Thermodynamics

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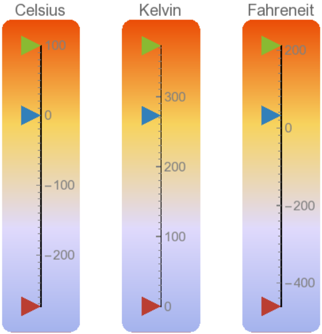
DIMES

Temperature and heat

Thermometric scales - zeroth principle



- Temperature is measured by thermometers
- Celsius: water triple point, $0.01°C$
- $T\,(°C) = T\,(K) - 273.$
- Kelvin: water triple point $273.16°K$
- Fahreneit :°F = °C × 1.8 + 32.

- If two objects at different temperatures are placed at thermal contact, they will reach the same temperature and will therefore be said to be in **thermal equilibrium**.
- If two objects are, separately, in thermal equilibrium with a third object, then they are also in thermal equilibrium between them

thermal expansion of materials

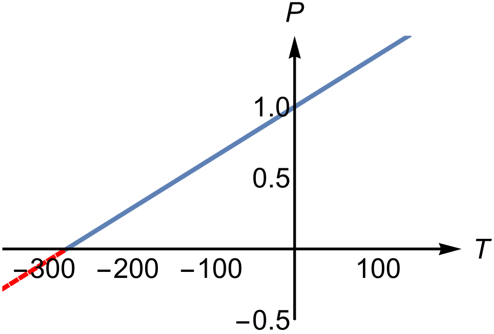
- If an object has linear size L at room temperature and gets warmed by a temperature ΔT, it will vary its size

$$L = L_0(1 + \alpha\Delta T)$$

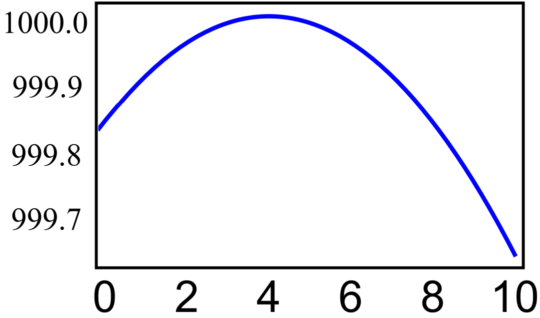
- α is a property of the material, represents the fraction of length it gains by degree of temperature
- α is a pure number
- this change actually occurs on all the dimensions: the volume changes!

the limit temperature of 0 K

- for gases, there is a similar law for pressure: $P = P_0(1 + \alpha t)$
- by interpolation, pressure and volume becomes zero at $-273.15°C$
- this was the first reason why the Kelvin scale was proposed
- there is a deeper physical meaning behind it, bound to the energy of the molecules



Anomalous behavior of water at $4°C$.

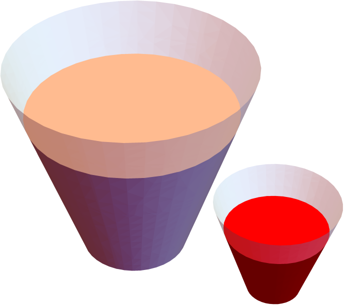


This is what keeps life possible in freezing temperatures: only the surface of the water freezes, while the bottom keeps at a stable temperature.

Temperature and energy

- How do two identical objects differ at different temperatures?
- From the mechanical point of view, there are no substantial differences.
- bodies have an internal (atomic) structure: these constituents move and interact through conservative forces: this system has a total kinetic energy (sum of the individual kinetic energies) and a total potential energy due to all possible pairs of interactions between particles.
- The sum of these kinetic energies and potential energies is called the **internal energy** of the body.
- The temperature is a *macroscopic* quantity that measures the *microscopic* property called internal energy.

Internal energy and temperature



- The heat content depends on the amount of mass.
- The larger vessel has a total kinetic energy greater than the smaller one, even if the latter is at a higher temperature (average kinetic energy).

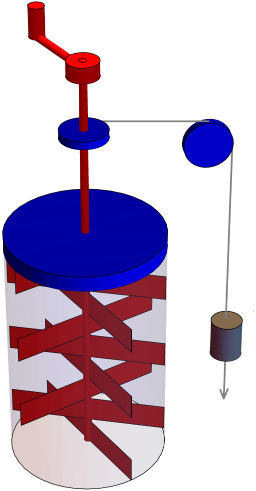
- Temperature: macroscopic quantity that measures only the **average** kinetic energy of the system.
- Internal energy: sum of all kinetic and potential energies of the N molecules constituting the system.

Internal energy

$$U = \sum_{i=0}^{N} E_{C_i} + E_{P_i}$$

- Where U is the internal energy and E_{C_i} and E_{P_i} are the kinetic and potential energy. The internal energy in I. S. is measured in $Joule$.
- Internal energy is a function of temperature: $U = U(T)$, and in simple systems such as ideal gas it assumes a very simple functional form, $U = nc_V T$, which depends linearly on the temperature T , from the number of particles n and from c_V, the specific heat measured at constant volume.

Joule's experiment: heat-work equivalence



- Work can produce heat and viceversa.
- The calorie *cal* is the amount of heat raising the temperature of $1g$ of water from $14.5°C$ to $15.5°C$.
- The great calorie ($kcal$ or Cal) is defined as the amount of heat needed to raise the temperature by $1kg$ of water in the same way.
- Mechanical equivalent of calorie:

$$1J = 0.238\ cal$$

Human metabolism

- Humans and animals perform work: movements, including cell and sub-cellular (e.g. active transport)
- The internal energy loss of the human body is mainly due to outwards heat flow.
- In open systems, like living organisms, both energy and matter can flow from the system or towards it.
- Food, through biochemical transformations, conveys internal energy to the human body, this internal energy is then transformed into heat or into mechanical work.

- The set of biochemical reactions that transform energy into an organism is called **metabolism**.
- **metabolic rate** is the rate at which internal energy is transformed inside the body ($kcal/h$ or Watt).
- adult human: $70W$ consumption in rest conditions, and about $460W$ in normal activity.
- Approximately 35% of energy introduced with food is stored as ATP molecules, and, due to energy transfer (dissipation) processes, the percentage that reaches cells is reduced to 27% .

Heat transfer

- Body at temperature T which is given a certain amount of heat Q and its temperature changes from T to $T + \Delta T$.
- Heat capacity of the body: ratio between the amount of heat absorbed Q and the temperature variation ΔT:

$$C = \frac{Q}{\Delta T} \tag{1}$$

- In S.I. thermal capacity is measured in $J°C^{-1}$.
- It is called **specific heat** c, the thermal capacity per unit mass:

$$c = \frac{C}{m} = \frac{Q}{m\Delta T} \tag{2}$$

- In S.I. specific heat is measured in $J/Kg°C$.
- While thermal capacity C also depends on mass, the specific heat c depends solely on the substance of which the body is made up.
- The specific heat of the water is 4186 $J/kg°C$ which, in calories, is $c_{H_2O} = 1000cal/kg°C$

Heat transfer mechanisms

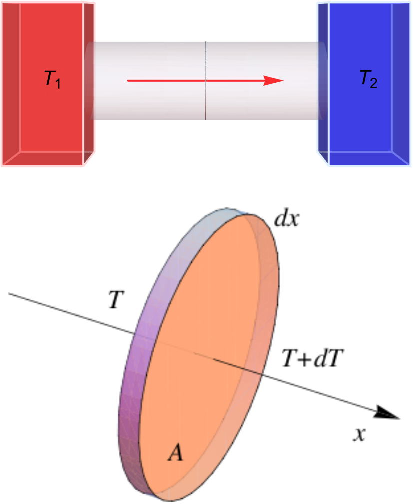
- Heat moves from one body to the other with three mechanisms:
    - Conduction (between solid bodies in contact)
    - Convection (in fluids)
    - Irradiation (between non-contact bodies)
- Skin dissipates heat through irradiation, conduction, convection through mechanisms such as evaporation (sweating) in addition to other mechanisms (vasoconstriction and vasodilation).

Heat exchange

- Two bodies at T_1 and T_2 in thermal contact reach a T_f (energy transfer)
- warmest body gives heat to coldest but also vice versa, even if with different fluxes, until equilibrium $\Delta Q_{12} = -\Delta Q_{21}$

$$m_1 c_{V1}(T_1 - T_f) = -m_2 c_{V2}(T_2 - T_f)$$

heat direct flow



- Heat conduction requires continuity between solid bodies, and heat flows from the warmest to the coldest.
- $\frac{dQ}{dt} = -KA\frac{dT}{dx}$
- $W = J/sec$
- K thermal conductivity
- Good heat conductors are usually good current conductors.

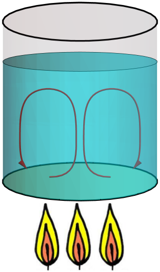
Material	K
Water	0.6
Air	0.026
Fat	0.2
Skin	0.3
Blood	0.5

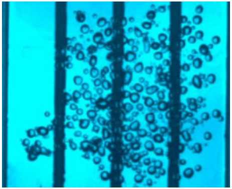
Table: Some values of K.

Multiple materials and surfaces

- If one tries to evaluate the heat loss from several exposed areas, or from layers of protection, one can combine the heat flow by defining the heat conductivity of a surface $C = K \cdot A$
- two surfaces with conductivities C_1 and C_2, one alongside the other (parallel composition) have a total C equal to $C_{tot} = C_1 + C_2$
- two layers of protection one on top of the other (series composition) have a total termal conductivity that can be obtained as
$$\frac{1}{C_{tot}} = \frac{1}{C_1} + \frac{1}{C_2}$$

Convection



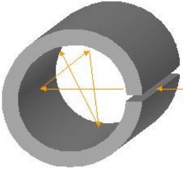


- Heat transmission in a fluid occurs through the motion of its molecules (convective currents).
- Natural: fluid moves because it changes its density with temperature.
- Forced: fluid motion is caused by a pump or a fan.
- $\frac{dQ}{dt} = K_C S(T_C - T_F)$.
- K_C convection coefficient $(W/m^{2o}C)$.

Irradiation: e.m. waves and photons: $E = h\nu$

- Heat transmission through emission and absorption of electromagnetic waves.
- λ wavelength depends on the body temperature: $T < 500°C$: infrared; larger T: visible light.
- emissive power $\mathcal{R}$: radiant energy emitted by a body per unit of time and surface $\mathcal{R}_{\mathcal{W}}$ at $2177°C$ is $500kW/m^2$.
- When radiation hits a body, it is partly absorbed, transmitted and reflected. Absorbed fraction is called the α absorbing power of the body and depends on its nature and surface.
- For example at $2477°C$, α_W is about 0.25.
- “Black body”; an ideal body with $\alpha = 1$ $(\alpha_B = 1)$.

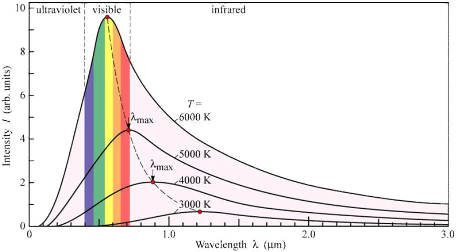
Stefan Boltzmann law: $\mathcal{R}_B = \sigma T^4$



- emissive power of a body is proportional to that of a black body with same T (Kirchoff's law).
- $\mathcal{R} = \alpha \mathcal{R}_B$. Proportionality constant is absorbing power of the body.
- Black body emissive power depends on T: Stefan-Boltzmann law

$$\mathcal{R}_B = \sigma T^4$$

Planck's law: photons energy distribution



- Photons: electromagnetic energy quanta
- Black body radiation distributed over different λ.

- Energy per time and surface unit in the wave length interval $\lambda - \lambda + d\lambda$ in W/m^2:
- $E_\lambda d\lambda = \frac{A}{\lambda^5 (e^{B/\lambda T} - 1)} d\lambda$ $(A = 3.74 \times 10^{-16} W/m^2 \mathrm{e} B = 1.44 \times 10^{-2} mK)$
- Maximum probability: $\lambda = C/T$ (C Wien constant:$2.8 \times 10^{-3} mK$)

Thermal exchanges in living organisms

- **heterotherms** are not able to maintain a constant temperature inside the body, so they need heat sources (mainly the sun) or move, so as not to lower their temperature too much.
- **homeotherms** (warm-blooded, like mammals) can regulate their temperature by exploiting the energy produced by their biochemical reactions (basal metabolism).
- Thermoregulation occurs by varying heat production inside the body and its exchange with the external environment (body surface).

- Blood perfusion allows nutrient exchange, but also to reduce thermal differences among body districts.
- Heat dissipation occurs through irradiation:
  When it's hot dissipation is increased through sweating
  When it's cold dissipation is reduced through clothes, or by restricting surface blood vessels, so to minimize blood heat exchange with neighbouring tissues
- Wet environment impairs thermoregulation in two ways: reducing sweating when it's hot, and making the skin more heat conducting when it's cold

Temperature and irradiation

- The electromagnetic radiation emitted by an object is indicative of its temperature and, at room temperature, this radiation falls mainly in the infrared.
- Some predators (such as reptiles) have organs sensitive to infrared radiation, which allow them to identify "warm", and therefore living, preys.
- Infrared cameras allow to record infrared emissions: these acquisitions give rise to images called "thermograms".
- Thermography is a diagnostic tool in medicine: for example, areas at higher temperatures than surrounding areas may be associated with malignant tumors, due to increased metabolic activity.

Temperature and irradiation

- Thermography can also highlight abnormalities in the distribution of blood in the tissues, caused by phenomena of vasoconstriction, which can cause temperature decreases up to $28°C$.
- There are biological sensors of temperature both at the receptor level, the so-called thermoreceptors, and at the subcellular level (Heat Shock Proteins, that recognize degraded proteins).
- There are also systems of proteins that can protect living organisms at low temperatures, the so-called anti-freeze proteins, observed for example in some species of Antarctic fishes.

First principle

Thermodynamic system

- A system that can be described through thermodynamics quantities: Pressure, Temperature, physical and chemical potentials, …
- Thermodynamic systems are divided into three categories, based on possible exchanges with the environment.
  - isolated systems (no energy or matter exchange);
  - closed systems (exchange of energy but not of matter);
  - open systems (both energy and matter exchange)
- A closed and thermally isolated vessel is the best approximation of an isolated system; a closed container in thermal contact with the environment is the typical example of a closed system.
- Living organisms are open thermodynamic systems (air, water, food, heat exchange) and it is possible to obtain useful information on their behavior through a thermodynamic approach.

Thermodynamic transforms

Variation of thermodynamic parameters (Temperature, Volume, etc.)

- **reversible transformations**: can be retraced in both directions, e.g. increasing or decreasing the temperature of a body and returning it to the same initial state.
- **irreversible transformations**: occur only one direction (e.g. mixing, spontaneous heat transfer).

Ideal gases:

- Isotherm (T constant)
- Isochore (V constant)
- Isobaric (constant P)
- Adiabatic (no heat exchange with the environment)

Change of thermodynamic state:

- Fusion (from solid to liquid)
- Liquefaction (from gas to liquid)
- Evaporation (from liquid to gas)
- Sublimation (from solid to gas)

Ideal gas

- Simplest thermodynamic system: non-interacting atoms/molecules (only kinetic energy)
- Work of a perfect gas (e.g. in a vessel with a moving wall): expansion/compression

$$L = P\Delta V$$

- pressure P is defined as the force F applied from a gas over a surface A

$$P = F/A$$

- pressure is measured in Pascal.

Ideal gas state equation

- Thermodynamic variables of an ideal gas are related by the **equation of state**:

$$PV = nRT$$

- where n is the number of moles, and $R = 8.33 J/^{o}K mole$ is the ideal gas constant
- all thermodynamic transforms (isothermal, isochore, isobaric, adiabatic) can be deduced from this equation

First principle of thermodynamics

- Two bodies at T_1 and T_2 in thermal contact reach a T_{eq} (energy transfer)
- Heat Q is defined as the energy exchanged between the bodies: internal energy U is a function of state (i.e. of thermodynamic variables), heat is not.
- mechanical work L is another way to change internal energy.
- The first principle of thermodynamics states the principle of **energy conservation**:

$$\Delta U = Q + L$$

- $Q > 0$ when it enters the system ($Q < 0$ when it goes out). $L > 0$ when performed on the system, $L < 0$ when performed by the system.
- Signs can be interpreted as the flow of energy from or to the system

Enthalpy:$H = U + P \cdot V$

- Enthalpy H is a state function that expresses the amount of energy that a thermodynamic system can exchange with the environment.
- Enthalpy is defined by the sum of the internal energy and the product of the volume and pressure of a system.
- For isobaric transformations (at constant P) the enthalpy variation is equal to the heat exchanged by the system with the environment.
- In chemical reactions, where $P \cdot V$ is negligible, enthalpy variation coincides with the change in internal energy.
- The ΔH sign tells us if the reaction is exothermic ($\Delta H < 0$) or endothermic $\Delta H > 0$

Hess law

- Since H is a function of state, its variation, in a complex reaction, is obtained as the algebraic sum of all enthalpy variations in the single reactions

$$\Delta H_{reaction} = \sum H_{\mathrm{f}(products)} - \sum H_{\mathrm{f}(reagents)}$$

- Example: Methane combustion $CH_4 + 2O_2 \to CO_2 + 2H_2O$
- from the enthalpies of formation of the products minus those of the reagents, it is deduced that this regulation releases $891kJ/mo$

- Metabolism and control of body temperature: balance between injected and consumed energy
- ATP produced by: combustion of carbohydrates, fatty acids and proteins
- The energy requirement varies between 2000 and 7000 kcal per day
- The temperature is controlled by the thermogenesis balance
- Irradiation, conduction, convection, evaporation, vasodilation, sweating
- Vasoconstriction, piloerection, increase in thermogenesis

Measure of body metabolism

- **direct calorimetry**: measurement of the heat released by the body as a function of time. The hot air produced by the body is removed and cooled by a thermal bath in which the temperature is constantly measured. The heat transferred to the thermal bath gives us the heat produced by the body.
- **Oxygen energy equivalent**. About 95% of body energy comes from combustion reactions. Metabolic rate can be measured on the basis of the oxygen used, calculated as the difference between the oxygen entering and exiting the lungs.

In a normal diet, the energy released by burning 1ℓ of oxygen is about $4.8kcal$: **energetic equivalent of oxygen** .

Second principle

Second principle

- The second principle defines the principle of *irreversibility* of certain thermodynamic transforms, depending on the microscopic (atomic) state of the system before and during transformation.
- It is related to the concept of thermodynamic potentials, that define the allowed direction of evolution of a system.

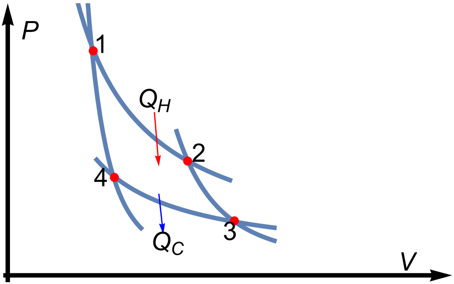
Second principle of Thermodynamics

- For a cyclic transform:
    - $\Delta U = 0 \Rightarrow Q = -L$
    - Q_H absorbed heat
    - Q_C dissipated heat

$$Q = Q_H + Q_C = Q_H - |Q_C| = -L$$

- $Q_H > |Q_C| \Rightarrow L < 0$ thermal machine $\Rightarrow$ KP
- It's impossible to have a thermal machine that converts into work L all the absorbed heat Q_H (Kelvin-Planck)
- $Q_H < |Q_C| \Rightarrow L > 0$ cooling machines $\Rightarrow$ C
- It's impossible to have a cooling machine that works without absorbing work L from environment (Clausius)

Carnot cycle and efficiency



- Carnot cycle is the prototype of a thermal machine, constituted by two isothermal and two adiabatic transforms
- efficiency of a thermal machine
- $\eta = \frac{|L|}{Q_H} = -\frac{L}{Q_H}$
- $-L = Q_H - |Q_C|$
- $\eta = \frac{Q_H - |Q_C|}{Q_H} = 1 - \frac{|Q_C|}{Q_H}$
- K-P proposition can be resumed as: it's impossible to realize a thermal machine with $\eta = 1$

Irreversibility

- The second principle introduces in Physics the concept of irreversible transformation, that does not exist in Mechanics.
- Irreversible transformations create a hierarchy of energy types: works can transform completely into heat but not viceversa.
- A hot body can provide heat to a colder one without work
- Whenever an irreversible process occurs, energy available for work diminishes.

Entropy and irreversibility

- We define the quantity called Entropy S to characterize changes in energy quality:

$$\Delta S = \frac{\Delta Q}{T}$$

- for a system of many bodies, $dS_{tot} = dS_1 + dS_2$
- if we describe heat flow, the energy increase of the cold body is greater than the entropy decrease of the hot body
- the exchanged Q is the same (with opposite signs), but the T at the denominator is different, and for the warmer body, being greater, the entropy change is smaller
- In an **isolated system** Entropy tends to a **maximum**

Thermodynamic potentials

- In Mechanics, system evolution is governed by Potential Energy minimization.
- In Thermodynamics we can define several potentials (i.e. state functions that drive system evolution) depending on the systems and its surrounding conditions:
    - Internal energy U
    - Entropy S (for isolated systems)
    - Enthalpy H (for closed systems)
    - Gibbs G and Helmholtz A free energy (for open systems)

Gibbs free energy

- It is a state function that represents a thermodynamic potential in transforms with constant temperature and pressure.
- It allows to state if a chemical reaction can occur spontaneously or not.
- $G = H - TS$: H enthalpy, T temperature and S entropy.

Gibbs free energy variations

- Variation in free energy:
  $\Delta G = \sum G(products) - \sum G(reactants)$
- 3 possible cases:
  - $\Delta G < 0$: spontaneous reaction
  - $\Delta G > 0$: non spontaneous reaction (additional energy required, e.g. through ATP)
  - $\Delta G = 0$: reaction at equilibrium
- Chemical reactions (at constant T and P) tend to **minimize** Gibbs free energy

spontaneous reactions due to entropy

- given the variation of both internal energy and entropy, some reactions might be spontaneous even when they would require energy from the environment
- this is the case for evaporation in dry air: it is favored by entropy, and takes energy away from the original system
- this is how sweat works

Biochemical reactions: enzymes and catalysis

- In biology, biochemical reactions may need an **activation energy**
- even if the total reaction is spontaneous ($\Delta G < 0$), there can be (almost always) an intermediate step that requires energy ($\Delta G > 0$ energy barrier).
- These barriers constitute **triggers** for the reaction to occur, since even if they are spontaneous their unperturbed kinetics can be very slow, so to make the reaction impossible.
- Enzymes are particular compounds (proteins, mRNA, chemicals) that act as *catalysts*, lowering the energy barrier and thus allowing the reaction to occur.
- Thus, cells, through the regulation of enzyme concentration, can regulate the **rate** of biochemical reaction advancement, allowing to **control** biological processes.

Entropy: statistical interpretation

- Statistical definition of entropy: link to the number of possible microscopic configurations W for a given macroscopic state (P, V, T).
- Statistically, the system achieves the macroscopic state that maximize the probability (count) of microscopic state configuration.

$$S = k \cdot log(W)$$

exercises

swimming in cold water

- a person is slowly swimming in cold water
- the skin temperature is around 35 °C
- the skin has a surface area of around $2m^2$
- the water temperature is 10 °C (ignore it warming up)
- fat has a thermal conductivity of $0.2W/(mK)$
- assuming a thickness of 6 mm of fat tissue,
- **how much heat is the person losing due to contact with the cold water?**

swimming in cold water - solution

- we can use the heat transfer equation.
- we can calculate the expression directly:

$$\frac{\Delta Q}{\Delta t} = \frac{K \cdot A \cdot \Delta T}{\Delta x}$$

  - thermal conductivity $K = 0.2W/(mK)$
  - thickness $\Delta x = 6 \cdot 10^{-3}m$
  - area $A = 2m^2$
  - temperature difference $\Delta T = 15$ °C
- the resulting heat flow is 1kW

meteorite in the bathtub

- A meteorite falls at high speed in a bathtub and warms it up
    - the meteorite has a mass o 0.1 Kg and a speed of 2000 m/s.
    - the bathtub has a size of 3m x 3m x 1m
    - the bathtub is filled with water (600 Joule per Kg per degree)
- **how much does the water warms up?**

meteorite in the bathtub - solution

- the increase in temperature is due to the kinetic energy of the meteorite is converted into the same amount of heat
- the kinetic energy is $\frac{1}{2}mv^2$
- that same amount of joules will become heat to warm up the water
- the change in temperature is related to the mass of the water: volume x density
- density $= 1000kg/m^3$
- volume $= 3 \cdot 3 \cdot 1 = 9m^3$
- $Q = mc\Delta T \Rightarrow \Delta T = \frac{Q}{m \cdot c}$