intro.pdf

GasProcesses.pdf

QuantumStatistics.pdf

Entropy.pdf

Ensembles.pdf

ThermodynamicPotentials.pdf

QuantumGases.pdf

LowTemperatureQuantumGases.pdf

RealGas.pdf

ElectromagneticField.pdf

ChemicalReactions.pdf

TransportPhenomena.pdf

Statistical physics is about the world of molecules

A few typical numbers

$$N = 6.022 \times 10^{23} \mathrm{mol}^{-1} \quad \text{Avogadro}$$

$$k = 1.38\ 10^{-23} \mathrm{JK}^{-1} = 1/11600\ \mathrm{eV/K} \quad \text{Boltzmann constant}$$

$$d = 0.1\mathrm{nm} \text{ typical molecular size}$$

$$\varepsilon = 1/50\mathrm{eV} \text{ typical kinetic energy}$$

$$v = 500\mathrm{ms}^{-1} \text{ typical velocity}$$

Please note, that since 2019 the Avogadro's number and the Boltzmann constant were redefined in the new SI system of units. These constants have now precisely fixed defined values (so they cannot be measured any more!)

Avogadro's number is exactly 6.02214076×10^{23} particles

Boltzmann constant is exactly 1.380649×10^{-23} J/K

Physics manifesto

(western civilization understanding of our world)

- We do **not** attempt for holistic approach to understand the world as a whole. We always identify a portion of universe, call it **“physical system”** and analyze it.
- It is possible to record a time instant snapshot of a physical system called **state of the system** (on paper, as a computer file,...) by recording a set of values of some physical quantities. From this record, the time instant of the system can be **completely reconstructed**, that means to calculate the “would-be” outcome of any measurement or observation of the system at that time instant
- The state of systems is generally changing with time either because of internal reasons or because of interaction with environment. **Time development** can be imagined as time sequence of states (better as a function which in any time provides the system state).
- The ambition of physics is to learn how to predict the time development of physical systems. We believe, it is possible. **It is possible to “forecast the future”.**
- The technology used to forecast the future are mathematical **equations of motion**. Often the equations of motion for a system are differential equations. We believe the time development of a system is found as (a unique) solution of the equations of motion satisfying the **initial condition**: knowing the state of a system at some (initial) time instant we aim to determine the future states.
- The words like “unique” and “predict” have to be **modified if quantum** mechanics has to be used to describe the system properly.

Physics manifesto

Classical (non quantum) point-like particle

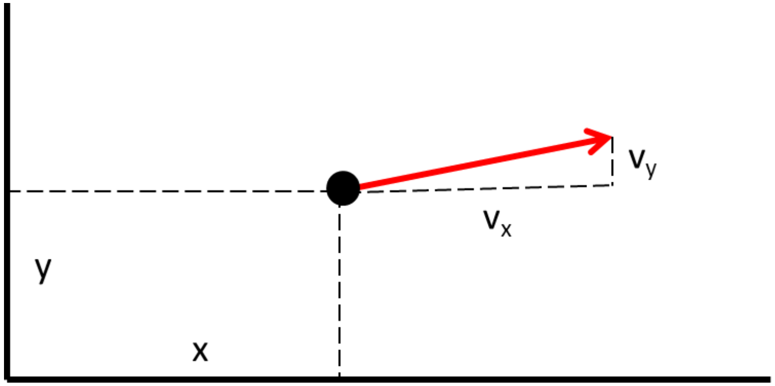
Particle state

- position $\{x, y, z\}$ (a point in the 3-dimensional space)
- velocity $\overrightarrow{v} = \{v_x, v_y, v_z\}$ (vector in the abstract space of velocities)

So the particle state can be represented by 6 numbers

$$\{x, y, z, v_x, v_y, v_z\}$$

It is a point in and abstract **6-dimensional space of states**



Physics manifesto

Classical (non quantum) point-like particle

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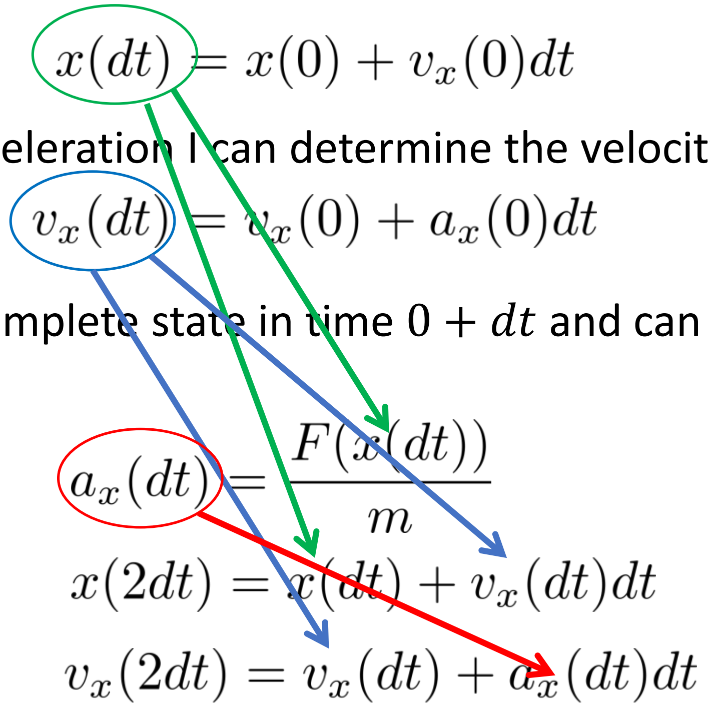
For a classical point-like particle the equation of motion is the Newton equation

$$\overrightarrow{a} = \frac{\overrightarrow{F}}{m}$$

For simplicity: one dimensional problem
Suppose I know $F_x(x)$ for all x, how I forecast the future?

- I know the initial state at t=0 $x(0), v_x(0)$
- I know $F(x(0))$
- Then, using Newton eq. I know the acceleration in time 0

$$a_x(0) = \frac{F(x(0))}{m}$$



- Knowing the initial velocity, I can determine the position after a short time interval dt.

$$x(dt) = x(0) + v_x(0)dt$$

- Knowing the acceleration I can determine the velocity in the new position

$$v_x(dt) = v_x(0) + a_x(0)dt$$

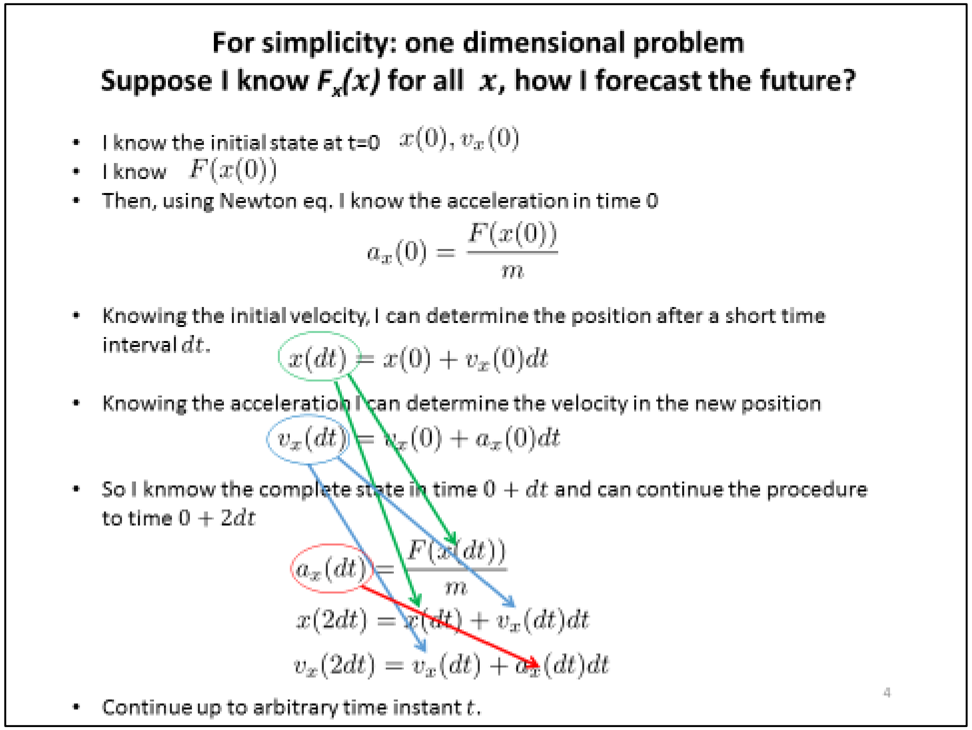
- So I know the complete state in time $0 + dt$ and can continue the procedure to time $0 + 2dt$

$$a_x(dt) = \frac{F(x(dt))}{m}$$

$$x(2dt) = x(dt) + v_x(dt)dt$$

$$v_x(2dt) = v_x(dt) + a_x(dt)dt$$

- Continue up to arbitrary time instant t.



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- Continue up to arbitrary time instant t.

Newtonian mechanics is enough to handle any (non-quantum) system made of particles. **But only in principle**. Real systems around us are often made of huge amount of particles, of the order of 10^{26}.

It is just technically impossible to write down a state using 10^{26} numbers and then solve 10^{26} differential equations simultaneously.

However, practical problems can still be handled using statistical methods. This is where **statistical physics** was born.

Statistical physics manifesto

- we have to handle systems with huge number of degrees of freedom $\approx 10^{26}$
- exact physical state of such a system ($\approx 10^{26}$ numbers) is called a **microstate**
- a complete information on microstate is experimentally unfeasible
- experimentally in a state of a large system we have just a few values of macroscopically measurable physical quantities
- these macroscopic numbers define what we call a **macrostate**
- macrostate is just drastically reduced information on microstate
- we have to live with the fact that we just know a macrostate instead of a microstate. Still, we want to “forecast the future” at least on the level of macrostates
- the technique how we handle macrostates in physics is statistics
- we know the macrostate, but the system is in fact in some unknown microstate
- there is tremendously huge number of microstates compatible with our information on macrostate
- a particular macrostate can be realized by tremendously huge number of different microstates. This set of compatible microstates is called a **statistical ensemble**. We shall see that the number of microstates in an ensemble is of the order $10^{10^{26}}$.
- We imagine a procedure which virtually forecast the future of each microstate from the ensemble, make a virtual average and get the average characteristics of the final macrostate which we assume will be the final macrostate of our particular initial macrostate.

Statistical physics manifesto

How do we know this:

- we have to handle systems with huge number of degrees of freedom $\approx 10^{26}$
- for a system with $\approx 10^{26}$ degrees of freedom there exist $\approx 10^{10^{26}}$ different microstates which cannot ne macroscopically distinguished from each other

At the beginning of the 19th century, we discovered that matter around us is composed of atoms and molecules and. Typical number of atoms or molecules is (by the rough order of magnitude) 10^{26}.

The major breakthrough was achieved by changing alchemy to chemistry essentially by introducing quantitative chemical recipes.

Here important phenomenological laws were discovered

- law of definite proportions
- law of multiple proportions
- Avogadro’s law

Beautiful collection of historical papers on these topics can be found here:
http://web.lemoyne.edu/~giunta/papers.html#atomic

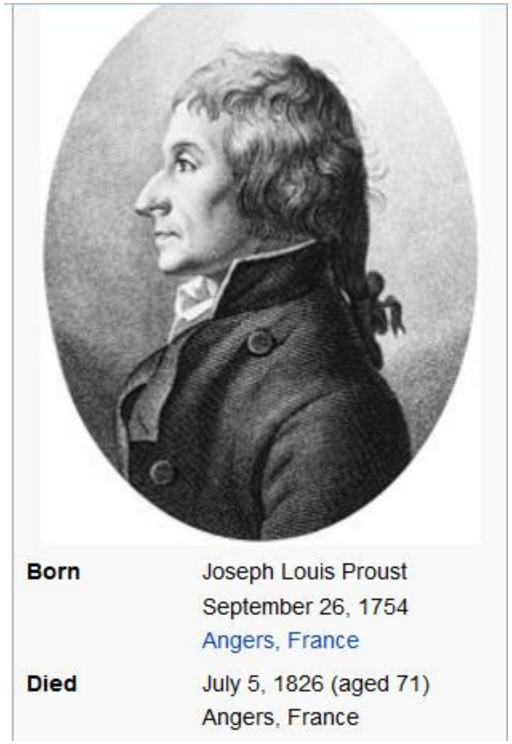
The law of definite proportions, sometimes called Proust's Law, states that a chemical compound always contains exactly the same proportion of elements by mass. This observation was first made by the French chemist **Joseph Proust**, based on several experiments conducted between 1798 and 1804.

In chemistry, the law of multiple proportions is one of the basic laws of stoichiometry used to establish the atomic theory, alongside the law of conservation of mass and the law of definite proportions. It is sometimes called Dalton's Law after its discoverer, the English, who published it in the first part of the first volume of his "New System of chemist **John Dalton** Chemical Philosophy" (1808). The statement of the law is:

If two elements form more than one compound between them, then the ratios of the masses of the second element which combine with a fixed mass of the first element will be ratios of small whole numbers.

Consider the difference between "chemical recipes" and "cooking recipes":
If the "chemical recipe says" take 1g hydrogen + 7.94 g oxygen and you get water than you cannot take 1g hydrogen + 10 g oxygen and hope to get "somewhat more dense water". What you observe is water and 2.06 g of "unused" oxygen.
This is different from "cooking recipes". If it says take 4 eggs and 200 g of flour to get pancakes, you can take 220 g of flour and still get pancakes but somewhat more dense.

A few slides follow on people who change alchemy to chemistry



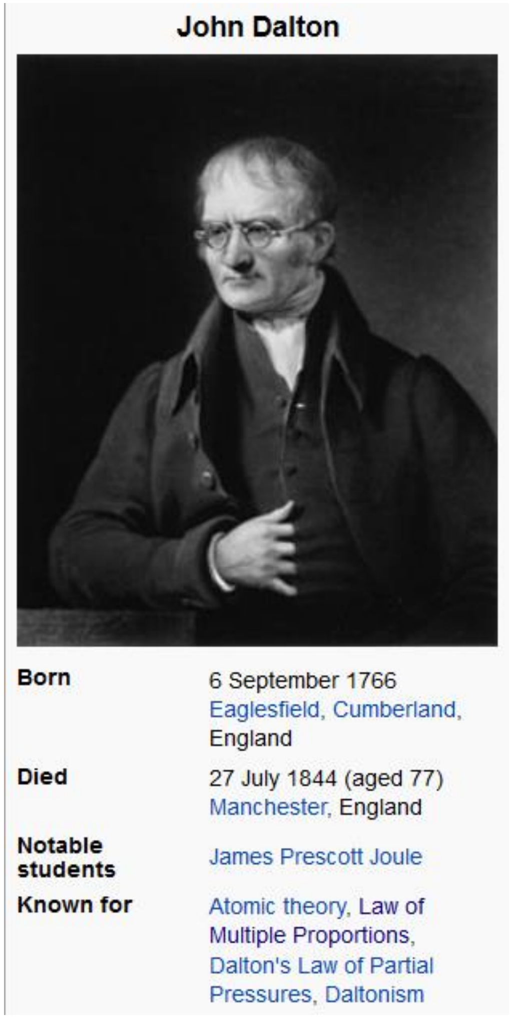
Born	Joseph Louis Proust September 26, 1754 Angers, France
Died	July 5, 1826 (aged 71) Angers, France

http://en.wikipedia.org/wiki/Joseph_Proust

Proust's best known work was derived from a controversy with C.L. Berthollet. Berthollet did not believe that substances always combine in constant and definite proportions as Proust did. Proust eventually was able to prove Berthollet wrong in 1799 and published his own hypothesis.

law of definite proportions, which is sometimes also known as Proust's Law

chemical compound always contains exactly the same proportion of elements by mass.



John Dalton

Born	6 September 1766 Eaglesfield, Cumberland, England
Died	27 July 1844 (aged 77) Manchester, England
Notable students	James Prescott Joule
Known for	Atomic theory, Law of Multiple Proportions, Dalton's Law of Partial Pressures, Daltonism

http://en.wikipedia.org/wiki/John_Dalton

He is best known for his pioneering work in the development of modern atomic theory, and his research into color blindness (sometimes referred to as Daltonism, in his honor).

In chemistry, the law of multiple proportions is one of the basic laws of stoichiometry used to establish the atomic theory, alongside the law of conservation of mass (matter) and the law of definite proportions. It is sometimes called Dalton's Law after its discoverer, the English chemist John Dalton, who published it in the first part of the first volume of his "New System of Chemical Philosophy" (1808). The statement of the law is:

If two elements form more than one compound between them, then the ratios of the masses of the second element which combine with a fixed mass of the first element will be ratios of small whole numbers.

In 1803 Dalton orally presented his first list of relative atomic weights for a number of substances. This paper was published in 1805, but he did not discuss there exactly how he obtained these figures.

Antoine Lavoisier

Line engraving by Louis Jean Desire Delaistre, after a design by Julien Leopold Boilly

Born	26 August 1743 Paris, France
Died	8 May 1794 (aged 50) Paris, France

http://en.wikipedia.org/wiki/Lavoisier

It is generally accepted that Lavoisier's great accomplishments in chemistry largely stem from the fact that he changed the science from a qualitative to a quantitative one. Lavoisier is most noted for his discovery of the role oxygen plays in combustion.

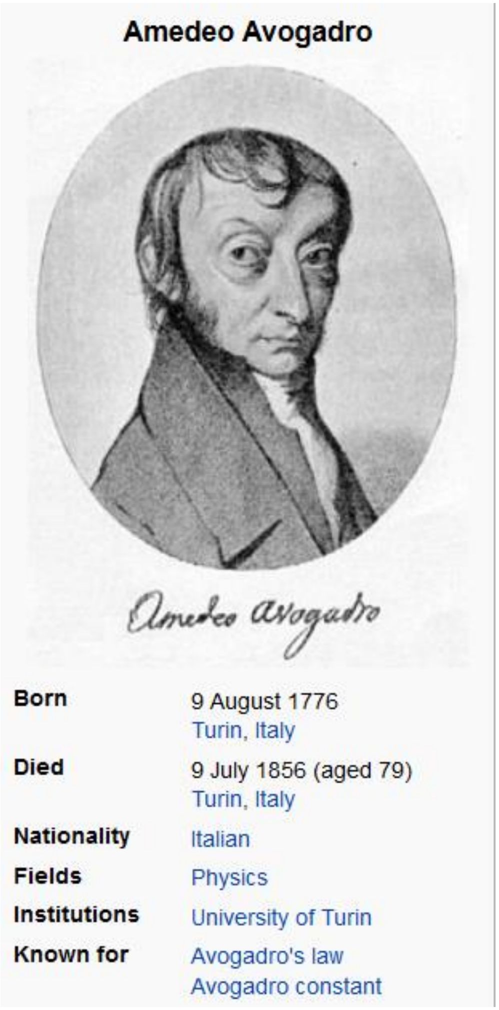
He recognized and named oxygen (1778) and hydrogen (1783)

At the height of the French Revolution, he was accused by Jean-Paul Marat of selling adulterated tobacco and of other crimes, and was eventually guillotined

Lavoisier's experiments supported the law of conservation of mass. In France it is taught as Lavoisier's Law and is paraphrased from a statement in his "Traité Élémentaire de Chimie" to "Rien ne se perd, rien ne se crée, tout se transforme." ("Nothing is lost, nothing is created, everything is transformed."). Mikhail Lomonosov (1711–1765) had previously expressed similar ideas in 1748 and proved them in experiments; others whose ideas pre-date the work of Lavoisier include Jean Rey (1583–1645), Joseph Black (1728–1799), and Henry Cavendish (1731–1810).

His Traité élémentaire de chimie (Elementary Treatise on Chemistry), published in 1789. This work represents the synthesis of Lavoisier's contribution to chemistry and can be considered the first modern textbook on the subject.

Lavoisier's Laboratory, Musée des Arts et Métiers, Paris



Amedeo Avogadro

Amedeo Avogadro

Born	9 August 1776 Turin, Italy
Died	9 July 1856 (aged 79) Turin, Italy
Nationality	Italian
Fields	Physics
Institutions	University of Turin
Known for	Avogadro's law Avogadro constant

http://en.wikipedia.org/wiki/Amedeo_Avogadro

He is most noted for his contributions to molecular theory, including what is known as Avogadro's law. In tribute to him, the number of elementary entities (atoms, molecules, ions or other particles) in 1 mole of a substance, $6.02214179(30) \times 10^{23}$, is known as the Avogadro constant

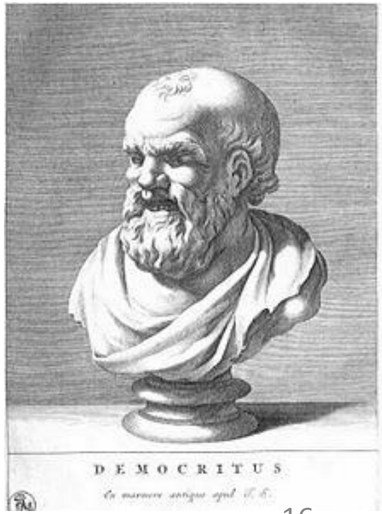
For an ideal gas, the volume and amount (moles) of the gas are directly proportional if the temperature and pressure are constant. In 1811, he published an article with the title Essai d'une manière de déterminer les masses relatives des molécules élémentaires des corps, et les proportions selon lesquelles elles entrent dans ces combinaisons ("Essay on Determining the Relative Masses of the Elementary Molecules of Bodies and the Proportions by Which They Enter These Combinations"), which contains Avogadro's hypothesis

Atomic hypothesis solves the enigma why “The law of definite proportions” (why chemical recipes are so strict with respect to cooking recipes). If “chemical cooking “ is just combining elementary discrete atoms then it is possible that 2 atoms of hydrogen combine with 1 atom of oxygen, but it is not possible that 2 atoms of hydrogen combine with 2.12 atoms of oxygen.

Combining stoichiometric rules are automatically rules of whole numbers

This automatically also solves the enigma why “the law of multiple proportions “ that is why the ratios of mass ratios are ratios of whole numbers.

In textbooks the atomic hypothesis is traced back to ancient Greeks (Democritus)



It is obvious that classical atomists would never have had a solid empirical basis for our modern concepts of atoms and molecules. Bertrand Russell states that they just hit on a lucky hypothesis. Well, maybe the belief that the observed immense diversity of the world around us should be based on simple principles gives you an “atomic hint” as a **LEGO principle**. Because of the combinatorial explosion you can build from just a few types of elementary LEGO blocks very diverse objects.

experiment:
1g hydrogen + 7.94 g oxygen = 8.94 g water
5g hydrogen + 39.68 g oxygen = 44.68 g water

$$\frac{1}{7.94} = \frac{5}{39.68}$$

The law of definite proportions

Experiment:
1g hydrogen + 15.87 g oxygen = 16.87 g hydrogen peroxide

$$\frac{\frac{1}{7.94}}{\frac{1}{15.87}} = 2.00$$

law of multiple proportions

Simplest atomic interpretation: water= HO, peroxide = HO_2

Experiment:
100 g iron + 28.65 g oxygen = 128.65 g iron oxide called wüstite
100 g iron + 42.98 g oxygen = 142.98 g iron oxide called hematite

$$\frac{\frac{100}{28.65}}{\frac{100}{42.98}} = 1.50 = \frac{3}{2}$$

Simplest atomic interpretation: wüstite = FeO, hematite = Fe_2O_3

Reminder:
1g hydrogen + 7.94 g oxygen = 8.94 g water
Simplest atomic interpretation: water= HO, peroxide = HO_2

Conclusion:
I atomic weight of hydrogen is assigned to be 1, than
atomic weight of O is 7.94
atomic weight of Fe is $100 \times \frac{7.94}{28.65} = 27.71$

Experiment:
10g oxygen + 7.56 g carbon = 17.51 g carbon oxide called carbonyl
10g oxygen + 3.78 g carbon = 44.68 g carbonic oxide

Simplest atomic interpretation: carbonyl = CO, carbonic oxide = CO_2

Atomic weight od carbon = $7.56 \times \frac{7.94}{10} = 6.00$

In this way we can in principle continue to include more chemical recipes and formulate more hypotheses on stoichiometric composition of molecules. The stoichiometric hypotheses, however, are not unambiguous and we can easily get wrong atomic weights, as we got here:
H ...1, O...7.94, C...6
Everybody today knows, that these numbers are wrong although the chemists originally considered them as right.
The way towards obtaining correct atomic weights was more complicated.

Solution of the problem is not simple:

atomic hypothesis of non-divisible atoms as combining to chemical products has to be corrected: even simple chemical elements like hydrogen or oxygen are made of not single atoms but molecules which are build from elementary atoms.

Hypothesis which leads to good stoichiometry is hydrogen and oxygen molecules are two-atomic, then water is H_2O , not HO and methane is CH_4.

Question:
If the chemical reactions are just combinations of the integer numbers of atoms, why only ratios of mass ratios are ratios of small integers and not the mass ratios themselves?

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Answer:
If the recipe for “standard fruit salad” is take 3 apples and 3 oranges, then the mass ratios of apples and oranges is not equal to 1:1 because an orange had different mass than an apple, so the mass ratio for this recipe might be 1:1.2.
But if the recipe for “French fruit salad” is take 3 apples and 6 oranges then the ratio of ratios would be

$$\frac{1/1.2}{1/2.4} = 2:1$$

Question:

Then why very often even the ratios of masses are close to ratios of integers, like for water 1g hydrogen + 7.94 g oxygen gives water, thus the mass ratio is almost 1:8?

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Answer:

This suggests that there might be integer numbers involved below the level of atoms, some “atomic principle” in the word of atoms. And indeed, there are particles inside the atoms: protons, neutrons and electrons. The trick is that protons and neutrons have almost equal masses (apples and oranges having equal mass) and electrons have negligible mass so ratios of masses of atoms are close to ratios of integers.

Questions:

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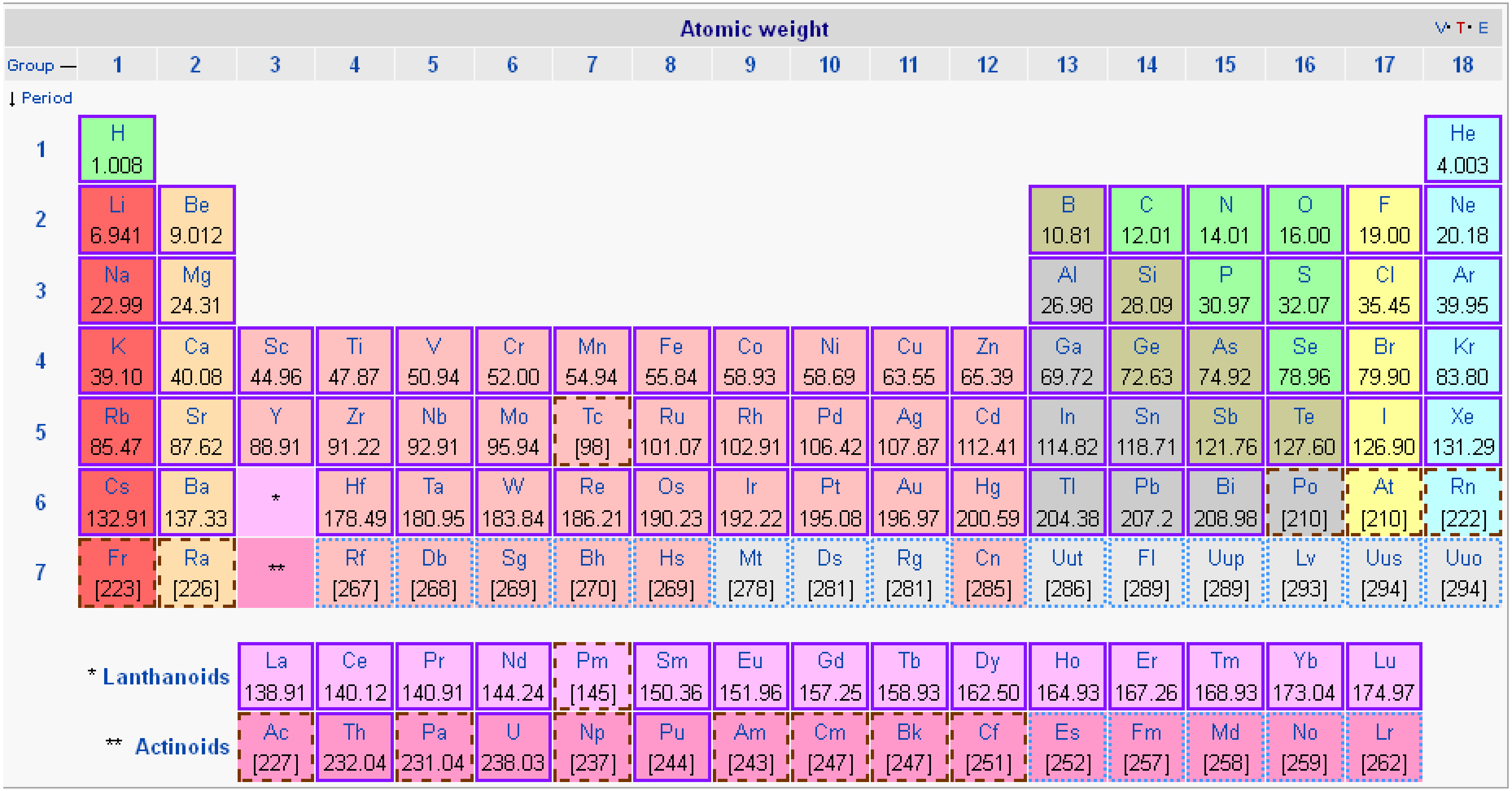
Question:

Then why sometimes the chemical mass ratios are sometimes significantly different from ratios of (small) integers?

Answer:

Mainly because the chemists find their input ingredients in nature, and these are mixtures of different isotopes, 76% of chlorine atoms have 18 neutrons, 24% have 20 neutrons. So an “average” chlorine atom has something like 18.48 neutrons, thus significantly non-integer atomic weight of “natural” chlorine 35.45.

Finding atomic weights from chemical recipes is a puzzle to be solved by making hypotheses on stoichiometry and checking that atomic weight thus found are consistent



Atomic weight

Group — ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1.008																	He 4.003
2	Li 6.941	Be 9.012											B 10.81	C 12.01	N 14.01	O 16.00	F 19.00	Ne 20.18
3	Na 22.99	Mg 24.31											Al 26.98	Si 28.09	P 30.97	S 32.07	Cl 35.45	Ar 39.95
4	K 39.10	Ca 40.08	Sc 44.96	Ti 47.87	V 50.94	Cr 52.00	Mn 54.94	Fe 55.84	Co 58.93	Ni 58.69	Cu 63.55	Zn 65.39	Ga 69.72	Ge 72.63	As 74.92	Se 78.96	Br 79.90	Kr 83.80
5	Rb 85.47	Sr 87.62	Y 88.91	Zr 91.22	Nb 92.91	Mo 95.94	Tc [98]	Ru 101.07	Rh 102.91	Pd 106.42	Ag 107.87	Cd 112.41	In 114.82	Sn 118.71	Sb 121.76	Te 127.60	I 126.90	Xe 131.29
6	Cs 132.91	Ba 137.33	*	Hf 178.49	Ta 180.95	W 183.84	Re 186.21	Os 190.23	Ir 192.22	Pt 195.08	Au 196.97	Hg 200.59	Tl 204.38	Pb 207.2	Bi 208.98	Po [210]	At [210]	Rn [222]
7	Fr [223]	Ra [226]	**	Rf [267]	Db [268]	Sg [269]	Bh [270]	Hs [269]	Mt [278]	Ds [281]	Rg [281]	Cn [285]	Uut [286]	Fl [289]	Uup [289]	Lv [293]	Uus [294]	Uuo [294]
* Lanthanoids			La 138.91	Ce 140.12	Pr 140.91	Nd 144.24	Pm [145]	Sm 150.36	Eu 151.96	Gd 157.25	Tb 158.93	Dy 162.50	Ho 164.93	Er 167.26	Tm 168.93	Yb 173.04	Lu 174.97	
** Actinoids			Ac [227]	Th 232.04	Pa 231.04	U 238.03	Np [237]	Pu [244]	Am [243]	Cm [247]	Bk [247]	Cf [251]	Es [252]	Fm [257]	Md [258]	No [259]	Lr [262]	

What are the reasons for non-integer atomic masses of natural elements?

- isotopic proportions
- non-equality of proton and neutron mass
- binding energy of nucleus: the mass of a nucleus the sum of masses of protons and neutrons minus the binding energy divided by c^2 (according to famous Einstein formula).
- non-negligible mass of electrons

Avogadro’s law

The law is named after Amedeo Avogadro who, in 1811, hypothesized that two samples of ideal gases, of the same volume and at the same temperature and pressure, contain the same number of molecules.

This law is a direct consequence of observation (Guy-Lussac, 1908) that chemical recipes expressed (for gases at equal pressure and temperature) not by gas masses but by gas volumes say that the volume ratios themselves are ratios of small integers (no need to do ratios of ratios).

It looks like saying that gasses of apples and oranges have the same volume. Since it is not plausible to assume that the sizes of atoms themselves are equal, it is natural to assume that **gas is presumably “empty space”,** so that careful distinction must be drawn between the volume *available to a particle* and the *volume of a particle*. Avogadro says, that **the volume available to a particle is the same for all particles while the total volume of particles is negligible (at usual conditions).**

Avogadro’s law has immediate consequence for elementary stoichiometry.

The chemical recipe for water expressed in volumes is

1 liter of hydrogen + 0.5 liter of oxygen gives 1 liter of water vapor

Since 1 liter of hydrogen has the same number of molecules than 1 liter of water vapor, there would be not enough molecules of oxygen to mate with hydrogen molecules in just 0.5 liter of oxygen. If each hydrogen particle (molecule) has to find its oxygen particle to mate with, the original oxygen particles must be somehow torn to two pieces to satisfy the Avogadro’s law.
Therefore the oxygen gas has two-atomic molecules and the stoichiometry for water reads

$$2H_2 + O_2 = 2H_2O$$

The mole

So far we have expressed the chemical recipes either in masses or in volumes. However since integer number of particles take part in the reaction, it would be most natural to express chemical recipes in integer numbers.

In fact, this is done in the stoichiometric expressions like

$$2H_2 + O_2 = 2H_2O$$

But experimentally not acceptable to read the recipe as “Take two molecules of hydrogen and let it react with one molecule of oxygen and you get one molecule of water”.

We need to work with very big numbers of molecules. Big numbers are usually given special names like million, billion etc. These are still too small numbers for practical chemical recipes. Practical big number would be for example 10^{23}.
One could call this number “chem” and the recipe would be “take two chems of hydrogen and one chem of oxygen and you get two chems of water.
This is again impractical, because an assistant cannot take “one chem” of atoms just counting them one, two, three, four, ..., chem.

But we know how to make it practical:

If we have to buy something like 10000 nails, the shop assistant do not start to count like one, two, three, four,... ,10000. Instead he counts something like 100 nails, then weights (determines the mass) of 100 nails and then gives you nails having 100 times larger mass.

And actually if you are experienced carpenter you go to the shop and ask directly for 10 kg of nails, because you have once counted the nails by the above described method.

So do the chemists, just they do not use “chems” but “moles”.

The old definition of one mole was: it is the amount of particles which is the same as the amount of molecules in 12 g of carbon isotope 12.

Since 2019 the SI system of units was reformulated, the new valid definition of mole is this: The mole (symbol: mol) is the base unit of amount of substance , defined as exactly 6.02214076×10^{23} particles, e.g., atoms, molecules, ions or electrons. The number of particles in one mole is called Avogadro’s number.
It took some time to count the number of molecules in one mole defined in the old way, Perrin has got the Nobel price for that, his Nobel lecture is worth to read (http://www.nobelprize.org/nobel_prizes/physics/laureates/1926/perrin-lecture.html).

Avogadro’s number by counting atoms

So today, measuring the Avogadro’s number is not a well-defined task, its value is just determined by definition. What one can do instead is to measure the mass of the carbon sample containing just one mole of molecules.
We have said something like “an assistant cannot take ‘one chem’ of atoms just counting them one, two, three, four, ..., chem. It is not quite true. **We can “check the Avogadro’s number” by really counting individual atoms**.

The idea is to count individual radioactive decays using a sample of radioactive element with known half-life.

Of course, we cannot take a sample having several grams and counting the clicks of some detectors. We would not distinguish individual decays if the half-life is small or we would have to run the experiment for time exceeding the cosmic age.

The idea is to use very small samples with short life times. It is possible in principle to prepare extremely small samples of radioactive liquid easily. The technique is called homeopathic dilution. Take 1 g of radioactive liquid, add 1 g pure water, stir, throw away 1 g of solution. Add 1 g of pure water, stir, throw away 1g. Repeat several times. After N repetitions you would have $1g/2^N$ radioactive matter in the solution. This can be a very very small number. You could really observe individual decays and count them. If you run the experiment for one halftime, you know the number of radioactive atoms in the solution. If you know the molecular weight you can check the consistency with Avogadro’s number.

Let’s repeat, the points of the “statistical physics manifesto”

- We want to “forecast the future” at least on the level of macrostates
- The technique how we handle macrostates in physics is statistics
- We know the macrostate, but the system is in fact in some unknown microstate
- There is tremendously huge number of microstates compatible with our information on macrostate
- A particular macrostate can be realized by tremendously huge number of different microstates. This set of compatible microstates is called a **statistical ensemble**. We shall see that the number of microstates in an ensemble is of the order $10^{10^{26}}$.
- We imagine a procedure which virtually forecast the future of each microstate from the ensemble, make a virtual average and get the average characteristics of the final macrostate which we assume will be the final macrostate of our particular initial macrostate.

What justifies usage of the mean value as a reliable prediction?

The mean value can be a good strategy **if it is very “sharp”**. To observe a microstate with value significantly different from the mean value is in fact highly improbable. So if you want to “survive in the jungle”, the best advice is to “**believe to mean values**”. If you meet something different, well, it’s just a bad luck.

We shall argue, that such a bad luck is very, very, very improbable.

To demonstrate the “dominance of the mean value” let’s consider the following problem “from the jungle”.
I want to open door to entre into the room behind. Well, should I do it? It may happen in principle, that all the molecules of the air inside will, by chance, be all located in the opposite half of the room and I would suffocate. Is that a real danger?

Well, no danger at all. The mean value 1:1(division of the molecules between the two halves) is so dominant, that I never find even a tiny difference in pressure between the two halves.

We shall demonstrate it using a highly simplified model.

Let’s assume that each molecule has just two possible states to choose from: be in the left half of the room or in the right half. We shall neglect velocities and the detailed positions of the molecules.

Let’s calculate the probability $p(n)$, to find exactly n molecules left and $N-n$ molecules right.

Note: we have to assume the particles to be distinguishable, since our assumptions are too crude to be used for undistinguishable particles.

Obviously:

$$p(n) = \binom{N}{n} \frac{1}{2^n}$$

Stirling formula

$$\ln n! \approx n \ln n - n + \frac{1}{2} \ln(2\pi n)$$

$$\ln p(\frac{N}{2}) \approx N \ln N - N + \frac{1}{2} \ln(2\pi N) \quad -2(\frac{N}{2} \ln \frac{N}{2} - \frac{N}{2} + \frac{1}{2} \ln(2\pi \frac{N}{2})) - N \ln 2$$

$$\ln p(\frac{N}{2}) \approx \frac{1}{2} \ln(2\pi N) - 2\frac{1}{2} \ln(2\pi \frac{N}{2}))$$

$$\ln p(\frac{N}{2}) \approx -\frac{1}{2} \ln(2\pi N) + \ln 2$$

$$p(\frac{N}{2}) \approx \sqrt{\frac{2}{\pi N}}$$

Oh! This looks like a disaster. For large N the probability to find half of the particles in the left half of the room is almost zero!

But wait! What we have calculated is the probability for **exactly half of the particles in half of the room.** This is not something we are interested it in order not to suffocate. What we need is the probability to find something like

$$0.999 \times \frac{N}{2} < n < 1.001 \times \frac{N}{2}$$

But even the above inequality describes "too many n-s". All those states cannot have the probability roughly equal to the probability of $n = \frac{N}{2}$, since there is too many of them. There are $0.002 \times \frac{N}{2}$ such states and if each of them had the probability

$$p(\frac{N}{2}) \approx \sqrt{\frac{2}{\pi N}}$$

their summary probability would be

$$p \approx 0.002 \frac{N}{2} \sqrt{\frac{2}{\pi N}} \approx 0.00005 \sqrt{N} \gg 1$$

Let's be more exact and calculate also the probabilities for n slightly different from $\frac{N}{2}$.

$$
\begin{aligned}
\ln p(n) \approx\ & N \ln N - N + \frac{1}{2}\ln(2\pi N) \\
& - \left(n \ln n - n + \frac{1}{2}\ln(2\pi n)\right) \\
& - \left((N-n)\ln(N-n) - (N-n) + \frac{1}{2}\ln(2\pi(N-n))\right) \\
& - N \ln 2
\end{aligned}
$$

denoting n=N/2+x

$$
\begin{aligned}
\ln p(n) \approx\ & N \ln N - N + \frac{1}{2}\ln(2\pi N) \\
& - \left((N/2+x)\ln(N/2+x) - (N/2+x) + \frac{1}{2}\ln(2\pi(N/2+x))\right) \\
& - \left((N/2-x)\ln(N/2-x) - (N/2-x) + \frac{1}{2}\ln(2\pi(N/2-x))\right) \\
& - N \ln 2
\end{aligned}
$$

Taylor series in x to the second order gives

$$
\ln p(n) \approx -\frac{1}{2}\ln\frac{N\pi}{2} + \frac{(2-2N)x^2}{N^2}
$$

so for large N we get

$$p(n) \approx \frac{1}{\sqrt{\frac{N\pi}{2}}} \exp(-\frac{(n-N/2)^2}{N/2})$$

$$\begin{aligned} P = p(n > (1+10^{-3})N/2)) &\approx \sum_{(1+10^{-3})N/2}^{N} \frac{1}{\sqrt{\frac{N\pi}{2}}} \exp(-\frac{(n-N/2)^2}{N/2}) \\ &\approx \int_{(1+10^{-3})N/2}^{N} \frac{1}{\sqrt{\frac{N\pi}{2}}} \exp(-\frac{(n-N/2)^2}{N/2}) dn \end{aligned}$$

We have approximated the required sum by an integral, but even the integral cannot be evaluated exactly. What we did is we have approximated the binomial distribution by Gauss distribution. We shall discuss Gauss distributions later it these series of lectures

$$P \approx \int_{(1+10^{-3})N/2}^{\infty} \frac{1}{\sqrt{\frac{N\pi}{2}}} \exp(-\frac{(n-N/2)^2}{N/2})dn - \int_{N}^{\infty} \frac{1}{\sqrt{\frac{N\pi}{2}}} \exp(-\frac{(n-N/2)^2}{N/2})dn$$

$$P \approx \int_{10^{-3}N/2}^{\infty} \frac{1}{\sqrt{\frac{N\pi}{2}}} \exp(-\frac{x^2}{N/2})dx - \int_{N/2}^{\infty} \frac{1}{\sqrt{\frac{N\pi}{2}}} \exp(-\frac{x^2}{N/2})dn$$

$$P \approx \int_{10^{-3}\sqrt{N/2}}^{\infty} \frac{1}{\sqrt{\pi}} \exp(-\xi^2)d\xi - \int_{\sqrt{N/2}}^{\infty} \frac{1}{\sqrt{\pi}} \exp(-\xi^2)d\xi$$

$$P \approx \frac{1}{2}\mathrm{erfc}(10^{-3}\sqrt{N/2}) - \frac{1}{2}\mathrm{erfc}(\sqrt{N/2})$$

Where erfc() is a special function (complementary error function, consult Wikipedia at http://en.wikipedia.org/wiki/Error_function), which has the following asymptotic behavior for large x

$$\mathrm{erfc}(x) \approx \frac{1}{x\sqrt{\pi}} \exp(-x^2)$$

for N=10^{23} we get $P \approx \exp(-5 \times 10^{16})$

That is the probability to find air pressure by more than 1 per mill higher than it should be. We can really rely on the mean value! Our universe is just exp(40) seconds old!

So let's estimate what can be a typical difference between the actual number and the mean number of molecules in the left compartment. The probability is given as

$$p(n) \approx \frac{1}{\sqrt{\frac{N\pi}{2}}} \exp(-\frac{(n - N/2)^2}{N/2})$$

So for what values of n the probability drops significantly as compared to the probability of the mean value $\frac{N}{2}$. Clearly it is a value for which the argument in the exponential function will be of the order of -1. This happens for

$$n \approx \frac{N}{2} \pm \sqrt{\frac{N}{2}}$$

Numerically we get something like

$$n \approx 10^{23} \pm 3 \times 10^{11}$$

So the number of molecules in the left part is constant up to some 12 most significant digits. Really fairly narrow variance with respect to the mean value.

Do remember the result:

Typical value is of the order N, typical deviation is of the order $\sqrt{N}$

Let’s summarize our findings:

- mean value of molecules in the left part(as calculated over all the possible microstates) is, as expected $\frac{N}{2}$.
- typical deviation is of the order $\sqrt{N}$

What is the reason for getting this result:

Big numbers!

The number of molecules is typically $N \sim 10^{23}$, a big number

The number of possible microstate was $2^N \sim 2^{10^{23}}$ a tremendously big number!

This situation is typical for statistical physics, we meet there three typical numerical values

- **normal numbers like 1, 4, 10^6**
- **big numbers like 10^{23}, typically number of molecules**
- **tremendously big numbers like $10^{10^{23}}$, typically number of possible microstates**

Random variables
discrete and continuous

States, variables, events

We shall not discuss here, what we mean by “physical system” and “the state of a physical system”
Physical variable is roughly any value which characterizes the state of some system, this value can be usually obtained by some measurement. For definiteness one can imagine some measuring apparatus with a digital display. The apparatus is somehow connected to the system and presents a value on its display: this is the value of the variable measured by that apparatus.

In classical physics the value of any variable is fully determined by the actual state (microstate) of the system, in quantum physics the value measured by some apparatus is not fully determined by the current state.

Obtaining a value of a physical variable needs two things

- obtaining a state
- applying the relevant measuring apparatus to the obtained state

These two “things” together we shall call **event.**

Random events

Sometimes events (= state + measurement) appear to be (or really are) random.

In classical physics everything is in principle deterministic, no space for “true randomness” there. Still, we are speaking about random events in classical physics as well.
What we mean by that? We usually assume that physics experiment should be reproducible, that is starting two experiments in exactly same conditions (same state and same environment) the outcome (event) should be the same.

Very often this is not so, the keyword in the preceding sentence is “exactly”. We simply do not have the initial conditions under the absolute control, so the initial conditions are usually at least “slightly different”. Sometimes a slight difference in the initial conditions can lead to significant difference in the outcome (event) Then the event looks random, even if there is no true randomness in the game.

In quantum mechanics, according to our present state of knowledge, there is true randomness in the measurement process. Measurements on two exactly same states can give different results. Knowing the state exactly, we still cannot deterministically predict the outcome of a measurement, we can only give probabilities for obtaining different values.

Random variables

If events (= state + measurement) are random, then the values obtained by measurement are also random, we speak about random variables.

Be careful and distinguish between event and variable. A variable (even if it is a multidimensional variable) need not characterize the event completely. There might be, for example, two states, giving the same value for the variable considered. So there are two different events having the same value of the variable.

So discussing random variables, we have to keep in mind, that the primary notion is random event and random variable is a value (maybe multidimensional) shown in that random event.

In what follows we shall distinguish two types of random events

- discrete
- continuous

In various texts people often do not distinguish between random events and random variable values. Especially for continuous events the **event identity** (event name) is often **given by a value of some (random) variable** if the correspondence between the event and the variable value is one-to-one. Even this, however, allows that more then one variable can be associated with the event.

From now on in this lecture, we shall consider classical (non-quantum) random events, that is an event is identical to the state. This can be done since the outcome of measurements is fully determined by the state

Discrete and continuous random events

In any physical experiment, which can lead to random events, we have to identify

the set of all possible events

which can be the outcome of that experiment.

The set of possible events may be
- finite or countable
- uncountable (for our purposes with the cardinality of continuum)

Using somewhat less precise language we shall use the notions of
- discrete random events
- continuous random events

To work with probabilities we need unique characterization (naming) of each event. Very often we use as names some numbers, but it is not essential, it is just practical
To identify (name) a discrete event, we can use integers. The continuous events cannot be named by integers, we have to use real numbers. To respect some natural structure of the set of continuous events we often use n-tuples off real numbers and we speak about n-dimensional random (continuous) variable.

Discrete and continuous random events

It is always good to have in mind some specific examples

Discrete random event:
throwing a dice

Continuous random event:
throwing a dart

If the tip of the dart is absolutely sharp, then it hits just an ideal point of the dartboard, so the event set is continuous.

Discrete and continuous random variables

According to the definition

event = state + measurement;

if the event set is discrete then the set of all possible variable values is also discrete, so we speak about discrete random variable

if the event set is continuous, the set of variable values might be discrete, but the mathematical treatment we should use is that of continuous random variables in any case

Naming the events

To identify the events we give them names. Very often we choose some specific variable which uniquely characterizes the event and use the variable value as a name. This variable looks as privileged among other variables, but it is not quite so: the variable just plays two roles.

Probability technology: Discrete random variables

Discrete random variables

Each event in the discrete set can be given a specific name. But since the whole set is countable, the events can also be enumerated or listed, even if the list might be infinite. Enumerability does not mean that we can actually write down the whole infinite list of names, but rather that we can write down a name at any wanted specific position in the list. In principle we can use integers to give names to any countable items, so the list of all the names of an infinite countable sets is just a list of all integers.

Probability technology requires, that we can assign a probability to any random event form the list. We shall not define exactly what is the probability, just that any probability is a nonnegative real number and the sum of all the probabilities of events from the list is equal to 1.

If we denote the names (imagine integers) of the events as i, the probabilities as $p(i)$, we get the conditions

$$p(i) \geq 0 \quad \sum_i p(i) = 1$$

The assignment of probabilities can be imagined as a table. For example for our dice example we might get

i	$p(i)$
1	0.15
2	0.15
3	0.15
4	0.15
5	0.15
6	0.25

We see, that the probabilities are not equal to each other, so the dice is not fair. How we can get (or at least estimate) the probabilities of discrete events? We perform N experiments and observe how many times (N_i) the event i happens. Then

$$p(i) \approx \frac{N_i}{N}$$

Now we shall discuss the variables. So the event i (with the measurement of the variable x (number-of-points) gave the value x_i.

i	$p(i)$	x_i
1	0.15	1
2	0.15	2
3	0.15	3
4	0.15	4
5	0.15	5
6	0.25	6

By the way, it is easy to imagine a number-of-points-meter. Take a web camera. Make a photo of the dice thrown. Binarize the image to black and white pixels. Count the number of white continuous regions. Show that number on the display as the value for the variable number-of-points.

One can easily imagine other variables like square-of-the-number-of-points and even a crazy variable like cosine-of-the-number-of-points. So our table can be extended like this

i	$p(i)$	x_i	$y_i = x_i^2$	$z_i = \cos x_i$
1	0.15	1	1	0.540
2	0.15	2	4	-0.416
3	0.15	3	9	-0.990
4	0.15	4	16	-0.654
5	0.15	5	25	0.284
6	0.25	6	36	0.960

In the table like this there one can find the full information about the random system "the dice". However, such tables might be huge for some system. Not an easy task to absorb the information in one's had. So very often, **we chose to present reduced information**, even squeezed to just one number: the mean value. The mean value of the random variable x is defined as

$$\boxed{\overline{x} = \sum_i x_i p(i)}$$

Notice, that using the “experimental determination of probability” we get

$$\overline{x} = \sum_i x_i p(i) = \sum_i \frac{x_i N_i}{N}$$

and this is exactly how we all used to calculate the “average mark” in the school: if you got 3 “one’s” and 4 “two’s” you calculated

$$\frac{1 \times 3 + 2 \times 4}{7}$$

Also be aware that the formula for the mean value is not a “natural law”. “Nature” is not aware of any such rule. The formula is our human definition. Well, it is not a completely arbitrary definition. We had some good reasons why we defined it like that, but we could chose something else equally well.
For example sometimes we use the “median value” for very similar purpose as we use the “mean value”.

In statistics and probability theory, **the median is the numerical value separating the higher half of a probability distribution (a data sample, a population), from the lower half**.

Denoting the median value of the variable x as $\tilde{x}$, we define it by the following:

- define the set of indices (names of random events) denoted by Low(ξ) as the set of all i for which $x_i \leq \xi$
- define the set of indices (names of random events) denoted by Hi(ξ) as the set of all i for which $x_i \geq \xi$
- Define median $\tilde{x}$ as any number for which

$$\sum_{i \in \mathrm{Low}(\tilde{x})} p(i) \geq \frac{1}{2} \qquad \text{and simultaneously} \qquad \sum_{i \in \mathrm{Hi}(\tilde{x})} p(i) \geq \frac{1}{2}$$

Do think over this definition and you find that it corresponds to the above mentioned informal “definition”. Just you have to accept, that in some situations the median value is not defined uniquely (that is why the words “any number” and not “the number” in the formal definition).

There are situations where the median value is “more descriptive” then the mean value.

Reducing the information about some probabilistic distribution to just one number, the mean value (or the median value) is very often too crude a reduction. We would like to know at least “how different” the individual random values are from the mean value. Something like a “typical difference” between a specific random value and the mean value.

For this purpose we define a “**standard deviation**” as the square root of **variance**. The variance σ^2 itself is defined as a “mean square of deviation” (or mean deviation squared).

$$\sigma^2 = \sum_i (x_i - \overline{x})^2 p(i)$$

So the standard deviation is defined as

$$\sigma = \sqrt{\sum_i (x_i - \overline{x})^2 p(i)}$$

Probability technology: Continuous random variables

Continuous random events

Continuous random event:
throwing a dart

If the tip of the dart is absolutely sharp, then it hits just and ideal point of the dartboard, so the event set is continuous. However the absolute sharpness of the dart tip means that the same random event never reappears. The chance to hit the same (ideal) point on the dartboard is just zero. Therefore we cannot assign probabilities to continuous random events.

This does not mean, however, that we cannot assign names to random events. Just the names should be elements of a "continuous set". The best way is to use some variable the value of which uniquely identifies the random event. For example for "one-dimensional dart game" the random event is a point on a line and as the "name of the event" we can use the coordinate of the point.

Continuous random events

Continuous random event:
throwing a dart

Coming back to the problem of “random event unrepeatability”:

Every event has a name which is a real number (a number with infinite number of decimal places). In principle, it may happen, that the hit point has the coordinate equal exactly to π. But it never happens again. Well, this example seems to be psychologically unacceptable, but do consider, that saying that the hit-point coordinate is exactly 2 (with infinite number of decimal zeros following) is equally unacceptable.
The psychological problem is due to the fact, that if I consider any real number as a possible hit-point coordinate before the dart is thrown, I will never observe it as a hit-point. However, if I throw the dart, it hits some point, and for the ideal case of absolutely sharp tip its coordinate is some real number with infinitely many decimal places.

Continuous random events

Continuous random event:
throwing a dart

The difference with respect to the discrete case is that the random events cannot be enumerated or listed (the set is not countable).

Having in mind that we cannot define the probabilities to individual random events, we have to introduce probabilities in some other way.

We can consider not individual events but some subset of events (with non zero measure) and assign probability to the "compound events" that any of the points from the subset was hit.

Let us discuss it more specifically for the one dimensional case. As the subsets we shall consider just intervals on the real line.

So suppose we can (for example experimentally) to assign probabilities that an arbitrary interval (a, b) was hit. Let is denote as the probability, that the coordinate (name of the event) ξ is within the interval (a, b)

$$p(a < \xi < b)$$

So to have the complete probabilistic information about the process, we need to collect the probabilities for arbitrary values of a, b. But if we think a bit more, we do not need a two dimensional set of probability data, what is enough to collect is just one dimensional function

$$F(x) = p(-\infty < \xi < x)$$

since then, of course

$$p(a < \xi < b) = F(b) - F(a)$$

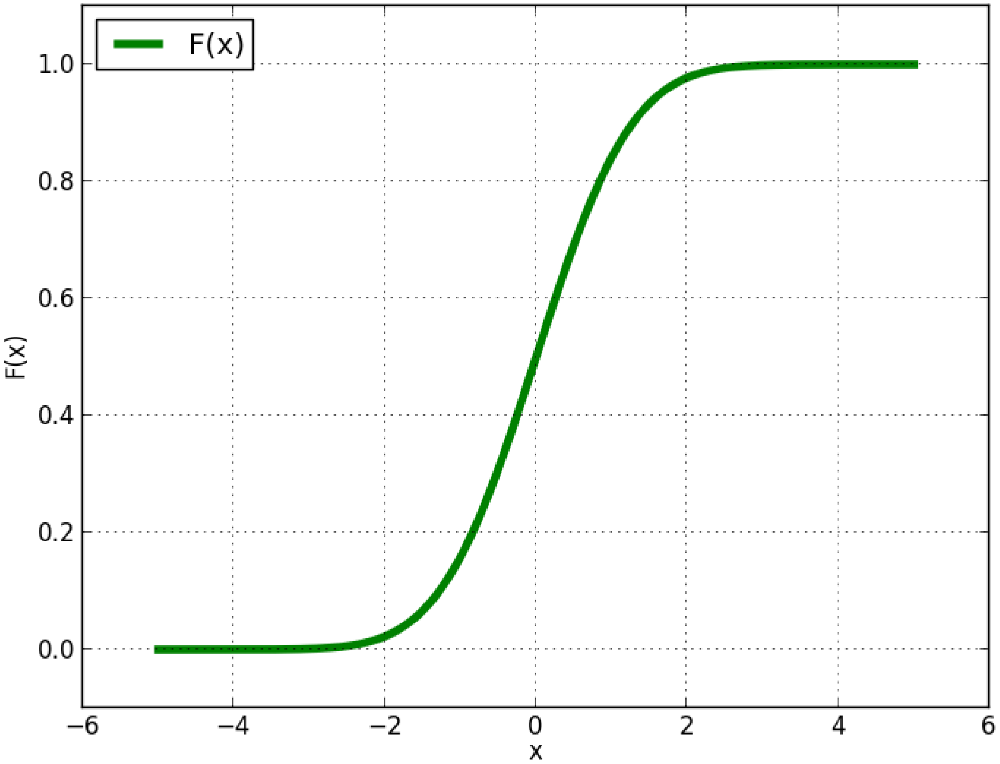
$F(x)$ is, obviously, a non-decreasing function, since

$$p(-\infty < \xi < x_1) \leq p(-\infty < \xi < x_2) \;\text{ if }\; x_1 < x_2$$

Also: $$F(-\infty) = 0, \quad F(+\infty) = 1$$

Function $F(x) = p(-\infty < \xi < x)$

is called cumulative distribution function (CDF). Other names like probability distribution function, cumulative probability distribution function are also used. Typically it looks like a “sigmoid curve”



For discrete events we could approximately determine the event probabilities experimentally. We perform N experiments and observe how many times (N_i) the event i happens. Then

$$p(i) \approx \frac{N_i}{N}$$

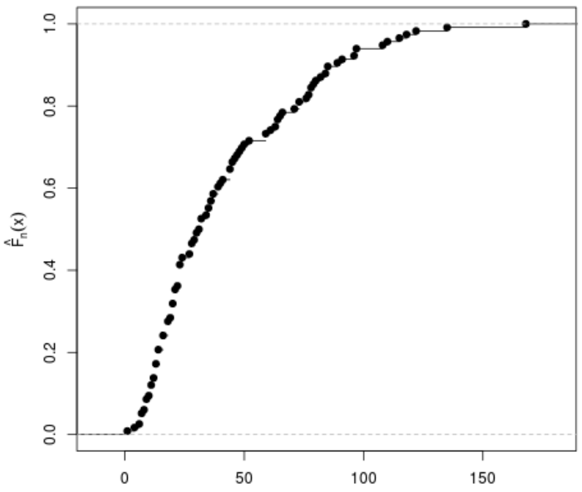
How we can determine the distribution function experimentally? We have to discretize the space x of the “event names”. Typically we define n discrete values

$$x_1, x_2, \ldots, x_n$$

We perform N “dart throws”, recording the coordinates of individual hits and calculate the numbers $\boldsymbol{N_i}$ **defined as the number of hits with coordinates less than** $\boldsymbol{x_i}$. Than

$$F(x_i) \approx \frac{N_i}{N}$$

Experimentally we get something like this



The true (theoretical) distribution function should somehow “smoothly interpolate” the experimental points. In the particular case represented by the figure the smooth interpolation is not easy to be drawn, due to experimental errors.

The error to our formula

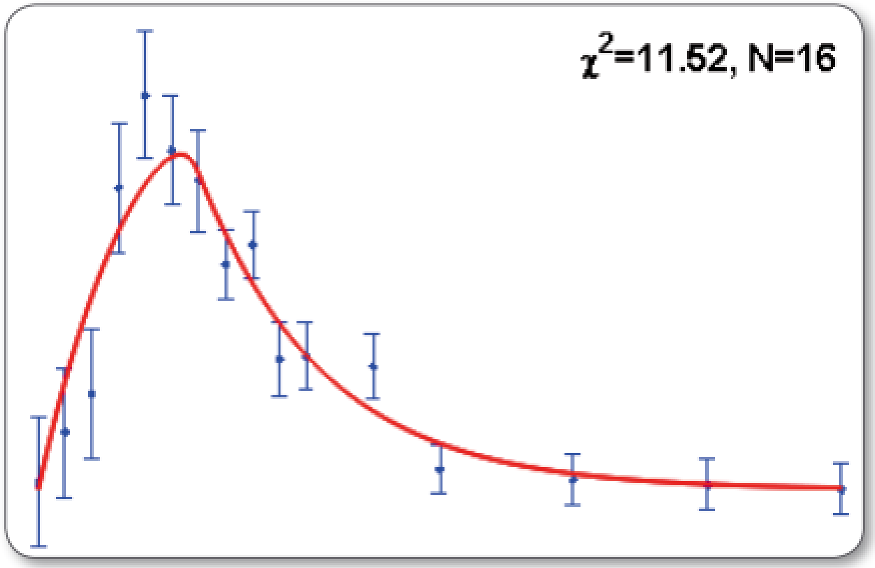
$$F(x_i) \approx \frac{N_i}{N}$$

is easy to estimate from binomial distribution and can be symbolically written as (see also http://en.wikipedia.org/wiki/Empirical_distribution_function)

$$F(x_i) \approx \frac{N_i}{N} \pm \frac{\sqrt{N_i(N-N_i)}}{\sqrt{N^3}}$$

Having data values and errors we can do “curve fitting” described on the next slide.

Supplement: curve fitting



Suppose we have some experimental data, a set of triplets $(x_i, y_i, \varepsilon_i)$ where ε_i are experimental errors of y_i, so that the measured values are

$$y_i \pm \varepsilon_i$$

Now we have a hypothesis, that the data points are to be described by a smooth curve

$$y = \mathrm{f}(x, \alpha)$$

where α is a set of parameters to be determined so that the data is optimally described. We do it like this. For any given value of α we calculate the test value

$$\chi^2(\alpha) = \sum_i \frac{(y_i - \mathrm{f}(x_i, \alpha))^2}{\varepsilon_i^2}$$

and we let the computer find optimal set of parameter values so that $\chi^2(\alpha)$ is minimal. Without going into the theory, the rule of thumb is that the fit is good when

$$\chi^2(\alpha) < N = n - p$$

where n is the number of experimental points and p is the number of fitting parameters α.

Probability density

The formula $p(a < \xi < b) = F(b) - F(a)$ suggest by its notation to play with the derivative of the cumulative probability distribution function. So let us define

$$\rho(x) = \frac{dF(x)}{dx}$$

It is clear, that the information contained in the function $\rho(x)$ enables to calculate any probability we need, in particular

$$p(a < \xi < b) = \int_a^b \rho(x)dx$$

Since $F(x)$ is a non-decreasing function, $\rho(x)$ is non-negative. Having in mind the analogy with mass density function for which the mass of any volume within a body is calculated as the integral of (non-negative) mass density over that volume, we call the function $\rho(x)$ **“probability density function”**. It is clear, that instead of the cumulative distribution function we can consider the probability density function as a primary carrier of the information on probability of the process considered. Actually, in many textbooks, the authors start the discussion of continuous random variables with introducing probability density and then derive the cumulative distribution function as a secondary concept. The normalization is obvious:

$$\int_{-\infty}^{\infty} \rho(x)dx = 1$$

Probability density

Having the formula

$$p(a < \xi < b) = \int_a^b \rho(x)dx$$

we can calculate the probability to hit a small interval around the value x as

$$p(x < \xi < x + dx) = \int_x^{x+dx} \rho(x)dx = \rho(x)dx$$

This is the closest analogy to the discrete-random-variable notion “probability of x” we have for the case of continuous random variables. This is how the proponents of the “priority of probability density over cumulative distribution” intuitively define the probability density. The argumentation is: for an infinitesimal interval dx the probability to hit that interval is “obviously” proportional to its length dx, so

$$p(x < \xi < x + dx) \propto dx$$

with the “factor of proportionality” possibly depending on the position x. Denoting this factor of proportionality as $\rho(x)$, we get

$$p(x < \xi < x + dx) = \rho(x)dx$$

Mean and variance

In analogy with the discrete case, where we have defined the mean value of a random variable x as

$$\overline{x} = \sum_i x_i p(i)$$

we define the mean value of any variable $f(x)$ (depending on the random event x as

$$\overline{f} = \int_{-\infty}^{\infty} f(x)\rho(x)dx$$

in particular for the random variable x (used to give a name to random events considered) we get

$$\overline{x} = \int_{-\infty}^{\infty} x\rho(x)dx$$

We define the variance of f as

$$\sigma_f^2 = \overline{(f-\overline{f})^2} = \int_{-\infty}^{\infty} (f(x)-\overline{f})^2\rho(x)dx$$

and for "the name" x

$$\sigma^2 = \overline{(x-\overline{x})^2} = \int_{-\infty}^{\infty} (x-\overline{x})^2\rho(x)dx$$

Examples

Uniform distribution

can be defined only on a finite interval (a, b):

$$\rho(x) = \frac{1}{b-a} \qquad\qquad \int_a^b \rho(x)dx = \int_a^b \frac{1}{b-a}dx = 1$$

We use this probability if we want to describe the situation when “no x is preferred with respect to others”. So something like “no bias”, “maximal democracy”, “equal chance”. However, one should be very careful here. For discrete random events, it is obvious what is meant under “no bias”:

$$p_i = \text{const}$$

Naively one would say that generalization to a continuous case is

$$\rho(x) = \text{const}$$

But one should be careful: generally there is **no canonical naming of continuous events**! We can use in principle any variable as “a name” for random events, but the probability density which is constant with respect to a certain variable is not constant with respect to an arbitrary other variable.

Supplement: probability density, change of variables

Suppose we have same probability density function $\rho(x)$ defined with respect to a variable x. Let us define a new variable y by the transformation formula.

$$y = f(x)$$

Since we are going to use the new variable y as a new “name” for the event x, the transformation should be one-to-one. Let us assume it is a rising function. Our task is to find the probability density with respect to the variable y, which we denote as $\tilde{\rho}(y)$. It is easy, by definition:

$$p(a < y < b) = \int_{f^{-1}(a)}^{f^{-1}(b)} \rho(x)dx$$

Now we make a substitution in the integral $x = f^{-1}(y)$ and get

$$p(a < y < b) = \int_{f^{-1}(a)}^{f^{-1}(b)} \rho(x)dx = \int_a^b \rho(f^{-1}(y)) \frac{1}{f'(f^{-}1(y))} dy$$

we should get, however

$$p(a < y < b) = \int_a^b \tilde{\rho}(y)dy$$

Supplement: probability density, change of variables

Comparing the two formulas, we get

$$\tilde{\rho}(y) = \rho(f^{-1}(y))\frac{1}{f'(f^{-1}(y)}$$

So the “new” probability density is not obtained just by inserting the inverse transformation as an argument to the “old” probability density: the **Jacobian of the transformation plays a role as well**!

So even if the original probability density was a constant function, the Jacobian need not be constant and so the “new” probability density will not be constant in general.

Conclusion:

“No-bias probability density” cannot be canonically defined for a general case of continuous random events!

Examples

Gauss (normal) distribution
is defined by the formula

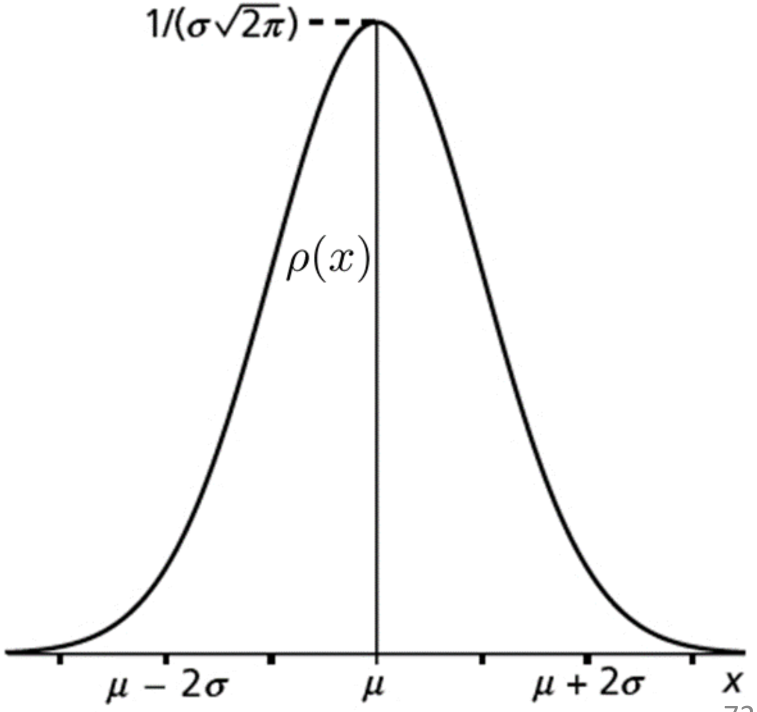
$$\rho(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp(-\frac{(x-\mu)^2}{2\sigma^2})$$

we see, that it is a whole "family" of probability distributions, differing by the choice of two parameters μ and σ. The meaning of these parameters is almost obvious:

$$\overline{x} = \int_{-\infty}^{\infty} x\rho(x)dx = \mu$$

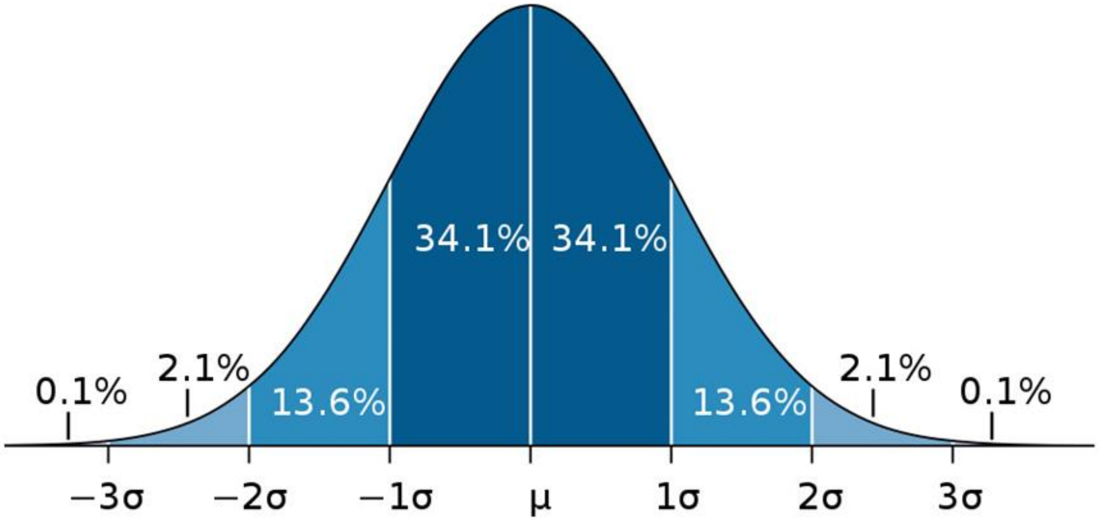
$$\overline{(x-\overline{x})^2} = \int_{-\infty}^{\infty} (x-\overline{x})^2 \rho(x)dx = \sigma^2$$

A typical shape is presented in the figure.



Examples: Gauss distribution

The following figure is instructive. It is worth to remember how often can one meet the deviation larger than a few standard deviations (assuming Gauss distribution)



Examples: Gauss distribution

Gauss (normal) distribution is frequently used in physics and generally in any science discipline.

- Sometimes we use Gauss distribution because we have good theoretical reasons that the probability density describing the random process we consider is a Gauss distribution
- Sometimes we use Gauss distribution because of a lack of any theoretical reasons. We just have a rough feeling about the mean and variance and the Gauss probability density is a nice bell-like shape corresponding to a simple analytical formula. Moreover, it is practically the only elementary formula known to a good high school student corresponding to a bell-like curve. Moreover, it is **fully specified by just two parameters: mean and variance**. So we use it having nothing better in the pocket.

Probability density: experimental determination

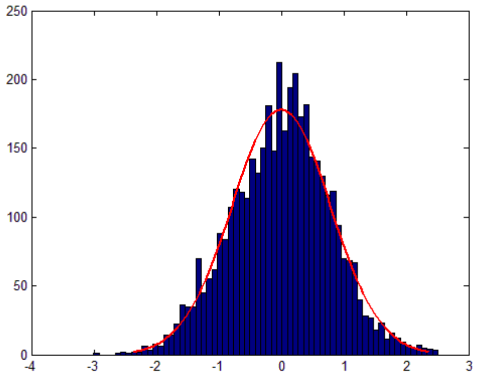
We have already discussed how to estimate experimentally the cumulative distribution function. We can estimate directly the probability density using essentially the same technique.

- discretize the space defining "bins" (intervals)

$$(-\infty, x_0), (x_0, x_1)(x_1, x_2), (x_2, x_3), \ldots, (x_{n-1}, x_n), (x_n, \infty)$$

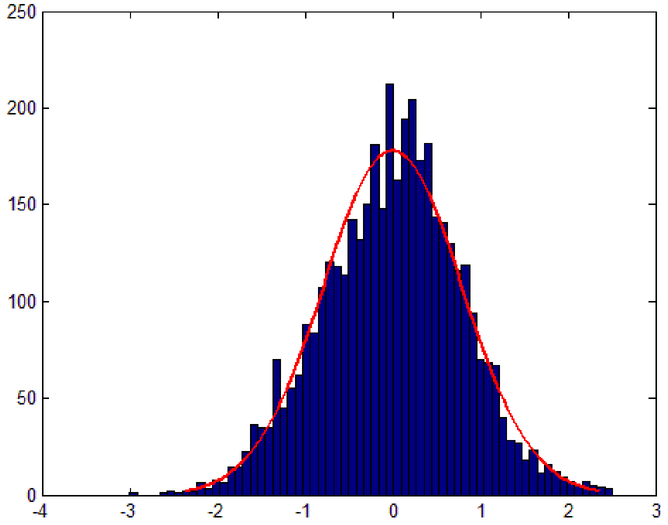
The bins $(-\infty, x_0), (x_n, \infty)$ are usually called "underflow bin" and "overflow bin", the bins in-between are usually (but not necessarily) chosen as equal-sized.

- Perform N experiments to obtain N random events and record the numbers N_i of how many times the event falls into the bin (x_{i-1}, x_i). (For simplicity we neglect underflows and overflows.)
- You can visualize the results in the form of a histogram



- Then let the computer to find a smooth curve describing the histogram

Probability density: experimental determination



- Then let the computer to find a smooth curve describing the histogram. To do this properly, wee need experimental errors of the number of hits in every bin.
- **If the bins are reasonably small**, we can estimate the errors as

$$N_i \pm \sqrt{N_i}$$

and the expected values are

$$N_i = N\rho(\frac{x_{i-1}+x_i}{2})(x_i - x_{i-1})$$

Assuming some formula for the probability density having a few free parameters α,

$$\rho(x,\alpha)$$

we write the test function (to be minimalized) as

$$\chi^2 = \sum_i \frac{(N\rho(\frac{x_{i-1}+x_i}{2},\alpha)(x_i - x_{i-1}) - N_i)^2}{N_i}$$

and find the optimal parameters α, thus estimating the probability density.

Continuous random events: more dimensions

Quite often the events from the event space considered cannot be properly named using just one real number. The event space might have more dimensions. We do not want to discuss here what is exactly meant by the dimensionality of the space considered. An intuitive feeling is enough to accept, that a good naming scheme requires n-tuples of real numbers like

$$(x_1, x_2, \ldots, x_n)$$

Those who want to know more about dimensionality and related things should read some textbook on manifolds, for example
M.Fecko, Differential Geometry and Lie Groups for Physicists,
http://www.amazon.com/Differential-Geometry-Lie-Groups-Physicists/dp/0521187966

The generalization of the probability machinery for more dimensions is straightforward. We use many-dimensional probability density function in the event space

$$\rho(x_1, x_2, \ldots, x_n)$$

and the probability to observe a random event within a subset S of the whole space is

$$p(S) = \int_S \rho(x_1, x_2, \ldots, x_n) dx_1 dx_2 \ldots dx_n$$

In some cases the volume element in the event space might be given by a more complicated formula instead of a simple

$$dx_1 dx_2 \ldots dx_n$$

Continuous random events: more dimensions
Example

A typical example is a multidimensional Gauss distribution as one finds, for example, in Maxwell distribution of the velocities of molecules in gas.

If I randomly select a molecule in gas and ask: “What is currently your velocity” I get an answer containing three numbers: projects of the velocity vector on three orthogonal axes.

$$\vec{v} = (v_x, v_y, v_z)$$

So I have a three-dimensional random variable: a velocity vector. Maxwell has derived a simple formula for the probability density in three-dimensional velocity space

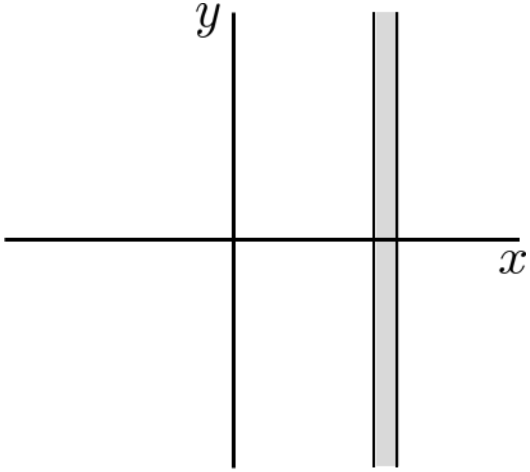
$$\rho(v_x, v_y, v_z) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2kT}\right)$$

Continuous random events: more dimensions
Marginal distribution

Sometimes I have a many-dimensional probability distribution and I am interested just for a subset of events having smaller dimension. For example having a two-dimensional probability density

$$\rho(x, y)$$

I want to now only how the variable x is distributed, so I need to find, what is the probability $p(x, x + dx)$ to find the coordinate x in the interval $(x, x + dx)$ irrespective of what is the value of y. Graphically it means, that the two-dimensional event hits the shadowed area below.



$$p(x, x + dx) = \int_{x}^{x+dx} dx \int_{-\infty}^{\infty} dy \rho(x, y) = dx \int_{-\infty}^{\infty} dy \rho(x, y)$$

We are searching for the probability density $\tilde{\rho}(x)$ defined as

$$p(x, x + dx) = \tilde{\rho}(x) dx$$

Comparing the two expressions we get

$$\tilde{\rho}(x) = \int_{-\infty}^{\infty} dy \rho(x, y)$$

$\tilde{\rho}(x)$ is called a **marginal distribution** derived from the more-dimensional distribution $\rho(x, y)$

Continuous random events: more dimensions
Conditional probability

Suppose we have a two-dimensional distribution $\rho(x,y)$

Suppose we have an interval X on the axis x, and an interval Y on the axis y. Then the joint probability to find $x \in X$ and $y \in Y$ is

$$p(x \in X, y \in Y) = \int_X dx \int_Y dy \rho(x,y)$$

The probability to find $y \in Y$ with x being anywhere is

$$p(y \in Y) = \int_{-\infty}^{\infty} dx \int_Y dy \rho(x,y)$$

The **conditional probability** to find $x \in X$ given that $y \in Y$ is defined as

$$p(x \in X | y \in Y) = \frac{p(x \in X, y \in Y)}{p(y \in Y)}$$

Experimentally what we speak about is to observe (x, y) events but record only those values of x which were accompanied by $y \in Y$. Then we analyze the probability distribution of the recorded values of x. What we get is the conditional probability.

Continuous random events: more dimensions
Independent variables

Variable **x is independent of y** if the conditional probability

$$p(x \in X | y \in Y)$$

does not depend on Y for any X. It means that knowing information about y does not change our expectation about x. We shall prove that x is independent of y if and only if the **two dimensional probability density factorizes**, that is if it can be written as

$$\rho(x,y) = \rho_x(x)\rho_y(y)$$

where on the right side we have the **marginal distributions**. First we prove the sufficient condition. Suppose $\rho(x,y)$ factorizes. Then

$$p(x \in X | y \in Y) = \frac{p(x \in X, y \in Y)}{p(y \in Y)} = \frac{\int\limits_X dx \int\limits_Y dy \rho(x,y)}{\int\limits_{-\infty}^{\infty} dx \int\limits_Y dy \rho(x,y)} = \frac{\int\limits_X dx \int\limits_Y dy \rho_x(x)\rho_y(y)}{\int\limits_{-\infty}^{\infty} dx \int\limits_Y dy \rho_x(x)\rho_y(y)}$$

$$= \frac{\int\limits_X dx \rho_x(x) \int\limits_Y dy \rho_y(y)}{\int\limits_{-\infty}^{\infty} dx \rho_x(x) \int\limits_Y dy \rho_y(y)} = \frac{\int\limits_X dx \rho_x(x)}{\int\limits_{-\infty}^{\infty} dx \rho_x(x)} = \int\limits_X dx \rho_x(x)$$

and the result obviously does not depend on Y.

Continuous random events: more dimensions
Independent variables

Now we prove the necessary condition. Let us choose the regions X, Y to be very small intervals around specific (but arbitrary) values x_0, y_0. Let us denote those small intervals as dx_0, dy_0. We get

$$p(x \in dx_0 | y \in dy_0) = \frac{p(x \in dx_0, y \in dy_0)}{p(y \in dy_0)} = \frac{\int\limits_{dx_0} dx \int\limits_{dy_0} dy \rho(x,y)}{\int\limits_{-\infty}^{\infty} dx \int\limits_{dy_0} dy \rho(x,y)}$$

$$= \frac{dx_0 dy_0 \rho(x_0, y_0)}{\int\limits_{-\infty}^{\infty} dx dy_0 \rho(x, y_0)} = \frac{dx_0 dy_0 \rho(x_0, y_0)}{dy_0 \rho_y(y_0)} = \frac{dx_0 \rho(x_0, y_0)}{\rho_y(y_0)}$$

Since the conditional probability is independent of Y, we can write

$$p(x \in dx_0 | y \in dy_0) = p(x \in dx_0 | y \in (-\infty, \infty)) = p(x \in dx_0) = dx_0 \rho_x(x_0)$$

Comparing the two results, we get

$$\frac{dx_0 \rho(x_0, y_0)}{\rho_y(y_0)} = dx_0 \rho_x(x_0)$$

$$\rho(x_0, y_0) = \rho_x(x_0) \rho_y(y_0)$$

since the values x_0, y_0 are arbitrary, we have proven the factorization.

Continuous random events: more dimensions
Mean values

We have two random variables x, y with probability density $\rho(x, y)$. Then the following is true **in general**

$$\overline{x+y} = \overline{x} + \overline{y}$$

Proof:

$$\begin{aligned}\overline{x+y} &= \iint dxdy\,(x+y)\rho(x,y) = \iint dx\,dy\,x\,\rho(x,y) = \iint dx\,dy\,y\,\rho(x,y)\\ &= \int dx\,x \int dy\,\rho(x,y) + \int dy\,y \int dx\,\rho(x,y)\\ &= \int dx\,x\,\rho_x(x) + \int dy\,y\,\rho_y(y) = \overline{x} + \overline{y}\end{aligned}$$

We have two **independent** random variables x, y with probability density Then the following is true

$$\overline{x.y} = \overline{x}.\overline{y}$$

Continuous random events: more dimensions
Mean values

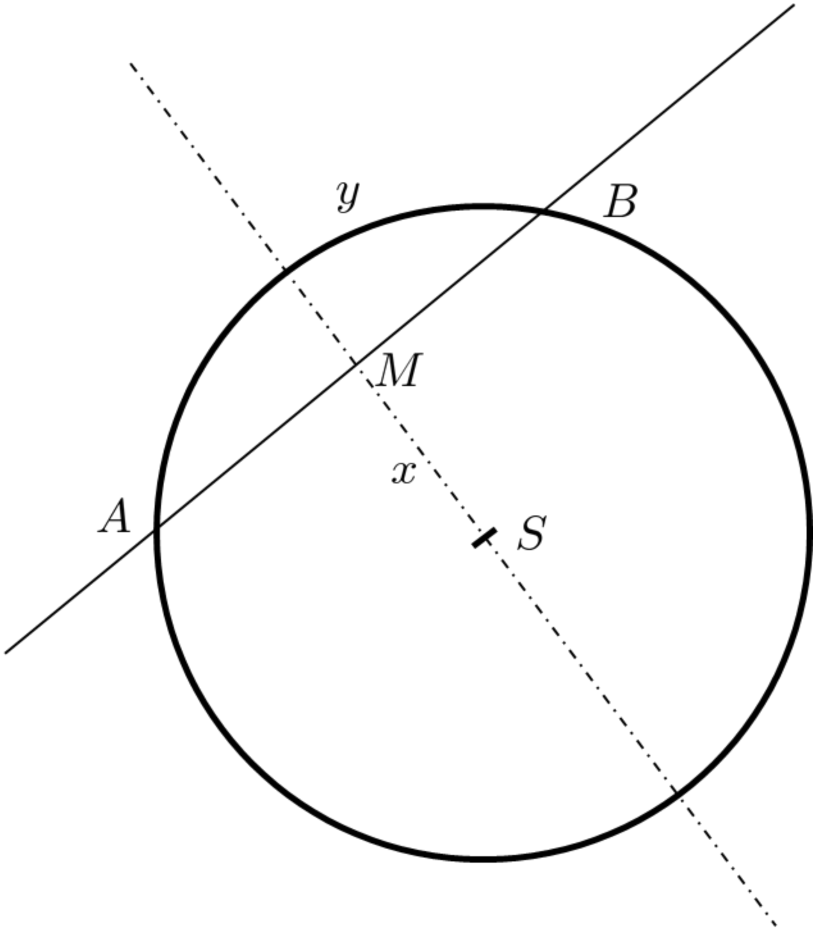
Proof: for independent variables $\rho(x,y) = \rho_x(x)\rho_y(y)$
and we get

$$\overline{x.y} = \iint dx dy\, x\, y \rho(x,y) = \iint dx\, dy\, xy\, \rho_x(x)\rho_y(y) = \int dx\, x\, \rho_x(x) \int dy\, y\, \rho_y(y)$$
$$= \overline{x}.\overline{y}$$

Note: if $\overline{x.y} = \overline{x}.\overline{y}$ holds, it does not necessarily mean that the variables are independent, even if it often considered as a strong hint for independence.

Continuous random events: no bias distribution counterexample

Consider the following problem. A thin long rigid rod is randomly thrown onto a circle and intersect the circle in two points A,B forming a chord (segment AB). Denote the length of the chord as ξ. Find the probability density for the random variable ξ.



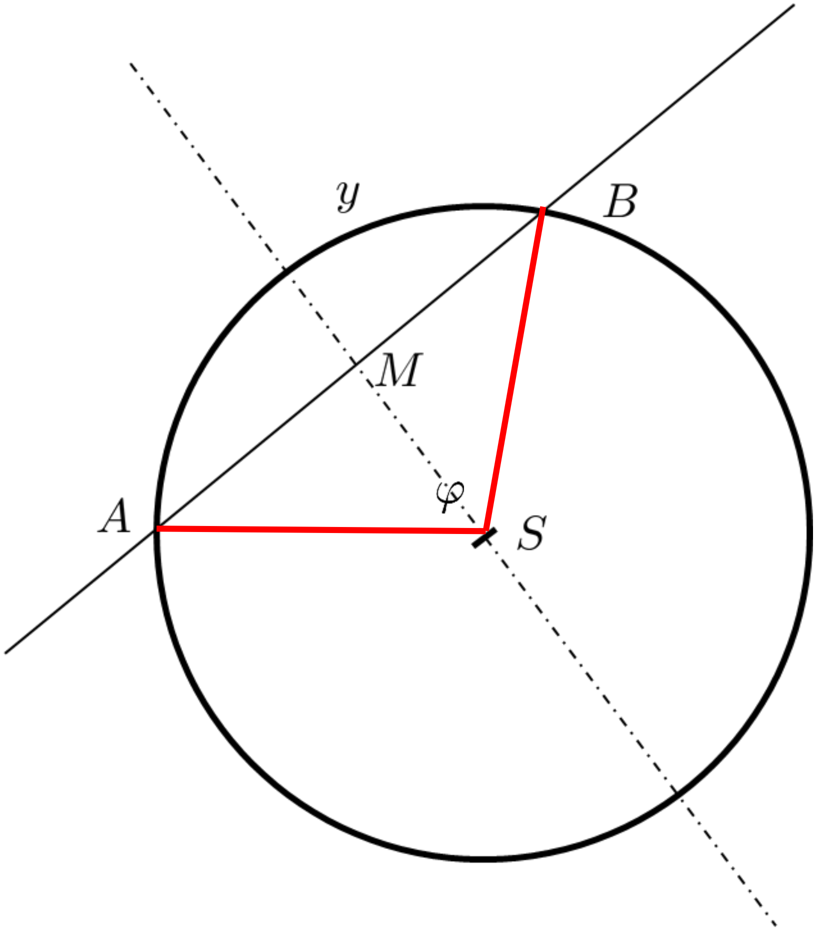
“Solution” 1:
Without loss of generality we can assume that all the thrown rods are parallel, perpendicular to the dash-dotted line in the figure. So the random event is fully specified by the size of the segment SB denoted as x. Using “non-biased” uniform distribution of $x \in (-r, r)$ we get

$$\xi = 2\sqrt{r^2 + x^2}$$

$$\overline{\xi} = \int_{-r}^{r} 2\sqrt{r^2 + x^2}\,\frac{1}{2r}dr \approx 1.57\,r$$

Continuous random events: no bias distribution counterexample

Consider the following problem. A thin long rigid rod is randomly thrown onto a circle and intersect the circle in two points A,B forming a chord (segment AB). Denote the length of the chord as ξ. Find the probability density for the random variable ξ.



“Solution” 2:
Without loss of generality we can assume that all the thrown rods intersect the circle in the specific point A. So the random event is fully specified by the angle ASB denoted as φ. Using “non-biased” uniform distribution of $\varphi \in (0, 2\pi)$ we get

$$\xi = 2r / \sin(\varphi/2)$$

$$\bar{\xi} = \int_0^\pi 2r\sin(\varphi/2)\frac{d\varphi}{\pi} \approx 1.27\, r$$

So two equally plausible “solutions”, two different results!

Demo random processes

Random walk in one dimension: Drunken sailor

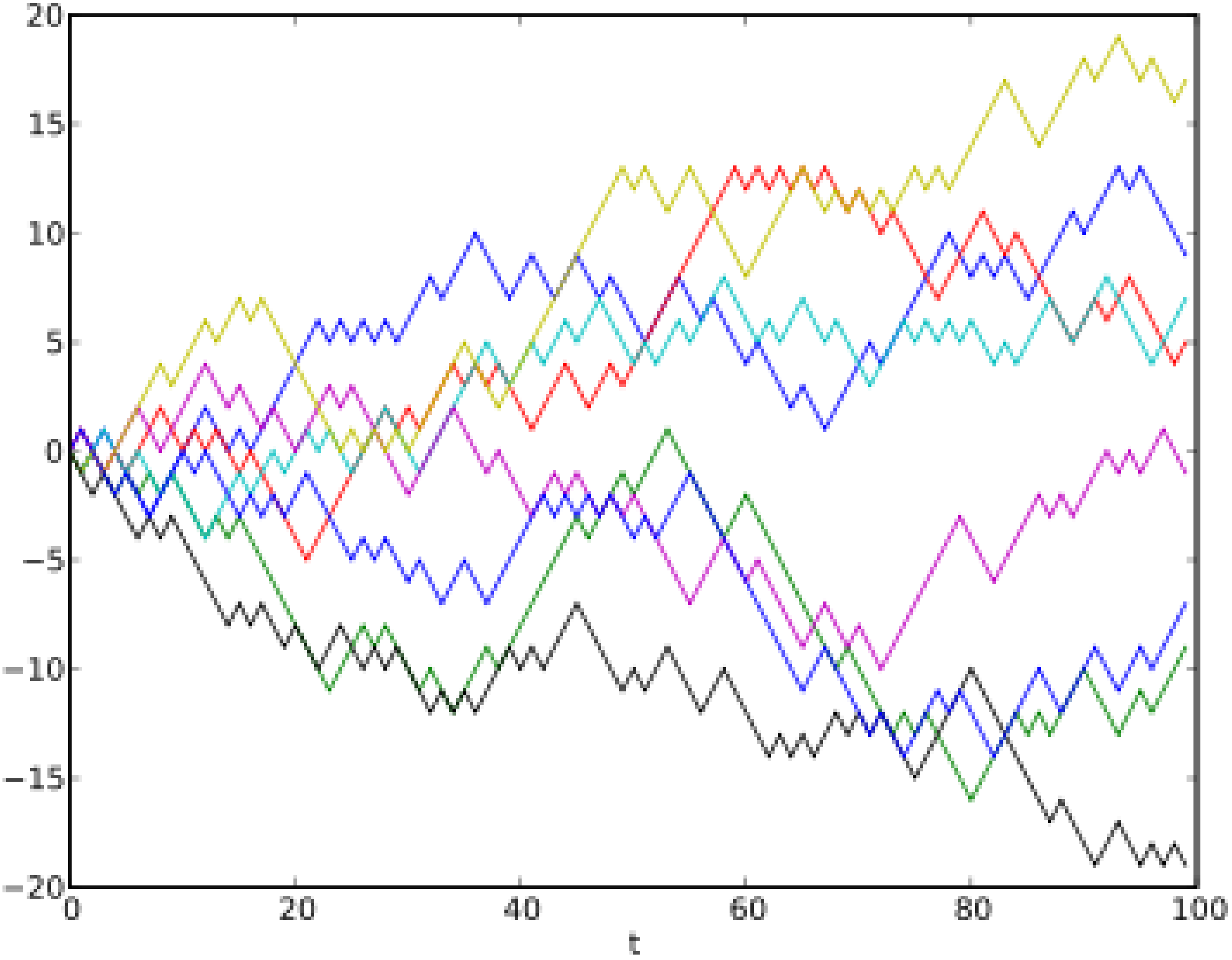
Consider one-dimensional world, a line with a coordinate denoted by x.
In the point $x = 0$ there is a pub. At time $n = 0$ (we use discrete time) a sailor gets out of the pub and starts to make random steps of equal size Δ but random direction (with equal probability either to the left or to the right).

Suppose that after making n steps he has got into the point with the coordinate x_n.
Then after making the next step he would be in the point

$$x_{n+1} = x_n + \delta_n, \quad \delta_n \in \{-\Delta, +\Delta\} \quad \text{randomly}$$

The equation describes the dynamics of what is called a random process. If we observe one sailor during his motion, we observe one particular realization of the random process. This means, that for this particular realization in each time step a particular sign (plus or minus) is randomly chosen (for example by tossing a coin) and a particular position history is realized. Observing another sailor, the random choices in each time step would be different and we get a different realization of the random process. Each realization is described by the same dynamical equation as presented above.

Random walk in one dimension: Drunken sailor



In the figure, there are 8 different realizations of the drunken sailor random process denoted by different colors. The plot shows the current position on the line (vertical axis) versus the time steps (horizontal axis).

Random walk in one dimension: Drunken sailor

$$x_{n+1} = x_n + \delta_n$$

We have observed in the figure that with increasing time (number of steps) there is a tendency that the sailors typically get to increasing distances from the origin.
Very often our primary interest is just one realization of the random process (one drunken sailor) and we would like to understand how his distance from the origin changes in time. We, of course, know, that for one sailor his particular distance from the origin is not a monotonic function of time. It might happen quite often that he would appear in the pub (at zero distance). Analyzing one particular trajectory with the aim to understand qualitatively its characteristics might be fairly complicated.
Instead of that we often switch to a different problem: to understand a typical behavior within a statistical ensemble of many realizations of the same random process (as it was visualized in the figure).

So we write dynamic equations for an ensemble of N sailors performing random walk synchronously in parallel (making their n-th step in the same time instant). We get a set of equations

Random walk in one dimension: Drunken sailor

$$
\begin{aligned}
x_{n+1}^{(1)} &= x_n^{(1)} + \delta_n^{(1)} \\
x_{n+1}^{(2)} &= x_n^{(2)} + \delta_n^{(2)} \\
&\dots \\
x_{n+1}^{(i)} &= x_n^{(i)} + \delta_n^{(i)} \\
&\dots \\
x_{n+1}^{(N)} &= x_n^{(N)} + \delta_n^{(N)}
\end{aligned}
$$

the superscript in the parenthesis is the index denoting individual sailors in the ensemble

Now we sum the equations and we get

$$
\begin{aligned}
\overline{x_{n+1}} &= \overline{x_n} + \overline{\delta_n} \\
\overline{x_{n+1}} &= \overline{x_n}
\end{aligned}
$$

The overlines denote the average values over the ensemble, that is $\overline{x_n}$ denotes the mean coordinate of the sailor ensemble after n steps. For very large N the mean step $\overline{\delta_n}$ is zero, since the random signs cancel.
The last recurrent equation is easily solved as

Random walk in one dimension: Drunken sailor

$$\overline{x_n} = \overline{x_{n-1}} = \ldots = \overline{x_0} = 0$$

This results can be qualitatively expressed as: In the mean the sailor is to be found in the pub in each time instance. The statement is almost obvious due to the left-right symmetry of the problem.

However this “first law of a drunken sailor” does not characterize the observed fact that with increasing time the probability to find a sailor in a distance larger than something increases. To investigate this effect it is useful to square all the ensemble equations before calculating the averages.

$$(x_{n+1}^{(1)})^2 = (x_n^{(1)})^2 + (\delta_n^{(1)})^2 + 2x_n^{(1)}\delta_n^{(1)}$$
$$(x_{n+1}^{(2)})^2 = (x_n^{(2)})^2 + (\delta_n^{(2)})^2 + 2x_n^{(2)}\delta_n^{(2)}$$
$$\ldots$$
$$(x_{n+1}^{(i)})^2 = (x_n^{(i)})^2 + (\delta_n^{(i)})^2 + 2x_n^{(i)}\delta_n^{(i)}$$
$$\ldots$$
$$(x_{n+1}^{(N)})^2 = (x_n^{(N)})^2 + (\delta_n^{(N)})^2 + 2x_n^{(N)}\delta_n^{(N)}$$

Random walk in one dimension: Drunken sailor

Averaging over the ensemble we get

$$\overline{x_{n+1}^2} = \overline{x_n^2} + \overline{\delta_n^2}$$
$$\overline{x_{n+1}^2} = \overline{x_n^2} + \Delta^2$$

The last recurrent equation is easily solved as

$$\boxed{\overline{x_n^2} = n\,\Delta^2}$$

The "second law of the drunken sailor" therefore reads:

Mean square of the distance of the sailor from the pub increases proportionally to the number of steps. Said alternatively **the typical distance of a drunken sailor from the pub increases as the square root of the number of steps.**

This contrasts with the **"law of non-random (directional) walk": the distance (and not the square of it) increases proportionally to the number of steps**.

So the characterizing logo of the drunken sailor is

$$\boxed{\sqrt{N}}$$

Drunken sailor application: Standard error of an arithmetic mean

In mathematics and statistics, the arithmetic mean is the **sum of a collection of numbers divided by the number of numbers in the collection**.
It is often use to decrease the measurement error of some quantity by performing the measurement several times and taking the arithmetic mean as a better estimate of the true value of the measured quantity compared to the result of a single measurement.

Let the statistical error of a single measurement be (symbolically) expressed by the formula

$$x_{\text{true}} = x_{\text{measured}} \pm \Delta$$

Let us make N individual independent measurements, denoted as

$$x_1, x_2, x_3, \dots, x_N$$

and calculate the arithmetic mean

$$x_{\text{average}} = \frac{1}{N}(x_1 + x_2 + x_3 + \cdots + x_N)$$

then the typical statistical error of the average can be estimated as

$$x_{\text{true}} = x_{\text{average}} \pm \frac{1}{\sqrt{N}}\Delta$$

Drunken sailor application: Standard error of an arithmetic mean - proof

Let us investigate the outcome of the i-th measurement, it differs from the true value by a random error

$$x_i = x_{\text{true}} + \delta_i$$

where δ_i is the (individual) measurement error, usually assumed to be Gaussian-distributed with mean $\bar{\delta} = 0$ and variance $\overline{\delta^2} = \Delta^2$. Then

$$x_{\text{average}} = \frac{1}{N}\sum_{1}^{N} x_i = \frac{1}{N}\sum_{1}^{N}(x_{\text{true}} + \delta_i) = x_{\text{true}} + \frac{1}{N}\sum_{1}^{N}\delta_i$$

The difference between the true value and the arithmetic mean is expressed through the sum of independent individual errors

$$\sum_{1}^{N}\delta_i$$

this expression is the same as that giving the coordinate of a drunken sailor after N random steps

Drunken sailor application: Standard error of an arithmetic mean - proof

$$\overline{(x_{\text{average}} - x_{\text{true}})^2} = \overline{(\frac{1}{N}\sum_i \delta_i)^2} = \overline{\frac{1}{N^2}\sum_i \delta_i \sum_j \delta_j}$$

$$\overline{(x_{\text{average}} - x_{\text{true}})^2} = \frac{1}{N^2}\overline{\sum_i \delta_i^2} + \frac{1}{N^2}\overline{\sum_{i\neq j} \delta_i \delta_j}$$

$$\overline{(x_{\text{average}} - x_{\text{true}})^2} = \frac{1}{N^2}\sum_i \overline{\delta_i^2} + \frac{1}{N^2}\sum_{i\neq j} \overline{\delta_i \delta_j}$$

$$\overline{(x_{\text{average}} - x_{\text{true}})^2} = \frac{1}{N^2} N\overline{\Delta^2} + 0 = \frac{1}{N}\overline{\Delta^2}$$

$$x_{\text{true}} = x_{\text{average}} \pm \frac{1}{\sqrt{N}}\Delta$$

In the final formula we clearly recognize the “drunken sailor $\sqrt{N}$ rule”.

Collisions in a one-dimensional world

In a one-dimensional world observe a collision of two pointlike particles: one with mass M and velocity V and another with mass m and velocity v. Let us stress that we are not using vector notations here, so the velocities mean, in fact, velocity projection on the coordinate axis and as such they can be also negative.

Let us denote the velocities after the collision as V', v'.

It is easy to find the velocities after the collision, one gets

$$V' = \frac{M-m}{M+m}V + \frac{2m}{M+m}v$$

Let us observe many particles of the type "M" denoted by index (i), then after n collisions one gets

$$V_n'^{(i)} = \frac{M-m}{M+m}V_n^{(i)} + \frac{2m}{M+m}v^{(i)}$$

Where we assume that in each collision the particle "m" is drawn from the same common pool of particles independently of the collision number n. Averaging over the ensemble:

$$\overline{V_n'} = \frac{M-m}{M+m}\overline{V_n} \quad \text{since we assume} \quad \overline{v} = 0$$

In different notation: $$\overline{V_{n+1}} = \frac{M-m}{M+m}\overline{V_n} \Longrightarrow \boxed{\overline{V_\infty} = 0}$$

Asymptotically the initial particle velocity is completely forgotten after many collisions.

$$V_n'^{(i)} = \frac{M-m}{M+m} V_n^{(i)} + \frac{2m}{M+m} v^{(i)}$$

Squaring this equation first and only then making the ensemble average we get:

$$\overline{V_{n+1}^2} = (\frac{M-m}{M+m})^2 \overline{V_n^2} + (\frac{2m}{M+m}) \overline{v^2}$$

Asymptotically we get

$$\overline{V_\infty^2} = (\frac{M-m}{M+m})^2 \overline{V_\infty^2} + (\frac{2m}{M+m}) \overline{v^2}$$

$$\overline{V_\infty^2} = \frac{m}{M} \overline{v^2}$$

The meaning oft the asymptotic solution is better understood, after we rewrite it as

$$\boxed{\frac{1}{2} M \overline{V_\infty^2} = \frac{1}{2} m \overline{v^2}}$$

We can read it as

“Ensemble-mean kinetic energy is asymptotically the same as the mean energy of the particles from the pool.”

Particle collisions: conclusions based on the demo

A particle randomly bombarded by particles having some mean kinetic energy asymptotically “forgets” its initial velocity and finally **reaches (mean) kinetic energy equal to the kinetic energy of the bombarding particles**. The word mean here describes a statistical average within an ensemble of similar particles undergoing same random bombardments. To be more precise here we speak about kinetic energies of the translational motion.

Conclusion 1: if we have an equilibrium system consisting of many types of particles (different masses) then the mean kinetic energy of all the particles will be the same.

Conclusion 2: if we start with a system of different types of particles with unequal kinetic energies then after some relaxation time the mean kinetic energies of all the particles will become the same.

Conclusion 3: If we have two physical systems in thermal contact (this means that they cannot exchange particles but the particles on the surface contact can collide with each other) then started from arbitrary macroscopic state the equilibrium will be reached where the mean kinetic energies of particles in the two systems will be equal

Equilibrium macrostate

In statistical physics we deal with macroscopic systems. Is is technically impossible to work with standard physical states (microstates). Technically we have at disposition tremendously reduced information, just values of a few macroscopic quantities, which define the **macrostate** of the system.

In principle, the values of those macrostate-defining quantities depend on time, thus describing the time development of the corresponding macrostate.

For isolated systems we observe a very interesting phenomenon:
Started from arbitrary (unknown) microstate we usually observe that the macrostate changes with time until after some time, which **we call relaxation time**, the macrostate does not change any more. Technically it means that all the macrostate-defining quantities are stable, their values do not change any more. We say that the system reached **equilibrium state**.

This does not mean that the situation is static: the microstates change all the time in macroscopic equilibrium (individual molecules collide, change their positions and velocities etc.) So the macroscopic equilibrium is a dynamical equilibrium. For all practical purposes we, however, can consider the situation as if it was static.

When we said “macroscopic quantities do not change with time” we have meant that no measuring devices are available to measure those quantities with a **precision of typically 13 digits**. Having such devices we would observe changes at the last digit even for macroscopically defined quantities.

Mutual thermal equilibrium

Consider two separately isolated physical systems. Both of them arrive, after some relaxation time, at the equilibrium state. Since the systems are individually isolated, those two equilibrium states are, a priori, in no relation with each other.

Now, bring those two systems into **thermal contact**. This means that they cannot exchange particles and **neither can perform macroscopically detectable work** on each other, but the particles on the contact surface can collide with each other and exchange energy by performing microscopic work.

After establishing the thermal contact, we start, in general, to observe macroscopic changes of states of both systems. The systems are not, in general, in a common equilibrium macrostate. But since the joined system is isolated, we should observe, after some relaxation time a new, common, equilibrium state with no macroscopic quantities changing in time anymore. We say the two systems **reached mutual thermal equilibrium**.

It may happen that initially the two isolated systems are in such (individual) macrostates, that after bringing them to thermal contact we do not observe any macroscopic changes. The systems are immediately in a mutual thermal equilibrium. So we say, that they are in the relation of mutual thermal equilibrium even before the thermal contact is established. The relation “being in mutual equilibrium” can be tested experimentally: no macroscopic changes are to be observed after bringing the two systems into thermal contact.

Thermal equilibrium, temperature.

The relation “being in mutual thermal equilibrium” **is experimentally found to be transitive**. That means, that if a system A is in equilibrium with B and B is in equilibrium with C, then A is found to be in equilibrium with C as well. This statement is called **Zeroth law of thermodynamics.**

The relation “being in mutual thermal equilibrium” is trivially also reflexive and symmetrical so the zeroth law of thermodynamics effectively says ”being in thermal equilibrium is equivalence (in mathematical sense). So all the systems can be classified into not overlapping classes of equivalence. The classes can be labeled. The label is called ”the temperature”. Temperature defined in this way is not unique: the only requirement is that different classes have different labels. (For example any function of the temperature will do the job.) We, however, usually require more, we need property of continuity in labeling the classes.
So the temperature is **the physical quantity which has the same value for all systems which are in mutual thermal equilibrium**.
We need to find some practical (experimental method) to label the classes. To do that we had to choose a suitable ”thermoscope”. By that we mean some system which can be find in many equivalence classes (in each class the system is, of course, in a different (macro)state. Ideally the system should be found in states having the same values of external parameters, differing by the value of some internal parameter (like pressure) in different equivalence classes. The system (and its chosen parameter) can be used as thermoscope: bringing it to thermal contact with any other system and reading the value of “pressure” we can recognize to which equivalence class the measured system belongs.

Thermoscope as a thermometer

We can do more, we can use the readings of our thermoscope to label the classes: so we use it effectively as a thermometer. Most often we first choose some (arbitrary) calibration to define our temperature scale.

Like this: we take the thermoscope of a defined prescribed size, put it into contact with a melt of ice and water and label the pressure reading by zero. Then we put it to contact with boiling water and label the pressure reading as 100. The other pressure readings are simply linearly interpolated or extrapolated.

The temperature defined in this way is rather arbitrary but can serve our purposes and is ”continuously defined”. Topology is introduced into the space of equivalence classes: the two classes are considered to be close to each other if the thermoscope readings are close to each other.

What the temperature really is

We have defined temperature as a label for equivalence classes as defined by the relation “being in mutual thermal equilibrium”.

This “definition” does not allow “theoretically” to assign the temperature value to a system just knowing the values of physical quantities characterizing its (equilibrium) macrostate. Having just an empirical definition of a suitable thermometer we have to find empirically a law how to calculate the “empirical temperature” from given set of macrostate-defining quantities.

What we would like to have is a generally valid “theoretical algorithm” how to define a macroscopic variable which could be used as a temperature in the spirit of the zeroth law of thermodynamics.

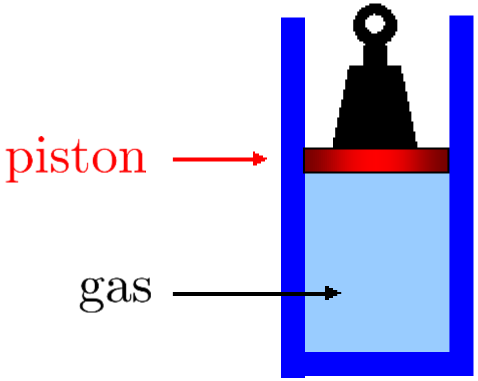
Our experience with molecular collisions allows us to formulate a hypothesis that **the kinetic energy of the translational motion of molecules can be used as temperature** for all systems composed of molecules. The reason is that this kinetic energy is equal for systems in mutual thermal equilibrium, so is the same within the class of equilibrium equivalence.

For systems **not composed of molecules** this definition cannot be used and we shall look for more general definitions.

Gas thermometer

As an example of an empirical thermometer we present here an ideal gas at constant external pressure. For one mole of gas we have the equation of state

$$pV = RT$$



In this discussion, when we just start to define empirical temperature we just use the fact that empirically the ideal gas (with fixed number of molecules) has just two macroscopic degrees of freedom p, V. If we design the thermometer with some fixed p, the gas volume will be the quantity we can use to label different classes of thermal equivalence. The gas constant R is just used to recalibrate the volume value to arbitrarily calibrated temperature. In the above equation of state we use the absolute temperature calibration in Kelvins by choosing

$$R = 8.3144598(48)\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$$

Historically the definition was different: extrapolation of isothermal law to very low temperatures has given that V= 0 for $t = -273.15$ degrees Celsius. Comparing with volume at 0 degrees Celsius has lead to the value of the gas constant as given.

Do ponder the subtleties of various definitions!

Gas constant, Avogadro constant, Boltzmann constant

We have written the ideal gas equation of state for one mole of molecules as

$$pV = RT$$

For the same pressure and temperature the ideal-gas volume obviously is proportional to the number of molecules, which for one mole is just the Avogadro constant N_A=6.02214076×10^{23}. So one can write for one mole

$$pV = N_A kT$$

Where k a suitable constant of proportionality. This constant is usually called Boltzmann constant and its value is

$$k = 1.380649 \times 10^{-23} \text{ J/K}$$

Boltzmann constant is sometimes referred to in textbooks as one of “fundamental constants of nature”. Actually “Nature” is not aware of any constant like that. Boltzmann constant is completely of a “human origin”. It just reflects our rather arbitrary definition of “one mole”. So we have the relation

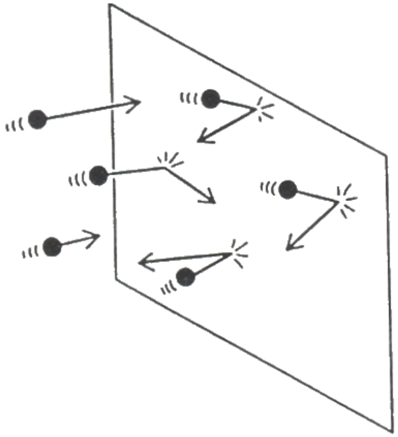
$$\boxed{R = N_A k}$$

Pressure: kinetic theory of gases

The molecular hypothesis explained where the integer numbers in chemical recipes come from. We have just seen how the molecular hypothesis enhanced our understanding what temperature “is”. Now we shall present the idea how the molecular hypothesis explains the origin of gas pressure. One can find this in textbooks in chapters like “Kinetic theory of gasses”.

The kinetic theory describes a gas as a large number of submicroscopic particles (atoms or molecules), all of which are in constant rapid motion that has randomness arising from their many collisions with each other and with the walls of the container.

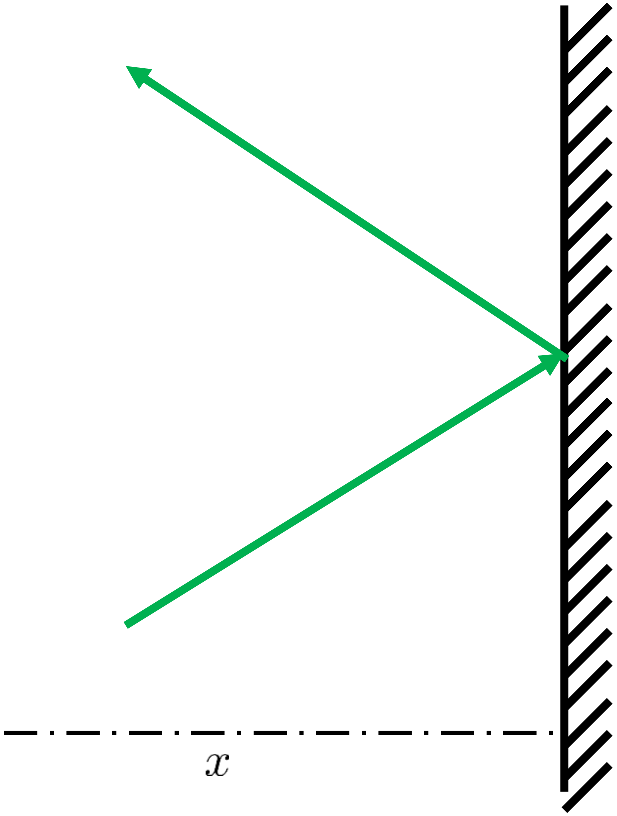
Kinetic theory explains macroscopic properties of gases, such as pressure, temperature, viscosity, thermal conductivity, and volume, by considering their molecular composition and motion.

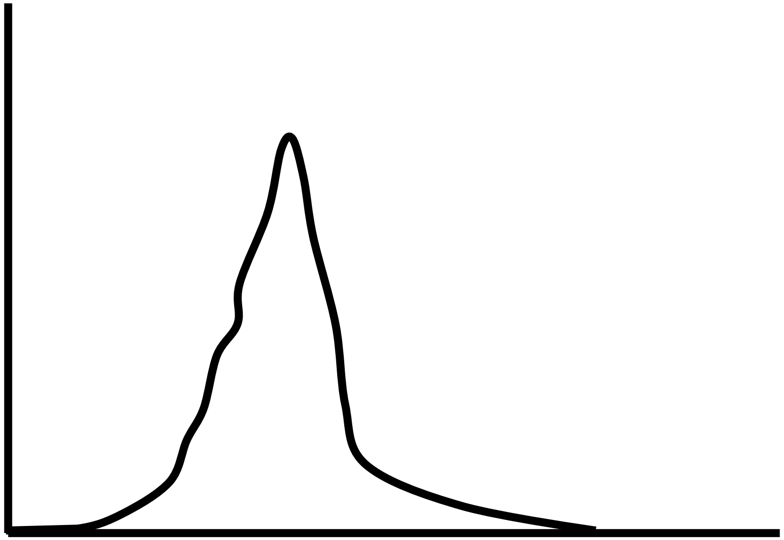


The theory proposes that gas pressure is due to the impacts, on the walls of a container, of molecules or atoms moving with random velocities.

Pressure: kinetic theory of gases

One-molecule impact and a typical corresponding force on the wall. The wall is perpendicular to the x axis. A molecule, after an elastic collision to the wall changes its velocity component v_x into opposite.

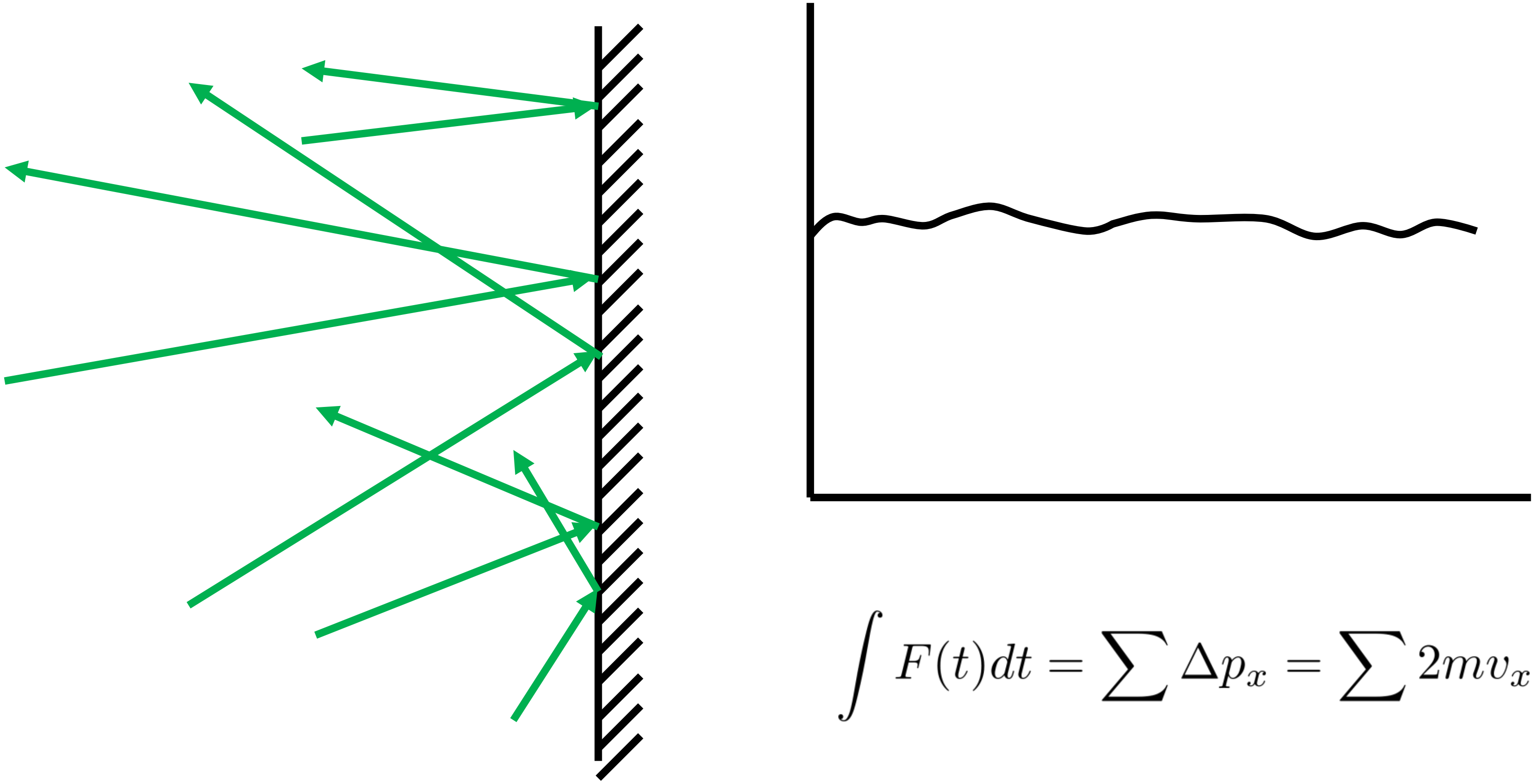




$$\int F(t)dt = \Delta p_x = 2mv_x$$

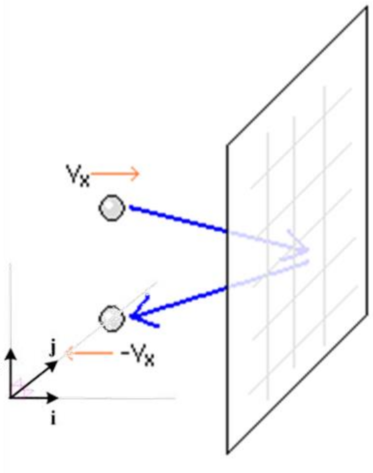
Pressure: kinetic theory of gases

Impact of many molecules and a typical corresponding force on the wall. Since our image is not a video, we cannot visualize that the impacts are not simultaneous but spread in time. In this way the forces due to individual impacts are smeared in time and we observe just an average force fluctuating a little.



$$\int F(t)dt = \sum \Delta p_x = \sum 2mv_x$$

Pressure: kinetic theory of gases

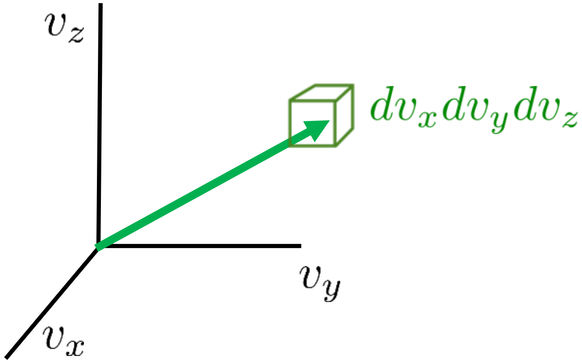


The wall is perpendicular to the x axis. A molecule, after an elastic collision to the wall changes its velocity component v_x into opposite, while the other two velocity components v_y, v_z are not changed by the collision.

The absolute value of the net impulse change of the molecule is therefore $|\Delta p_x| = 2mv_x$

Notice that we consider here only $v_x > 0$since for negative values the molecule does not hit the wall.

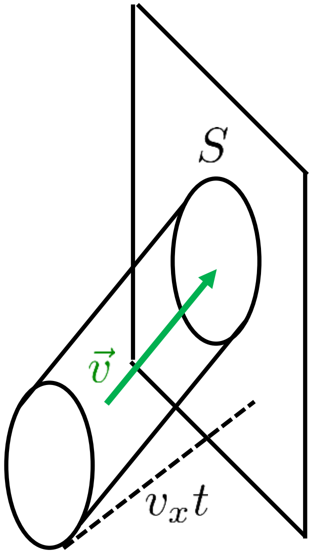
The velocity of a molecule is a random vector (random 3-dimensional continuous quantity) with probability density $\varrho(v_x, v_y, v_z)$. To simplify our formulation we shall say "a molecule with velocity $\vec{v}$" and we shall mean by that "a molecule whose velocity is any vector with the endpoint in a small box $dv_x dv_y dv_z$ around the endpoint of the vector $\vec{v}$ in the abstract velocity space" (see figure).



Let us denote the volume density of all the molecules as n. Then the number of molecules with velocity $\vec{v}$ is

$$n\varrho(\vec{v})dv_x dv_y dv_z$$

Pressure: kinetic theory of gases



Let us consider just molecules with velocity $\vec{v}$ and calculate how many of them hits the area S on the wall during some small time t. Those would be the molecules contained in the inclined cylinder whose height is $v_x t$. So he number of these molecules will be

$$n\varrho(\vec{v})v_x t S dv_x dv_y dv_z$$

and the total change of momentum of those molecules would be

$$2mv_x n\varrho(\vec{v})v_x t S dv_x dv_y dv_z$$

Now consider all molecules, not just with a particular velocity. Then the total change of momentum of all the molecules which would hit the surface S within the time t will the sum (integral)

$$\Delta p = \int_{v_x>0} 2mv_x n\varrho(\vec{v})v_x t S dv_x dv_y dv_z$$

We have included only molecules with $v_x > 0$, since those with $v_x < 0$ do not hit the wall at all. By Newton law the change of momentum is given by the impulse (force multiplied by time) of (average) force, and by dividing the force by S we get the gas pressure P

$$P = \int_{v_x>0} 2mv_x n\varrho(\vec{v})v_x dv_x dv_y dv_z$$

Pressure: kinetic theory of gases

$$P = \int_{v_x>0} 2mv_x n\varrho(\vec{v})v_x dv_x dv_y dv_z$$

$$P = 2mn\int_{v_x>0} v_x^2\varrho(\vec{v})dv_x dv_y dv_z = 2mn\frac{1}{2}\int v_x^2\varrho(\vec{v})dv_x dv_y dv_z$$

$$P = mn\overline{v_x^2} = \frac{1}{3}nm\overline{\vec{v}^2} = \frac{2}{3}n\frac{1}{2}m\overline{\vec{v}^2}$$

$$P = \frac{2}{3}\frac{N}{V}\frac{1}{2}m\overline{\vec{v}^2}$$

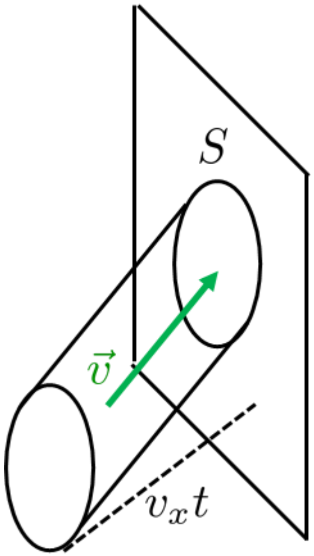
where N is the total number of molecules in the container. If we compare this with the gas equation of state

$$PV = NkT$$

we get the relation between the mean kinetic energy of the translational motion of molecules and the temperature

$$\boxed{\frac{1}{2}m\overline{\vec{v}^2} = \frac{3}{2}kT}$$

Pressure: kinetic theory of gases



We have, in fact, derived the equation of state for the ideal gas. However, we did not mention, that the gas we have considered, was ideal. Our derivation looked perfectly general. Since real gases do not behave according to the ideal-gas equation, we must have cheated somewhere.

The problem was how we have calculated the number of collisions with the wall. We have assumed that all the molecules in the inclined cylinder hit the wall with the velocity $\vec{v}$. This is not true.

The reasons are quite complex, let us just present one.

Imagine the molecule, which is just about to hit the wall. There are less molecules in front of that molecule then behind it. So the other molecules from behind attract the molecule more then the molecules in front of it an effectively decelerate it. So the considered molecule hits the wall with slightly different velocity then it had far from the wall.

Maxwell velocity distribution

The velocity of a molecule is a random vector (random 3-dimensional continuous quantity) with probability density $\varrho(v_x, v_y, v_z)$. The distribution was first derived by Maxwell in 1860 on heuristic grounds. Maxwell used two essential assumptions: rotational symmetry and statistical independence of the variables v_x, v_y, v_z.

Rotational invariance requires that the distribution function can depend only on rotational invariants, which can be constructed from v_x, v_y, v_z. There is only one such variable $v^2 = \vec{v}.\vec{v}$, what means, that the probability density, which a priori is a function of three variables, can be expressed as just a function of one variable

$$\varrho(v_x, v_y, v_z) = \tilde{\varrho}(v^2)$$

Assuming independence of the three random variables v_x, v_y, v_z we get, that the probability density factorizes

$$\varrho(v_x, v_y, v_z) = \varrho_1(v_x)\varrho_1(v_y)\varrho_1(v_z)$$

Taking these two assumptions together we get

$$\tilde{\varrho}(v_x^2 + v_y^2 + v_z^2) = \varrho_1(v_x)\varrho_1(v_y)\varrho_1(v_z)$$

Without trying to do some fancy mathematical reasoning we can simply ask what function makes product from a sum, with the obvious answer “the exponential”. So the obvious hypothesis is

$$\varrho(v_x, v_y, v_z) = C \exp(-\alpha(v_x^2 + v_y^2 + v_z^2))$$

with C, α some arbitrary (for the moment) parameters.

Maxwell velocity distribution

We arrived at a Gaussian distribution. The kinetic theory of pressure has lead to the relation

$$\frac{1}{2}m\overline{\vec{v}^2} = \frac{3}{2}kT$$

The Gaussian probability distribution must be consistent with this, so (together with the requirement of a proper normalization) the distribution is uniquely given as

$$\varrho(\vec{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp(-\frac{mv^2}{2kT})$$

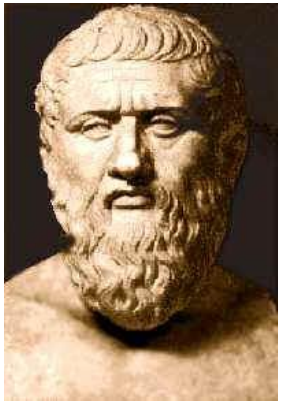
Let us stress that the requirement of spherical symmetry is more-or-less unavoidable. The requirement of statistical independence of the variables v_x, v_y, v_z is, on the other hand, not forced by any general physics arguments. It was a clever hypothesis justified a posteriori by agreement of many of its consequences with experiment.

We add a note that the Maxwell distribution can be seen as a direct consequence of canonical distribution we shall meet later on, so canonicity leads directly to independence of directions.

For experts we add a note that a careful analysis of physical kinetics (Boltzmann kinetic equation and its collision term in particular) leads to independence of directions directly.

Reversible processes in gas

Consider an equilibrium state (macrostate) of gas. By definition it is a macroscopically static situation, the values of macroscopic physical quantities do not change with time.
Now consider some action of an outside agent changing some external parameters. After such a change the gas state is no more in the equilibrium state, because it is not in equilibrium with outer conditions. So the macrostate starts to change and after some relaxation time it becomes consistent with the outer conditions and becomes a new equilibrium state. However when the action of the outer agent is such, that the outer conditions change by only a small (infinitesimal) amount, then the relaxation time to reach a new equilibrium is very (infinitesimally) small and we would see **rather contradictory situation**. The state of the system will be **constantly in the equilibrium state but still it would be changing** all the time.
This seeming contradiction is in fact the same contradiction as recognized by ancient philosophers like Zeno of Elea, who felt the contradiction between the "current position" and the "current velocity".



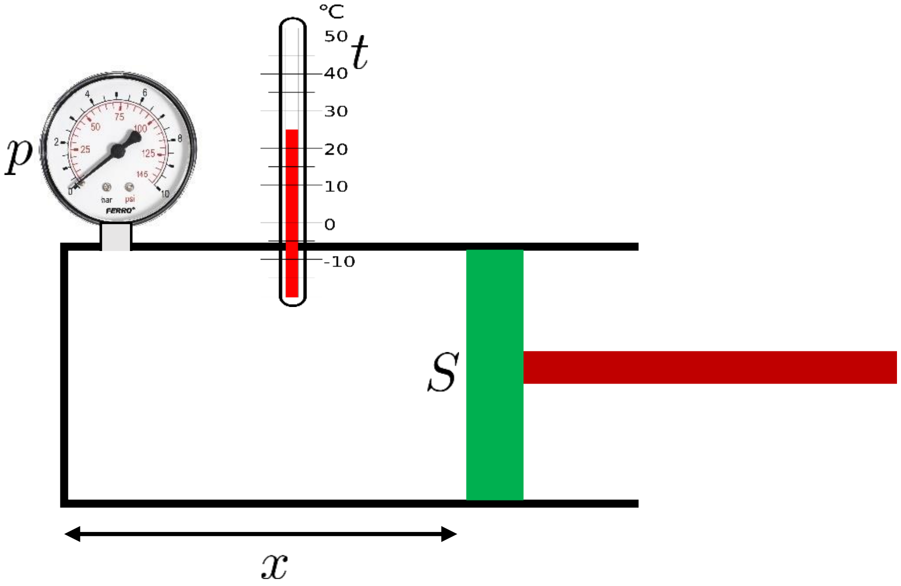
So we have arrived at the notion of equilibrium process or **reversible process**. It is a process controlled by an outer agent in such a way that the **process can be changed to a reversed one by an infinitesimal change of the agent's action**.

Equilibrium states of gas

Experimental practice shows, that for a fixed amount of gas (mass, number of molecules) the equilibrium states are uniquely determined by just two macroscopic parameters. Most often we choose two of the three common variables

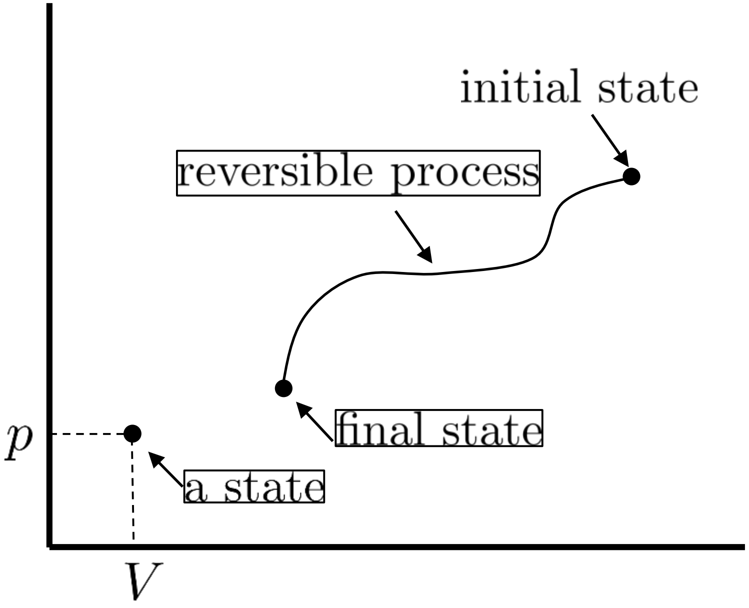
- volume
- pressure
- temperature

Pressure is measured by pressure gauge, volume can be calculated from dimensions of the container $V = S \times x$, and temperature is measured by a thermometer. If we want to observe macrostates at different volumes, we use a piston instead of a fixed wall of a container



PV diagram

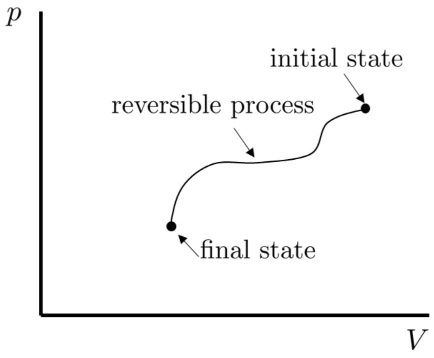
Since the space of equilibrium macrostates of gas is two-dimensional, we can visualize them in a plane diagram, most often by a pV diagram. A point in a pV plane represents an equilibrium state.

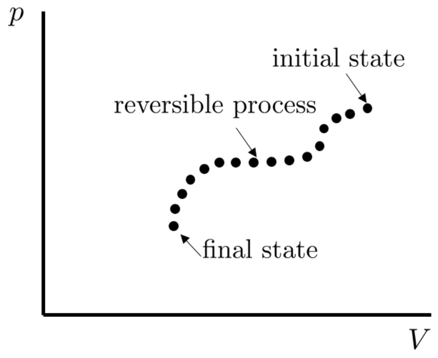


Do take into account that only equilibrium states can be fully visualized on a pV diagram. The non-equilibrium states have more degrees of freedom. To specify them we have to add some variables describing the "difference from equilibrium". For example we shall not have just one value of pressure if the gas is not yet homogenous. Places with higher density of molecules would have higher pressure: so two pressure gauges introduced to different points in the gas would show different values of pressure. So **only reversible processes can be fully visualized as lines in a pV diagram**

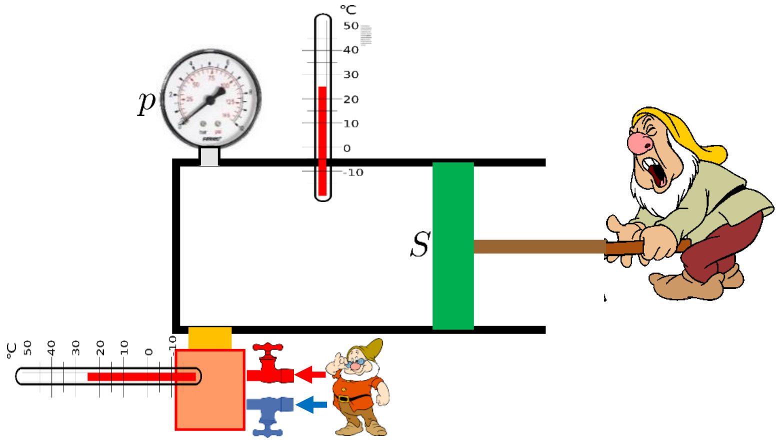
Reversible processes in gas – experimental setup

If we want to study reversible processes in gas, we need to have control over two parameters, let us say p, V.
Suppose we want to perform the process visualized in the following figure (left).

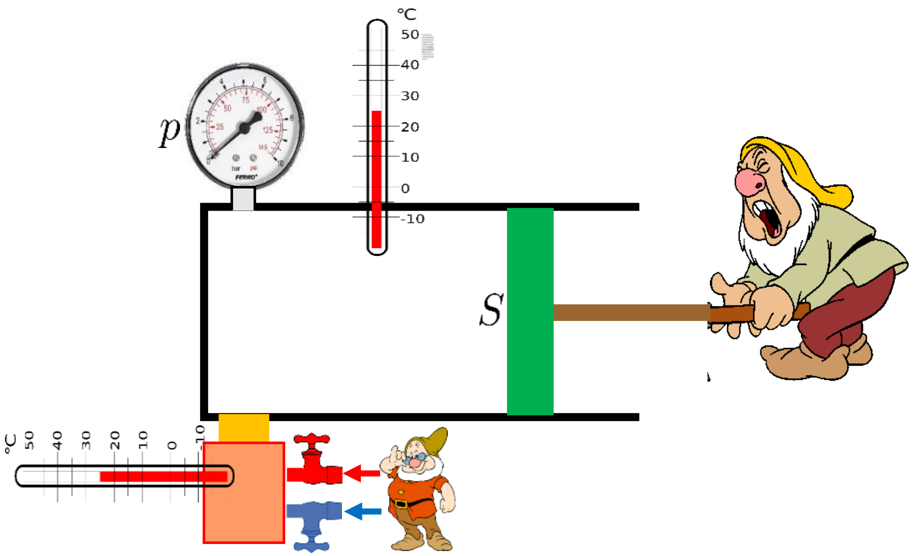




We can consider the continuous reversible process as if it was a discrete process through a sequence of equilibrium states (right figure). We need an experimental setup to perform such a step by step reversible process. We hire two dwarfs (external agents) as presented in the next figure



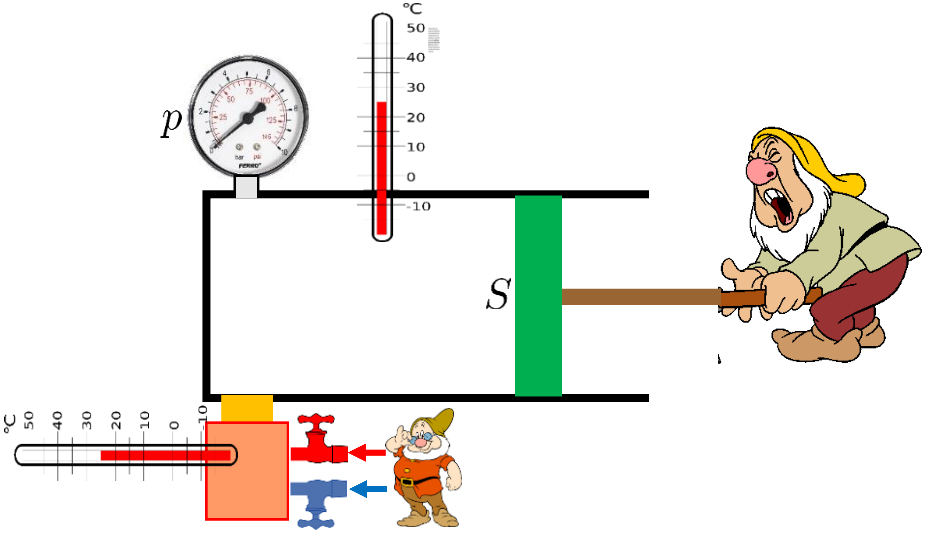
Reversible processes in gas – experimental setup

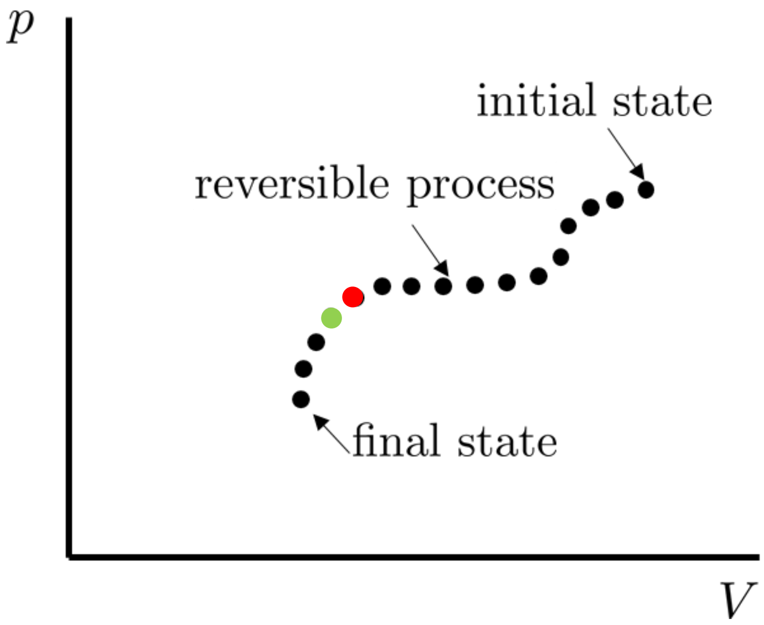


The first dwarf (**piston-pusher**) can set any V value (in the vicinity of the current value) by moving carefully the piston by small amount. He has to act by a proper force on the piston: a bit higher then corresponding to the gas pressure (if he wants to decrease V) or a bit lower then corresponding to the gas pressure (if he wants to increase V).

The second dwarf (**boiler attendant**) can set any pressure p (in the vicinity of the current value) indirectly by increasing or decreasing the current temperature of the gas. To control temperature in a reversible manner is a tricky task. Here it is how it can be done. The boiler attendant controls roughly the boiler water temperature (by manipulating the valves with hot and cold water) in an external boiler which serves as a heat exchanger. The boiler is in thermal contact with the gas through an interface with low coefficient of heat transfer. If the boiler water is a bit hotter then the gas, energy slowly flows from the boiler to the gas thus increasing its temperature. If the boiler is colder then the gas, energy slowly flows from the gas into the boiler thus decreasing slowly the gas temperature. The **energy exchange** between the boiler and the gas is **an irreversible process** (the boiler and the gas are not in the state of mutual equilibrium), **but the gas remains in internal equilibribrium** because the energy transfer is slow.

Reversible processes in gas – experimental setup

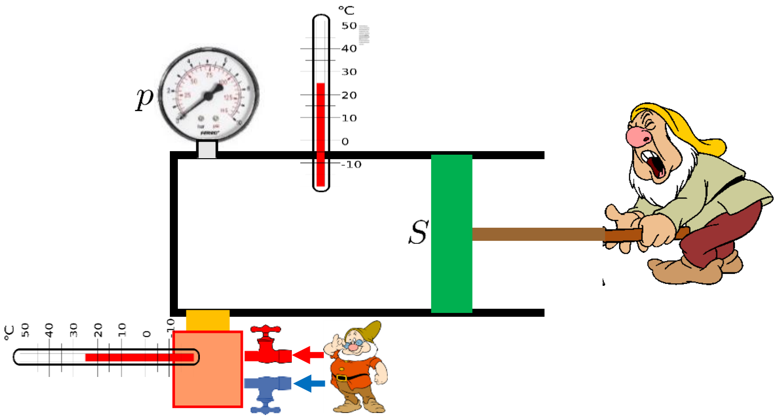




The dwarfs observe all the time the pressure gauge and the temperature of the gas and by coordinated action they can manage to change the gas state from, say, the red point to the green point in the figure.

Note, that we have used the term **energy flow** and **not the heat flow** as it would seem to be natural for a common generally educated person. We shall discuss this very thoroughly later on. Here we just stress that the heat cannot flow, since it is an **action (kind of work), not a substance** (which could be stored somewhere and then transfered to some other place).

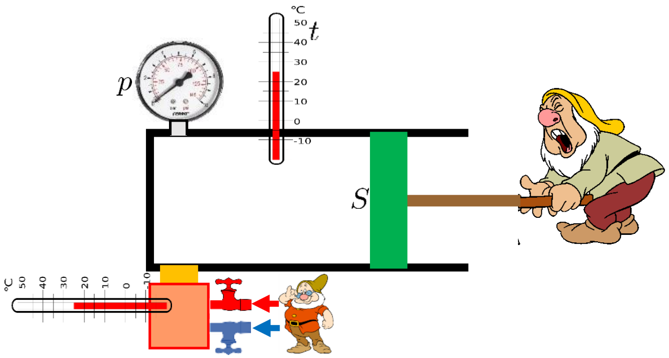
Example: isothermal reversible process



Let’s discuss in detail the instructions for the piston pusher and boiler attendant to perform a reversible isothermal process. The task is to increase the volume $V_1 \rightarrow V_2, \quad V_2 > V_1.$

Instructions for the boiler attendant: Before starting the process prepare the temperature in your boiler to be equal to the gas temperature. During the process observe the gas thermometer. If, due to actions of the piston-pusher, the gas temperature starts to decrease, add hot water to the boiler so that the gas temperature would increase back to designed value due to energy transfer from boiler to the gas. If the gas temperature starts to increase, add some cold water to the boiler. What we have described in the form of “instructions for the heat attendant” is in technical praxis how a gadget called **thermostat** works.
Instructions for the piston pusher: At the beginning push the piston by force $F = p.S$ what just compensate the gas pressure thus keeping the piston at rest. Then decrease by a small amount your force what causes the piston to move to the right thus increasing the volume a little. Constantly watch the pressure gauge and maintain your pushing force just “infinitesimally” below the $p.S$ value thus enabling the piston to increase the volume continuously until the designed volume V_2 is reached.

Thought experiments



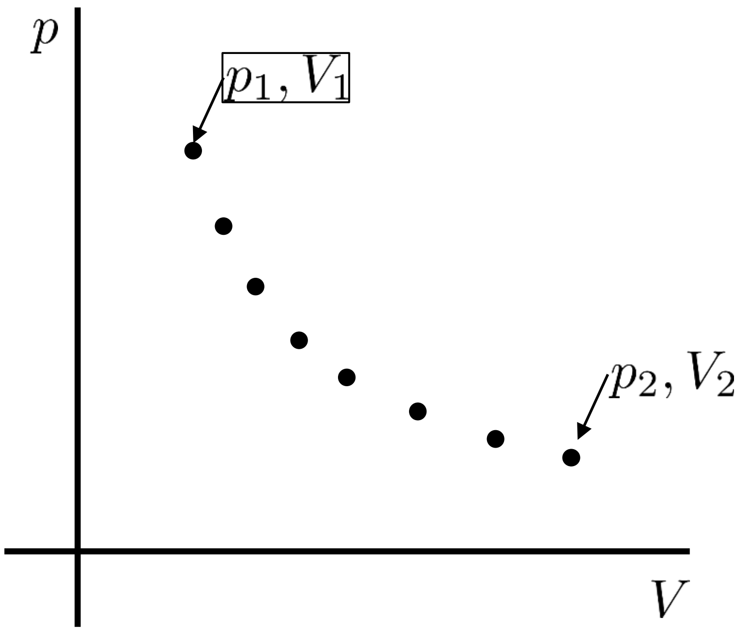
The previous, maybe a bit infantile, discussion wanted to demonstrate the technique of "thought experiment". The purpose of doing thought experiments is to check consistency or consequences of some hypothesis, theory, intuitive formulation of ideas etc.

In our case we wanted to check the viability of performing isothermal process reversibly. It could well happen that some briefly sketched idea like "we perform a reversible isothermal process" cannot be realized in reality. True realizations might be technically difficult due to technical engineering complications of non-principal character which could be overcome at least to an acceptable level. The thought experiment tries to check principal aspects of the idea by virtually doing an experiment free of technical complications.

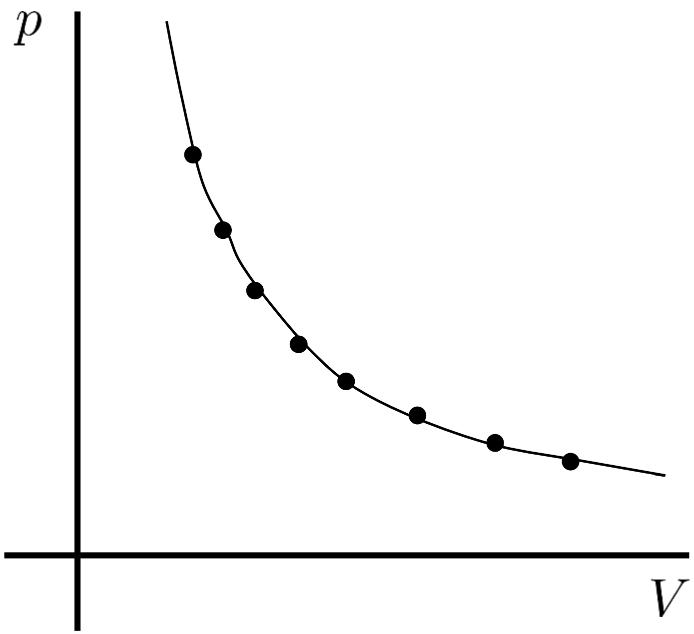
Einstein and Feynman were real masters of thought experiments.

For a student a thought experiment can be a test "do I really understand the lecture?" Do the intellectual exercises like "how would I experimentally test the theorem I am studying". Translating abstract notions into real world structures may discover, that you are, in fact, not fully understanding what you are speaking about.

Isothermal reversible process



This is how the experimental points from the isothermal process might look.



Having the experimental points we can try to find suitable formula (continuous curve) going through the points. We can do it by blind try-and-error method or we can use some more sophisticated computer program to **"fit the data"**.

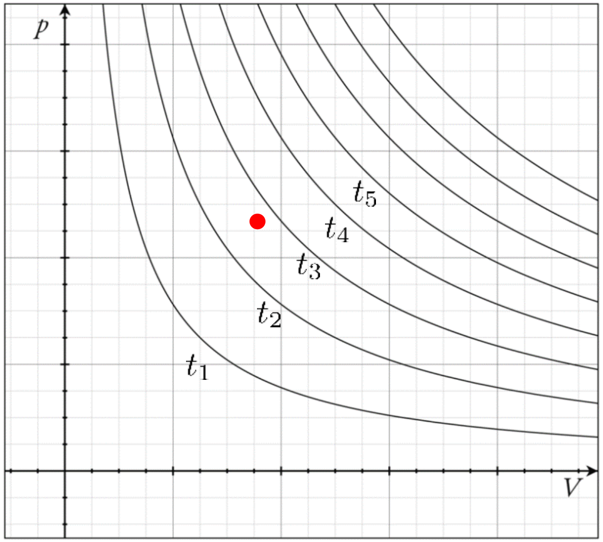
Phenomenologically, the isothermal process of an ideal gas satisfies the Boyle-Mariotte law:

$$\boxed{\begin{gathered} pV = \text{const} \\ p_1 V_1 = p_2 V_2 \end{gathered}}$$

Isotherms of ideal gas

Boyle-Mariotte law is strictly valid only for ideal gas. On the pV diagram of an ideal gas we can draw a system of isotherms for various temperatures like in the following figures for

$$t_1 < t_2 < t_3 < t_4 < t_5 < \cdots$$



A point in the pV diagram corresponds to an equilibrium macrostate. Seeing a point we can directly read the corresponding values of p, V. B With the help of isotherm curves we can also read the corresponding temperature. We find the closest isotherms and then by interpolation we can find the temperature even with higher precision. For example, the red point in the figure divides the distance between the t_2, t_3 isotherms roughly as 2:1, so its temperature is roughly

$$t = \frac{2}{3}t_3 + \frac{1}{3}t_2$$

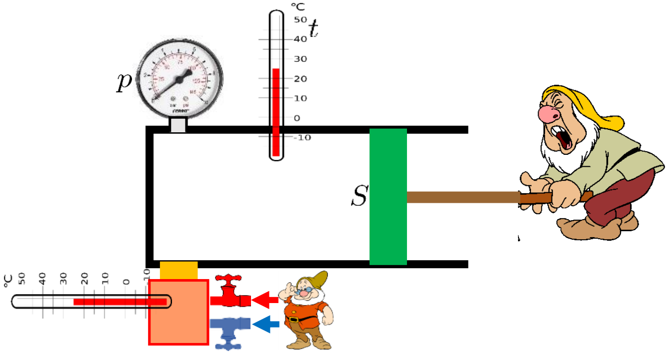
Isobaric process

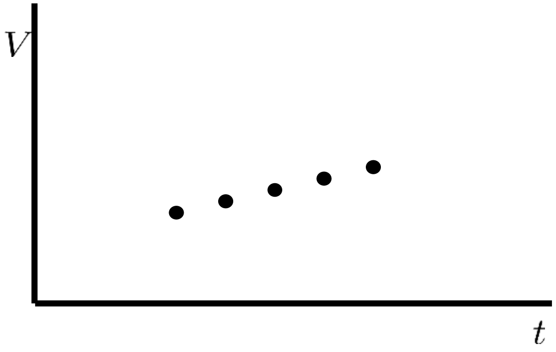
This process is better visualized on a tV diagram. Suppose we want reversibly change the state t_1V_1 to $t_2V_2,\ t_2 > t_1$, at constant pressure.

Instructions for the boiler attendant: Starting with the boiler temperature t_1 slowly add hot water to your boiler until you reach t_2. Do it slowly so that the piston-pusher be able to maintain constant pressure and the process be reversible.

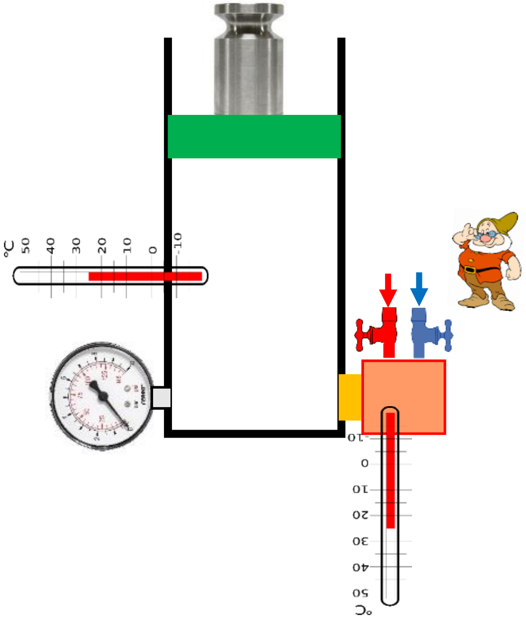
Instructions for the piston pusher: Keep watching the pressure gauge. If, due to actions of the boiler attendant, the gas pressure starts to increase, increase the volume so that the pressure drops back to required constant. If you overdo it and the pressure drops more, do decrease the volume a little. The piston-pusher works like a **barostat** (constant pressure-keeping device).

The observation record in the tV diagram might look like this:

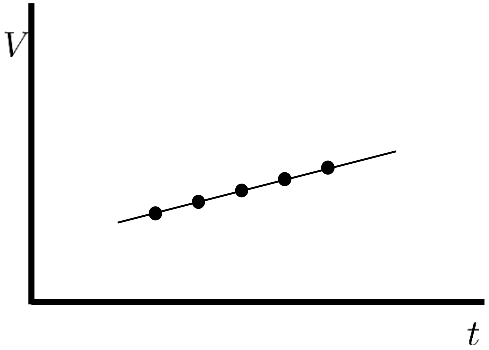




Isobaric process



A barostat function is technically easy to realize without any intelligent piston-pusher. One can use weight-loaded piston calculated so that the weight plus the atmospheric pressure add up to the desired pressure value.



Gay-Lussac

The experimental points can be fitted by a direct line (Gay-Lussac’s law)

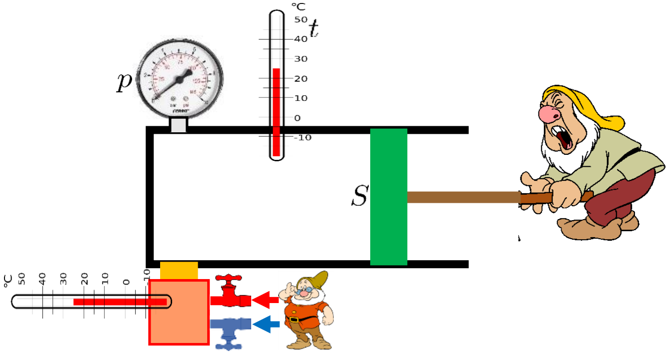
$$V = V_0(1 + \gamma(t - t_0))$$

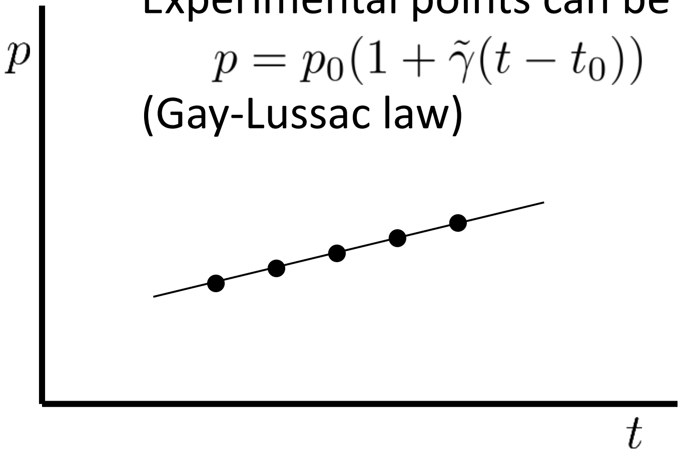
This formula already respects the fact, that if we start the process with the initial volume doubled, the volume will be doubled through the whole process. Experimentally we would also find, that the coefficient γ (coefficient of volumetric thermal expansion) is independent of the pressure value and independent of the type of molecules provided the gas is “ideal enough”.

Isochoric process

Isochoric process is experimentally quite difficult. One cannot jus fix the position of the piston: the container itself changes its dimensions with changing temperature. So the instructions for the piston-pusher are: constantly measure the container dimensions and keep adjusting the piston position so that the gas volume remains constant

The experiment visualized on a pt diagram looks as follows





Experimental points can be fitted as

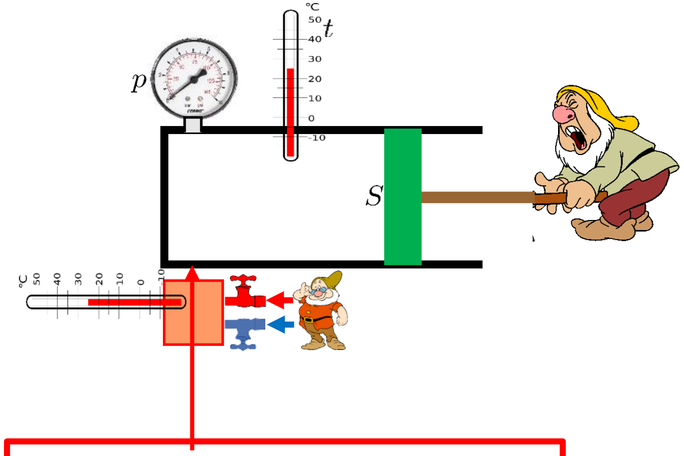
$$p = p_0(1 + \tilde{\gamma}(t - t_0))$$

(Gay-Lussac law)

Gay-Lussac

The formula already respects the fact, that if we start the process with the initial pressure doubled, the pressure will be doubled through the whole process. Experimentally we would also find, that the coefficient $\tilde{\gamma}$ (isochoric thermal pressure coefficient) is independent of the volume value and also independent of the type of molecules provided the gas is "ideal enough", and, as we shall discuss shortly, its value for ideal gasses is the same as that of the coefficient of thermal expansion γ.

Adiabatic process



No thermal contact here!

Adiabatic process is a process performed on a thermally isolated gas. In the figure we see that the thermal coupling of the heating boiler to the gas was removed, so the boiler attendant is superfluous, he does not do anything. All the process is performed by the piston pusher.
We shall postpone to write the equation of adiabatic curve on the pV diagram for later discussion.

But the piston pusher can arbitrarily change just one variable, the volume. He adjusts his pushing force according to the current gas pressure so that the process be reversible. Setting the volume to the desired value, he could read the final values of pressure and temperature.

Empirically we find that during the adiabatic process (thermal isolation, no boiler attendant) final temperature would be different from the initial one. So the **adiabatic process is different from isothermal process**. **To maintain a constant temperature we have to employ the boiler attendant to heat or cool the gas**.

The lesson of an adiabatic process (process in thermal isolation) is that one can **change the temperature by performing just a macroscopic mechanical work.** We shall come back to this observation when we shall speak about calorimetry.

Reversible processes in ideal gas, summary

The following laws has been established for reversible processes in ideal gas

- Isothermal process $pV = p_0V_0$
- Isobaric process $V = V_0(1+\gamma(t-t_0))$
- Isochoric process $p = p_0(1+\tilde{\gamma}(t-t_0))$

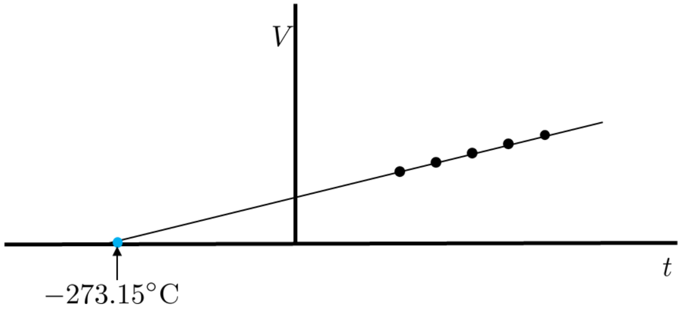
The coefficient of isobaric thermal expansion γ and the coefficient of isochoric thermal pressure $\tilde{\gamma}$ have the same value for an ideal gas and are universal, that is have the same value for all ideal gasses (provided we use the same value of the reference temperature t_0).

Their common value for t_0 =0°C is

$$\gamma_{0^\circ C} = \frac{1}{273.15^\circ C}$$

The **consequence of this universality** is, that the extrapolated straight lines for isobaric and isochoric processes in ideal gasses intercept the temperature axis at a universal point at $-273.15^\circ\mathrm{C}$.

Kelvin suggested to shift zero temperature to this point and leave the size of "one degree" the same as for Celsius scale. In this way the Kelvin temperature scale was defined.



New kelvin

Later we abandoned the use of boiling point and freezing point of water as reference temperatures and the “size” of one Kelvin temperature difference was defined by **defining** the temperature of **the triple point of water as 273.16K**. So the connection to “degree of Celsius” was abandoned although practically the two „degrees“ have equal size.

The latest development is still different. Since 2019 SI system of units was redefined and was Kelvin defined anew:

The kelvin is defined by fixing the numerical value of the Boltzmann constant k to 1.380 649×10^{-23} J·K^{-1}

Equation of state

Isobaric (Gay-Lussac) law $V = V_0(1+\gamma(t-t_0))$ $\gamma_{0^\circ C} = \dfrac{1}{273.15^\circ C}$

has a very simple form when rewritten using absolute temperature in Kelvin. Freezing point of water in Kelvin is $T_0 = 273.15$K and so γ can be written as $\gamma = 1/T_0$.
Guy-Lussac law will be

$$V = V_0(1+\frac{1}{T_0}(T-T_0)) \qquad \text{or} \qquad \frac{V}{T} = \frac{V_0}{T_0} = \text{const}$$

In a same way we can rewrite the isochoric Guy-Lussac law as

$$\frac{p}{T} = \frac{p_0}{T_0} = \text{const}$$

Now we shall perform a compound process: starting at p_1, V_1, T_1 we isothermally go to p_2, V', T_1 and from there isobarically to p_2, V_2, T_2. Applying the corresponding laws we get

$$P_1V_1 = p_2V' \qquad \frac{V'}{T_1} = \frac{V_2}{T_2}$$

and from there $\dfrac{p_1V_1}{T_1} = \dfrac{p_2V_2}{T_2} = \text{const}$ what is the ideal gas equation of state.

Equation of state

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} = \text{const}$$

Now recall the Avogadro's law: **equal volumes of all gases, at the same temperature and pressure, have the same number of molecules.** From there it is clear that the constant on in the last equation is proportional to the number of molecules and some universal constant

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} = \text{const} = Nk$$

The constant k is called the **Boltzmann constant**: $k = 1.380649\times10^{-23}$ J/K

The number of molecules N can be easily expressed through the Avogadro number N_A:

$$N = \frac{m}{M}N_A$$

and so the ideal gas equation of state reads

$$\boxed{pV = \frac{m}{M}N_AkT}$$

Historically it used to be written using a different constant R (so called gas constant) as

$$pV = \frac{m}{M}RT \qquad R = N_Ak = 8.3144598 \text{ J mol}^{-1} \text{ K}^{-1}$$

The reason was that the Avogadro number (and so neither the Boltzmann constant) was not known with acceptable precision, while R can be measured easily.
After the redefinition of mol by the new SI, the equation $N = mN_A/M$ **is not exact**, even though the error is experimentally negligible. The problem is not yet officially settled, if you want to know more, consult Wikipedia.

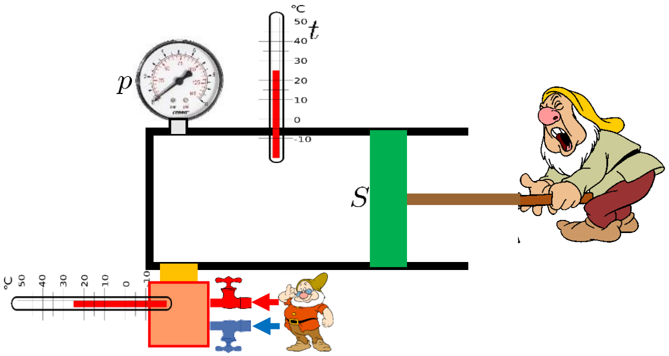
Work at reversible gas processes

In thermodynamics and in statistical physics when we say “work” we have in mind macroscopically observable work **related to our piston-pusher dwarf**.
The piston pusher (when manipulating the piston) has to use force to ensure, that the piston movement is slow enough for the process to be reversible. Applying force on a moving piston means that some work is performed.

We stress, however, that there are two parties involved: the gas and the dwarf. In the same way as the dwarf acts on the gas by force the gas acts on the dwarf by force. These two forces are, by Newton’s action-reaction principle, equal in size but opposite in direction.

Therefore we can calculate “two klinds” of work. One which is performed by the dwarf on the gas, the other one which is performed by the gas on the dwarf. Speaking about a work, we have to specify whom we consider to be **“the performer of work”** and who is considered to be **“the receiver of the work”**. There are two possible choices: the dwarf as a performer and the gas as a receiver, or the dwarf as a receiver and the gas as a performer. Depending on our choice we get two different definitions of the work, differing by the sign.

Work at reversible gas processes



Suppose we have chosen the gas to be the performer. The gas acts by a force from left to right. If the piston moves to the right by a distance dx, the gas performs the work

$$\delta A = pSdx = pdV$$

Where dV is the change of the gas volume. If we choose the dwarf to be the performer, he performs the work

$$\delta A' = -pSdx = -pdV$$

The standard choice in textbooks is **“gas as a performer”** so the standard formula used for “work performed during the gas process” is

$$\boxed{\delta A = pdV}$$

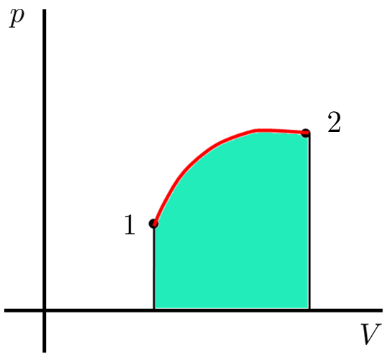
Work at reversible gas processes

Work performed during an infinitesimal reversible process in gas is

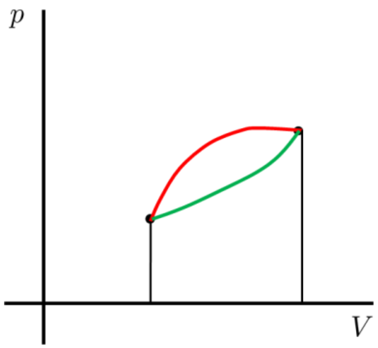
$$\delta A = pdV$$

Now consider a non-infinitesimal process from the state “1” to the state “2” as represented by the red path on the figure below. The total macroscopic work performed during that process would be

$$A = \int_1^2 pdV$$



The total work is obviously equal to the area below the curve representing the process.



Now consider a different process between the same initial and final states, represented by the green curve. The area below the green curve is obviously different from the area below the red curve and therefore the total work performed along the green curve is different from that performed along the red curve. So the **work depends on path, it is not a function of just the initial and finale states**.

Macroscopic work in general

Studying the work related to piston-pusher dwarf we have studied one specific example of macroscopically performed work.
In general the term macroscopic work is used for any work required to change a (macroscopic) external parameter (like volume of gas).
What is called external parameter was never quite clear to me on a phenomenological level in thermodynamics. In statistical physics, and particularly in quantum statistical physics, it is more clearly defined. We have a system with very many degrees of freedom (like 10^{26}) We consider its stationary states and the corresponding energy spectrum. The energy spectrum values might depend on some macroscopic parameters (like volume, magnetic field etc.). Those parameters are, by definition , called **external parameters**. If an external agent (dwarf) changes the value of an external parameter, it leads to changes of the energy spectrum, and therefore it changes the total energy of the system.
Therefore work must be performed to change the external parameter value. Since the external parameter (V) is a macroscopic parameter, the change of its value (dV) is also macroscopic and the corresponding work ($\delta A = pdV$) is "macroscopically observable". In the formula p denotes a force parameter conjugated to the external parameter V. In particular: if the system is in its i-th stationary state with energy E_i, the conjugated force value (in the state i) is defined as

$$p_i = -\frac{\partial E_i}{\partial V}$$

Microscopic work: heat

There is, however, also a different way how to change the energy of a system, not by changing the external parameters values.

If we bring the system considered to a thermal contact with some external objects, then the interaction of molecules (collisions) of the two systems can change of the energy of the system being considered. How it is done? Of course by performing work on the molecular level. It is a simple mechanical work as known from the courses of mechanics, but typically this work is performed on a microscopic level and is not directly observable macroscopically.

According to present-day terminology this **work performed on a microscopic molecular level** is called **heat**. However, there was a complicated historical development until the physicist arrived at the knowledge, that **what they phenomenologically called heat is not a sort of (kind of) energy, it is rather a kind of work**.

The difference between “the work” and “the energy” is principal. **Common people still speak about heat as a kind of energy**. So some more notes about the history of “heat” are necessary now.

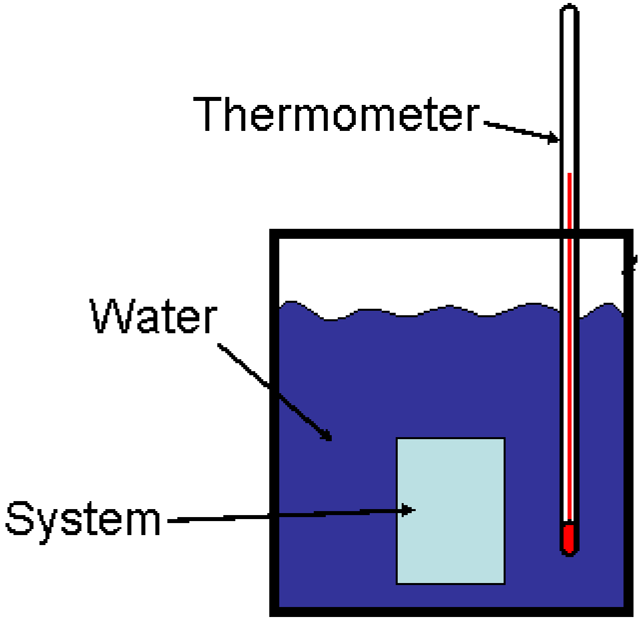
Historical notes

We have at least intuitive feeling about temperature. So it was in the history. People learned how to measure temperature **without properly understanding what “temperature really is”.** The invention of a thermometer was not a single act. Various thermoscopes were known by old Greeks. But only much later people introduced some arbitrary scales to thermoscope leading gradually to the development of thermometer. Our practical scale was introduced by Celsius at the first half of the 18 century.

The invention of thermometer opened the way to gather empirical facts related to temperature and how it can be changed.

It was obvious that temperature of some object could be changed by heating it or cooling it, what essentially meant **to bring it into a thermal contact** with something hotter (with higher temperature) or something cooler (with lower temperature). Again what physical process is hidden behind the heating or cooling was not understood at all.

Calorimetry



Quantitative experiments about heating or cooling were done using calorimeters.
A calorimeter is a thermally isolated vessel. Inside the vessel we bring into contact two physical objects having initially different temperatures. Typically one object is a liquid like water, the other may be some solid body.
After some time the thermal equilibrium is established, both object having the same temperature which we measure.

So the experiment looks like this
Water: mass m_1, initial temperature t_1. Solid body: mass m_2, initial temperature $t_2 > t_1$.
The final temperature is t.
Empirical facts show that there is a material constant for water c_1 and for the body c_2, so that a following calorimetric equation holds

$$\boxed{m_1 c_1 (t - t_1) = m_2 c_2 (t_2 - t)}$$

The material constants c_1, c_2 are called specific heat constants.

Calorimetric equation as a conservation law

Calorimetric equation can be rewritten as: $m_1 c_1 t_1 + m_2 c_2 t_2 = m_1 c_1 t + m_2 c_2 t$

Inspecting that equation it looks like a conservation law. Some quantity calculated like mct is the same at the beginning an at the end of the process. This something looks like to be hidden inside the objects but distributed differently between the two objects during the process, the total sum being conserved.

We certainly cannot resist the temptation to introduce a new physical quantity: **the heat**. The heat is hidden inside the objects, can be transferred between the objects, the total amount of heat is conserved. More heat inside the object means higher temperature. It led to terminology like **heat transfer, loss of heat, "heat is transferred through conduction, flow or radiation"**. **All this was found to be wrong!**

The crucial point was, that the first calorimetric measurements were done using fluids or solid bodies both having the property that they change their volumes with temperature only slightly. The situation is dramatically different with gases.

We have seen during a qualitative discussion of an adiabatic process **that we can change the temperature of some gas just by changing its volume by the "piston pusher" who is acting by force on a moving piston therefore performing mechanical work.**

So the lesson is simple, to change the temperature, we do not need to increase the "heat content" of the body, we **can just perform mechanical work**.

Phenomenological units of heat

Historically, when people defined heat as “something that is conserved according to the calorimetric equation

$$m_1c_1(t - t_1) = m_2c_2(t_2 - t)$$

it was obvious, that there is not any “natural” physical unit of heat, The content of heat in a body defined as mct is not well defined until we define the physical unit for the heat capacity.

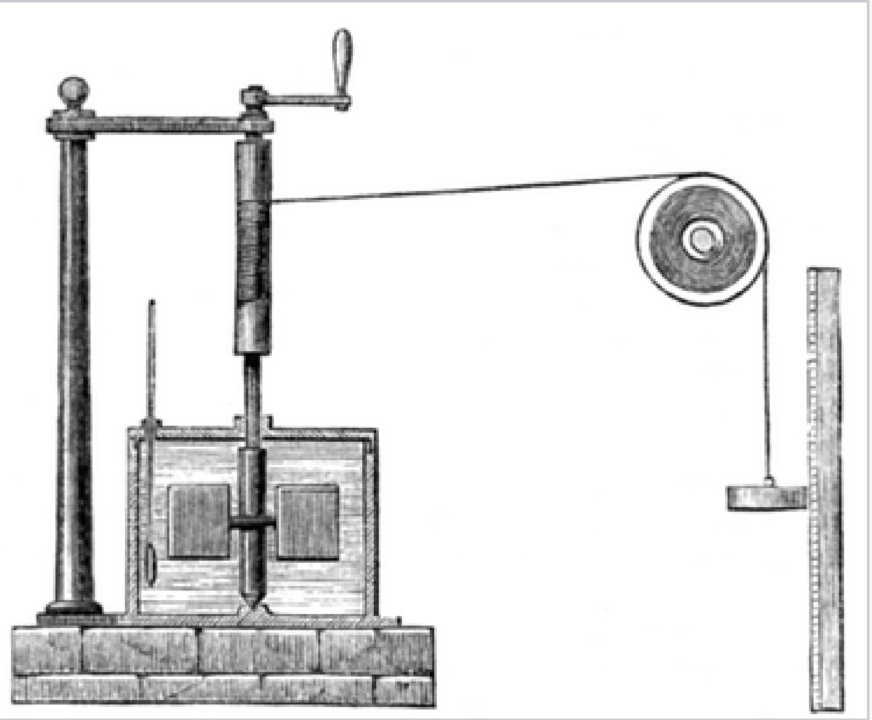
It is obvious, that if we multiply the heat capacities of all materials by the same constant, the calorimetric equation would still hold, That means the unit for heat capacity can be arbitrary, since the heat capacity and/or heat itself is (at this level of physics knowledge) not directly connected to any other physical quantity (with already defined physical unit).

So the unit of heat was chosen arbitrarily to be one calorie “cal” defined as the amount of heat needed to increase the temperature of one gram of water by one degree.

Therefore the specific heat of water was defined as 1 cal/g/K. The specific heat of any other material can then be measured by a suitable calorimetric measurement.

Mechanical equivalent of heat

Benjamin Thompson, Count Rumford, had observed the frictional heat generated by boring cannon at the arsenal in Munich, Germany circa 1797. More precise measurements were done by James Prescott Joule in the 1840s.



Joule's apparatus for measuring the mechanical equivalent of heat in which the "work" of the falling weight is converted into the "heat" of agitation in the water.

Finally it was found that the same increase of temperature of some object as achieved by “transfer of heat” of **1 kcal can be achieved by performing a mechanical work of 4186 J**.

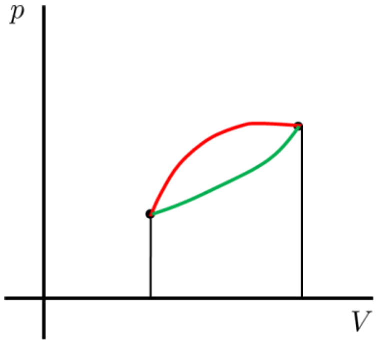
So it was found that the “amount od heat” can be more naturally measured by the units of work, Joules. In this way a “mechanical equivalent of heat” was found. **Calories can be universally converted to Joules by the conversion constant 4186 J/kcal.**

Work and heat for reversible processes in gas

We have found that the work performed by the “piston-pusher” during a reversible process changing the state of gas from the state “1” to the state “2” can be calculated as

$$A = \int_1^2 p dV$$

and this work depends on “the trajectory” of the process between the initial and final states, as it is clearly seen from the figure below.



The obvious question is how much heat is to be provided by the boiler attendant on a particular process (trajectory). A careful investigation of this problem has led to precise specification of the concept of energy formulating the law called “first law of thermodynamics”.

First law of thermodynamics

For any process between the two states “1” and “2” we can calculate the work performed by the piston pusher

$$A = \int_1^2 p dV$$

and we can measure the heat “transferred” to the gas by calorimetric consideration of the actions performed by the boiler attendant. The following empirical law was established.

The sum of mechanical work and heat (converted to Joules) depends only on the initial and final states of the system and so this sum is the same for any (reversible) process (trajectory) between those two states.

Let us stress again: the work by itself and the heat by itself depend on the specific trajectory, their sum does not.

This means that the sum of work and heat must be calculable from the characteristics of the initial and final states only.

This means that we can define a physical quantity of state in such a way, that the difference of this quantity between the two states is equal to the sum of work and heat performed during (any reversible) process between the two states.

First law of thermodynamics

Repeating: the first law of thermodynamics says, that there must be a physical quantity of state such that **the sum of work and heat is calculable as a difference** of this quantity between the final and initial state.

This quantity was given a name: **energy**. More precisely, the phenomenological thermodynamics used the name **internal energy**. The reason perhaps was, that it was not obvious that the state function “energy” as found by thermodynamical considerations has anything common with the quantity “energy” as found in the studies of Newtonian mechanics of particles.

Of course, there was a connection: the internal energy can be changed at the expense of mechanical work, the same work as found in classical mechanics.

Only after molecules were discovered, it was clear that the **“internal energy” is a “standard” mechanical energy of molecules**, just macroscopically “not directly visible”.

In what follows we shall use the terminology “energy”, without the attribute internal.

First law of thermodynamics

The obvious task for a phenomenologist is to find the formula for energy as a function of quantities defining the macrostate.

Obviously, the first law of thermodynamics can determine only the difference of energies of two states, so energy in thermodynamics is defined up to an arbitrary additive constant.

The phenomenologist has to define some arbitrary reference macrostate whose energy is set to 0 by definition. Then he has to measure the sum of work and heat going from the reference state to an arbitrary macrostate. Based on experimental data he has to “guess” a formula for energy.

A theoretician, who already knows that behind the macrostate there is some microstate of molecules can in principle calculate the (mechanical) energy of molecules in the chosen representing microstate and**, based on statistical considerations, express the energy of the macrostate through the macroscopic quantities defining the macrostate considered**.

First law of thermodynamics

we shall present the statistical analysis later; here we will just quote (without proof) formulas for the energy of ideal gasses.

Gas of N moecules has energy

$$\boxed{\begin{aligned} E &= \frac{3}{2}NkT \quad \text{for gas whose molecues are just single atoms} \\ E &= \frac{5}{2}NkT \quad \text{for gas whose molecues consist of two atoms} \\ E &= \frac{6}{2}NkT \quad \text{for gas whose molecues consists from more than two atoms} \end{aligned}}$$

These formulas are just approximate, more exact quantum mechanical expressions should take into account details of internal structure of atoms and molecules. We introduce a universal notation as

$$\boxed{E = C_V T \quad \text{where } C_V = \frac{3}{2}Nk \text{ or } C_V = \frac{5}{2}Nk \text{ or } C_V = \frac{6}{2}Nk}$$

The rationale for this notation will be clear when we shall discuss the isochoric process energy heat balance.

First law of thermodynamics

Let us finally present a formula corresponding to the first law of thermodynamics as it is usually presented in standard textbooks.

Let us consider an infinitesimal change of state between two close macrostates. The energy difference will be dE, the mechanical work preformed by the physical system will be δA, and heat performed by an external agent (boiler attendand) δQ. The first law of thermodynamics then reads

$$\boxed{dE = \delta Q - \delta A}$$

Do notice that the first law of thermodynamics is, in fact, the generalized law of energy conservation: any change of energy has to be balanced by work of external agents. Do notice the negative sign of the mechanical work. This is due to a standard convention that when speaking of the mechanical work we speak about work performed by the system (gas) upon an external agent (piston pusher), while the convention for heat is that it is the (microscopic) work performed by an external agent (boiler attendant) upon the physical system (gas).

Do also notice, that we use the terminology “performed heat” and not “transferred heat”. **Heat is a form of work: it is not a form of energy**.
A few words to notations. d in dE **means the difference** of two (infinitesimally close) values of energy. Symbol δ in δA means that it is an infinitesimally small value, **but it is not a difference of any two values**. The amount of work depends on the trajectory, so it is not a difference of a final and initial values of any state quantity. Similarly for heat.

Heat is a form of work, not of energy

The fact that heat is not a form of energy we consider to be so important, that we devote to it a special slide.
The difference between “work” and “energy” is essential. Energy is a state quantity, work is not. We can say that energy is “stored” in a physical system as are goods in some warehouse. The energy can be “taken out” of this warehouse and transferred to some other object to be stored inside it.
The way, how the energy can be transferred from one object to another is by performing work. Work is the property of some process. Once the process ends, the work is no more there.

If you go with your car to a service, you get an invoice. There are two groups of items mentioned in the invoice: **spare parts and work**. Spare parts were stored in the service warehouse, were taken out of there and mounted to your car. From then on, the spare parts are stored in your car and they are there long after the service operations were finished, you take them to your home with your car.
On the other hand the invoice mentions performed work (usually expressed in man-hours). The work was not stored anywhere in any warehouse. It was just performed during the service operations. You did not take the “performed work” to your home with your car. The work is nowhere after service operations ended.
Well, this is exactly the difference between “energy” and “work”, or “energy” and “heat”. So if you get an invoice saying **“we delivered to you 1 GJ of heat” it is nonsense**. The invoice should read **“we performed for you 1 GJ of heat”**. Unfortunately, nobody speaks like that. People just do not follow my lectures.

First law of thermodynamics as a definition of heat

The first law of thermodynamics
is often written as

$$dE = \delta Q - \delta A$$

$$\delta Q = dE + \delta A$$

In this form it can be interpreted as the definition of heat. The point is that we can easily calculate the mechanical work δA for any process (just using the formula $\delta A = p\ dV$.
We also often know (either by phenomenological analysis or by theoretical calculation) the formula for energy. What is less obvious is calculation of heat for an arbitrary process. **So we easily define that heat is the missing work needed to complete the energy – work balance**.

We shall demonstrate the energy – work – heat calculations for standard gas processes.

Energy – work – heat for the isochoric process

Isochoric process means constant volume, $dV = 0$. So no mechanical work is performed.

For ideal gas we have the energy formula

$$E = C_V T$$

so $dE = C_V dT$ and from the first law of thermodynamics we get for heat at isochoric process

$$\delta Q = C_V dT$$

This is a typical calorimetric formula, so we now know the meaning of the constant C_V: it is the heat capacity of ideal gas for isochoric process.

Please, do remember, that the formula $dE = C_V \, dT$ is valid for **any process with ideal gas**, since the energy difference is process independent. So there is always the constant C_V in this formula, it is just an “accident” that this constant has a special meaning for isochoric process. So, for example, for isobaric process we still have $dE = C_V dT$ and **not** something like $dE = C_p dV$.

Energy – work – heat for the isobaric process

Isobaric process means constant pressure, $p = \mathrm{const}$. Calculation of mechanical work is trivial

$$A = \int p\, dV = p \int dV = p\Delta V = Nk\Delta T$$

For ideal gas we have the energy formula $E = C_V T$ and so

$$\Delta E = C_V \Delta T = \frac{1}{Nk} p\Delta V$$

The firs law of thermodynamics then gives

$$Q = \Delta E + A = C_V \Delta T + Nk\Delta T = C_p \Delta T$$

This is a typical calorimetric formula, however, for isobaric process. We have denoted the corresponding heat capacity (at constant pressure) as

$$C_p = C_V + Nk.$$

The last relation is called Mayer relation and for **one mole** it reads

$$C_p = C_V + R$$

Energy – work – heat for the isothermal process

Isothermal process means constant temperature, $T = \text{const}$. Calculation of mechanical work is not difficult

$$A = \int p \, dV = \int \frac{p_1 V_1}{V} = p_1 V_1 \ln \frac{V_2}{V_1} = NkT \ln \frac{V_2}{V_1}$$

For ideal gas we have the energy formula $E = C_V T$ and so

$$\Delta E = 0$$

The firs law of thermodynamics then gives for the isothermal process

$$Q = \Delta E + A = A = NkT \ln \frac{V_2}{V_1}$$

Adiabatic process

Now he have enough knowledge to calculate everything about adiabatic process which is defined as $\delta Q = 0$. From the first law of thermodynamics we get

$$\delta Q = dE + \delta A = C_V dT + pdV = 0$$
$$\frac{dT}{dV} = -\frac{p}{C_V} = \frac{NkT}{VC_V}$$

What we got is a differential equation for an unknown function $T(V)$ describing an adiabatic process on a VT diagram. We are willing to use a pV diagram, so we need a differential equation in pV variables. We swap VT for pV using the equation of state:

$$dpV + pdV = NkdT$$
$$0 = C_V dT + pdV = C_V \frac{dpV + pdV}{Nk} + pdV$$
$$C_V V dp + (C_V + Nk)pdV = 0$$
$$\frac{dp}{dV} = -\frac{C_V + Nk}{C_V}\frac{p}{V}$$

Using the Mayer relation $C_p = C_V + Nk$ we get

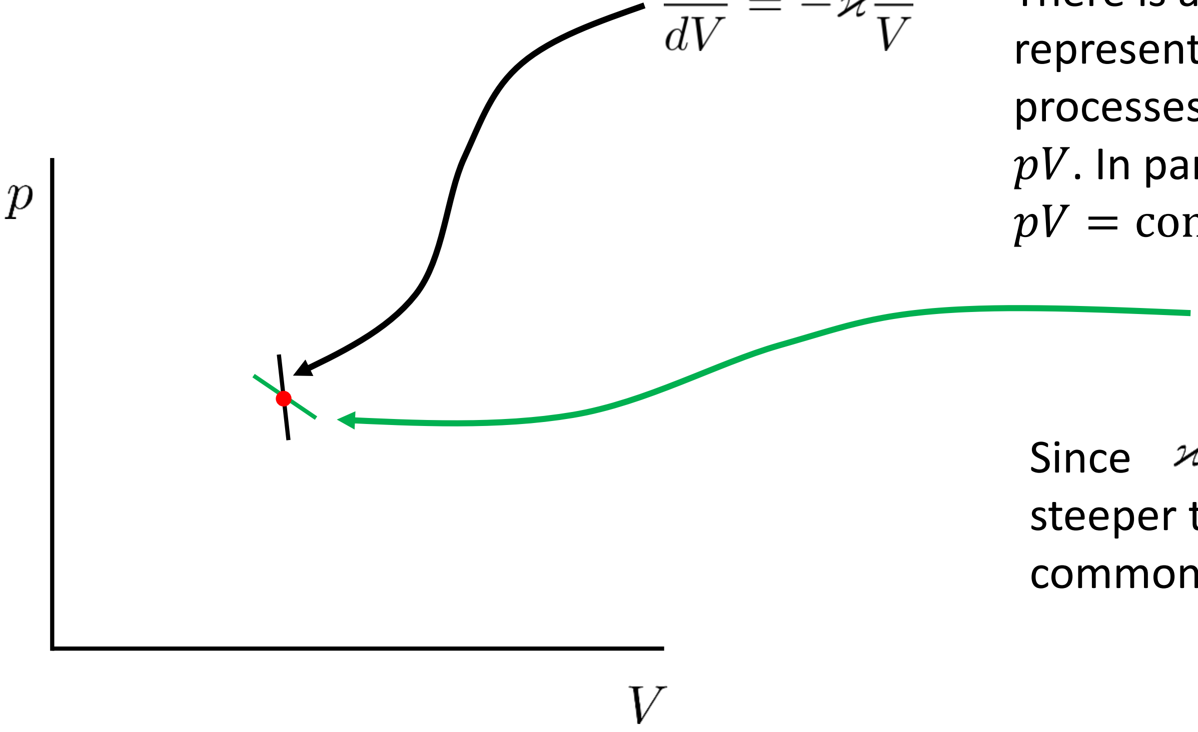
$$\frac{dp}{dV} = -\frac{C_P}{C_V}\frac{p}{V} = -\varkappa\frac{p}{V}$$

where we introduced **Poisson constant** $\boxed{\varkappa = \frac{C_P}{C_V}}$

Adiabatic process

$$\frac{dp}{dV} = -\varkappa \frac{p}{V} \qquad\qquad \varkappa = \frac{C_P}{C_V}$$

What we have got? It is a differential equation for the unknown function $p(V)$ representing an adiabatic process on a pV diagram. We are looking for a curve, which starts at a given initial state $p_1 V_1$ and in each pV point through which it goes it has the derivative (slope)



$$\frac{dp}{dV} = -\varkappa \frac{p}{V}$$

There is an infinite number of curves representing different reversible processes going through arbitrary point pV. In particular there is an isotherm $pV = \text{const}$, the slope of which is

$$\frac{dp}{dV} = -\frac{p}{V}$$

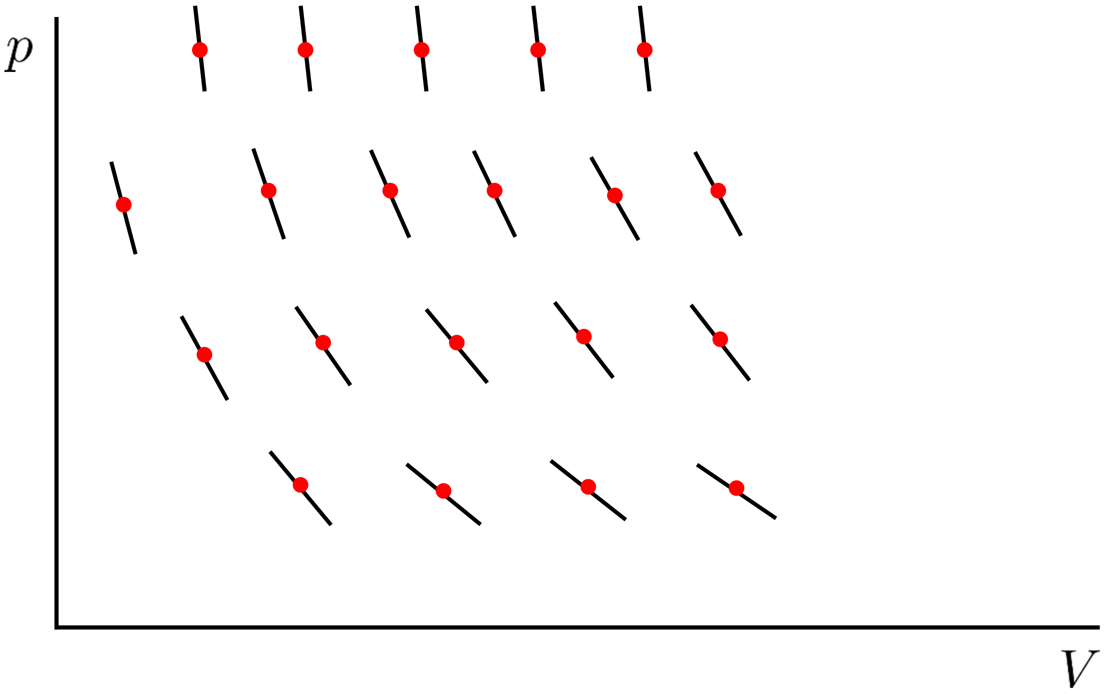
Since $\varkappa > 1$ the adiabatic curve is steeper than the isotherm in a common pV point.

Adiabatic process

in principle we can draw in any point in the pV diagram a short line showing the slope of the adiabat curve going through that point as given by the formula

$$\frac{dp}{dV} = -\varkappa \frac{p}{V}$$

We should get something like this (the figure is just a sketch, not exact drawing)



Now imagine we have a figure with a very dense population of local slope lines. If we choose one point as a starting state for an adiabatic process, we can **simply draw a continuous curve going through the points** and get the whole adiabat.

Adiabatic process

in principle we can draw in any point in the pV diagram a short line showing the slop of the adiabat curve going through that point as given by the formula

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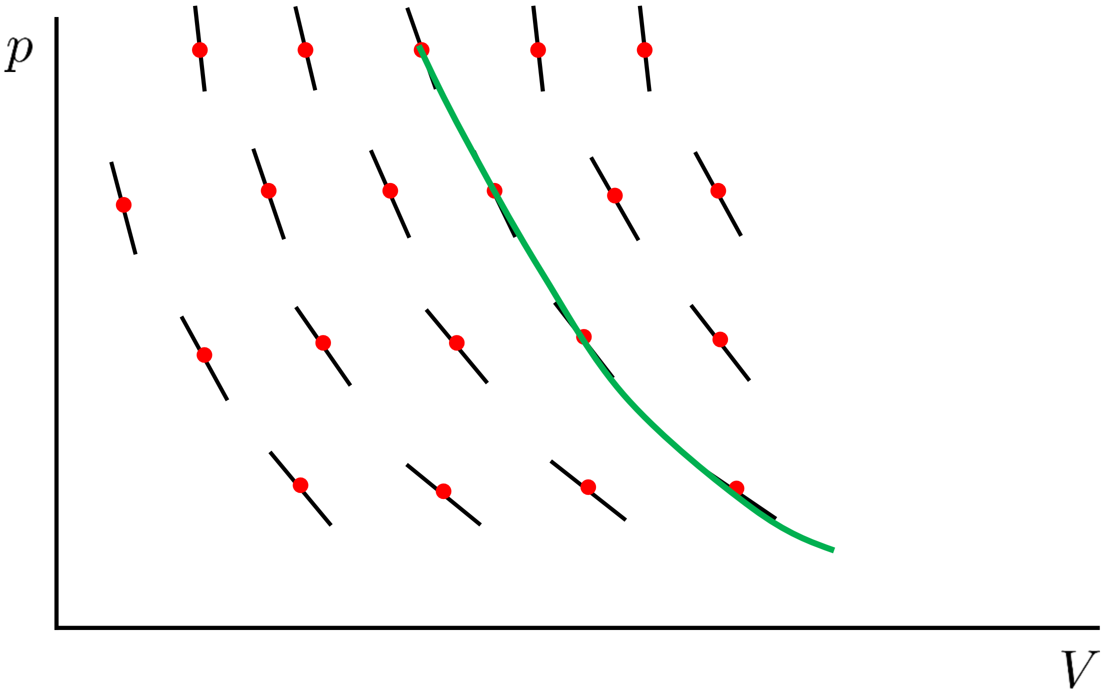


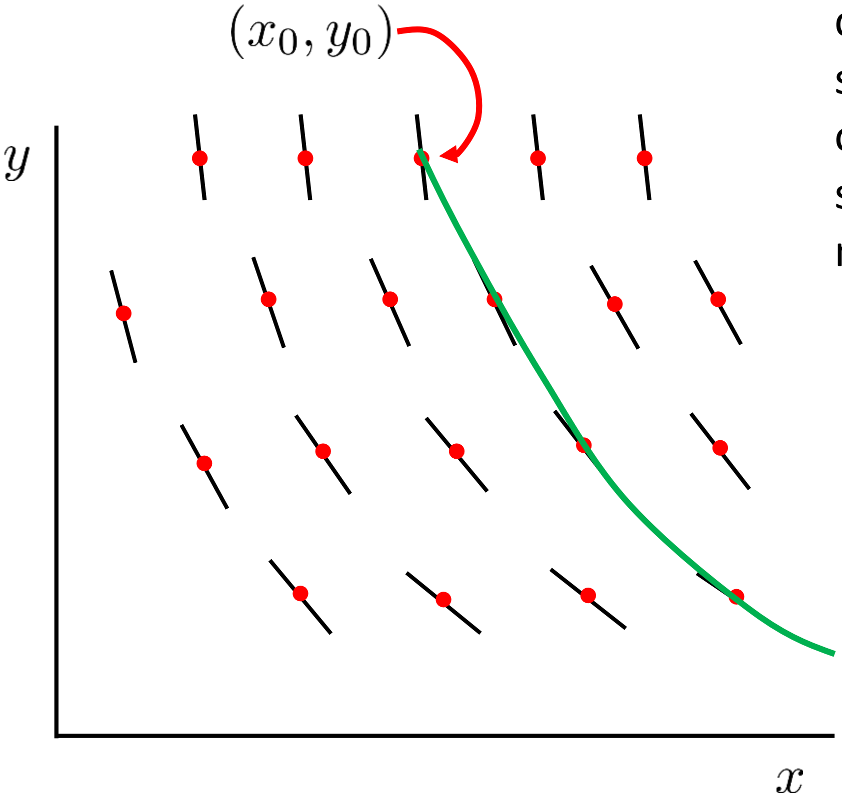
Now imagine we have a figure with a very dense population of local slope lines. If we choose one point as a starting state for an adiabatic process, we can simply draw a continuous curve going through the points and get the whole adiabat.

The green curve is a smooth curve going through the points and having in each point the slope as given by the short slope line in that point

A note on differential equations

Solving a first order differential equation $\frac{dy}{dx} = f(x, y)$

we are looking for a curve $y(x)$, which starts at the point (x_0, y_0) and in each point (x, y) through it goes it has the slope $f(x, y)$. The visualization of this problem in the x, y plane is the same as we have seen when looking for the adiabat curve



Instead of drawing a curve by hand we can use a computer to make many small steps finding a sequence of points (x_i, y_i) which approximately lay on the curve we are looking for. A simple recursive stepping algorithm does the job (Euler numerical method for solving differential equations)

$$\boxed{\begin{aligned} x_{i+1} &= x_i + \Delta \\ y_{i+1} &= y_i + f(x_i, y_i)\Delta \end{aligned}}$$

A higher order differential equation can be easily rewritten as a first order equation in a higher dimensional space and the Euler method can be used.

Adiabatic process

The differential equation for the adiabat

$$\frac{dp}{dV} = -\varkappa \frac{p}{V}$$

can easily be solved analytically.

$$\frac{dp}{p} = -\varkappa \frac{dV}{V}$$

$$\int_{p_0}^{p} \frac{dp}{p} = -\int_{V_0}^{V} \varkappa \frac{dV}{V}$$

$$\ln \frac{p}{p_0} = -\varkappa \ln \frac{V}{V_0} = -\ln \left(\frac{V}{V_0} \right)^{\varkappa}$$

$$\boxed{pV^{\varkappa} = p_0 V_0^{\varkappa}}$$

This is the adiabat curve (for ideal gas) which goes through a given point (p_0, V_0).

Carnot cycle

The **Carnot cycle** is a theoretical thermodynamic cycle proposed by French physicist Sadi Carnot in 1824. It provides an upper limit on the efficiency that any classical thermodynamic engine can achieve during the “conversion of heat into work”, or conversely, the efficiency of a refrigeration system in creating a temperature difference (e.g. refrigeration) by the application of work to the system.

The analysis by Carnot is an example of “intellectual beauty”. Using very simple considerations, without any heavy mathematics, Carnot was able to demonstrate, that there is an upper limit for the efficiency of any thermodynamic engine which has access just to two reservoirs: hot at temperature T_1 and cold at temperature T_2. What is really striking is that “any engine” means even engines not yet proposed and even engines working on some new (not yet discovered) physical interactions of matter. **A demonstration of power of human intellect.**

Technical praxis needs a lot of machines able to perform mechanical work: lifting or moving objects, pumping fluids, machining (turning, drilling, milling) materials etc. To perform work, one needs a source of energy. Sometimes it is just a form of mechanical energy like in the watermill. However, sources of mechanical energy (which are simple to use to perform mechanical work) are rare. We have much richer resources of chemical energy, which can simply be used to perform heat but not so easily to perform macroscopic mechanical work.

Thermodynamic cyclic engine

We have used the expression “conversion of heat into work”. This expression is scientifically not quite correct. Heat is not a form of energy; it is a form of (microscopic) work. A **heat engine** (thermodynamic engine) is a device, which receives work in the form of heat and performs macroscopic mechanical work.

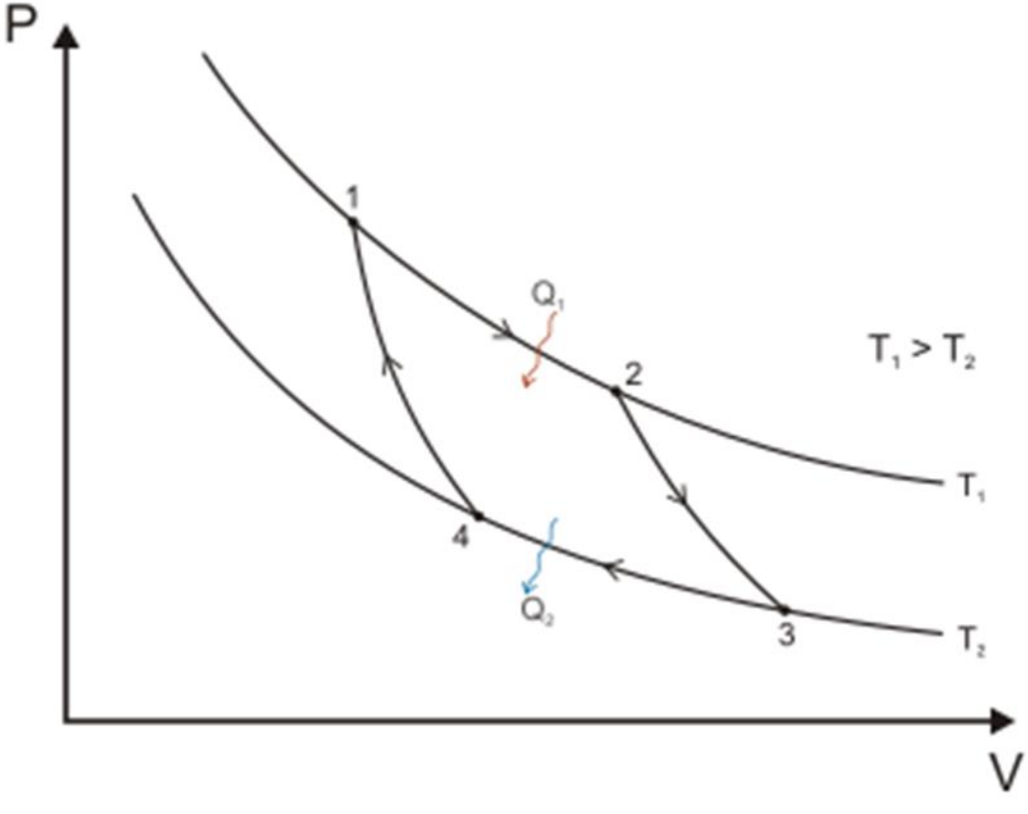
Speaking about the efficiency of such a machine we have in mind how many “Joules of mechanical work” can be produced receiving some amount of Joules of heat work.

Carnot engine is a hypothetical cyclic thermodynamic machine which has access just to two reservoirs: hot at temperature T_1 and cold at temperature T_2. Its cycle consists of 4 steps.

It is worth to stress, that the **size of the machine** (how many moles of working gas is used) is arbitrary. **The amount of useful work the machine provides during one cycle depends on its size**.

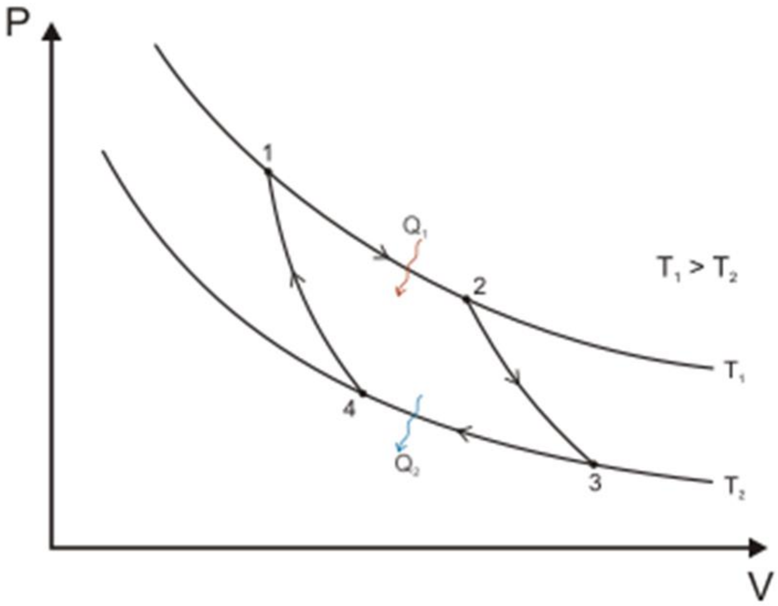
Carnot cycle

The Carnot cycle starts (end ends) in the point (p_1, V_1, T_1). All three parameters can be chosen arbitrarily. The size of the machine (N) is then uniquely given by the equation of state $pV = NkT$. The cycle consist of four reversible steps



1. The isothermal expansion on $T_1$to arbitrarily chosen volume V_2. The Pressure p_2 is then uniquely determined.
2. The adiabatic expansion to temperature T_2, point (p_3, V_3) is then uniquely determined.
3. The isothermal compression on T_2 to a point p_4, V_4 which is uniquely determined by the requirement that from there one can get adiabatically to the initial point p_1, V_1.
4. The adiabatic compression to the point p_1, V_1.

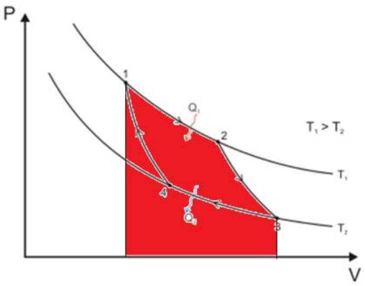
Carnot cycle



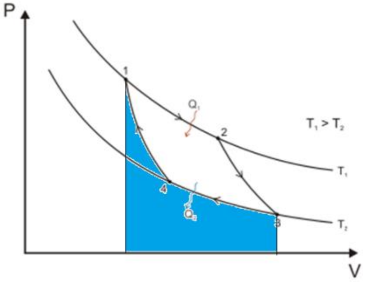
1. The isothermal expansion on T_1 to arbitrarily chosen volume V_2. The Pressure p_2 is then uniquely determined.
2. The adiabatic expansion to temperature T_2, point (p_3, V_3) is then uniquely determined.
3. The isothermal compression on T_2 to a point p_4, V_4 which is uniquely determined by the requirement that from there one can get adiabatically to the initial point p_1, V_1.
4. The adiabatic compression to the point p_1, V_1.

The machine performs positive mechanical work during the expansion steps 1 and 2 and negative mechanical work during the compression steps 3 and 4.
It is an easy but a bit tedious work to calculate all the state parameters p_2, p_3, V_3, p_4, V_4 from a given set p_1, V_1, T_1, T_2, V_2. Once we have those values it is easy to calculate heat and work for each step of the Carnot cycle.

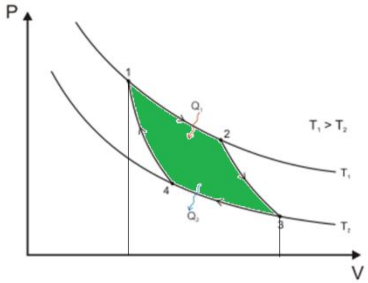
Carnot cycle



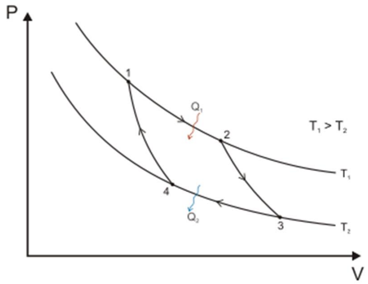
The machine performs positive mechanical work during the expansion steps 1 and 2, the total amount of the positive work is given by the area marked as red in the figure.



The machine performs negative mechanical work during the compression steps 3 and 4, the total amount of the negative work is given by the area marked as blue in the figure.



The net amount of work (A), which can be used during one cycle is given by the area marked as green in the figure.

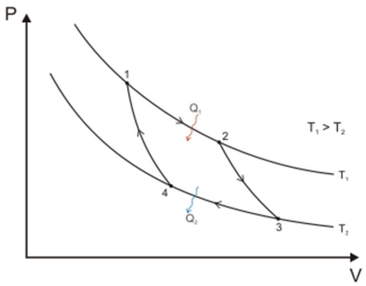


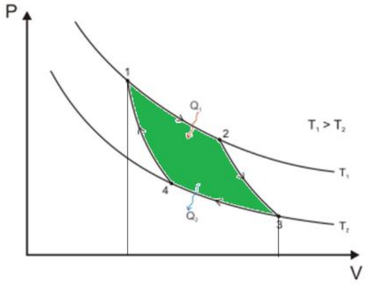
There is a positive heat $Q_1 > 0$, performed by the thermostat keeping the temperature T_1 during the step 1 and a negative heat $Q_2 < 0$ at temperature T_2 during the step 3. Heat is zero during the adiabatic steps 2 and 4.

Since the machine gets to the initial state after performing the cycle, the useful work A can be calculated as $A = Q_1 - |Q_2|$.

Carnot cycle: efficiency

Carnot main motivation to study heat engines was the problem how to increase the efficiency of real thermodynamic machines. He designed the Carnot cycle to study the efficiency in general.
The efficiency of the Carnot machine is defined as





$$\eta = \frac{A}{Q_1} = \frac{Q_1 - |Q_2|}{Q_1}$$

Once we calculate all the state parameters relevant to the Carnot cycle it is easy to calculate the efficiency. One gets a simple formula

$$\boxed{\eta = \frac{T_1 - T_2}{T_1}}$$

Note on efficiencies

There are frequent misconceptions concerning the notion efficiency:

- that it is a physics notion defined like (power output)/(power input)
- that efficiency is always less than 100 %

There is no unique technical definition of efficiency: it is more an economics notion than a physics notion. The idea can perhaps be symbolically defined as

$$\boxed{\text{efficiency} = \frac{\text{performance}}{\text{price}}}$$

To be mathematically consistent one has to quantitatively express both “performance” and “price” in same units. It may be dollars, watts, amount of water (like amount of water pumped out of a mine compared to the amount of water needed to turn the water wheel driving the pump), etc.

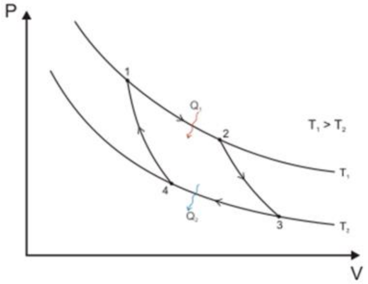
The efficiency can easily be much larger than 100%. A drastic example might be a picklock priced 100 $ to steel a luxury car priced 1 million $. The efficiency is 10000 % (until you get caught by the police).

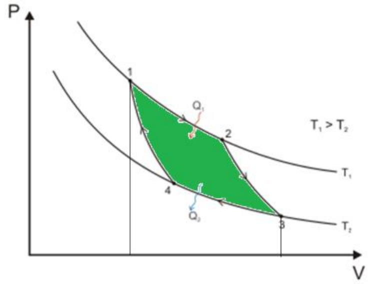
Carnot cycle: efficiency

We have defined the efficiency of the Carnot machine as

$$\eta = \frac{A}{Q_1} = \frac{Q_1 - |Q_2|}{Q_1}$$

$$\boxed{\eta = \frac{T_1 - T_2}{T_1}}$$





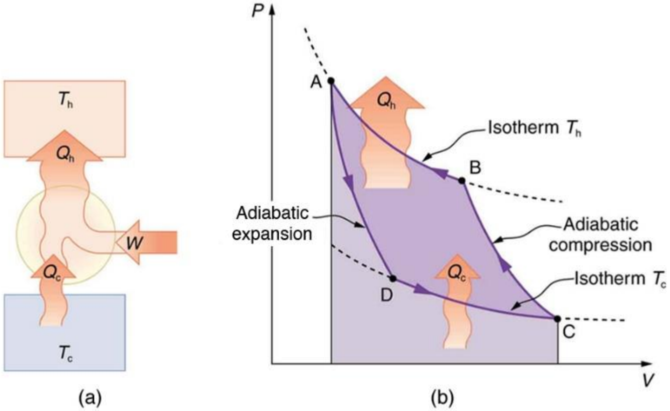
The reason for this definition is simple. The purpose for the thermodynamic engine is to get useful mechanical work A. And we have to pay cost for burning some fuel to provide heat Q_1.
At the time being the cooling (Q_2) is free of charge, we use the atmosphere as heat absorber. It may happen in future that we will have to pay charges for “heat pollution”, then the definition of the engine efficiency would be something like

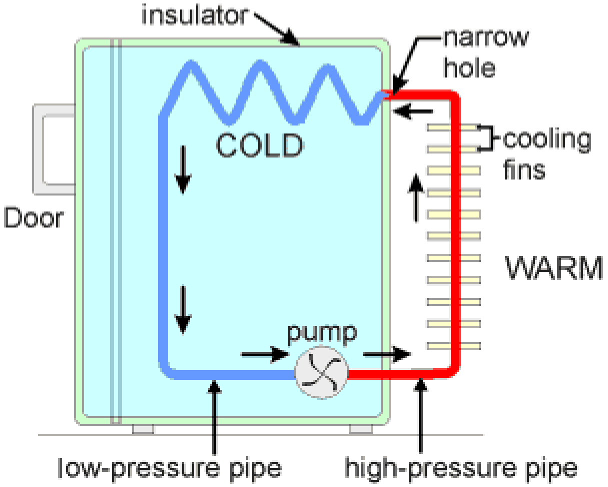
$$\eta = \frac{A}{Q_1 + \alpha Q_2} = \frac{Q_1 - |Q_2|}{Q_1 + \alpha Q_2}$$

where α would be a “penalty price factor” for heat pollution determined by the state government.

Carnot engine as a refrigerator

Carnot cycle is reversible so the engine can run in the opposite direction. Instead of producing useful work it consumes mechanical work, “receives” heat from the cold body and heats the hot body. So it works as a refrigerator: the cold body becomes even colder, the hot body (“kitchen environment”) gets even hotter. You have certainly noticed the heat radiator on the back of a kitchen refrigerator.





Since the Carnot cycle is run exactly in the opposite way, all the quantities have the same absolute value, jut opposite signs ($Q_1 < 0, Q_2 > 0, A < 0$).

Think about the efficiency of a refrigerator. The purpose is the heat Q_2 “pumped out” from inside and the cost is the mechanical work (we pay for the electricity to drive the compressor). So we get

$$\eta = \frac{Q_2}{|A|} = \frac{Q_2}{|Q_1| - Q_2} = \frac{T_2}{T_1 - T_2}$$

Carnot engine as a heat pump

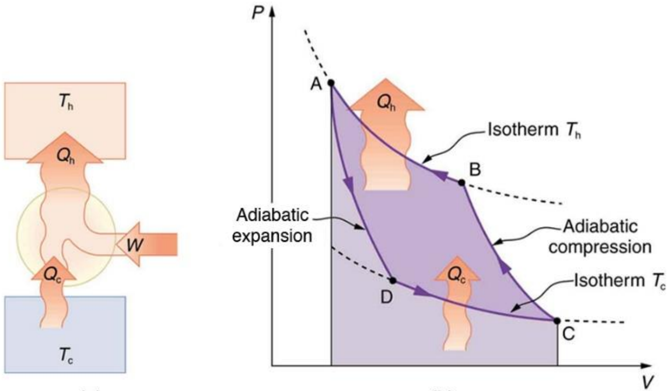
Carnot engine run in the reverse direction can be used not only as a refrigerator to cool the cold but also as a heater to heat the hot.

To get a heat pump for heating you can in principle take a standard refrigerator, throw away its door, open the balcony and insert the refrigerator into the balcony door so that the interior of the refrigerator is seen from outside the building like here in the picture.

If you look from inside the room, you will see the backward side of the refrigerator with the (black) heat exchanger replacing the balcony door.

If you switch on the refrigerator it will start to cool the outside atmosphere and heat the room by the hot heat exchanger

Carnot engine as a heat pump



(a) (b)

A heat pump works exactly as a refrigerator: it “takes out” heat Q_2 from outside, consumes the mechanical work $|A|$ and “injects” heat $|Q_1|$ into the room. What is its efficiency?

The purpose is $|Q_1|$ and the cost is $|A|$.

$$\eta = \frac{Q_1}{|A|} = \frac{Q_1}{|Q_1| - Q_2} = \frac{T_1}{T_1 - T_2} > 1$$

The efficiency of a heat pump is larger than 100% ! We get more Joules into the room than we pay for the Joules of A !

Carnot theorem

The Carnot theorem states: No engine operating between two heat reservoirs can be more efficient than a Carnot engine operating between the same reservoirs.

The Carnot theorem has to be read carefully. It says, that the Carnot engine is a winner of a competition between all possible heat engines. However, one has to read carefully the rules for that competition.

The rules to be observed by all engines willing to take part in the competition are here:

- the heat engine must be a cyclically working machine, each cycle starting and ending in the same state
- the machine is allowed to interact only with two outer systems: two heat reservoirs, one having temperature T_1, the other temperature T_2, or be thermally isolated during some parts of its cycle.

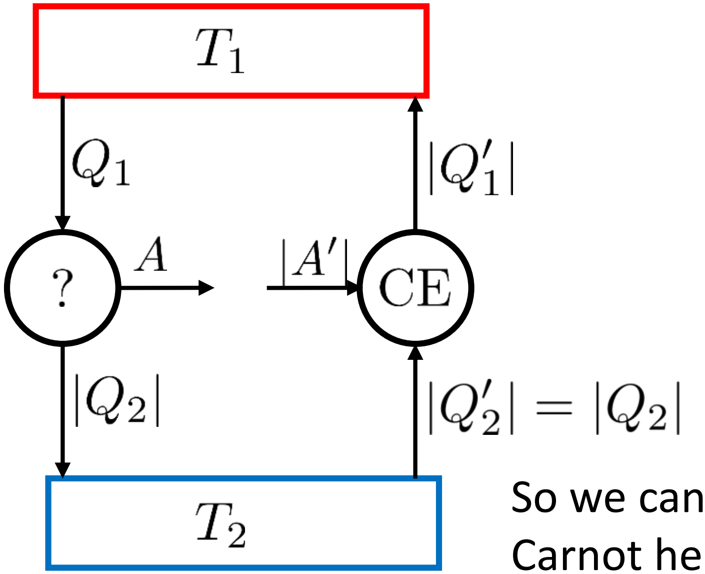
The proof of the Carnot theorem is by reductio ad absurdum. That means that we assume that a better machine exist and then we show that we can derive from that some physically unacceptable consequence. The key is in the words physically unacceptable: we **do not get any logical contradiction**. We just get a consequence which **we believe not to be true** in the world around us. This kind of belief is based on our historical experience, limited as it is. Limited experience does not mean absolute knowledge. Keep in mind: **maybe we are wrong**.

You have been warned, so we can continue with the proof of the Carnot theorem.

Carnot theorem: "proof"

Suppose somebody claims that his (hypothetical) machine is better than Carnot machine. His parameters are $Q_1 > 0$ (heat "taken out from the hot reservoir) and $Q_2 < 0$ ($|Q_2|$ is returned to the cold reservoir) and performs useful work A.
We take a Carnot engine of such a size, that when operated as a heat engine its parameters are $Q_1' > 0$ and $\boldsymbol{Q_2' = Q_2 < 0}$. We run the Carnot engine as a heat pump (reversed run) consuming mechanical work $A' = Q_1' - |Q_2|$ per cycle.
We shall prove that $A > A'$ if the hypothetical machine is indeed more efficient. Here is the proof:

according to the assumption: $\frac{A}{Q_1} > \frac{A'}{Q_1'}$



$$\frac{Q_1 - |Q_2|}{Q_1} > \frac{Q_1' - |Q_2|}{Q_1'}$$

$$1 - |Q_2|/Q_1 > 1 - |Q_2|/Q_1'$$

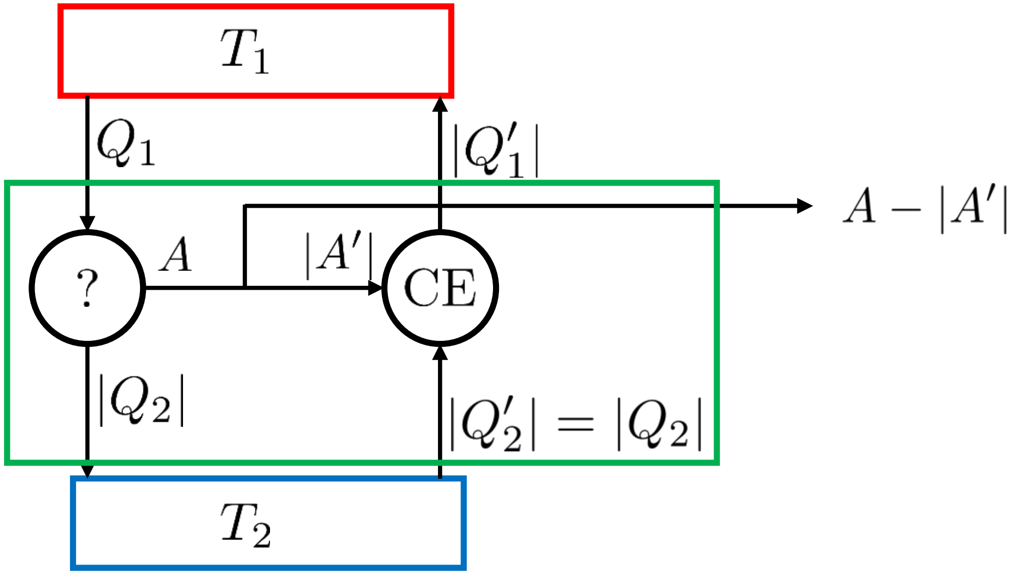
$$Q_1 > Q_1'$$

$$Q_1 - |Q_2| > Q_1' - |Q_2|$$

$$A > A'$$

So we can use the hypothetical efficient machine to feed the Carnot heat pump and we still can use the work access $A - A'$ to for some useful purpose like pumping out water from a mine.

Carnot theorem: “proof”



So we have shown that if the hypothetical machine is indeed more efficient than the Carnot machine, we can combine the hypothetical machine with a Carnot heat pump to form a compound heat machine (framed by green in the figure) that produces useful mechanical work $A - A'$ just by “consuming “ heat $Q_1 - |Q_2|$ from the hot reservoir but does not “return” any heat to the cold reservoir, since the same heat which is returned by the hypothetical machine is taken out by the Carnot heat pump. The cold reservoir is, in fact, not needed for the work of such a compound machine.

By that we would be able to construct a **perpetuum mobile of the second kind**. **This is defined as a heat machine which “converts” heat into mechanical work without the need to “return” some heat into outer environment.** This is believed to be a **physical contradiction**.

Second law of thermodynamics

We arrived at the statement that it is not possible to construct perpetuum mobile of the second kind. Notice that we did not prove it. We just said we **believe** it cannot be constructed. We believe it so strongly that we have promoted this statement to be a deep principle of physics: **the second law of thermodynamics**. All our experience suggest, that perpetuum mobile of the second kind is not possible. As anything in physics, we cannot prove it. Just saying "it would be too good to be true" is just a cliché, not a proof.

Impossibility of perpetuum mobile of the second kind is just one possible formulation of the second law of thermodynamics. There are many other, physically equivalent, formulations. Like this one:

Heat cannot spontaneously "flow" from cold system to hot system without external work being performed.

This can be reformulated as: It is not possible to construct absolute refrigerator, which would be a device able to "pump heat" from cold region to hot region without need "to pay" for some mechanical work. Refrigerators are possible, we have one at home. But we have to pay for the electricity. It is easy to demonstrate the connection to the Carnot theorem.

Carnot theorem: absolute refrigerator is impossible

Suppose somebody claims that his (hypothetical) machine is better than Carnot machine. His parameters are $Q_1 > 0$ (heat “taken out from the hot reservoir) and $Q_2 < 0$ ($|Q_2|$ is returned to the cold reservoir). We take a Carnot engine of such a size, that when operated as a heat engine its parameters are $Q_1' > 0$ and $Q_2' < 0$ such that $A' = A$. We run the Carnot engine as a heat pump (reversed run) consuming mechanical work $A' = A$ per cycle Here is the proof that if the hypothetical machine is more efficient, we would be able to construct absolute refrigerator:

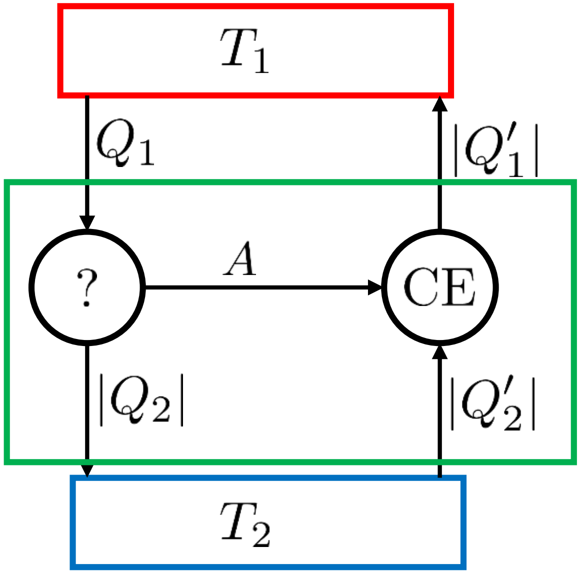
according to the assumption:

$$\frac{A}{Q_1} > \frac{A}{Q_1'}$$

$$Q_1' > Q_1$$

$$Q_1' - A > Q_1 - A$$

$$\boxed{|Q_2'| > |Q_2|}$$



The framed statement says that the net heat is “pumped out” from the cold reservoir by the green framed compound machine without need of external work, so we have got absolute refrigerator.

Thermodynamic temperature

The second law of thermodynamics allows us to define temperature independently of the medium.

Up to now we had defined the temperature for gas like this:

Temperature of gas in equilibrium is given by the mean kinetic energy of the translational movement of molecules as

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$$

This definition of temperature is medium-specific, since it refers to the structure of gas as being composed of molecules. For systems not composed of molecules this definition is not applicable. **Of course, we can define in principle the temperature of any system like the temperature of gas which is in equilibrium with the system considered**.

The second law of thermodynamics allows us to define temperature in a medium-independent way. We can use the system whose temperature we want to measure as the hot reservoir with unknown temperature T_1, a system consisting of water at the state of triple point as a cold reservoir with $T_2 = 273.16\ K$ and let a Carnot machine work between these two reservoirs. If we were able to measure its efficiency η , the unknown temperature T_1 would be given as the temperature which satisfies the formula

$$\eta = \frac{T_1 - T_2}{T_1}$$

Thermodynamic temperature

The definition of the thermodynamic temperature through the efficiency of Carnot machine is perhaps not directly usable for practical metrology. It serves as a unique theoretical definition and for practical purposes we have to use some device (perhaps different devices for different temperature regions) for which we have a reasonable statistical theory which can be directly related to the thermodynamic definition of temperature.

Actually the term “thermodynamic temperature” is not uniquely defined in physics literature. During our lectures we shall meet several other definitions also referred to as “thermodynamic temperature”. All of them are theoretically equivalent. Strangely enough even the official legal document defining SI units by **International Bureau of Weights and Measures** (French: Bureau international des poids et mesures, BIPM) is of no help to uniquely identify the notion of “thermodynamic temperature. In the official definition of Kelvin it just says (https://www.bipm.org/en/measurement-units/):

The Kelvin (K) is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.

There is no further specification of what the notion thermodynamic temperature means. It is implicitly assumed that “it is explained somewhere” in the physics literature.

The notion of temperature is abstract enough that one feels rather unsure like “what they speak about”.

On the other hand, BIPM uses the same strategy in defining other, more common, units like meter

The meter is the length of the path travelled by light in vacuum during a time interval of 1/299 792 458 of a second.

Here one first does not feel unsafe, what is meant under the definition “length of the path”, which seems to be intuitively clear. However, anyone interested in more careful thinking will recognize that the precise definition is not simple at all and soon he will be trapped in the labyrinth of general relativity.

Quantum mechanics: some postulates

We shall need basic knowledge of quantum mechanics. Here we shall present a few elementary facts about quantum mechanics. In principle you will be able to follow our statistical physics course if you accept these facts.

- Microworld is discrete in the following sense: there exist special stationary states of a quantum system which are discrete. These states are usually identified by a set of (a few) discrete "quantum numbers".
- Quantum mechanics usually predicts experimental results only probabilistically. This is not due to some incompleteness of the quantum theory; it is fundamental property of the microworld. However, if a system is in one of its stationary states, then its energy is precisely predictable. Since the stationary states are discrete this means that the energy spectrum (set of possible energy values) is discrete.
- The stationary states are not the only possible states of a quantum system. There are so called superposition states not having uniquely predictable energy. However, it can be proved that **for the purpose of describing statistical physics equilibrium states it is enough to consider only stationary states**.
- There may be different stationary states having the same energy. This is called energy degeneration. The energy level belonging to several different stationary states is called degenerated.

Quantum mechanics

- One of the first attempts to understand the discrete character of stationary states was de'Broglie's hypothesis of describing particles as localized packets of some (de'Broglie's) waves. Today, we do not think that particles are waves. **The waves which appear in quantum theory are just mathematical tools** to arrive at prediction of outcomes of physical experiments by solving Schrodinger wave equation and decoding by well defined operations those predictions from the wave function found. The details are not necessary to be able to follow our statistical physics explanations. It is however useful to remember the relation between the energy of a free moving particle and the frequency of the corresponding de'Broglie's wave

$$E = \hbar\omega$$

and the relation between the particle momentum and the wavelength of the corresponding wave

$$p = \frac{2\pi\hbar}{\lambda}$$

$\hbar$ is the Planck constant $\hbar = h/(2\pi)$. The new SI **defines**: h =6.62607015×10^{-34} Js

Quantum mechanics

- Stationary states of a (spinless point-like) particle confined to a line segment of a length L (model of a gas particle in a box in a one-dimensional world) are labeled by a single quantum number n with possible values $1,2,3,4,\ldots$ with corresponding energies given by the formula

$$E_n = \frac{\pi^2\hbar^2}{2mL^2}n^2$$

- Stationary states of a **spinless point-like particle** in a 3-dimensional cubic box with the edge size L are labeled by 3 independent integer quantum numbers n_1, n_2, n_3 with energies given by the formula

$$E_{n_1,n_2,n_3} = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2)$$

- Stationary states of many non-interacting spinless point-like particles in a box (model of an ideal gas) can be expressed using the one-particle states as described above.

Quantum mechanics: further postulates

- Describing stationary states of a many non-interacting particle system one has to distinguish two cases: **distinguishable particles and indistinguishable particles**
- Indistinguishable particles, also called identical particles or indiscernible particles, are particles that cannot be distinguished from one another, even in principle. We cannot distinguish them from one another physically by “painting a different-color dots on two electrons”. But **we cannot distinguish them even virtually by giving them a different name** as we do it with human identical twins.
- The impossibility of assigning different names to two indistinguishable particles needs a more detailed commentary. When we give different names to human identical twins, we can in principle track their movements (trajectories) for whole their lives and so at any moment we can know “who is who”. With two electrons it is not possible. Even if at some initial time moment we observe them well separated in space and therefore we may try to give them two different names, we generally cannot track their trajectories from then on. More precisely, if we keep continuously measuring their positions, **we would get “different future”** with respect to the case when we do not measure their positions continuously. In microworld one is not able to comply with the requirement of old experimental gurus “good measurement must not influence the measured system”. So since we cannot follow the particle trajectories, we loose the initial knowledge of “who is who”.

Quantum mechanics

- Describing stationary states of N **non-interacting distinguishable** particles is straightforward. We make a numbered list of all particles and assign to each particle its one-particle state n_1, n_2, n_3. So the state is a list of N triplets n_1, n_2, n_3. Do notice that we have effectively **gave a name to each particle, its ordering number**. This is allowed for distinguishable particles.
- Describing stationary states of N **non-interacting indistinguishable** particles is trickier. Let us assume that we deal with spinless particles, so there is not any additional one-particle state quantum number other than a triplet n_1, n_2, n_3. We start with making a list of all possible one-particle states. It will look like an infinite column

1,1,1
1,1,2
1,2,1
1,2,2
2,1,1
2,1,2
2,2,1
2,2,2
⋮

The list of one-particle states is infinite, since there are infinitely many integer triplets. Now we add additional column and write there the occupational numbers, that is **how many particles are in the corresponding one-particle state**

1,1,1	1
1,1,2	3
1,2,1	0
1,2,2	2
2,1,1	0
2,1,2	0
2,2,1	12
2,2,2	4
⋮	⋮

$$\Sigma = N$$

The sum of occupational numbers is equal to the total number of particles considered.

So the state of indistinguishable spinless non-interacting particles is given by the **list of one-particle states each with its occupational number**

Quantum mechanics: bosons and fermions

Bosons are those particles which have an integer spin (0, 1, 2...). Fermions are those particles that have an odd half-integer (like 1/2, 3/2, …) spin.

One-particle states for spinless (spin=0) bosons are those states we have used so far. Their complete identification is given just by a triplet of integers n_1, n_2, n_3.
For particles with spin their one-particle state is identified with a triplet of integers n_1, n_2, n_3 (this specifies the spatial part of the particle state), but additional specification of the spin state is required as well. Usually a quantum number s_z is used for that specification, it gives the projection of the spin to the z-axis. s_z can be given using explicit SI units through $\hbar$ (like $s_z = \frac{1}{2}\hbar$), but more often we omit $\hbar$ and write something like $s_z = \frac{1}{2}$.
Examples of possible values are given in the table:

Total spin	**Possible s_z values**
1/2	1/2, -1/2
1	1, 0, -1
3/2	3/2, 1/2, -1/2, -3/2
2	2, 1, 0, -1, -2

For spin 1/2, we often use instead of $s_z = \frac{1}{2}, -\frac{1}{2}$ the notation $s_z = \uparrow, \downarrow$.

Quantum mechanics: bosons and fermions

Bosons and fermions behave differently what concerns possible values of occupational numbers.

- **Bosons can have any value as occupational number** in a one-particle state
- **Fermions can have just 0 or 1 as occupational number** in a one-particle state. This principle is called Pauli exclusion principle

Do not forget that there are no spinless fermions, so one-particle states of fermions do have also s_z quantum number in addition to “spatial” quantum numbers n_1, n_2, n_3. So the table describing a state of spin 1/2 fermions can look like the following

$1,1,1,\uparrow$	1
$1,1,1,\downarrow$	0
$1,1,2,\uparrow$	0
$1,1,2,\downarrow$	1
$1,2,1,\uparrow$	1
$1,2,1,\downarrow$	0
$1,2,2,\uparrow$	1
$1,2,2,\downarrow$	0
⋮	⋮

$$\Sigma = N$$

The sum of all occupational numbers is equal to the total number of fermions ion the box.

Ideal gas quantum state: shorter notation

Repeating: the quantum state of an ideal gas of point-like particles is given by a table of one-particle states with filled occupational numbers. The one-particle states of point-like particles are fully described as n_1, n_2, n_3, s_z. A particle occupying that state would have the energy

$$\varepsilon = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2)$$

We stress that we use the quantum mechanical formula for point-like particles. This means that we can use the formula for ideal gasses consisting of monoatomic molecules (molecules consisting of single atoms like He and not like O_2. Somebody might disagree with that saying that even a He atom is not "point-like", since it contains many protons, neutrons and electrons. The complaint would be very relevant for atoms satisfying Newton mechanics. However the real atoms behave according to quantum mechanics. **For the usual laboratory conditions the quantum mechanics tells us, that we can handle such atoms as if they were point-like particles.** The detailed explanation is behind the scope of this introductory text.

We shall often use a shorter notation, the one particle states will be identified just by one number j, understood for example as the line **order number in the list of the one particle states**. The corresponding occupational number will then be denoted as n_j and the state energy as ε_j. The **gas state** will then be given as **list of the occupational numbers** $\{\boldsymbol{n_j}\}$, the total number of particles as $N = \sum_j n_j$

and the total energy as $E = \sum_j n_j \varepsilon_j$

$n!$

We repeat: For indistinguishable particles one has to identify the many-particle-ideal- gas state by a set of occupational numbers.

It is not legal to identify individual particles by naming them by numbers and give the gas state as a list of one particle states of individual numbered particles.

However, it is often possible to simplify some calculation by using such an illegal gas state definition. By that we would get too many gas microstates: two microstates distinguished only by different permutation of particles would be considered as different microstates what is not allowed for indistinguishable particles. We can, however, often rectify this by **dividing** number of microstates on a proper place by the “Gibbs factor” $N!$. Gibbs found this trick just empirically without knowing the true quantum-mechanical reason. (Quantum mechanics was invented many years later!) He said something like “statistical physics considers many particle states **as if** the particles were indistinguishable”.
Today, we know, that **it is not “as if”**. Identical particles are indeed indistinguishable.

Statistical physics manifesto

- we have to handle systems with huge number of degrees of freedom $\approx 10^{26}$
- exact physical state of such a system ($\approx 10^{26}$ numbers) is called a **microstate**
- a complete information on microstate is experimentally unfeasible
- experimentally in any state of a large systems we have just a few values of macroscopically measurable physical quantities
- these macroscopic numbers define what we call a **macrostate**
- macrostate is just drastically reduced information on microstate
- we have to live with the fact that we just know a macrostate instead of a microstate. Still, we want to "forecast the future" at least on the level of macrostates
- the technique how we handle macrostates in physics is statistics
- we know the macrostate, but the system is in fact in some unknown microstate
- there is tremendously huge number of microstates compatible with our information on macrostate
- **a particular macrostate can be realized by tremendously huge number of different microstates**. This set of compatible microstates is called a **statistical ensemble**. We shall see that the number of microstates in an ensemble is of the order $10^{10^{26}}$.
- We imagine a procedure which virtually forecast the future of each microstate from the ensemble, then make a virtual average and get the average characteristics of the ensemble which we assume will be useful characteristics of the final macrostate of our particular initial macrostate.

Let’s repeat, the last two points of the “statistical physics manifesto”

- A particular macrostate can be realized by tremendously huge number of different microstates. This set of compatible microstates is called a **statistical ensemble**. We shall see that the number of microstates in an ensemble is of the order $10^{10^{26}}$.
- We imagine a procedure which virtually forecast the future of each microstate from the ensemble, make a virtual average and get the average characteristics of the final macrostate which we assume will be the final macrostate of our particular initial macrostate.

What justifies usage of the mean ensemble value as a reliable prediction?

The mean value can be a good strategy **if it is very “sharp”**. To observe a microstate with value significantly different from the mean ensemble value is in fact highly improbable. So if you want to “survive in the jungle”, the best advice is to **“believe to mean values”**. If you meet something different, well, it’s just a very bad luck.

We shall argue, that such a bad luck is very, very, very improbable.

We have observed the typical sharpness of the value of a physical quantity when we calculated the probability of finding n molecules out of N in the left half of a box.

Let’s summarize our findings:

- mean value of molecules in the left part(as calculated over all the possible microstates) is, as expected $\frac{N}{2}$.
- typical deviation is of the order $\sqrt{N}$

What was the reason for getting this result:
Big numbers!
The number of molecules is typically $N \sim 10^{23}$, a big number
The number of possible microstates was $2^N \sim 2^{10^{23}}$ a tremendously big number!

This situation is typical for statistical physics, we meet there three typical numerical values

- **normal numbers like 1, 4, 10^6**
- **big numbers like 10^{23}, typically number of molecules**
- **tremendously big numbers like $10^{10^{23}}$, typically number of possible microstates**

Calculating the number of one-particle states

We have observed that a typical microstate of a large system can be realized by a huge number of possible microstates. The number of microstates is typically 10^N, where N is of the order of number of degrees of freedom $N \approx 10^{23}$. Let us estimate the number of microstates somewhat more precisely for a most simple statistical system: ideal gas of spinless particles.
A microstate of an ideal gas is a list of occupational values for all one-particle states. So to calculate the number of microstates we have to develop a technique for handling numbers of one particle states.

Let us denote as $\varphi(\varepsilon)$ the number of one-particle states in a box which have energies less than ε. Let us estimate this number for the case when ε is large. We know that

$$\varepsilon_{n_1,n_2,n_3} = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2)$$

Let us imagine an abstract space formed by three-dimensional vectors $\vec{n} = (n_1, n_2, n_3)$

In this abstract space the one-particle states correspond to points with **positive integer coordinates**. States with energies less than ε are therefore integer-coordinate points inside the "positive octant" of the sphere with the radius

$$|\vec{n}_\varepsilon| = (\frac{2mL^2}{\pi^2\hbar^2}\varepsilon)^{1/2}$$

In the abstract $\vec{n}$ space the integer-valued coordinates correspond to vertexes of unit cubes (with volume 1). Each such cube has 8 vertexes, but each vertex is shared by 8 cubes, so on average there is 1 integer-valued point per unit volume cube. So there is one one-particle state per unit volume cube.

States with energies less than ε are integer-coordinate points inside the "positive octant" of the sphere with the radius

$$|\vec{n}_\varepsilon| = (\frac{2mL^2}{\pi^2\hbar^2}\varepsilon)^{1/2}$$

So for large enough ε (to neglect surface effects) the number of such one-particle states is given by the volume

$$\varphi(\varepsilon) = \frac{1}{8}\frac{4}{3}\pi|\vec{n}_\varepsilon|^3 = \frac{1}{6}\pi(\frac{2mL^2}{\pi^2\hbar^2}\varepsilon)^{3/2}$$

This is true for spinless particles. For particles with spin their one-particle state is identified not only by with a triplet of integers n_1, n_2, n_3 (this specifies the spatial part of the particle state), but additional specification of the spin state s_z is required as well. So each state n_1, n_2, n_3 is g-times degenerated where g is the number of possible s_z values. g equals 2 for spin 1/2 particles, equals to 3 for spin 1 particles etc. So finally we have

$$\boxed{\varphi(\varepsilon) = g\frac{1}{6}\pi(\frac{2mL^2}{\pi^2\hbar^2}\varepsilon)^{3/2}}$$

Number of microstates of an ideal gas

We shall estimate the number of microstates which correspond to one macrostate of an **ideal monoatomic gas**. We shall consider an isolated gas in a box of the volume V. Since the gas is isolated its total (internal) energy E is fixed, it is a “given number”. However, aa absolutely perfect isolation is technically not feasible, so the macroscopic energy is not a precise real number, it is fixed within some very small (with respect to the value E) interval $\Delta\mathrm{E}$. We shall not specify the interval ΔE more precisely, we shall see that the result which would interest us will not depend on the precise value of ΔE.

So let us denote as $\Omega(E)$ the number of microstates of an ideal gas with energy E **within an unspecified interval $\boldsymbol{\Delta E}$**. We shall estimate the number of typical (dominating) microstates. We have seen for example, that the macrostate of a gas in a large box is dominated by microstates with one half of molecules in the left part of the box and one half in the right part. So we guess that a molecule of our gas will typically occupy a one particle state with energy $\bar{\varepsilon} = E/N$, within some interval $\Delta\bar{\varepsilon} \approx \alpha\bar{\varepsilon}$, where α is some small constant independent of $\bar{\varepsilon}$. The number of one-particle microstates with energy $\bar{\varepsilon}$ within the interval $\Delta\bar{\varepsilon}$ is clearly

$$\varphi'(\bar{\varepsilon})\Delta\bar{\varepsilon}$$

A simple combinatorics then tells us that the total number of relevant microstates is

$$\Omega(E) = \frac{1}{N!}(\varphi'(\bar{\varepsilon})\Delta\bar{\varepsilon})^N = \frac{1}{N!}C^N L^{3N}(\bar{\varepsilon})^{N/2}(\alpha\bar{\varepsilon})^N$$

Note that we have used the formula for $\varphi(\varepsilon)$ derived for **monoatomic spinless gas**. The spinelessness is not so important, since the spin g-factor would get hidden into the constant C.

The $N!$ is the Gibbs trick to satisfy indistinguishability of the gas particles. Our estimate was very rough and therefore too unprecise. We shall, however, later see, that if we **limit our interests just to the logarithm of this number**, then our estimate will be quite reasonable. We get

$$\ln\Omega(E) = (-N\ln N + N) + N\ln(\alpha C) + N\ln V + \frac{3}{2}N\ln(\bar{\varepsilon})$$

where we merged some state independent constants into one constant denoted as C.

$$\ln\Omega(E) = N\ln\frac{V}{N} + \frac{3}{2}N\ln(\frac{E}{N}) + N\ln\alpha C$$

A **note concerning physical units** is in order. The last equation is wrong what concerns physical units. For example the unit of volume is m^3 and we certainly do not know what is the logarithm of m^3. The point is that the constant C also contains some physical units and if we would distribute those units into the two logarithms $\ln V$ and $\ln E$, we would get correct dimensionless expressions under all the logarithms.

Entropy for monoatomic spinless ideal gas

For the number of microstates we got the formula

$$\ln \Omega(E,V) = N \ln \frac{V}{N} + \frac{3}{2} N \ln(\frac{E}{N}) + N \ln \alpha C$$

Similar formula was known in phenomenological thermodynamics for monoatomic ideal gas (spin was not known at the time). **The corresponding physical quantity was called entropy**. The main difference was in physical units, a complete match can be achieved, if we **define the entropy in statistical physics** adding the Boltzmann constant k:

$$S(E,V) = k \ln \Omega(E,V) = kN \ln \frac{V}{N} + \frac{3}{2} kN \ln(\frac{E}{N}) + kN \ln \alpha C$$

Our formula was derived for ideal gas using crude approximations. That is why it contains unknown constants α, C. Later we shall derive exact formula for ideal gas in classical (non-quantum) approximation.

Here we add just a formal definition valid for any isolated physical system:

Entropy for an isolated physical system is defined as k-times the logarithm of the number of microstates corresponding to the macrostate considered.

Since we speak here abut the number of microstates, we are considering a quantum system, where the (discrete, stationary) states can be counted. We also repeat our previous statement: **a particular macrostate can be realized by tremendously huge number of different microstates**.

$$\ln \Omega(E) = N \ln \frac{V}{N} + \frac{3}{2} N \ln(\frac{E}{N}) + N \ln \alpha C$$

The fact, that a microstate can be realized by tremendously **huge number** of microstates is clear from the above formula. The logarithm of the number of microstates is proportional to number of degrees of freedom $N \approx 10^{23}$. Therefore the **number of states $\boldsymbol{\Omega(E)}$** itself will really be **tremendously huge**

$$\boxed{\Omega(E) \approx \exp(10^{23})}$$

Let us also notice, that the entropy for a large system

$$S(E, V) = kN \ln \frac{V}{N} + \frac{3}{2} kN \ln(\frac{E}{N}) + kN \ln \alpha C$$

is additive. That is the entropy of two systems considered as one common system is twice the entropy of one of those systems: for the compound system the number of particles N is doubled, the volume V is doubled and the energy E is doubled. So we see, that the common entropy will be doubled. It was the requirement of additivity which forced Gibbs to introduce his "$N!$ trick”. It is essential for the additivity that the volume V is divided by N under the logarithm in our formula.

A note about Gibbs' $N!$ trick

I do not know the exact story how Gibbs invented his $N!$ trick. Most probably he wanted to understand the meaning of the phenomenological entropy within the framework of statistical physics. He derived the formula and found that it does not have the expected additivity property. He must have said to himself something like: "How could I get N into the denominator under the logarithm to make the formula additive?" And he probably realized that the Stirling approximation to $N!$ can put N under the logarithm. So he realized, that putting (artificially) $N!$ to the formula like

$$\Omega(E) = \frac{1}{N!}(\varphi'(\bar{\varepsilon})\Delta\bar{\varepsilon})^N$$

will make the entropy formula additive. So he invented the rule "statistical physics considers many particle states **as if** the particles were indistinguishable". Later quantum mechanics gave justification for such artificial empirical rule.

Phenomenological entropy is defined only up to an arbitrary additive constant

Using rather crude approximations we were able to derive the entropy formula

$$S(E,V) = kN\ln\frac{V}{N} + \frac{3}{2}kN\ln(\frac{E}{N}) + kN\ln\alpha C$$

containing unknown constants α, C. Actually the phenomenological thermodynamics was not able to specify entropy in an absolute way. It was able only to specify the difference of entropies between two macroscopic states.
Our formula enables us to do exactly the same

$$\boxed{S(E_2,V_2) - S(E_1,V_1) = kN\ln\frac{V_2}{V_1} + \frac{3}{2}kN\ln(\frac{E_2}{E_1})}$$

Here the arbitrary constants dropped out. Later we will be able to derive the exact formula without any arbitrary constants. In this way we shall show, that the statistical physics is able to get stronger (absolute) formula for entropy in contrast to phenomenological thermodynamics.

A note about “teachers’ tricks”

This note is a warning: do not believe too strongly to “simple derivations” found in textbooks. I cheated a lot deriving entropy formula.

I new the correct formula (derived in a more rigorous way) and so I knew “what I wanted to get”. And I twisted the argumentation to get it right. Be extremely prudent. **Logics teaches us that getting the correct result does not validate the arguments leading to that correct results**. The main dirty trick used by myself was to write $\Delta\bar{\varepsilon} \approx \alpha\bar{\varepsilon}$. Proportionality to $\bar{\varepsilon}$ gave me the required factor 3/2 in front of $\ln(E)$ in the final formula!

So do not be disappointed if reading my text you did not quite understand all the motivations on the way! Writers of textbooks sometimes do such dirty tricks without warning the reader that even they do not quite understand what they do.

On the other hand, not every time when the reader does not understand the text in the textbook he can just say “well, another dirty trick”. **He should first try harder** to get more deeply inside the story. Because the authors **quite often do understand** what they write.

Repetition: Equilibrium macrostate

In statistical physics we deal with macroscopic systems for which its is technically impossible to work with microstates. We have at disposition tremendously reduced information, just values of a few macroscopic quantities, which define the **macrostate** of the system.

In principle, the values of those macrostate-defining quantities depend on time, thus describing the time development of the corresponding macrostate.

For **isolated systems** we observe a very interesting phenomenon:
Started from arbitrary microstate we usually observe that the corresponding macrostate changes with time until after some time (which **we call relaxation time)** the macrostate does not change any more. Technically it means that all the macrostate-defining quantities are stable, their values do not change any more. We say that the system reached **equilibrium macrostate**.

This does not mean that the situation is static: the microstates change all the time in macroscopic equilibrium (individual molecules collide, change their positions and velocities etc.) So the macroscopic equilibrium is a dynamical equilibrium. For all practical purposes we, however, can consider the situation as if it was static.

When we said "macroscopic quantities do not change with time" we have meant that no measuring devices are available to measure those quantities with a **precision of typically 13 digits**. Having such devices we would observe changes (fluctuations) at the last digit even for macroscopically defined quantities.

Entropy of the equilibrium macrostate

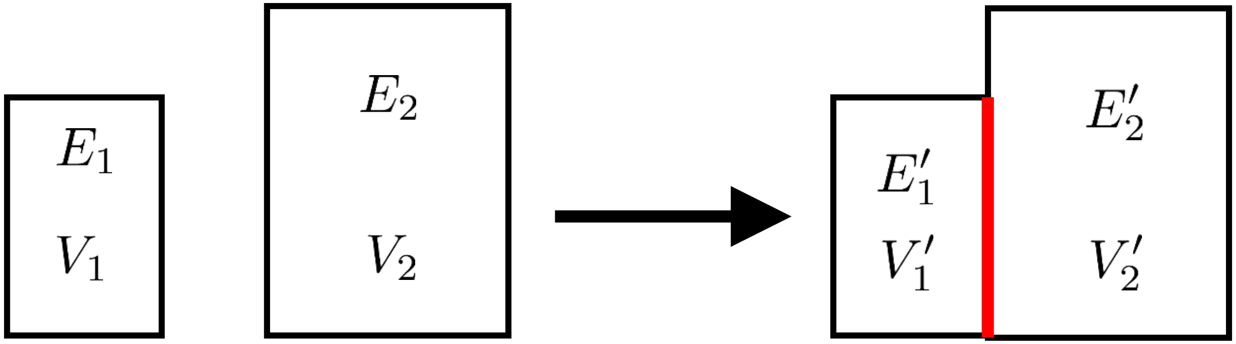
Observing the time development of a microstate we notice irreversible behavior. Once the equilibrium microstate is reached, the microstates continue to change, but never leave the equilibrium macrostate domain of microstates. We may ask why it is so. Starting from a random microstate the changing microstates arrive at the set of equilibrium macrostate domain. A possible “explanation” is that the equilibrium macrostate is so huge, in terms of the number of its realizing microstates, that the **probability of leaving this microstate domain by random microstate dynamics is negligible**.

Therefore the hypothesis: The equilibrium macrostate of an isolated system is the macrostate realizable by the largest number of available microstates.

The equilibrium macrostate of an isolated system has the largest entropy with respect to the entropies of all non-equilibrium macrostates.

We can use this entropy property to find which macrostate – **under given conditions for an isolated system** – is the equilibrium macrostate.

We consider two isolated statistical systems, each of them being individually in equilibrium. Their energies and volumes (representing any general external parameters) are E_1, E_2, V_1, V_2. We bring them into **a thermal contact** enabling to redistribute energy between them by performing heat. The new energies will be E_1', E_2', satisfying, of course energy conservation $E_1' + E_2' = E_1 + E_2$. The volumes will be unchanged.



Thermal contact between the two systems is symbolized by the red line

Performing heat the systems exchange energy until new common equilibrium is reached. So we have a new compund isolated system and we would like to calculate the final energies E_1', E_2'. We do it by finding the maximal entropy of the compound system. The original systems have their entropy functions $S_1(E,V), S_2(E,V)$. Those two system might be very different, one may be for example an ideal gas, the other a box containing free electromagnetic field. So the functions $S_1(.,.)$ and $S_2(.,.)$ might be **different functional prescripts**. Our notation suggests that the function prescript expects two variables inserted into the dotted slots. After the values are inserted, the “functional machine” produces the resulting entropy value out of them. It is good to imagine even in “pure mathematics” under the word “function” a computer programming notion “function”: as a program expecting that its formal parameters are substituted by some actual values, then the program starts and returns the resulting value.

We already know how the “entropy program” looks for ideal gas:

$$S(E,V) = kN\ln\frac{V}{N} + \frac{3}{2}kN\ln(\frac{E}{N}) + kN\ln\alpha C$$

For the electromagnetic field it would be something completely different.

Entropy is additive, so the total entropy before the thermal contact is

$$S = S_1(E_1, V_1) + S_2(E_2, V_2)$$

After the final common equilibrium is established the total entropy will be

$$S' = S_1(E_1', V_1) + S_2(E_2', V_2)$$

We may consider the final entropy as a function of one unknown variable E_1' , since the other variable E_2' is fixed by the energy conservation $E_2' = E_1 + E_2 - E_1'$.

$$S'(E_1') = S_1(E_1', V_1) + S_2(E_1 + E_2 - E_1', V_2)$$

We are looking for the value E_1' for which the final entropy will be maximal

$$\frac{dS'(E_1')}{dE_1'} = \left.\frac{\partial S_1}{\partial E}\right|_{E=E_1'} - \left.\frac{\partial S_2}{\partial E}\right|_{E=E_1+E_2-E_1'} = 0$$

Note our (maybe over-prudent) notation. The right-hand side means that we differentiate the first entropy function with respect to its first “formal parameter”, the energy, and then we insert for the energy the value E_1'. Then we differentiate the second entropy function with respect to its first formal parameter, the energy, and then we insert for the energy the value $E_1 + E_2 - E_1'$. The minus sign in front of the derivative is due to the “differentiating of a composite function” rule.

In the maximum the total derivative must be zero, so we get

$$\left.\frac{\partial S_1}{\partial E}\right|_{E=E_1'} - \left.\frac{\partial S_2}{\partial E}\right|_{E=E_2'} = 0$$

$$\boxed{\left.\frac{\partial S_1}{\partial E}\right|_{E=E_1'} = \left.\frac{\partial S_2}{\partial E}\right|_{E=E_2'}}$$

What is the physical meaning of this equation?
Entropy function $S(E,V)$ when differentiated with respect to E gives some other function $f(E,V)$ of the (macro)state variables E,V. So it is some state function of the macrostate, it is some physical quantity characterizing the macrostate. The equation says that this state variable has the same value in the two systems in thermal contact in equilibrium. So the two system in mutual equilibrium have the same value of the physical quantity $f(E,V)$. Discussing the zeroth law of thermodynamics we found that temperature is **the physical quantity which has the same value for all systems which are in mutual thermal equilibrium**. So the quantity

$$f(E,V) = \frac{\partial S}{\partial E}$$

must be **either the temperature itself or some unique function of temperature**. We can check what function of temperature it is, since we have explicit entropy function for ideal gas, so we can check the physical meaning of it for ideal gas.

For ideal monoatomic gas we got

$$S(E,V) = kN\ln\frac{V}{N} + \frac{3}{2}kN\ln(\frac{E}{N}) + kN\ln\alpha C$$

$$\left(\frac{\partial S}{\partial E}\right)_V = \frac{3}{2}kN\frac{N}{E}\frac{1}{N} = \frac{3kN}{2E}$$

For monoatomic ideal gas its energy is given by the formula

$$E = \frac{3}{2}NkT$$

and so finally we get

$$\boxed{\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T}}$$

However, the formula

$$\left.\frac{\partial S_1}{\partial E}\right|_{E=E_1'} = \left.\frac{\partial S_2}{\partial E}\right|_{E=E_2'}$$

should be true for arbitrary two systems in mutual equilibrium, so the formula $\frac{\partial S}{\partial E} = \frac{1}{T}$ must be **true for any physical system**.

Repetition: Thermodynamic temperature

The second law of thermodynamics allows us to define temperature independently of the medium.
Up to now we had defined the temperature for gas like this:
Temperature of gas in equilibrium is given by the mean kinetic energy of the translational movement of molecules as

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$$

This definition of temperature is medium-specific, since it refers to the structure of gas as being composed of molecules. **For systems not composed of molecules this definition is not applicable**. Of course, we can define in principle the temperature of any system like the temperature of gas which is in equilibrium with the system considered.

We have already seen a medium-independent temperature definition:
The second law of thermodynamics allowed us to define temperature in a medium-independent way. We can use the system whose temperature we want to measure as the hot reservoir with unknown temperature T_1 and some a system consisting of water at the state of triple point as a cold reservoir with $T_2 = 273.16\ K$ and let a Carnot machine work between these two reservoirs. If we were able to measure its efficiency η , the unknown temperature T_1 would be given as the temperature which satisfies the formula

$$\eta = \frac{T_1 - T_2}{T_1}$$

Thermodynamic temperature

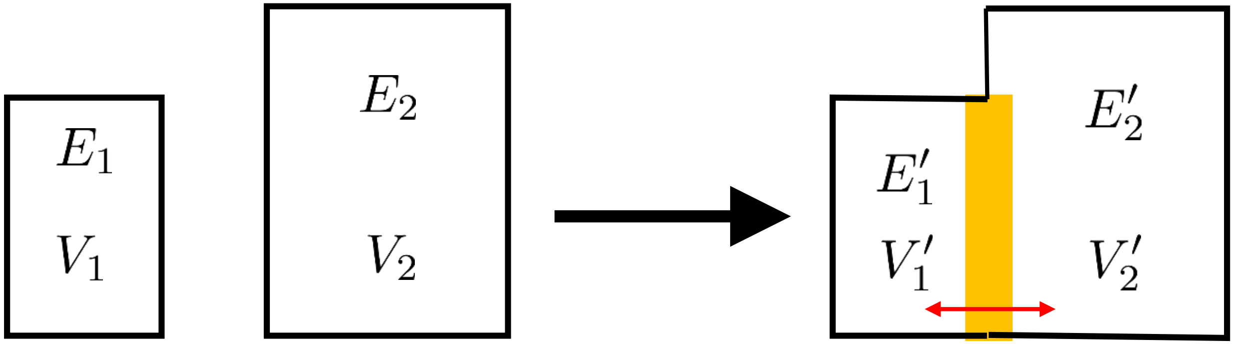
Now we have another formula which can serve as a bases for definition of temperature

$$\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T}$$

In this formula the symbol V represents in general any external parameter. So if for a general system we know its entropy function, we can define what is the temperature of some macrostate: we calculate its entropy and then we have to know the entropy also for a close macrostate at a somewhat different energy. We calculate the difference of entropies, divide by the difference of energies and thus get $\frac{1}{T}$.

This definition is also often called "**thermodynamic temperature**" and is completely equivalent to the definition using efficiency of an ideal heat engine we have already discussed in these lectures.

Another example of entropy maximization. We consider two isolated statistical systems, each of them being individually in equilibrium. Their energies and volumes (representing any general external parameters) are E_1, E_2, V_1, V_2. This time we bring them into a contact realized by a piston what enables to **redistribute volume between them**. The piston, of course, provides (by microscopic movements) also a heat contact. The new energies will be E_1', E_2', satisfying, of course energy conservation $E_1' + E_2' = E_1 + E_2$. The new volumes will be V_1', V_2' with the total volume unchanged $V_1' + V_2' = V_1 + V_2$.



After the final common equilibrium is established the total entropy will be

$$S' = S_1(E_1', V_1') + S_2(E_2', V_2')$$

the final values of energies will be the same as in the case when we have considered just a thermal contact. The only unknown value in this relation is V_1', since V_2' is given by the total volume conservation $V_2' = V_1 + V_2 - V_1'$.

We get the final value V_1' by maximizing the entropy

$$\frac{dS'(V_1')}{dV_1'} = \left.\frac{\partial S_1}{\partial V}\right|_{V=V_1'} - \left.\frac{\partial S_2}{\partial V}\right|_{V=V_1+V_2-V_1'} = 0$$

Finally we get

$$\boxed{\left.\frac{\partial S_1}{\partial V}\right|_{V=V_1'} = \left.\frac{\partial S_2}{\partial V}\right|_{V=V_2'}}$$

What is the physical meaning of this equation?
Entropy function $S(E,V)$ when differentiated with respect to V gives some other function $\tilde{f}(E,V)$ of the (macro)state variables E,V. So it is some state function of the macrostate, it is some physical quantity characterizing the macrostate. The equation says that this state variable has the same value in the two subsystems for the final position of the piston. But we know when the piston stops moving. It is when the pressure on both its sides will be the same. So the physical quantity $\tilde{f}$ must be somehow related to pressure. However, since the piston provides also a heat contact, the temperatures will also be equal, so the function $\tilde{f}$ may be some combination of temperature and pressure.

For ideal monoatomic gas we got

$$S(E,V) = kN\ln\frac{V}{N} + \frac{3}{2}kN\ln(\frac{E}{N}) + kN\ln\alpha C$$

$$\left(\frac{\partial S}{\partial V}\right)_E = kN\frac{N}{V}\frac{1}{N} = \frac{kN}{V}$$

From the equation of state for ideal gas we have

$$\frac{kN}{V} = \frac{p}{T}$$

So finally we get

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_E = \frac{p}{T}}$$

This formula must be true for any system, which can have a “piston contact” with ideal gas system. By knowing for example the entropy function for electromagnetic field in a box, **this formula gives us the pressure in the box provided by the electromagnetic field inside.**

System and state variables

We shall include here notes from the methodology (or philosophy, if you want) of physics.

Physics does not have the ambition to study the entire world in one complex attempt. It rather tries to **focus on some smaller part of the world, called a physical system**, which is well identified and can be meaningfully studied how it behaves due to its internal functioning and due to its interactions with the rest of the world, which is not included into the system studied.

So the first task of any physical study is to define (identify) the physical system of interest. Just a very specific example: let the system of interest will be the hydrogen gas of N molecules contained in a box of the volume V.

Now the key point of physics is that even if we identified sharply the system of interest which "keeps its identity constant" during the time we observe it, **the system can be found in different states** in different times.

This is philosophically not a simple assumption. How a system which we considered to be identical system in two instants of time can be "in different states"? What is then the meaning of "identical"? The problem was already recognized by the antique philosophy. There is the famous quote by Heraclitus: **You could not step twice into the same river.** I do not have satisfying solution to this problem. Anyhow, every physicist just intuitively uses the notion "same system in different states".

System and state variables

Let us come back to the notion of "physical system". How the system is characterized, identified? It is by defining the values of a set of **"system variables"**. This set of values should be unique, so that the system is well defined. Those values must be constant in time so that the system "keeps its identity". (Let me note that the notion of "system variables" you would hardly find in physics textbooks. People usually are satisfied with intuitive interpretation of "system" and "state". I do not want to pretend that I have something beyond the intuitive approach. This discussion just wanted to point that there is a problem.)

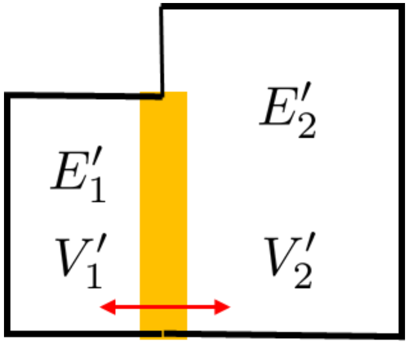
In addition to system variables there are the "state variables". These variables define a specific "state of the system" considered. If the state is changed, we recognize it by the change of some of the state variables.

So an example: let the system of interest will be the hydrogen gas of N molecules contained in a box of the volume V. Here "hydrogen", "N" and "V" are the system variables, considered to be fixed. The state variables mat be the temperature T and pressure p.

However, we have already studied the changes of gas state due to **changing volume**. This just shows that the division into sets of "system" and "state" variables is somewhat arbitrary. Some originally system variables can be reconsidered to be state variables and their change then considered as the change of state of the (more mutable) system.

System and state variables

We have already met the situation, where the volume of the box with gas started to be considered as mutable. So instead of system definition “N molecules of hydrogen gas in a box of the volume V”. we can redefine the system as “N molecules of hydrogen gas in a box”. The volume of the box is not considered to be fixed, so if the volume is changed, we say “it is the same system”. Then the state variables might be temperature T, pressure p and volume V. This is what we implicitly did when discussing common equilibrium of two systems in contact allowing to redistribute volumes between them



Variable number of particles

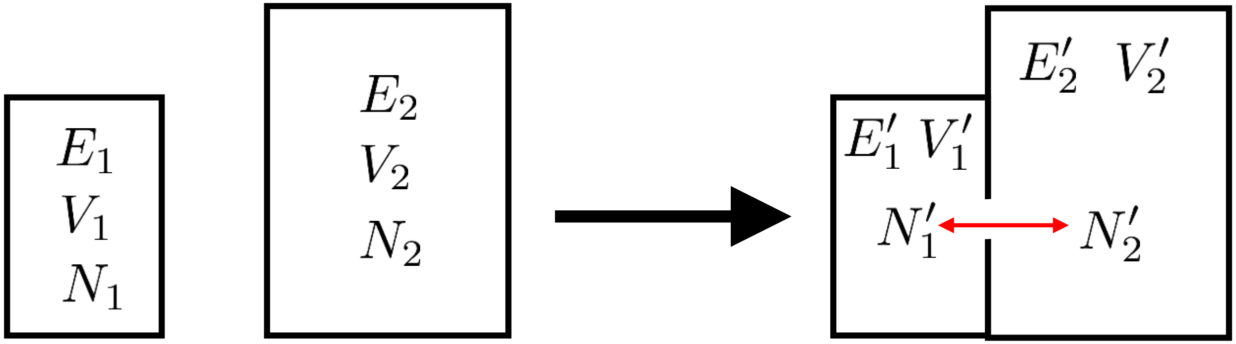
Let us now be even more flexible and consider the number of particles N of gas not as a system variable but as a state variable. The system will be "hydrogen gas in a box" and the state variables will be temperature T, pressure p, volume V and the number of particles N.

Experimentally such a system may be realized as a box with a small hole through which it is connected to some reservoir of particles. Another possibility is a chemical reaction. For example system (artificially) prepared as system of N molecules of water H_2O. You will find that that is not an equilibrium macrostate. Water molecules can dissociate

$$H_2O \leftrightarrow H^+ + OH^-$$

so the number of water molecules in the equilibrium will be smaller than the initial number due to dissociation. Even more: the number of molecules of some type is not constant and (microscopically) fluctuates even in an equilibrium macrostate.

We consider two isolated statistical systems, each of them being individually in equilibrium. Their energies, volumes and particle numbers are E_1, E_2, V_1, V_2, N_1, N_2. We bring them into a contact enabling to redistribute particles between them through some hole. Of course redistributing particles also redistributes energy. The new energies will be E_1', E_2', the new particle numbers will be N_1', N_2' .The volumes will be unchanged. We shall consider a case when the total number of particles will be fixed (no chemical reactions), so $N_1 + N_2 = N_1' + N_2'$.



After the final common equilibrium is established the total entropy will be

$$S' = S_1(E_1', V_1, N_1') + S_2(E_2', V_2, N_2')$$

The final values of energies will be the same as in the case when we have considered just a thermal contact. The only unknown value in this relation is N_1', since N_2' is given by the total number of particles conservation $N_2' = N_1 + N_2 - N_1'$.

Chemical potential

We get the final value N_1' by maximizing the entropy

Finally we get

$$\frac{dS'(N_1')}{dN_1'} = \left.\frac{\partial S_1}{\partial N}\right|_{N=N_1'} - \left.\frac{\partial S_2}{\partial N}\right|_{N=N_1+N_2-N_1'} = 0$$

$$\left.\frac{\partial S_1}{\partial N}\right|_{N=N_1'} = \left.\frac{\partial S_2}{\partial N}\right|_{N=N_2'}$$

What is the physical meaning of this equation?
Entropy function $S(E,V,N)$ when differentiated with respect to N gives some other function $\tilde{f}(E,V,N)$ of the (macro)state variables E,V,N. So it is some state function of the macrostate, it is some physical quantity characterizing the macrostate. The equation says that this state variable has the same value for the two systems in contact. The problem is that in cases of energy and volume redistributions we had an intuitive feeling what are the relevant physical quantities which emerge to be the same after reaching common equilibrium. Here we normally (unless we are constructors of chemical reactors) do not have everyday experience **what is the particle-redistribution-controlling quantity**.
At this moment we accept that it is the quantity which can be **defined** using the formula $\frac{\partial S}{\partial N}$ and we define the name **chemical potential μ** for the relevant quantity by the formula

$$\boxed{\frac{\mu}{T} = -\frac{\partial S}{\partial N}}$$

Equilibrium entropy changes

Equilibrium entropy of an isolated system is naturally a function of energy and external parameters. As an external parameter we shall generically consider volume.
We can easily express the total differential of equilibrium entropy $S(E, V)$. **For fixed number of particles** we get

$$dS = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV$$

We have just expressed the partial derivatives in equilibrium, so we get

$$dS = \frac{1}{T}dE + \frac{p}{T}dV$$

Rearranging this equation a bit we get

$$dE = TdS - pdV$$

we compare this to the first law of thermodynamics

$$dE = \delta Q - pdV$$

and get

$$\boxed{\delta Q = TdS}$$

and also

$$\boxed{dS = \frac{1}{T}\delta Q}$$

both equations are valid for reversible processes only

$1/T$ as an integrating factor

The relation

$$dS = \frac{1}{T}\delta Q$$

deserves more detailed discussion. The symbol d in dS means that dS is a total differential. Physically it means that it is a difference of entropies of two close equilibrium states. (Entropy is a state variable). On the other hand the symbol δ in δQ means that **here we do not have a differential**. Heat is not a state variable! δQ is the small amount of microscopic work performed in a (here reversible) process!

Temperature has a magic property: multiplying by $1/T$ a non-differential δQ we get a differential dS!

The other way how to express the same thing is to say that δQ is non-integrable, so that

$$\int \delta Q \neq Q_2 - Q_1$$

but dS is integrable

$$\int dS = \int \frac{1}{T}\delta Q = S_2 - S_1$$

This is why $1/T$ is called "**integrating factor**". The trivial consequence is that the integral around a closed curve is zero

$$\boxed{\oint \frac{1}{T}\delta Q}$$

Still another definition of thermodynamic temperature

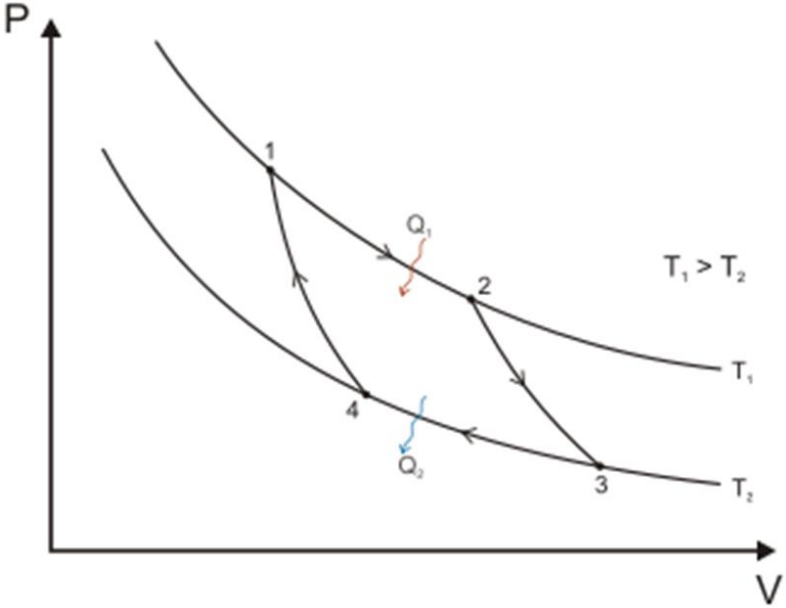
$$dS = \frac{1}{T}\delta Q$$

We can use the above formula to alternatively define temperature. Like this:
temperature is the physical quantity which one has to put into the denominator like

$$\frac{1}{T}\delta Q$$

to get full differential (for a reversible process) d{something} from δQ which is not a full differential.

Carnot engine again using entropy



Carnot machine is a cyclic device, so after one cycle we get

$$\oint dS = 0$$

$$\oint \frac{1}{T}\delta Q = 0$$

$$\int_1^2 \frac{1}{T}\delta Q + \int_3^4 \frac{1}{T}\delta Q = 0$$

W have omitted contribution from the adiabats 23 and 41, since heat is zero on adiabat. On isotherms the temperature is constants, so integrals are trivial

$$\int_1^2 \frac{1}{T}\delta Q + \int_3^4 \frac{1}{T}\delta Q = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \implies \frac{Q_2}{Q_1} = -\frac{-T_2}{T_1}$$

$$\eta = \frac{A}{Q_1} = \frac{Q_1 + Q_2}{Q_1} = 1 + \frac{Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

Do not forget that $Q_2 < 0$.

So we have trivially derived the formula for the efficiency (without the need to calculate volumes and pressures).

Equilibrium entropy changes

Equilibrium entropy of an isolated system is naturally a function of energy and external parameters. As an external parameter we shall generically consider volume.
We can easily express the total differential of **equilibrium entropy** $S(E,V,N)$. **For variable number of particles** we get

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN$$

Substituting for the partial derivatives in equilibrium, we get

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$$

Rearranging this equation a bit we get $\boxed{dE = TdS - pdV + \mu dN}$

Looking at this equation we can formally define the chemical potential as the energy change required to increase the number of particles by $dN = 1$ for fixed volume and fixed entropy on the system:

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$$

The problem is in magic words "fixed entropy". Fixed entropy usually means just $\delta Q = 0$, what means thermally isolated system. But if we want to add particles into the system, we have to push particles through some hole in the wall and this means that some microscopic work is to be performed and a **part of it might be $\boldsymbol{\delta Q}$**! So it is not easy to experimentally secure both constant entropy and variable number of particles. We shall come back to this question later.

Statistical ensemble

This is the central chapter of our lectures on statistical physics. It demonstrates the basic methodological idea: instead of analyzing a single system with many degrees of freedom in some specific macrostate **we shall study an ensemble** of identical macroscopic systems each of them being in some (different) microstate representing the macrostate considered. We shall then **statistically analyze the ensemble** calculating for example some mean macroscopic values of interest and assume that the real macroscopic values of the single system we experimentally observe will be very close to the mean statistical values we have calculated.

The art of statistical physics is hidden in prescripts **how to construct the representing statistical ensemble**. The prescripts for the construction of the representing statistical ensemble will depend on how the considered macrostate is defined through values of macroscopic variables.

We shall consider here quantum microstates to build the representing ensemble. Statistical physics emerged well before quantum mechanics and everything was formulated in terms of classical states (in phase space of the system considered). Since quantum stationary states are discrete, it is conceptually simpler to think in terms of quantum states. Though, in many situations we shall formulate the rules in terms of quantum states but then we shall use **continual approximation** (and the techniques of calculus) for real calculations.

We shall study in some details three situations:

- isolated system: its macrostate will be represented by so called **microcanonical ensemble**
- system in contact with thermal reservoir keeping its temperature constant: its macrostate will be represented by so called **canonical ensemble**
- system in contact with thermal reservoir as well as with particle reservoir which keeps its temperature and chemical potential constant: its macrostate will be represented by so called **grand canonical ensemble**

Microcanonical ensemble

We start with a macrostate of an isolated system. An isolated system has its energy fixed, so we can consider its **energy E as a given macroscopic parameter.** In addition to energy all external parameters shall be considered as given and fixed. The external parameters will be generically represented by a macroscopic variable V. For better imagination we can think about the volume (of a gas). The statistical ensemble representing an isolated system is called **microcanonical ensemble**.

Let us stress that the system considered must be large having very big number of degrees of freedom, typically 10^{23}. Then the number of relevant number of representing microstates will be of the order of $10^{10^{23}}$. Then the statistical predictions based on evaluating mean values calculated for the representing statistical ensemble will be sharp enough to be useful to represent the observed values of macroscopic physical quantities of the (single!) system we have at hand.

As we stressed several times the role of physics is to provide “good advice” to users. The advice provided by statistical physics is: **assume the macroscopic values you meet in reality to be equal to mean values calculated for the representing statistical ensemble**. What we just said is that **such an advice would be useful if the system considered is large enough**.

Microcanonical ensemble

As it is usual in physics, we cannot rigorously prove how to construct the microcanonical ensemble representing some specific statistical system. The general rule (guessed as a hypothesis and found to lead to "good advice" in many practical situations) is here:

Take all microstates having the energy equal to the macroscopic energy E of the system considered, each of them once (or each of them with equal probability).

This rule is sometimes considered to be one of the basic postulates of statistical physics. It is based on the assumption that once the isolated system reaches thermal equilibrium it randomly wanders through the subset of microstates having the same energy.

Well, this cannot be a rigorous truth. For absolutely isolated system its time evolution is controlled by its (internal) Hamiltonian through the Schrodinger equation. At some moment (for a fixed given energy) it must be in some superposition of stationary states corresponding to that energy. According to the Schrodinger equation it remains in the same superposition of states with phases changing. The weights of the stationary states need not have the same value, so the probability to find the system in a particular stationary state does not need to be the same for all the stationary states with the given energy.

In reality, however, no system can be strictly isolated from its environment. Any interaction, however weak, with the environment, can change the state to a state with energy differing just a little from the "given energy E".

Microcanonical ensemble

So some weak interaction with the environment can in principle make the “isolated system in equilibrium” wander through all the microstates with energy equal or very close to the ”given energy” E.

The interaction with environment we usually do not have under control. The interaction Hamiltonian in special situations may not be able to guarantee that the system considered would visit **all** the microstates having the “given energy”.

A typical example is a magnetized ferromagnet. Its macrostate is realized by microstates where almost all the local magnetic moments are oriented in a fixed direction. However to each such microstate there exist a complementary microstate where the local magnetic moments are oriented in exactly the opposite direction. These complementary microstates have the same energy, but they are certainly not representing the same macrostate. Normally we do not observe that a piece of magnetized material becomes spontaneously magnetized in an opposite direction.

The reason is, that the interaction with environment is not able to simultaneously flip all the local magnetic moments. To do that the interaction Hamiltonian would have to be highly non-local. The interaction with environment is usually able to flip just a few local magnetic moments. So the complete flip of all the moments would have to be achieved by many local consecutive flips. This is highly improbable, because “on the way” the system would have to go through states with very high energies: something like half of the moments “up” and the other half “down”.

Microcanonical ensemble

If we form the microcanonical ensemble for a ferromagnet according to the rule “each microstate with the given energy”, there will be microstates with exactly opposite magnetization and the **mean magnetization calculated for the ensemble would be zero**. Contrary to the experimental experience: we know there are magnetized materials in equilibrium.

So using microcanonical ensembles might be tricky and, in some situations, good physical intuition is required. We shall not dwell on it more here; this was just a warning.

We may be, however, suspicious of general rule “each microstate with the given energy” because of other reasons as well.

For example we know that for a gas macrostate in equilibrium the distribution of molecules in the container is uniform. However, there are microstates with all the molecules having the same energy as they have in a typical microstate but by chance, they occupy just one half of the container. Such microstate will enter the microcanonical ensemble, although they do not represent the studied macrostate properly. They are even macroscopically distinguishable from the “typical microstate” they in fact represent other, highly non-equilibrium macrostate. We have however seen, that the number of such untypical microstate is negligibly small: **we can safely calculate the mean values through the ensemble containing such non-typical microstates and get the correct typical values**.
Our notes in the last few slides are conceptually beyond the level of these lectures. We just presented them as a warning that the world is often more complex then it is described in basic textbooks. It is here, where the intuition of physics gurus is vitally important.

Microcanonical ensemble

Well, let us forget about exceptional situations and show that **the basic hypothesis of equal probabilities of all available microstates for isolated system can be used as an extremely valuable tool to obtain "good advice" when dealing with systems with huge amount of degrees of freedom**.

We have already introduced the function $\Omega(E)$ as the number of microstates having its energy within some small not exactly specified interval around the value E.

It is typical for statistical physics, that it operates with not precisely defined approximations. However one has to be sure that the inaccuracies do cancel in resulting values.

Suppose for example we want to calculate the mean value of some physical quantity A, which in the microstate i has the value A_i. The mean value is for the microcanonical ensemble given as

$$\bar{A} = \frac{1}{\Omega(E)} \sum_{i, E_i = E} A_i$$

Here the summation is restricted over microstates whose energy $E_i = E$. However this condition is not to be taken rigorously. We rather mean the states having its energy within some small not exactly specified interval around the value E. The same inaccuracy of definition is hidden in the function $\Omega(E)$. But if we consider $\Omega(E)$ to be the number of terms in the sum, everything is consistent. But is it also useful? Well, experience show that yes. The point is, that **for real situations we find that the result does not depend on how large the "interval around E" is, provided it is "reasonably small"**.

Microcanonical ensemble - entropy

We have defined the entropy of an isolated macroscopic system as

Entropy for an isolated physical system is defined as k-times the logarithm of the number of microstates corresponding to the macrostate considered.

$$\boxed{S = k \ln \Omega(E)}$$

Here we use the imprecisely defined function $\Omega(E)$ **alone**, so one would naively say that the inaccuracy cannot get canceled against some other inaccuracy in the formula.

The mystery is hidden in the use of logarithm. For huge numbers the logarithm is a very very slowly increasing function. Here is an example. Let us have two huge numbers $e^{10^{23}}$ and $1000\ e^{10^{23}}$ These two numbers are obviously grossly unequal. But look:

$$\ln(\exp 10^{23}) = 10^{23} \qquad \ln(1000 \times \exp 10^{23}) = 10^{23} + \ln 1000 \approx 10^{23}$$

So with a very good precision we get that the logarithms of these two grossly unequal numbers are practically equal!

$$\boxed{\ln(\exp 10^{23}) = \ln(1000 \times \exp 10^{23})}$$

So the logarithm in the definition of entropy is blind to the inaccuracy in the definition of $\Omega(E)$.

Approximations in statistical physics

In mechanics we have worked with exact equations, like $s = vt$. This is an equation in space of real numbers and is perceived as exact. We normally are not aware of the fact that this equation is not about the real world, it is an equation in some mathematical model. The mathematical model in mechanics is rigorous and exact. What is not exact is the mapping of the mathematical model to some real-world situation.

The equation $s = vt$ is by no means about a real-world train: the position of the train cannot be given with arbitrary precision, the train never moves exactly uniformly etc. So even the mathematical-model equations are exact, the results interpreted in terms of the real world are just approximate.

In statistical physics where we deal with systems of many degrees of freedom even the mathematical equations are often just approximate. The definition of entropy $S = k\,\ln\Omega(E)$ is not strictly exact since its right hand side is not rigorously defined. We do not mind, because the logarithm is blind enough to this inaccuracy. But if we naively do exponentiation like

$$\exp\frac{1}{k}S = \Omega(E)$$

we have to be very careful about the interpretation (validity) of the resulting equation. When we know experimentally the entropy to a good precision it does not mean that we do know precisely “the number of relevant microstates”. The equations of statistical physics are usually **valid only in logarithmic approximation**.

Microcanonical ensemble - calculations

So let us do some calculations with microcanonical ensemble.
N number of microstates in the ensemble can clearly be expressed as

$$\Omega(E) = \sum_{i, E_i = E} 1$$

This formula is not used for practical calculations, it is useful for theoretical manipulations.
Mean energy through the ensemble is

$$\bar{E} = \frac{1}{\Omega(E)} \sum_{i, E_i = E} E_i = \frac{1}{\Omega(E)} E \sum_{i, E_i = E} 1 = \frac{1}{\Omega(E)} E \Omega(E) = E$$

We got a consistent result.
Now to less trivial quantity. Let us consider an ideal gas of monoatomic spinless particles and calculate the (mean) pressure. Just formally

$$\bar{p} = \frac{1}{\Omega(E)} \sum_{i, E_i = E} p_i$$

where p_i is the pressure of gas in a specific microstate i. **So first we have to learn, how to calculate $\boldsymbol{p_i}$.**

Gas in a microstate, calculating its pressure

This is an exercise of elementary quantum mechanics.
We start with calculating the pressure of a gas in a box consisting of just a single molecule in the state $j = (n_1, n_2, n_3)$. To calculate the pressure we use the trick from elementary mechanics: to calculate force it is often easier to calculate the work the force performs during an infinitesimal change of state using the energy conservation principle.
The energy in the considered state is

$$E_j = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2) = \frac{\pi^2\hbar^2}{2mV^{2/3}}(n_1^2 + n_2^2 + n_3^2)$$

Now consider our piston-pusher dwarf changing reversibly the volume a bit. He has to perform an infinitesimal work $\delta A = -p_j dV$, where p_j is the pressure in the one-particle microstate j. The energy of the gas is changed by

$$dE_j = -\frac{2}{3}\frac{\pi^2\hbar^2}{2mV^{5/3}}(n_1^2 + n_2^2 + n_3^2)dV = -\frac{2}{3}\frac{E_j}{V}dV$$

The relation $dE_j = -p_i dV$ gives $$p_j = \frac{2}{3}\frac{E_j}{V}$$

For gas containing many molecules the energy of a (total) specific microstate i is given by the sum over all one-particle states. Repeating the above procedure it is obvious that the pressure in the total microstate i will be again given by the formula

$$\boxed{p_i = \frac{2}{3}\frac{E_i}{V}}$$

Microcanonical ensemble - calculations

For gas in the microstate i we got $p_i = \frac{2}{3}\frac{E_i}{V}$

so the mean pressure will be

$$\bar{p} = \frac{1}{\Omega(E)} \sum_{i,E_i=E} p_i = \frac{1}{\Omega(E)} \sum_{i,E_i=E} \frac{2}{3}\frac{E_i}{V} = \frac{2}{3}\frac{1}{V}\frac{1}{\Omega(E)} \sum_{i,E_i=E} E_i = \frac{2}{3}\frac{1}{V}\bar{E} = \frac{2}{3}\frac{1}{V}E$$

Even if we have not yet calculated the temperature for microcanonical gas we know that for monoatomic gas we expect $E = \frac{3}{2}NkT$ so for the pressure we get the equation of state

$$\boxed{\bar{p} = \frac{1}{V}NkT}$$

We have done the calculation for ideal gas. In general, for arbitrary external parameter V we shall find that changing its value requires to do work. (Remember, an external parameter is a parameter which is contained in the formula for energies of the stationary states!). So for infinitesimal changes we get something like $dE_i = -p_i dV$ where p_i is **conjugated force parameter** to the external parameter V so in general we get

$$p_i = -\frac{\partial E_i}{\partial V}$$

and so

$$\boxed{\bar{p} = \frac{1}{\Omega(E)} \sum_{i,E_i=E} -\frac{\partial E_i}{\partial V}}$$

Microcanonical ensemble - temperature

We said that we calculate the macroscopic quantities expected in equilibrium macrostate as mean values of the microstate values of the corresponding physical quantities over the microcanonical ensemble.

However there are physical quantities which are **well defined only for macrostates, they have no analog for microstates**. These are for example entropy, temperature and chemical potential.

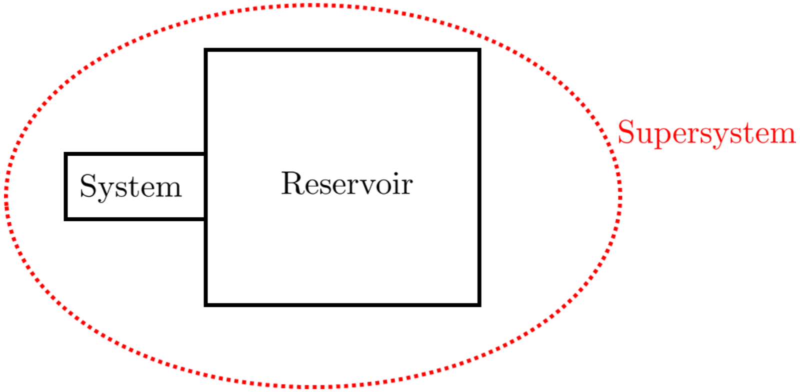
This is not obvious especially for temperature: one might try to define temperature for example for an isolated gas microstate as the total energy divided by the number of molecules (perhaps adding some factors like $\frac{3}{2}k$). But this is just expressing energy in units of Kelvin. This does not respect the definition of temperature by the zeroth law of thermodynamics: its role of the quantity controlling the mutual equilibrium. Equilibrium state is a property of macrostate.
So we have to calculate temperature of a microcanonical ensemble system using a thermodynamic definition like

- first calculate the entropy as $$S(E) = k \ln \Omega(E) = k \ln \sum_{i, E_i = E} 1$$
- then calculate the temperature as $$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_V$$

Technically, however, it is almost impossible to calculate entropy using the above formula, we shall calculate the entropy of gas later using technology of **grandcanonical ensemble**.

Canonical ensemble

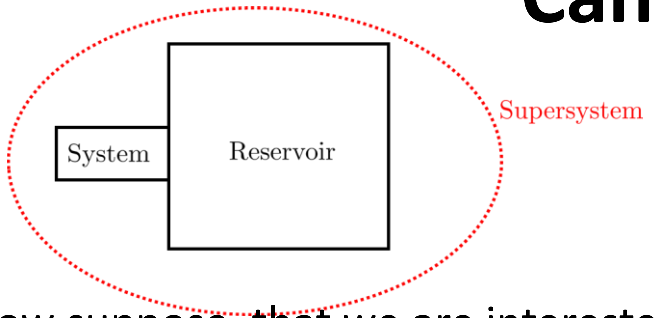
We shall now consider a system whose temperature is kept constant by a thermostat ("dwarf boiler attendant"). To make the theoretical analysis easier, we shall not consider real technologic thermostat but an abstract model: **our system in thermal contact with a very large system called reservoir**. Energy exchange through the thermal contact are negligible for the extremely large reservoir. So we can consider the temperature of the reservoir as constant and given. So we have a theoretically analyzable model of thermostat. System of our interest will be called just "system", it is in thermal contact with a large "reservoir". The system and the reservoir together form "supersystem". The supersystem can be considered as isolated, the total energy of the supersystem E_{super} is considered to be fixed, so **we can represent the supersystem by a microcanonical ensemble**.



The energy of the system will be denoted as E, of the reservoir as E_{res} and of the supersystem as E_{super}.

The microstate of the supersystem is composed by the state of the system i and by the state of the reservoir I. **So the supersystem state is a pair $(\boldsymbol{i}, \boldsymbol{I})$**.

Canonical ensemble



The supersystem microstate is a pair $(\boldsymbol{i},\boldsymbol{I})$.

Now suppose, that we are interested in a quantity, which is defined for the system alone. That is its value depends only on the system state i and not on the reservoir state I. Still, we can calculate its mean value using a the microcanonical ensemble for the whole supersystem:

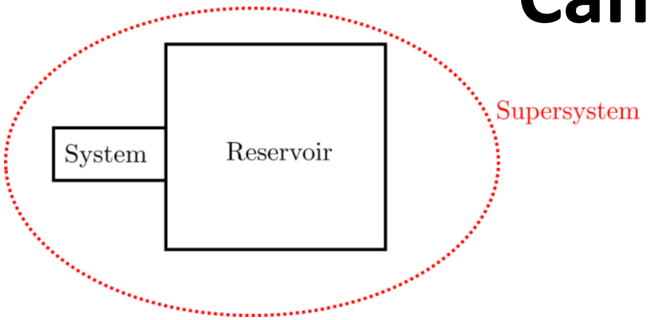
$$\bar{A} = \frac{1}{\Omega_{super}(E_{super})} \sum_{(i,I),E_{iI}=E_{super}} A_i$$

Do notice, that the value A_i does not have the index I, since the value of A does not depend on the reservoir state I. Still, in the formula above, we have to sum over all the values of the index I. This means, that the terms in the sum above having the same index i but different values of I contribute to the sum by a same value. So we can group the terms to groups having the same value of i and express the mean A value as

$$\bar{A} = \frac{1}{\Omega_{super}(E_{super})} \sum_{i} \Omega_{res}(E_{super} - E_i) A_i$$

Here $\Omega_{res}(E_{super} - E_i)$ is the number of states of the reservoir such that combined with the system state i they have the right total energy E_{super}. So it is the number of terms in the original sum containing the system state i. So the rewritten sum is correct.

Canonical ensemble



$$\bar{A} = \frac{1}{\Omega_{super}(E_{super})} \sum_i \Omega_{res}(E_{super} - E_i) A_i$$

Now we rewrite Ω_{res} through the entropy S_{res} and get

$$\bar{A} = \frac{1}{\Omega_{super}(E_{super})} \sum_i \exp\left(\frac{1}{k} S_{res}(E_{super} - E_i)\right) A_i$$

Since the reservoir is much larger than the system $E_i \ll E_{super}$ and we expand the function in the exponent to the first order in Taylor series:

$$\bar{A} = \frac{1}{\Omega_{super}(E_{super})} \sum_i \exp\left(\frac{1}{k} S_{res}(E_{super}) - \frac{1}{k}\frac{\partial S_{res}}{\partial E} E_i\right) A_i$$

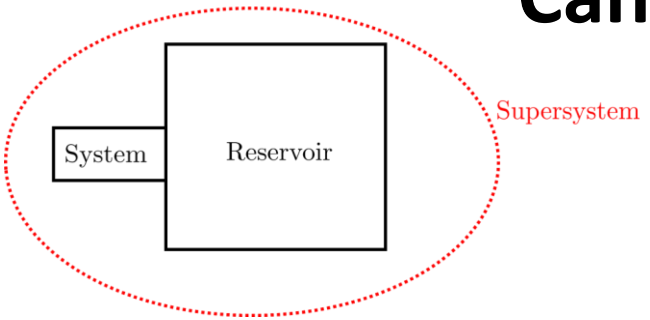
Using the formula $\frac{\partial S}{\partial E} = \frac{1}{T}$ we get

$$\bar{A} = \frac{\exp\left(\frac{1}{k} S_{res}(E_{super})\right)}{\Omega_{super}(E_{super})} \sum_i \exp\left(-\frac{E_i}{kT}\right) A_i$$

The factor in front of the sum “does not feel” the system at all neither it feels what quantity A we are interested in; it is just a constant. It is in fact a normalization constant.

$$\bar{A} = \text{const} \sum_i \exp\left(-\frac{E_i}{kT}\right) A_i$$

Canonical ensemble



$$\bar{A} = \text{const} \sum_i \exp\left(-\frac{E_i}{kT}\right) A_i$$

So what have we got? In the formula T is the temperature of the reservoir but because of the equilibrium through the thermal contact it is also the temperature of the system. So we can calculate any mean value concerning the system by forgetting about the reservoir: there is no more any mentioning of the reservoir in the above formula.
The formula looks like a standard formula for calculating the mean values if we interpret the factor

$$\text{const}\exp\left(-\frac{E_i}{kT}\right)$$

as a probability of the system microstate i. So the rule:

The ensemble representing a macrostate of a system with a given temperature (kept constant by a suitable thermostat) can be constructed taking all the possible microstates (with arbitrary energy E_i, but fixed number of particles $N_i = N$), each with the probability

$$p(i) = \text{const}\exp\left(-\frac{E_i}{kT}\right)$$

Such an ensemble is called canonical ensemble.

Canonical ensemble – comments

- Deriving canonical distribution from the microcanonical we did a “forbidden operation”:

Now we rewrite Ω_{res} through the entropy S_{res}

We have exponentiate the entropy. This is dangerous, since Ω is “fuzzy defined” what makes no problems after taking logarithm of it what gives entropy. We have already warned that exponentiating back the entropy returns Ω which again is “fuzzy”, but we have no control on it. So maybe the effective probabilities of the system states are not correct !? The point is that we are not interested in probabilities, we want to calculate mean values: summing over probabilities. And the states with debatable probabilities are anyhow those with marginal probabilities which do not contribute to the sums significantly. The problem might be only with normalization, but we have to recalculate normalization anyhow (see next slides) and that will be done with probabilities already fixed.

- We expanded the entropy in the exponent only to the first order in E. Could we get “a more precise” canonical distribution doing the expansion to the second order? Actually not. The reservoir is very big: you can check that the second order would be negligible. You can investigate it for some model of reservoir like ideal gas and find that the correction in the exponent would be proportional to $1/N$ and therefore negligible

Canonical ensemble – Statistical sum

$$p(i) = \mathrm{const}\exp\left(-\frac{E_i}{kT}\right)$$

The normalization constant can be calculated from the condition

$$\sum_i p(i) = 1$$

From there we get $\boxed{p(i) = \frac{1}{Z}\exp\left(-\frac{E_i}{kT}\right)}$ where $\boxed{Z = \sum_{i, N_i = N} \exp\left(-\frac{E_i}{kT}\right)}$

Z is sometimes called the statistical sum and it is the first thing one has to calculate when one wants to use the canonical ensemble. We have explicitly written the condition that the sum is taken only over the states with fixed $N_i = N$. Usually one writes just $\sum_i$ and the **condition $N_i = N$ is understood implicitly**.

A **short summary of the canonical ensemble usage**:

- canonical ensemble is to be used when the given quantities for the system are **temperature T and volume (or external parameter) V**
- the first step is to calculate the **statistical sum Z**
- then the mean value of any quantity A is calculated as $\bar{A} = \frac{1}{Z}\sum_i A_i \exp\left(-\frac{E_i}{kT}\right)$

Canonical ensemble – mean values

In particular the mean energy of a canonical system is given as

$$\bar{E} = \frac{1}{Z} \sum_i E_i \exp\Big(- \frac{E_i}{kT} \Big)$$

The mean pressure (more generally the man value of the canonical force quantity conjugated to the external parameter V is given as

$$\bar{p} = \frac{1}{Z} \sum_{i, E_i = E} - \frac{\partial E_i}{\partial V} \exp\Big(- \frac{E_i}{kT} \Big)$$

Canonical ensemble – small system

Deriving the canonical ensemble probabilities we have used an auxiliary large system, the reservoir, playing the role of thermostat. Inspecting the derivation we can see, that using the statistical methods and calculating the means we used the fact that the reservoir and therefore also the supersystem was large macroscopic system. We in fact did not need the system to be macroscopic.

Therefore the canonical ensemble can be used also for small systems in contact with reservoir or thermostat. Even for such a small system as one particle.

Let us consider gas of classical (non quantum) particles. In that case we can define a particular particle as the system of interest. (For quantum indistinguishing particles we cannot limit attention to one specific particle!) The chosen particle collides with many other particles of the gas, so we can say our particle is in thermal contact with the rest of the gas which would play the role of the reservoir (or thermostat).

So we can use the technique of canonical ensemble for a small system containing just one particle. This, however, requires classical (non-quantum) statistical physics, that is classical analogue of our quantum formula which uses discrete quantum states. We shall write the relevant classical formula just intuitively, without deep discussion on the relation between quantum and classical statistics. Actually, we have already seen the Maxwell velocity distribution, so we just will point at the canonical ensemble interpretation of the Maxwell distribution

Canonical ensemble – Maxwell distribution

We shall consider one classical particle in contact with rest of the particles in gas as a reservoir. Let us first assume there is no external field (like gravitation). Then what concerns position the particles are uniformly distributed in the container. The microstate of a particle is then given by its velocity. So we are interested to get the probability that our selected particle has velocity $\vec{v}$. Classical velocity is a continuous variable, so we have to use the probability technology for continuous variables: probability densities. Intuitively we expect that in parallel to quantum canonical distribution the probability density for velocities will be proportional to the "Boltzmann factor"

$$\exp\left(-\frac{E}{kT}\right)$$

For one particle and no external field the relevant energy in the formula should be just the kinetic energy so we get

$$\varrho(\vec{v}) = C\exp\left(-\frac{mv^2}{2kT}\right)$$

We got what we expected: the Maxwell distribution. The normalization constant (analog of statistical sum) we get from the condition

$$\int d^3\vec{v}\varrho(\vec{v}) = 1$$

and get what we have already seen:

$$\boxed{\varrho(\vec{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2}\exp(-\frac{mv^2}{2kT})}$$

Canonical ensemble – Boltzmann distribution

In external field the gas particle distribution is no more uniform in space, the microstate of the particle is given by its position and velocity. So for one classical particle we get the probability density in the $(\vec{r},\vec{v})$ space

$$\varrho(\vec{r},\vec{v}) = C\exp\left(-\frac{E_{kin}+E_{pot}}{kT}\right)$$

$$\boxed{\varrho(\vec{r},\vec{v}) = C\exp\left(-\frac{\frac{1}{2}mv^2+U(\vec{r})}{kT}\right)}$$

This is called the **Boltzmann distribution**. The normalization constant is to be obtained from the condition

$$\int d^3\vec{r}d^3\vec{v}\varrho(\vec{r},\vec{v}) = 1$$

If we are not interested by the velocity distribution, we can integrate over velocities and get the marginal spatial probability density

$$\boxed{\varrho(\vec{r}) = \tilde{C}\exp\left(-\frac{U(\vec{r})}{kT}\right)}$$

Canonical ensemble – barometric formula

Applied to homogenous gravitational field $U(z) = mgz$ we get for the marginal probability density of the z-coordinate of a particle

$$\varrho(z) = C \exp\left(-\frac{mgz}{kT}\right)$$

where m is the mass of the particle. Then for the gas spatial particle density at the height z (number of particles per unit volume) we get

$$n(z) = n_0 \exp\left(-\frac{mgz}{kT}\right)$$

where n_0 is obviously the particle density at $z = 0$. Since ideal gas pressure is proportional to the particle density, we get for the pressure distribution in isothermal atmosphere (temperature not dependent on z)

$$\boxed{p(z) = p_0 \exp\left(-\frac{mgz}{kT}\right)}$$

This barometric formula can be used as the bases for the construction of pressure altimeter. The altitude of a plane can be determined by comparing the pressure at unknown altitude z with the pressure at the ground.

Canonical ensemble – classical harmonic oscillator

Let us consider a single harmonic oscillator in contact with a thermostat. It is “a small system at constant temperature” so we can apply the Boltzmann distribution. Without doing “too much science” around it we shall apply it just intuitively, assuming that the probability distribution in the two-dimensional space of states (x, v) is

$$\varrho(x,v) = C\exp\left(-\frac{\frac{1}{2}mv^2+\frac{1}{2}Kx^2}{kT}\right)$$

The normalization constant is to be get from the condition $\int \varrho(x,v)dx\,dv = 1$

The probability density is just a double Gaussian, so the calculation is easy, and we get

$$C = \sqrt{\frac{mK}{(2\pi kT)^2}}$$

Having this we can easily calculate the mean energy and get

$$\overline{E} = \int \left(\frac{1}{2}mv^2+\frac{1}{2}Kx^2\right)\varrho(x,v)dx\,dv = kT$$

Here is the summary of results for single harmonic oscillator at temperature T

$$\overline{\frac{1}{2}mv^2} = \frac{1}{2}kT \qquad \overline{\frac{1}{2}Kx^2} = \frac{1}{2}kT \qquad \overline{E} = kT$$

Canonical ensemble – entropy

We have defined **entropy for isolated system as k-times the logarithm of the number of microstates corresponding to the macrostate considered (equivalently the number of states in the corresponding microcanonical ensemble).**
This definition cannot be extrapolated to the system in contact with the thermal reservoir: the corresponding ensemble is the canonical ensemble which is formed by all - that is an infinite number - of microstates. We have to look for some alternative definition of entropy.
The notion of entropy is conceptually relevant only for macrostates of systems with very large degrees of freedom. **The canonical distribution can be used also for small systems in contact with reservoir, but we need to define entropy only for very large systems**.
For very large systems the macroscopic values are very sharp: the values fluctuate but typically on the level of 13-th decimal place.
In particular: **the energy of a large canonical system is practically constant**. We are unable to observe fluctuations on the 13-th decimal place. Experimentally we cannot just by measurements distinguish a canonical system with fixed given temperature from a microcanonical system with a given fixed energy. Therefore the idea:

The entropy for a canonical system can be defined in two consecutive steps

1. Determine the mean energy $\bar{E}$ of the canonical system considered.
2. Imagine the same system **as if** an isolated system with a fixed energy $E = \bar{E}$ and determine what would be its entropy $S(E = \bar{E})$. This is to be called the entropy of the original canonical system.

Canonical ensemble – entropy

The above mentioned two-step process for calculating the canonical entropy can be rewritten by a single compact formula. Its derivation is a bit tricky. Here it is.
We start with the definition of the statistical sum

$$Z = \sum_i \exp\Big(- \frac{E_i}{kT}\Big)$$

where the summation is over the states. We can regroup the terms in this sum according to the energy of states and rewrite the sum as a sum over energies as

$$Z = \sum_E \Omega(E) \exp(-\frac{E}{kT})$$

In this sum the function $\Omega(E)$ is a sharply rising function of E while the exponent is a sharply decreasing function of E. Therefore the main contribution to the whole sum comes from the terms with $E \approx \bar{E}$. The domination of the terms around $\bar{E}$ is such, that in the logarithmic precision the logarithm of the sum is given by a single term (we write just $=$ instead of $\approx$ as it is usual in statistical physics where most of the equations are only approximate anyhow).

$$\ln Z = \ln\left(\Omega(\bar{E}) \exp(-\frac{\bar{E}}{kT}) \right) = \ln \Omega(\bar{E}) - \frac{\bar{E}}{kT}$$

From there we get

$$S = k \ln \Omega(\bar{E}) = k \ln Z + \frac{\bar{E}}{T}$$

This formula could be used as the definition of entropy of a canonical system. But we will derive still a nicer formula.

Canonical ensemble – entropy

We start with the formula we just got

$$S = k\ln\Omega(\bar{E}) = k\ln Z + \frac{\bar{E}}{T}$$

and we play more with it:

$$S = k\ln Z + \frac{1}{T}\sum_i E_i p(i)$$

$$S = k\ln Z\sum_i p(i) - k\sum_i \frac{-E_i}{kT}p(i)$$

$$S = k\ln Z\sum_i p(i) - k\sum_i \ln\exp(\frac{-E_i}{kT})p(i)$$

$$S = -k\sum_i \ln\frac{\exp(-E_i/kT)}{Z}p(i)$$

$$\boxed{S = -k\sum_i(\ln p(i))p(i)}$$

see the nice trick, using $1 = \sum_i p(i)$

The last formula is very nice and compact, and it can be shown that it is very general. For example it also holds for a microcanonical system where we have $p(i) = \frac{1}{\Omega(E)}$ so we get

$$S = -k\sum_i(\ln\frac{1}{\Omega(E)})\frac{1}{\Omega(E)} = k(\ln\Omega(E))\frac{1}{\Omega(E)}\sum_i 1 = k\ln\Omega(E)$$

what is just “k times the logarithm of the number of states” as it should be.

General ensemble – entropy

The formula for entropy we have derived for the canonical ensemble can be used as a general definition of entropy for any macroscopic state, represented by a suitable statistical ensemble.

Statistical ensemble in general is a set of microstates i with assigned probability $p(i)$. Then the man value of any physical quantity A which has a well-defined value A_i for any microstate i from the ensemble is defined as

$$\bar{A} = \sum_i A_i p(i)$$

and the entropy of that macrostate **is defined** as $S = -k \sum_i (\ln p(i)) p(i)$

It looks as if it was a mean value of some physical quantity (entropy?) of individual microstates. This is not true. The probability $p(i)$ is not a state variable of an individual microstate. It cannot be calculated just from microstate-defining variables. The probability $p(i)$ is given by the weight of the microstate i in the ensemble characterizing the macrostate. So one has to know the macrostate before assigning the probabilities $p(i)$.

Actually, many textbooks basically start the introduction to statistical physics with something like the above framed text as “the basic postulate”. The general formula for entropy which looks a priori like a miraculous guess is in fact very natural for anyone who is familiar with the theory of information, where it is called “the information entropy”. The interested reader may find more in my text on advanced statistical physics.

Canonical ensemble – first law of thermodynamics

We start with the formula for the mean energy:

$$\bar{E} = \sum_i E_i p(i)$$

Now suppose our “external dwarfs” infinitesimally change the macrostate in a general way. The corresponding ensemble will be changed, that is the probabilities of the microstates will be changed by $dp(i)$ and the energies of the microstates will also be changed in general by dE_i due to some changes of external parameters (like V). The mean energy of the macrostate will be changed by

$$d\bar{E} = \sum_i \left(dE_i p(i) + E_i dp(i)\right) = \sum_i dE_i p(i) + \sum_i E_i dp(i)$$

The physical interpretation of the first sum is clear: energies E_i are changed due to the change of the external parameter dV, so we can write

$$d\bar{E} = \sum_i \frac{\partial E_i}{dV} dV\, p(i) + \sum_i E_i dp(i) = -\sum_i p_i dV\, p(i) + \sum_i E_i dp(i) = -\bar{p} dV + \sum_i E_i dp(i)$$

We know the first term; it is the mechanical work (extracted e.g. by the dwarf piston-pusher). So the second term must be heat (performed by the boiler attendant)

$$\boxed{\delta Q = \sum_i E_i dp(i)}$$

Canonical ensemble – first law of thermodynamics

Now for a canonical system we perform an ingenious trick writing

$$E_i = -kT \ln \exp\left(\frac{-E_i}{kT}\right) = -kT \ln\left(Zp(i)\right)$$

Using this in the just derived formula for heat we get

$$\delta Q = \sum_i E_i dp(i) = -kT \sum_i \ln\left(Zp(i)\right) dp(i) = -kT \ln Z \sum_i dp(i) - kT \sum_i \ln(p(i)) dp(i)$$

The first term is 0 since $\sum_i dp(i) = d \sum_i p(i) = d1 = 0$

The second term needs another ingenious insight:

$$\delta Q = -kT \sum_i \ln(p(i)) dp(i) = -kTd \sum_i \ln p(i) p(i)$$

indeed:

$$d \sum_i \ln p(i) p(i) = \sum_i \left(d \ln p(i) p(i) + \ln p(i) dp(i)\right) =$$

$$= \sum_i \left(\frac{1}{p(i)} dp(i) p(i) + \ln p(i) dp(i)\right) = \sum_i \ln p(i) dp(i)$$

So we have got, as expected $\boxed{\delta Q = TdS}$

Canonical ensemble – partition function

We have defined the statistical sum as a "normalization constant"

$$Z = \sum_i \exp\Big(- \frac{E_i}{kT} \Big)$$

This evokes impression that Z is a constant. It is to some extent true. However, a canonical system has a given temperature T and volume (external parameter) V. If we evaluate Z for arbitrary values T, V, we get a function $Z(T, V)$. Z as a function is called **partition function**. We shall show that this function carries a lot of useful information about the canonical system considered. Let us start with calculating the mean energy:

$$\bar{E} = \frac{1}{Z} \sum_i E_i \exp(-\frac{E_i}{kT}) = \frac{1}{Z} \frac{\partial}{\partial(-1/kT)} \sum_i \exp(-\frac{E_i}{kT}) = \frac{1}{Z} \frac{\partial}{\partial(-1/kT)} Z$$

$$\boxed{\bar{E} = \frac{\partial}{\partial(-1/kT)} \ln Z}$$

So the information on the mean energy "is coded" in the partition function. The above formula is the instruction how to decode it. In the same way one can easily prove that even higher moments are coded in the partition function. For variance one gets

$$\overline{(\Delta E)^2} = \frac{\partial^2}{\partial(-1/kT)^2} \ln Z$$

Canonical ensemble – free energy

Similarly for the mean pressure we get

$$\bar{p} = \frac{1}{Z} \sum_i -\frac{\partial E_i}{\partial V} \exp(-\frac{E_i}{kT}) = kT \frac{1}{Z} \frac{\partial}{\partial V} \sum_i \exp(-\frac{E_i}{kT})$$

$$\boxed{\bar{p} = kT \frac{\partial}{\partial V} \ln Z}$$

We see that the logarithm of the partition function carries a lot of useful information. Therefore it was given a special name: free energy. More precisely

free energy *F* is defined by the expression

$$\boxed{Z = \exp -\frac{F}{kT}}$$

Similarly all higher moments of probability distribution of p can be obtained by derivatives of Z and its logarithm. If we expand $\ln Z$ as a Taylor series in V, the coefficients of the expansion will be so called **cumulants** (find in Wikipedia, how cumulants are related to moments) of p. Therefore $\ln Z$ is called generating function of the cumulants of p. Remember the term **generating function**, you will meet it often in theoretical physics.

Canonical ensemble – free energy

Free energy is closely related to the entropy. We have expressed entropy of the canonical system as

$$S = k \ln \Omega(\bar{E}) = k \ln Z + \frac{\bar{E}}{T}$$

Substituting for $\ln Z$ from the definition of free energy

$$Z = \exp -\frac{F}{kT}$$

we get

$$F = \bar{E} - TS$$

Actually the free energy was defined already in phenomenological thermodynamics as

$$\boxed{F = E - TS}$$

Since for macroscopic systems (entropy is defined only for macroscopic systems!) there is no practical experimental difference between $\bar{E}$ and E, the statistical and thermodynamical expressions are equivalent.

Canonical ensemble – quantum harmonic oscillator

Stationary states of a quantum harmonic oscillator can be labeled by integers n and the energies are

$$\boxed{E_n = (n + \frac{1}{2})\hbar\omega}$$

Now we consider one quantum harmonic oscillator in thermostat at temperature T. The calculation of the statistical sum is easy

$$Z = \sum_n \exp\left(-\frac{(n+1/2)\hbar\omega}{kT}\right) = \exp\left(\frac{-\hbar\omega}{2kT}\right)\sum_n\left(\exp\left(\frac{-\hbar\omega}{kT}\right)\right)^n$$

$$Z = \exp\left(\frac{\hbar\omega}{2kT}\right)\frac{1}{1-\exp\left(-\frac{\hbar\omega}{kT}\right)}$$

The mean energy is

$$\overline{E} = \frac{\partial}{\partial\left(\frac{-1}{kT}\right)}\ln Z$$

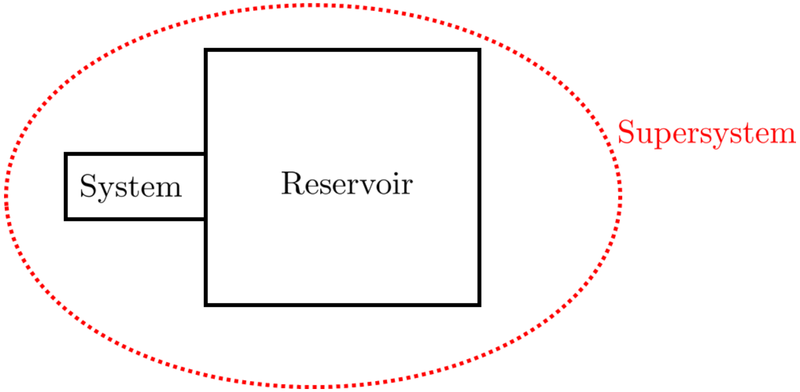
After a bit tedious calculations we get

$$\boxed{\overline{E} = \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{kT}\right)-1} + \frac{\hbar\omega}{2}}$$

In the classical limit $\hbar \to 0$ we get $\bar{E} \approx kT$, the same value as we got using Boltzmann distribution for a classical harmonic oscillator.

Grand canonical ensemble

We shall now consider a system with variable number of particles N. The system will be **in thermal and diffusion contact with a very large system called reservoir**. The thermal contact means energy exchange and the diffusion contact particle exchange between the system and the reservoir. Since the reservoir is considered to be much larger than the system, we can assume the temperature and the chemical potential of the reservoir to be constant and given. The system and the reservoir together form "supersystem". The supersystem can be considered as isolated, the total energy of the supersystem E_{super} is considered to be fixed as well as the total number of particles N_{super} of the supersystem to be fixed, so **we can represent the supersystem by a microcanonical ensemble**.



The energy of the system will be denoted as E, of the reservoir as E_{res} and of the supersystem as E_{super}, the number of particles of the system will be denoted by N, of the reservoir by N_{res} and of the supersystem N_{super}.

Our discussion will be a close parallel to our derivation of the canonical distribution.

The microstate of the supersystem is composed by the state of the system i and by the state of the reservoir I. **So the supersystem state is a pair $(\boldsymbol{i}, \boldsymbol{I})$.**

Grand canonical ensemble

We are interested in a quantity, which is defined for the system alone. That is its value depends only on the system state i and not on the reservoir state I. Still, we can calculate its mean value using a the microcanonical ensemble for the whole supersystem:

$$\bar{A} = \frac{1}{\Omega_{super}(E_{super,N_{super}})} \sum_{(i,I),E_{iI}=E_{super},N_{iI}=N_{super}} A_i$$

We can group the terms to groups having the same value of i and express the mean A value as

$$\bar{A} = \frac{1}{\Omega_{super}(E_{super}, N_{super})} \sum_i \Omega_{res}(E_{super} - E_i, N_{super} - N_i) A_i$$

Here $\Omega_{res}(E_{super} - E_i, N_{super} - N\_i)$ is the number of states of the reservoir such that combined with the system state i they have the right total energy E_{super} and the right total number of particles N_{super}. So it is the number of terms in the original sum containing the system state i. So the rewritten sum is correct.

Now we rewrite Ω_{res} through the entropy S_{res} and get

$$\bar{A} = \frac{1}{\Omega_{super}(E_{super,N_{super}})} \sum_i \exp\left(\frac{1}{k} S_{res}(E_{super} - E_i, N_{super} - N_i)\right) A_i$$

Grand canonical ensemble

$$\bar{A} = \frac{1}{\Omega_{super}(E_{super,N_{super}})} \sum_i \exp\left(\frac{1}{k} S_{res}(E_{super} - E_i, N_{super} - N_i)\right) A_i$$

Since the reservoir is much larger than the system $E_i \ll E_{super}$ and $N_i \ll N_{super}$ we expand the function in the exponent to the first order in Taylor series:

$$\bar{A} = \frac{1}{\Omega_{super}(E_{super})} \sum_i \exp\left(\frac{1}{k} S_{res}(E_{super,N_{super}}) - \frac{1}{k}\frac{\partial S_{res}}{\partial E} E_i - \frac{1}{k}\frac{\partial S_{res}}{\partial N} N_i\right) N_i A_i$$

Using the formulas $\frac{\partial S}{\partial E} = \frac{1}{T}, \frac{\partial S}{\partial N} = -\frac{\mu}{T}$ we get

$$\bar{A} = \frac{\exp\left(\frac{1}{k} S_{res}(E_{super}, N_{super})\right)}{\Omega_{super}(E_{super})} \sum_i \exp\left(-\frac{E_i}{kT} + \frac{\mu}{kT} N_i\right) A_i$$

The factor in front of the sum “does not feel” the system at all neither it feels what quantity A we are interested in; it is just a constant. It is in fact a normalization constant.

$$\bar{A} = \mathrm{const} \sum_i \exp\left(-\frac{E_i}{kT} + \frac{\mu}{kT} N_i\right) A_i$$

Grand canonical ensemble

$$\bar{A} = \mathrm{const} \sum_i \exp\Big(-\frac{E_i}{kT} + \frac{\mu}{kT} N_i\Big) A_i$$

So what have we got? In the formula T is the temperature of the reservoir and μ is the chemical potential of the reservoir. Because of the equilibrium through the thermal and diffusion contact these are also the temperature and the chemical potential of the system. So we can calculate any mean value concerning the system by forgetting about the reservoir: there is no more any mentioning of the reservoir in the above formula.
The formula looks like a standard formula for calculating the mean values if we interpret the factor

$$\mathrm{const} \exp\Big(-\frac{E_i}{kT} + \frac{\mu}{kT} N_i\Big)$$

as a probability of the system microstate i. So the rule:

The ensemble representing a macrostate of a system with a given temperature and chemical potential (kept constant by a suitable external reservoir) can be constructed taking all the possible microstates (with arbitrary energy E_i and arbitrary number of particles N_i), each with the probability

$$p(i) = \mathrm{const} \exp\Big(-\frac{E_i}{kT} + \frac{\mu}{kT} N_i\Big)$$

such an ensemble is called grand canonical ensemble.

Grand canonical ensemble – grand partition function

$$p(i) = \text{const} \exp\Big(-\frac{E_i}{kT} + \frac{\mu}{kT} N_i\Big)$$

The normalization constant can be calculated from the condition $\sum_i p(i) = 1$

From there we get

$$\boxed{p(i) = \frac{1}{\mathcal{Z}} \exp\Big(-\frac{E_i}{kT} + \frac{\mu}{kT} N_i\Big)}$$

$$\boxed{\mathcal{Z} = \sum_i \exp\Big(-\frac{E_i}{kT} + \frac{\mu}{kT} N_i\Big)}$$

$\mathcal{Z}$ is sometimes called the grand statistical sum. As a function of T, V, μ it is called **grand partition function** and it is the first thing one has to calculate when one wants to use the grand canonical ensemble.

A **short summary of the grand canonical ensemble usage**:

- grand canonical ensemble is to be used when the given quantities for the system are **temperature T volume (or external parameter) Vm and chemical potential μ**
- the first step is to calculate the grand partition function $\mathcal{Z}$
- then the mean value of any quantity A is calculated as

$$\bar{A} = \frac{1}{\mathcal{Z}} \sum_i A_i \exp\Big(-\frac{E_i}{kT} + \frac{\mu}{kT} N_i\Big)$$

Grand canonical ensemble – practical usage

We have said that we use the grand canonical ensemble when we have a macrostate with given T, V, μ. This is somewhat a symbolic statement. We usually do not have direct knowledge about the value of the chemical potential for a given system. (Try to buy a μ-meter in a laboratory-equipment shop!).

Normally we know the number of particles N together with T, V. So we should use the canonical ensemble. However for technical reasons we might prefer the grand canonical ensemble. The reason is the following: compare the two expressions

$$Z = \sum_{i, N_i = N} \exp\Big(-\frac{E_i}{kT}\Big) \qquad\qquad \mathcal{Z} = \sum_i \exp\Big(-\frac{E_i}{kT} + \frac{\mu}{kT} N_i\Big)$$

Technically it is usually easier to calculate the grand canonical sum **over all the states without any restriction** than the canonical sum **with the states restricted** by the condition $N_i = N$. The way how we use the grand canonical ensemble even for systems with given N and not μ is the following. We **just pretend that $\boldsymbol{\mu}$ is given** (without knowing its numerical value) and do the calculations with the parameter μ as a symbolic number. Then calculate the mean number of particles as a function of (pretended given but unknown) μ

$$\overline{N}(\mu) = \frac{1}{\mathcal{Z}(\mu)} \sum_i N_i \exp\Big(-\frac{E_i}{kT} + \frac{\mu}{kT} N_i\Big)$$

and find the “good” value of μ by inverting the equation $\overline{N}(\mu) = N$. This value of μ we then insert to all other results obtained by the grand-canonical calculation and we get the correct answer. The reason is that **for macroscopic system $\boldsymbol{\overline{N}}$ is undistinguishable from fixed $\boldsymbol{N}$**.

How to measure chemical potential

We can in principle experimentally determine the chemical potential for some type of particles for a system for which we are able to do the grand-canonical calculation. From the equation

$$\overline{N}(\mu) = N$$

we can in principle get the value of μ if we can measure (for example by suitable electrochemical method like by the lambda sensor) the concentration of the relevant particles to obtain N.

One may argue that **“this is not a direct measurement of $\boldsymbol{\mu}$**! “ since we need the theoretical formula connecting μ and N. Well, actually most of the measurements (and measuring devices) do not “measure directly” the required physical quantity. Directly measurable are for example length and angle. Even the old-fashioned ammeter does not measure the electric current directly: it measures the angle of the pointing needle and we have some theory to connect the measured angle and the current going through the ammeter. In a standard thermometer we do not directly measure temperature but rather the length of the mercury column in a glass tube. And we have some phenomenological formula connecting the temperature and the length of the mercury column.

Grand partition function

Similarly to the partition function of the canonical distribution useful information on moments of physical quantities is coded in the grand partition function. For example, the mean number of particles can be calculated as follows

$$\overline{N}(\mu) = \frac{1}{\mathcal{Z}(\mu)} \sum_i N_i \exp\Big(-\frac{E_i}{kT} + \frac{\mu}{kT} N_i \Big) = \frac{kT}{\mathcal{Z}} \frac{\partial}{\partial \mu} \sum_i \exp\Big(-\frac{E_i}{kT} + \frac{\mu}{kT} N_i \Big)$$

$$\boxed{\overline{N}(\mu) = kT \frac{\partial}{\partial \mu} \ln \mathcal{Z}}$$

The grand partition function can be expressed thorough the canonical partition function:

$$\mathcal{Z}(\mu, T, V) = \sum_i \exp\Big(-\frac{E_i}{kT} + \frac{\mu}{kT} N_i \Big) = \sum_N \sum_{i, N_i = N} \exp\Big(-\frac{E_i}{kT} + \frac{\mu}{kT} N_i \Big)$$

$$= \sum_N \exp\Big(\frac{\mu}{kT} N \Big) \sum_{i, N_i = N} \exp\Big(-\frac{E_i}{kT} \Big) = \sum_N \exp\Big(\frac{\mu}{kT} N \Big) Z(N, T, V)$$

Using again the argument on domination of mean values for the logarithm of the sum:

$$\boxed{\ln \mathcal{Z}(\mu, T, V) == \frac{\mu}{kT} \bar{N} + \ln Z(\bar{N}, T, V) = \frac{\mu}{kT} \bar{N} - \frac{1}{kT} \bar{E} + \frac{1}{k} S}$$

Grand canonical potential

Similarly to the definition of free energy through the logarithm of canonical partition function we define the **grand canonical potential *Ω*** as

$$\mathcal{Z}(\mu, T, V) = \exp\Big(-\frac{\Omega}{kT}\Big)$$

There is an inconsistency in the notation (overall in the statistical physics books): symbol *Ω* was already used to denote the number of microstates in the microcanonical ensemble. The reader has to resolve from the context the two omegas from each other.

Thermodynamic potentials

In the preceding lectures we have met several functions of the state like energy E, entropy S, free energy F and canonical potential Ω with the property that their partial derivatives with respect to their natural variables gave us the possibility to calculate various macroscopic physical quantities. For example we have met the following relations:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} \qquad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$$

Now we shall discuss various thermodynamic potentials more systematically. We start with the first law of thermodynamics written for reversible processes.

$$dE = TdS - pdV + \mu dN \qquad dS = \frac{1}{T}dE + \frac{1}{T}pdV - \frac{1}{T}\mu dN$$

These relations suggest, that the “native” variables for energy are S, V, N and for entropy E, V, N. In this context energy and entropy are called **thermodynamic potentials**.
If the thermodynamic potentials are expressed through their “native” variables, we get the following relations

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N} \qquad p = -\left(\frac{\partial E}{\partial V}\right)_{V,S} \qquad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} \qquad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} \qquad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V}$$

Thermodynamic potentials

Energy as and thermodynamic potential has intuitively clear meaning, but its “native” variables are not nice: the entropy is experimentally inaccessible. One would prefer to replace entropy to something experimentally comfortable like temperature.
There is a general mathematical tool to manage such replacements: the Legendre transform (remember how one does that in theoretical mechanics: Lagrangian as a function of $q, \dot{q}$, is replaced by Hamiltonian as a function of q, p). The Legendre transform to swap S for T: $F(T,V,N) = E(S,V,N) - TS$

We have already seen such function; it is called **free energy**. Do not be confused: it looks there are 4 variables on the right but only 3 on the left! S on the right is not a variable, it should be written as a function of T, V, N by inverting the relation $T = \left(\frac{\partial E}{\partial S}\right)_{V,N}$

One has to solve this for S as a function of T, V, N and insert it to the Legendre transform. Let us calculate the differential of F:

$$dF = dE - dTS - TdS = TdS - pdV + \mu dN - dTS - TdS$$

$$\boxed{dF = -SdT - pdV + \mu dN}$$

The native variables of F are T, V, N and we get relations

$$\boxed{S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \qquad p = -\left(\frac{\partial F}{\partial V}\right)_{V,T} \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}}$$

Free energy

$$F(T,V,N) = E(S,V,N) - TS \qquad dF = -SdT - pdV + \mu dN$$

For isothermal processes with fixed N get

$$dF = -pdV = \delta A$$

So **for isothermal process** infinitesimal pieces of work can be easily integrate to get

$$A = F_1 - F_2$$

Free energy can be understood as the **isothermal potential of work**. It says how much mechanical work can be extracted from a device in an isothermal process. This is perhaps the motivation for its name “free energy”.

Further thermodynamic potentials

Free energy is a useful thermodynamic potential if we need the native parameters to be T, V, N. For other purposes we might need other native parameters. For example if we require S, p, N, we can do the following Legendre transformation

$$H(S, p, N) = E + pV$$

H is called **enthalpy** (actually H is the capital Greek letter eta, not our Latin H) and we get

$$dH = TdS + Vdp + \mu dN$$

$$\boxed{T = \left(\frac{\partial H}{\partial S}\right)_{p,N} \qquad V = \left(\frac{\partial H}{\partial p}\right)_{S,N} \qquad \mu = \left(\frac{\partial H}{\partial N}\right)_{S,p}}$$

For isobaric processes with fixed N we get

$$dH = TdS = \delta Q$$

So for isobaric processes infinitesimal pieces of performed heat can easily be integrated to get

$$Q = H_2 - H_1$$

Further thermodynamic potentials

The thermodynamic potential with native parameters T, P, N is the Gibbs potential (sometimes called free enthalpy)

$$G(T,p,N) = E - TS + pV = H - TS$$

$$dG = -SdT + Vdp + \mu dN$$

$$\boxed{S = -\left(\frac{\partial G}{\partial T}\right)_{p,N} \qquad V = \left(\frac{\partial G}{\partial p}\right)_{T,N} \qquad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,p}}$$

G as any thermodynamic potential is an extensive variable. But its only extensive parameter is N, its two other native parameters p, T are intensive, so G must be proportional to N. So it must look like $G = N\,f(p,T)$, where f is some suitable function of p, T. However from the relation

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,p}$$

we get $f = \mu$, so we see, that G can be expressed as

$$\boxed{G(T,p,N) = N\mu(p,T)}$$

Further thermodynamic potentials

The thermodynamic potential with native variables T, V, μ is the grand canonical potential

$$\Omega(T, V, \mu) = E - TS - N\mu$$

$$d\Omega = -SdT - pdV - Nd\mu$$

$$\boxed{S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} \qquad p = -\left(\frac{\partial\Omega}{\partial V}\right)_{V,\mu} \qquad N = -\left(\frac{\partial\Omega}{\partial \mu}\right)_{T,V}}$$

Comparing the Legendre transformation defining Ω with the expression we got for the logarithm of the grand canonical partition function

$$\ln \mathcal{Z}(\mu, T, V) = \frac{\mu}{kT}\bar{N} - \frac{1}{kT}\bar{E} + \frac{1}{k}S$$

we see that the grand canonical potential is related to the grand canonical partition function similarly as the free energy is related to the canonical partition:

$$\boxed{\mathcal{Z} = \exp\left(-\frac{\Omega}{kT}\right)}$$

There are other ways how to express Ω:

$$\Omega = E - TS - N\mu = F - N\mu = F - G = F - (F + pV) = -pV$$

Later we shall be able to calculate the grand canonical function for ideal gas in classical approximation and we shall get $\ln \mathcal{Z} = N$. It is due to the ideal gas equation of state $pV = NkT$.

Non-equilibrium macrostates - entropy

So far, we have discussed equilibrium thermodynamic potentials. These potentials can be defined even for non-equilibrium macrostates.

We have already defined the entropy for arbitrary (equilibrium as well as non-equilibrium) macrostates of an isolated system. The definition was universal:

Entropy for an isolated physical system is defined as k-times the logarithm of the number of microstates corresponding to the macrostate considered.

We have used this definition to study evolution towards equilibrium of two systems after putting into contact.

More generally entropy for arbitrary macrostate can be defined, when we define a statistical ensemble of microstates representing the macrostate considered (equilibrium or non-equilibrium). The statistical ensemble is defined by assigning the probabilities $p(i)$ to arbitrary microstate i. (In general some probabilities might be 0.) We defined the entropy as

$$S = -k \sum_i (\ln p(i)) p(i)$$

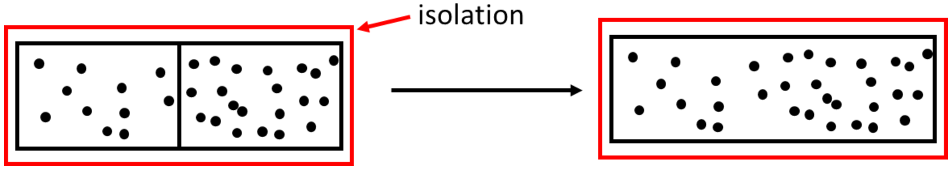
The difference between the equilibrium and non equilibrium macrostates is manifested by the fact that **we need more macroscopic variables** to define a non-equilibrium macrostate than for the equilibrium macrostate. For example the macrostate of a gas in equilibrium is given by three variables like N, T, V. Any other macroscopic variable in equilibrium can be calculated as a function of the equilibrium variables. Like pressure

$$p = \frac{1}{V} NkT$$

Non-equilibrium macrostates

Non equilibrium macrostate of a gas needs more variables for its specification. These additional variables characterize how the non-equilibrium state differs from the equilibrium. Consider gas in an **isolated container** having two compartments separated by a non-penetrable diaphragm. The temperature is the same in both compartments, but the number of molecules and therefore the pressure might be prepared as different.

Free expansion:



If **we suddenly remove the diaphragm**, the gas in the container will get into a non-equilibrium state which (immediately after the diaphragm removal) will be given by 5 parameters N, T, V, p_1, p_2, where p_1, p_2 give pressure in the left half and the right half of the container. Then an irreversible process starts. Finally a common equilibrium state is achieved, which is characterized by just 3 parameters N, T, V. The resulting p is given by the equation of state.

By the way the final temperature T will be the same as the initial temperature: neither heat nor mechanical work is performed (the diaphragm is removed by pulling it down, in the direction perpendicular to the gas pressure, so no work is needed for the removal). Therefore the final energy of the gas will be the same as the initial energy. There is no potential energy of interaction for ideal gas, so the kinetic energy of the molecules is not changed, so **the final temperature for an ideal gas free expansion is the same as the initial temperature**.

Non-equilibrium macrostates – thermodynamic potentials

We have defined entropy for arbitrary macrostate, equilibrium or non-equilibrium. It is trivial to define the energy for a non-equilibrium macrostate characterized by an ensemble of microstates with probabilities $p(i)$. The mean non-equilibrium macrostate energy is then

$$E = \sum_i E_i p(i)$$

All other non-equilibrium thermodynamic potentials are defined by the appropriate Legendre transformations from energy and entropy.

$$\boxed{F = E - TS \qquad G = E - TS + pV \qquad H = E + pV \qquad \Omega = E - TS - \mu N}$$

Now what about the differentials (potential changes during infinitesimal processes). For reversible (equilibrium) processers we had for example

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$$

This cannot be a correct expression for the differential of a non-equilibrium entropy, since there are more independent (non-equilibrium) parameters and their differential are missing in the above expression. So the correct formula has to look like this

$$\boxed{dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN + \text{terms with differentials of non-equilibrium parameters}}$$

Even this formula is debatable for states far from equilibrium: it is not clear what is the meaning of T, p, μ for such states.

Non-equilibrium macrostates – extremal entropy

Now consider isolated system in fixed volume with fixed number of particles. This means $dE = 0, dV = 0, dN = 0$. For nonequilibrium processes for such system we get from

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN + \text{terms with differentials of non-equilibrium parameters}$$

$$dS = \text{terms with differentials of non-equilibrium parameters}$$

We know, however, that an isolated system spontaneously increases its entropy, so we expect $dS \geq 0$, so for isolated system

$$dS = \text{terms with differentials of non-equilibrium parameters} \geq 0$$

Therefore we **formulate the hypothesis**, that for arbitrary infinitesimal processes the following inequality holds

$$\boxed{dS \geq \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN}$$

The equality holds for equilibrium (reversible) processes. The above inequality express our starting hypothesis that the isolated system increases its entropy during its approach to equilibrium and **the entropy of an isolated system is maximal for the equilibrium macrostate.**

Non-equilibrium macrostates – Clausius inequality

$$dS \geq \frac{1}{T}dE + \frac{p}{T}dV + \frac{\mu}{T}dN$$

First law of thermodynamics (energy conservation) says

$$\delta Q = dE + pdV - \mu dN$$

So we get for a general (reversible or irreversible) process the Clausius inequality

$$\boxed{dS \geq \frac{\delta Q}{T}}$$

Actually the Clausius inequality can be proven from the second law of thermodynamics, we shall not present the proof here.

Thermodynamic potentials – irreversible processes

The Clausius inequality for entropy

$$dS \geq \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$$

can be rearranged for the inequality for differential of energy for reversible and irreversible processes

$$dE \leq TdS - pdV + \mu dN$$

Remainder: $\boldsymbol{TdS \neq \delta Q}$ **for irreversible processes!** The other thermodynamic potentials we get from energy by Legendre transformations and from there one can easily derive the corresponding inequalities

$$dF \leq -SdT - pdV + \mu dN$$

$$dH \leq TdS + Vdp + \mu dN$$

$$dG \leq -SdT + Vdp + \mu dN$$

$$d\Omega \leq -SdT - pdV - Nd\mu$$

From there we directly see the extremal properties

- F is minimal in equilibrium for a system with given T, V, N
- H is minimal in equilibrium for a system with given S, p, N
- G is minimal in equilibrium for a system with given T, V, N
- Ω is minimal in equilibrium for a system with given T, V, μ
- S is maximal in equilibrium for a system with given E, V, N
- E is minimal in equilibrium for a system with given S, V, N

Finding equilibrium by minimizing the free energy

Let us demonstrate how we can use the non-equilibrium free energy to find equilibrium state for a system in contact with a heat reservoir (thermostat). We first start using standard canonical technique and then proceed to minimizing the non-equilibrium free energy to see that we get equivalent results.

Consider a system of mutually non-interacting spins in external magnetic field B, in thermostat with temperature T. Each spin has just two states $-\mu, \mu$ with energies $-\mu\mathrm{B}, \mu B$. (Here μ is the spin magnetic moment, not some chemical potential!). Since the spins are noninteracting (independent) we can first consider just one spin j, calculate its statistical sum and then the statistical sum of the whole system of spins is a product of individual sums

$$Z_j(T,B) = \sum_{\mu_j=-\mu}^{\mu} \exp(-\frac{-\mu_j B}{kT})$$

$$Z(T,B) = \prod_j \sum_{\mu_j} \exp(\frac{\mu_j B}{kT})$$

$$Z(T,B) = \prod_j 2\cosh(\frac{\mu B}{kT})$$

$$\ln Z(T,B) = N \ln 2\cosh(\frac{\mu B}{kT})$$

The total magnetic moment in equilibrium we get as a generalized force conjugated to the external fields B

Finding equilibrium by minimizing the free energy

$$\overline{M} = \frac{\partial \ln Z}{\partial B}$$

$$\overline{M} = N \tanh\left(\frac{\mu B}{kT}\right)$$

Now let us consider the same system in **an artificially maintained non-equilibrium state**. The non-equilibrium parameter will be magnetization M, different from its equilibrium value $\overline{M}$. How this could be achieved? We can just virtually imagine little dwarfs each controlling one of the spins. They observe their spins, permanently collectively evaluate the total magnetization and if they find that in the time instant the magnetization value is different from the prescribed non-equilibrium value M, they randomly choose some dwarfs and order them to flip the spins they control to restore the magnetization to the prescribed value. By this dwarf mechanism the system is maintained in the non-equilibrium macrostate without being forced to be in a fixed microstate. The microstates dynamically change (by interaction with the reservoir) without relaxation to the equilibrium macrostate.

Now the **hypothesis**: we shall calculate the statistics of the described non-equilibrium macrostate by **as if a canonical technique,** but all the sums will be not over all the microstates but **only over the microstates having the prescribed total magnetization** $\boldsymbol{M_i = M}$**.**

Finding equilibrium by minimizing the free energy

individual spin states will be denoted as $\mu_j \in \{-\mu, \mu\}$. Then the microstate of the whole system will be given by the list $\{\mu_j\} \equiv \{\mu_1, \mu_2, \mu_3, \dots, \mu_j, \dots\}$.

$$Z_{noneq} = Z(T,B,M) = \sum_{\{\mu_j\}, fix\ M=\sum_j \mu_j} \exp(\frac{\sum_j \mu_j B}{kT})$$

$$Z(T,B,M) = \sum_{\{\mu_j\}, fix\ M=\sum_j \mu_j} \exp(\frac{MB}{kT})$$

$$Z(T,B,M) = \exp(\frac{MB}{kT}) \sum_{\{\mu_j\}, fix\ M=\sum_j \mu_j} 1$$

$$Z(T,B,M) = \exp(\frac{MB}{kT}) \Omega(M)$$

where $\Omega(M)$ is the number of states (number of lists $\{\mu_j\}$) with the total magnetization equal to the prescribed value M. When n denotes the number of "up" spins (that is $\mu_j = \mu$) then the total magnetization will be

$$M = n\mu - (N-n)\mu = 2n\mu - N\mu \quad \Longrightarrow \quad n = \frac{N}{2} + \frac{M}{2\mu}$$

$$\Omega(M) = \binom{N}{\frac{N}{2} + \frac{M}{2\mu}}$$

Finding equilibrium by minimizing the free energy

The nonequilibrium free energy will be

$$F_{noneq}(T,B,M) = \ln Z_{noneq} = \ln\left(\exp(\frac{MB}{kT})\Omega(M)\right)$$

$$\begin{aligned} F_{noneq}(T,B,M) &= \frac{MB}{kT} + \ln\binom{N}{\frac{N}{2}+\frac{M}{2\mu}} \\ &\approx \frac{MB}{kT} + N\ln N - N - \left((\frac{N}{2}+\frac{M}{2\mu})\ln(\frac{N}{2}+\frac{M}{2\mu}) - (\frac{N}{2}+\frac{M}{2\mu})\right) - \\ &- \left((\frac{N}{2}-\frac{M}{2\mu})\ln(\frac{N}{2}-\frac{M}{2\mu}) - (\frac{N}{2}-\frac{M}{2\mu})\right) \end{aligned}$$

differentiating with respect to M we find the value $\bar{M}$, which minimizes F_{noneq}. After some work we get

$$\overline{M} = \underset{M}{\operatorname{argmin}}\, F_{noneq}(T,B,M) = N\tanh(\frac{\mu B}{kT})$$

This is exactly the same as we got using standard “canonical mean” technique.

Quantum ideal gas

For classical (non-quantum) ideal gas we could use canonical distribution for just one particle (Maxwell-Boltzmann distribution). The reason is that molecules do not interact (except for very short time during collisions) and so they are statistically independent. **Classical particle is well identifiable**, so we can use one-particle distribution.

For quantum particles we have a problem even for non-interacting particles: particles are usually undistinguishable. So we cannot well identify just one particle, therefore one-particle distributions are meaningless.

Still, classical one-particle distributions are very useful, so we would be happy to have some quantum analogue. Some small one-particle-like gas subsystem.

The key idea is this: **take as a subsystem one one-particle state**. The one particle states are well identifiable as (n_1, n_2, n_3, s_z). We can speak about the **"state of the one-particle state"**: it is given by the occupational number of the one-particle state considered.
Different one-particle states are statistically independent of each other, that is their occupational numbers are independent.

In different microstates of the whole gas the occupational number of one specifically chosen one-particle states are generally different: we can speak about the **occupational-number-probability distribution for a specific one-particle state** for a particular gas macrostate.
The occupational number is the number of particles in that chosen state. We can consider the chosen one-particle state as a small system in thermal and diffusion contact with the rest of the gas and **use grand canonical distribution as the relevant probability distribution**.

Quantum ideal gas

One-particle states will be denoted in brief as j. It can be understood as the order number in a sorted list of all one-particle states as shown in the table below for fermions with spin 1/2.

j	n_1, n_2, n_3, s_z
1	1,1,1,↑
2	1,1,1,↓
3	1,1,2,↑
4	1,1,2,↓
5	1,2,1,↑
6	1,2,1,↓
7	1,2,2,↑
8	1,2,2,↓
⋮	⋮

The energy of a particle in the state n_1, n_2, n_3, s_z is

$$E_{n_1,n_2,n_3} = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2)$$

Fermi gas: Fermi-Dirac distribution

We shall now consider Fermi gas at the temperature T with the chemical potential μ. We apply the grand canonical distribution to a particular one-particle state j, its energy will be denoted as ε_j. The allowed occupational numbers are $n_j \in \{0, 1\}$ so there are just two possible "states of the one particle state". The total energy of n_j particles in the state j is, of course $n_j \varepsilon_j$, and the sum will have just two terms for $n_j = 0$ and $n_j = 1$. The grand statistical sum for the chosen one one-particle state j will be:

$$\mathcal{Z} = \sum_{n_j=0}^{1} \exp\left(-\frac{\varepsilon_j n_j}{kT} + \frac{\mu}{kT} n_j\right) = 1 + \exp\left(\frac{\mu - \varepsilon_j}{kT}\right)$$

The probabilities for the two values of n_j will be $p(n_j) = \dfrac{1}{1 + \exp\left(\frac{\mu - \varepsilon_j}{kT}\right)} \exp\left(\dfrac{\mu - \varepsilon_j}{kT} n_j\right)$

The mean value of the occupational number will be

$$\overline{n_j} = \frac{1}{1 + \exp\left(\frac{\mu - \varepsilon_j}{kT}\right)} \left(0 + \exp\left(\frac{\mu - \varepsilon_j}{kT}\right)\right)$$

$$\boxed{\overline{n_j} = \frac{1}{\exp\left(\frac{\varepsilon_j - \mu}{kT}\right) + 1}}$$

This formula is called **Fermi-Dirac distribution**. To repeat: it gives the **mean occupational number** of the one-particle state j of Fermi gas.

Bose gas: Bose-Einstein distribution

We shall now consider Bose gas at the temperature T with the chemical potential μ. We apply the grand canonical distribution to a particular one-particle state j. The allowed occupational numbers are $n_j \in \{0, 1, 2, 3, \dots\}$ so there is an infinite number of possible "states of the one particle state". The grand canonical statistical sum is an infinite series. Fortunately it is geometric series, so it can easily be calculated. We get

$$\mathcal{Z} = \sum_{n_j} \exp\left(-\frac{\varepsilon_j n_j}{kT} + \frac{\mu}{kT} n_j\right) = \sum_{n_j} \left(\exp\left(\frac{\mu - \varepsilon_j}{kT}\right)\right)^{n_j} = \frac{1}{1 - \exp\left(\frac{\mu - \varepsilon_j}{kT}\right)}$$

This result is, of course, valid only for convergent series, so the following must be true

$$\exp\left(\frac{\mu - \varepsilon_j}{kT}\right) < 1 \quad \text{for all } j \implies \mu - \varepsilon_j < 0 \quad \text{for all } j$$

For increasing j the ε_j are increasing, so it is enough if $\mu < \varepsilon_0$.

So the chemical potential for any Bose gas must satisfy the condition $\mu < \varepsilon_0$. Since ε_0 is almost 0, we practically get the condition $\mu < 0$.

Bose gas: Bose-Einstein distribution

The probabilities of occupational numbers $n_j \in \{0, 1, 2, 3, \dots\}$ will be

$$p(n_j) = \frac{1}{1 - \exp\left(\frac{\mu - \varepsilon_j}{kT}\right)} \exp\left(\frac{\mu - \varepsilon_j}{kT} n_j\right)$$

The mean value of the occupational number will be

$$\overline{n_j} = \frac{1}{1 - \exp\left(\frac{\mu - \varepsilon_j}{kT}\right)} \sum_{n_j} n_j \exp\left(\frac{\mu - \varepsilon_j}{kT} n_j\right) = \frac{1}{1 - \exp\left(\frac{\mu - \varepsilon_j}{kT}\right)} \frac{\partial}{\partial\left(\frac{\mu - \varepsilon_j}{kT}\right)} \sum_{n_j} \exp\left(\frac{\mu - \varepsilon_j}{kT} n_j\right)$$

We did a clever trick with the derivative after which we got a geometrical series. The rest of the calculation is trivial. Finally we get

$$\boxed{\overline{n_j} = \frac{1}{\exp\left(\frac{\varepsilon_j - \mu}{kT}\right) - 1}}$$

This formula is called **Bose-Einstein distribution**. To repeat: it gives the **mean occupational number** of the one-particle state *j* of Bose gas.

Quantum ideal gas – classical limit

we shall now investigate the situation, when the mean occupancy of all one-particle states is much less than 1. We expect that then the quantum effects can be neglected and get results as for classical particles with the exception of the Gibbs paradox: indistinguishability is manifested even in the classical limit.

So we look for situations where

$$\overline{n_j} = \frac{1}{\exp\left(\frac{\varepsilon_j - \mu}{kT}\right) \pm 1} \ll 1$$

This requirement leads to the same condition for bosons and fermions

$$\overline{n_j} \approx \exp\left(\frac{\mu - \varepsilon_j}{kT}\right) \ll 1$$

If this condition holds for $j = 0$, then it holds for all j, so the classical limit is good when

$$\exp\left(\frac{\mu}{kT}\right) \ll 1$$

As usual, we just pretend to know μ. The mean number of all particles in the considered gas is

$$\overline{N} = \sum_j \overline{n_j} = \sum_j \exp\left(\frac{\mu - \varepsilon_j}{kT}\right)$$

The sum is over all the one-particle states. It can be rewritten as a sum over energies of the one particle states using the degeneracy $\Omega(\varepsilon)$

$$\overline{N} = \sum_\varepsilon \Omega(\varepsilon) \exp\left(\frac{\mu - \varepsilon}{kT}\right)$$

The sum is over all the (discrete) values of the energies of the one-particle states.

Quantum ideal gas – classical limit

The discrete summation $$\overline{N} = \sum_{\varepsilon} \Omega(\varepsilon) \exp\left(\frac{\mu - \varepsilon}{kT}\right)$$

can be approximate by integrating over almost continuous spectrum of energies as

$$\overline{N} = \int d\varepsilon \varphi'(\varepsilon) \exp\left(\frac{\mu - \varepsilon}{kT}\right)$$

where $\varphi(\varepsilon)$ is our standard notation for the number of one-particle states with energies less than ε. For spinless particles we have (m is the mass of the particles $L = V^{2/3}$).

$$\varphi(\varepsilon) = \frac{1}{6}\pi\left(\frac{2mL^2}{\pi^2\hbar^2}\right)^{3/2}\varepsilon^{1/2}$$

Let us note that the spin degeneracy survives the classical limit so for particles with spin we should include also the spin degeneracy factor g (2 for the spin 1/2, 3 for the spin 1 etc.). The integration is trivial, we get

$$\boxed{\overline{N} = \frac{V}{V_Q} \exp \frac{\mu}{kT}}$$

where we have denoted

$$V_Q = \left(\frac{2\pi\hbar^2}{mkT}\right)^{3/2}$$

The index *Q* in the notation suggests “quantum volume”. V_Q is the volume corresponding to the de’Broglie’s wavelength of a particle having the energy by the order of magnitude equal to kT. It is roughly a **minimum volume required so that the particle can have such energy**. Restricting to a smaller volume would lead (by uncertainty principle) to larger energy.

Quantum ideal gas – classical limit

The relation $\overline{N} = \frac{V}{V_Q} \exp \frac{\mu}{kT}$ we more often use in the inverse form: to calculate μ when we know N:

$$\boxed{\mu = kT \ln \frac{NV_Q}{V}} \qquad V_Q = \left(\frac{2\pi\hbar^2}{mkT} \right)^{3/2}$$

We have calculated the chemical potential! Of course, the result is valid only in the classical limit, what requires

$$\exp\left(\frac{\mu}{kT}\right) \ll 1 \qquad \text{or} \qquad \boxed{V \gg NV_Q}$$

Intuitively we understand why this is the condition of classicality. NV_Q is the minimal volume required by quantum mechanics for the gas so that its temperature (roughly kinetic energy per molecule) can be T. If the available total volume is much larger than that, the de'Broglie's waves "are not squeezed" by the gas container and particles behave as classical. Of course, this is a "hand-waving" argument, but perhaps there is a piece of truth in it.

Ideal gas – classical limit – grand partition function

We shall demonstrate now the calculation of the grand partition function for an ideal gas in the classical limit. The gas microstate is given by **the list of the occupational numbers**, which we shall denote as $\{n_j\} \equiv \{n_0, n_1, n_2, \ldots, n_j, \ldots\}$

The grand partition function is the sum over all gas microstates (over all possible lists}:

$$\mathcal{Z} = \sum_{\{n_j\}} \exp\left(\frac{1}{kT}(\mu \sum_j n_j - \sum_j n_j \varepsilon_j)\right) = \sum_{\{n_j\}} \exp\left(\frac{1}{kT}(\sum_j n_j (\mu - \varepsilon_j))\right)$$

Be careful and understand well what the symbols mean! The overall sum is over all possible infinite lists of occupational numbers. The sums in the exponent are over the **occupational numbers in one specific list**. Now exponent of a sum is a product of exponents:

$$\mathcal{Z} = \sum_{\{n_j\}} \prod_j \exp\left(\frac{1}{kT}(n_j (\mu - \varepsilon_j)\right)$$

Now the most difficult (for understanding) rearrangement according to the distributive law. Symbolically but imprecisely: "sum of products is the product of sums".

$$\mathcal{Z} = \prod_j \sum_{n_j} \exp\left(\frac{1}{kT}(n_j (\mu - \varepsilon_j)\right)$$

Observe the difference: in the original expression the sum is **over lists** of numbers, in the transformed expression the sum is **over all possible occupational number values** for the specific state j. So for fermions it is the sum of just two numbers 0, 1. You can understand that **this is correct** by inspecting small specific examples for the distributive law. **Try hard**, finally you will understand the distributive law!

Ideal gas – classical limit – grand partition function

So far, our calculations were exact. Now we will do approximations of the classical limit. Firstly, in the classical limit there is no difference between bosons and fermions because the mean occupational numbers are very low. So we continue the calculations with fermions, where the sums are only over $n_j = 0{,}1$.

$$\mathcal{Z} = \prod_j \sum_{n_j=0}^{1} \exp\left(\frac{1}{kT}(n_j(\mu - \varepsilon_j)\right) = \prod_j \left(1 + \exp\left(\frac{\mu - \varepsilon_j}{kT}\right)\right)$$

$$\ln \mathcal{Z} = \sum_j \ln\left(1 + \exp\left(\frac{\mu - \varepsilon_j}{kT}\right)\right)$$

The classical limit also means $\overline{n_j} \approx \exp\left(\frac{\mu - \varepsilon_j}{kT}\right) \ll 1$ so we approximate the logarithms $\ln(1+x) \approx x$

$$\ln \mathcal{Z} = \sum_j \left(\exp\left(\frac{\mu - \varepsilon_j}{kT}\right)\right)$$

We got just the sum over mean occupational numbers, what gives the total number of particles. So **in the classical limit**

$$\boxed{\ln \mathcal{Z} = N}$$

We have calculated the grand partition function! We were able to do it because of the classical limit but also because in the grand statistical sum there is no restriction for the one-particle states we sum over. For the canonical sum the restriction $N_j = N$ would make a similar calculation more difficult. (Later we shall see that in classical (non-quantum) statistics the calculation of the canonical sum for ideal gas is easy!)

Ideal gas – classical limit – entropy

Summarizing the results we have obtained

$$\mu = kT \ln \frac{NV_Q}{V} \qquad V_Q = \left(\frac{2\pi\hbar^2}{mkT}\right)^{3/2} \qquad \ln \mathcal{Z} = N$$

we continue by calculating the entropy of an ideal gas in the classical limit. We start with the relation

$$\ln \mathcal{Z}(\mu, T, V) == \frac{\mu}{kT}\bar{N} + \ln Z(\bar{N}, T, V) = \frac{\mu}{kT}\bar{N} - \frac{1}{kT}\bar{E} + \frac{1}{k}S$$

After substitution for μ and $\ln \mathcal{Z}$ we get

$$\boxed{S = kN \ln \frac{V}{N} + \frac{3}{2}kN \ln \frac{E}{N} + 3/2kN \ln \frac{m}{3\pi\hbar^2} + \frac{5}{2}}$$

This formula is called **Sackur-Tetrode equation** for the entropy of monoatomic classical ideal gas. It demonstrates that the statistical physics is able to calculate the entropy absolutely: there is no arbitrary additive constants, while the phenomenological thermodynamics is able to determine entropy only up to an additive constant.

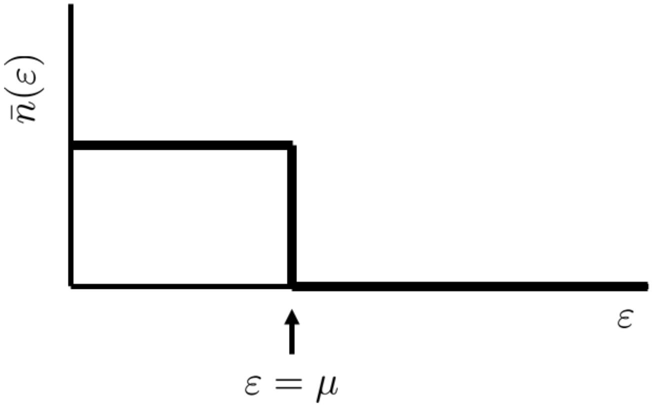
Fermi ideal gas at low temperatures

Fermi-Dirac distribution

$$\bar{n}(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon-\mu}{kT}\right)+1}$$

in the limit $T \to 0$ gives

$$\bar{n}(\varepsilon) = \begin{cases} 1 & \text{for } \varepsilon < \mu \\ 0 & \text{for } \varepsilon > \mu \end{cases}$$



At $T = 0$ all one-particle states below $\varepsilon = \mu$ are occupied, all states above μ are empty.
So at $T = 0$ chemical potential **μ is equal to the energy of the highest occupied one-particle state**.
This energy is called the **Fermi energy** ε_F .

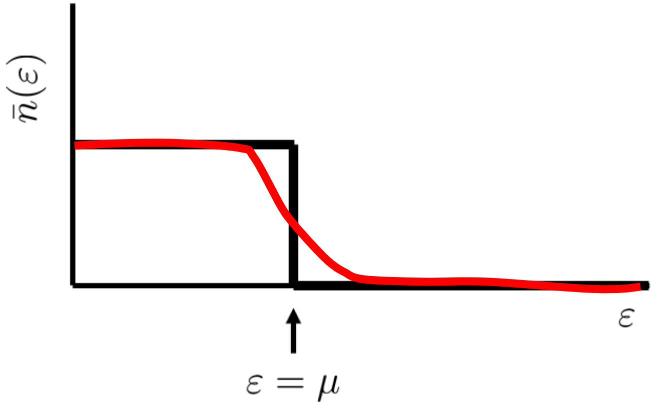
The Fermi energy can easily be calculated if we realize that the number of one-particle states below ε_F must be equal to the total number of particles. (Do not forget $g = 2$ for spin 1/2 particles.)

$$N = \varphi(\varepsilon_F)$$

$$\boxed{\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}}$$

Fermi ideal gas at low temperatures

or temperatures slightly above $T = 0$ the chemical potential will be slightly higher then ε_F so the occupation numbers will be only slightly different from their values at $T = 0$ for ε around ε_F in the interval with a width $\approx kT$. (Red curve.)



This qualitative picture will not change until the temperature reaches Fermi temperature $T \approx T_F = \varepsilon_F / k$. Fermi gas below the Fermi temperature is called **degenerate Fermi gas**.

As an example of degenerate fermi gas we can consider conduction electrons in metal. Of course, the electron gas is not ideal, the electron feel each other. We use this example only to demonstrate some features qualitatively.

For metal potassium the electron density in the lattice is $1.34 \times 10^{22}\ \mathrm{cm}^{-3}$ and for the Fermi temperature we get $T_F \approx 24000$ K.

Fermi ideal gas at low temperatures

We shall calculate the degenerate fermion gas heat capacity work in the approximation $\mu = \varepsilon_F$.

$$C_V = \frac{d\overline{E}}{dT} = \int d\varepsilon \varphi'(\varepsilon)(\varepsilon - \varepsilon_F) \frac{d}{dT} \frac{1}{\exp(\frac{\varepsilon - \varepsilon_F}{kT}) + 1}$$

We have intelligently written zero as

$$0 = \varepsilon_F \frac{dN}{dT} = \varepsilon_F \frac{d}{dT} \int d\varepsilon \varphi'(\varepsilon) \frac{1}{\exp(\frac{\varepsilon - \varepsilon_F}{kT}) + 1}$$

this trick enables us to use the substitution $x = \frac{\varepsilon - \varepsilon_F}{kT}$

For temperatures much lower than T_F Fermi-Dirac function is constant (either 1 or 0) almost everywhere except around ε_F. So the derivative of the Fermi-Dirac function is nonzero only around ε_F.Therefore the slowly varying function $\varphi'(\varepsilon)$ can be replaced by the constant value $\varphi'(\varepsilon_F)$ and we get

$$C_V = k^2 T \varphi'(\varepsilon_F) \int_{-\varepsilon_F/kT}^{\infty} dx x^2 \frac{\exp(x)}{(\exp(x) + 1)^2}$$

For $T \ll T_F$ we can replace the lower bound by $-\infty$

$$C_V = k^2 T \varphi'(\varepsilon_F) \int_{-\infty}^{\infty} dx x^2 \frac{\exp(x)}{(\exp(x) + 1)^2} = k^2 T \varphi'(\varepsilon_F) \frac{\pi^2}{3}$$

$$\boxed{C_V = \frac{1}{2} \pi^2 N k \frac{T}{T_F}}$$

Fermi ideal gas at low temperatures

The obtained result

$$C_V = \frac{1}{2}\pi^2 Nk\frac{T}{T_F}$$

shows that the heat capacity of the conduction electron gas is negligible for $T \ll T_F$.

This is how quantum mechanics (which was not yet known) saved the statistical physics from being thrown away. The heat capacity of electrons (which were not yet known) did not influenced the heat capacity of the metal as given by the lattice of atoms and everything was ok with the predictions of statistical physics at normal temperatures.

Bose condensation

Bosons are particles which can have any occupation numbers of the one-particle states. It means that at very low temperatures practically all bosons of an ideal bose gas can occupy the lowest-energy one particle state.
It is, however, not a priori clear whether at low but finite temperatures like 1K still a majority of particles would occupy the lowest-energy one-particle state.
We shall estimate what happens for liquid helium which we shall very roughly consider to be an ideal gas in a box 1 cm^3 containing 10^{22} particles.
The energy of the lowest one-particle states will be $\varepsilon_0 = 10^{-18}$ eV, the first higher state will have energy twice that big $\varepsilon_1 = 2\varepsilon_0$.
The mean occupation number of the lowest state is

$$n(\epsilon_0) = \frac{1}{\exp(\frac{\varepsilon_0 - \mu}{kT}) - 1}$$

Let us assume that a significant number of particles $\approx 10^{22}$ is in the lowest state, then

$$\frac{\varepsilon_0 - \mu}{kT} = 10^{-22}$$

Bose condensation

Let us calculate for this value of μ the occupancy of the first higher state at $T = 1\mathrm{K}$.

$$n(\varepsilon_1) = \frac{1}{\frac{\varepsilon_1 - \mu}{kT}}$$

$$n(\varepsilon_1) = \frac{1}{\frac{2\varepsilon_0 - \mu}{kT}}$$

$$n(\varepsilon_1) = \frac{1}{\frac{\varepsilon_0 - \mu}{kT} + \frac{\varepsilon_0}{kT}}$$

$$n(\varepsilon_1) = \frac{1}{10^{-22} + 10^{-13}}$$

$$n(\epsilon_1) = 10^{13}$$

So really even at 1K almost all particles can be in the lowest one-particle state. This effect is called **Bose condensation**.

Bose condensation

If low-state occupation numbers are very high, we cannot approximate various summations by integration like this

$$N = \int d\varepsilon \varphi'(\varepsilon) \frac{1}{\exp(\frac{\varepsilon-\mu}{kT}) - 1}$$

A more appropriate approximation would be to include the contribution by the lowest state explicitly (in a discrete way, the lowest state does not contribute to the integral) as

$$N = n(\varepsilon_0) + \int d\varepsilon \varphi'(\varepsilon) \frac{1}{\exp(\frac{\epsilon-\mu}{kT}) - 1}$$

We have seen in our numerical estimates that for low temperatures both ε_0 and μ are approximately zero, so we can write

$$N = n(\varepsilon_0) + \int d\epsilon \varphi'(\varepsilon) \frac{1}{\exp(\frac{\varepsilon}{kT}) - 1}$$

The integral gives the number of particles in higher one-particle states N_e. After suitable substitution we get for it

$$N_e = \frac{V}{4} \left(\frac{2mkT}{\pi\hbar^2}\right)^{3/2} \int dx \frac{x^{1/2}}{\pi^{1/2}(\exp(x) - 1)}$$

Bose condensation

The integral can be calculated numerically and we get

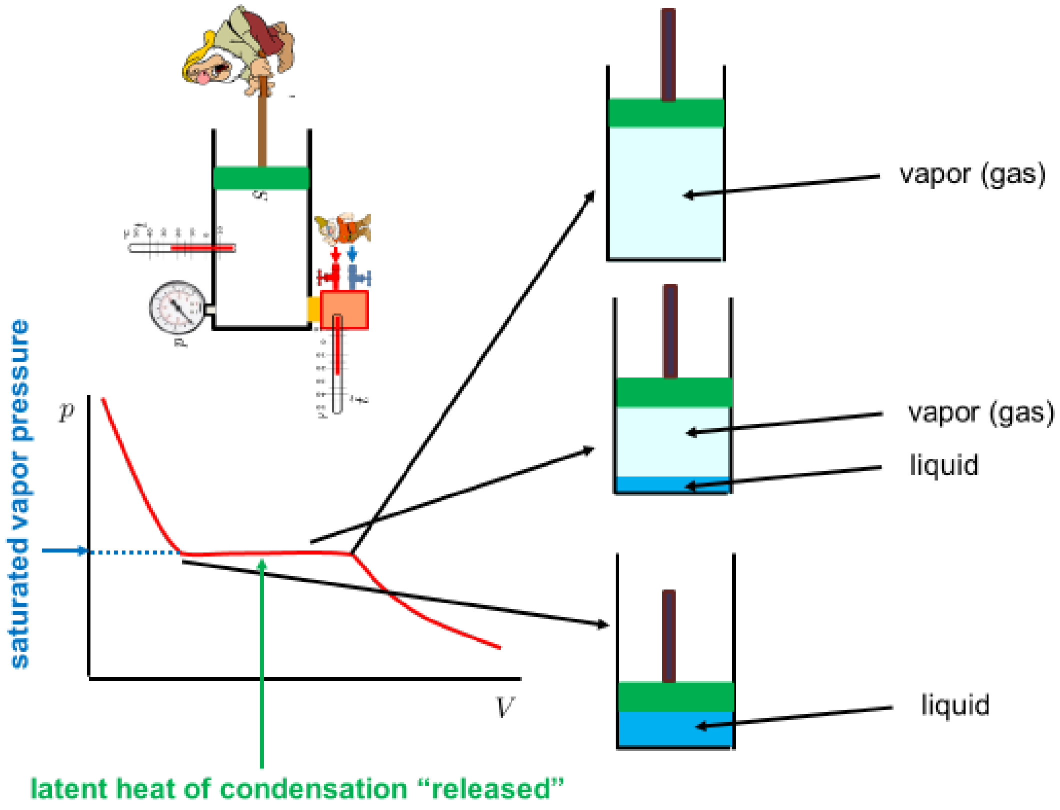
$$N_e = 2,612V\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}$$

The Bose condensation will disappear for temperatures for which already practically all the particles are in higher states: $N_e \approx N$. So the Bose condensation is present (very roughly) for temperatures lower than

$$\boxed{T_0 = \frac{2\pi\hbar^2}{km}\left(\frac{N}{2,612V}\right)^{2/3}}$$

Real gases, condensation

Real gases do not satisfy the ideal gas equation of state $pV = NkT$. Real isotherms are not simple hyperbolas. For sufficiently small temperatures the real isotherm has a flat horizontal segment corresponding to condensation. The piston pusher dwarf will observe a strange phenomenon: he will be able to decrease the volume of the container at a constant pressure. The reason is that a new phase will appear at the bottom of the container: a liquid phase. When pushing the piston more an more molecules from the gas phase above the liquid enter the liquid phase thus decreasing the number of molecules in the gas phase. The gas phase having smaller number of molecules keeps constant pressure in the decreasing gas volume in the container.



saturated vapor pressure

p

V

vapor (gas)

vapor (gas)

liquid

liquid

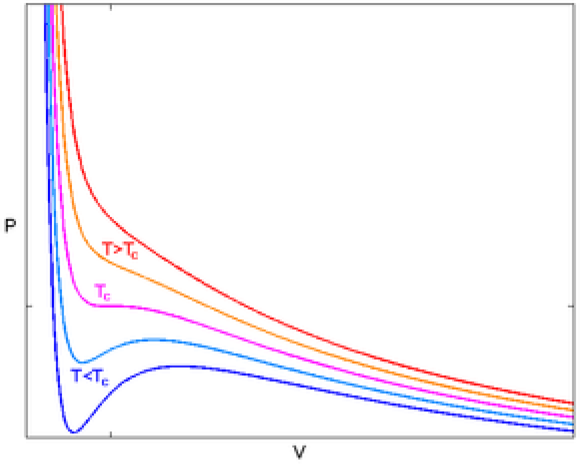
latent heat of condensation “released”

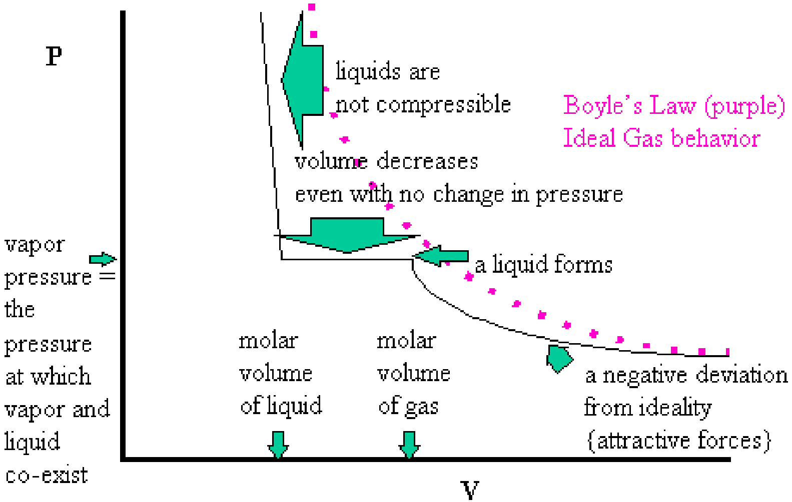
van der Waals equation

There were several attempts to “invent formulas” for the real gas equation of states. The most popular in textbooks is the van der Waals equation

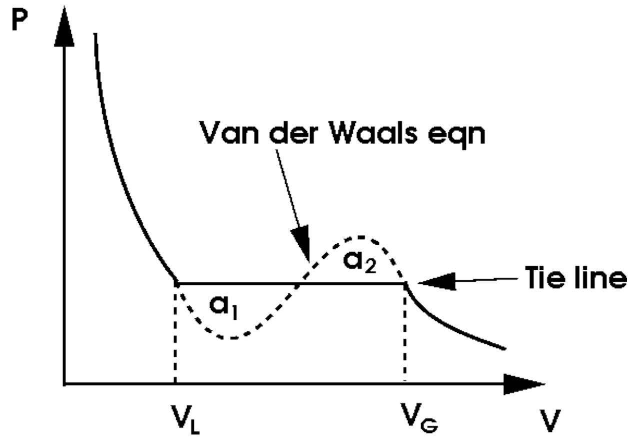
$$\left(p+\frac{N^2a}{V^2}\right)(V-Nb)=NkT$$

where a, b are empirical constants characterizing the specific gas. The equation is of the third order in V and for the temperatures below certain critical temperature T_c does not have a flat horizontal segment in the region where condensation is expected. Instead an **upward rise and a downward dip** is “predicted” by the formula. This region in the isotherm is usually interpreted as corresponding to a metastable equilibrium of overheated liquid or overcooled vapor which can be observed for very clean samples of the substance. Usually, however a flat horizontal segment of isotherm is observed.





Van der Waals equation: Maxwell construction



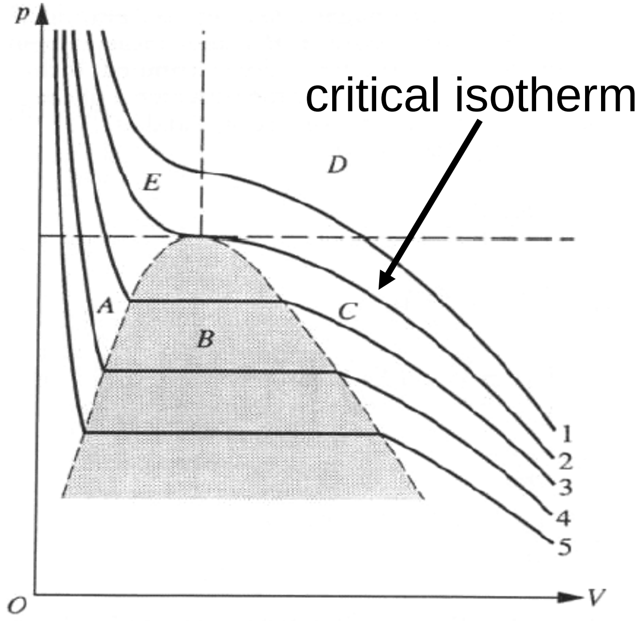
It is possible to predict the position of the horizontal flat segment on the isotherm using the Van der Waals curve with the rise and dip. Maxwell construction says: substitute the rise-dip area with a horizontal line in such a way, that the **areas above and below the horizontal line are equal**.

The pressure as given by the position of the flat horizontal line is called **saturated vapor pressure**. If we artificially prepare a non-equilibrium state such that the pressure of vapor is less than the saturated pressure, then during the relaxation molecules from the liquid phase will escape into the vapor phase more often then from the vapor phase into the liquid phase. This causes increasing the vapor pressure until it reaches the saturated vapor pressure, that is equilibrium. The **equilibrium is dynamical**: macroscopically we do not observe and changes, but on the molecular level the molecules continue to migrate between the liquid and the vapor phase in equal amounts.

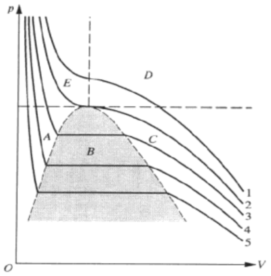
Van der Waals equation: critical isotherm

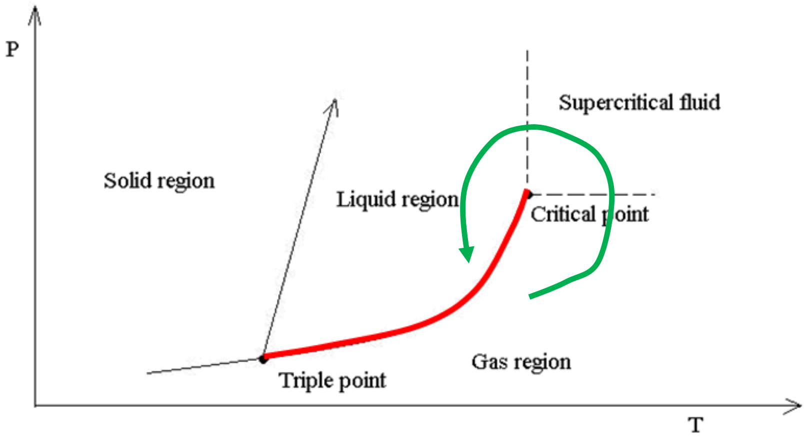
If we draw several isotherms as given by the van der Waals equation (with Maxwell modification) we observe that the higher the temperature the shorter is the flat horizontal segment and for certain temperature the flat segment is degenerated to a point. It is the isotherm marked as “2” it the figure below. This isotherm is called the critical isotherm and corresponds to the critical temperature T_c. For the critical isotherm there is no need to do the Maxwell construction, since the rise-dip area degenerates to just a point: it is an inflex point on the isotherm. The point corresponds to the critical volume V_c and critical pressure p_c. For still higher temperatures is no rise-dip area, therefore no coexistence of liquid-vapor phases. **For temperatures higher than critical it is not possible to liquify the gas just by decreasing volume and increasing pressure**: one must first lower the temperature below critical value.

The position of the critical point T_c, V_c, p_c can be calculated from the van der Waals equation. One can for example look for temperature T_c for which the isotherm has an inflex point. Technically easier way is to **rewrite the van der Waals equation to a third order equation for the variable V** with p, T as parameters and **find the values of these parameters for which this third order equation has a triple (real) root V_c .**



Phase diagram

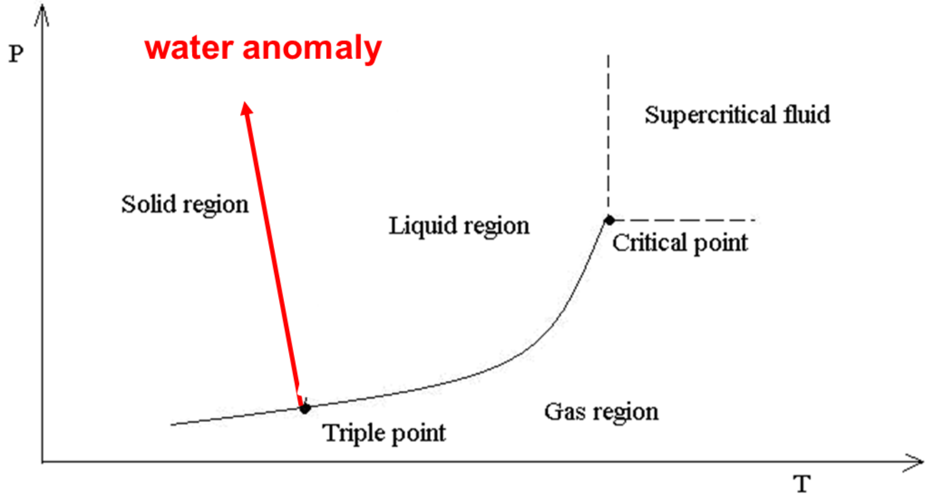




It is clear that the saturated vapor pressure is uniquely determined by the temperature. The equilibrium between the liquid and gas phase is determined by just one macroscopic parameter, temperature or pressure. Therefore one can visualize the liquid-gas coexistence equilibrium states by a curve in a pT diagram, called **phase diagram** . The liquid-gas coexistence curve is visualized in the figure below by the red curve. The curve is at high temperatures ended by the critical point. There is no liquid-gas coexistence above the critical temperature. At the critical point itself there is already no difference in physical properties between the liquid and the gas phase. The point is that **there are no absolute differences between the liquid and the gas** phase, only relative. So if I have liquid and gas next to each other, I can tell for example that the liquid phase is the one with higher mass density. When common people say that gas has low mass **density it has just comparative meaning** “lower than liquid”. That is why I can reversibly go from the gas phase to the liquid phase without seeing any discontinuity: it is enough to go around the critical point (the green path in the figure).

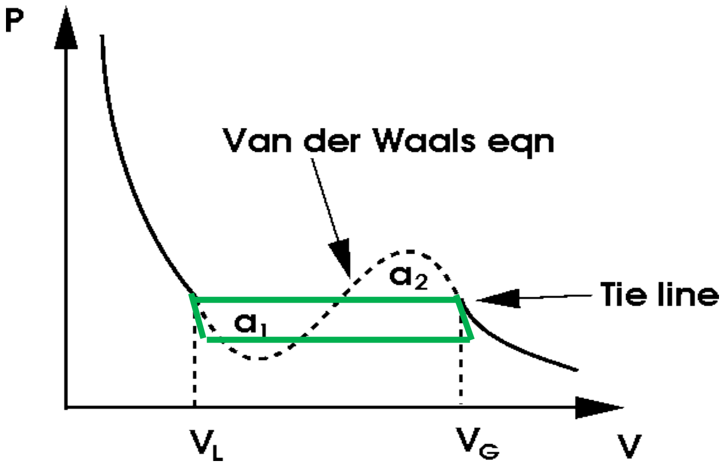
Similarly to the liquid-gas coexistence curve, there are liquid-solid and gas-solid coexistence curves. The three curves meet at the **triple point** with p, V, T uniquely determined

Phase diagram for water



On the above figure showing water phase diagram we can see the water anomaly: the solid – liquid (ice – water) coexistence curve has a negative slope. This means that the ice melting temperature decreases with increasing pressure. The reason is that the ice mass density is lower than the liquid water density at the same temperature (ice is floating on water). We shall see it in the next slide with Clausius Clapeyron equation.

Clausius - Clapeyron equation



Imagin a Carnot cycle working between two gas liquid coexistence temperatures $T, T - dT$, that is at saturated vapor pressures $p, p - dp$. The cycle is represented by the green cyclic path in the figure. The mechanical work produced is equal to the area inside the cycle $A = dp(V_G - V_L)$. The heat obtained at the higher temperature T is equal to the latent heat l. From the efficiency formula for the Carnot cycle we get

$$A = \eta l$$

$$dp(V_G - V_L) = \frac{T - (T - dT)}{T} l$$

$$\boxed{\frac{dp}{dT} = \frac{l}{T(V_G - V_L)}}$$

This is the Clausius Clapeyron equation giving the slope of the coexistence curve in the phase diagram. Similar equation holds for the liquid solid curve. For water where the solid volume is larger than the liquid volume, we get negative slope: the water anomaly.

Electromagnetic radiation in a hot cavity

Heating stove: even if the fuel is burned out, no fire there, if you open the door you see red light. **There is electromagnetic field inside heated to temperature T**. This is all we know about the field inside. We do not know the detailed state (microstate). We just have very reduced information:

There is **radiation in the box of volume V, having temperature T**. This sentence describes the current macrostate. We assume that some relaxation time has already passed, so it is an **equilibrium macrostate**. A priori we do not know if V, T specify the equilibrium macrostate sufficiently, so that we can start statistical physics machinery. Just assume that yes and we shall see later that V, T is really enough.

Physics manifesto

- **Select some part of the outer world, call it the system**
- **Find how to describe state of the system**
- **Find the equation of motion**
- **Predict future states**

Now we go to work with a new physical system: electromagnetic field. It is a new animal in the physics ZOO. So we have to show how the physics manifesto works for this new animal.

System: electromagnetic field

State of electromagnetic field: two vector fields $\vec{E}(\vec{r})\ \vec{B}(\vec{r})$
What are the equations of motion, how to predict future? (This is something which is usually not much discussed in the course "Theory of electromagnetic field".)

Let us try our standard strategy: starting from the current state find the new state after infinitesimal time interval dt.
Suggestion: try to use Maxwell equations.

Maxwell equations

$$\mathrm{div}\vec{E}(\vec{r}) = \frac{1}{\varepsilon_0}\rho(\vec{r})$$

$$\mathrm{div}\,\vec{B}(\vec{r}) = 0$$

$$\mathrm{rot}\vec{E}(\vec{r}) = -\frac{\partial\vec{B}(\vec{r})}{\partial t}$$

$$\mathrm{rot}\,\vec{B}(\vec{r}) = \mu_0\vec{j}(\vec{r}) + \mu_0\varepsilon_0\frac{\partial\vec{E}(\vec{r})}{\partial t}$$

The first two equations do not contain derivatives with respect to time. They must be true in each time instant. Therefore they pose **a condition on state of the electromagnetic field which must be satisfied in each time instant** (in particular in “initial state”).
This means that the six functions describing the state

$$E_x(\vec{r}), E_y(\vec{r}), E_z(\vec{r}), B_x(\vec{r}), B_y(\vec{r}), B_z(\vec{r})$$

cannot be chosen arbitrarily at will at each spatial point. Very imprecisely it means that because of two conditions only four of the six functions are independent. To work wit six functions of state is just technically practical in applications. In theoretical physics we, however, often describe the state by just four other functions (potentials).

Electromagnetic field – time development

The second pair of the Maxwell equations contains time derivatives, so let us try to rewrite those equations to use them to determine a new state after infinitesimal time interval dt.

$$\frac{\partial \vec{E}}{\partial t} = \frac{1}{\mu_0 \varepsilon_0} \mathrm{rot}\, \vec{B} - \frac{1}{\varepsilon_0} \vec{j} \qquad \frac{\partial \vec{B}}{\partial t} = -\mathrm{rot}\, \vec{E}$$

Suppose we know the state $\vec{E}(t,\vec{r}), \vec{B}(t,\vec{r})$. The state after time dt should be

$$\boxed{\begin{aligned} \vec{E}(t+dt,\vec{r}) &= \vec{E}(t,\vec{r}) + \frac{1}{\mu_0 \varepsilon_0} \mathrm{rot}\, \vec{B}(t,\vec{r})\; dt - \frac{1}{\varepsilon_0} \vec{j}(t,\vec{r})\; dt \\ \vec{B}(t+dt,\vec{r}) &= \vec{B}(t,\vec{r}) - \mathrm{rot}\, \vec{E}(t,\vec{r})\; dt \end{aligned}}$$

The right-hand sides concern only the “current time” t. Therefore they can be evaluated just knowing the current (initial) state. So we are happy: we can move forward in time. We should just check whether the first pair of the Maxwell equations will be satisfied after the time shift if they were satisfied in the initial state. One can easily check that it is true provided the charges and currents satisfy the continuity equation (which is the consequence of the charge conservation). Notice that we have considered the currents to be “external entities”, their time and space dependence are considered here “to be given”.

By the way: do notice that when we want to make the time shift, we have to do it simultaneously for both electric field and magnetic field. So these two fields are not “individual entities” they form together a common “electromagnetic field”.

Note: boundary conditions

$$\vec{E}(t+dt,\vec{r}) = \vec{E}(t,\vec{r}) + \frac{1}{\mu_0\varepsilon_0}\mathrm{rot}\,\vec{B}(t,\vec{r})\;dt - \frac{1}{\varepsilon_0}\vec{j}(t,\vec{r})\;dt$$
$$\vec{B}(t+dt,\vec{r}) = \vec{B}(t,\vec{r}) - \mathrm{rot}\vec{E}(t,\vec{r})\;dt$$

These equations can in principle be used to predict the state after a small time interval dt knowing the current state at the time t. And then iterate to further future, next dt, and next dt and so on. We can try to do it at least numerically on a computer. However, we meet two problems:

- numerical instabilities. We either have be very careful with the choice of steps in time and space or we have to choose more sophisticated numerical methods. This is not a sign of some essential problem
- we will not be able to numerically approximate the rotations in points at the boundaries. We have to use boundary conditions for the boundary points instead. **This is essential and it helps us to understand why the partial differential equations force us to specify the boundary conditions. To know the initial state is not enough to predict the future.**

Statistical physics of a new physical object: electromagnetic field

So we have described a new physical object: the electromagnetic field. We know how to define its state and we know how to predict its time development.

So far there was no need of statistical methods.

A new situation arises when the electromagnetic field interacts with some thermal reservoir: we can imagine a stow with hot walls and the red light inside. This red light is just electromagnetic field in statistical equilibrium with the hot walls. We expect to use the technology of the canonical ensemble.

It is not, however, straightforward: we were not told how to create the canonical ensemble for object whose state is described by a field theory. Fortunately there is a way how to **describe the state of the free electromagnetic field in a cavity by discrete mathematical objects similar to harmonic oscillators** (even if there are infinitely many oscillators required) and for such objects the application of statistical physics is well understood.

Free electromagnetic field

Let us now consider some area of space where there are neither charges nor currents. Still, electromagnetic field may be there. It is true, that the field had to be created somewhere sometimes by some charges, but this is not interesting for us for the moment. An example might be light moving through the empty space which originated far away by a distant star. Another example is the electromagnetic field in a microwave cavity. The field was created by a magnetron outside the cavity and injected into the cavity through a wave guide. But from then on it can be considered as a free electromagnetic field inside a cavity within brass (conducting) walls. The Maxwell equations for a free field read

$$\mathrm{div}\vec{E}(\vec{r}) = 0 \qquad \mathrm{div}\,\vec{B}(\vec{r}) = 0$$

$$\mathrm{rot}\vec{E} = -\frac{\partial \vec{B}}{\partial t} \qquad \mathrm{rot}\,\vec{B} = \mu_0\varepsilon_0\frac{\partial \vec{E}}{\partial t}$$

Since the spatial area is limited, we need to consider the physical conditions on the border of the area. These border conditions are necessary supplement to the Maxwell equations, without them the equations themselves are useless.

Free electromagnetic field – wave equation

For completeness we show, that the Maxwell equations of a free field can be rewritten to the form of a wave equation.

$$\mathrm{rot}\vec{E} = -\frac{\partial \vec{B}}{\partial t}$$

we apply another rotation:

$$\mathrm{rot}\ \mathrm{rot}\ \vec{E} = -\frac{\partial}{\partial t}\mathrm{rot}\ \vec{B} = -\frac{\partial}{\partial t}\mu_0\varepsilon_0\frac{\partial \vec{E}}{\partial t} = -\mu_0\varepsilon_0\frac{\partial^2 \vec{E}}{\partial t^2}$$

Now the well know relation $\mathrm{rot}\ \mathrm{rot}\ \vec{E} = \nabla \mathrm{div}\ \vec{E} - \mathrm{div}\ \nabla \vec{E}$

For those who are not familiar with nablas, here is the derivation in coordinate formalism (if you still do not recognize some formulas, consult web)

$$(\mathrm{rot}\ \mathrm{rot}\ \vec{E})_i = \sum_{jk}\varepsilon_{ijk}\frac{\partial}{\partial x_j}(\mathrm{rot}\ \vec{E})_k = \sum_{jk}\varepsilon_{ijk}\frac{\partial}{\partial x_j}\sum_{mn}\varepsilon_{kmn}\frac{\partial}{\partial x_m}E_n =$$

$$= \sum_{jmn}\sum_{k}\varepsilon_{ijk}\varepsilon_{kmn}\frac{\partial}{\partial x_j}\frac{\partial}{\partial x_m}E_n = \sum_{jmn}(\delta_{im}\delta_{jn} - \delta_{in}\delta_{jm})\frac{\partial}{\partial x_j}\frac{\partial}{\partial x_m}E_n =$$

$$= \sum_j(\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}E_j - \frac{\partial}{\partial x_j}\frac{\partial}{\partial x_j}E_i) = \frac{\partial}{\partial x_i}\mathrm{div}\ (\vec{E}) - \Delta E_i$$

Free electromagnetic field – wave equation

$$\text{rot rot } \vec{E} = -\mu_0 \varepsilon_0 \frac{\partial^2 \vec{E}}{\partial t^2}$$

$$\text{rot rot } \vec{E} = \nabla \text{div } \vec{E} - \text{div } \nabla \vec{E}$$

since $\text{div } \vec{E} = 0$ we get

$$\text{rot rot } \vec{E} = -\text{div } \nabla \vec{E} = -\Delta \vec{E}$$

So finally

$$\boxed{\frac{\partial^2 \vec{E}}{\partial t^2} = \frac{1}{\mu_0 \varepsilon_0} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial z^2}{\partial z^2} \right) \vec{E}}$$

So the free field satisfies the wave equation. The phase velocity is

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

c= 299 792 458 m/s, what is the velocity of light

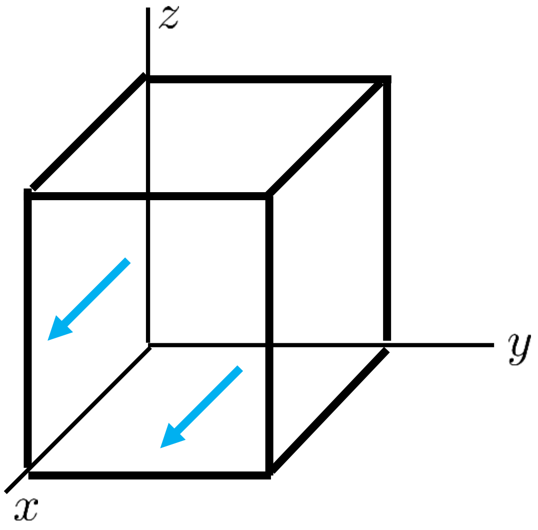
Deriving the wave equations we have used only two of the four Maxwell equations, so in addition to the wave equation **there are additional constrains** for the electromagnetic wave to be fulfilled!

Free electromagnetic field in a conducting box

Free electromagnetic field in a conducting box (like microwave) satisfies wave equation inside the box. The more difficult part of the problem are the boundary condition.

Let us investigate the x-component of the electric field $E_x(x, y, z)$ in a cube-like conducting box $a \times a \times a$.

Tangential components on the boundary have to be zero



$$E_x(x,0,z) = E_x(x,a,z) = E_x(x,y,0) = E_x(x,y,a) = 0$$

According to **Fourier**: function $E_x(x, y, z)$ satisfying such conditions can be constructed from the set of functions (cyclically for other components)

$$\tilde{E}_{x;n,l} = f_{x;n,l}(x)\sin(\frac{n\pi y}{a})\sin(\frac{l\pi z}{a})$$ where f-s are so far unknown functions

The electric field has to satisfy the condition div $\vec{E} = 0$ also in points with $x = 0, x = a$. There the y and z field components do not contribute since their sinuses are 0 there, therefore we get the condition for the derivative of f

$$f'_{x;n,l}(0) = f'_{x;n,l}(a) = 0$$

so the derivatives of f can be constructed from sinuses, so f from cosines.

Free electromagnetic field in a conducting box

We have found that the electric field automatically satisfying the boundary conditions can be looked for in the form

$$E_x(x,y,z,t) = \sum_{mnl} E_{x;mnl}(t)\cos(\frac{m\pi x}{a})\sin(\frac{n\pi y}{a})\sin(\frac{l\pi z}{a})$$

$$E_y(x,y,z,t) = \sum_{mnl} E_{y;mnl}(t)\sin(\frac{m\pi x}{a})\cos(\frac{n\pi y}{a})\sin(\frac{l\pi z}{a})$$

$$E_z(x,y,z,t) = \sum_{mnl} E_{z;mnl}(t)\sin(\frac{m\pi x}{a})\sin(\frac{n\pi y}{a})\cos(\frac{l\pi z}{a})$$

where $E_{x;mnl}(t), E_{y;mnl}(t), E_{z;mnl}(t)$ are so far unknown functions. Actually not all these functions are independent, because of the zero-divergence condition, which gives the conditions

$$\frac{m\pi}{a}E_{x;mnl}(t) + \frac{n\pi}{a}E_{y;mnl}(t) + \frac{l\pi}{a}E_{z;mnl}(t) = 0$$

so for any mnl only two of these functions are independent (for example the x and y component). The third one can be expressed from the other two.

What have we got? We have found that in each time t the state of the electric field in the boxed is uniquely given by two infinite discrete sets of functions $E_{x;mnl}(t)$ and $E_{y;mnl}(t)$ where mnl are triplets of arbitrary integers.

Originally, we have described the state of an electric field as a field: a vector in each spatial point xyz in the given time t. Now we have **discrete sets** of functions of time.

Free electromagnetic field in a conducting box

What are the equations of motion for the state functions $E_{x;mnl}(t), E_{y;mnl}(t)$? The electric field has to satisfy the wave equation

$$\triangle E_x(x,y,z,t) - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}E_x(x,y,z,t) = 0$$

and similarly for the y component. (The z component is expressed through the other two components and will satisfy the wave equation automatically.) After substituting the fields by the discrete sums containing the $E_{x;mnl}(t), E_{y;mnl}(t)$ into the wave equations we get the equations

$$\frac{d^2}{dt^2}E_{x;mnl}(t) = -\omega_{mnl}^2 E_{x;mnl}(t)$$
$$\frac{d^2}{dt^2}E_{y;mnl}(t) = -\omega_{mnl}^2 E_{y;mnl}(t)$$

where

$$\omega_{mnl}^2 = \frac{c^2\pi^2}{a^2}(m^2+n^2+l^2)$$

These are equations of motions for harmonic oscillators!

The time dependence will be $$E_{x;mnl}(t) = \exp(-i\omega_{mnl}t)E_{x;mnl}(0)$$

What have we got? The electric field in a box is mathematically equivalent to two sets of independent harmonic oscillators, labeled by integer triplets mnl. We shell show that magnetic part of the electromagnetic filed is fully determined by the "electric" functions $E_{x;mnl}(t), E_{y;mnl}(t)$ so the oscillators describe the state of field completely!

Free electromagnetic field in a conducting box

We have the solution for the electric field in a box**. Now we show very briefly that the magnetic field is fully given by the electric field**. From the Maxwell equation

$$\mathrm{rot}\vec{E} = -\frac{\partial}{\partial t}\vec{B}$$

We get for the mnl term in the sums and for the expected time dependence $\exp(-i\omega_{mnl}t)$

$$i\omega_{mnl}B_{z;mnl} = \frac{m\pi}{a}E_{y,mnl}\cos(\frac{m\pi x}{a})\cos(\frac{n\pi y}{a})\sin(\frac{l\pi z}{a}) +$$
$$-\frac{n\pi}{a}E_{x,mnl}\cos(\frac{m\pi x}{a})\cos(\frac{n\pi y}{a})\sin(\frac{l\pi z}{a})$$

$$\boxed{B_{z;mnl} = -i\left(\frac{m\pi}{a\omega_{mnl}}E_{y,mnl} - \frac{n\pi}{a\omega_{mnl}}E_{x,mnl}\right)\cos(\frac{m\pi x}{a})\cos(\frac{n\pi y}{a})\sin(\frac{l\pi z}{a})}$$

The x, y components of the magnetic field we get by the cyclic permutation.
So we have shown that the electric field solution generates the magnetic field solution.

Free electromagnetic field in a conducting box

Why did we do the rewriting of the field into sets of harmonic oscillators? Because we want to study what kind of field is formed in the box, if the box walls are heated to temperature T and so we have the electromagnetic field in thermal contact with thermostat. We would like to use canonical ensemble technology, bat we do not know how to do that if the microstates of the electromagnetic field are described as fields in space.

On the other hand we know how to do statistics of independent harmonic oscillators in contact with the thermal reservoir taking the oscillator as either classical or quantum objects. Since the oscillators are independent, they do not feel each other and we can do the canonical calculation for just one harmonic oscillator (an easy task) and then do the summation through the set (infinitely large) of all the harmonic oscillators. Here are the results for one oscillator labeled as mnl

Classical result for the mean energy at temperature T: $\bar{E} = kT$

Quantum result for the mean energy at temperature T: $\overline{E} = \dfrac{\hbar\omega_{mnl}}{\exp\left(\frac{\hbar\omega_{mnl}}{kT}\right) - 1} + \dfrac{1}{2}\hbar\omega_{mnl}$

Observe the difference: all classical oscillators have the same mean energy not dependent on their ω_{mnl}. Quantum oscillators mean energies do depend on ω_{mnl} .

Free electromagnetic field in a conducting box: canonical ensemble

Since the microstate of the free electromagnetic field is the same as the microstate of (an infinite) set of harmonic oscillators the statistical physics of the field in contact with the thermal reservoir is straightforward: one just uses the canonical ensemble for independent harmonic oscillators. But we immediately see some problems.

If the oscillators are considered to be classical, then the mean energy for each of them is kT, independently of ω_{mnl}. Since there is an infinite number of these oscillators, we get infinite mean energy of the electromagnetic field in a hot box. Even worse: this infinite value is not a constant but depends on T. So to increase the temperature in a stove would need to add infinite amount of energy. Even worse: since the mean energy of the oscillators does not depend on ω_{mnl}, even the very high frequencies of the electromagnetic field will be highly excited even at moderate temperatures. Very high frequencies mean ultraviolet, roentgen, gamma frequencies. It would mean "open the window to a stove" and you get irradiated by deadly radiation. Disaster, which got the name "ultraviolet catastrophe". It means that either the statistical physics is completely wrong or that the electromagnetic field is not a classical, but a quantum object and quantum version of oscillators should be used.

Free electromagnetic field in a conducting box: canonical ensemble

Even **considering the oscillators to be quantum objects** is not without problems! The mean energy of a quantum oscillator is

$$\overline{E} = \frac{\hbar\omega_{mnl}}{\exp\left(\frac{\hbar\omega_{mnl}}{kT}\right) - 1} + \frac{1}{2}\hbar\omega_{mnl}$$

The problem is the constant additive term $\hbar\omega/2$. Which again gives infinite contribution to the total energy. However, this term is a constant not depending on any state characteristics like the temperature, so can be considered as a meaningless energetical additive constant. Well, this is a rather cheap solution to an essential problem, it is more like sweeping the problem under the carpet. **We shall omit this constant term in what follows in this formula and in the formula for energy of a harmonic oscillator.**

Historically the problem with the classical statistics was found by **Max Planck around 1900**. Curiously enough it was not the youngest theory to be blamed for the disaster (statistical physics) but older and well-established theories: Newton mechanics and Maxwell theory of electromagnetism, which had to be replaced by their quantum versions. Max Planck was the first who “quantized” the old theory for black body radiation. It started the quantum era of physics.

Black body radiation

After all the preparatory work let us study the electromagnetic field in a box in contact with thermal reservoir. In physics the problem is known under the name “black body radiation”.

The experiment shows, that all bodies heated to some temperature emit electromagnetic waves. Our sun emits visible light from its surface having some 6000 K. Our own bodies emit infrared radiation corresponding to our temperature of 37 Celsius. This radiation is detected by mosquito sensors which then recognize us as the object to attack. This radiation is also detected by motion detector in the alarm systems.


Motion detector

The spectral characteristics of radiation emitted by a hot body is theoretically simplest if it is so called black body. A black body is an idealized physical body that absorbs all incident electromagnetic radiation, not reflecting any part of it. In thermal equilibrium it emits radiation called **black body radiation.** An approximate realization of a black surface is a hole in the wall of a large cavity. Any light entering the hole is reflected within the internal surface of the body indefinitely or absorbed within the body and is unlikely to re-emerge, making the hole a nearly perfect absorber. In thermal equilibrium radiation is emitted from such hole equivalent to black body radiation. **If the electromagnetic field inside a cavity is in thermal equilibrium with its walls the spectral characteristic of the electromagnetic field inside are equal to the black body radiation**.

Quantum states of a free electromagnetic field in a box

We have shown that the electromagnetic field states are equivalently described as states of a set of harmonic oscillators. So we know, how to make a quantum theory of electromagnetic field in a box: we just take those oscillators to be quantum oscillators and the general state of the field will be some general quantum state of those oscillators.
We know that a quantum state of a harmonic oscillator is given by a single integer n (called excitation number) and its energy in the state n is $E_n = n\hbar\omega$. (We have omitted the $\hbar\omega/2$ term). **A quantum state of electromagnetic field can be therefore given as the list of all the equivalent oscillators together with the excitation number of each of them.**

mnl,s	excit.number
111,x	n_{111x}
111,y	n_{111y}
112,x	n_{112x}
112,y	n_{112y}
121,x	n_{121x}
121,y	n_{121y}
…	…

One particular (micro)state of the electromagnetic field in a box is given by the table like this.
The table is an infinite list of oscillators. Each raw contains the label of a particular oscillator and its quantum excitation number.

The total energy of the field in such state is given by the sum

$$E = \sum_{mnls} (n_{mnls}\hbar\omega_{mnl}) \qquad \omega_{mnl} = \frac{c\pi}{a}\sqrt{m^2+n^2+l^2}$$

In the sum mnl are integers, s runs through just two values x, y.

We know what are all possible microstates and what are their energies, so we can use canonical ensemble technology.

We have quantized the electromagnetic field !!! Very advanced physics !!!

Thermal radiation in a cavity - energy

Thermal radiation is equivalent to a set of independent oscillators. We can calculate the mean energy of each one separately, we get

$$\overline{E}_{mnls} = \frac{\hbar\omega_{mnl}}{\exp\left(\frac{\hbar\omega_{mnl}}{kT}\right) - 1}$$

By the way the energy of an oscillator in the state with excitation number n is $\hbar\omega$, therefore we see that **the mean excitation number** at the temperature T is

$$\overline{n}_{mnls} = \frac{1}{\exp\left(\frac{\hbar\omega_{mnl}}{kT}\right) - 1}$$

The total energy of all the oscillators (the total energy of radiation in the cavity) is

$$\overline{E} = \sum_{mnls} \frac{\hbar\omega_{mnl}}{\exp\left(\frac{\hbar\omega_{mnl}}{kT}\right) - 1} \qquad \omega_{mnl} = \frac{c\pi}{a}\sqrt{m^2 + n^2 + l^2}$$

The sum runs over all triplets mnl of integers and over two values of s: x, y. Now we do a standard trick: we approximate the sum by an integral over ω. To do this we have to know how many oscillators have the frequency less than some value ω. We see that the various ω values correspond to points in the abstract mnl space with integer coordinates. The trick is the same as we used when calculating the number of one-particle states. So we get (the factor 2 is for two states x, y for each mnl).

$$\varphi(\omega) = 2\frac{1}{8}\frac{4}{3}\pi r_\omega^3 = 2\frac{1}{8}\frac{4}{3}\pi\left(\frac{a}{c\pi}\omega\right)^3$$

Thermal radiation in a cavity - energy

The total energy of the thermal radiation in a cavity is

$$U = \int d\omega \varphi'(\omega) \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{kT} - 1\right)} = \int d\omega \frac{1}{3}\pi \frac{a^3}{\pi^3 c^3} 3\omega^2 \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{kT} - 1\right)}$$

a^3 is the cavity volume, so we get for the **energy density** of the thermal radiation in the cavity

$$\boxed{u = \int d\omega \frac{\omega^2}{\pi^2 c^3} \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{kT} - 1\right)}}$$

The energy density is expressed as an integral (a sum) over frequencies ω. So the function under the integral can be interpreted as the **spectral energy density $u(\omega)$**, that means the **energy per unit volume per frequency interval $d\omega$ around the frequency ω** is

$$\boxed{u(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{\hbar\omega}{\exp\left(\frac{1}{kT} - 1\right)}}$$

Thermal radiation in a cavity - energy

After integration over ω we get for the total energy density

$$U = \frac{\pi^2 k^4}{15\hbar^3 c^3} T^4$$

If we make a small hole into the cavity with equilibrium thermal radiation, the radiation will be emitted through that hole. The energy density flow peer unit of time will be

$$J = \frac{1}{4} c U = \frac{\pi^2 k^4}{60\hbar^3 c^2} T^4$$

We derived the formula in a rather hand-waving way: the energy with density U flows out of the hole with the velocity of light c. The factor 1/4 we got by averaging over angles of the outgoing radiation.

The formula is called Stefan's low and is usually written in the form

$$\boxed{J = \sigma T^4 \qquad \sigma = \frac{\pi^2 k^4}{60\hbar^3 c^2}}$$

σ is called Stefan-Boltzmann constant

Free electromagnetic field: alternative description of the state

We found that the electromagnetic field in a box is mathematically equivalent to two sets of independent harmonic oscillators, labeled by integer triplets mnl and an additional label x or y.

$$E_x(x,y,z,t) = \sum_{mnl} E_{x;mnl}(t)\cos(\frac{m\pi x}{a})\sin(\frac{n\pi y}{a})\sin(\frac{l\pi z}{a})$$

$$E_y(x,y,z,t) = \sum_{mnl} E_{y;mnl}(t)\sin(\frac{m\pi x}{a})\cos(\frac{n\pi y}{a})\sin(\frac{l\pi z}{a})$$

$$E_z(x,y,z,t) = \sum_{mnl} E_{z;mnl}(t)\sin(\frac{m\pi x}{a})\sin(\frac{n\pi y}{a})\cos(\frac{l\pi z}{a})$$

$E_{x;mnl}(t) = \exp(-i\omega_{mnl}t)E_{x;mnl}(0)$ and similarly for y, z

We called the "items" oscillators due to the fact that we have concentrated on the time dependence of the coefficients $E_{x;mnl}(t)$ not giving too much meaning to the "spatial" sinuses and cosines. But equally well we could call the "defining items" as **stationary waves**, when we include the spatial dependence into the "state". We see stationary waves with frequencies $\boxed{\omega_{mnl} = \frac{c\pi}{a}\sqrt{m^2+n^2+l^2}}$ and wave vectors $\boxed{\vec{k}_{mnl} = (\frac{m\pi}{a}, \frac{n\pi}{a}, \frac{l\pi}{a})}$

We see the relation $\boxed{\omega_{mnl} = c|\vec{k}_{mnl}|}$

Free electromagnetic field: alternative description of the state

Se we have two alternative description of electromagnetic field state

The electromagnetic field in a box is mathematically equivalent to two sets of independent harmonic oscillators, labeled by integer triplets mnl and an additional label x or y with frequencies $\omega_{mnl} = \frac{c\pi}{a}\sqrt{m^2+n^2+l^2}$

Alternatively

The electromagnetic field in a box is mathematically equivalent to two sets of independent stationary waves, labeled by integer triplets mnl and an additional label x or y with frequencies and wave vectors

$$\omega_{mnl} = \frac{c\pi}{a}\sqrt{m^2+n^2+l^2} \qquad \vec{k}_{mnl} = \left(\frac{m\pi}{a}, \frac{n\pi}{a}, \frac{l\pi}{a}\right)$$

What concerns the creation of the canonical ensemble both the alternatives are the same. The oscillators and the stationary waves are considered here as individual objects, individual independent subsystems. The quantum states of individual oscillators as well as individual stationary waves are given identically by the excitation number n. The energy of the state n is $\varepsilon_n = \hbar\omega_{mnl}$. So the alternative descriptions of the states of the electromagnetic field give the same statistical physics results.

Free electromagnetic field:
still another alternative description - photons

The complete (micro)state of the electromagnetic field we have represented by the table where the excitation numbers are any integers. If you see the table do you recall that you have already met a similar table in a very different context? Here it is: The state of non-interacting indistinguishable spinless bosons was given by the list of one-particle states each with its occupational number which could be any integer. The total energy was

mnl,s	excit.number
111,x	n_{111x}
111,y	n_{111y}
112,x	n_{112x}
112,y	n_{112y}
121,x	n_{121x}
121,y	n_{121y}
…	…

one particle state	occup. number
1,1,1	1
1,1,2	3
1,2,1	0
1,2,2	2
2,1,1	0
2,1,2	0
2,2,1	12
2,2,2	4
⋮	⋮

$$E = \sum_{n_1,n_2,n_3} n_{n_1,n_2,n_3} \varepsilon_{n_1,n_2,n_3}$$

For the electromagnetic field the total energy is

$$E = \sum_{mnl} n_{mnl} \hbar\omega_{mnl} = \sum_{mnl} n_{mnl} \varepsilon_{mnl}$$

The same (almost) description of the states, the same formula for the energy.

Free electromagnetic field: still another alternative description - photons

mnl,s	excit.number
111,x	n_{111x}
111,y	n_{111y}
112,x	n_{112x}
112,y	n_{112y}
121,x	n_{121x}
121,y	n_{121y}
…	…

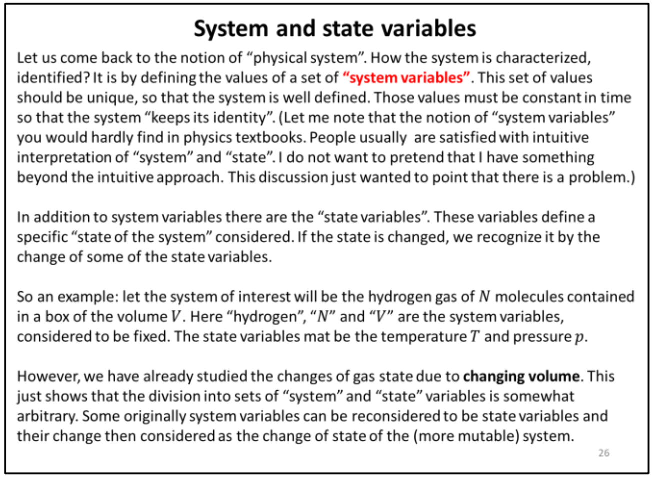
one particle state	occup. number
1,1,1	1
1,1,2	3
1,2,1	0
1,2,2	2
2,1,1	0
2,1,2	0
2,2,1	12
2,2,2	4
⋮	⋮

The table giving the state of the electromagnetic field via the states of stationary waves is very similar to the table giving some state of a ideal spinless boson gas. **However there are some dissimilarities as well**:

- Each row in the stationary wave table represents a different stationary wave. Different stationary waves are considered as **different objects**, different physical systems. The rows in the boson table represents different one **particle states of one physical object**: the bosonic particle
- the rows in the stationary waves table have additional label $s \in \{x, y\}$. We can have additional label for bosons with spins. But the closest to spin zero boson is a spin 1 boson which **should have 3 spin states**, not just 2.

To disclose our aim: we want to show that there is another alternative description of the electromagnetic field in a box: ideal bosonic gas of particles called photons. To do that we have to handle the above-mentioned dissimilarities of the two tables.

Free electromagnetic field:
still another alternative description - photons



System and state variables

Let us come back to the notion of "physical system". How the system is characterized, identified? It is by defining the values of a set of **"system variables"**. This set of values should be unique, so that the system is well defined. Those values must be constant in time so that the system "keeps its identity". (Let me note that the notion of "system variables" you would hardly find in physics textbooks. People usually are satisfied with intuitive interpretation of "system" and "state". I do not want to pretend that I have something beyond the intuitive approach. This discussion just wanted to point that there is a problem.)

In addition to system variables there are the "state variables". These variables define a specific "state of the system" considered. If the state is changed, we recognize it by the change of some of the state variables.

So an example: let the system of interest will be the hydrogen gas of N molecules contained in a box of the volume V. Here "hydrogen", "N" and "V" are the system variables, considered to be fixed. The state variables mat be the temperature T and pressure p.

However, we have already studied the changes of gas state due to **changing volume**. This just shows that the division into sets of "system" and "state" variables is somewhat arbitrary. Some originally system variables can be reconsidered to be state variables and their change then considered as the change of state of the (more mutable) system.

mnl,s	excit.number
111,x	n_{111x}
111,y	n_{111y}
112,x	n_{112x}
112,y	n_{112y}
121,x	n_{121x}
121,y	n_{121y}
…	…

one particle state	occup. number
1,1,1	1
1,1,2	3
1,2,1	0
1,2,2	2
2,1,1	0
2,1,2	0
2,2,1	12
2,2,2	4
⋮	⋮

First to the problem "different objects versus different states". Here is the reminder of the slide where we discussed the freedom of reconsidering what are the "system variables" and what are the "state variables". It was about chemical potential and considering the number of particles N not as a fixed system characteristics but rather as a state variable.

We can do a similar trick with the mnl labels of the stationary waves. We considered different mnl labels as "names" for different physical objects, different oscillators or different stationary waves. We can consider all the stationary waves "in the box" as instances of one type of "physical animal" – a stationary wave – in different states mnl. Similarly to gas particles being same "physical animals" in different one-particle state. **So this dissimilarity disappeared**.

Free electromagnetic field:
still another alternative description - photons

mnl,s	excit.number
111,x	n_{111x}
111,y	n_{111y}
112,x	n_{112x}
112,y	n_{112y}
121,x	n_{121x}
121,y	n_{121y}
…	…

one particle state	occup. number
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1,1,2	3
1,2,1	0
1,2,2	2
2,1,1	0
2,1,2	0
2,2,1	12
2,2,2	4
⋮	⋮

Now to the problem of “spin labels”. The particles we want to “invent and introduce” must be bosons, since the excitation numbers interpreted as occupational numbers are any integers. The bosons should not be spinless since we have to interpret the labels x, y as some spin-state labels. So far, we do not know any bosons which would have just two spin states. Spin 1 bosons should have 3 “spin projections”. Two spin projections suggest spin 1/2, but spin 1/2 particles are fermions!

However, the above-mentioned classification is valid if we consider only nonrelativistic particles. Relativistic particles with the mass equal to zero with the total spin 1 have only two spin-projection states +1 and -1. Projection 0 is not possible. The reason is hidden deeply in relativistic quantum mechanics (better: field theory). We skip the detailed argumentation, just take it as a fact.

So there is a chance for a particle-like alternative description of the states of the electromagnetic field introducing relativistic mass=0 particles with spin 1 named photons. The “spin-projection labels” for photons do not necessarily mean true spin projections: other quantum mechanical base of “spin states” can be used equally well. For photons we most ly use the “polarization basis”.

Free electromagnetic field:
alternative descriptions of the state

Se here are now three alternative description of electromagnetic field state

The electromagnetic field in a box is mathematically equivalent to two sets of independent harmonic oscillators, labeled by integer triplets mnl and an additional label x or y with frequencies $\omega_{mnl} = \frac{c\pi}{a}\sqrt{m^2 + n^2 + l^2}$

The electromagnetic field in a box is mathematically equivalent to two sets of independent stationary waves, labeled by integer triplets mnl and an additional label x or y with frequencies and wave vectors

$$\omega_{mnl} = \frac{c\pi}{a}\sqrt{m^2 + n^2 + l^2} \qquad \vec{k}_{mnl} = (\frac{m\pi}{a}, \frac{n\pi}{a}, \frac{l\pi}{a})$$

The electromagnetic field in a box is mathematically equivalent to an ideal gas of relativistic mass=0 bosons. Their one-particle states are labeled as $mnls$ where the mnl are integers and s can have two values describing two possible polarizations. The frequencies and the wave vectors are interpreted using the de'Broglie relations as the energy and the momentum of particles. A boson in the one-particle-state $mnls$ would have the energy and momentum

$$\varepsilon_{mnl} = \frac{c\hbar\pi}{a}\sqrt{m^2 + n^2 + l^2} \qquad \vec{p}_{mnl} = \hbar(\frac{m\pi}{a}, \frac{n\pi}{a}, \frac{l\pi}{a})$$

Free electromagnetic field: photons

We found that the energy and momentum formulas for photons should be

$$\varepsilon_{mnl} = \frac{c\hbar\pi}{a}\sqrt{m^2+n^2+l^2} \qquad \vec{p}_{mnl} = \hbar(\frac{m\pi}{a}, \frac{n\pi}{a}, \frac{l\pi}{a})$$

This gives us the following relation between energy and momentum

$$\boxed{\varepsilon = c|\vec{p}|}$$

Such a relation is expected for relativistic massless particle because of the general relativistic formula for the particle rest mass

$$\boxed{m_0^2 = \frac{1}{c^4}\varepsilon^2 - \frac{1}{c^2}|\vec{p}|^2}$$

For photons this gives the rest mass 0. The general formula for the relation between the energy, rest mass and velocity of a particle is $\varepsilon = \frac{m_0c^2}{\sqrt{1-\frac{v^2}{c^2}}}$

To get non-zero energy, the zero-mass particle velocity must always be $v = c$. So photons always move with the velocity c.

We have discovered photons !!!

Thermal radiation in a cavity as a photon gas

We have arrived at a conclusion that we can consider the electromagnetic field in a cavity as a photon gas. So we can try to calculate the properties of the thermal radiation by calculating the properties of a photon gas in equilibrium with the cavity walls at the temperature T.

How to do that? we certainly do not know a priori the total number of photons in the cavity so we try to work within the grand canonical technology pretending to know the chemical potential of photons, calculate with it as with a symbolical abstract number μ and finally find the correct value of it by adjusting this value to get the correct thermal radiation results which we already know.

So we have the photon gas with one-particle-states mnls. The mean occupational number a one-particle-state will be

$$n_{mnls} = \frac{1}{\exp\left(\frac{\hbar\omega_{mnl}-\mu}{kT}\right) - 1}$$

The total energy of the photon gas will be

$$\overline{E} = \sum_{mnls} \frac{\hbar\omega_{mnl}}{\exp\left(\frac{\hbar\omega_{mnl}-\mu}{kT}\right) - 1}$$

Thermal radiation in a cavity as a photon gas

Let us compare the formula we have just got with the formula we have got for "equivalent oscillators" where we had "mean excitation numbers" instead of "mean occupational numbers"

$$\overline{E} = \sum_{mnls} \frac{\hbar\omega_{mnl}}{\exp\left(\frac{\hbar\omega_{mnl}-\mu}{kT}\right) - 1} \qquad \leftrightarrow \qquad \overline{E} = \sum_{mnls} \frac{\hbar\omega_{mnl}}{\exp\left(\frac{\hbar\omega_{mnl}}{kT}\right) - 1}$$

The formula for ω_{mnl} is the same in both cases, the only difference is that there is μ in the formula on the left. The conclusion is: we get exactly the same results for the thermal radiation if calculated as for oscillators and if calculated as for photons **if we set $\boldsymbol{\mu = 0}$**.

We discovered a new law of nature: chemical potential of photons is (always) zero.

Putting $\mu = 0$ we continue in exactly the same way as we did for the "equivalent oscillators": we replace the sum by an integral using formula for the **density of one-particle-states which would be for photons the same as was the formula for the density of oscillators** and we will get the same result

$$u(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{\hbar\omega}{\exp\left(\frac{1}{kT} - 1\right)}$$

Chemical potential in an external field

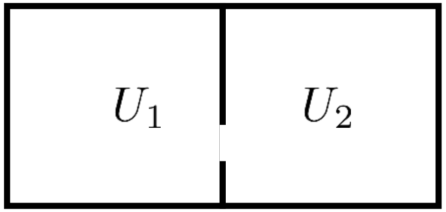
We have calculated chemical potential for an ideal gas in the classical approximations as

$$\mu = kT \ln \frac{NV_Q}{V} \qquad\qquad V_Q = \left(\frac{2\pi\hbar^2}{mkT}\right)^{3/2}$$

For gas in an external constant potential U, the chemical potential would be

$$\mu = kT \ln \frac{NV_Q}{V} + U$$

The reason is that the chemical potential has the meaning of the energy needed to increase the number of molecules by 1, and if the energy per molecule is higher by U due to external potential, the chemical potential has to be increased by U as well. This trick is often used by solid state physicists. The simplest example of its usage is an alternative derivation of the barometric formula. Imagine gas in two compartments connected by a hole enabling to exchange particles. Suppose in one compartment is a constant external potential U_1, in the other compartment U_2. In equilibrium the chemical potential has to be equal in both compartments, so we get



$$\mu_1 = \mu_2$$

$$kT \ln \frac{N_1 V_Q}{V_1} + U_1 = kT \ln \frac{N_2 V_Q}{V_2} + U_2$$

$$\boxed{\frac{N_1/V_1}{N_2/V_2} = \exp\left(-\frac{U_1 - U_2}{kT}\right)}$$

We have got the well-known barometric formula if U is the potential of gravity

Chemical reactions

Let us consider the chemical reaction $H_2 + Cl_2 \leftrightarrow 2HCl$

The reaction can run in both directions. We assume everything happens in gas phase. If the reaction runs from left to right the binding energy U per one molecule of HCl is released which is manifested by the fact that the molecules HCl are born in the reaction with the kinetic energies by U higher than it would correspond to the temperature T. We can mathematically model it that there is a constant external potential -U which is not felt neither by H_2 nor by Cl_2 molecules but is felt by HCl molecules.

The stoichiometric relations we express by integers ν_i defined negative for molecules entering the reaction from left and positive for molecules leaving the reaction on the right. So we have $\nu_{H_2} = -1$ $\nu_{Cl_2} = -1$ $\nu_{HCl} = 2$

Let us assume we at the beginning have filled the chemical reactor with the initial concentrations of molecules $n_{H_2;0}, n_{Cl_2;0}, n_{HCL;0}$

This would be the initial non equilibrium state. Let the container is kept at constant pressure and temperature. After reaching the equilibrium certain number N_{eq} of reactions have to take place. Assume that at some time instant just N reactions took place. We shall count N as positive for reactions from left to right and negative otherwise. We can take ***N* to be the parameter of non-equilibrium** and our task will be to **find its equilibrium value** N_{eq}. We shall find it by minimizing the Gibbs potential.

Chemical reactions - equilibrium

So suppose we are in the non-equilibrium state given by a certain value N and in the next small time of development this parameter changedas

$$N \to N + dN$$

This means that the numbers of molecules considered must have changed by

$$N_i \to N_i + dN_i \qquad dN_i = \nu_i dN \qquad \text{where} \qquad i \in \{H_2, Cl_2, HCl\}$$

At constant temperature and pressure the Gibbs potential will be changed by

$$dG = \sum_i \mu_i dN_i = \sum_i \mu_i \nu_i dN$$

At equilibrium the Gibbs potential should be extremal, so it has to be stationary for small changes of N. We get as a condition of equilibrium

$$\boxed{\sum_i \mu_i \nu_i = 0}$$

In our example we have (notice that the volumes V_Q do not depend on concentrations)

$$\mu_{H_2} = kT \ln(n_{H_2} V_{Q,H_2})$$
$$\mu_{Cl_2} = kT \ln(n_{Cl_2} V_{Q,Cl_2})$$
$$\mu_{HCl} = kT \ln(n_{HCl} V_{Q,HCl}) - U$$

Chemical reactions - equilibrium

From the equilibrium condition we get

$$\ln(n_{H_2}V_{Q,H_2}) + \ln(n_{Cl_2}V_{Q,Cl_2}) - 2(\ln(n_{HCl}V_{Q,HCl}) + 2U/(kT) = 0$$

$$\boxed{\frac{n_{H_2}n_{Cl_2}}{n^2_{HCl}} = \exp(-\frac{2U}{kT})\frac{V^2_{Q,HCl}}{V_{Q,H_2}V_{Q,Cl_2}}}$$

The given initial conditions are $n_{H_2;0}, n_{Cl_2;0}, n_{HCL;0}$

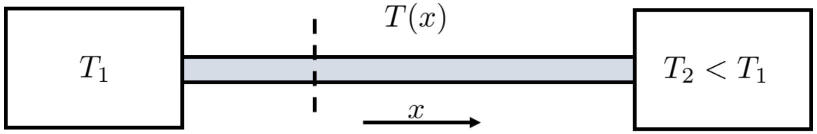
The unknown parameter which we should find is the number of reactions till the equilibrium N_{eq}. The final concentrations satisfy the stoichiometry relation

$$n_i = n_{i;0} + \nu_i \frac{N_{eq}}{V}$$

after inserting this into the equilibrium condition we can determine N_{eq} and the final equilibrium concentrations.

Theory of smuggling through the border

We shall study a non-equilibrium effect: transport phenomena. There are situations where there is no relaxation to equilibrium because the non-equilibrium state is artificially maintained by the external conditions. Imagine a long tube with gas connected at the ends to two reservoirs at different temperatures T_1, T_2.

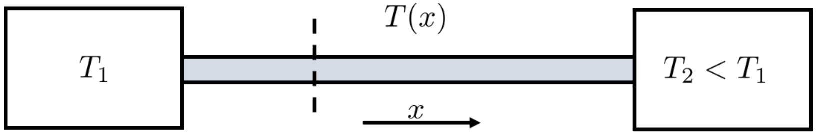


Obviously, the gas will not get into an equilibrium state. What happens after some relaxation time is a stationary state. The local macroscopic variables do not change any more, but for example the temperature will not be homogenous. It will depend on the coordinate x. What is, however, not directly “seen” is that there is a steady flow of energy through the gas tube from left to right. The energy current density is phenomenologically found to be

$$j_Q = -K\frac{dT}{dx}$$

The units of j_Q are J $\mathrm{s}^{-1}\mathrm{m}^{-2}$. The mechanism of this energy transfer is that the mean kinetic energy carrying by the gas molecules through the plane represented by the dashed line from left to right is higher than from right to left. The molecules are “smuggling energy” through the virtual boundary. If you are a real smuggler at the real border you cannot buy, say, cigarettes just close in front of the border and sell it immediately after the border, because the cigarette price is often continuous around the border. **You have to buy your goods in a distance before the border and to sell it in a distance after the border to get your profit**.

Smuggling the energy



We want to study the energy transfer through the virtual border represented by the dashed line. Molecules randomly cross the border. At the stationary state there is no net flow of the molecules, the number of molecules crossing from left to right is the same as the number crossing in the opposite direction. It is the same as for real smugglers on a real border. All the smugglers crossing the border return (with emptied backpacks) back. (Unless they are caught and jailed by the finance police .) The flow of molecules from left to right (per second per unit of area) is $n_{left}v_{left}$ where n_{left} is a typical density of molecules and v_{left} is the typical velocity of molecules left from the border. The net flow through the border is zero if

$$n_{left}v_{left} = n_{right}v_{right}$$

Now the smuggler-molecules crossing from the left carry "backpacks" filled by the energy ε_{left}. Those crossing from the right carry the energy ε_{right}. So the net flow of energy through the border taken as positive from left to right and expressed in units $\mathrm{J\,s^{-1}m^{-2}}$ is

$$\boxed{j_Q = n_{left}v_{left}\varepsilon_{left} - n_{right}v_{right}\varepsilon_{right}}$$

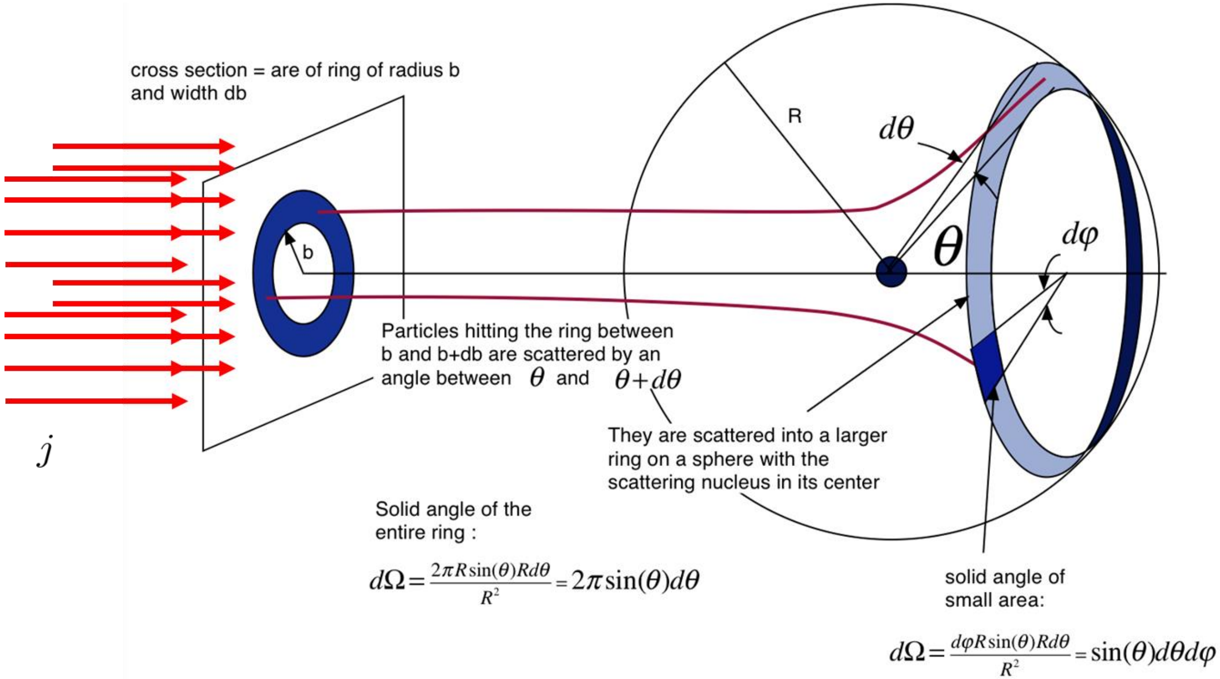
Smuggling the energy

The question is where the backpacks of the smuggler-molecules are filled with energy. The energy we are speaking about is, of course, the kinetic energy of the molecule as it was "obtained" in the last collision before crossing the border. This means that ε_{letf} is typically the mean kinetic energy of molecules **at a distance of the mean free molecular path** to the left from the border.

Warning: you have certainly noticed that we always used the word "typical" characterizing various physical quantities. We stress by that that our reasoning is an "order-of-magnitude" reasoning. We do not care to distinguish between for example mean absolute velocities or square roots of mean quadratic velocities or whatever. Therefore our results will not contain such factors as $\sqrt{2}, \pi$ you will find in some textbooks. The authors of those books do not often present more rigorous arguments than we do here, but they know more exact results and do some cheating to get "better results".

So to continue with our reasoning we have to repeat basic facts about molecular mean free path. **Next, we present some slides from the course of mechanics**

Scattering cross section



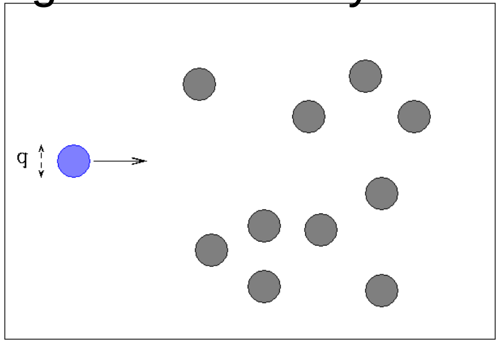
If the whole 4π spatial angle around the target is covered by detectors, then the number of detector “clicks” per second n can be expressed as

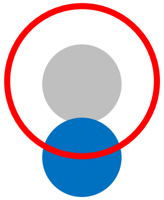
$$n = j\sigma_{\mathrm{tot}}$$

where j is the incoming particle beam flow density (in particles per second per area unit) and σ_{tot} (in area units) is so called total cross section which one can imagine as the area in the plane perpendicular to the beam: beam particles going through this area induce detector clicks, beam particles which miss this area do not induce clicks in the detectors.

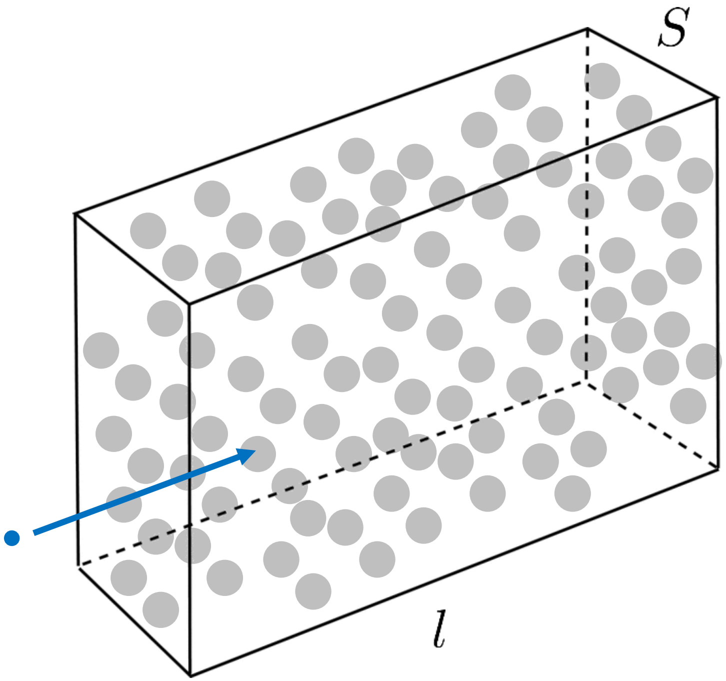
Mean free path estimate from the total cross section

Imagine the following experiment. A particle (the blue one in the figure) is shot into a gas of randomly moving particles (the grey ones in the figure).





$$\sigma = \pi(2r)^2$$



Each gas particle represents a target of area σ. Gas particle density is n.
The total area of targets on the path of the length l is $nlS\sigma$
The projectile will not get out of the gas container if the total area covered by the targets will cover the area of the back wall S. (We have neglected mutual concealing of targets.)

$$nlS\sigma = S \qquad \boxed{l = \frac{1}{n\sigma}}$$

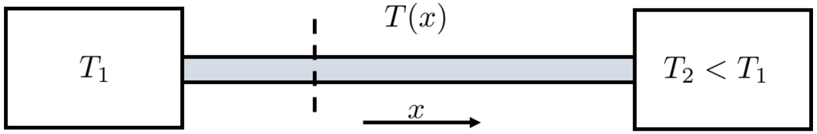
For shorter containers it will get out. So what we have crudely estimated is the **typical mean free path of a particle in gas**

Typical mean free path

$$l = \frac{1}{n\sigma}$$

- typical gas particle density $n = 0{,}3.\,10^{26}$ m^{-3}
- typical radius of a molecule $0.2\ \mathrm{nm}$
- typical cross section $\sigma = 0.5\ \mathrm{nm}^2$
- typical mean free path $l =\ \ 70$ nm
- typical time between collisions $\tau =$ 0.2 ns

Energy (“heat”) transfer



$$n_{left}v_{left} = n_{right}v_{right}$$

$$j_Q = n_{left}v_{left}\varepsilon_{left} - n_{right}v_{right}\varepsilon_{right}$$

$$j_Q = nv(\varepsilon_{left} - \varepsilon_{right}) = nv\frac{C_V}{N_A}(T_{left} - T_{right})$$

The two temperatures are the temperatures at two locations at a mean free path distance from each other

$$(T_{left} - T_{right}) = -\frac{dT}{dx}l$$

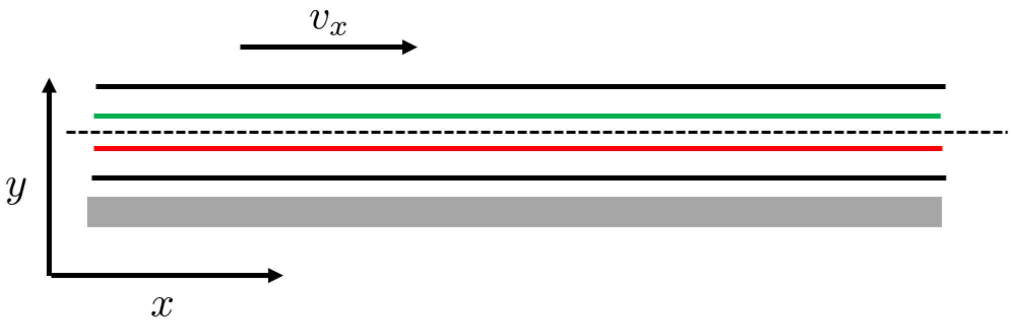
$$j_Q = -nv\frac{C_V}{N_A}l\frac{dT}{dx}$$

So the heat transfer coefficient is

$$\boxed{K - nv\frac{C_V}{N_A}l}$$

Note: everybody calls it “heat transfer coefficient” even if it better should be thermal energy transfer coefficient.

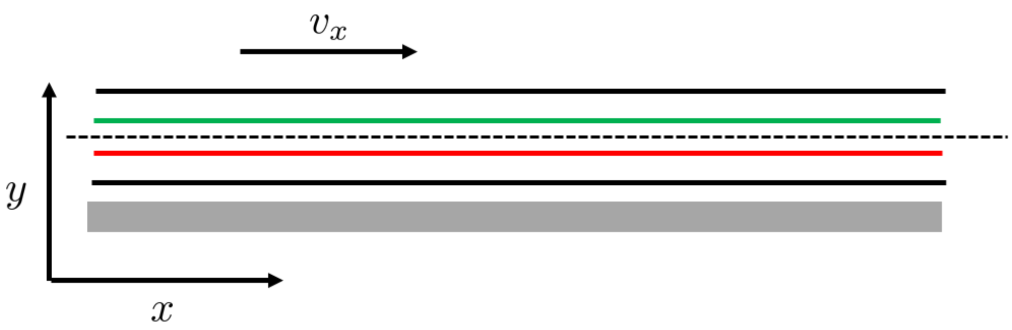
Viscosity



Let us consider gas laminar flow. Viscous gas will not flow homogeneously. We shall observe that its flow velocity v_x is zero just above the bed and then increases with increasing coordinate y. So there is a flow velocity gradient.

The flow velocity is a drift velocity superimposed on the random thermal movement of the molecules. The drift velocity might be of the order of a few ms^{-1} the chaotic thermal velocity might be of the order 500 ms^{-1}. The drift velocity is in the direction x, the chaotic velocity has random direction. That means, that slow molecules from the bottom layers can by their random movement infiltrate the top layers and decelerate the molecules there and the fast molecules from the top layers can infiltrate the bottom layers and accelerate the molecules there. The random chaotic movement of the molecules leads to the transfer of the x-direction momentum through the virtual boundary (represented by the dashed line) between the flowing layers. Transfer of momentum per time means the force acting between the layers in the x-direction what leads to **tangential tension between the layers manifested as the viscosity.**

Smuggling the momentum: viscosity



Not repeating the detailed discussion we had on energy transfer we just write the expression for the momentum flow density (in kgms^{-1} per unit of time per unit of the border area)

$$j_{p_x} = nv(mv_{drift;bottom} - mv_{drift;top}) = -mnv\frac{dv_{drift}}{dy}l$$

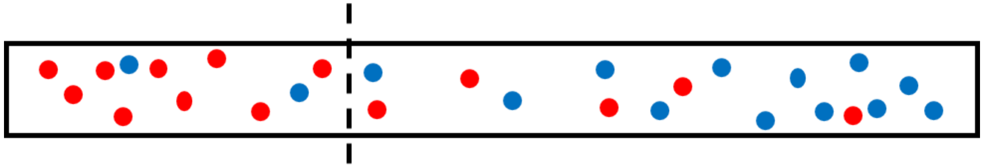
Phenomenologically we define the coefficient of viscosity η by the relation for the tangential tension between the layers in the form

$$\tau = -\eta\frac{dv_{drift}}{dy}$$

So we got for the coefficient of gas viscosity

$$\boxed{\eta = mnvl}$$

Smuggling themselves: diffusion



Let us consider a rather artificial situation. We have two types of molecules in the container. They are not uniformly distributed but in such a way, that the pressure is homogenous, therefore there is no “blow of the wind” in the container. We prepared such a thought experiment to be able to observe diffusion in a pure form free of a molecular transport by a macroscopic flow of gas.
We shall monitor just one type of molecules (for example the red ones) how they randomly move through the virtual border represented by the dashed line.
“The smugglers” do not carry anything in their backpacks, they smuggle themselves: there is a non-zero net flow of the smugglers through the border what leads to gradual homogenization of the concentration of the red molecules in the container.
We can directly write the formula for the net molecular diffusion current density (in units of molecules per the time unit per the area unit):

$$j_n = vn_{left} - vn_{right} = -v\frac{dn}{dx}l$$

So the diffusion current is

$$j_n = -D\frac{dn}{dx}$$

$$\boxed{D = nvl}$$

D is called the diffusion coefficient.