 A^{2/3} - c_3 \frac{Z(Z-1)}{A^{1/3}} - - c_4 \frac{(2Z - A)^2}{A} + \delta(Z, A)$$

[11] Sometimes if the atom ${}^{\text{A}}_{\text{Z}}\text{X}$ is well-known, we simply refer to it as ${}^{\text{A}}\text{X}$.
[12] Unified atomic mass unit.

where

$$\delta(Z,A) = \begin{cases} -c_5 A^{-1/2} & \text{if } N,Z \text{ are odd} \\ 0 & \text{if } A \text{ is odd} \\ +c_5 A^{-1/2} & \text{if } N,Z \text{ are even} \end{cases}$$

empirically, it can be seen that $c_1 \approx 15.56$ MeV, $c_2 \approx 17.23$ MeV, $c_3 \approx 0.697$ MeV, $c_4 \approx 23.285$ MeV and $c_1 \approx 12.00$ MeV.

Definition 57 (Q value). The Q *value* for a reaction is defined as:

$$Q = (m_i - m_f)c^2$$

where m_i is the sum of the reactant masses and m_f is the sum of the product masses. The decay will be spontaneous if $Q > 0$ and in this case, the decay will have a net release of energy.

Definition 58 (α-decay). An α particle is a nucleus of ${}^4_2\mathrm{He}$, which has a short range. The decay is:

$${}^A_Z\mathrm{X} \to {}^{A-4}_{Z-2}\mathrm{Y} + \alpha$$

In this case:

$$\begin{aligned} Q &= \left[M_{\text{nuc}}\left({}^A_Z\mathrm{X}\right) - M_{\text{nuc}}\left({}^{A-4}_{Z-2}\mathrm{Y}\right) - M_{\text{nuc}}\left({}^4_2\mathrm{He}\right)\right]c^2 = \\ &= \left[M_{\text{at}}\left({}^A_Z\mathrm{X}\right) - M_{\text{at}}\left({}^{A-4}_{Z-2}\mathrm{Y}\right) - M_{\text{at}}\left({}^4_2\mathrm{He}\right)\right]c^2 = \\ &= K_Y + K_\alpha \end{aligned}$$

where $M_{\text{at}}\left({}^A_Z\mathrm{X}\right)$ is the mass of the atom ${}^4_2\mathrm{X}$, $M_{\text{nuc}}\left({}^A_Z\mathrm{X}\right)$ is the mass of its nucleus (and the same for the atom Y), K_Y is the kinetic energy of the particle Y and K_α is the kinetic energy of the α particle. Moreover we have:

$$K_\mathrm{Y} \approx \frac{4}{A}Q \qquad K_\alpha \approx \frac{A-4}{A}Q$$

Definition 59 (β-decay).

1. β^- *decay*: $\mathrm{n} \to \mathrm{p} + e^- + \bar{\nu}_e$

   The decay:

   $${}^A_Z\mathrm{X} \to {}^A_{Z+1}\mathrm{Y} + e^- + \bar{\nu}_e$$

   Q factor[13]:

   $$Q = \left[M_{\text{at}}\left({}^A_Z\mathrm{X}\right) - M_{\text{at}}\left({}^A_{Z+1}\mathrm{Y}\right)\right]c^2$$

2. β^+ *decay*: $\mathrm{p} \to \mathrm{n} + e^+ + \nu_e$

   The decay:

   $${}^A_Z\mathrm{X} \to {}^A_{Z-1}\mathrm{Y} + e^+ + \nu_e$$

   Q factor:

   $$Q = \left[M_{\text{at}}\left({}^A_Z\mathrm{X}\right) - M_{\text{at}}\left({}^A_{Z-1}\mathrm{Y}\right) - 2m_e\right]c^2$$

[13] Since neutrino's mass is around 2 eV, we can neglect it.

3. *Electron capture*: $\mathrm{p} + e^- \to \mathrm{n} + \nu_e$

   The decay:

   $${}^A_Z\mathrm{X} + e^- \to {}^A_{Z-1}\mathrm{Y} + \nu_e$$

   Q factor:

   $$Q = \left[M_{\text{at}}\left({}^A_Z\mathrm{X}\right) - M_{\text{at}}\left({}^A_{Z-1}\mathrm{Y}\right)\right]c^2 - B_n$$

   where B_n is the ionization energy at the shell n where the electron is captured.

Definition 60 (γ-decay). A γ particle is a photon which has long range. The decay is produced when the nucleus goes from an excited state to a less excited state. The decay is:

$${}^A_Z\mathrm{X}^* \to {}^A_Z\mathrm{X} + \gamma$$

Definition 61 (Radioactive activity). The *radioactive activity* of a substance is defined as the number of decays it has per unit of time. Its unit in the SI is the Bq ($[\mathrm{Bq}] = [\mathrm{s}^{-1}]$). The probability for a radionuclide to decay per unit of time is constant and unique for each radionuclide. This constant λ is called *decay constant*. Moreover if $N(t)$ is the number of radionuclide to decay at time t and $A(t)$ is the activity of the substance at time t, we have:

$$A(t) = \lambda N(t) = -\frac{\mathrm{d}N(t)}{\mathrm{d}t}$$

And therefore:

$$N(t) = N_0 \mathrm{e}^{-\lambda t} \qquad A(t) = A_0 \mathrm{e}^{-\lambda t}$$

where N_0 is the initial number of radionuclides and $A_0 = \lambda N_0$ is the initial activity of the substance.

Definition 62 (Half-time). We define the *half-time* $t_{1/2}$ as the time in which the number of radionuclide has reduced by half.

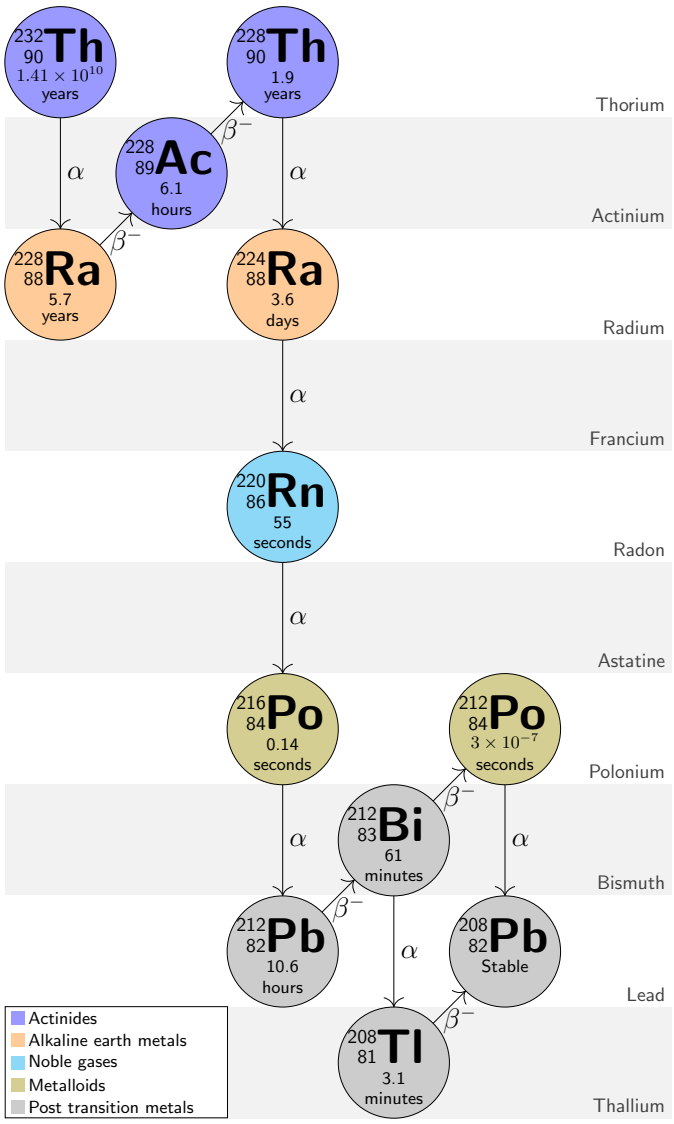
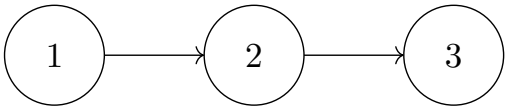


Figure 3: Decay chain of Thorium or *Thorium series* corresponding to nuclei with $A = 4n$, $n \in \mathbb{N}$.

Proposition 63 (Decay chain). Consider the decay chain:



where the third nucleus is stable. Let $N_i(t)$ be the number of radionuclides of the substance i at time t, $A_i(t)$ be the activity of the substance i at time t and λ_i be the decay constance of the substance i, all of this for $i = 1, 2$. Then, if $N_1(0) = N_0$ and $N_2(0) = N_3(0) = 0$, we have:

$$N_1(t) = N_0 \mathrm{e}^{-\lambda_1 t} \quad N_2(t) = N_0 \frac{\lambda_1}{\lambda_2 - \lambda_1} \left(\mathrm{e}^{-\lambda_1 t} - \mathrm{e}^{-\lambda_2 t}\right)$$

$$A_1(t) = N_0 \lambda_1 \mathrm{e}^{-\lambda_1 t} \quad A_2(t) = N_0 \frac{\lambda_1 \lambda_2}{\lambda_2 - \lambda_1} \left(\mathrm{e}^{-\lambda_1 t} - \mathrm{e}^{-\lambda_2 t}\right)$$

We may have three possible situations:

1. *Secular equilibrium*: $\lambda_1 \ll \lambda_2$. This implies that over short time (compared to the half-life time of the substance 1),

$$\mathrm{e}^{-\lambda_1 t} \approx 1 \implies A_2(t) \approx N_0 \lambda_1 (1 - \mathrm{e}^{-\lambda_2 t})$$

2. *Transient equilibrium*: $\lambda_1 < \lambda_2$.

$$\frac{A_2(t)}{A_1(t)} = \frac{\lambda_2}{\lambda_2 - \lambda_1} \left(1 - \mathrm{e}^{-(\lambda_2 - \lambda_1)t}\right)$$

3. If $\lambda_1 > \lambda_2$, there is no equilibrium.

Definition 64 (Nuclear reactions). A nuclear reaction is a reaction of the form:

$$\mathrm{a} + \mathrm{X} \to \mathrm{Y} + \mathrm{b}$$

It is sometimes abbreviated as X(a,b)Y. The Q value of the reaction may behave in two ways:

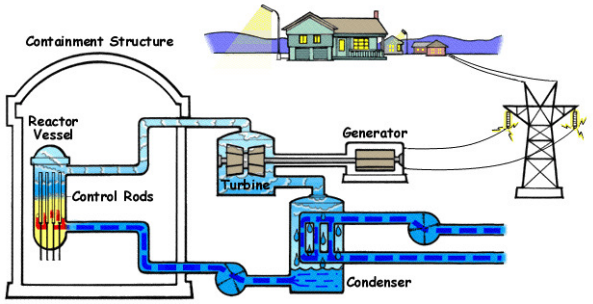
1. *Exothermic reaction* ($Q > 0$): kinetic energy may be released during the course of a reaction.
2. *Endothermic reaction* ($Q < 0$): kinetic energy may have to be supplied for the reaction to take place.

Definition 65 (Nuclear fission). *Nuclear fission* is a reaction in which the nucleus of an atom splits into two or more smaller nuclei. Nuclear fissions are usually initialized hitting a stable atom with a neutron, turning the atom excited. In fact, nuclear fissions involve a few neutrons which play an important role. The *reproduction factor* k is the number of neutrons produced from a nuclear fission.

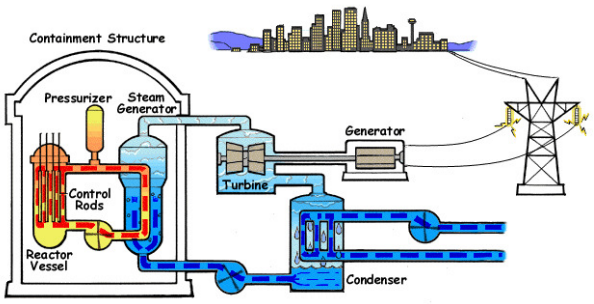
- If $k < 1$, the reaction will stop itself.
- If $k = 1$, the reaction is self-sustained.
- If $k > 1$, the reaction can be uncontrolled[14].

Definition 66 (Nuclear reactors). There are mainly two types of nuclear reactors:

1. BWR (*Boiling Water Reactor*):



2. PWR (*Pressurized Water Reactor*):



[14] Because of that, in nuclear reactors there are *control roads* of some metal that absorbs neutrons. Therefore, if at any time $k > 1$, the control rods are introduced causing a decrease of the value of k.

Definition 67 (Nuclear fusion). *Nuclear fusion* is a reaction in which two or more atomic nuclei are combined to form one or more different atomic nuclei and subatomic particles (neutrons or protons)[15]. The most interesting fusion reactions are:

$$^2\mathrm{H} + {}^2\mathrm{H} \to \mathrm{n} + {}^3\mathrm{He} \qquad (Q = 3.3 \text{ MeV})$$
$$^2\mathrm{H} + {}^2\mathrm{H} \to \mathrm{p} + {}^3\mathrm{H} \qquad (Q = 4.0 \text{ MeV})$$
$$^2\mathrm{H} + {}^1\mathrm{H} \to {}^3\mathrm{He} + \gamma \qquad (Q = 5.49 \text{ MeV})$$
$$^2\mathrm{H} + {}^3\mathrm{H} \to \mathrm{n} + {}^4\mathrm{He} \qquad (Q = 17.6 \text{ MeV})$$

Elementary particles

Definition 68 (Elementary particles). All the matter is composed by 12 fermions (6 quarks and 6 leptons) and all of these have an associated antiparticle. Quarks and Leptons can interact with each other by exchanging Gauge bosons which are carriers of the 4 fundamental forces.

Definition 69 (Antimatter). Each elementary particle has an associated *antiparticle* which has the same properties as the initial particle but has different sign on all the charges.

Definition 70 (Quark). A *quark* is a fermion with fractional electric charge by 1/3. There are 6 types of quarks, known as *flavors*: *up* u and *down* d (first generation); *charm* c and *strange* s (second generation), and *top* t and *bottom* b (third generation)[16].

Definition 71 (Lepton). A *lepton* is a fermion which does not undergo strong interaction. There are 6 types of leptons, known as *flavors*: *electron* e^- and *electron neutrino* ν_e (first generation); *muon* μ^- and *muon neutrino* ν_μ (second generation), and *tau* τ^- and *tau neutrino* ν_τ (third generation).

Definition 72 (Lepton number). *Lepton number* L is a quantum number that is conserved in all interactions. It is defined as:

$$L = n_\ell - n_{\bar{\ell}}$$

where where n_ℓ is the number of leptons and $n_{\bar{\ell}}$ is the number of antileptons in a reaction. In addition to lepton number, *lepton family numbers* are defined as:

- *Electron number* L_e: for the electron and electron neutrino.
- *Muon number* L_μ: for the muon and muon neutrino.
- *Tau number* L_τ: for the tau and tau neutrino.

These numbers are also preserved during collisions.

	L_e	L_μ	L_τ
e^-	$+1$	0	0
ν_e	$+1$	0	0
e^+	-1	0	0
$\bar{\nu}_e$	-1	0	0
μ^-	0	$+1$	0
ν_μ	0	$+1$	0
μ^+	0	-1	0
$\bar{\nu}_\mu$	0	-1	0
τ^-	0	0	$+1$
ν_τ	0	0	$+1$
τ^+	0	0	-1
$\bar{\nu}_\tau$	0	0	-1

Table 2: Lepton family numbers

Definition 73 (Hadron). A *hadron* is a subatomic particle made of two or three quarks held together by the strong force. There are two types of hadrons:

- Baryons: made of three quarks.
- Mesons: made of two quarks.

Definition 74 (Color charge). The *color charge*[17] is a property of quarks and gluons (see Theorem 75) that is related to the particles' strong interactions. There are three types of colors (*red*, *green* and *blue*) and three types of anticolors (*antired*, *antigreen* and *antiblue*). This two families of colors mixed together, or one color with its anticolor, produces the color *white* or, equivalently, has a net color charge of zero.

Definition 75 (Fundamental interactions). Fundamental interactions are characterized by the exchange of bosons. The 4 fundamental interactions are:

- Electromagnetic interaction: Based on emission and absorption of photons. The particles with which it interacts have nonzero electric charge. This interaction is described by quantum electrodynamics (QED).
- Strong interaction: It is transported by gluons. The particles with which it interacts have nonzero color charge. This interaction is described by quantum chromodynamics (QCD)[18].
- Weak interaction: It is transported by bosons W^+, W^- and Z^0. It modifies the flavour of a particle.
- Gravity: Te particles wit which it interacts have nonzero mass. The carrier particle of this forces is the graviton, which hasn't been observed yet.

[15] Even that nuclear fusion is still being the energetic promise of the future, its production is very costly. Indeed, we have to put together the nuclei in the way that the strong interaction overcome the electrostatic force, that is, put the nuclei together at a distance of $\sim 10^{-15}$ m.

[16] An important fact of quarks is that they cannot be isolated due to the *color confinement* property (see definition Theorem 74).

[17] The color charge of quarks and gluons is completely unrelated to the everyday meaning of color.

[18] In particular, strong interaction is the responsible of maintaining the atomic nucleus unified: since protons have charge $+e$, they experience an electric force that tends to push them apart, but at short range ($\sim 10^{-15}$ m) the attractive nuclear force is strong enough to overcome the electromagnetic force.

Interaction	Relative intensity	Boson
Strong	1	Gluon g
Electromagnetic	10^{-2}	Photon γ
Weak	10^{-7}	W^+ W^- Z^0
Gravitational	10^{-39}	Graviton G

Table 3: Relative intensity of fundamental forces

Definition 76 (Grand Unified Theory). Electromagnetic and weak forces join together in a unique *electroweak theory* for energies $\gg 100$ GeV. This one join with strong force in the *Grand Unified Theory* for energies $\sim 10^{15}$ GeV. And finally, the 4 interaction join together at energies $> 10^{20}$ GeV or distances $\sim 10^{-34}$ m.

Solids

Definition 77. A solid is *crystalline* if atoms form a regular and structured patron. A solid is *amorphous* if the arrangement of atoms is not regular.

Proposition 78 (Classical interpretation of resistivity). Consider a metal of resistivity ρ with n_e electrons per unit of volume moving at an average speed of v_{av}. Then:

$$\rho = \frac{m_e v_{\text{av}}}{n_e e^2 \lambda}$$

where $\lambda = v_{\text{av}}\tau$ is the mean free path of electrons between collisions with the lattice ions and τ is the average time between these collisions[19].

Proposition 79 (Quantum interpretation of resistivity). Free electrons do not interact neither with ions nor with themselves. Indeed they behave as a particles in a gas (*fermi gas*). Moreover by Pauli exclusion principle, there can only be two electrons in each energy state. At $T = 0$ K the energy E_F of the last filled (or half-filled) energy state is called *Fermi energy*:

$$E_F = \frac{h^2}{8m_e}\left(\frac{3N}{\pi V}\right)^{2/3}$$

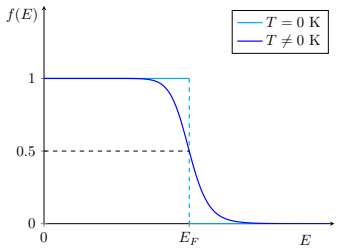
where N is the number of free electrons and V is the volume they occupy. That is, $\frac{N}{V}$ is the density of free electrons. The average energy E_{av} at $T = 0$ K is:

$$E_{\text{av}} = \frac{3}{5}E_F$$

Definition 80. The *Fermi factor* $f(E)$ is defined as the probability of a state being occupied. At $T = 0$ K we have:

$$f(E) = \begin{cases} 1 & \text{if } E < E_F \\ 0 & \text{if } E > E_F \end{cases}$$

If $T \neq 0$ K some electrons gain enough energy to level up and therefore we should redefine E_F in the following way: energy in which the probability of its corresponding state being occupied is $1/2$. Therefore the Fermi factor becomes:



Proposition 81 (Band Theory of Solids). When many atoms are brought together to form a solid, the individual energy levels are split into bands of allowed energies. The splitting depends on the type of bonding and the lattice separation. The highest energy band that contains electrons is called the *valence band* (*VB*). The lowest energy band that is not filled with electrons is called the *conduction band* (*CB*).

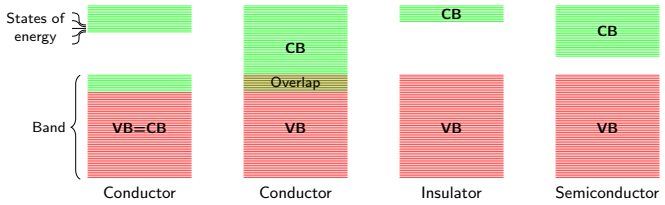
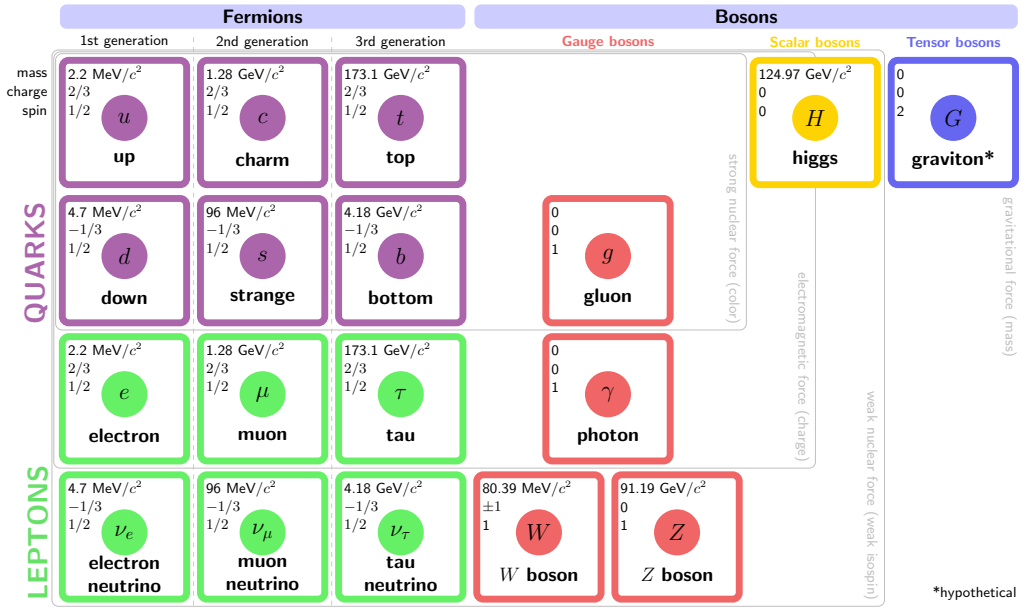


Figure 4: Band of levels on a conductor, insulator and semiconductor. In red there are the levels occupied by electrons and in green the levels empty.

- In a conductor, the valence band is only partially filled, so there are many available empty energy states for excited electrons which can move freely through these states.
- In an insulator, the valence band is completely filled and there is a large energy gap between it and the next allowed band, the conduction band. Therefore, the electrons can barely move.
- In a semi-conductor, the energy gap between the filled valence band and the empty conduction band is small; so, at ordinary temperatures, an appreciable number of electrons are thermally excited into the conduction band.

[19] We know that $\rho \propto v_{\text{av}} \propto \sqrt{T}$ but empirically it is observed that $\rho \propto T$. The classical model is, therefore, inconsistent.



2. | Heat transfer

Definition 82 (Heat). The *heat* is the transport of thermal energy due to the temperature difference. The fundamental modes of heat transfer are: *conduction*, *convection* and *radiation*.

Conduction

Definition 83 (Conduction). *Thermal conduction* is the heat transfer produced by the contact of two object at different temperatures in the absence of matter transfer. Microscopically, energy is transferred throughout the material due to collisions of particles and the movement of electrons within the body.

Law 84 (Fourier's law). The law of heat conduction states that

$$\boldsymbol{\nabla \Phi}_q = -\lambda \boldsymbol{\nabla} T$$

where $\boldsymbol{\Phi}_q$ is the heat flux density (energy transferred per unit of surface and time) and λ is the material's *thermal conductivity* ($[\lambda] = \mathrm{W} \cdot \mathrm{m}^{-1} \cdot \mathrm{K}^{-1}$).

Proposition 85 (Heat equation). For a medium at a temperature $T(\mathbf{r}, t)$ we have:

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho c_s} \Delta T =: \alpha \Delta T$$

where ρ is the density of the material; c_s, its specific heat capacity; λ, its thermal conductivity, and α its *thermal diffusivity*.

Law 86 (Fick's law). The solute in a solvent at rest will move from a region of high concentration to a region of low concentration across a concentration gradient. Mathematically, if $\mathbf{J}$ is the diffusion flux; D, the diffusion coefficient, and c, the concentration, then:

$$\mathbf{J} = -D \boldsymbol{\nabla} c$$

Proposition 87 (Diffusion equation). The diffusion equation is:

$$\frac{\partial c}{\partial t} = D \Delta c$$

Proposition 88. Suppose that inside a material there is a source of heat which generates an amount of heat $\dot{q}$ per unit of volume and time. Then:

$$\rho c_s \frac{\partial T}{\partial t} = \lambda \Delta T + \dot{q}$$

where ρ is the density of the material; c_s, its specific heat capacity, and λ, its thermal conductivity. For the case of creating matter instead of energy and measuring the solute c of the solvent we have:

$$\frac{\partial c}{\partial t} = D \Delta c + f(c, t)$$

where D is the diffusion coefficient and $f(c, t)$ is the function that measures the net solute created and destructed per unit of volume and time.

Convection

Definition 89 (Convection). *Thermal convection* is the heat transfer from one place to another due to the movement of fluid.

Proposition 90 (Newton's law of cooling). A body subjected to a forced convection exchanges heat with its surroundings as:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = hA(T - T_0)$$

where h is the *heat transfer coefficient*; A, the heat transfer surface area; T, the temperature of the body on its surface, and T_0, the temperature of the environment.

Radiation

Definition 91 (Radiation). *Thermal radiation* is the emission of electromagnetic waves from all matter that has a temperature greater than absolute zero. Moreover, the power radiated from an object in a vacuum is:

$$P = \varepsilon \sigma T^4$$

where $0 < \varepsilon < 1$ is the emissivity of the object;σ, the Stefan-Boltzmann constant, and T, the temperature of the object.

3. | Thermodynamics

Basic definitions

Definition 92 (Thermodynamic system). A *thermodynamic system* is a region of the universe confined by walls. There are three types of systems:

- *Open system*: can exchange energy and matter with its surroundings (made of permeable and diathermic walls).
- *Closed system*: can exchange energy with its surroundings but not matter (made of impermeable and diathermic walls).
- *Isolated system*: can exchange neither energy nor matter with its surroundings (made of impermeable and adiabatic walls).

Definition 93. Variables which measure the macroscopic measurable properties of the state of a system are called *state variables* and can be of two types:

1. *Extensive*: are additive and scale the size of the system. Examples of such variables are: mass, volume, energy...
2. *Intensive*: do not depend on the system size or the amount of material in the system. Examples of such variables are: temperature, density, pressure...

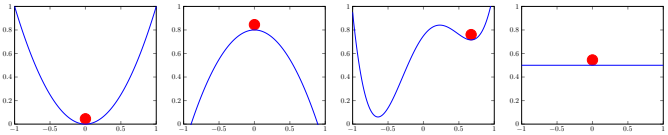
Moreover, *specific variables* are those created from an extensive variable and divided by the volume, number of moles, mass... Examples of such variables are: specific volume, density, specific heat capacity...

Definition 94. A system is in

1. *mechanical equilibrium* if the net force acting on the system is zero.
2. *thermal equilibrium* if there is no net flow of thermal energy inside it or between it and its surroundings.
3. *chemical equilibrium* if there are no chemical reactions on the system.
4. *thermodynamical equilibrium* if it is in mechanical, thermal and chemical equilibrium simultaneously.

Definition 95. There are different types of equilibrium:

- *Stable*: after a slight disturbance, the system returns to the equilibrium.
- *Unstable*: after a slight disturbance, the system get away from the equilibrium.
- *Metastable*: after a slight disturbance, the system returns to the equilibrium but if the disturbance is strong enough the system may get away from the equilibrium.
- *Neutral*: a slight disturbance does not displace the system from the equilibrium.



Stable Unstable Metastable Neutral

Definition 96 (Thermodynamic process). A *thermodynamic process* is the passage between two states of equilibrium. We distinguish the following types of processes:

- *Quasi-static process*: the system passes through states infinitely close to the equilibrium.
  - *Reversible process*: the system can be inverted in each infinitesimally step by changing the sign of the external parameters.
  - *Irreversible process*: the system cannot be inverted in each infinitesimally step by changing the sign of the external parameters.
- *Non-quasi-static process*: the system passes through non-equilibrium states.

Zeroth law of thermodynamics

Definition 97. We say that two systems are in *thermal contact* if they are separated by a diathermic wall.

Law 98 (Zeroth law of thermodynamics). If two systems are both in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.

Corollary 99. Being in thermal equilibrium is an equivalence relation.

Definition 100. The *empirical temperature* is a common state variable between the systems that are in thermal equilibrium.

Proposition 101. The conversions between Celsius, Fahrenheit and Kelvin scales are:

$$T(^\circ\mathrm{C}) = \frac{5}{9}\left(T(^\circ\mathrm{F}) - 32\right) \qquad T(^\circ\mathrm{C}) = T(^\circ\mathrm{K}) - 273.15$$

Proposition 102. Let $z = z(x, y)$ be a function. Then:

$$\left(\frac{\partial z}{\partial y}\right)_x = \frac{1}{\left(\frac{\partial y}{\partial z}\right)_x} \qquad \left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

Definition 103 (Thermal expansion). The *volumetric coefficient of thermal expansion* is given by

$$\alpha := \alpha_{\mathrm{V}} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

where the subscript p indicates that the pressure is held constant during the process.

Definition 104 (Compressibility). *Isothermal compressibility* is defined as

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

where the subscript T indicates that the temperature is held constant during the process.

Definition 105 (Thermal pressure). The *thermal pressure coefficient* is defined as:

$$\beta = \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

where the subscript V indicates that the volume is held constant during the process.

Work

Definition 106. The work done by a hydrostatic system is:

$$\mathrm{d}W = -p\,\mathrm{d}V \implies W = -\int_{V_\mathrm{i}}^{V_\mathrm{f}} p\,\mathrm{d}V$$

where V_i and V_f are the initial and final volumes of the system, respectively.

Lemma 107 (Sign convention of work). Given a system we have:

- $W > 0$, if the surroundings of the system do work on the system.
- $W < 0$, if the system do work on its surroundings.

Proposition 108. Depending on the type of process, we get different values for the total work done on the process:

- Isochoric process ($V = \text{const.}$):

  $$\mathrm{d}V = 0 \implies W = 0$$

- Isobaric process ($p = \text{const.}$):

  $$W = -p\Delta V$$

  where p is the pressure of the system and ΔV is the difference of volume between the initial and final states.

- Isothermal process ($T = \text{const.}$):

  $$W = -nRT\ln\left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right)$$

  where n is the number of moles of present gas, R is the ideal gas constant, T is the temperature of the system and V_i and V_f are the initial and final volumes of the system, respectively.

First law of thermodynamics

Law 109 (First law of thermodynamics in isolated systems). In an isolated system, the work done by a process between two arbitrary states is independent of that process and depends only on the initial and final states.

Corollary 110. We define the *internal energy* U_B of the state B as:

$$U_B = U_A + W^{\mathrm{ad}}_{A\to B} \implies \Delta U = W^{\mathrm{ad}}_{A\to B}$$

where U_A is the internal energy of the state A, and $W^{\mathrm{ad}}_{A\to B}$ is the work done to go form A to B through an adiabatic process.

Law 111 (First law of thermodynamics in closed systems). In a closed system, the work done to go from an initial state to a final state does depend on the process followed and not only on the initial and final states.

Corollary 112. In a closed system, we define the *heat supplied to the system* Q in a process between two states A and B as:

$$Q_{A\to B} = \Delta U - W_{A\to B}$$

Or in differential form:

$$\delta Q = \mathrm{d}U - \delta W$$

where δ is not exactly the differential of a function.

Lemma 113 (Sign convention of heat). Given a system we have:

- $Q > 0$, if the heat is added to the system.
- $Q < 0$, if the heat is rejected from the system.

Definition 114. Relating the heat capacity of a substance we have:

$$C_X = \frac{\mathrm{d}Q_X}{\mathrm{d}T}$$

where the subscript X indicates that the variable X is held constant during the expansion.

Definition 115. *Latent heat* is the amount of heat required to completely change the phase of a kilogram of a substance.

Definition 116 (Enthalpy). We define the *enthalpy* H of a system as:

$$H = U + pV$$

where U is the internal energy, p is the pressure and V is the volume.

Proposition 117. Relating the heat capacities C_V and C_p holding constant the volume and the pressure, respectively, we have:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

And in general:

$$C_p = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_p$$

Proposition 118 (Reversible adiabatic equation for an ideal gas). The equation for an ideal gas undergoing a reversible adiabatic process is:

$$\mathrm{d}U + p\,\mathrm{d}V = 0 \implies nc_V\,\mathrm{d}T + \frac{nRT}{V}\,\mathrm{d}V = 0$$
$$\implies \begin{cases} pV^\gamma = \text{const.} \\ V^{\gamma-1}T = \text{const.} \\ p^{1-\gamma}T^\gamma = \text{const.} \end{cases}$$

Second law of thermodynamics

Law 119 (Second law of thermodynamics). No system can absorb heat from a single reservoir and convert it entirely into work without additional net changes in the system or its surroundings.

Definition 120. A *heat engine* is a cyclic device whose purpose is to convert as much heat into work as possible. Heat engines contain a working substance (water in a steam engine) that absorbs a quantity of heat Q_h (hot) from a high temperature reservoir, does work W on its surroundings, and releases heat Q_c (cool) as it returns to its initial state. Its efficiency η is given by:

$$\eta = \frac{W}{Q_\mathrm{h}} = 1 - \frac{Q_\mathrm{c}}{Q_\mathrm{h}}$$

Definition 121. A *refrigerator engine* absorbs heat Q_c (cold) from the interior of a refrigerator and releases heat Q_h (hot) to the surroundings. This process requires work W to be done on the refrigerator. Its efficiency η is given by:

$$\eta = \frac{Q_\mathrm{c}}{W}$$

Definition 122. A *heat pump* is a refrigerator with a different objective. It absorbs heat Q_c from the outside (cold reservoir) and releases heat Q_h into the object or region of interest. This process requires work W to be done on the heat pump. Its efficiency η is given by:

$$\eta = \frac{Q_\mathrm{h}}{W}$$

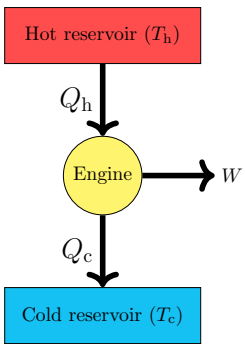


Figure 5: Heat engine

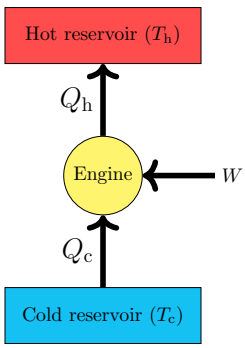


Figure 6: Heat pump

Definition 123 (Carnot cylce). *Carnot cycle* is a reversible thermodynamic process that consists of the following steps:

1. Isothermal expansion
2. Adiabatic expansion
3. Isothermal compression
4. Adiabatic compression

The efficiency η_C of Carnot cycle is:

$$\eta_\mathrm{C} = 1 - \frac{T_\mathrm{c}}{T_\mathrm{h}}$$

where T_h and T_c are the temperatures at the isothermal processes (see **??**). Moreover it is satisfied that:

$$\frac{Q_\mathrm{c}}{Q_\mathrm{h}} = \frac{T_\mathrm{c}}{T_\mathrm{h}}$$

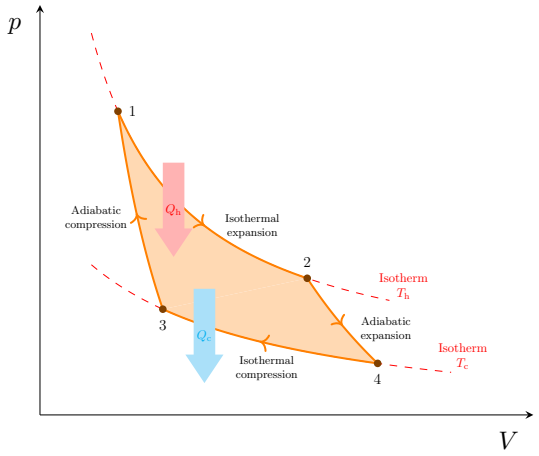


Figure 7: Carnot cycle

Theorem 124 (Carnot's theorem). All heat engines between two heat reservoirs are less or equally efficient than a Carnot heat engine operating between the same reservoirs.

Corollary 125. All reversible machines working between two heat reservoirs has the same efficiency.

Proposition 126. Consider a machine that realizes a Carnot cycle. Let T_1 and T_2 be the temperatures of the two reservoirs and $T_{1,\mathrm{w}}$ and $T_{2,\mathrm{w}}$ the temperatures of the machine when it is in touch with reservoirs of temperatures T_1 and T_2, respectively. Then, the power of this cycle[20] is:

$$P = \lambda \frac{(T_1 - T_{1,\mathrm{w}})(T_{2,\mathrm{w}} - T_2)(T_{1,\mathrm{w}} - T_{2,\mathrm{w}})}{T_1(T_1 - T_{1,\mathrm{w}}) + T_2(T_{2,\mathrm{w}} - T_2)}$$

where λ is the material's conductivity. The efficiency when the power is maximum is:

$$\eta = 1 - \sqrt{\frac{T_2}{T_1}} < \eta_\mathrm{C}$$

[20] In a reversible cycle the efficiency is maximum but because of it is extremely slow the power is null.

Entropy

Theorem 127 (Clausius theorem). For a thermodynamic system exchanging heat with external reservoirs and undergoing a thermodynamic cycle we have:

$$\oint \frac{\delta Q}{T} \leq 0$$

where δQ is the heat exchange with a reservoir at a temperature T. Moreover if the cycle is reversible, we have:

$$\oint \frac{\delta Q_{\text{rev}}}{T} = 0$$

Definition 128 (Entropy). There exists a new state function, called *entropy* S, such that:

$$S(B) - S(A) = \int_A^B \frac{\delta Q_{\text{rev}}}{T} \quad \text{or} \quad \mathrm{d}S = \frac{\delta Q_{\text{rev}}}{T}$$

Law 129 (Second law of thermodynamics in terms of entropy). In an isolated system, the entropy cannot decrease: $\Delta S \geq 0$. Moreover:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$$

Proposition 130. Entropy in different processes:

- Cyclic process:
$$\Delta S = 0$$
- Reversible adiabatic process:
$$\Delta S = 0$$
- Reversible isothermal process at temperature T:
$$\Delta S = \frac{Q}{T}$$
where Q is the heat exchanged on the process.
- Thermal contact between two reservoirs at temperatures T_1 and T_2:
$$\Delta S = Q\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
where Q is the heat exchanged on the process.
- Change on temperature at constant volume:
$$\Delta S = C_V \ln \frac{T_2}{T_1}$$
where T_1 is the initial temperature and T_2 the final temperature.
- Change on temperature at constant pressure:
$$\Delta S = C_p \ln \frac{T_2}{T_1}$$
where T_1 is the initial temperature and T_2 the final temperature.
- Free adiabatic expansion of an ideal gas:
$$\Delta S = nRT \ln \frac{V_2}{V_1}$$
where V_1 is the initial volume and V_2 the final volume.
- Arbitrary process of an ideal gas:
$$\Delta S = nRT \ln \frac{V_2}{V_1} + nc_p \ln \frac{T_2}{T_1}$$

Definition 131. We define the *Helmholtz free energy* F as:

$$F = U - TS$$

At equilibrium, Helmholtz free energy is minimized.

Definition 132. We define the *Gibbs free energy* G as:

$$G = H - TS$$

Proposition 133. 2nd law of thermodynamics applied to non-isolated systems:

$$\Delta G = \Delta U + p\Delta V - T\Delta S \leq 0$$

Proposition 134. For a non-isolated system, we have different criteria to know whether or not a the system is spontaneous.

- If $T, p = \text{const.}$, then $\Delta G \leq 0$.
- If $T, V = \text{const.}$, then $\Delta F \leq 0$.
- If $S, p = \text{const.}$, then $\Delta H \leq 0$.
- If $S, V = \text{const.}$, then $\Delta U \leq 0$.
- If $U, V = \text{const.}$, then $\Delta S \geq 0$.

Proposition 135. The maximum amount of work that the system can perform in a thermodynamic process in which temperature is held constant is $|\Delta F|$.

Proposition 136 (Gibbs equation). For a closed system we have:

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V$$

For an open system we have:

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N$$

where μ is the chemical potential and N is the number of particles in the system.